1-(Organosulfonyloxy)-3(1*H*)-1,2-benziodoxoles: Preparation and Reactions with Alkynyltrimethylsilanes

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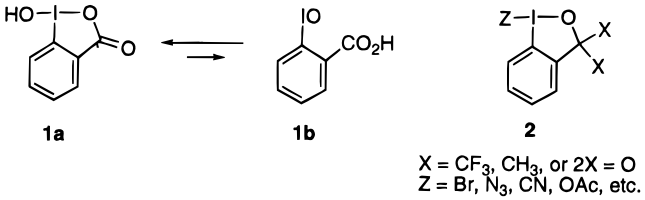
Organosulfonyloxy derivatives of 1,2-benziodoxol-3(1*H*)-one (**3a**−**c**) and 3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (**5a**−**c**) can be prepared in high yield by the reaction of 1-hydroxybenziodoxoles **1** or **4** and the corresponding sulfonic acids or Me_3SiOTf in the form of stable, but moderately hygroscopic, microcrystalline solids. Reaction of the triflate derivatives **3a** and **5a** with alkynyltrimethylsilanes affords either alkynyliodonium triflates **6**, or (*E*)-*β*-(trifluoromethanesulfonyloxy)-alkenyliodonium triflates **7**, while the same reaction in the presence of pyridine selectively gives the respective 1-alkynylbenziodoxoles **8** and **9** in 82−90% yield.

Introduction

In the past decade, there has been a considerable interest and research activity centered on the chemistry of five-membered iodine heterocycles, derivatives of benziodoxole.[1−9] The most important and best investigated heterocyclic iodane is 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (**1a**), the cyclic tautomer of 2-iodosylbenzoic acid (**1b**). In particular, benziodoxole **1** and its analogues are premier reagents for catalytic cleavage and decontamination of toxic phosphates and reactive esters due to a pronounced *O*-nucleophilicity of the anion of 1-hydroxybenziodoxole.[2,3] Another important feature of heterocyclic iodanes is a considerably higher stability than that of their acyclic analogs.[1,4−9] This stabilization effect due to the incorporation of the hypervalent iodine into a five-membered heterocycle made possible the isolation of several otherwise unstable iodine(III) derivatives. Martin and co-workers have first prepared stable bromoiodanes, derivatives of benziodoxoles (**2**, Z = Br; X = CF_3 or CH_3).[4] More recently, Ochiai and co-workers reported the preparation, X-ray structural investigation, and some chemical properties of (alkylperoxy)benziodoxole (**2**, Z = OOR, 2X = O).[6] The newest examples include synthesis and X-ray structural analysis of stable azidobenziodoxoles (**2**, Z = N_3; X = CF_3, CH_3 or 2X = O)[7] and cyanobenziodoxoles (**2**, Z = CN; X = CF_3 or 2X = O).[8,9] Azidobenziodoxoles are useful radical azidating reagents toward alkanes and alkenes,[7c] while cyanobenziodoxoles can serve as efficient cyanating reagents in the reactions with *N*,*N*-dimethylanilines.[8a]



Much less is known about derivatives of benziodoxole and strong acids. Cyclic carboxylates and phosphates **2** [Z = OCOR or $OP(O)(OPh)_2$, 2X = O] have been proposed as reactive intermediates in the catalytic cleavage of reactive esters or phosphates on the basis of spectral and kinetic mechanistic studies.[2b,c] However, with the exception of acetate (**2**, Z = OAc, 2X = O)[10] none of adducts **2**, derivatives of strong acids, such as organosulfonic, were reported in the literature as individual compounds. In this paper we wish to report the preparation of sulfonates **3a**−**c**[11] and **5a**−**c** and the use of triflates **3a**, **5a** as electrophilic reagents for the preparation of alkynyliodonium salts *via* the reaction with (trimethylsilyl)alkynes.

Results and Discussion

Sulfonate derivatives **3**, **5** can be conveniently prepared by a simple, one-step procedure starting from the commercial 2-iodosylbenzoic acid **1** or benziodoxole **4**[12] and the corresponding sulfonic acids or trimethylsilyl triflate (Schemes 1 and 2). The reaction conditions vary in each case. Triflates **3a**, **5a** are best prepared by the reaction

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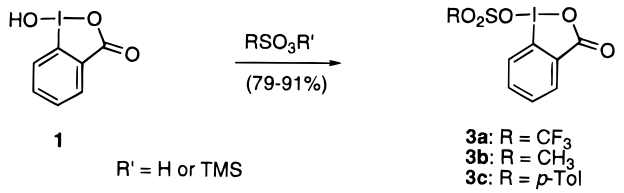
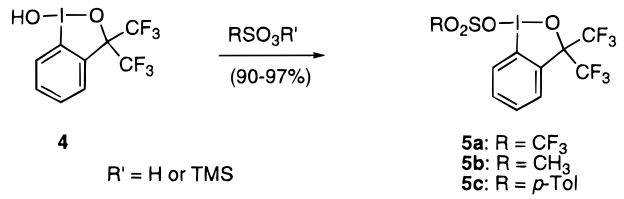
Scheme 1



Scheme 2

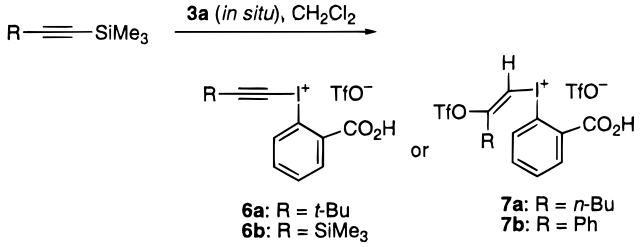


of **1** or **4** with trimethylsilyl triflate in methylene chloride at room temperature. Mesylate **3b** slowly crystallizes from the solution of **1** in neat methanesulfonic acid in the form of large, colorless crystals, while tosylate **3c** is obtained in the form of a white, microcrystalline precipitate in an exothermic reaction of **1** with $TsOH \cdot H_2O$ in acetic anhydride. Mesylate **5b** and tosylate **5c** precipitate from the mixture of **4** and the respective sulfonic acid in methylene chloride at 0 °C. All six adducts are isolated as hygroscopic, but thermally stable, crystalline solids. The most stable to moisture are tosylates **3c** and **5c**. According to elemental analyses and spectral data, tosylates **3c** and **5c** do not form crystallohydrates upon a brief exposure to an open air. Only extended contact of **3c** with moist air for several hours results in the formation of a microcrystalline dihydrate, $\mathbf{3c} \cdot 2H_2O$. Mesylates **3b**, **5b** and triflates **3a**, **5a** are highly hygroscopic and can be isolated only in the form of crystallohydrates; however, for further reactions triflates **3a**, **5a** (presumably as monohydrates) can be conveniently used *in situ*.

All adducts **3** and **5** were identified by spectral data and elemental analyses. In particular, proton NMR spectra of these compounds showed signals and splitting pattern typical of *ortho*-substituted benzene rings as well as the respective signals of the R-group in mesylates (**3b**, **5b**) and tosylates (**3c**, **5c**). The presence of the triflate group in **3a** and **5a** was confirmed by ^{19}F NMR. We propose the cyclic, benziodoxole structure for all adducts **3** and **5** based on the available X-ray data for the other 1-substituted benziodoxoles, such as hydroxy,[13a] methoxy,[13b] azido,[7c] and cyanobenziodoxoles.[8b] The cyclic structure of products **3** is further confirmed by IR spectra in which the carbonyl peak is observed at 1610−1615 cm^{-1}. In contrast, the carbonyl absorption in the noncyclic 2-iodosyl benzoate derivatives, such as 3-alkyl-2-iodosylbenzoic acids, has a much higher wavenumber at 1710 cm^{-1}.[3]

It is known from the literature that the noncyclic aryliodosyl sulfonates, such as Koser's reagent PhI(OH)OTs and Zefirov's reagent PhI(OTf)O(OTf)IPh, are highly reactive toward unsaturated organic substrates and other carbon nucleophiles.[14] The noncyclic aryliodosyl sulfonates are especially useful reagents for the preparation of alkynyliodonium salts by the reaction with silylated

Scheme 3



or stannylated alkynes.[15,16] Assuming that the cyclic aryliodosyl sulfonates **3**, **5** have a similar reactivity pattern, we investigated reactions of sulfonates **3** and **5** with silylacetylenes. Mesylates (**3b**, **5b**) and tosylates (**3c**, **5c**) were found to have low reactivity in these reactions. In particular, mesylate **3b** and tosylate **3c** slowly reacted with bis(trimethylsilyl)acetylene only at temperatures above 50 °C to afford a complex mixture of products due to significant decomposition under the reaction conditions. Triflates **3a** and **5a** were much more reactive in these reactions. Thus, triflate **3a** (generated *in situ*) was reacted with (3,3-dimethyl-1-butynyl)trimethylsilane at room temperature to afford alkynyliodonium salt **6a** in high yield (Scheme 3). A similar reaction of bis(trimethylsilyl)acetylene furnished alkynyliodonium salt **6b** as the major product. We propose the noncyclic structure for products **6** based on the relatively high frequency of the carbonyl stretch (1670−1684 cm^{-1}) in their IR spectra. Proton and ^{13}C NMR, IR, and elemental analysis are all consistent with the proposed structure **6** and are in good agreement with the previously reported data on alkynyl(aryl)iodonium triflates.[15]

Further investigation of this reaction revealed that only alkynes with a bulky substituent R (R = *t*-Bu or TMS) afforded alkynyliodonium salts as major products. In contrast, similar reactions of hexynyl- and phenylethynyl trimethylsilanes led exclusively to the vinylic compounds **7** (Scheme 3), the products of electrophilic addition of **3a** to the alkyne in the presence of HOTf. The formation of (*E*)-*β*-(trifluoromethanesulfonyloxy)alkenyliodonium triflates in the reactions of phenyliodosyl triflates, $PhIO \cdot Tf_2O$ or PhIO·HOTf, with alkynes has been well documented in the literature.[17,18] In particular, Kitamura, Taniguchi, and co-workers have found that the reaction of PhIO·HOTf with terminal, nonsterically hindered alkynes, such as 1-hexyne or phenylacetylene, afforded (*E*)-[*β*-(trifluoromethanesulfonyloxy)alkenyl](phenyl)iodonium triflates, while the analogous reaction of the sterically hindered *tert*-butylacetylene produced the respective alkynyliodonium salt as major product.[17a]

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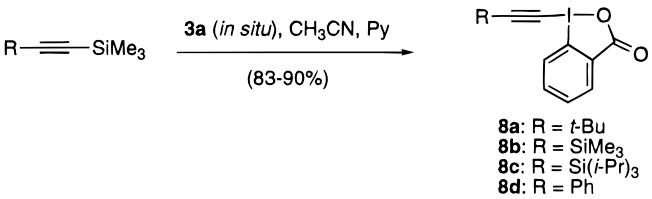
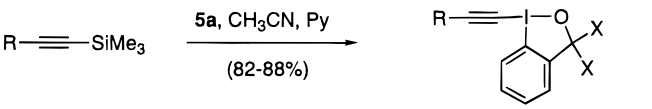
Scheme 4



8a: R = *t*-Bu
8b: R = $SiMe_3$
8c: R = Si(*i*-Pr)$_3$
8d: R = Ph

Scheme 5



9a: R = *t*-Bu
9b: R = $SiMe_3$
9c: R = Si(*i*-Pr)$_3$
9d: R = Ph
9e: R = 1-cyclohexenyl

Norton and co-workers have reported an X-ray crystal structure for (*E*)-*β*-(trifluoromethanesulfonyloxy)alkenyliodonium triflate obtained from the reaction of Zefirov's reagent, $2PhIO{\cdot}Tf_2O$, with an internal alkyne.[18] The formation of similar (*E*)-alkenyl adducts in the analogous reaction of trimethylsilylated alkynes has also been reported.[19]

The outcome of this reaction can be changed by carrying it out in the presence of pyridine. Thus, the reaction of reagent **3a** (generated *in situ*) with trimethylsilylated alkynes followed by addition of pyridine selectively affords 1-alkynylbenziodoxoles **8** in a high preparative yield (Scheme 4).

Products **8** were identified by elemental analyses and spectral data. In particular, IR spectra of these compounds showed triple bond absorption at 2133−2164 cm^{-1} and the carbonyl stretch at 1611−1640 cm^{-1} which is consistent with their cyclic structure. In ^{13}C NMR of **8**, the acetylenic signals have chemical shifts 46−65 (C≡*C*I) and 114−116 (*C*≡CI) ppm, which are typical of alkynyliodonium salts.[5,15,20] The preparation of several examples of 1-alkynyl-1,2-benziodoxol-3(1*H*)-ones (**8**, R = cyclo-C_6H_{11}, *n*-C_8H_{17}, *t*-Bu) was recently reported by Ochiai and co-workers.[5] Previously these compounds were prepared by a single step reaction of **1** with alkynyltrimethylsilanes and $BF_3{\cdot}Et_2O$ in only 22−35% yield.[5] Our procedure affords 1-alkynylbenziodoxoles **8** in much better yield. The closely related 1-alkynylbenziodoxathiole dioxides were recently prepared by Koser and co-workers from the reaction of terminal alkynes with 1-hydroxybenziodoxathiole dioxide and TsOH in 26−66% yield.[20]

Triflate **5a** reacts with alkynyltrimethylsilanes under similar conditions to afford the respective alkynylbenziodoxoles **9** in good yield (Scheme 5). These products were identified by their spectral data and elemental analyses. An X-ray structure for a similar 1-cyanobenziodoxole was recently reported in the literature.[8b]

In conclusion, we have prepared and isolated as individual, stable compounds adducts of 1-hydroxybenziodoxoles with sulfonic acids. These compounds are potentially useful reagents for the selective preparation of 1-alkynylbenziodoxoles by the reaction with alkynyltrimethylsilanes in the presence of pyridine.

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Experimental Section

General. All melting points were determined in an open capillary tube and are uncorrected. NMR spectra were recorded at 300 MHz (^1H NMR), 75 MHz (^{13}C NMR), and 282.2 MHz (^{19}F NMR). Chemical shifts are reported in parts per million (ppm); ^1H chemical shifts are referenced to the proton resonance due to the residual protons in the deuteriated NMR solvent; ^{19}F chemical shifts are given relative to external $CFCl_3$. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

All commercial reagents were ACS reagent grade and used without further purification. 1-Hydroxy-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (**4**) was prepared by oxidation of 2-(2-iodophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol[12] with peracetic acid. Methylene chloride and acetonitrile were distilled from CaH_2 immediately prior to use. Other solvents were of commercial quality from freshly opened containers. The reaction flasks were flame-dried and flushed with nitrogen.

1-(Trifluoromethanesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (3a). To a stirred mixture of 2-iodosylbenzoic acid **1** (0.53 g, 2 mmol) in dry CH_2Cl_2 (20 mL) was added trimethylsilyl triflate (0.43 mL, 2.2 mmol) under nitrogen at room temperature. The resulting mixture turned into a clear solution after 10−20 min stirring, and then a yellow precipitate of **3a** formed. The precipitate was filtered under nitrogen and dried in vacuum; yield 0.67 g (85%), mp 166−168 °C dec; IR (CCl_4): 3071, 1614, 1271, 1233, 1166, 1024 cm^{-1}; ^1H NMR ($CDCl_3$/CF_3COOH, 20:1): δ 8.32 (d, 1H, J = 8 Hz), 8.11 (t, 1H, J = 8 Hz), 7.98 (d, 1H, J = 8 Hz), 7.80 (t, 1H, J = 8 Hz); ^{13}C NMR (DMSO-d_6): δ 167.9, 134.6, 131.4, 131.1, 130.4, 126.3, 120.5, 121.82 (q, J = 320 Hz); ^{19}F NMR (CD_3CN): δ −78.61 (s). Compound **3a** is highly hygroscopic. After brief exposure to air the original yellow color of **3a** disappears and a white, microcrystalline crystallohydrate $\mathbf{3a}{\cdot}2H_2O$ forms. For $\mathbf{3a}{\cdot}2H_2O$: ^1H NMR (CD_3CN): δ 8.27 (d, 1H), 8.06 (t, 1H), 7.94 (d, 1H), 7.77 (t, 1H), 7.45 (br s, 4H). Anal. Calcd for $C_8H_8IF_3O_7S$: C, 22.24; H, 1.87. Found: C, 22.25; H, 1.80.

1-(Methanesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (3b). 2-Iodosylbenzoic acid **1** (4.22 g, 16 mmol) was dissolved in 5−7 mL of neat methanesulfonic acid at room temperature with stirring. Then dry acetonitrile (10 mL) and anhydrous ether (20 mL) were added, and the resulting solution was left for several hours at 0 °C for crystallization of the product. Colorless crystals of **3b** were filtered under nitrogen, washed with anhydrous ether, and dried in vacuum; yield 4.98 g (91%), mp 174−176 °C dec. Compound **3b** is hygroscopic. After exposure to air the original colorless crystals turn into white, microcrystalline crystallohydrate $\mathbf{3b}{\cdot}5H_2O$, mp 140−145 °C dec. For $\mathbf{3b}{\cdot}5H_2O$: IR (CCl_4): 3383 (br), 3074, 2927, 1615, 1337, 1206, 1149, 1039 cm^{-1}; ^1H NMR ($CDCl_3$/CF_3COOH, 20:1): δ 8.31 (d, 1H, J = 8 Hz), 8.09 (t, 1H, J = 8 Hz), 8.00 (d, 1H, J = 8 Hz), 7.82 (t, 1H, J = 8 Hz), 2.99 (s, 3H, Me); ^{13}C NMR ($CDCl_3$/CF_3COOH, 20:1): δ 174.6, 138.4, 128.7, 126.8, 126.4, 124.9, 120.6, 39.2. Anal. Calcd for $C_8H_{17}ISO_{10}$ ($\mathbf{3b}{\cdot}5H_2O$): C, 22.23; H, 3.96; I, 29.36. Found: C, 22.23; H, 3.80; I, 29.57.

1-(*p*-Toluenesulfonyloxy)-1,2-benziodoxol-3(1*H*)-one (3c). To a stirred mixture of 2-iodosylbenzoic acid **1** (3.17 g, 12 mmol) in acetic anhydride (6 mL), $TsOH{\cdot}H_2O$ (4.56 g, 24 mmol) was added at room temperature. After 5 min stirring a slightly exothermic reaction began, and the mixture turned into a clear solution. The solution was additionally stirred for 30 min until a white microcrystalline precipitate formed. Then the reaction mixture was diluted with dry ether (20 mL), the precipitate was filtered, washed with anhydrous ether (3 × 20 mL), and dried in vacuo to afford analytically pure product **3c**; yield 3.90 g (79%), mp 178−180 °C dec; IR (CCl_4): 3062, 2921, 1610, 1341, 1250, 1120, 1027 cm^{-1}; ^1H NMR ($CDCl_3$/CF_3COOH, 20:1): δ 8.30 (d, 1H, J = 8 Hz), 8.09 (t, 1H, J = 8 Hz), 7.94 (d, 1H, J = 8 Hz), 7.80 (t, 1H, J = 8 Hz), 7.71 (d, 2H, J = 8 Hz), 7.29 (d, 2H, J = 8 Hz), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$/CF_3COOH, 20:1): δ 174.6, 144.0, 138.7, 138.6, 136.2, 129.6, 128.7, 126.3, 126.0, 124.5, 120.6, 21.2. Anal. Calcd for $C_{14}H_{11}ISO_5$: C, 40.21; H, 2.65; I, 30.35. Found: C, 39.95; H, 2.77; I, 30.20. Compound **3c** is slightly hygroscopic: its

extended exposure to moist air affords white, microcrystalline crystallohydrate **3c**·$2H_2O$, mp 169−174 °C dec.

1-(Trifluoromethanesulfonyloxy)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (5a). To a stirred suspension of 1-hydroxy-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole **4** (0.20 g, 0.52 mmol) in dry CH_2Cl_2 (15 mL) was added trimethylsilyl triflate (0.11 mL, 0.57 mmol) under nitrogen at room temperature. After stirring 10−20 min, the resulting clear yellow solution was evaporated, and product **5a** was collected and dried under vacuum; yield 0.26 g (97%), mp 143−145 °C; IR (KBr): 3089, 1377, 1258, 1185, 1105, 1037 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.93 (m, 2H), 7.77 (m, 2H); ^{19}F NMR ($CDCl_3$): δ −75.50 (s) and 78.60 (s). Anal. Calcd for $C_{10}H_4IF_9O_4S·H_2O$: C, 22.40; H, 1.13; I, 23.67. Found: C, 22.45; H, 1.14; I, 23.76.

1-(Methanesulfonyloxy)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (5b). To a stirred suspension of benziodoxole **4** (0.20 g, 0.52 mmol) in dry CH_2Cl_2 (15 mL) was added methanesulfonic acid (0.04 mL, 0.57 mmol) at room temperature. After stirring 10−20 min, the resulting clear colorless solution was cooled to 0 °C and a white precipitate of **5b** formed. The precipitate was filtered and dried under vacuum; yield 0.22 g (92%), mp 172−178 °C; IR (CCl_4): 3088, 3033, 2944, 1261, 1200, 1161, 1139, 1105, 1038 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03 (d, 1H, J = 8 Hz), 7.91 (m, 2H), 7.74 (d, 1H, J = 8 Hz), 3.09 (s, 3H, Me); ^{19}F NMR (CD_3CN): δ −75.59 (s). Anal. Calcd for $C_{10}H_7IF_6O_4S·H_2O$: C, 24.91; H, 1.88; I, 26.32. Found: C, 24.73; H, 1.95; I, 26.15.

1-(*p*-Toluenesulfonyloxy)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (5c). To a stirred suspension of benziodoxole **4** (0.20 g, 0.52 mmol) in dry CH_2Cl_2 (15 mL), $TsOH·H_2O$ (0.11 g, 0.57 mmol) was added at room temperature. After 10−20 min stirring, the resulting clear colorless solution was cooled to 0 °C, and a white precipitate of **5c** formed. The precipitate was filtered and dried under vacuum; yield 0.25 g (90%), mp 158−160 °C; IR (KBr): 3088, 2922, 1383, 1266, 1200, 1150, 1105, 1038 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.97 (t, 1H, J = 8 Hz), 7.91 (d, 1H, J = 8 Hz), 7.85 (t, 1H, J = 8 Hz), 7.82 (d, 2H, J = 8 Hz), 7.71 (d, 1H, J = 8 Hz), 7.32 (d, 2H, J = 8 Hz), 2.45 (s, 3H); ^{19}F NMR (CD_3CN): δ −75.60 (s). Anal. Calcd for $C_{16}H_{11}IF_6O_4S$: C, 35.57; H, 2.05; I, 23.49; S, 5.93. Found: C, 35.56; H, 2.05; I, 23.58; S, 6.01.

General Procedure for Reactions of Triflate 3a with Alkynyltrimethylsilanes *in situ*. Trimethylsilyl triflate (0.64 mL, 3.3 mmol) was added to a stirred suspension of 2-iodosylbenzoic acid **1** (0.79 g, 3 mmol) in dry CH_2Cl_2 (10 mL) at room temperature. The resulting yellow mixture was stirred for 1 h followed by addition of the respective alkynyltrimethylsilane (3.3 mmol). The reaction mixture was stirred for 6 h, solvent was evaporated, and the resulting oil was crystallized from ether−hexane 1:1 mixture. Analytically pure materials were obtained by recrystallization from a concentrated solution of the iodonium salt in CH_2Cl_2 by addition of ether−hexane mixture.

2-[3,3-Dimethylbutynyl(trifluoromethanesulfonyloxy)-iodo]benzoic Acid (6a). Reaction of 2-iodosylbenzoic acid (0.79 g, 3 mmol), trimethylsilyl triflate (0.64 mL, 3.3 mmol), and (3,3-dimethyl-1-butynyl)trimethylsilane (0.36 mL, 3.3 mmol) gave 1.35 g (94%) of **6a** as a white microcrystalline solid, mp 149−151 °C dec; IR (CCl_4): 3104, 3064, 2971, 2535 (br), 2183, 2149, 1684, 1288, 1233, 1219, 1162 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.39 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.92 (t, J = 8.0 Hz, 1H), 7.83 (t, J = 8.1 Hz, 1H), 6.35 (br s, ∼2H), 1.38 (s, 9H); ^{19}F NMR ($CDCl_3$): δ −78.65 (s); ^{13}C NMR ($CDCl_3$): δ 170.8, 137.9, 133.2, 132.2, 128.4, 125.3, 123.9, 121.1 (q, J = 318 Hz), 113.9, 40.1, 29.7, 28.5. Anal. Calcd for $C_{14}H_{14}F_3IO_5S·0.5H_20$: C, 34.51; H 3.10. Found: C, 34.50; H, 2.97.

2-[(Trimethylsilylethynyl)(trifluoromethanesulfonyloxy)iodo]benzoic Acid (6b). Reaction of 2-iodosylbenzoic acid (0.79 g, 3 mmol), trimethylsilyl triflate (0.64 mL, 3.3 mmol), and bis(trimethylsilyl)acetylene (0.39 mL, 3.3 mmol) gave 1.38 g (93%) of **6b** as a white microcrystalline solid, mp 121−123 °C dec; IR (CCl_4): 3104, 2966, 2515 (br), 2107, 1670, 1286, 1217, 1172, 1026 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.30 (br s, 1H) 8.30 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.90 (t, J = 8.0 Hz, 1H), 7.80 (t, J = 8.0 Hz, 1H), 0.27 (s, 9H); ^{19}F NMR (CD_3CN): δ −78.60 (s); ^{13}C NMR (CD_3CN): δ 172.1, 139.5, 134.1, 133.4, 130.1, 126.1, 125.5, 121.0 (q, J = 318 Hz), 115.7, 47.4, 0.0; FAB HRMS m/z 344.980639 [M − $CF_3SO_3^-$]$^+$, calcd for $C_{12}H_{14}IO_2Si$ 344.980661. Anal. Calcd for $C_{13}H_{14}F_3IO_5SSi$: C, 31.59; H 2.85. Found: C, 31.41; H, 2.78.

2-[[(*E*)-2-(Trifluoromethanesulfonyloxy)-1-hexenyl](trifluoromethanesulfonyloxy)iodo]benzoic Acid (7a). Reaction of 2-iodosylbenzoic acid (0.53 g, 2 mmol), trimethylsilyl triflate (0.42 mL, 2.2 mmol), and (1-hexynyl)trimethylsilane (0.24 mL, 2.2 mmol) gave 0.56 g (45%) of **7a** as a white microcrystalline solid, mp 149 °C dec; IR (CCl_4): 3098, 2972, 2659 and 2507 (br), 1667, 1629, 1288, 1220, 1200, 1139, 1041 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.05 (br s, 1H), 8.45 (d, J = 8.0 Hz, 1H), 7.85 (m, 3H), 7.01 (s, 1H), 2.80 (m, 2H), 1.60 (m, 2H), 1.30 (m, 2H), 0.9 (m, 3H); ^{19}F NMR ($CDCl_3$): δ −73.63 (s) and 78.60 (s). Anal. Calcd for $C_{15}H_{15}F_6IO_8S_2$: C, 28.68; H 2.41. Found: C, 28.77; H, 2.43.

2-[[(*E*)-2-(Trifluoromethanesulfonyloxy)-1-phenylethenyl](trifluoromethanesulfonyloxy)iodo]benzoic Acid (7b). Reaction of 2-iodosylbenzoic acid (0.79 g, 3 mmol), trimethylsilyl triflate (0.64 mL, 3.3 mmol), and (phenylethynyl)trimethylsilane (0.38 mL, 3.3 mmol) gave 0.95 g (47%) of **7b** as a white, microcrystalline solid, mp 150−152 °C dec; IR (CCl_4): 3081, 2668 and 2506 (br), 1661, 1620, 1270, 1230, 1196, 1171, 1135 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.0 (br s, 1H), 8.47 (d, J = 8.0 Hz, 1H), 7.90 (m, 3H), 7.60 (m, 5H) 7.28 (s, 1H); ^{19}F NMR ($CDCl_3$): δ −73.52 (s) and 78.61 (s). Anal. Calcd for $C_{17}H_{11}F_6IO_8S_2$: C, 31.50; H 1.71. Found: C, 31.56; H, 1.69.

General Procedure for Reactions of 2-Iodosylbenzoic Acid with Alkynyltrimethylsilanes and Trimethylsilyl Triflate in the Presence of Pyridine. To a stirred solution of 2-iodosylbenzoic acid **1** (0.42 g, 1.60 mmol) in dry CH_3CN (12 mL) was added trimethylsilyl triflate (0.34 mL, 1.76 mmol). After stirring 15 min the appropriate alkynyltrimethylsilane (0.5 mmol) was added. The reaction mixture was additionally stirred for 10−20 min, and then pyridine (0.14 mL, 1.76 mmol) was added and the solvent was evaporated. The residual crude oil was washed with water to afford a white, microcrystalline product **8**, which was collected and dried under vacuum. Analytically pure materials were obtained by recrystallization from acetonitrile.

1-(3,3-Dimethylbutynyl)-1,2-benziodoxol-3(1*H*)-one (8a). Reaction of 2-iodosylbenzoic acid **1** (0.54 g, 2.03 mmol) with trimethylsilyl triflate (0.43 mL, 2.24 mmol), (3,3-dimethylbutynyl)trimethylsilane (0.47 mL, 2.24 mmol), and pyridine (0.18 mL, 2.24 mmol) gave 0.60 g (90%) of **8a**, mp 195−200 °C dec; IR (KBr): 2978, 2932, 2164, 2133, 1619, 1560, 1298, 1248 cm^{-1}; ^1H NMR ($CDCl_3$/CD_3CN, 7:1): δ 8.32 (dd, J_1 = 5 Hz, J_2 = 2 Hz, 1H), 8.17 (dd, J_1 = 5 Hz, J_2 = 1.5 Hz, 1H), 7.79 (m, 2H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 166.0, 134.3, 131.3, 130.8, 125.7, 116.8, 116.1, 114.9, 37.17, 29.84, 28.93. Anal. Calcd for $C_{13}H_{13}IO_2$: C, 47.58; H, 3.99. Found: C, 47.61; H, 3.81.

1-[(Trimethylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (8b). Reaction of 2-iodosylbenzoic acid **1** (0.42 g, 1.60 mmol), trimethylsilyl triflate (0.34 mL, 1.76 mmol), bis(trimethylsilyl)acetylene (0.34 mL, 1.76 mmol), and pyridine (0.14 mL, 1.76 mmol) afforded 0.49 g (89%) of **8b** after standard workup, mp 140−143 °C (dec); IR (KBr): 3068, 2921, 2854, 2028, 1615 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 20:1): δ 8.27 (m, 2H), 7.79 (m, 2H), 0.32 (s, 9H); ^{13}C NMR ($CDCl_3$/DMSO-d_6, 20:1): δ 166.8, 134.9, 131.5, 131.2, 126.2, 117.4, 115.3, 114.2, 47.1, 0.0. Anal. Calcd for $C_{12}H_{13}IO_2Si$: C, 41.87; H, 3.81. Found: C, 41.82; H, 3.79.

1-[(Triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (8c). Reaction of 2-iodosylbenzoic acid **1** (0.41 g, 1.56 mmol) with trimethylsilyl triflate (0.33 mL, 1.71 mmol), (triisopropylsilyl)(trimethylsilyl)acetylene (0.44 g,1.71 mmol), and pyridine (0.14 mL, 1.71 mmol) afforded 0.55 g (83%) of **8c**, mp 162−165 °C. IR (KBr): 3070, 2946, 1621, 1583 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.39 (m, 1H), 8.29 (m, 2H), 7.76 (m, 2H), 1.17 (s, 21H); ^{13}C NMR ($CDCl_3$): δ 166.4, 134.5, 132.3, 131.5, 126.1, 115.6, 114, 96.8, 64.66, 18.1, 11.09. Anal. Calcd for $C_{18}H_{25}IO_2Si$: C, 50.47; H 5.88; I, 29.62. Found: C, 50.29; H, 5.94; I, 29.70.

1-(Phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (8d). Reaction of 2-iodosylbenzoic acid **1** (0.58 g, 2.21 mmol) with trimethylsilyl triflate (0.47 mL, 2.43 mmol), (phenylethynyl)-trimethylsilane (0.48 mL, 2.43 mmol), and pyridine (0.19 mL, 2.43 mmol) afforded 0.67g (87%) of **8d**, mp 153−155 dec; IR (KBr): 3063, 2141, 1639, 1585 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.42 (m, 1H), 8.26 (m, 1H), 7.77 (m, 2H), 7.61 (m, 2H), 7.47 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 166.4, 134.8, 132.8, 132.4, 131.5, 131.4, 130.7, 128.7, 126.3, 120.5, 116.2, 106.5, 50.16. Anal. Calcd for $C_{15}H_9IO_2$: C, 51.75; H 2.61; I, 36.45. Found: C, 51.69; H, 2.64; I, 36.54.

General Procedure for Reactions of Triflate 5a with Alkynyltrimethylsilanes. To a stirred solution of 1-(trifluoromethanesulfonyloxy)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (**5a**) (0.20 g, 0.39 mmol) in dry CH_3CN (15 mL), the appropriate alkynyltrimethylsilane (0.5 mmol) was added under nitrogen at 0 °C. After stirring 10−20 min, two drops of pyridine were added and the solvent was evaporated. The residual crude product **9** was redissolved in ether and filtered through a short silica gel plug in order to remove pyridinium triflate. The ether solution was evaporated, and the white, microcrystalline solid product collected and dried under vacuum. Analytically pure materials were obtained by recrystallization from ether−hexane.

1-(3,3-Dimethylbutynyl)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (9a). Reaction of benziodoxole **5a** (0.20 g, 0.39 mmol) with (3,3-dimethylbutynyl)trimethylsilane (0.10 mL, 0.6 mmol) and pyridine at 0 °C afforded 0.200 g (85%) of **9a**, mp 190−194 °C; IR (KBr): 3089, 2972, 2860, 2158, 2128, 1265, 1255, 1179, 1149, 1129 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.17 (d, J = 8 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 7.67 (m, 2H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 132.7, 130.9, 130.1, 129.8, 127.9, 123.7 (q, J = 290 Hz), 115.9, 111.0, 81.7 (septet, J = 29.7 Hz), 41.9, 30.7, 29.4. Anal. Calcd for $C_{15}H_{13}F_6IO$: C, 40.02; H 2.91; I, 28.19. Found: C, 39.76; H, 2.97; I, 28.44.

1-[(Trimethylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (9b). Reaction of benziodoxole **5a** (0.20 g, 0.39 mmol) with bis(trimethylsilyl)acetylene (0.15 mL, 0.66 mmol) and pyridine at 0 °C afforded 0.157 g (86%) of **9b**, mp 163−177 °C dec; IR (KBr): 3089, 2972, 2905, 2128, 1264, 1223, 1183, 1152, 1122 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.27 (d, J = 8 Hz, 1H), 7.82 (d, J = 8 Hz, 1H), 7.71 (m, 2H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 132.7, 130.8, 130.1, 129.4, 128.0, 123.3 (q, J = 290 Hz), 116.2, 114.9, 110.3, 81.2 (septet, J = 29.7 Hz), 68.4, −0.8. Anal. Calcd for $C_{14}H_{13}F_6IOSi$: C, 36.07; H 2.81; I, 27.22. Found: C, 34.79; H, 2.59; I, 29.72.

1-[(Triisopropylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (9c). Under similar conditions, reaction of benziodoxole **5a** (0.200 g, 0.39 mmol) with (triisopropylsilyl)(trimethylsilyl)acetylene (0.127 g, 0.5 mmol) afforded 0.177 g (82%) of **9c**, mp 127−131 °C; IR (KBr): 3089, 2941, 2862, 2124, 1461, 1264, 1215, 1180, 1151, 1136, 1116 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.33 (d, J = 8 Hz, 1H), 7.83 (d, J = 8 Hz, 1H), 7.67 (m, 2H), 1.12 (s, 21H); ^{13}C NMR ($CDCl_3$): δ 141.2, 135.1, 132.5, 130.8, 129.9, 127.7, 123.3 (q, J = 290 Hz), 110.6, 81.2 (septet, J = 29.7 Hz), 68.9, 18.4, 11.2. Anal. Calcd for $C_{20}H_{25}F_6IOSi$: C, 43.64; H 4.58; I, 23.06. Found: C, 43.51; H, 4.51; I, 23.28.

1-(Phenylethynyl)-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (9d). Reaction of benziodoxole **5a** (0.200 g, 0.39 mmol) with (phenylethynyl)trimethylsilane (0.15 mL, 0.76 mmol) afforded 0.162 g (88%) of **9d**, mp 128−133 °C; IR (KBr): 3079, 2133, 1292, 1264, 1182 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.29 (m, 1H), 7.83 (m, 1H), 7.67 (m, 2H), 7.77 (m, 2H), 7.41 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 132.9, 132.6, 132.2, 131.1, 130.0, 129.8, 128.6, 128.3, 123.3 (q, J = 290 Hz), 121.3, 111.4, 105.2, 81.2 (septet, J = 29.7 Hz), 54.3. Anal. Calcd for $C_{17}H_9F_6IO$: C, 43.43; H 1.93; I, 26.99. Found: C, 42.92; H, 2.04; I, 27.82.

1-[(1-Cyclohexenyl)ethynyl)]-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (9e). Reaction of benziodoxole **5a** (0.200 g, 0.39 mmol) with (1-cyclohexen-1-ylethynyl)trimethylsilane (0.10 mL, 0.5 mmol) afforded 0.161 g (87%) of **9e**, mp 131−135 °C dec; IR (KBr): 3072, 3025, 2938, 2914, 2123, 1567, 1267, 1225, 1181 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.19 (d, J = 8 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 7.69 (m, 2H), 6.35 (s, 1H), 2.3−1.5 (m, 8H); ^{13}C NMR ($CDCl_3$): δ 140.0, 132.7, 129.7, 129.5, 128.0, 127.7, 123.3 (q, J = 290 Hz), 119.6, 111.1, 107.6, 81.2 (septet, J = 29.7 Hz), 50.3, 28.6, 25.6, 21.8, 20.9. Anal. Calcd for $C_{17}H_{13}F_6IO$: C, 43.06; H, 2.76; I, 26.76. Found: C, 42.99; H, 2.82; I, 26.89.

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