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1-[Hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes: Stable, Fluoroalkyl Analogs of Koser's Reagent

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1-[Hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes **3** [$R_fCH_2I(OH)OSO_2R$; R = CH_3, CF_3, *p*-$CH_3C_6H_4$, R_f = CF_3, C_2F_5] can be prepared in two steps from the appropriate iodofluoroalkanes by oxidation with peroxytrifluoroacetic acid and subsequent reaction with TsOH, MsOH, or Me_3SiOTf. The tosylate derivative **3a** reacts with silyl enol ethers under mild conditions to give the respective α-(tosyloxy) ketones. A similar reaction of cyclohexene furnishes *cis*-1,2-bis(tosyloxy)cyclohexane as the major product. Triflates **3c**,**f** react with (trimethylsilyl)arenes under mild conditions to afford the respective (fluoroalkyl) (aryl)iodonium triflates **7**, while the analogous reaction with alkynyltrimethylsilanes leads to novel (fluoroalkyl)(alkynyl)iodonium salts **8**.

Introduction

There is considerable current interest and research activity in the development of new reagents and synthetic methods based on the organic chemistry of hypervalent iodine.[1] The overwhelming majority of the known, stable organic polyvalent iodine compounds have a benzene ring as a carbon ligand linked to the iodine atom. Derivatives of polyvalent iodine with an alkyl substituent at the iodine generally are highly unstable and can exist only as short-lived reactive intermediates in the oxidation of alkyl iodides. However, introduction of an electron-withdrawing substituent in the alkyl moiety may lead to significant stabilization of the molecule. Especially interesting and useful representatives of such stabilized compounds with $I{-}C_{sp3}$-bonding are (fluoroalkyl)iodanes.[1a,b] The first representatives of stable (fluoroalkyl)iodanes, namely 1-[bis(trifluoroacetoxy)iodo]perfluoroalkanes, $R_fI(OCOCF_3)_2$, and (perfluoroalkyl)(phenyl)iodonium salts, R_fIPhX, were reported by Yagupolskii and co-workers in 1970.[2] A few years later, Umemoto and co-workers demonstrated that (fluoroalkyl)(phenyl)iodonium sulfonates can be used as efficient electrophilic fluoroalkylating reagents.[3,4] One of the more recent developments in the area of (fluoroalkyl)iodonium chemistry has been the preparation of 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes, $R_fCH_2ICl_2$, relatively stable alkyl derivatives of trivalent iodine, that can serve as precursors to useful (1*H*,1*H*-perfluoroalkyl)(phenyl)iodonium triflates.[5] However, these compounds, $R_fCH_2ICl_2$, have only limited synthetic value since they generally require conversion to more electrophilic trifluoroacetates by $AgOCOCF_3$.[5a] In this paper we wish to report the preparation and properties of sulfonates **3a**−**f** (Table 1),[6] which are more stable then 1-(dichloroiodo)-1*H*,1*H*-perfluoroalkanes and have a useful reactivity pattern, similar to Koser's reagent,[1a−c] PhI(OH)OTs.

Table 1. 1-[Hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes 3

product	*n*	R	mp, °C	yield,[a] %
3a	1	Tol	123−125	90
3b	1	Me	105−107	86
3c	1	CF_3	58−61	70
3d	2	Tol	124−125	96
3e	2	Me	97−99	97
3f	2	CF_3	105−109	92

[a] Preparative yield.

Results and Discussion

Sulfonates **3a**−**f** can be conveniently prepared in two steps from the commercially available 1*H*,1*H*-perfluoroalkyl iodides **1** (Scheme 1). In the first step, starting iodides **1** are oxidized with peroxytrifluoroacetic acid to trifluoroacetates **2** in almost quantitative yield by a known procedure.[4b] The subsequent treatment of trifluoroacetates **2** with the monohydrate of *p*-toluenesulfonic acid or methanesulfonic acid in acetonitrile at low temperature results in the formation of tosylates **3a,d** or mesylates **3b,e** in high yield. In contrast to starting trifluoroacetates **2**, tosylates **3a,d** have a substantially higher thermal stability, melting at about 124 °C without decomposition. Both tosylates **3a,d** and mesylates **3b,e** are not water sensitive, can be purified by crystallization

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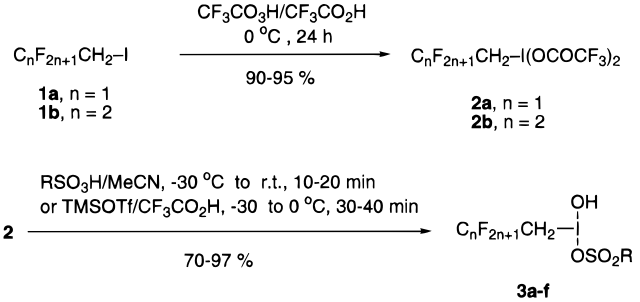
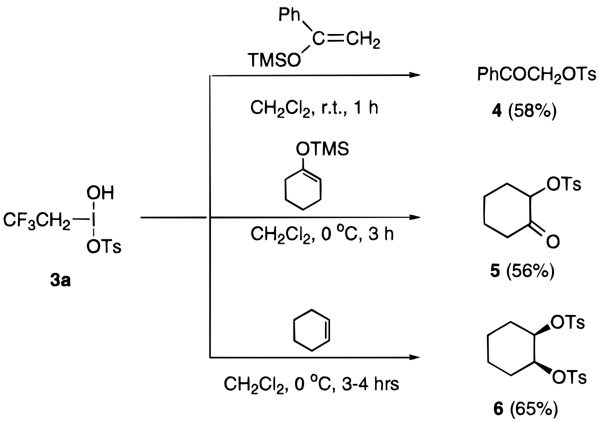
Scheme 1



Scheme 2



from acetonitrile, and can be stored for several months in a refrigerator. The analogous triflates **3c,f** were prepared in good yield by the reaction of trifluoroacetates **2** with trimethylsilyl triflate in dichloromethane and were isolated as colorless, stable, nonhygroscopic solids. The structures of compounds **3a**−**f** were determined by IR, NMR, and elemental analysis. In particular, the ^{1}H NMR displayed the characteristic signals of methylene protons at $\delta = 4.9$-5 ppm as a quartet ($n = 1$) or a triplet ($n = 2$) with $J_{H-F} = 10$ Hz. The broad signal of the hydroxyl proton was observed at about 3 ppm for all compounds **3**, as well as the respective signals of Ts or Ms groups for **3a,d** and **3b,e**.

Investigation of chemical properties of compounds **3** has shown that their reactivity pattern is similar to Koser's reagent, PhI(OH)OTs, and Zefirov's reagent, PhI(OTf)O(OTf)IPh.[1a−c] Similar to their phenyl−substituted analogs, compounds **3** are highly reactive toward electron-rich organic substrates, such as silyl enol ethers, alkenes, aryltrimethylsilanes, and alkynyltrimethylsilanes. We have found that reagent **3a** reacts with the silyl enol ethers of acetophenone and cyclohexanone under mild conditions to afford α-(tosyloxy) ketones **4** and **5** as major products (Scheme 2). These reactions give only volatile byproducts (bp of CF_3CH_2I is 55 °C), which significantly facilitates reaction workup. Products **4** and **5** were identified by comparison of their melting points and NMR spectra with literature data.[7]

Similar to Koser's reagent, tosylate **3a** reacts with cyclohexene to afford *cis*-1,2-bis(tosyloxy)cyclohexane **6**[8] (Scheme 2) as the major product. This reaction is completed in 3−4 h at 0 °C, while the analogous reaction of Koser's reagent requires 4 days at room temperature for completion, which indicates substantially higher reactivity of tosylate **3a** compared to PhI(OH)OTs. It is also interesting to compare the reactivity of tosylate **3a** and its perfluoroalkylated analog, $C_4F_9I(OH)OTs$,[9,10] in the reaction with cyclohexene. In contrast to tosylate **3a** and Koser's reagent, $C_4F_9I(OH)OTs$ reacts with cyclohexene under similar conditions to afford *trans*-1-iodo-2-(tosyloxy)cyclohexane, but not *cis*-ditosylate **6**, as the major product.[9]

Scheme 3

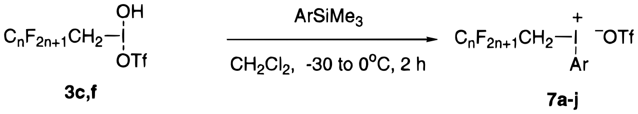


Table 2. (1*H*,1*H*-Perfluoroalkyl)(aryl)iodonium Triflates 7

product	*n*	Ar	mp, °C	yield,[a] %
7a[4b]	1	Ph	91−93 (88−89)[4b]	85
7b	1	4-TMSC$_6$H$_4$	88−90	62
7c	1	2-MeC$_6$H$_4$	75−77	72
7d	1	4-MeC$_6$H$_4$	77−80	78
7e	1	4-MeOC$_6$H$_4$	92−94	77
7f[4b]	2	Ph	127−129 (130)[4b]	71
7g	2	4-TMSC$_6$H$_4$	130−132	75
7h	2	2-MeC$_6$H$_4$	106−108	75
7i	2	4-MeC$_6$H$_4$	124−126	65
7j	2	4-MeOC$_6$H$_4$	147−148	74

[a] Preparative yield.

Similar to their phenyl−substituted analogs, compounds **3** can be used for the preparation of iodonium salts via reaction with the respective trimethylsilane derivatives. We have found that triflates **3c** and **3f** can serve as convenient precursors to (1*H*,1*H*-perfluoroalkyl)(aryl)iodonium triflates **7** (Scheme 3, Table 2) which are useful electrophilic fluoroalkylating agents.[4,5] Reagents **3c**,**f** smoothly react with aryltrimethylsilanes in methylene chloride under very mild conditions to give iodonium salts **7** in high yields. Products **7** were crystallized from ether−hexane and characterized by IR, NMR, and elemental analysis. In contrast to previously reported methods,[4,5] the preparation of **7** does not require the presence of triflic acid. Therefore, our method can, in principle, be generalized to acid-sensitive substrates.

It is noteworthy that triflates **3c,f** are more reactive toward arylsilanes than the previously reported (perfluoroalkyl)iodonium triflates, $C_nF_{2n+1}I(OH)OTf$.[10] Reaction of $C_nF_{2n+1}I(OH)OTf$ with ArTMS generally require the presence of Me_3SiOTf or trifluoroacetic acid as a catalyst, whereas triflates **3c,f** smoothly react with ArTMS without the presence of a catalyst and at low temperatures.

Under similar conditions, triflates **3c,f** react with various substituted (trimethylsilyl)acetylenes to afford novel (fluoroalkyl)(alkynyl)iodonium salts **8** (Table 3). Products **8** are substantially less stable than their aryl-substituted analogs, decomposing after only 2−3 days of storage in a refrigerator. Nevertheless, all compounds **8** were characterized by their IR and NMR spectra. All IR spectra displayed the typical C≡C stretch[1k] between 2165 and 2145 cm^{-1}, along with CF absorbances from 1250 to 1000 cm^{-1}. ^{1}H NMR spectra showed the signal

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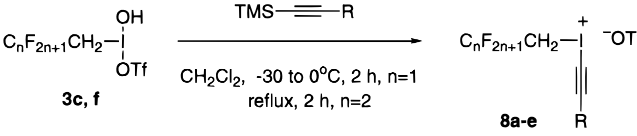
Table 3. (1*H*,1*H*-Perfluoroalkyl)(alkynyl)iodonium Triflates 8

product	*n*	R	mp, °C	yield,[a] %
8a	1	*t*-Bu	70−72	74
8b	1	TMS	54−57	70
8c	1	Ph	66−68	65
8d	2	*t*-Bu	122−124	76
8e	2	Ph	101−102	55

[a] Preparative yield.

Scheme 4



of R_fCH_2 protons as a quartet or a triplet at 4.7−4.9 ppm with $J_{H-F} = 10$ Hz. In the ^{13}C NMR spectrum of **8**, the acetylenic signals have chemical shifts −8 to 20 ($C{\equiv}CI$) and 94 to 104 ($C{\equiv}CI$) ppm, which are typical of alkynyliodonium salts.[1k]

Considering the useful properties of alkynyliodonium salts,[1k,1] the preparation of products **8a**−**e** is of particular interest. It is noteworthy that the previously reported (perfluoroalkyl)iodonium triflates, $C_nF_{2n+1}I(OH)OTf$[10] did not react with (trimethylsilyl)acetylenes, and we were therefore not able to prepare the analogous (perfluoroalkyl)(alkynyl)iodonium salts, $C_nF_{2n+1}I(C{\equiv}CR)OTf$.

It should be emphasized that reactivity of sulfonates **3** toward organic substrates is different from the previously reported [hydroxy(sulfonyloxy)iodo]perfluoroalkanes, $C_nF_{2n+1}I(OH)OSO_2R$. Specifically, $C_4F_9I(OH)OTs$ reacts with cyclohexene to afford *trans*-1-iodo-2-(tosyloxy)cyclohexane,[9] while a similar reaction of $CF_3CH_2I(OH)OTs$ gives *cis*-ditosylate **6** as the major product. This reactivity difference is most likely explained by the higher electronegativity of the C_nF_{2n+1} group compared to the $C_nF_{2n+1}CH_2$ moiety. As a result, the C−I bond in C_nF_{2n+1}−I(OH)OX has more ionic character than in $C_nF_{2n+1}CH_2$−I(OH)OX and will cleave easier under polar conditions. In general, we can speculate that the C−I bond polarities in **3** and in Koser's reagent are similar, which explains the observed similarities in their reactivity.

In conclusion, we have prepared and isolated as individual, stable compounds 1-[hydroxy(sulfonyloxy)iodo]-1*H*,1*H*-perfluoroalkanes **3**, a new structural type of iodine(III) sulfonate. These compounds have a reactivity pattern similar to Koser's reagent and therefore are useful for vicinal oxytosylations and for the synthesis of α-(tosyloxy) ketones. Triflates **3c,f** react with (trimethylsilyl)arenes under mild conditions to afford the respective (fluoroalkyl)(aryl)iodonium triflates **7**, while the analogous reaction with alkynyltrimethylsilanes leads to novel (fluoroalkyl)(alkynyl)iodonium salts **8**.

Experimental Section

General Procedures. All melting points were determined in an open capillary tube and are uncorrected. NMR spectra were recorded at 200 MHz (^1H NMR) and 50 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm); ^1H and ^{13}C chemical shifts are referenced to the proton resonance due to the residual protons in the deuteriated NMR solvent. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, GA.

All commercial reagents were ACS reagent grade and used without further purification. 1-[Bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroalkanes **2** were prepared by oxidation of the appropriate, commercial iodofluoroalkanes with peroxytrifluoroacetic acid according to a known procedure[4b] and were used without additional purification. (Trimethylsilyl)arenes were prepared from the corresponding bromo- or iodoarenes by lithiation with butyllithium followed by quenching with chlorotrimethylsilane.[11] 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-[Hydroxy(tosyloxy)iodo]-1*H*,1*H*-perfluoroethane (3a): Typical Procedure. To a stirred solution of $TsOH{\cdot}H_2O$ (0.23 g, 1.2 mmol) in acetonitrile (15−20 mL) was added 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroethane (**2a**) (0.500 g, 1.15 mmol) at −30 °C. The mixture was warmed to room temperature and stirred until a white crystalline precipitate of **3a** formed. The product was filtered, washed with dry CH_2Cl_2 (10 mL), and dried in vacuo to afford 0.41 g (90%) of analytically pure **3a** as white needles: mp 123−124 °C; IR (KBr) 3467, 3044, 2944, 2922, 1383, 1289, 1250, 1183, 1128, 1039, 1011 cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 5:1) δ 7.65 (d, 2H, $J = 8$ Hz), 7.15 (d, 2H, $J = 8$ Hz), 4.93 (q, 2H, $J_{H-F} = 10$ Hz), 2.8 (br s, 1H, OH), 2.3 (s, 3H). Anal. Calcd for $C_9H_{10}IF_3O_4S$: C, 27.15; H, 2.53; I, 31.87. Found: C, 27.17; H, 2.54; I, 31.78.

1-[Hydroxy(tosyloxy)iodo]-1*H*,1*H*-perfluoropropane (3d). According to the above typical procedure, $TsOH{\cdot}H_2O$ (0.23 g, 1.2 mmol) was reacted with 1-bis(trifluoroacetoxy)-iodo]-1*H*,1*H*-perfluoropropane (**2b**) (0.559 g, 1.15 mmol) to afford 0.494 g (96%) of **3d** as white needles: mp 124−125 °C; IR (KBr) 3467, 3044, 2944, 2922, 1383, 1289, 1250, 1183, 1128, 1039, 1011 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 5:1) δ 7.67 (d, 2H, $J = 8$ Hz), 7.17 (d, 2H, $J = 8$ Hz), 4.73 (t, 2H, $J_{H-F} = 10$ Hz), 2.36 (s, 3H), 2.08 (br s, 1H, OH). Anal. Calcd for $C_{10}H_{10}IF_5O_4S$: C, 26.80; H, 2.25; I, 28.32. Found: C, 26.47; H, 2.15; I, 28.04.

1-[Hydroxy(methanesulfonyloxy)iodo]-1*H*,1*H*-perfluoroethane (3b): Typical Procedure. To a stirred solution of 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroethane (**2a**) (0.5 g, 1.15 mmol) in acetonitrile (15−20 mL) was added neat methanesulfonic acid (0.1 mL, 1.4 mmol) dropwise at −30 °C. The mixture was then warmed to room temperature and stirred until a white crystalline precipitate of **3b** formed. The product was filtered, washed with dry CH_2Cl_2 (10 mL), and dried in vacuo to afford 0.32 g (86%) of analytically pure **3b** as white needles: mp 105−107 °C; IR (KBr) 3433, 2944, 1233, 1189, 1117, 1061 cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 5:1) δ 4.91 (q, 2H, $J_{H-F} = 10$ Hz), 3.2 (br s, 1H, OH), 2.9 (s, 3H). Anal. Calcd for $C_3H_6IF_3O_4S$: C, 11.19; H, 1.88; I, 39.41. Found: C, 11.09; H, 1.83; I, 39.47.

1-[Hydroxy(methanesulfonyloxy)iodo]-1*H*,1*H*-perfluoropropane (3e). According to the above typical procedure, 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoropropane (**2b**) (0.559 g, 1.15 mmol) was reacted with neat methanesulfonic acid (0.1 mL, 1.4 mmol) to afford 0.415 g (97%) of analytically pure **3e** as white needles: mp 107−109 °C; IR (KBr) 3433, 2944, 1233, 1189, 1117, 1061 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6, 5:1) δ 7.35 (br s, 3H, OH), 4.79 (t, 2H, $J_{H-F} = 10$ Hz), 2.81 (s, 3H). Anal. Calcd for $C_4H_6IF_5O_4S{\cdot}H_2O$: C, 12.32; H, 2.07; I, 33.53. Found: C, 12.70; H, 2.08; I, 33.80.

1-[Hydroxy[(trifluoromethanesulfonyl)oxy]iodo]-1*H*,1*H*-perfluoroethane (3c): Typical Procedure. To a stirred mixture of 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoroethane (**2a**) (0.559 g, 1.15 mmol) in 15−20 mL of dry CH_2Cl_2 was added 0.3 mL (1.5 mmol) of trimethylsilyl triflate at −30 °C. The resulting mixture was warmed to room temperature and stirred until a white precipitate of **3c** formed. The product was filtered, washed with dry hexane (10 mL), and dried under high vacuum to afford 0.3 g (70%) of analytically pure **3c** as a white waxy solid: mp 111−113 °C dec; IR (KBr) 3444, 2956, 1261, 1178, 1117, 1033 cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 5:1) δ 4.93 (q, 2H, $J_{H-F} = 10$ Hz), 3.9 (br s, 1H, OH). Anal. Calcd for $C_3H_3IF_6O_4S$: C, 9.58; H, 0.80; I, 33.75. Found: C, 9.49; H, 0.79; I, 33.69.

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1-[Hydroxy[(trifluoromethanesulfonyl)oxy]iodo]-1*H*,1*H*-perfluoropropane (3f). According to the above typical procedure, 1-[bis(trifluoroacetoxy)iodo]-1*H*,1*H*-perfluoropropane-(**2b**) (0.559 g, 1.15 mmol) was reacted with 0.3 mL (1.5 mmol) of trimethylsilyl triflate to afford 0.452 g (92%) of **3f** as a white, waxy solid: mp 105−109 °C dec; IR (KBr) 3444, 2956, 1261, 1178, 1117, 1033 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3CN$, 5:1) δ 6.02 (br s, 1H, OH), 4.93 (t, 2H, J_{H-F} = 10 Hz). Anal. Calcd for $C_4H_3IF_8O_4S$: C, 11.28; H, 0.71; I, 29.79. Found: C, 11.12; H, 0.70; I, 29.38.

Reactions of 1-[Hydroxy(tosyloxy)iodo]-1*H*,1*H*-perfluoroethane (3a) with Silyl Enol Ethers and Cyclohexene: Typical Procedure. To a stirred mixture of tosylate **3a** (0.300 g, 0.76 mmol) in methylene chloride (20 mL) was added 1-phenyl-1-[(trimethylsilyl)oxy]ethylene (0.17 mL, 0.78 mmol) dropwise at room temperature. The mixture was stirred for 1 h until a clear solution formed. The solvent was then evaporated, and the crude product was recrystallized from ether−hexane to give (tosyloxy)acetophenone (**4**) as a white microcrystalline solid: yield 0.127 g (58%); mp 92−94 °C (lit.[7] mp 91−92 °C).

Similarly, reaction of tosylate **3a** (0.2 g, 0.5 mmol) in methylene chloride (20 mL) with (1-cyclohexenyloxy)trimethylsilane (0.11 mL, 0.55 mmol) was carried out at 0 °C to give α-(tosyloxy)cyclohexanone (**5**) as a white microcrystalline solid: yield 0.075 g (56%); mp 73−75 °C (lit.[7] mp 74−76 °C). Under similar conditions, reaction of tosylate **3a** (0.300 g, 0.76 mmol) with cyclohexene (0.1 mL, 1.0 mmol) at 0 °C afforded *cis*-1,2-bis(tosyloxy)cyclohexane **6**: yield 0.094 g (65%); mp 115−118 °C (lit.[8] mp 115−117 °C, α-form).

(1*H*,1*H*-Perfluoroethyl)[4-(trimethylsilyl)phenyl]iodonium Triflate (7b): Typical Procedure. To a stirred mixture of 1-[hydroxy[(trifluoromethanesulfonyl)oxy]iodo]-1*H*,1*H*-perfluoroethane (**3c**) (0.200 g, 0.53 mmol) in methylene chloride (20 mL) was added 1,4-bis(trimethylsilyl)benzene (0.130 g, 0.6 mmol) in portions at −20 °C. The mixture was warmed to room temperature and allowed to stir for 1−2 h until a clear solution formed. The solvent was then evaporated, and the crude product **7b** was recrystallized from ether−hexane to give a white microcrystalline solid. The solid was filtered and dried in vacuo: yield 0.191 g (62%); mp 88−90 °C; IR (KBr) 3060, 2951, 2889, 1566, 1371, 1248, 1172, 1034, 1001, 840, 801, 749, 706, 650, 645, 578, 516, 479 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.15 (d, 2H, J = 8 Hz), 7.69 (d, 2H, J = 8 Hz), 4.75 (q, 2H, J = 10 Hz), 0.29 (s, 9H). Anal. Calcd for $C_{12}H_{15}F_6IO_3SSi$: C, 28.36; H, 2.97; I, 24.97. Found: C, 27.99; H, 2.93; I, 24.88.

(1*H*,1*H*-Perfluoroethyl)(2-methylphenyl)iodonium Triflate (7c). According to the above typical procedure, **3c** (0.200 g, 0.53 mmol) was reacted with 2-(trimethylsilyl)toluene (0.12 mL, 0.58 mmol) to give **7c** as a white microcrystalline solid: yield 0.171 g (72%); mp 75−77 °C dec; IR (KBr) 3044, 2970, 1383, 1267, 1177, 1130, 1066, 1035, 1008, 745, 645, 576, 518 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, 1H, J = 8 Hz), 7.56 (m, 2H), 7.24 (t, 1H, J = 8 Hz), 4.57 (q, 2H, J = 10 Hz), 2.62 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 141.4, 139.0, 129.8, 128.1, 127.4, 120.9 (q, J = 278 Hz), 118.4 (q, J = 320 Hz), 101.1, 68.5 (q, J = 39 Hz), 28.0. Anal. Calcd for $C_{10}H_9F_6IO_3S$: C, 26.68; H, 2.02; I, 28.19. Found: C, 26.57; H, 2.04; I, 28.28.

(1*H*,1*H*-Perfluoroethyl)(4-methylphenyl)iodonium Triflate (7d). According to the above typical procedure, **3c** (0.200 g, 0.53 mmol) was reacted with 4-(trimethylsilyl)toluene (0.12 mL, 0.58 mmol) to give **7d** as a white microcrystalline solid: yield 0.185 g (78%); mp 76−80 °C dec; IR (KBr) 3031, 2955, 1481, 1381, 1262, 1177, 1115, 1034, 1001, 797, 645, 578, 517, 474 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 2H, J = 8 Hz), 7.32 (d, 2H, J = 8 Hz), 4.67 (q, 2H, J = 10 Hz), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3/CD_3CN$, 10:1) δ 137.1, 136.7, 130.8, 120.9 (q, J = 278 Hz), 118.4 (q, J = 320 Hz), 89.4, 68.5 (q, J = 39 Hz), 20.3. Anal. Calcd for $C_{10}H_9F_6IO_3S$: C, 26.68; H, 2.02. Found: C, 27.04; H, 2.08.

(1*H*,1*H*-Perfluoroethyl)(4-methoxyphenyl)iodonium Triflate (7e). According to the above typical procedure, **3c** (0.200 g, 0.53 mmol) was reacted with 4-(trimethylsilyl)anisole (0.15 mL, 0.59 mmol) at −40 °C to give **7e** as a white microcrystalline solid: yield 0.190 g (77%); mp 92−94 °C dec; IR (KBr) 3028, 2959, 2837, 1584, 1485, 1286, 1259, 1247, 1177, 1129, 1033, 995, 830, 811, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 2H, J = 8 Hz), 6.98 (d, 2H, J = 8 Hz), 4.65 (q, 2H, J = 10 Hz), 3.89 (s, 3H). Anal. Calcd for $C_{10}H_9F_6IO_4S$: C, 25.77; H, 1.95; I, 27.22. Found: C, 25.69; H, 2.00; I, 27.31.

(1*H*,1*H*-Perfluoropropyl)[4-(trimethylsilyl)phenyl]iodonium Triflate (7g). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 1,4-bis(trimethylsilyl)benzene (0.116 g, 0.52 mmol) at 0 °C to give **7g** as a white microcrystalline solid: yield 0.197 g (75%); mp 130−132 °C dec; IR (CCl_4) 3023, 2952, 1328, 1268, 1248, 1212, 1172, 1045, 1010, 853, 843, 803, 752, 707, 651, 515 cm^{-1}; ^{1}H NMR ($CDCl_3$ δ 8.17 (d, 2H, J = 8 Hz), 7.62 (d, 2H, J = 8 Hz), 4.70 (t, 2H, J = 10 Hz), 0.29 (s, 9H). Anal. Calcd for $C_{13}H_{15}F_8IO_3SSi$: C, 27.97; H, 2.71; I, 22.73. Found: C, 27.85; H, 2.69; I, 22.87.

(1*H*,1*H*-Perfluoropropyl)(2-methylphenyl)iodonium Triflate (7h). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 2-(trimethylsilyl)toluene (0.10 mL, 0.52 mmol) at 0 °C to give **7h** as a white microcrystalline solid: yield 0.176 g (75%); mp 106−108 °C dec; IR (KBr) 3023, 2952, 1335, 1270, 1245, 1230, 1211, 1195, 1171, 1034, 1012, 795, 707, 650 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3CN$, 10:1) δ 8.17 (d, 1H, J = 8 Hz), 7.56 (m, 2H), 7.24 (t, 1H, J = 8 Hz), 4.62 (t, 2H, J = 10 Hz), 2.68 (s, 3H). Anal. Calcd for $C_{11}H_9F_8IO_3S$: C, 26.42; H, 1.81; I, 25.37. Found: C, 26.53; H, 1.85; I, 25.46.

(1*H*,1*H*-Perfluoropropyl)(4-methylphenyl)iodonium Triflate (7i). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 4-(trimethylsilyl)toluene (0.10 mL, 0.52 mmol) at 0 °C to give **7i** as a white microcrystalline solid: yield 0.152 g (65%); mp 124−126 °C dec; IR (KBr) 3043, 2952, 1333, 1268, 1248, 1235, 1212, 1197, 1172, 1035, 1010, 798, 707, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.96 (d, 2H, J = 8 Hz), 7.32 (d, 2H, J = 8 Hz), 4.67 (t, 2H, J = 10 Hz), 2.45 (s, 3H). Anal. Calcd for $C_{11}H_9F_8IO_3S$: C, 26.42; H, 1.81; I, 25.37. Found: C, 26.30; H, 1.85; I, 25.44.

(1*H*,1*H*-Perfluoropropyl)(4-methoxyphenyl)iodonium Triflate (7j). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 2-(trimethylsilyl)toluene (0.10 mL, 0.52 mmol) at 0 °C to give **7j** as a white, microcrystalline solid, which was filtered directly out of the reaction mixture: yield 0.179 g (74%); mp 147−148 °C dec; IR (CCl_4) 3098, 3010, 2951, 2833, 1572, 1488, 1459, 1439, 1405, 1331, 1306, 1267, 1238, 1223, 1164, 1056, 1046, 1012, 638, 574, 515 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 2H, J = 8 Hz), 7.04 (d, 2H, J = 8 Hz), 4.70 (t, 2H, J = 10 Hz), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3/CF_3CO_2H$, 10:1) δ 164.8, 139.4, 120.9 (q, J = 278 Hz), 119.0, 118.4 (q, J = 320 Hz), 93.9, 56.0, 35.7 (q, J = 39 Hz), 20.3. Anal. Calcd for $C_{11}H_9F_8IO_4S$: C, 25.60; H, 1.76; I, 24.59. Found: C, 25.48; H, 1.79; I, 24.70.

(1*H*,1*H*-Perfluoroethyl)[(trimethylsilyl)ethynyl]iodonium Triflate (8b): Typical Procedure. To a stirred mixture of 1-[hydroxy[(trifluoromethanesulfonyl)oxy]iodo]-1*H*,1*H*-perfluoroethane (**3c**) (0.200 g, 0.53 mmol) in methylene chloride (20 mL) was added bis(trimethylsilyl)acetylene (0.14 mL, 0.6 mmol) in portions at −10 °C. The mixture was warmed to room temperature and allowed to stir for 1−2 h until a clear solution formed. The solvent was then evaporated, and the crude product **8b** was recrystallized from dichloromethane−hexane to give a white microcrystalline solid. The solid was filtered and dried in vacuo: yield 0.169 g (70%); mp 54−57 °C dec; IR (CCl_4): 2966, 2900, 2100, 1560, 1414, 1250, 1004, 857, 840, 699, 623 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.72 (q, 2H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 120.7 (q, J = 278 Hz), 118.6 (q, J = 320 Hz), 104.1, 68.4 (q, J = 39 Hz), 20.2, −0.2.

(1*H*,1*H*-Perfluoroethyl)(3,3-dimethylbutynyl)iodonium Triflate (8a). According to the above typical procedure, **3c** (0.200 g, 0.53 mmol) was reacted with 1-(trimethylsilyl)-3,3-dimethylbutyne (0.15 mL, 0.6 mmol) to give **8a** as a white microcrystalline solid: yield 0.165 g (74%); mp 70−72 °C dec; IR (CCl_4) 3034, 2976, 2937, 2908, 2869, 2180, 2151, 1455, 1401, 1367, 1285, 1217, 1173, 1135, 1062, 1023, 834, 635, 577, 514 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.72 (q, 2H, J = 10 Hz), 1.23 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 120.9 (q, J = 278 Hz), 118.7 (q, J = 320 Hz), 102.9, 68.4 (q, J = 39 Hz), 30.8, 29.8, −8.3.

(1*H*,1*H*-Perfluoroethyl)(phenylethynyl)iodonium Triflate (8c). According to the above typical procedure, **3c** (0.200 g, 0.53 mmol) was reacted with 1-phenyl-2-(trimethylsilyl)ethyne (0.15 mL, 0.6 mmol) to give **8c** as a white microcrystalline solid: yield 0.155 g (65%); mp 66−68 °C dec; IR (CCl_4) 3067, 3028, 2158, 1490, 1438, 1419, 1237, 1213, 1136, 1064, 1021, 959, 854, 686, 596, 519 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42 (m, 2H), 7.31 (m, 3H), 4.72 (q, 2H, $J = 10$ Hz); ^{13}C NMR ($CDCl_3/CD_3CN$, 10:1) δ 131.9, 128.5, 128.0, 123.0, 120.9 (q, $J = 278$ Hz), 118.7 (q, $J = 320$ Hz), 93.6, 68.3 (q, $J = 39$ Hz), 6.6.

(1*H*,1*H*-Perfluoropropyl)(3,3-dimethylbutynyl)iodonium Triflate (8d). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 1-(trimethylsilyl)-3,3-dimethylbutyne (0.10 mL, 0.56 mmol) to give **8d** as a white microcrystalline solid: yield 0.174 g (76%); mp 122−124 °C dec; IR (CCl_4) 3027, 2968, 2939, 2909, 2870, 2180, 2151, 1406, 1332, 1283, 1219, 1180, 1057, 1017, 707, 633, 574, 515 cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$, 10:1) δ 4.73 (t, 2H, $J = 10$ Hz), 1.30 (s, 9H).

(1*H*,1*H*-Perfluoropropyl)(phenylethynyl)iodonium Triflate (8e). According to the above typical procedure, **3f** (0.200 g, 0.47 mmol) was reacted with 1-phenyl-2-(trimethylsilyl)ethyne (0.11 mL, 0.56 mmol) to give **8f** as a white microcrystalline solid: yield 0.165 g (74%); mp 102−104 °C dec; IR (CCl_4) 3040, 2970, 2162, 1405, 1329, 1286, 1229, 1213, 1192, 1174, 1055, 1015, 793, 784, 757, 713, 683, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (m, 5H), 4.85 (t, 2H, $J = 10$ Hz); ^{13}C NMR ($CDCl_3/CD_3CN$, 10:1) δ 131.9, 128.4, 128.0, 123.0, 121−105 (a group of multiplets), 118.7 (q, $J = 320$ Hz), 93.9, 67.8 (t, $J = 39$ Hz), 6.9.

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Supporting Information Available: Copies of ^1H NMR for compounds **8a**,**b,d** and copies of ^{13}C NMR for **8a,c,e** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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