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A General and Convenient Preparation of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes and [Bis(trifluoroacetoxy)iodo]arenes by Oxidation of Organic Iodides Using Oxone and Trifluoroacetic Acid

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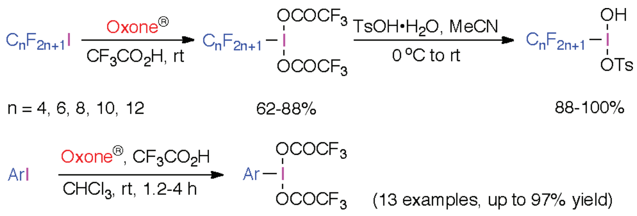
Received January 11, 2010



[Bis(trifluoroacetoxy)iodo]perfluoroalkanes $C_nF_{2n+1}I(OCOCF_3)_2$ (n = 4, 6, 8, 10, 12) can be conveniently prepared by the oxidation of the corresponding perfluoroalkyl iodides with Oxone in trifluoroacetic acid at room temperature and subsequently converted to the stable [hydroxy(tosyloxy)iodo]perfluoroalkanes, $C_nF_{2n+1}I(OH)OTs$, by treatment with *p*-toluenesulfonic acid. This general and convenient procedure has been further extended to the synthesis of various [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$.

[Bis(acyloxy)iodo]arenes and other polyvalent iodine carboxylates belong to the most important class of hypervalent iodine compounds, which are widely used in organic synthesis.[1] In a series of recent publications,[2] it has been demonstrated that [bis(trifluoroacetoxy)iodo]perfluoroalkanes as well as other fluorous iodine(III) derivatives[3] are particularly useful recyclable oxidizing reagents that can be easily recovered from the reaction mixture using fluorous techniques. The most common synthetic approach to the fluorous bis(trifluoroacetoxy) iodides involves the oxidation of appropriate perfluoroalkyl iodides with 80% hydrogen peroxide and trifluoroacetic anhydride,[2,4] which is a potentially hazardous and inconvenient procedure. Herein we report a straightforward experimental protocol for preparation of [bis(trifluoroacetoxy)iodo]perfluoroalkanes **2** by the oxidation of corresponding perfluoroalkyl iodides **1** with Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) in trifluoroacetic acid at room temperature. The relatively unstable and hygroscopic trifluoroacetates **2** can be subsequently converted to the stable [hydroxy(tosyloxy)iodo]perfluoroalkanes **3** in almost quantitative yields by treatment with *p*-toluenesulfonic acid (Scheme 1).

The yields and melting points of the fluorous iodine(III) products **2** and **3** are summarized in Table 1. Trifluoroacetates **2** were separated from inorganic salts by extraction with acetonitrile (for **2a**−**c**) or acetone (for **2d**,**e**) after evaporation of the reaction mixture. Crude products **2** were converted to tosylates **3** by treatment with $TsOH{\cdot}H_2O$ in acetonitrile or acetone. Analytically pure tosylates **3** were obtained by recrystallization from acetonitrile. All previously reported products were identified by comparison of their NMR spectra and mp with literature data;[4b] new products **3d**,**e** were identified by ^1H, ^{19}F, and ^{13}C NMR spectra and elemental analysis. The fluorous tosylates **3** are generally stable for storage at room temperature and, in contrast to the trifluoroacetates **2**, are not sensitive to light and moisture.

In the next step, we investigated the applicability of this convenient procedure to the synthesis of various [bis(trifluoroacetoxy)iodo]arenes, $ArI(OCOCF_3)_2$. The most general known synthetic approaches to $ArI(OCOCF_3)_2$ consist of heating (diacetoxyiodo)arenes in trifluoroacetic acid[5a,b] or the oxidation of the respective iodoarenes with peroxytrifluoroacetic acid in trifluoroacetic acid.[5b−d] A less common procedure involves the reactions of arenes with $I(OCOCF_3)_3$.[5e] Recently, Hossain and Kitamura reported a more convenient and safe method for preparing $ArI(OCOCF_3)_2$ in 36−87% yield from some iodoarenes by using a $K_2S_2O_8/CF_3CO_2H/CH_2Cl_2$ system at 38 °C for 20 h.[6] We have found that Oxone in chloroform and trifluoroacetic acid is a more efficient oxidizing system providing [bis(trifluoroacetoxy)iodo]arenes **5a**−**m** from iodoarenes **4** in generally excellent yields in 1−4 h at room temperature (Scheme 2). For example, our procedure affords

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DOI: 10.1021/jo902733f

SCHEME 1. Preparation of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes 2 and Tosylates 3

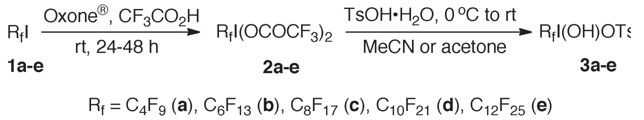


TABLE 1. Yields and Melting Points of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes $2^{a,b}$ and Tosylates 3^{c}

R_fI	yield of $2^{d,e}$ (%)	mp of 2^{e} (° C)	yield of $3^{d,e}$ (%)	mp of 3^{f} (° C)
1a	62	55−57	100	135−137
1b	88	65−67	99	141−143
1c	67	85−87	88	147−149
1d	63	65.5−66.5	99	97−99
1e	68	98−99	98	97^{g}

[a] Products **2a**−**c** were prepared by stirring **1a**−**c** (1 g) with Oxone (1 molar equiv) in trifluoroacetic acid (5 mL) at rt for 24 h at room temperature. [b] Products **2d**,**e** were prepared by stirring **1d**,**e** (0.5 g) with Oxone (0.5 molar equiv) in trifluoroacetic acid (7 mL) at rt for 48 h. [c] Tosylates **3** were prepared similarly to the previously reported procedure[4b] using acetonitrile (**3a**−**c**) or acetone (**3d**,**e**) as a solvent. [d] Isolated yields of analytically pure products. [e] Recrystallized from trifluoroacetic acid−hexane, 1:10. [f] Recrystallized from acetonitrile. [g] With decomposition (turns dark).

$PhI(OCOCF_3)_2$ **4a** in 97% yield after 1.2 h at room temperature (Table 2), compared to 76% yield using Hossain and Kitamura's procedure.[6]

The reaction conditions, yields, and melting points of [bis(trifluoroacetoxy)iodo]arenes **5** are summarized in Table 2. Trifluoroacetates **5** were separated from inorganic salts by extraction with chloroform after evaporation of the reaction mixture. Analytically pure products **5** were obtained by recrystallization from hexane in the presence of a small amount of trifluoroacetic acid. All previously reported products were identified by comparison of their NMR spectra and melting points with literature data; new products **5e**, **5f**, and **5k** were identified by NMR spectra and elemental analysis. The pentafluorophenyl derivative **5m** was additionally identified by conversion to [hydroxy(tosyloxy)iodo]pentafluorobenzene **6** using a reaction with $TsOH \cdot H_2O$ in acetonitrile (Scheme 3).

In conclusion, we have reported a safe, convenient, and efficient method for preparing fluorous [bis(trifluoroacetoxy)iodo]perfluoroalkanes **2** by the oxidation of the corresponding perfluoroalkyl iodides **1** with Oxone in trifluoroacetic acid at room temperature. The trifluoroacetates **2** can be further converted to [hydroxy(tosyloxy)iodo]perfluoroalkanes **3**, which are stable for storage at room temperature and, in contrast to the trifluoroacetates **2**, are not sensitive to light and moisture. This general and convenient procedure has been further extended to the synthesis of various [bis(trifluoroacetoxy)iodo]arenes **5** in good to excellent yields.

Experimental Section

Additional experimental details can be found in the Supporting Information.

General Procedure for Preparation of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes 2a−c. To a solution of an appropriate iodoperfluoroalkane **1a**−**c** (1 g) in trifluoroacetic acid (5 mL) was added Oxone (1 molar equiv) under stirring at room temperature. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the solvent was evaporated under vacuum and the residue was treated with acetonitrile (15 mL). The insoluble residue of inorganic salts was collected by filtration, washed with acetonitrile (10 mL), and discarded. Evaporation of combined acetonitrile extracts under reduced pressure afforded microcrystalline crude products **2**, which could be used for the preparation of tosylates **3d**,**e** without additional purification.

SCHEME 2. Preparation of [Bis(trifluoroacetoxy)iodo]arenes

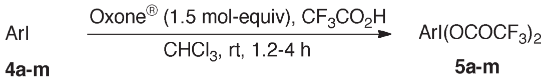
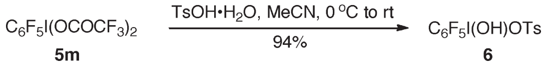


TABLE 2. Yields and Melting Points of Trifluoroacetates 5^{a}

ArI (**4**)	Ar	time (h)	yield of 5^{b} (%)	mp of $5^{c,d}$ (°C)
a	C_6H_5	1.2	97	118−120
b	$4\text{-}FC_6H_4$	1	80	94−96
c	$4\text{-}BrC_6H_4$	1.5	94	123−125
d	$4\text{-}ClC_6H_4$	1.5	69	128−130
e	$3\text{-}ClC_6H_4$	1.2	91	95−97
f	$2\text{-}ClC_6H_4$	1.2	97	98−100
g	$4\text{-}CF_3C_6H_4$	1.5	68	121−123
h	$3,5\text{-}(CF_3)_2C_6H_3$	1.5	94	82 dec
i	$4\text{-}NO_2C_6H_4$	1.5	69	157−159
j	$3\text{-}NO_2C_6H_4$	1.5	58	141−143
k	$4\text{-}HOOCC_6H_4$	4	54	109−111
l	$3\text{-}HOOCC_6H_4$	4	41	159−161
m	C_6F_5	2	94	$95.5−96.5^{e}$

[a] All reactions of iodoarenes **4a**−**m** (0.5 mmol) were performed at room temperature in the presence of Oxone (1.5 mol-equiv) in CF_3CO_2H (1.5 mL) and $CHCl_3$ (0.5 mL). [b] Isolated yields of analytically pure products. [c] All previously reported products **5** were identified by comparison of their NMR spectra and/or melting points with literature data; for analytical and spectroscopic characterization of new products (**5e**, **5f**, **5k**) see Experimental Section. [d] Recrystallized from trifluoroacetic acid-hexane, 1:10. [e] Additionally identified by conversion to $C_6F_5I(OH)OTs$, mp 160 °C.

SCHEME 3. Preparation of [Hydroxy(tosyloxy)iodo]pentafluorobenzene 6



[Bis(trifluoroacetoxy)iodo]perfluorobutane (2a). Reaction of perfluorobutyl iodide **1a** (1.00 g, 2.89 mmol) with Oxone (1.78 g, 2.89 mmol) according to the general procedure afforded 1.02 g (62%) of product **2a**, isolated as a microcrystalline solid. ^{19}F NMR (282 MHz, CD_3CN): δ −75.3 (br s), −76.2 (s), −80.2 (s), −115.4 (m), −125.0 (m).[7]

[Bis(trifluoroacetoxy)iodo]perfluorohexane (2b). Reaction of perfluorohexyl iodide **1b** (1.00 g, 2.24 mmol) with Oxone (1.38 g, 2.24 mmol) according to the general procedure afforded 1.32 g (88%) of product **2b**, isolated as microcrystalline solid. Mp: 65−67 °C (lit.[2c] mp 67 °C dec). ^{19}F NMR (282 MHz, CD_3OD): δ −75.2 (s), −75.8 (s), −80.7 (s), −113.1 (br s), −120.5 (br s), −122.2 (br s), −125.7 (br s). ^{13}C NMR (selected peaks) (125.6 MHz, CD_3OD): δ 115.6 (q, J_{CF} = 283 Hz).

[Bis(trifluoroacetoxy)iodo]perfluorooctane (2c). Reaction of perfluorooctyl iodide **1c** (1.00 g, 1.83 mmol) with Oxone (1.13 g, 1.83 mmol) according to the general procedure afforded 0.95 g (67%) of product **2c**, isolated as microcrystalline solid. ^{19}F NMR (282 MHz, acetone-d_6): δ −74.8 (s), −75.6 (s), −80.5 (s), −113.1 (br s), −120.3 (br s), −121.3 (br s), −122.1 (br s), −125.6 (br s).[2a]

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General Procedure for Preparation of [Bis(trifluoroacetoxy)iodo]perfluoroalkanes 2d,e. To a solution of an appropriate iodoperfluoroalkane (0.5 g) in trifluoroacetic acid (7 mL) was added Oxone (0.5 molar equiv) added under stirring at room temperature. The reaction mixture was stirred at room temperature for 48 h. After completion of the reaction, the solvent was evaporated under vacuum and the residue was treated with acetone (15 mL). The insoluble residue of inorganic salts was collected by filtration, washed with acetone (10 mL), and discarded. Evaporation of combined acetone extracts under reduced pressure afforded a solid crude product **2**, which could be used for the preparation of tosylates **3d**,**e** without additional purification.

[Bis(trifluoroacetoxy)iodo]perfluorodecane (2d). Reaction of perfluorodecyl iodide **1d** (0.50 g, 0.77 mmol) with Oxone (0.24 g, 0.385 mmol) according to the general procedure afforded 0.43 g (63%) of product **2d**, isolated as a microcrystalline solid. ^{19}F NMR (282 MHz, acetone-d_6): δ −63.9 (s), −75.5 (s), −80.6 (s), −113.1 (br s), −120.3 (br s), −121.1 (br s), −122.1 (br s), −125.6 (br s).[2a]

[Bis(trifluoroacetoxy)iodo]perfluorododecane (2e). Reaction of perfluorododecyl iodide **1e** (0.50 g, 0.67 mmol) with Oxone (0.21 g, 0.385 mmol) according to the general procedure afforded 0.44 g (68%) of product **2e**, isolated as a microcrystalline solid. ^{19}F NMR (282 MHz, acetone-d_6): δ −63.9 (s), −75.8 (s), −80.6 (s), −113.1 (br s), −120.3 (br s), −121.1 (br s), −122.0 (br s), −125.6 (br s). ^{13}C NMR (selected peaks) (125.6 MHz, acetone-d_6): δ 158.5 (q, J_{CF} = 40.3 Hz), 115.9 (q, J_{CF} = 286 Hz).[2a]

General Procedure for Preparation of [Hydroxy(tosyloxy)iodo]perfluoroalkanes 3a−c. To a stirred solution of TsOH·H$_2$O (1.25 molar equiv) in acetonitrile (5−10 mL) was added the appropriate trifluoroacetate **2** (1.14−1.82 mmol) at 0 °C. The mixture was warmed to room temperature and stirred until formation of a white crystalline precipitate. Evaporation of the solvent under reduced pressure afforded a crude product **3**. Analytically pure materials were obtained by recrystallization from acetonitrile.

[Hydroxy(tosyloxy)iodo]perfluorobutane (3a). Reaction of [bis(trifluoroacetoxy)iodo]perfluorobutane **2a** (0.92 g, 1.60 mmol) according to the general procedure afforded 0.85 g (100%) of product **3a**, isolated as a microcrystalline solid. Mp: 135−137 °C (lit.[4b] mp 137−139 °C). ^{1}H NMR (500 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ 7.70 (d, J = 7.4 Hz, 2H), 7.28 (d, J = 7.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (125.6 MHz, CDCl$_3$): δ 143.6, 137.2, 129.8, 125.5, 21.4. ^{19}F NMR (282 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ −80.5 (s), −83.7 (s), −116.2 (s), −125.1 (s).

[Hydroxy(tosyloxy)iodo]perfluorohexane (3b). Reaction of [bis(trifluoroacetoxy)iodo]perfluorohexane **2a** (1.22 g, 1.82 mmol) according to the general procedure afforded 1.14 g (99%) of product **3b**, isolated as a microcrystalline solid. Mp: 141−143 °C (lit.[4b] mp 142−144 °C). ^{1}H NMR (500 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ 7.68 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (selected peaks) (125.6 MHz, CD$_3$CN/DMSO-d_6, 22:1): δ 140.5, 128.9, 125.9, 20.5. ^{19}F NMR (282 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ −63.7 (s), −80.2 (s), −112.8 (br s), −120.3 (s), −121.9 (br s), −125.3 (br s).

[Hydroxy(tosyloxy)iodo]perfluorooctane (3c). Reaction of [bis(trifluoroacetoxy)iodo]perfluorooctane **2c** (0.877 g, 1.14 mmol) according to the general procedure afforded 0.73 g (88%) of product, isolated as a microcrystalline solid. Mp: 147−149 °C (lit.[4b] mp 147−149 °C). ^{1}H NMR (500 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ 7.68 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (selected peaks) (125.6 MHz, CD$_3$CN/DMSO-d_6, 22:1): δ 140.1, 128.8, 125.9, 20.5. ^{19}F NMR (282 MHz, CD$_3$CN/DMSO-d_6, 20:1): δ −75.4 (s), −80.2 (s), −82.7 (s), −112.9 (s), −119.9 (s), −121.0 (s), −121.9 (br s), −125.3 (s).

General Procedure for Preparation of [Hydroxy(tosyloxy)iodo]perfluoroalkanes 3d,e. To a stirred solution of TsOH·H$_2$O (1.25 molar equiv) in acetone (5−10 mL) was added the appropriate trifluoroacetate **2** (0.19−0.43 mmol) at 0 °C. The mixture was warmed to room temperature and stirred until the formation of a slightly yellow crystalline precipitate. Evaporation of the solvent under reduced pressure afforded a pure product.

[Hydroxy(tosyloxy)iodo]perfluorodecane (3d). Reaction of [bis(trifluoroacetoxy)iodo]perfluorodecane **2d** (0.375 g, 0.43 mmol) according to the general procedure afforded 0.355 g (99%) of product **3d**, isolated as a microcrystalline solid. Mp: 97−99 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.78 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (selected peaks) (125.6 MHz, acetone-d_6): δ 144.2, 138.9, 130.4, 127.5, 21.4. ^{19}F NMR (282 MHz, acetone-d_6): δ −63.9 (s), −80.6 (s), −113.1 (s), −120.3 (s), −121.2 (s), −122.2 (br s), −125.7 (s). Anal. Calcd for C$_{17}$H$_8$F$_{21}$IO$_4$S: C, 24.48; H, 0.97. Found: C, 24.21; H, 0.90.

[Hydroxy(tosyloxy)iodo]perfluorododecane (3e). Reaction of [bis(trifluoroacetoxy)iodo]perfluorododecane **2e** (0.19 g, 0.195 mmol) according to the general procedure afforded 0.18 g (98%) of product **3e**, isolated as a microcrystalline solid. Mp: 97 °C dec. ^{1}H NMR (500 MHz, acetone-d_6): δ 7.78 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (selected peaks) (125.6 MHz, acetone-d_6): δ 130.3, 127.5, 21.4. ^{19}F NMR (282 MHz, acetone-d_6): δ −63.9 (s), −80.5 (s), −113.0 (s), −120.3 (s), −121.1 (s), −122.1 (s), −125.6 (s). Anal. Calcd for C$_{19}$H$_8$F$_{25}$IO$_4$S: C, 24.43; H, 0.86; F, 50.84; S, 3.43. Found: C, 24.02; H, 0.89; F, 50.49; S, 3.32.

General Procedure for Preparation of [Bis(trifluoroacetoxy)iodo]arenes 5. To a solution of an appropriate iodoarene **4** (0.5 mmol) in a mixture of trifluoroacetic acid (1.5 mL) and chloroform (0.5 mL) was added Oxone (1.5 molar equiv) under stirring at room temperature. The reaction mixture was stirred at room temperature for a period of time as indicated in Table 1 (the reaction was monitored by TLC using hexane/EtOAc 3:1 as eluent by disappearance of the iodoarene). After completion of the reaction, the solvent was evaporated under vacuum, and the residue was treated with chloroform (10 mL). The insoluble residue of inorganic salts was collected by filtration, washed with chloroform (5 mL), and discarded. Evaporation of combined chloroform extracts under reduced pressure afforded crude products **4**, which could be further purified by recrystallization from CF$_3$CO$_2$H/hexane, 1:10.

[Bis(trifluoroacetoxy)iodo]benzene (5a). Reaction of iodobenzene **4a** (0.10 g, 0.50 mmol) according to the general procedure afforded 0.21 g (97%) of product **5a**, isolated as a microcrystalline solid. Mp: 118−120 °C (lit.[6] mp 119−120 °C). ^{1}H NMR (300 MHz, CDCl$_3$/CF$_3$CO$_2$D, 22:1): δ 8.22 (d, J = 7.8 Hz, 2H), 7.75 (t, J = 7.8 Hz, 1H), 7.64 (t, J = 7.8 Hz, 2H). ^{13}C NMR (125.6 MHz, CDCl$_3$): δ 161.1 (q, J_{CF} = 42 Hz), 135.2, 133.7, 132.1, 122.8, 112.9 (q, J_{CF} = 287 Hz).

1-[Bis(trifluoroacetoxy)iodo]-3-chlorobenzene (5e). Reaction of 1-chloro-3-iodobenzene **4e** (0.12 g, 0.50 mmol) under general conditions afforded 0.21 g (91%) of product **5e**, isolated as a microcrystalline solid. Mp: 95−97 °C. ^{1}H NMR (300 MHz, CDCl$_3$/CF$_3$CO$_2$D, 22:1): δ 8.21 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 8.5 Hz, 1H). ^{13}C NMR (125.6 MHz, CDCl$_3$): δ 161.3 (q, J_{CF} = 42 Hz), 136.8, 134.7, 133.1, 132.8, 132.1, 121.8, 112.9 (q, J_{CF} = 288 Hz). Anal. Calcd for C$_{10}$H$_4$ClF$_6$IO$_4$: C, 25.86; H, 0.87; I, 27.32; F, 24.54. Found: C, 25.64; H, 0.89; I, 27.55; F, 24.30.

1-[Bis(trifluoroacetoxy)iodo]-2-chlorobenzene (5f). Reaction of 1-chloro-2-iodobenzene **4f** (0.12 g, 0.50 mmol) under general conditions afforded 0.23 g (97%) of product **5f**, isolated as a microcrystalline solid. Mp: 98−100 °C. ^{1}H NMR (300 MHz, CDCl$_3$/CF$_3$CO$_2$D, 22:1): δ 8.37 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 8.1 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H). ^{13}C NMR (125.6 MHz, CDCl$_3$): δ 161.3 (q, J_{CF} = 41 Hz), 138.7, 137.6, 135.7, 130.6, 129.8, 126.1, 113.0 (q, J_{CF} = 286 Hz).

1-[Bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene (5h). Reaction of 1-iodo-3,5-bis(trifluoromethyl)benzene **4h** (0.17 g, 0.50 mmol) under general conditions afforded 0.27 g (94%) of product **5h**, isolated as a microcrystalline solid. Mp: 82 °C dec (lit.[5c] mp 82 °C dec). ^{1}H NMR (300 MHz, $CDCl_3/CF_3CO_2D$, 22:1): δ 8.60 (s, 2H), 8.21 (s, 1H). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 161.5 (q, J_{CF} = 40 Hz), 135.2 (q, J_{CF} = 35 Hz), 134.83, 127.5 (q, J_{CF} = 4 Hz), 121.9 (q, J_{CF} = 274 Hz), 121.5, 112.9 (q, J_{CF} = 287 Hz).

4-[Bis(trifluoroacetoxy)iodo]benzoic Acid (5k). Reaction of 4-iodobenzoic acid **4k** (0.12 g, 0.50 mmol) under general conditions afforded 0.13 g (54%) of product **5k**, isolated as a microcrystalline solid. Mp: 109−111 °C. ^{1}H NMR (300 MHz, $CDCl_3/CF_3CO_2D$, 22:1): δ 8.34 (s, 4H). ^{13}C NMR (125.6 MHz, $CDCl_3/CF_3CO_2D$, 60:1): δ 170.0, 160.7 (q, J_{CF} = 43 Hz), 135.2, 133.7, 133.2, 127.5, 112.9 (q, J_{CF} = 288 Hz).

3-[Bis(trifluoroacetoxy)iodo]benzoic Acid (5l). Reaction of 3-iodobenzoic acid (0.12 g, 0.5 mmol) under general conditions afforded 0.10 g (41%) of product, isolated as a microcrystalline solid. Mp: 159−161 °C. ^{1}H NMR (300 MHz, $CDCl_3/CF_3CO_2D$, 22:1): δ 8.96 (s, 1H), 8.47−8.52 (m, 2H), 7.82 (t, J = 8.2 Hz, 1H). ^{13}C NMR (125.6 MHz, $CDCl_3/CF_3CO_2D$, 60:1): δ 169.2, 160.3 (q, J_{CF} = 43 Hz), 140.1, 136.8, 135.2, 132.4, 132.3, 122.2, 112.9 (q, J_{CF} = 290 Hz).[8]

1-[Bis(trifluoroacetoxy)iodo]pentafluorobenzene (5m). Reaction of iodopentafluorobenzene **4m** (0.15 g, 0.5 mmol) under general conditions afforded 0.245 g (94%) of crude product **5m**, initially isolated as an oil, which was sublimed to afford a microcrystalline solid. Mp: 95.5−96.5 °C (lit.[9] mp 96 °C). ^{19}F NMR (300 MHz, DMSO-d_6): δ −73.9 (s), −123.6 (s), −144.8 (s), −157.3 (s). ^{13}C NMR (125.6 MHz, DMSO-d_6): δ 159.7 (q, J_{CF} = 37 Hz), 148.2 (m), 146.3 (m), 138.2 (m), 136.2 (m), 115.6 (q, J_{CF} = 289 Hz). Crude product **5m** was additionally identified by conversion to [hydroxy(tosyloxy)iodo]pentafluorobenzene **6**.

[Hydroxy(tosyloxy)iodo]pentafluorobenzene (6). Reaction of [bis(trifluoroacetoxy)iodo]pentafluorobenzene **5m** (0.20 g, 0.385 mmol) with $TsOH \cdot H_2O$ according to the general procedure for preparation of tosylates **3a**−**c** afforded 0.17 g (94%) of product **6**, isolated as a microcrystalline solid. Mp: 160 °C dec. ^{1}H NMR (500 MHz, CD_3CN/DMSO-d_6, 20:1): δ 7.57 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.7 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$/DMSO-d_6, 24:1): δ 141.1, 140.4, 128.8, 125.9, 21.3. ^{19}F NMR (282 MHz, CD_3CN/DMSO-d_6, 20:1): δ −120.5 (s), −153.9 (s), −160.4 (s). Anal. Calcd for $C_{13}H_8F_5IO_4S$: C, 32.38; H, 1.67; S, 6.65. Found: C, 32.73; H, 1.67; S, 6.82.

Acknowledgment. This work was supported by a research grant from the National Science Foundation.

Supporting Information Available: Details of the experimental procedures and spectroscopic data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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