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# Practical method for the synthesis of β-[(trimethylsilyl)ethynyl]-λ$^3$-iodane

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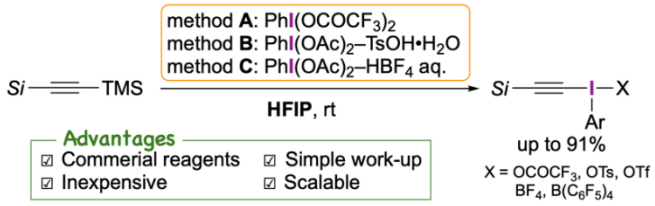
## Abstract

A practical, highly reliable method for the synthesis of β-[(trimethylsilyl)ethynyl]-λ$^3$-iodane from (diacetoxyiodo)arene has been developed using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a solvent. Exposure of bis(trimethylsilyl)acetylene to (diacetoxyiodo)arene and TsOH·$H_2O$ in HFIP at room temperature results in the clean formation of β-[(trimethylsilyl)ethynyl](aryl)(tosyloxy)-λ$^3$-iodanes in high yields. Other acids-assisted approaches (e.g. using TMSOTf or $HBF_4$) is also applicable in this medium. The high stability of β-[(trimethylsilyl)ethynyl](aryl)(tosyloxy)-λ$^3$-iodanes enables the development of one-pot synthesis from iodobenzene in good yield.




**Keywords:** hypervalent iodine; ethynyl-λ$^3$-iodane; (diacetoxyiodo)arene; 1,1,1,3,3,3-hexafluoro-2-propanol; iodoarene

## Introduction

β-[(Trimethylsilyl)ethynyl](phenyl)-λ$^3$-iodane **3a** has serves as a privileged electrophilic ethynylating agent toward a variety of carbon and heteroatom nucleophiles,[1] dienophile/dipolarophile for dienes,[2] diazoketones,[3a] alkyl/aryl azides,[3a] and nitrones[3b] owing to the potent electron-withdrawing character of phenyl-λ$^3$-iodanyl group (Hammett $\sigma_p$ of 1.37).[4] Recently, we also revisited the utility of **3a**-$BF_4$ as a precursor of a high-energy intermediate: diatomic carbon ($C_2$) in the presence of fluoride ion sources.[5] Because of the extremely high leaving group ability of phenyl-λ$^3$-iodanyl group (-I(Ph)$BF_4$, ca. $10^6$ times greater than triflate (-OTf) group),[6] **3a** undergoes linear β-elimination yielding singlet $C_2$ even at room temperature.

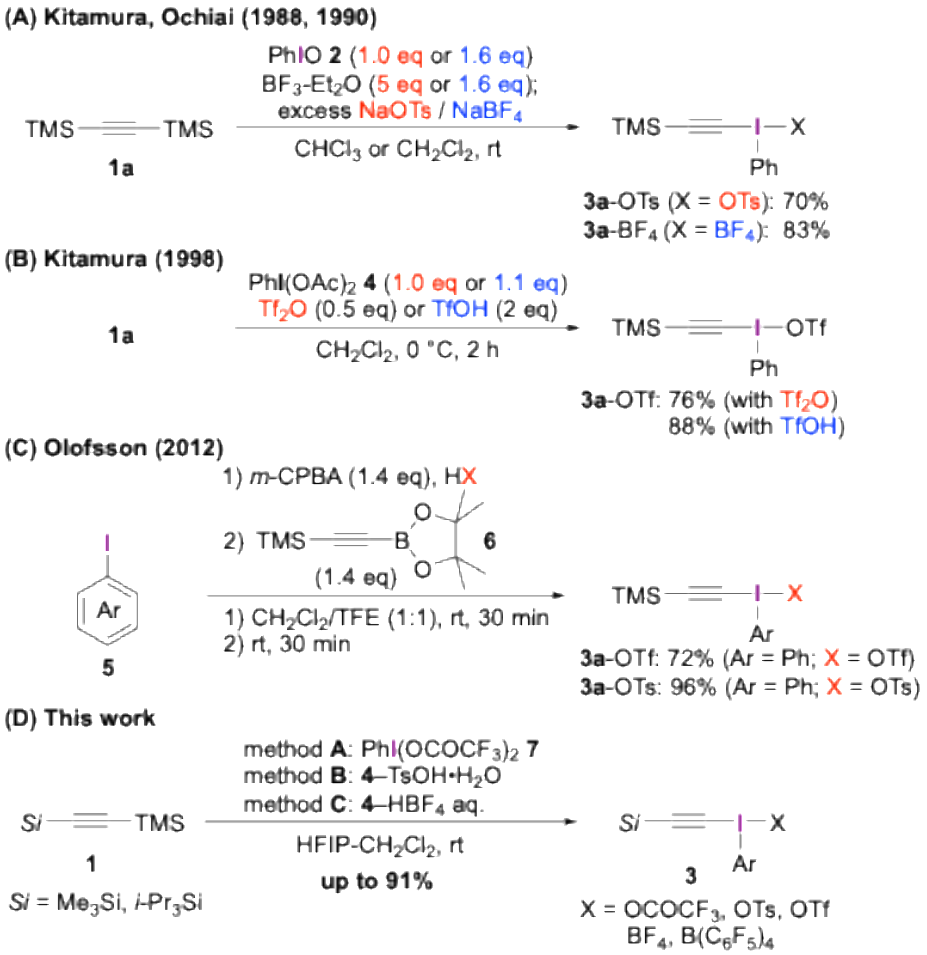


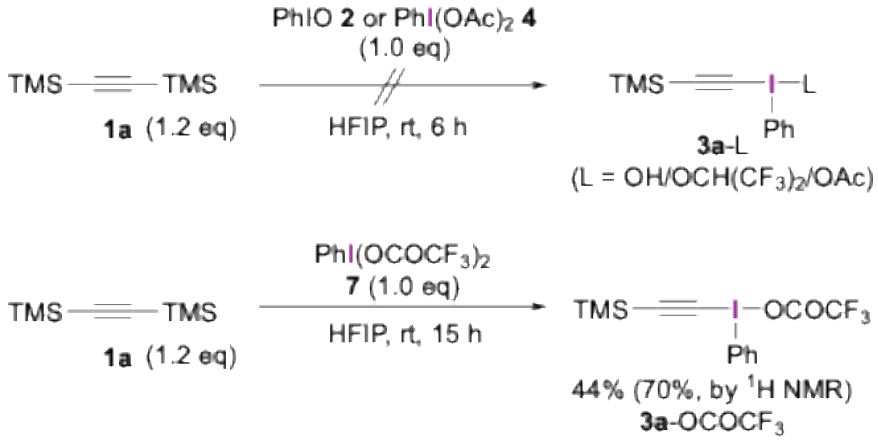

**Figure 1.** Approaches for the synthesis of **3** with (A) PhIO–$BF_3$-$Et_2O$, (B) $Ph(OAc)_2$–$Tf_2O$/TfOH, (C) ArI–*m*-CPBA and alkynylborane **6**. (D) This work.

On the other hand, despite the high synthetic utility of **3a**, a truly user-friendly synthesis of **3** remains under investigation. In the end of 1980$^{th}$, the first efficient approach for the synthesis of **1a** were reported by Kitamura and Ochiai independently,[7,8] where the electrophilic substitution of bis(trimethylsilyl)acetylene (**1**) with $BF_3$-$Et_2O$-activated iodosylbenzene (**2**) afforded **3a**-OTs/$BF_4$ in high yields (Fig 1A). In 1998, Kitamura *et al.* improved the approach more practically:[9] they utilized commercially available stable (diacetoxyiodo)benzene (**4**) and superacid TfOH or $Tf_2O$ (Fig 1B). While this approach represents one of the primary methods for preparing **3a**-OTf, conditions using milder Lewis or Brønsted acid remains underexplored. Later, Olofsson and co-workers

developed the one-pot time-/cost effective synthesis of **3a**-OTf from corresponding iodoarene **5** (Fig 1C).[10] The keys to this achievement are 1) the use of co-solvent 2,2,2-trifluoroethanol (TFE), which facilitates both the oxidation of iodoarene and the subsequent electrophilic substitution with I(III) species, and 2) the use of a superior alkynyl group donor, alkynyl(pinacolato)boronate **6**, which enables the efficient synthesis of both acyclic and cyclic alkynyl-λ³-iodanes. We report herein that the use of solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) significantly accelerates the formation of **3** under mild conditions. The enhanced rate of Silicon-Iodine(III) exchange in the media allows practical synthesis of **3** with a variety of ligands ($OCOCF_3$, OTf, $BF_4$, $B(C_6F_5)_4$).

## Results and Discussion

Although iodosylbenzene (**2**), which forms a polymeric intermolecular I···O network, is essentially insoluble in common organic solvents,[11] various alcohols– such as methanol, TFE, and HFIP– can dissolve it, generating soluble species denoted as $PhI(OR)_2$.[12] Especially (fluoroalkoxy)iodanes are known to exhibit superior oxidizing ability toward heteroatoms/arenes.[13] Inspired by this insight, we commenced our study by the activation-free synthesis of **3** by the reaction of **2** or (diacetoxyiodo)benzene (**4**) with bis(trimethylsilyl)acetylene (**1a**) in HFIP. However, these trials resulted in fruitless. These I(III) reagents and **1a** were recovered intact, except for partial decomposition (Scheme 1). In contrast, use of more electrophilic agent bis(trifluoroacetoxyiodo)benzene (**7**) cleanly afforded corresponding **3a**-$OCOCF_3$ in acceptable yield. Although this alkynyl-λ³-iodane was isolable compound at room temperature, it slowly decomposed to iodobenzene within days when it was kept at benchtop.

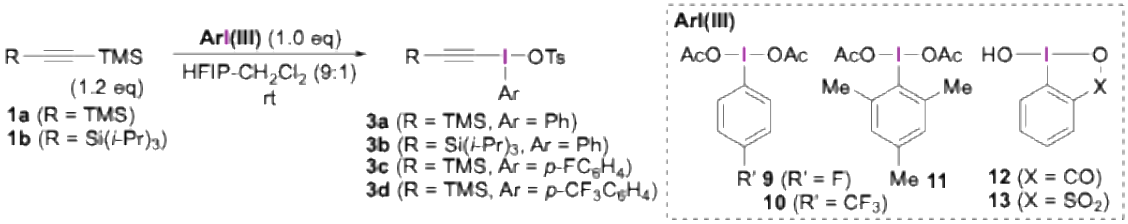



**Scheme 1.** Reaction of iodosyl-/(diacyloxyiodo)arene with silylacetylene **1** in HFIP.

Gratifyingly, the yield and stability of **3a** were greatly improved when *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$) was used as an additive (Table 1). Thus, exposure of silylacetylene **1a** to a mixture of **4** and $TsOH{\cdot}H_2O$ in HFIP resulted in the formation of **3a**-OTs in high yields (entry 1). The work-up procedure is straightforward: removal of the solvents followed by the addition of a diethyl ether-hexane mixture, which precipitates **3a**-OTs in pure form. This process can be easily scaled up to a gram-scale without any loss of efficiency, partly due to the improved moisture-/thermal stability of this species (entry 2). The quantitative formation of **3a**-OTs from

Koser's reagent, hydroxy(tosyloxy)iodobenzene (**8**), suggests the intermediary of this species **8** in the above system (entry 3). Use of powerful Lewis acid: TMSOTf worked nicely in this media to give **3a**-OTf within 10 minutes (entry 4). More sterically crowded β-TIPS-substituted trimethylsilylacetylene **1b** also selectively afforded **3b**-OTs in high yield (entry 5). During our investigation of the substituent effects on (diacetoxyiodo)arenes, we found that the electron-deficient **9** and **10** reacted similarly, whereas (diacetoxyiodo)mesitylene (**11**) did not afford the corresponding alkynyl-λ³-iodanes **3**-OTs (entries 6–8). It is reasonable to attribute this result to electron transfer from the electron-rich mesityl ring to the activated iodine(III) center.[14] Further, neither *o*-iodosylbenzoic acid (**12**) nor *o*-iodosylbenzenesulfonic acid **13** yielded corresponding alkynyl-λ³-iodanes **3**-OTs in any appreciable amount (entries 9 and 10). In these cases, due to the lower reactivity of these neighboring σ-donating groups-stabilized cyclic-λ³-iodanes, protodesilylation of **1a** with TsOH proceeded preferentially under the conditions.

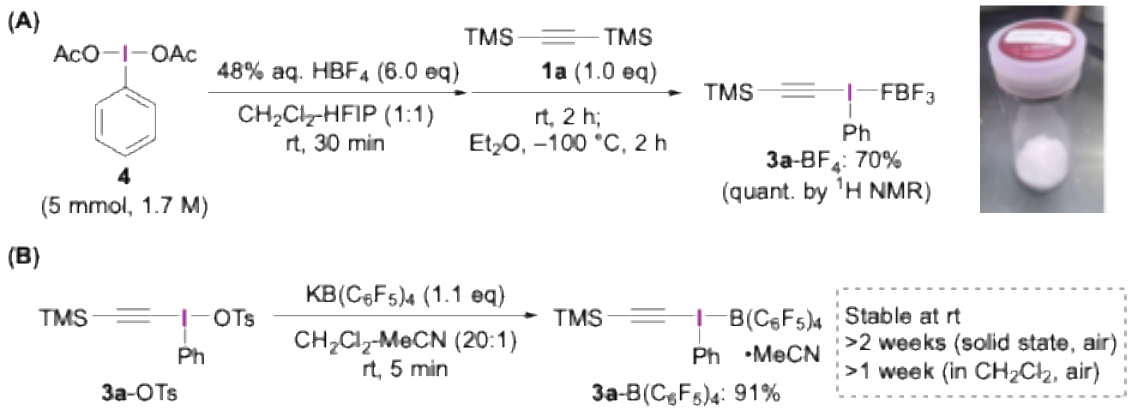
**Table 1.** Synthesis of **3**-OTs in the presence of HFIP.




| entry | ArI(III) | additive (equiv) | time (h) | product | yield (%)[a] |
|---|---|---|---|---|---|
| 1 | $PhI(OAc)_2$ **4** | $TsOH{\cdot}H_2O$ (1.0) | 15 | **3a**-OTs | 90[b] |
| 2[c] | **4** | $TsOH{\cdot}H_2O$ (1.0) | 19 | **3a**-OTs | 91 |
| 3[d] | PhI(OH)OTs **8** | – | 3 | **3a**-OTs | 97 |
| 4 | **4** | TMSOTf (1.0) | 0.1 | **3a**-OTf | 71 |
| 5[e] | **4** | $TsOH{\cdot}H_2O$ (1.0) | 18 | **3b**-OTs | 85 |
| 6 | **9** | $TsOH{\cdot}H_2O$ (1.0) | 15 | **3c**-OTs | 81 |
| 7 | **10**[f] | $TsOH{\cdot}H_2O$ (1.0) | 21 | **3d**-OTs | 75 |
| 8 | **11** | $TsOH{\cdot}H_2O$ (1.0) | 18 | – | 0 |
| 9 | **12** | $TsOH{\cdot}H_2O$ (1.0) | 40 | – | 0 |
| 10 | **13** | $TsOH{\cdot}H_2O$ (1.0) | 24 | – | 0 |

Unless otherwise noted, reactions were performed on 0.7 mmol scale in HFIP (0.7 M) under air. [a]Isolated yields. [b]Average of 3 runs. [c]5.2 mmol scale. [d]0.2 M. [e]0.4 M. [f]A mixture of **10** and its μ-oxo dimer (1:1.7) was used.

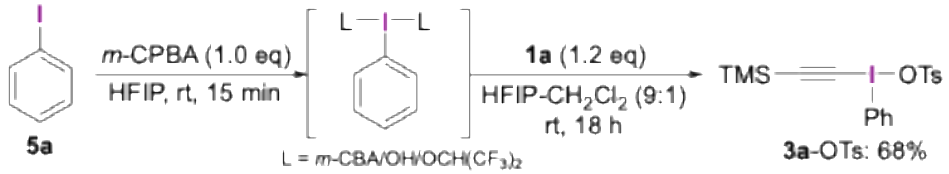
With the effective method to access alkynyl-λ³-iodanes **3**-OTs was in hand, we next optimized the conditions for the synthesis of **3a**-$BF_4$ as it serves as $C_2$-precursor both in the solid state and in solution.[5,15] After the extensive research, we were pleased to find the efficient conditions yielding very pure **3a**-$BF_4$ in gram scale (Scheme 2A). Thus, treatment of **1a** to a solution of **4** activated with excess 48% $HBF_4$ in $CH_2Cl_2$-HFIP (1:1) resulted in the clean formation of **3a**-$BF_4$ within 1–2 hours. The dilution of organic phase with excess diethyl ether and store at –100 °C ceases pure crystals of **3a**-$BF_4$ in good yield. This result is in marked contrast to the PhIO–$BF_3$-$Et_2O$ system, which required a prolonged reaction time (>24 h).[8] The enhanced reactivity would be partly due to the in situ formation of highly electrophilic species $PhI[OCH(CF_3)_2]^+$ ions.[16]




**Scheme 2**. (A) Synthesis of **3a**-$BF_4$ using **4**-$HBF_4$-HFIP system. (B) Synthesis of **3a**-$B(C_6F_5)_4$ by a ligand exchange.

It is noteworthy that the ligand exchange reaction of **3a**-OTs with potassium tetrakis(pentafluorophenyl)borate afforded novel **3a**-$B(C_6F_5)_4$ as a 1:1 complex with MeCN in high yield (Scheme 2B). This species is surprisingly stable at room temperature both in solution (>1 week, $CH_2Cl_2$ or $CDCl_3$ solution) and in the solid state. No detectable decomposition was observed when it was left standing on a benchtop (at room temperature, without shielding from light) for more than 1 months (Figure S1 and S2 in Supporting Information).

From the synthetic point of view, rapid and highly efficient synthesis of alkynyl-$\lambda^3$-iodane reminds us the installation of unprecedented platforms (caged alkyl iodide/perfluoroalkyl iodide/iodoalkyne, etc.) into the alkynyl-$\lambda^3$-iodane family. Inspired by the Olofsson's one-pot approach,[10] preliminary study on the direct synthesis of **3a**-OTs from iodobenzene **5a** was commenced (Scheme 3). Thus, exposure of **5a** with equimolar amount of *m*-CPBA in HFIP leads to the smooth conversion to ArI(III) species within 15 minutes and following ligand exchange with **1a** cleanly afforded desired **3a**-OTs in 68% yield.




**Scheme 3**. One-pot synthesis of **3a**-OTs from iodobenzene **5a**.

## Conclusions

In conclusion, we have developed a practical method for the synthesis of alkynyl-$\lambda^3$-iodane **3** with silylacetylene **1** in HFIP. The approach allows facile access to "ethynyl cation/$C_2$" synthon with commercially available reagents. We believe this procedure would be a powerful tool not only in the field of organic synthesis but also in material science, chemical biology, medicinal chemistry, and related areas. Further studies on the use of other oxidant (selectfluor, Oxone, $NaBO_3$, $NaClO\text{-}5H_2O$, etc.) in one-pot approach to oxidize $C_{sp}$/$C_{sp2}$/$C_{sp3}$–I species is underway in our laboratory.

## Experimental Section

**General**: $^{1}H$, $^{19}F$, and $^{13}C$ spectra were recorded either on a BRUKER ACANCE NEO 400 OneBay, AVANCE III HD 500, ACANCE NEO 600, or JEOL ECZL600 spectrometer (TMS, $CHCl_3$, $CHD_2CN$ as an internal standard). Samples were recorded in $CDCl_3$ or $CD_3CN$ at room temperature. Chemical shifts are expressed in δ (ppm) values. Melting points were determined with the Melting Point System MP70 or SANSYO Melting Point Apparatus SMP-300 and were uncorrected. IR spectra were recorded on a JASCO FT/IR-4700 spectrometer.

**Materials**: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., LLC., and other commercial suppliers. (Diacetoxyiodo)arene **9** and **10** were prepared from corresponding iodoarenes with NaClO-$5H_2O$ according to the reported procedure.[17] $KB(C_6F_5)_4$ was prepared from commercially available [(4-isopropyl)phenyl](tolyl)[tetrakis(pentafluorophenyl)borato]-$\lambda^3$-iodane according to the reported procedure.[18]

**General Procedure for Synthesis of 3-OTs. A typical example (3a-OTs, 0.7 mmol scale).** To a stirred solution of $PhI(OAc)_2$ **4** (228.3 mg, 0.70 mmol) in HFIP (0.9 mL) was added *p*-toluenesulfonic acid monohydrate (134.8 mg, 0.70 mmol) under air at room temperature, and the mixture was vigorously stirred for 5 minutes. The resulting yellow solution was added bis(trimethylsilyl)acetylene **1a** (135.0 mg, 0.79 mmol) in $CH_2Cl_2$ (0.1 mL) and the mixture was stirred for 15 h. After the solution was concentrated under reduced pressure, the oil was washed several times with hexane and then with $Et_2O$ by decantation to afford **3a**-OTs (289.7 mg, 78%) as a white microcrystalline solid. Recrystallization from $CH_2Cl_2$-hexane at –20 °C gave colorless needles.

**3a**-OTs:[7] mp. 112–113 °C (dec.); IR (ATR): 3074, 2957, 1460, 1439, 1226, 1147, 1030, 1147, 1030, 1002, 988, 851, 837, 815, 683, 568 $cm^{-1}$; $^{1}H$ NMR (600 MHz, $CD_3CN$): δ 8.12 (d, *J* = 8.3 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.56–7.45 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 0.19 (s, 9H); $^{13}C$ NMR (151 MHz, $CD_3CN$): δ 141.3, 140.4, 133.6, 132.2, 132.0, 128.8, 126.0, 118.8, 117.2, 51.9, 21.3, –0.70; $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 141.3, 140.4, 133.9, 132.0, 131.9, 128.8, 126.1, 118.7, 116.5, 51.5, 21.4, –0.6.

**3a**-OTf:[9] mp. 128–138 °C (dec.) ($CH_2Cl_2$-hexane); IR (ATR): 3083, 2959, 2900, 1561, 1471, 1446, 1289, 1215, 1174, 1165, 1020, 845, 710, 632, 575, 513 $cm^{-1}$; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.55 (dd, *J* = 8.0, 7.2 Hz, 2H), 0.24 (s, 9H). $^{19}F$ NMR (564 MHz, $CDCl_3$): δ –78.0 (s, 3F); $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 134.1, 132.7, 132.6, 120.4 (q, $^{1}J_{CF}$ = 317.9 Hz), 119.8, 116.9, 44.1, –0.8.

**3a**-$OCOCF_3$: mp. 73–79 °C (dec.) ($CH_2Cl_2$-hexane); IR (ATR): 3075, 2967, 1656, 1183, 1130, 836, 739, 694 $cm^{-1}$; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (dd, *J* = 8.2, 7.4 Hz, 2H), 0.21 (s, 9H); $^{19}F$ NMR (564 MHz, $CDCl_3$): δ -75.1 (s, 3F); $^{13}C$ NMR (151 MHz, $CD_3CN$): δ 162.6 (q, $^{2}J_{CF}$ = 36.1 Hz), 133.5, 132.1, 131.9, 116.5, 115.5 (q, $^{1}J_{CF}$ = 295.8 Hz), 114.6, 58.3, –0.6.

**3b**-OTs: mp. 166.5–167 °C (dec.) ($CH_2Cl_2$-hexane); IR (ATR): 3088, 3071, 1460, 1444, 1222, 1157, 1120, 1007, 723, 676, 567, 550 $cm^{-1}$; $^{1}H$ NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 8.1, 7.4 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 1.12–1.00 (m, 3H), 1.03 (d, *J* = 5.8 Hz, 18H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 141.4, 140.4, 133.5, 132.1, 131.9, 128.8, 126.0, 119.4, 114.8, 114.7, 52.7, 21.4, 18.4 11.1.

**3c**-OTs: mp. 122–128 °C (dec.) ($CH_2Cl_2$-hexane); IR (ATR): 3067, 3050, 2962, 2904, 1574, 1477, 1216, 1168, 1119, 1028, 1004, 845, 812, 713, 678, 564 552, 509 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.10–8.05 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.17–7.12 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H), 0.21 (s, 9H). $^{19}F$ NMR (564 MHz, $CDCl_3$): δ –105.4 (s, 1F); $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 165.2 (d, $^1J_{CF}$ = 254.1 Hz), 142.0, 141.1, 137.3 (d, $^3J_{CF}$ = 8.8 Hz), 129.5, 126.8, 119.9 (d, $^2J_{CF}$ = 23.3 Hz), 116.6, 112.5 (d, $^4J_{CF}$ = 3.2 Hz), 52.1, 22.1, 0.0.

**3d**-OTs: mp. 141–149 °C (dec.) ($CH_2Cl_2$-hexane); IR (ATR): 3096, 3049, 2965, 1594, 1398, 1316, 1225, 1155, 1118, 1065, 1001, 844, 824, 715, 679, 632, 563 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H), 0.26 (s, 9H); $^{19}F$ NMR (564 MHz, $CDCl_3$): δ –63.2 (s, 3F); $^{13}C$ NMR (151 MHz, $CDCl_3$): δ 140.9, 140.8, 134.6, 133.9 ($^2J_{CF}$ = 33.5 Hz), 129.0, 128.5 (d, $^3J_{CF}$ = 3.2 Hz), 123.2 (d, $^1J_{CF}$ = 272.9 Hz), 121.6, 117.3, 51.1, 21.4, –0.7.

**Large-scale synthesis of 3a-Ots.** To a stirred solution of $PhI(OAc)_2$ **4** (1.67 g, 5.2 mmol) in HFIP (7.0 mL) was added *p*-toluenesulfonic acid monohydrate (1.00 g, 5.3 mmol) under air at room temperature, and the mixture was vigorously stirred until all reagents has dissolved. To the resulting yellow solution was added **1a** (1.02 g, 6.0 mmol) in a small amount of HFIP, and the mixture was stirred for 15 h. After the solution was concentrated under reduced pressure, the oil was washed several times with hexane and then with $Et_2O$ by decantation to afford **3a**-OTs (2.22 g, 91%) as a white microcrystalline solid.

**Large-scale Synthesis of 3a-$BF_4$.** To a vigorously stirred solution of $PhI(OAc)_2$ **4** (1.61 g, 5.0 mmol) in $CH_2Cl_2$ (2.5 mL) and HFIP (1.5 mL) was added 42% aqueous $HBF_4$ (4.8 mL, 30 mmol). To the resulting canary yellow emulsion was added **1a** (852 mg, 5 mmol) and stirred for 2 hours. The pale yellow organic phase was poured into cold $Et_2O$ (40 mL, –100 °C) and kept for 2 hours to precipitate **3a**-$BF_4$. Removal of the supernatant by decantation, followed by washing of the crystals with hexane several times and drying under vacuum, afforded pure **3a**-$BF_4$ (1.36 g, 70%) as colorless needles.
**3a**-$BF_4$:[8,19] mp. 161–163 (dec.); IR (ATR): 3093, 2965, 1469, 1444, 1252, 1200–900, 843, 763, 740, 720, 673, 644, 518 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.57 (dd, *J* = 8.0, 7.2 Hz, 2H), 0.27 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 134.2, 133.1, 132.9, 122.2, 115.1, 38.3, –0.8.

**Ligand exchange of 3a-OTs to 3a-B($C_6F_5$)$_4$.** To a stirred solution of **3a**-OTs (29.0 mg, 0.061 mmol) in $CH_2Cl_2$ (1.0 mL) was added K($C_6F_5$)$_4$ (48.5 mg, 0.068 mmol) and MeCN (50 µL) and the resulting suspension was stirred for 5 minutes. Filtration of the reaction mixture (eluted with $CH_2Cl_2$), followed by concentration under reduced pressure, afforded **3a**-B($C_6F_5$)$_4$·MeCN 1:1 complex (53.2 mg, 89%) as a white microcrystalline solid.
**3a**-B($C_6F_5$)$_4$·MeCN: mp. 104–109 °C (dec.) ($CH_2Cl_2$-hexane); $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.65 (dd, *J* = 7.8, 7.2 Hz, 2H), 2.01 (s, 3H), 0.28 (s, 9H); $^{19}F$ NMR (564 MHz, $CDCl_3$): δ -132.2 – -132.5 (m, 8F), –162.0 to –162.2 (m, 4F), –165.9 to –166.2 (m, 8F); $^{13}C$ NMR (142 MHz, $CDCl_3$): δ 148.3 (m), 139.3 (dt, $^1J_{CF}$ = 246.5 Hz, $^2J_{CF}$ = 12.7 Hz, 4C), 136.4 (m), 125 to 123 (br), 134.4, 134.3, 133.9, 125.5, 116.8, 115.4, 34.6, 1.6, –1.1.

**One-pot synthesis of 3a-OTs from iodobenzene.** To a stirred solution of iodobenzene **5a** (85.8 µL, 0.77 mmol) in HFIP (0.9 mL) was added *p*-toluenesulfonic acid monohydrate (145.0 mg, 0.77 mmol) and *m*-chloroperbenzoic acid (70%, 197.0 mg, 0.80 mmol) and the solution was vigorously stirred for 15 minutes. During this time, the formation of white precipitate ceased. To the resulting suspension was then added **1a** (157 mg, 0.92 mmol) in $CH_2Cl_2$ (0.1 mL) and stirred for 18 hours. After the solution was concentrated under reduced pressure, the oil

was washed several times with $Et_2O$ by decantation to afford **3a**-OTs (244 mg, 68%) as a white microcrystalline solid.

## References


1. Selected reviews and books:
   (a) Yoshimura A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. https://doi.org/10.1021/acs.chemrev.5b00547
   (b) Ochiai, M. *Topics in Current Chemistry*, Vol. 224 (Ed.: T. Wirth), Springer: Berlin, Germany, 2003, p. 5.
   (c) Ochiai, M. *Chemistry of Hypervalent Compounds* (Ed.: K. Akiba); Wiley-VCH: New York, US, 1999, p. 359.
   (d) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927. https://doi.org/10.1016/S0040-4020(98)00410-4
   (e) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: San Diego, US, 1996.
   (f) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, US, 1992.
2. (a) Williamson, B.L.; Stang, P.J.; Arif, A. M. *J. Am. Chem. Soc.* **1993**, *115*, 2590. https://doi.org/10.1021/ja00060a007
   (b) Murch, P.; Arif, A. M.; Stang, P. J. *J. Org. Chem.* **1997**, *62*, 5959. https://doi.org/10.1021/jo970651m
   (c) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 4571. https://doi.org/10.1021/ja00012a028
3. (a) Maas, G.; Regitz, M.; Moll, U.; Rahm, R.; Krebs, F.; Hector, R.; Stang, P. J.; Crittell, C. M.; Williamson, B. L. *Tetrahedron* **1992**, *48*, 3527. https://doi.org/10.1016/S0040-4020(01)88491-X
   (b) Kotali, E.; Varvoglis, A.; Bozopoulos, A. *J. Chem. Soc. Perkin Trans.* 1 **1989**, 827. https://doi.org/10.1039/p19890000827
4. Mironova, A. A.; Maletina, I. I.; Iksanova, S. V.; Orda, V. V.; Yagupolskii, L. M. *Zh. Org. Chem.* **1989**, *25*, 306.
5. (a) Miyamoto, K.; Narita, S.; Masumoto, Y.; Hashishin, T.; Osawa, T.; Kimura, M.; Ochiai, M.; Uchiyama. M. *Nat. Commun.* **2020**, *11*, 2134. https://doi.org/10.1038/s41467-020-16025-x
   (b) Rzepa, H. S. Arita, M.; Miyamoto, K.; Uchiyama, M. *Phy. Chem. Chem. Phys.* **2022**, *24*, 25816. https://doi.org/10.1039/D2CP01214F
6. Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360. https://doi.org/10.1021/ja00117a006
7. Kitamura, T.; Stang, P. J. *J. Org. Chem.* **1988**, *53*, 4105. https://doi.org/10.1021/jo00252a042
8. Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Chem. Soc. Chem. Commun.* **1990**, 118. https://doi.org/10.1039/c39900000118
9. Kitamura, T.; Kotani, M.; Fujiwara, Y. *Synthesis* **1998**, 1416. https://doi.org/10.1039/c39900000118
10. Bouma, M. J.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14242. https://doi.org/10.1002/chem.201202977

11. Carmalt, C. J.; Crossley, J. G.; Knight, J. G.; Lightfoot, P.; Martin, A.; Muldowney, M. P.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2367. https://doi.org/10.1039/C39940002367
12. (a) Kajiyama, D.; Inoue, K.; Ishikawa, Y.; Nishiyama, S. *Tetrahedron* **2010**, *66*, 9779. https://doi.org/10.1016/j.tet.2010.11.015 (b) Cardenal, A. D.; Maity, A.; Gao, W.-Y.; Ashirov, R.; Hyun, S.-M.; Powers, D. C. *Inorg. Chem.* **2019**, *58*, 10543. (c) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563. https://doi.org/10.1021/acs.inorgchem.9b01191
13. Selected examples of the oxidation with di[(fluoroalkoxy)iodo]arenes:
    (a) Kajiyama, D.; Saitoh, T.; Nishiyama, S. *Electrochemistry* **2013**, *81*, 319. https://doi.org/10.5796/electrochemistry.81.319
    (b) Broese, T.; Francke, R. *Org. Lett.* **2016**, *18*, 5896. https://doi.org/10.1021/acs.orglett.6b02979
    (c) Kita, Y.; Morimoto, K.; Ito, M.; Ogawa, C.; Goto, A.; Dohi, T. *J. Am. Chem. Soc.* **2009**, *131*, 1668. https://doi.org/10.1021/ja808940n
    (d) Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 8605. https://doi.org/10.1002/anie.201102984
14. (a) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684. https://doi.org/10.1021/ja00088a003 (b) Xie, J.; Zhang, J.; Kasemthaveechok, S.; López-Resano, S.; Cots, E.; Maseras F.; Pérez-Temprano, M. H. *Nat. Synth.* **2024**, *3*, 1021. https://doi.org/10.1038/s44160-024-00566-w
15. Gorantla, S.-M. N. V. T.; Pan, S.; Mondal, K. C.; Frenking, G. *Pure Appl. Chem.* **2022**; *94*, 767. https://doi.org/10.1515/pac-2021-1102
16. The PhI[OCH$(CF_3)_2$]$^+$-related species has been detected by CSI-MS under similar conditions. See, Miyamoto, K.; Tada, N.; Ochiai, M. *J. Am. Chem. Soc.* **2007**, *129*, 2772. https://doi.org/10.1021/ja070179e
17. Watanabe, A.; Miyamoto, K.; Okada, T.; Asawa, T.; Uchiyama, M. *J. Org. Chem.* **2018**, *83*, 14262. https://doi.org/10.1021/acs.joc.8b02541
18. Watanabe, Y.; Takagi, T.; Miyamoto, K.; Kanazawa, J.; Uchiyama, M. *Org. Lett.* **2020**, *22*, 3469 https://doi.org/10.1021/acs.orglett.0c00924
19. $^1$H NMR data for **3a**-$BF_4$·18-crown-6 complex were reported by Ochiai, M.; Miyamoto, K.; Suefuji, T.; Shiro, M.; Sakamoto, S.; Yamaguchi, K. *Tetrahedron Lett.* **2003**, *59*, 10153. https://doi.org/10.1016/j.tet.2003.10.074