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Paper

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

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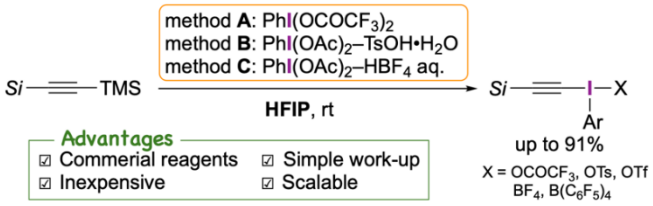
Received 11-14-2025 **Accepted** 01-06-2026 **Published on line** 01-23-2026

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

Cite as *Arkivoc* **2025** (4) 202512493

DOI: https://doi.org/10.24820/ark.5550190.p012.493

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,[1-6] dienophile/dipolarophile for dienes,[7-9] diazoketones,[10] alkyl/aryl azides,[10] and nitrones[11] owing to the potent electron-withdrawing character of phenyl-λ^3-iodanyl group (Hammett σ_p of 1.37).[12] 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.[13,14] 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),[15] **3a** undergoes linear β-elimination yielding singlet C_2 even at room temperature.

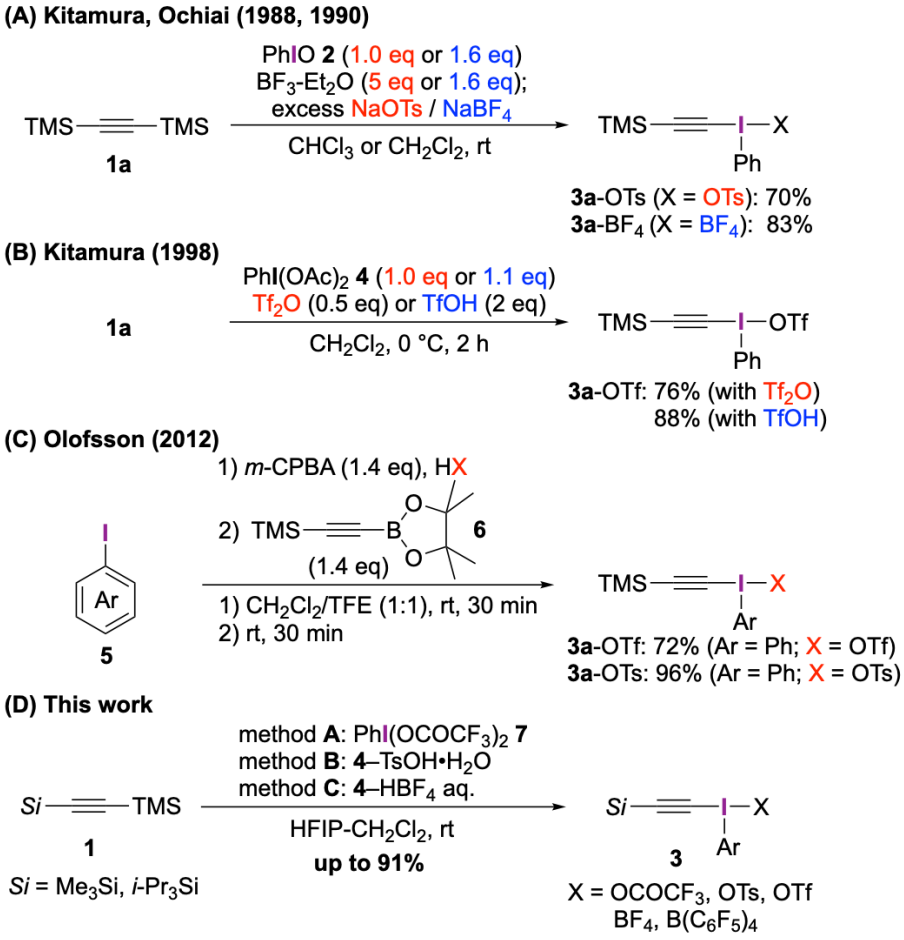


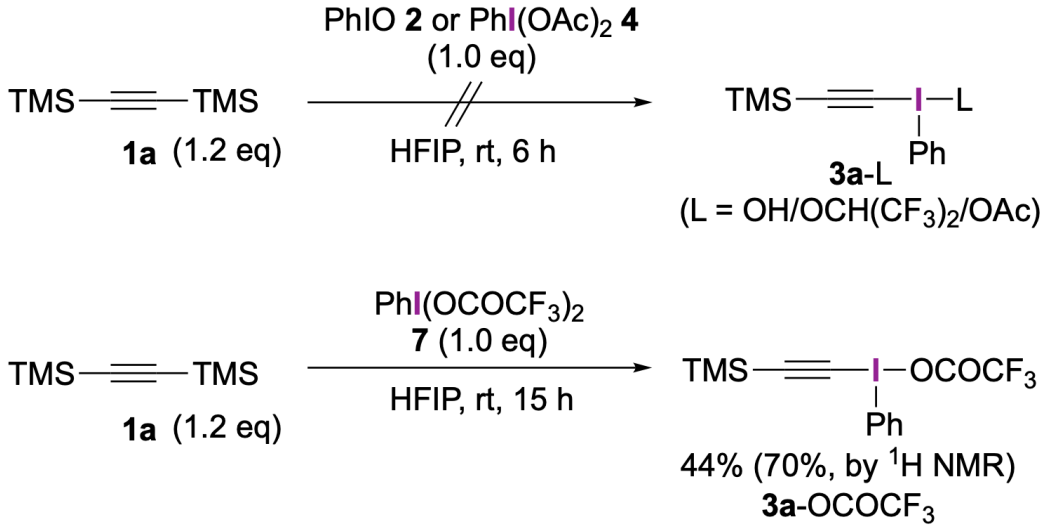
Figure 1. Approaches for the synthesis of **3** with (A) PhIO–BF_3-Et_2O, (B) $Ph(OAc)_2$–Tf_2O/TfOH, (C) ArI–*m*-CPBA and alkynylborane **6**. (D) This work.

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 1980th, the first efficient approach for the synthesis of **1a** were reported by Kitamura and Ochiai independently,[16,17] 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 (Figure 1A). In 1998, Kitamura *et al.* improved the approach more practically:[18] they utilized commercially available stable (diacetoxyiodo)benzene

(**4**) and superacid TfOH or Tf_2O (Figure 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** (Figure 1C).[19] 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

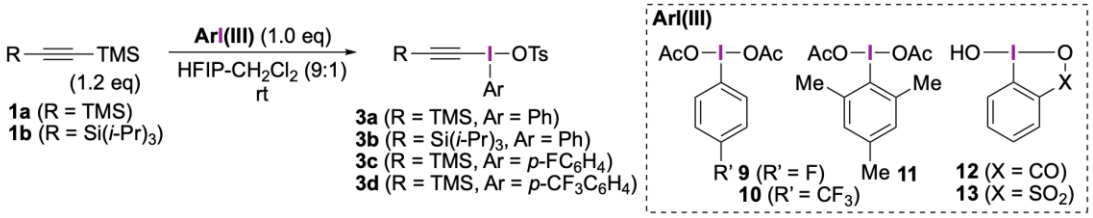
Although iodosylbenzene (**2**), which forms a polymeric intermolecular I···O network, is essentially insoluble in common organic solvents,[20] various alcohols– such as methanol, TFE, and HFIP– can dissolve it, generating soluble species denoted as $PhI(OR)_2$.[21,22] Especially (fluoroalkoxy)iodanes are known to exhibit superior oxidizing ability toward heteroatoms/arenes.[23-26] 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-λ^3-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.[27,28] Further, neither *o*-iodosylbenzoic acid (**12**) nor *o*-iodosylbenzenesulfonic acid **13** yielded corresponding alkynyl-λ^3-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-λ^3-iodanes, protodesilylation of **1a** with TsOH proceeded preferentially under the conditions.

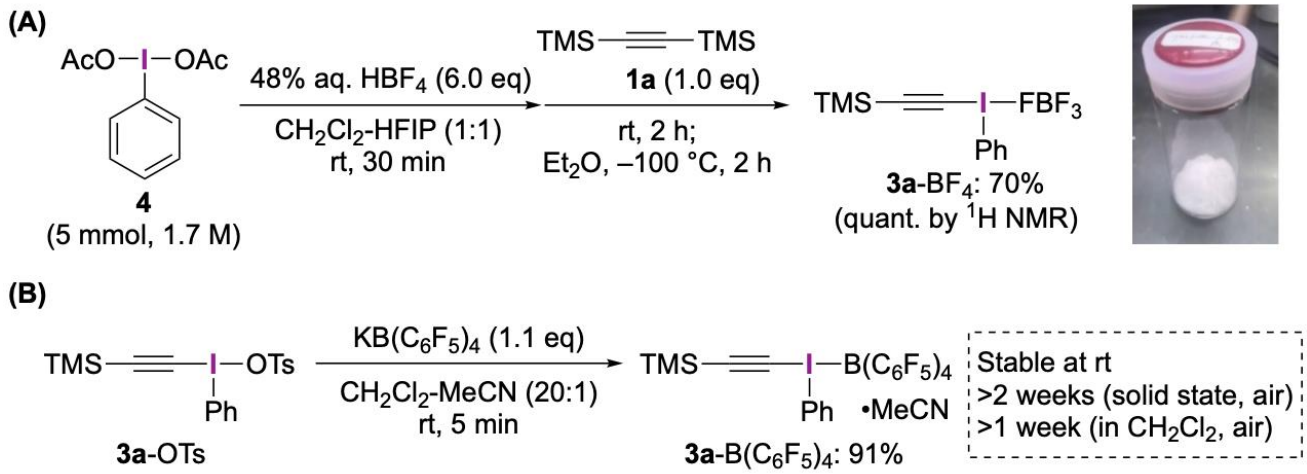
Table 1. Synthesis of **3**-OTs in the presence of HFIP



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.

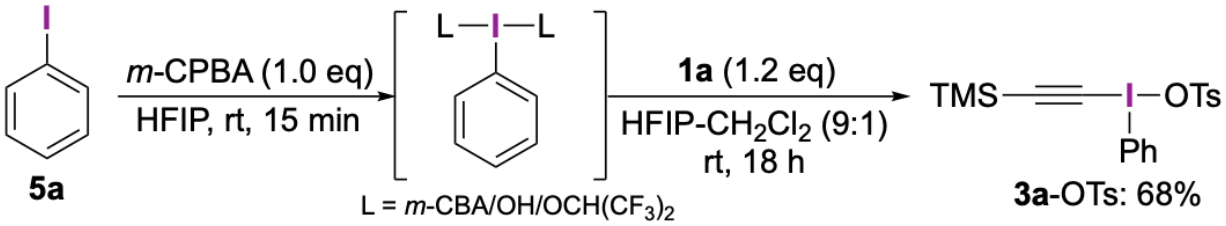
With the effective method to access alkynyl-λ^3-iodanes **3**-OTs was in hand, we next optimized the conditions for the synthesis of **3a**-BF_4 as it serves as C_2-precursor both in the solid state and in solution.[13,14,29] After the extensive research, we were pleased to find the efficient conditions 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.[30]



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-λ^3-iodane reminds us the installation of unprecedented platforms (caged alkyl iodide/perfluoroalkyl iodide/iodoalkyne, etc.) into the alkynyl-λ^3-iodane family. Inspired by the Olofsson's one-pot approach,[19] 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-λ^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-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]-λ^3-iodane according to the reported procedure.[32]
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:[16] 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}; ^1H 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:[18] 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}; ^1H 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, $^1J_{CF}$ = 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}; ^1H 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, $^2J_{CF}$ = 36.1 Hz), 133.5, 132.1, 131.9, 116.5, 115.5 (q, $^1J_{CF}$ = 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}; ^1H 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:[17,33] 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 $KB(C_6F_5)_4$ (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.

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