Facile Synthesis of Iodonium Salts by Reaction of Organotrifluoroborates with *p*-Iodotoluene Difluoride

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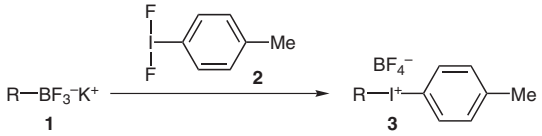
Abstract: A simple and easy method for the synthesis of various iodonium salts was developed, and involves the reaction of potassium organotrifluoroborates with *p*-iodotoluene difluoride under mild conditions. The one-pot synthesis of a (*Z*)-(2-fluoroalkenyl)iodonium salt from an alkynyltrifluoroborate was also carried out.

Key words: alkenes, alkynes, arenes, boron, iodine

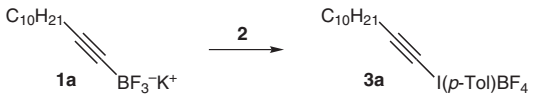
Hypervalent iodine(III) compounds, especially alkynyl-, alkenyl-, or diaryliodonium salts, are known as useful reagents for a number of organic syntheses, since phenyliodanyl is an excellent leaving group.[1,2] Generally, they are synthesized by reaction of organometals, such as organostannanes,[3] organosilanes,[4] or organoboranes,[5] with aryl–iodine(III) compounds ($ArIX_2$). However, the reaction of organosilanes or organoboranes with $ArIX_2$ generally needs activation with acids,[6] and the use of organostannanes sometimes causes handling problems, due to its high toxicity. Therefore, it would be worthwhile to develop an easier and safer method for the synthesis of iodonium salts. Recently, potassium organotrifluoroborates ($RBF_3^-K^+$) have been employed instead of organoboronic acids or esters in organic synthesis, since organotrifluoroborates have many advantages with regard to handling and reactivity compared to the other organoboranes.[7] Organotrifluoroborates are readily obtainable from the corresponding organoboronic acids, and some of them are commercially available.[8] We were interested in the nucleophilicity of organotrifluoroborates,[9] and planned to synthesize the iodonium salts **3** by reaction of organotrifluoroborates **1** with *p*-iodotoluene difluoride (**2**),[10] which is known as a mild and safe oxidizing reagent (Scheme 1).

To optimize reaction conditions, potassium dodec-1-ynyltrifluoroborate (**1a**) was employed as a starting material to give dodec-1-ynyl(4-methylphenyl)iodonium tetrafluoroborate (**3a**) (Table 1). To our delight, the reaction of **1a** with one equivalent of **2** in dichloromethane was complete within 15 minutes at room temperature to afford **3a** in good yield (Table 1, entry 1). A solvent screen found acetonitrile to be a suitable solvent for this reaction (Table 1, entries 1–3). Attempted optimization of reaction temperature gave no improvement in the yield of **3a** (Table 1, entries 3–5). Finally, we successfully obtained **3a** in 95% yield by tuning the substrate concentration in acetonitrile to 0.05 molar (Table 1, entry 7); a higher substrate concentration resulted in a decrease in the yield of **3a** (Table 1, entry 6).



Scheme 1

Table 1 Optimization of the Reaction Conditions with **1a**[a]



Entry	Solvent	Concn of **1a**	Temp	Yield[b] (%)
1	CH_2Cl_2	0.1	r.t.	66
2	acetone	0.1	r.t.	89
3	MeCN	0.1	r.t.	90
4	MeCN	0.1	40 °C	82
5	MeCN	0.1	0 °C	89
6	MeCN	0.2	r.t.	83
7	MeCN	0.05	r.t.	95

[a] Reagents and conditions: **1a** (1 mmol), **2** (1 mmol), 15 min.
[b] Isolated yield of **3a**.

The scope of this iodonium salt synthesis was studied with various organotrifluoroborates (Table 2). Under these reaction conditions, alkynyltrifluoroborate **1b** prepared from propargyl alcohol was converted into iodonium salt **3b** in 83% yield (Table 2, entry 1). The reaction with potassium (*E*)-trifluoro(hex-1-enyl)borate (**1c**) as starting material gave a better result at –20 °C than at room temperature (Table 2, entries 2 and 3). Under the same reaction conditions, potassium (*E*)-trifluoro(styryl)borate (**1d**) and the internal alkenyltrifluoroborate potassium (4-*tert*-butylcyclohex-1-enyl)trifluoroborate (**1e**) provided the corresponding alkenyliodonium salts **3d** and **3e** in 82% and 69% yields, respectively (Table 2, entries 4 and 5). Then, the reactions of aryltrifluoroborates giving diaryliodonium salts were investigated. The reaction of potassium trifluoro(phenyl)borate (**1f**) with **2** proceeded well at 60 °C to give (4-methylphenyl)(phenyl)iodonium tetra-

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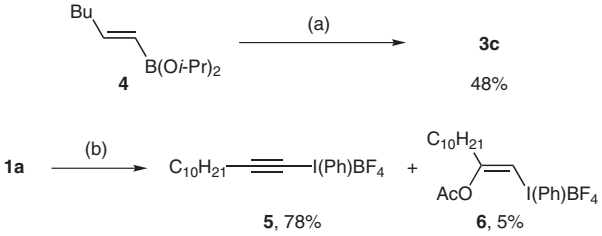
fluoroborate (**3f**) in 60% yield, although the reaction was sluggish at room temperature (Table 2, entry 6). To study the substituent effect, *p*-methyl- (**1g**), *p*-methoxy- (**1h**), and *p*-chloro-substituted (**1i**) trifluoro(phenyl)borates were used as starting materials (Table 2, entries 7–9). These results confirmed that an electron-donating group increases the reactivity of organotrifluoroborate **1** towards **2**, while an electron-withdrawing group decreases it. The reaction of the hetaryltrifluoroborate potassium trifluoro(5-methyl-2-thienyl)borate (**1j**) proceeded smoothly at room temperature to give the thienyliodonium salt **3j** in 88% yield (Table 2, entry 10). Thus, it was found that a variety of organotrifluoroborates **1** react with **2** without the requirement of the addition of acids to give iodonium salts **3** in good yields.

Table 2 Synthesis of **3b–j**

Entry	Borate **1**	R	Conditions	Yield[a] (%)
1	**1b**	C≡CCH$_2$OBn	r.t., 15 min	83
2	**1c**	(*E*)-CH=CHBu	r.t., 15 min	69
3	**1c**	(*E*)-CH=CHBu	–20 °C, 15 min	73
4	**1d**	(*E*)-CH=CHPh	–20 °C, 15 min	82
5	**1e**	4-*tert*-butylcyclohex-1-enyl	–20 °C, 15 min	69
6	**1f**	Ph	60 °C, 6 h	60
7	**1g**	Tol	60 °C, 2 h	67
8	**1h**	PMP	60 °C, 15 min	83
9	**1i**	*p*-ClC$_6$H$_4$	60 °C, 15 h	65
10	**1j**	5-methyl-2-thienyl	r.t., 15 min	88

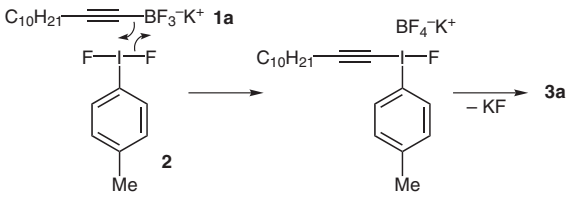
[a] Isolated yield of **3**.

Next, we attempted the reactions of diisopropyl hexenylboronate (**4**) with **2**, and of alkynyltrifluoroborate **1a** with iodobenzene diacetate, to investigate if these reactions proceed without activation by acids (Scheme 2). Alkenylboronate **4** reacted with **2** in the absence of acids; however, the yield of alkenyliodonium salt **3c** from **4** was only 48%, while alkenyltrifluoroborate **1c** gave **3c** in 73% yield, as shown in Table 2. On the other hand, the reaction of alkynyltrifluoroborate **1a** with iodobenzene diacetate also proceeded without the addition of acids; however, a mixture of alkynyliodonium salt **5** (78%) and (2-acetoxyalkenyl)iodonium salt **6** (5%) was obtained,[11] while the reaction between **1a** and **2** afforded only alkynyliodonium salt **3a** in 95% yield (see Table 1). These investigations confirmed that both of these reactions, between **4** and **2** and between **1a** and iodobenzene diacetate, could be carried out without activation by acids. However, it revealed that the combination of an organotrifluoroborate and **2** is essential for various iodonium salts to be obtained in good yields.



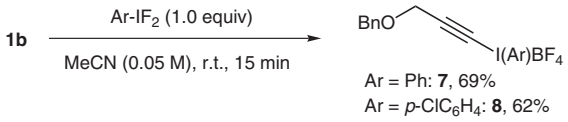
Scheme 2 *Reagents and conditions*: (a) 1. **2** (1.0 equiv), MeCN (0.05 M), –20 °C, 15 min; 2. aq $NaBF_4$; (b) 1. $PhI(OAc)_2$ (1.0 equiv), MeCN (0.05 M), r.t., 15 min; 2. aq $NaBF_4$.

A possible reaction mechanism for **1a** is presented in Scheme 3. At first, nucleophilic attack of the alkynyl group on **1a** occurs at the iodine(III) atom of **2** to give an alkynyliodonium fluoride along with potassium tetrafluoroborate. Then, ligand exchange at the iodine atom gives alkynyliodonium tetrafluoroborate **3a**, which is more stable than the fluoride salt.[1e]



Scheme 3

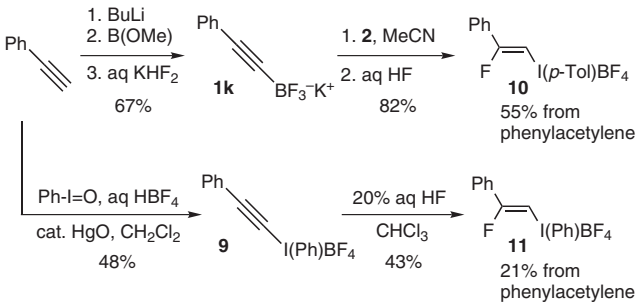
To carry out the iodonium salt synthesis more effectively, we employed relatively electronegative iodoarene difluorides[10] in the reaction of **1b** (Scheme 4); however, the yields of the alkynyliodonium salts **7** and **8** were lower than in the reaction with **2**, because of decomposition of alkynyliodonium salts **7** and **8**.



Scheme 4

We previously reported the synthesis of (*Z*)-(2-fluoroalkenyl)iodonium salts in good yields by Michael-type addition of the fluoride anion to alkynyliodonium salts when aqueous hydrogen fluoride was used.[12] However, hydrogen fluoride addition to (phenylethynyl)iodonium salt **9** resulted in a low yield of (*Z*)-(2-fluoro-2-phenylethenyl)iodonium salt **11** (Scheme 5), because of the low stability of **9**. Therefore, we attempted a one-pot synthesis of (*Z*)-(2-fluoro-2-phenylethenyl)(4-methylphenyl)iodonium tetrafluoroborate (**10**) from potassium (phenylethynyl)trifluoroborate (**1k**) to evaluate our iodonium salt synthesis (Scheme 5). First, alkynyltrifluoroborate **1k** was prepared from phenylacetylene in 67% yield by a published procedure (Scheme 5).[8a] Then, the reaction of **1k** with **2** was carried out in acetonitrile at room temperature. After 15 minutes, without prior isolation of the (phe-

nylethynyl)iodonium salt, 10 equivalents of 20% aqueous hydrogen fluoride was added to the reaction vessel, and the reaction mixture was stirred at 60 °C for 16 hours. This gave us (fluoroalkenyl)iodonium salt **10** in 55% yield from phenylacetylene (82% yield from **1k**). By our previous method, (fluoroalkenyl)iodonium salt **11** was synthesized in 43% yield from **9**, which had been prepared in 48% yield from phenylacetylene; this gave **11** in a total yield of only 21% from phenylacetylene (Scheme 5). When hydrogen fluoride addition proceeded without prior isolation of **9**, only a complex mixture resulted, and the formation of **11** was not observed. Thus, we improved the yield of the (*Z*)-(2-fluoro-2-phenylethenyl)iodonium salt by using a one-pot synthesis via alkynyltrifluoroborate.



Scheme 5

In summary, we successfully synthesized alkenyl-, alkynyl-, and diaryliodonium salts in good yields by reaction of the corresponding organotrifluoroborates with *p*-iodotoluene difluoride. A (phenylethynyl)iodonium salt was also synthesized by this method, and was used for a Michael-type addition of hydrogen fluoride without prior isolation of the alkynyliodonium salt. By this one-pot synthesis, (*Z*)-(2-fluoro-2-phenylethenyl)iodonium salt was obtained in good yield.

IR spectra were recorded on a JASCO FT/IR-410 instrument. The ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL JNM-A400II FT NMR spectrometer and the chemical shifts δ are relative to TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F). The high-resolution mass spectra were measured on a JEOL JMS-700TZ, JMS-FABmate, or JMS-HX110 instrument. Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Alkynyltrifluoroborates **1a**, **1b**, and **1k** were prepared by literature procedures.[8a] Alkenyltrifluoroborates **1c** and **1d** were synthesized from the corresponding alkenylboronic acids,[8b] which were prepared from hex-1-yne[13a] and phenylacetylene.[13b] Aryltrifluoroborates **1f–i** were prepared by literature procedures.[8b] Potassium trifluoro(5-methyl-2-thienyl)borate (**1j**) was purchased from Aldrich. *p*-Iodotoluene difluoride ($TolIF_2$, **2**) is commercially available from Aldrich. The spectral data of **1c**,[14a] **1d**,[13b] **1f**,[8b,14b] **1g**,[14b] **1i**,[8a] **1k**,[14c] **3f**,[15] and **3i**[15] have been reported previously.

Potassium (4-*tert*-Butylcyclohex-1-enyl)trifluoroborate (1e)
To a soln of 4-*tert*-butyl-1-chlorocyclohexene[16] (3.45 g, 20 mmol) in anhyd Et_2O (80 mL) was added $(MeO)_3B$ (4.2 mL, 40 mmol) and Na cuttings (3.00g, 130 mmol) at r.t. After the mixture had stirred for 3 d at r.t., excess Na was removed by decantation. To the resulting soln was slowly added aq KHF_2 (12.5 g, 40 mL, 160 mmol) at 0 °C. The mixture was warmed to r.t. and stirred for 30 min. Evaporation of the mixture at 40 °C gave a crude product, which was, then, dissolved in hot acetone. After hot filtration and evaporation, pure **1e** was obtained.

Yield: 2.19 g (45%); mp >300 °C.

IR (KBr): 2966, 2912, 2871, 2834, 1703, 1647, 1469, 1433, 1364, 1246, 1234, 1193, 1165, 1050, 1018, 976, 918, 897, 826, 811 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.75–0.96 (m, 10 H), 1.04–1.11 (m, 1 H), 1.57–1.67 (m, 2 H), 1.73–1.84 (m, 2 H), 1.99–2.05 (m, 1 H), 5.44 (s, 1 H, H-2).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 24.4, 27.1 (3 C), 28.3, 30.7, 32.0, 44.3, 122.5.

HRMS–FAB: *m/z* [M – K]$^-$ calcd for $C_{10}H_{17}BF_3$: 205.1375; found: 205.1382.

Potassium Dodec-1-ynyltrifluoroborate (1a)
Mp >300 °C.

IR (KBr): 2956, 2921, 2852, 2189, 1469, 1146, 1126, 968, 721 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.85 (t, *J* = 6.7 Hz, 3 H, 12-H), 1.21–1.35 (m, 16 H), 1.94–1.98 (m, 2 H, 3-H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.9, 18.9, 22.1, 28.5, 28.8 (2 C), 29.05, 29.08 (2 C), 31.3, 88.8 (m, 1 C).

HRMS–FAB: *m/z* [M – K]$^-$ calcd for $C_{12}H_{21}BF_3$: 233.1688; found: 233.1694.

Potassium [3-(Benzyloxy)prop-1-ynyl]trifluoroborate (1b)
Mp >300 °C.

IR (KBr): 3061, 3032, 2874, 2854, 2229, 1497, 1454, 1405, 1383, 1367, 1353, 1255, 1207, 1114, 963, 731, 695 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.02 (s, 2 H, 3-H), 4.48 (s, 2 H, H-5), 7.28–7.37 (m, 5 H, Ph).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 58.0, 70.0, 84.7 (m, 1 C), 127.4, 127.6 (2 C), 128.2 (2 C), 138.2.

HRMS–FAB: *m/z* [M – K]$^-$ calcd for $C_{10}H_9BF_3O$: 213.0699; found: 213.0692.

Potassium (4-Methylphenyl)trifluoroborate (1g)
Mp 293–294 °C.

IR (KBr): 3040, 3016, 2982, 2924, 2867, 1663, 1613, 1387, 1233, 1200, 1022, 973, 923, 809 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.20 (s, 3 H, CH_3), 6.88 (d, *J* = 7.6 Hz, 2 H), 7.19 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.0, 127.0 (2 C), 131.3 (m, 2 C), 133.0, 159.4.

HRMS–FAB: *m/z* [M – K]$^-$ calcd for $C_7H_7BF_3$: 159.0593; found: 159.0588.

Dodec-1-ynyl(4-methylphenyl)iodonium Tetrafluoroborate (3a); Typical Procedure
$TolIF_2$ (**2**) (256 mg, 1 mmmol) was dissolved in anhyd MeCN (20 mL) in a Teflon PFA vessel. Borate **1a** (272 mg, 1 mmol) was added, and the mixture was stirred for 15 min at r.t. Then the mixture was poured into 5% aq $NaBF_4$ (30 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in a little CH_2Cl_2 (2 mL), followed by the addition of a large quantity of hexane (40 mL). The upper clear part was removed by decantation, and the remaining viscous oil was washed with hexane. Finally, complete removal of the solvent under reduced pressure gave **3a**.

Yield: 447 mg (95%); mp 42 °C.

IR (paraffin): 2187, 1465, 1377, 1060, 986, 803, 720 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H, H-12), 1.22–1.35 (m, 14 H), 1.54–1.61 (m, 2 H, H-4), 2.44 (s, 3 H, $C_6H_4CH_3$), 2.62 (t, *J* = 7.1 Hz, 2 H, H-3), 7.33 (d, *J* = 8.6 Hz, 2 H), 7.93 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 15.9, 20.7, 21.3, 22.6, 27.5, 28.7, 28.8, 29.2, 29.3, 29.4, 31.8, 110.6, 113.2, 133.3 (2 C), 134.0 (2 C), 144.1.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{19}H_{28}I$: 383.1236; found: 383.1241.

[3-(Benzyloxy)prop-1-ynyl](4-methylphenyl)iodonium Tetrafluoroborate (3b)
Mp 79–81 °C.

IR (KBr): 3089, 3059, 3032, 2906, 2870, 2202, 1741, 1578, 1477, 1454, 1390, 1354, 1284, 1259, 1208, 1066, 905, 804, 748, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, $C_6H_4CH_3$), 4.45 (s, 2 H, H-3), 4.57 (s, 2 H, H-5), 7.29–7.33 (m, 7 H), 7.92 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 24.4, 57.9, 72.5, 106.6, 110.5, 128.2, 128.3 (2 C), 128.5 (2 C), 133.5 (2 C), 134.6 (2 C), 136.3, 144.5.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{17}H_{16}IO$: 363.0246; found: 363.0245.

Hex-1-enyl(4-methylphenyl)iodonium Tetrafluoroborate (3c)
Oil.

IR (neat): 3086, 2959, 2932, 2872, 1631, 1584, 1483, 1463, 1397, 1283, 1210, 1065, 918, 804 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3 H, H-6), 1.24–1.34 (m, 2 H, H-5), 1.39–1.47 (m, 2 H, H-4), 2.30–2.35 (m, 2 H, H-3), 2.43 (s, 3 H, $C_6H_4CH_3$), 6.76 (d, *J* = 13.7 Hz, 1 H, H-1), 6.89–6.96 (m, 1 H, H-2), 7.30 (d, *J* = 8.5 Hz, 2 H), 7.87 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 21.7, 22.3, 30.0, 35.2, 97.1, 105.8, 133.6 (2 C), 136.0 (2 C), 144.3, 154.8.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{13}H_{18}I$: 301.0453; found: 301.0454.

(4-Methylphenyl)(2-phenylethenyl)iodonium Tetrafluoroborate (3d)
Oil.

IR (neat): 3085, 2960, 2925, 2871, 1684, 1591, 1566, 1483, 1447, 1396, 1283, 1038, 804, 731 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, $C_6H_4CH_3$), 7.24–7.47 (m, 8 H), 7.71 (d, *J* = 14.2 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 96.6, 106.6, 128.4 (2 C), 129.3 (2 C), 131.4, 133.5 (2 C), 134.4, 136.1 (2 C), 144.2, 151.1.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{15}H_{14}I$: 321.0140; found: 321.0137.

(4-*tert*-Butylcyclohex-1-enyl)(4-methylphenyl)iodonium Tetrafluoroborate (3e)
Mp 75–76 °C.

IR (KBr): 3089, 3066, 2961, 2868, 1627, 1579, 1479, 1436, 1399, 1366, 1083, 1057, 1022, 801, 692 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84 (s, 9 H, *t*-Bu), 1.36–1.53 (m, 2 H), 1.89–1.93 (m, 1 H), 2.22–2.31 (m, 1 H), 2.42–2.48 (m, 4 H), 2.60–2.71 (m, 2 H), 6.98–7.00 (m, 1 H, H-2), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 26.9 (3 C), 27.2, 31.8, 32.2, 35.2, 41.9, 104.3, 119.0, 133.3 (2 C), 135.8 (2 C), 144.1, 147.2.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{17}H_{24}I$: 355.0923; found: 355.0929.

Bis(4-Methylphenyl)iodonium Tetrafluoroborate (3g)
Mp 113–114 °C.

IR (KBr): 3086, 3048, 2954, 2927, 2867, 1666, 1579, 1479, 1447, 1396, 1282, 1211, 1188, 1060, 999, 801 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 6 H, CH_3), 7.21 (d, *J* = 8.6 Hz, 4 H), 7.90 (d, *J* = 8.6 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7 (2 C), 109.0 (2 C), 133.6 (4 C), 135.7 (4 C), 144.3 (2 C).

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{14}H_{14}I$: 309.0140; found: 309.0138.

(4-Chlorophenyl)(4-methylphenyl)iodonium Tetrafluoroborate (3i)
Mp 46–47 °C.

IR (KBr): 3092, 2954, 2927, 1918, 1742, 1635, 1585, 1556, 1471, 1391, 1282, 1213, 1190, 1089, 990, 803 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 3 H, $C_6H_4CH_3$), 7.26 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.8 Hz, 2 H), 7.88–7.93 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 108.4, 109.1, 132.1 (2 C), 132.9 (2 C), 135.3 (2 C), 136.2 (2 C), 139.3, 143.8.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{13}H_{11}ClI$: 328.9594; found: 328.9597.

(4-Methylphenyl)(5-methyl-2-thienyl)iodonium Tetrafluoroborate (3j)
Mp 105–107 °C.

IR (KBr): 3102, 2959, 2925, 2862, 1910, 1632, 1576, 1528, 1477, 1444, 1420, 1395, 1283, 1223, 1188, 1074, 934, 801 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, $C_6H_4CH_3$), 2.59 (s, 3 H, thienyl-CH_3), 6.79 (d, *J* = 3.9 Hz, 1 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 3.9 Hz, 1 H), 7.87 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 21.3, 88.1, 112.3, 128.7, 133.0 (2 C), 134.1 (2 C), 142.9, 143.7, 153.9.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{12}H_{12}IS$: 314.9704; found: 314.9714.

[3-(Benzyloxy)prop-1-ynyl](phenyl)iodonium Tetrafluoroborate (7)
Mp 46–47 °C.

IR (KBr): 3090, 3062, 3030, 2925, 2858, 2186, 1724, 1561, 1500, 1456, 1377, 1077, 983, 739, 700 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.48 (s, 2 H, H-3), 4.59 (s, 2 H, H-5), 7.30–7.36 (m, 5 H), 7.54 (t, *J* = 8.1 Hz, 2 H), 7.68 (t, *J* = 7.5 Hz, 1 H), 8.06 (d, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 57.9, 72.5, 107.0, 114.4, 128.2, 128.3 (2 C), 128.5 (2 C), 132.7 (2 C), 133.1, 134.5 (2 C), 136.3.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{16}H_{14}IO$: 349.0089; found: 349.0088.

[3-(Benzyloxy)prop-1-ynyl](4-chlorophenyl)iodonium Tetrafluoroborate (8)
Mp 89–90 °C.

IR (KBr): 3085, 3061, 3033, 2927, 2871, 2197, 1638, 1473, 1392, 1352, 1264, 1086, 994, 971, 809, 744, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.46 (s, 2 H, H-3), 4.58 (s, 2 H, H-5), 7.30–7.33 (m, 5 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 8.00 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.0, 58.3, 72.9, 107.6, 111.2, 128.60, 128.64 (2 C), 128.9 (2 C), 133.0 (2 C), 136.3 (2 C), 136.6, 140.5.

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{16}H_{13}ClIO$: 382.9700; found: 382.9707.

One-Pot Synthesis of (*Z*)-(2-Fluoro-2-phenylethenyl)(4-methylphenyl)iodonium Tetrafluoroborate (10)

$TolIF_2$ (**2**) (256 mg, 1 mmmol) was dissolved in anhyd MeCN (20 mL) in a Teflon PFA vessel. Borate **1k** (208 mg, 1 mmol) was added, and the mixture was stirred for 15 min at r.t. Then 20% aq HF (1.0 g, 10 mmol) was added, and the mixture was stirred for 16 h at 60 °C. The resulting soln was poured into 5% aq $NaBF_4$ (30 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. To the residue was added a little CH_2Cl_2 (2 mL), followed by the addition of a large quantity of hexane (40 mL). The upper clear part was removed by decantation, and the remaining solid was washed with hexane. Finally, complete removal of the solvent under reduced pressure gave **10**.

Yield: 342 mg (82%); mp 144–145 °C.

IR (KBr): 3114, 1629, 1575, 1496, 1477, 1449, 1287, 1190, 1083, 1038, 799, 782, 743, 694 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3 H, $C_6H_4CH_3$), 7.37 (d, *J* = 8.2 Hz, 2 H), 7.38–7.60 (m, 3 H), 7.74 (d, *J* = 7.4 Hz, 2 H), 7.90 (d, *J* = 37.6 Hz, 1 H, H-1), 8.04 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 80.6 (d, $^2J_{C-F}$ = 21.7 Hz, 1 C, C-1), 111.8, 125.9 (d, $^3J_{C-F}$ = 6.6 Hz, 2 C, *o*-Ph), 127.4, (d, $^2J_{C-F}$ = 27.8 Hz, 1 C, *ipso*-Ph), 129.4 (2 C), 132.5 (3 C), 135.1 (2 C), 142.6, 164.5 (d, $^1J_{C-F}$ = 260.5 Hz, 1 C, C-2).

^{19}F NMR (376 MHz, DMSO-d_6): δ = –84.2 (d, *J* = 37.6 Hz, 1 F, F-2).

HRMS–FAB: *m/z* $[M - BF_4]^+$ calcd for $C_{15}H_{13}FI$: 339.0046; found: 339.0042.

References

(1) For reviews on iodonium salts, see: (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (b) Wirth, T.; Hirt, U. H. *Synthesis* **1999**, 1271. (c) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927. (d) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179. (e) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123. (f) Varvoglis, A. *Synthesis* **1984**, 709.

(2) For books on iodonium salts, see: (a) *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; Wiley-VCH: Weinheim, **1999**. (b) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; Wiley-VCH: Weinheim, **1992**.

(3) For recently published papers concerned with iodonium salt synthesis, see: (a) Kitamura, T.; Inoue, D.; Wakimoto, I.; Nakamura, T.; Katsuno, R.; Fujiwara, Y. *Tetrahedron* **2004**, *60*, 8855. (b) Zhdankin, V. V.; Koposov, A. Y.; Su, L.; Boyarskikh, V. V.; Netzel, B. C.; Young, V. G. Jr. *Org. Lett.* **2003**, *5*, 1583.

(4) (a) Kitamura, T.; Aoki, Y.; Isshiki, S.; Wasai, K.; Fujiwara, Y. *Tetrahedron Lett.* **2006**, *47*, 1709. (b) Klein, M.; König, B. *Tetrahedron* **2004**, *60*, 1087. (c) Abe, T.; Yamaji, T.; Kitamura, T. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2175. (d) Radhakrishnan, U.; Stang, P. J. *J. Org. Chem.* **2003**, *68*, 9209. (e) Kitamura, T.; Abe, T.; Fujiwara, Y.; Yamaji, T. *Synthesis* **2003**, 213. (f) Ochiai, M.; Miyamoto, K.; Suefuji, T.; Shiro, M.; Sakamoto, S.; Yamaguchi, K. *Tetrahedron* **2003**, *59*, 10153. (g) Carroll, M. A.; Pike, V. W.; Widdowson, D. A. *Tetrahedron Lett.* **2000**, *41*, 5393.

(5) (a) Fujita, M.; Lee, H. J.; Okuyama, T. *Org. Lett.* **2006**, *8*, 1399. (b) Ochiai, M.; Miyamoto, K.; Yokota, Y.; Suefuji, T.; Shiro, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 75. (c) Abo-Amer, A.; Adonin, N. Y.; Bardin, V. V.; Fritzen, P.; Frohn, H.-J.; Steinberg, C. *J. Fluorine Chem.* **2004**, *125*, 1771.

(6) Benziodoxole and its acetoxy derivative can react with alkynylboronates to afford iodonium salts in the absence of acids; however, excess boronate and reflux temperature in acetonitrile are required. See: Zhdankin, V. V.; Persichini, P. J. III; Cui, R.; Jin, Y. *Synlett* **2000**, 719.

(7) For reviews on trifluoro(organo)borates, see: (a) Molander, G. A.; Figueroa, R. *Aldrichimica Acta* **2005**, *38*, 49. (b) Darses, S.; Genet, J.-P. *Eur. J. Org. Chem.* **2003**, 4313.

(8) (a) Darses, S.; Michaud, G.; Genet, J.-P. *Eur. J. Org. Chem.* **1999**, 1875. (b) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020.

(9) (a) Batey, R. A.; Quach, T. D.; Shen, M.; Thadani, A. N.; Smil, D. V.; Li, S.-W.; MacKay, D. B. *Pure Appl. Chem.* **2002**, *74*, 43. (b) Kerverdo, S.; Gingras, M. *Tetrahedron Lett.* **2000**, *41*, 6053.

(10) Sawaguchi, M.; Ayuba, S.; Hara, S. *Synthesis* **2002**, 1802; and references cited therein.

(11) The iodonium salts **5** and **6** were obtained as an inseparable mixture. The yields were determined by ^1H NMR spectroscopy; for the spectral data of the (*Z*)-(2-acetoxyalkenyl)iodonium salt, see: Ochiai, M.; Kitagawa, Y. *J. Org. Chem.* **1999**, *64*, 3181.

(12) (a) Yoshida, M.; Komata, A.; Hara, S. *Tetrahedron* **2006**, *62*, 8636. (b) Yoshida, M.; Hara, S. *Org. Lett.* **2003**, *5*, 573.

(13) (a) Brown, H. C.; Cambell, J. B. Jr. *J. Org. Chem.* **1980**, *45*, 389. (b) Petasis, N. A.; Yudin, A. K.; Zavialov, I. A.; Prakash, G. K. S.; Olah, G. A. *Synlett* **1997**, 606.

(14) (a) Bardin, V. V.; Idemskaya, S. G.; Frohn, H.-J. *Z. Anorg. Allg. Chem.* **2002**, *628*, 883. (b) Smoum, R.; Rubinstein, A.; Srebnik, M. *Org. Biomol. Chem.* **2005**, *3*, 941. (c) Molander, G. A.; Katona, B. W.; Machrouhi, F. *J. Org. Chem.* **2002**, *67*, 8416.

(15) Kasumov, T. M.; Brel, V. K.; Koz'min, A. S.; Zefirov, N. S. *Synthesis* **1995**, 775.

(16) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.