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Synthesis of Multifunctional Aryl(trifloxyalkenyl)iodonium Triflate Salts

Balázs L. Tóth,*[,†] Ferenc Béke,[†] Orsolya Egyed,[‡] Attila Bényei,[§] András Stirling,[‡] and Zoltán Novák*[,†]

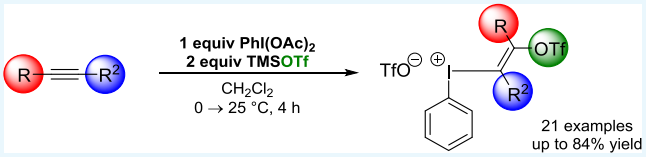
[†]ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry, Eötvös Loránd University, Faculty of Science, Pázmány Péter stny. 1/A, H-1117 Budapest, Hungary

[‡]Research Centre for Natural Sciences of the Hungarian Academy of Sciences, Magyar Tudósok körútja 2, H-1117 Budapest, Hungary

[§]Department of Pharmaceutical Chemistry, University of Debrecen, Egyetem tér 1, H-4032 Debrecen, Hungary

Supporting Information

ABSTRACT: A convenient procedure for the synthesis of aryl(trifloxyalkenyl)iodonium triflate salts from commercially available (diacetoxyiodo)benzene, trimethylsilyl trifluoromethanesulfonate, and acetylenes under mild conditions was developed. The obtained multifunctional hypervalent vinyliodonium salts equipped with electrophilic and nucleophilic functions could serve as novel C2 synthons for organic transformations. The structure of the iodonium salts was identified by multidimensional NMR spectroscopy and X-ray crystallography.



INTRODUCTION

In the last decade, the synthesis and application of hypervalent iodine reagents became a hot topic in synthetic organic chemistry. Due to their electrophilic character, high reactivity, general low toxicity, and easy preparation, +3 oxidation state organic iodonium salts are frequently used in arylation, alkenylation, alkynylation, or alkylation reactions.[1] Although the number of applications of these hypervalent reagents increases, the synthesis and utilization of alkenyl derivatives[2] are still a less explored topic of hypervalent iodine chemistry.[3] However, the alkenyl function appears as an important molecular motif in innumerable syntheses of valuable chemical compounds.[4] Therefore, the design of direct alkenylation reactions and multifunctional alkenyl building blocks has great synthetic potential.[5] To fulfill this synthetic demand, (trifloxyalkenyl)iodonium triflate salts[6] were designed and utilized in ligand exchange reactions resulting various diaryliodonium species,[7] palladium-catalyzed cross-coupling reactions,[8] and also in metal-free substituted oxazole ring formation reaction.[9]

Although the synthesis of aryl(trifloxyalkenyl)iodonium triflate salts can be achieved starting from iodosylbenzene, trifluoromethanesulfonic acid, and acetylenes,[10] their synthesis is based on the utilization of less available I(III) species (prepared from DIB) and highly sensitive TfOH. Most importantly, the efficiency of the synthesis is limited to 50% maximum theoretical yield because of the 1:1 ratio of λ^3 iodane source to triflate anion (Scheme 1). Of note, there are three examples for the syntheses of the target alkenes, starting from ArI or $PhI(OAc)_2$, but the first strategy uses special FXeOTf reagent,[6e] and there are only two reactions of DIB with 2 equiv of TfOH and terminal alkyne, which reportedly reach 55 and 56% isolated yield, respectively.[7a,c]

To overcome the limitations of the aforementioned existing procedures and expand the chemical space of available alkenyl(aryl)iodonium salts, we aimed to design new procedure and synthetic approach for the efficient synthesis of novel multifunctional alkenyl synthons using less corrosive trimethylsilyl triflate (TMSOTf) as triflate source and readily available aryliodonium source such as (diacetoxyiodo)benzene (DIB, **3**) (Scheme 2). Our synthetic strategy is based on the utilization of both internal and terminal acetylenes containing versatile alkyl, aryl, and hetaryl fragments equipped with various synthetically useful functional groups (OH, Br, Cl, CN).

RESULTS AND DISCUSSION

We began the synthetic investigation with the preparation of phenyl(trifloxyalkenyl)iodonium triflate salt from DIB and phenylacetylene using TMSOTf as activator. Compared to the final, optimized reaction conditions, the following modifications resulted in lower than 41% yield: the concentration of DIB higher than 0.5 mol/L, less inert or polar solvents, higher or lower reaction temperatures, longer reaction time, and less equivalent of added acetylene or TMSOTf (Scheme 3).

Additionally, increasing the amount of phenylacetylene up to 1.5 equiv did not give the target product in higher yield. Drawing the lessons, we determined the best synthetic

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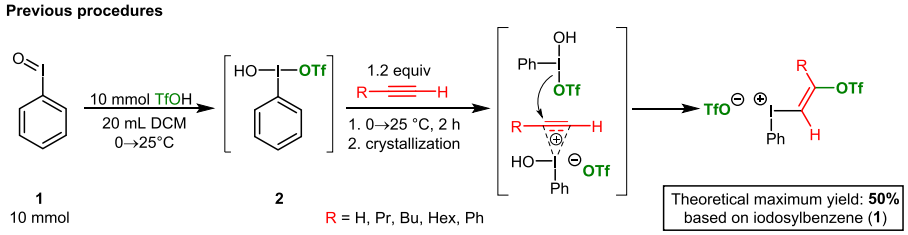
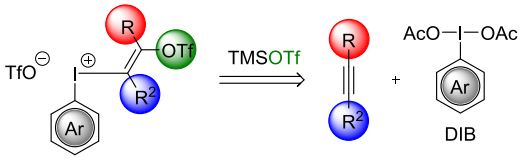
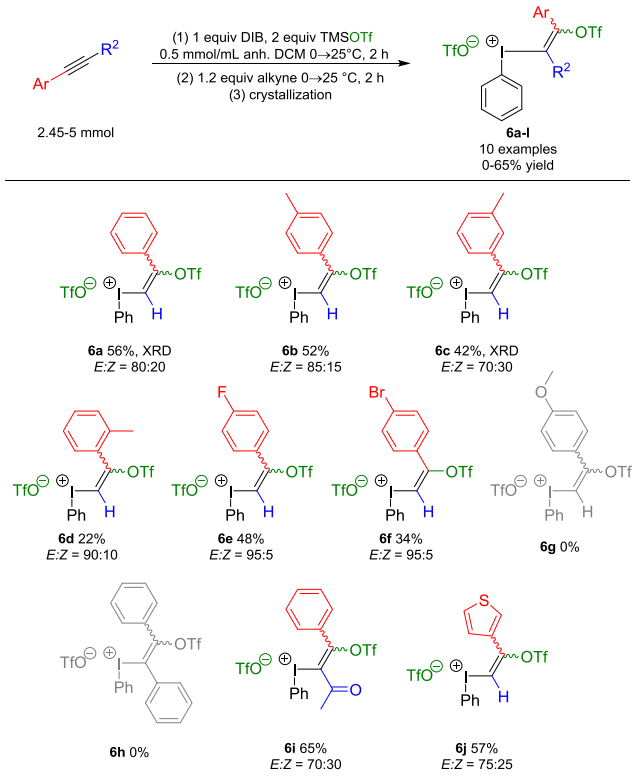
Scheme 1. Previous Literature Procedures, Highlighting the Formation of Trifloxyalkenyl(aryl)iodonium Triflates from Two Hypervalent Iodine Reagent



Scheme 2. Retrosynthetic Approach to the Access of Multifunctional Aryl(trifloxyalkenyl)iodonium Triflate Salts



Scheme 4. Scope of Aryl-Substituted Phenyl(vinyltrifloxy)iodonium Triflate Salts

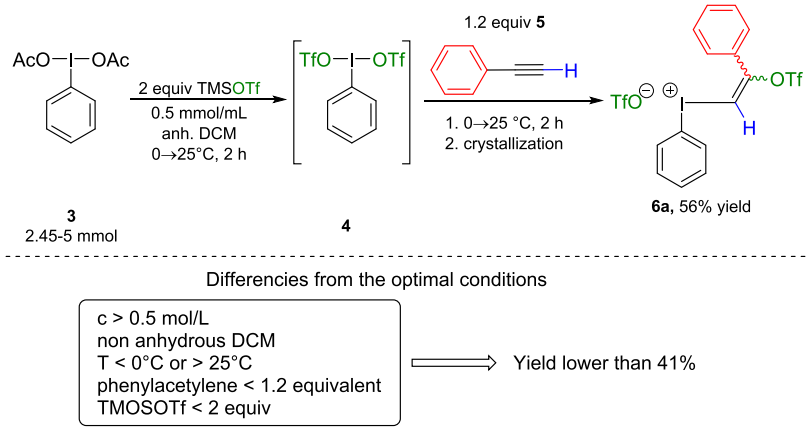


conditions to the access of the target compounds **6a**. To the anhydrous dichloromethane solution of DIB, 2 equiv of trimethylsilyl trifluoromethanesulfonate have been added at 0 °C and the temperature increased to 25 °C. The colorless solution turns yellow by forming bis(trifloxy)iodobenzene (**4**).[11] The solution was cooled again to 0 °C, and the acetylene derivative was added dropwise. The reaction mixture darkened while the desired aryl(trifloxyalkenyl)iodonium triflate product forms and may precipitate from the solution at 0 °C. For the completion of the reaction, we allowed to warm up the mixture to 25 °C. As shown in Scheme 3, after the evaporation of solvent and recrystallization procedure, we obtained the unsubstituted phenyl derivative **6a** as a white solid with 56% yield.

In general, the reaction took place in a similar manner, resulting in off-white solids after crystallization; nevertheless, the determination of their structure was a more complex task. To study the influence of steric and electronic effect of substituents on aromatic systems, a series of hypervalent iodonium salts have been synthesized (Scheme 4).

The methyl group in para position has no significant effect on the reaction and gave **6b** in 52% yield, but the yields of **6c** meta or **6d** ortho methyl product were 42 and 22%, respectively. However, the presence of methyl group reduced the yields, and under the reaction conditions, the formation of *E* product gained advantage over *Z* isomer. The structure of

Scheme 3. Study of the Conditions of the Preparation of 6a



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the *E*-**6a** and *E*-**6c** product has been determined also by X-ray crystallography (Figure 1).[12]

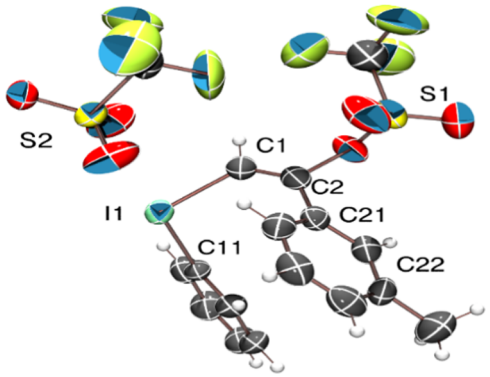


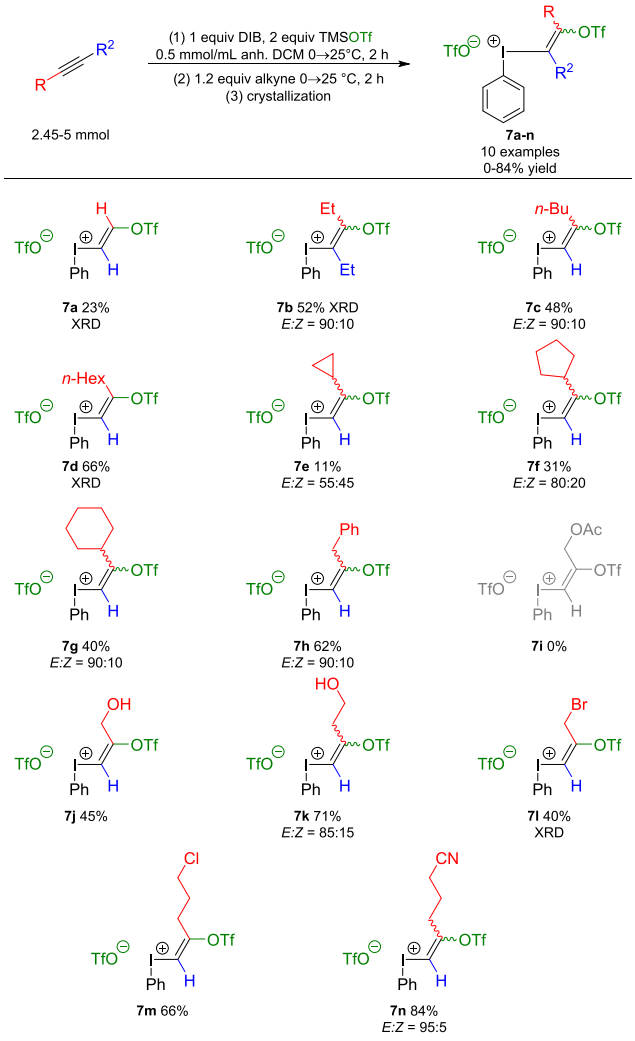
Figure 1. ORTEP view of **6c** at 50% probability level with partial numbering scheme. Selected bond distance [Å] and bond angle [deg] data: I1-C1 2.091 (9); C1-C2 1.298 (14); I1-C11 2.112 (7); C2-C21 1.472 (13); I1-C1-C2 121.6 (7); C1-C2-C21 132.0 (9); C1-I1-C11 97.0 (3).

The *para*-fluoro **6e** and bromo-substituted **6f** aryl derivatives were synthesized in 48 and 34% yields, respectively. Pushing the limits further, we have experienced similar consequences in the case of the electron-rich *para*-methoxyphenyl **6g** and the bulky diphenylethyne **6h**, and no product isolated. However, the steric hindrance does not appear in the reaction of 4-phenylbut-3-yn-2-one and the **6i** product formed effectively with 65%. There is one example to show the opportunity of the transformation of heterocyclic acetylenes: we have synthesized 3-ethynylthiophene to the corresponding **6j** product with 57% efficiency.

Fortunately, the reaction was not limited to the aromatic acetylenes; therefore, we investigated the synthesis of phenyl-(alkenyltrifloxy)iodonium triflate salts utilizing alkyl acetylene reactants. With the best reaction conditions in hand, we started to examine the effect of structural diversity on acetylene derivatives (Scheme 5). First, we synthesized the simplest and unsubstituted phenyl(vinyltrifloxy)iodonium triflate salt (**7a**) by bubbling acetylene gas into the reaction mixture, which yielded the vinyl salt in 23% yield. This low yield is understandable since the product (**7a**) is highly soluble in most of organic solvents and decomposes quickly. Increasing the length of side chains on vinyl moiety by the application of different terminal alkylacetylenes resulted in higher stability, lower solubility, and better yields. The transformation of hex-3-yne, hex-1-yne, and oct-1-yne yielded the desired products in 52% (**7b**), 48% (**7c**), and 66% (**7d**) yields, respectively. The experiments have shown that the external and internal acetylene can be utilized, and the presence of ethyl groups has no steric hindrance effect on the formation of the salts. The molecular structures of selected iodonium species were identified by X-ray measurement.[12]

Next, we reacted cycloalkyl acetylenes with DIB in the presence of TMSOTf under the optimal reaction conditions. Similarly to the previous experimental experiences, we found analogous tendency of the yields as a function of ring size. The cyclopropyl-substituted phenyl(vinyl)iodonium triflate salt (**7e**) was obtained with only 11% yield; nevertheless, the extension of alkyl chain decreased the solubility of the salts and increased the yield as well. Accordingly, the cyclopentyl (**7f**, 31%), cyclohexyl (**7g**, 40%), and benzyl (**7h**, 62%) derivatives resulted in higher yields.

Scheme 5. Scope of Alkyl-Substituted Phenyl(vinyltrifloxy)iodonium Triflate Salts



Moving forward to the synthesis of more challenging multifunctional alkenyliodonium salts, we studied the synthetic applicability of different terminal alkylacetylenes functionalized with OAc, OH, Br, Cl, and CN groups at the alkyl terminal. These functions enable further transformations on the side chain with the utilization of nucleophilic or electrophilic reagents. Although under the reaction conditions the ester functionality (**7i**) was not tolerated, the unprotected propargyl alcohol and but-3-yn-1-ol underwent reaction and gave the corresponding hypervalent iodine product **7j** in 45% yield and **7k** in 71% yield. Interestingly, we observed diminished stability at 25 °C in the case of **7k** compared to **7j**, which can be rationalized by the more flexible alkyl chain and a potential intramolecular cyclization side reaction. Next, we studied the reactivity of alkynes bearing halogen and pseudohalogen functional groups. It was found that the propargyl bromide can be transformed into compound **7l** with 40% yield. The structure of this trifunctional alkenyliodonium salt has been confirmed by X-ray measurements.[12]

The longer alkyl chain primary chloro **7m** and cyano **7n** products formed in good yields, 66 and 84%, respectively.

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As the NMR measurements revealed, under the reaction conditions, the *Z* isomer formed in the same way as the *E* isomer. However, the DFT calculations showed that the energy gap between the *Z* and *E* product is very low.[12] We found that the presence of an alkyl or aryl group in (vinyltrifloxy)-iodonium moiety favored in *E* position. The separation of *Z* and *E* products is not feasible by crystallization.

CONCLUSIONS

In summary, we developed a new synthetic method for the preparation of substituted trifloxyvinyliodonium triflates using commercially available, easy-to-handle starting materials such as acetylene, (diacetoxyiodo)benzene, and trimethylsilyl triflate. The synthesis of the target compounds was performed under mild reaction conditions, and the procedure ensures a novel synthetic route to multifunctional alkynyliodonium salts with wide structural diversity, which were identified by multidimensional NMR measurements and X-ray crystallography. The obtained hypervalent vinyliodonium salts containing electrophilic and nucleophilic functions could serve as novel alkenyl building blocks for versatile organic transformations.

EXPERIMENTAL SECTION

General Conditions. Analytical thin-layer chromatography (TLC) was performed on Merck DC precoated TLC plates with 0.25 mm Kieselgel 60 F254. Visualization was performed with a 254 nm UV lamp.

The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Agilent (Varian) VNMRS-400 and VNMR-600 spectrometers in CD_2Cl_2. Measurements were performed on indirect detection Z-gradient probes. Chemical shifts are expressed in parts per million (δ). The ^{1}H and ^{13}C chemical shifts are referenced to the residual solvent signals; for ^{19}F chemical shifts, $CFCl_3$ internal standard is used. Coupling constants (J) are reported in hertz (Hz). Splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The structure determination is based on one- (^{1}H, ^{13}C, ^{19}F NMR, selective 1d-noesy) and two-dimensional (^{1}H-^{13}C-gHSQCAD, ^{1}H-^{13}C-gHMBCAD, ^{1}H-zqTOCSY) NMR experiments. NMR assignments refer in each case to the main (trans) component except in the case of **6j** where both the trans and *Z* isomers could be fully assigned.

IR spectra were obtained in dichloromethane solutions on a Mettler Toledo ReactIR 15, AgX DiComp probe, 6 mm × 1.5 m Fiber (silver halide), MCT detector. The in situ reactions were conducted in the following setup: sampling interval, 15 s; 2500−650 cm^{-1} (resolution, 8 cm^{-1}); scan option, AutoSelect; gain, 1×. Data were processed by Mettler Toledo iC IR.

All melting points were measured on Büchi 501 apparatus and are uncorrected.

High-resolution mass spectra were acquired on an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive-ion mode. Injections of 0.1−0.3 μL were directed to the mass spectrometer at a flow rate of 0.5 mL/min (70% acetonitrile−water mixture, 0.1% formic acid), using an Agilent 1260 Infinity HPLC system. Jet Stream parameters: drying gas (N_2) flow and temperature, 10.0 L/min and 325 °C, respectively; nebulizer gas (N_2) pressure, 10 psi; capillary voltage, 4000 V; sheath gas flow and temperature, 325 °C and 7.5 L/min, respectively; TOFMS parameters: fragmentor voltage, 120 V; skimmer potential, 120 V; OCT 1 RF Vpp, 750 V. Full-scan mass spectra were acquired over the m/z range of 100−2500 at an acquisition rate of 250 ms/spectrum and processed by Agilent MassHunter B.03.01 software.

Preparation of Aryl(trifloxyalkenyl)iodonium Triflate Salts. A 30 mL vial was charged with (diacetoxyiodo)benzene (98%, 1 equiv, 5 mmol, 1643 mg), equipped with a stirring bar, and then sealed with a cap. The reaction atmosphere changed to argon by three consecutive evacuation and argon backfillation processes. Then, 10 mL of absolute dichloromethane was added by a syringe and stirred at 25 °C for 5 min. The solution was cooled to 0 °C and stirred vigorously for 10 min. Trimethylsilyl trifluoromethanesulfonate (98%, 2 equiv, 10 mmol, 2268 mg, 1.85 mL) was added dropwise in 1 min. The solution turned to a clear yellow solution. The reaction mixture was allowed to warm up to 25 °C and stirred for 2 h. Then, the solution was cooled to 0 °C and acetylene derivative (1.2 equiv, 6 mmol) was added dropwise by a syringe in 2 min under vigorous stirring. The reaction mixture was allowed to warm up to 25 °C. The yellow solution turned to a dark-colored mixture. After 2 h, the solvent was evaporated and cold diethyl ether and pentane were added and cooled in a freezer to crystallize the salts. The precipitates were collected by filtration, and in case the solid was not white due to the decomposition products, it was washed with absolute 1,2-dichloroethane (in case of aryl derivatives), diethyl ether, and pentane to obtain pure white compound. The materials were dried quickly in high vacuum at 25 °C, capped tightly, and stored in a freezer at −20 °C. In these conditions, the salts remained usable for more than half of year.

***6a**, (E)-Phenyl(2-phenyl-2-(((trifluoromethyl)sulfonyl)-oxy)vinyl)iodonium trifluoromethanesulfonate[8−10] and (Z)-Phenyl(2-phenyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-iodonium trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (98%, 625 mg, 672 μL) phenylacetylene; 1700 mg (2.18 mmol, 56% yield, 80% *E*, 10% *Z*) white solid. MP: 132−134 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 7.39 (2H, m, H3′ + H5′); 7.47 (1H, s, H1); 7.48−7.56 (4H, m, H2″ + H3″ + H5″ + H6″); 7.58−7.67 (4H, m, H4″ + H2′ + H4′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 95.2 (C1); 114.8 (C1′);); 118.0 (q, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 129.8 (C2″ + C6″); 130.2 (C3″ + C5″); 130.3 (C1″); 132.6 (C3′ + C5′); 133.4 (C4′); 133.6 (C4″); 135.7 (C2′ + C6′); 158.6 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.5; −79.0. IR 1430, 1266, 1240, 1221, 1180, 1171, 1163, 1139, 1132, 1029, 988, 850, 779, 742, 734, 703, 677, 654 cm^{-1}. HRMS calculated for $C_{15}H_{11}O_3F_3SI$ [M]$^{+}$ 4549426; found 454.9422. XRD: see in SI.

***6b**, (E)-Phenyl(2-(p-tolyl)-2-(((trifluoromethyl)sulfonyl)-oxy)vinyl)iodonium Trifluoromethanesulfonate and (Z)-Phenyl(2-(p-tolyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (98%, 711 mg, 776 μL) 4-ethynyltoluene; 1594 mg (2.58 mmol, 52% yield, 85% *E*, 15% *Z*) white solid. MP: 121−124 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 2.46 (3H, s, CH_3); 7.33 (1H, s, H1); 7.34 (2H, m, H3″ + H5″); 7.38−7.45 (4H, m, H2″ + H6″ + H3′ + H5′); 7.66 (3H, m, H2′ + H4′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 22.0

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(CH_3); 93.9 (C1); 114.9 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 127.3 (C1″), 129.7 (C2″ + C6″); 130.9 (C3″ + C5″); 132.7 (C3′ + C5′); 133.5 (C4′); 135.7 (C2′ + C6′); 145.1 (C4″); 158.9 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.5; −79.0. IR 1424, 1255, 1236, 1219, 1176, 1133, 1027, 990, 969, 852, 826, 742, 729, 716, 660 cm^{-1}. HRMS calculated for $C_{16}H_{13}O_3F_3SI$ $[M]^+$ 468.9582; found 468.9576.

***6c**, (E)-Phenyl(2-(m-tolyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate and (Z)-Phenyl(2-(m-tolyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (97%, 719 mg, 798 μL) 3-ethynyltoluene; 1594 mg (2.11 mmol, 42% yield, 70% *E*, 30% *Z*) white solid. MP: 127−132 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 600 MHz), δ (ppm): 2.41 (3H, s, CH_3); 7.24 (1H, s, H2″); 7.33 (1H, d, *J* = 7.1 Hz, H6″); 7.35 (1H, s, H1); 7.40−7.50 (4H, m, H4″ + H5″ + H3′ + H5′); 7.63−7.70 (3H, m, H2′ + H4′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 150 MHz), δ (ppm): 21.6 (CH_3); 94.5 (C1); 114.8 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 126.8 (C6″); 129.9 (C2″); 130.2 (C1″ + C5″); 132.8 (C3′ + C5′); 133.5 (C4′); 134.6 (C4″); 135.7 (C2′ + C6′); 140.8 (C3″), 158.7 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 565 MHz), δ (ppm): −73.4; −79.0. IR 1430, 1268, 1243, 1223, 1180, 1169, 1161, 1141, 1130, 1029, 1010, 990, 895, 833, 742, 707, 680, 673, 664 cm^{-1}. HRMS calculated for $C_{16}H_{13}O_3F_3SI$ $[M]^+$ 468.9589; found 468.9582. XRD: see in the SI.

***6d**, (E)-Phenyl(2-(o-tolyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate and (Z)-Phenyl(2-(o-tolyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 3.48 mmol (98%, 1144 mg) (diacetoxyiodo)benzene and 4.18 mmol (97%, 500 mg, 542 μL) 2-ethynyltoluene; 477 mg (0.77 mmol, 22% yield, 90% *E*, 10% *Z*) white solid. MP: 98−102 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 600 MHz), δ (ppm): 2.05 (3H, s, CH_3); 7.29 (1H, d, *J* = 7.9 Hz, H3″); 7.36−7.40 (2H, m, H5″ + H6″); 7.42 (2H, m, H3′ + H5′); 7.50 (1H, s, H1); 7.50−7.60 (3H, m, H4″ + H2′ + H6′); 7.67 (1H, m, H4′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 150 MHz), δ (ppm): 19.4 (CH_3); 97.2 (C1); 113.8 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 126.9 (C1″); 127.5 (C5″); 129.5 (C2″); 131.2 (C6″); 132.0 (C3″); 132.8 (C3′ + C5′); 133.7 (C4″); 133.8 (C4′); 136.1 (C2′ + C6′); 159.8 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.6; −78.8. IR 1426, 1271, 1240, 1217, 1167, 1137, 1109, 1025, 992, 973, 861, 809, 800, 775, 740, 733, 712, 680, 669, 660 cm^{-1}. HRMS calculated for $C_{16}H_{13}O_3F_3SI$ $[M]^+$ 468.9582; found 468.9581.

***6e**, (E)-(2-(4-Fluorophenyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(2-(4-Fluorophenyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 3.33 mmol (98%, 1094 mg) (diacetoxyiodo)benzene and 4 mmol (98%, 490 mg, 467 μL) 1-ethynyl-4-fluorobenzene; 996 mg (1.6 mmol, 48% yield, 95% *E*, 5% *Z*) white solid. MP: 134−137 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 600 MHz), δ (ppm): 7.27 (2H, m, H3″ + H5″); 7.39 (1H, s, H1); 7.48 (2H, m, H3′ + H5′); 7.56 (2H, m, H2″ + H6″), 7.65−7.75 (3H, m, H2′ + H4′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 150 MHz), δ (ppm): 94.8 (C1); 114.6 (C1′); 117.8 (d, $^2J_{C,F}$ = 22.0 Hz, C3″ + C5″); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 126.4 (d, $^4J_{C,F}$ = 3.0 Hz, C1″); 132.4 (d, $^3J_{C,F}$ = 10.0 Hz, C2″ + C6″); 133.0 (C3′ + C5′); 133.8 (C4′); 135.6 (C2′ + C6′); 157.7 (C2); 165.9 (d, $^1J_{C,F}$ = 254.3 Hz, C4″). ^{19}F NMR (CD_2Cl_2, 25 °C, 565 MHz), δ (ppm): −73.3; −79.0. IR 1435, 1262, 1251, 1242, 1217, 1184, 1161, 1135, 1029, 990, 857, 844, 815, 744, 712, 656 cm^{-1}. HRMS calculated for $C_{15}H_{10}O_3F_4SI$ $[M]^+$ 472.9332; found 472.9340.

***6f**, (E)-(2-(4-Bromophenyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(2-(4-Bromophenyl)-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 2.5 mmol (98%, 822 mg) (diacetoxyiodo)benzene and 3 mmol (98%, 554 mg) 1-bromo-4-ethynylbenzene; 576 mg (0.84 mmol, 34% yield, 95% *E*, 5% *Z*) white solid. MP: 143−147 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 7.38 (2H, m, H2″ + H6″); 7.43 (2H, m, H3′ + H5′); 7.46 (1H, s, H1); 7.60−7.72 (5H, m, H2′ + H4′ + H6′ + H3″ + H5″). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 95.6 (C1); 114.8 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 128.6 + 129.2 (C1″ + C4″); 131.3 (C2″ + C6″); 132.8 (C3′ + C5′); 133.6 (C4′ + C3″ + C5″); 135.6 (C2′ + C6′), 157.5 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.3; −79.0. IR 1426, 1264, 1242, 1234, 1227, 1174, 1133, 1027, 1014, 992, 979, 850, 738, 693, 654 cm^{-1}. HRMS calculated for $C_{15}H_{10}O_3F_3SBrI$ $[M]^+$ 532.8531; found 532.8531.

***6i**, (E)-(3-Oxo-1-phenyl-1-(((trifluoromethyl)sulfonyl)oxy)but-1-en-2-yl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(3-Oxo-1-phenyl-1-(((trifluoromethyl)sulfonyl)oxy)but-1-en-2-yl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (96%, 901 mg, 910 μL) 4-phenyl-3-butyn-2-one; 2111 mg (3.27 mmol, 65% yield, 70% *E*, 30% *Z*) white solid. MP: 125−128 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 2.77 (3H, s, CH_3); 7.40 (2H, m, H3′ + H5′); 7.47 (2H, m, H2″ + H6″), 7.50−7.60 (4H, m, H2′ + H6′ + H3″ + H5″); 7.63 (1H, m, H4′); 7.70 (1H, m, H4″). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 30.0 (C4); 114.8 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 125.8 (C2); 128.4 (C1″); 129.9 (C3″ + C5″); 130.2 (C2″ + C6″); 132.4 (C3′ + C5′); 133.5 (C4′); 134.1 (C4″); 136.5 (C2′ + C6′); 159.9 (C1); 191.3 (C3). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −72.6; −78.8. IR 1445, 1434, 1279, 1219, 1169, 1130, 1038, 1022, 984, 934, 913, 880, 844, 783, 766, 736, 703, 686, 677 cm^{-1}. HRMS calculated for $C_{17}H_{13}O_4F_3SI$ $[M]^+$ 496.9526; found 496.9531.

***6j**, (E)-Phenyl(2-(thiophen-3-yl)-2-(((trifluoromethyl)-sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate and (Z)-Phenyl(2-(thiophen-3-yl)-2-(((trifluoromethyl)-sulfonyl)oxy)vinyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 3.85 mmol (98%, 1265 mg) (diacetoxyiodo)benzene and 4.62 mmol (97%, 515 mg, 474 μL) 3-ethynyltiophene; 1347 mg (2.21 mmol, 57% yield, 75% *E*, 25% *Z*) brownish deep green solid, MP: 84−87 °C (dec.). *E*-isomer: ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 7.30 (1H, dd, *J* = 5.1, 1.3 Hz, H4″); 7.35 (1H, s, H1); 7.44 (2H, m, H3′ + H5′); 7.56 (1H, dd, *J* = 5.1, 3.0 Hz, H5″); 7.64 (1H, m, H4′); 7.72 (2H, m, H2′ + H6′); 7.96 (1H, dd, *J* = 3.0, 1.3 Hz, H2″). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 93.2 (C1); 114.6 (C1′);

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118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 127.4 (C4″); 129.6 (C5″); 132.9 (C3′ + C5′); 133.1 (C2″); 133.6 (C4′); 135.5 (C2′ + C6′); 138.0 (C3″); 154.0 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −72.5; −78.9. *Z*-isomer: ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 7.30 (1H, dd, *J* = 5.1, 1.2 Hz, H4″); 7.47 (1H, s, H1); 7.48 (1H, dd, *J* =5.1, 2.8 Hz, H5″); 7.54 (2H, m, H3′ + H5′); 7.70 (1H, m, H4′); 7.85 (1H, dd, *J* = 2.8, 1.2 Hz, H2″); 8.08 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 89.2 (C1); 114.1 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 126.3 (C4″); 129.1 (C5″); 131.1 (C2″); 133.1 (C3′ + C5′); 133.7 (C4′); 136.0 (C2′ + C6′); 138.0 (C3″); 153.8 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.5; −78.9. *E-Z*: IR 1430, 1275, 1238, 1217, 1167, 1152, 1137, 1025, 1003, 990, 913, 878, 848, 822, 807, 787, 762, 748, 733, 708, 677 cm^{-1}. HRMS calculated for $C_{13}H_9O_3F_3S_2I$ [M]$^+$ 460.8988; found 460.8990.

***7a**, (E)-Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-iodonium Trifluoromethanesulfonate.*[6a,7b,8,10] The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene. Acetylene gas was generated from 6 mmol CaC_2 (80%, 481 mg); 545 mg (1.03 mmol, 21% yield) white solid. MP: 110−116 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 7.09 (1H, d, *J* = 12.3 Hz, H1); 7.54 (2H, m, H3′ + H5′), 7.68 (1H, d, *J* = 12.3 Hz, H2); 7.72 (1H, m, H4′); 8.03 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 91.3 (C1); 113.1 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 133.7 (C4′); 136.1 (C2′ + C6′); 149.9 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.3; −79.0. IR 1422, 1249, 1219, 1180, 1169, 1133, 1022, 1008, 990, 906, 856, 761, 740, 686, 679, cm^{-1}. HRMS calculated for $C_9H_7O_3F_3SI$ [M]$^+$ 378.9113; found 378.9107. XRD: see in the SI.

***7b**, (E)-Phenyl(4-(((trifluoromethyl)sulfonyl)oxy)hex-3-en-3-yl)iodonium Trifluoromethanesulfonate*[10] *and (Z)-Phenyl-(4-(((trifluoromethyl)sulfonyl)oxy)hex-3-en-3-yl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (97%, 508 mg, 703 μL) 3-hexyne; 1531 mg (2.62 mmol, 52% yield, 90% *E*, 10% *Z*) white solid. MP: 85−87 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 1.19 (3H, t, *J* = 7.1 Hz, CH_3); 1.33 (3H, t, *J* = 7.1 Hz, CH_3); 2.76 (2H, q, *J* = 7.1 Hz, CH_2); 3.04 (2H, q, *J* = 7.1 Hz, CH_2); 7.55 (2H, m, H3′ + H5′), 7.71 (1H, m, H4′); 7.95 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 11.3 (CH_3); 13.7 (CH_3); 28.7 (CH_2); 30.8 (CH_2); 112.6 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 123.8 (C3); 133.0 (C3′ + C5′); 133.5 (C4′); 135.4 (C2′ + C6′); 157.4 (C4). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −72.3; −76.9. IR 1415, 1279, 1234, 1223, 1206, 1165, 1146, 1132, 1085, 1025, 1010, 990, 956, 878, 742, 680, 665 cm^{-1}. HRMS calculated for $C_{13}H_{15}O_3F_3SI$ [M]$^+$ 434.9739; found 434.9746. XRD: see in the SI.

***7c**, (E)-Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)iodonium Trifluoromethanesulfonate*[6a,e,f,8,10] *and (Z)-Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)-iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (97%, 508 mg, 711 μL) 1-hexyne; 1390 mg (2.38 mmol, 48% yield, 90% *E*, 10% *Z*) white solid. MP: 114−118 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 0.91 (3H, m, CH_3); 1.37 (2H, m, $H5_{x,y}$); 2.18 (2H, m, $H4_{x,y}$); 2.82 (2H, t, *J* = 7.2 Hz, $H3_{x,y}$); 7.06 (1H, br. s, H1); 7.53 (2H, m, H3′ + H5′), 7.71 (1H, m, H4′); 7.98 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 13.9 (CH_3); 22.6 (C5); 28.6 (C4); 35.2 (C3); 92.1 (C1); 114.3 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.2 (C3′ + C5′); 133.7 (C4′); 135.3 (C2′ + C6′); 163.4 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.6; −78.9. IR 1430, 1269, 1242, 1223, 1210, 1165, 1139, 1122, 1061, 1023, 984, 900, 856, 828, 755, 742, 731, 675, 654 cm^{-1}. HRMS calculated for $C_{13}H_{15}O_3F_3SI$ [M]$^+$ 434.9739; found 434.9742.

***7d**, (E)-Phenyl(2-(((trifluoromethyl)sulfonyl)oxy)oct-1-en-1-yl)iodonium Trifluoromethanesulfonate.*[6a,9,10] The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (99%, 668 mg, 894 μL) 1-octyne; 2030 mg (3.32 mmol, 66% yield) white solid. MP: 121−123 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 0.88 (3H, t, *J* = 6.9 Hz, CH_3); 1.20−1.40 (6H, m, $H7_{x,y}$ + $H6_{x,y}$ + $H5_{x,y}$); 1.53 (2H, m, $H4_{x,y}$); 2.81 (2H, t, *J* = 7.6 Hz, $H3_{x,y}$); 7.14 (1H, s, H1); 7.53 (2H, m, H3′ + H5′); 7.69 (1H, m, H4′); 8.00 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 14.2 (CH_3); 22.9 + 29.0 + 31.8 (C7 + C6 + C5); 26.6 (C4); 35.4 (C3); 93.0 (C1); 114.5 (C1′); 118.9 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.6 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 133.4 (C4′); 135.3 (C2′ + C6′); 163.3 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −71.7; −77.0. IR 1432, 1271, 1245, 1221, 1208, 1163, 1143, 1128, 1027, 951, 899, 856, 835, 751, 731, 675, 654 cm^{-1}. HRMS calculated for $C_{15}H_{19}O_3F_3SI$ [M]$^+$ 434.9739; found 434.9742. XRD: see in the SI.

***7e**, (E)-(2-Cyclopropyl-2-(((trifluoromethyl)sulfonyl)oxy)-vinyl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(2-Cyclopropyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (98%, 405 mg, 519 μL) cyclopropylacetylene; 317 mg (0.558 mmol, 11% yield, 55% *E*, 45% *Z*) beige solid. MP: 73−76 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 0.9−1.25 (4H, m, $H2''_{x,y}$+$H3''_{x,y}$); 2.24 (1H, m, H1″); 7.07 (1H, s, H1); 7.53 (2H, m, H3′ + H5′), 7.69 (1H, m, H4′); 8.00 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 9.3 (C2″ + C3″); 16.3 (C4″); 90.3 (C1); 114.2 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 133.5 (C4′); 135.9 (C2′ + C6′); 162.6 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.6; −78.9. IR 1417, 1273, 1242, 1217, 1182, 1167, 1137, 1092, 1048, 1025, 1005, 990, 930, 912, 856, 796, 761, 733, 677 cm^{-1}. HRMS calculated for $C_{12}H_{11}O_3F_3SI$ [M]$^+$ 418.9426; found 418.9429.

***7f**, (E)-(2-Cyclopentyl-2-(((trifluoromethyl)sulfonyl)oxy)-vinyl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(2-Cyclopentyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 4 mmol (98%, 1315 mg) (diacetoxyiodo)benzene and 4.8 mmol (90%, 502 mg, 618 μL) cyclopentylacetylene; 748 mg (1.25 mmol, 31% yield, 80% *E*, 20% *Z*) off-white solid. MP: 102−106 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 1.60 (2H, m, $H2''_y$ + $H5''_y$); 1.66 (2H, m, $H3''_y$ + $H4''_y$); 1.72 (2H, m, $H3''_x$ + $H4''_x$); 1.84 (2H, m, $H2''_x$ + $H5''_x$); 3.44 (1H, m, H1″); 7.05 (1H, s, H1); 7.55 (2H, m, H3′ + H5′), 7.69 (1H, m, H4′);

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7.98 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 26.5 (C3″ + C4″); 31.0 (C2″ + C5″); 45.1 (C1″); 89.9 (C1); 114.6 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 133.4 (C4′); 135.3 (C2′ + C6′); 165.3 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.8; −78.9. IR 1426, 1277, 1249, 1215, 1165, 1135, 1077, 1025, 992, 928, 856, 798, 781, 751, 734, 679, 654 cm^{-1}. HRMS calculated for $C_{14}H_{15}O_3F_3SI$ $[M]^+$ 446.9739; found 446.9745.

***7g**, (E)-(2-Cyclohexyl-2-(((trifluoromethyl)sulfonyl)oxy)-vinyl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(2-Cyclohexyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)-(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 3.75 mmol (98%, 1233 mg) (diacetoxyiodo)benzene and 4.5 mmol (98%, 497 mg, 600 μL) cyclohexylacetylene; 910 mg (1.49 mmol, 40% yield, 90% *E*, 10% *Z*) off-white solid. MP: 153−156 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 1.19 (1H, m, H4″y); 1.30 (2H, m, $H3''_y$ + $H5''_y$); 1.37 (2H, m, $H2''_y$ + $H6''_y$); 1.59 (2H, m, $H2''_x$ + $H6''_x$); 1.71 (1H, m, $H4''_x$); 1.80 (2H, m, $H3''_x$ + $H5''_x$); 2.98 (1H, m, H1″); 7.03 (1H, s, H1); 7.55 (2H, m, H3′ + H5′), 7.70 (1H, m, H4′); 8.00 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 25.5 (C4″); 25.6 (C3″ + C5″); 29.5 (C2″ + C6″), 44.9 (C1″); 89.8 (C1); 114.8 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.1 (C3′ + C5′); 133.5 (C4′); 135.4 (C2′ + C6′); 166.0 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.7; −78.9. IR 1428, 1271, 1251, 1214, 1184, 1159, 1133, 1081, 1027, 992, 977, 921, 899, 846, 809, 796, 777, 759, 749, 734, 710, 679, 656 cm^{-1}. HRMS calculated for $C_{15}H_{17}O_3F_3SI$ $[M]^+$ 460.9895; found 460.9895.

***7h**, (E)-Phenyl(3-phenyl-2-(((trifluoromethyl)sulfonyl)-oxy)prop-1-en-1-yl)iodonium Trifluoromethanesulfonate and (Z)-Phenyl(3-phenyl-2-(((trifluoromethyl)sulfonyl)oxy)-prop-1-en-1-yl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 3.4 mmol (98%, 1117 mg) (diacetoxyiodo)benzene and 4.08 mmol (95%, 499 mg, 531 μL) 3-phenyl-1-propyne; 1310 mg (2.12 mmol, 62% yield, 90% *E*, 10% *Z*) white solid. MP: 133−139 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 4.16 (2H, s, $H3_{x,y}$); 7.15 (1H, s, H1); 7.20 (2H, m, H2″ + H6″); 7.38 (3H, m, H3″ + H4″ + H5″); 7.50 (2H, m, H3′ + H5′), 7.69 (1H, m, H4′); 7.87 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 41.2 (C3); 93.5 (C1); 114.5 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 129.3 (C4″), 129.8 (C2″ + C6″); 130.1 (C3″ + C5″); 133.1 (C3′ + C5′); 133.6 (C4′); 135.6 (C2′ + C6′); 160.1 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.5; −78.9. IR 1426, 1275, 1258, 1240, 1219, 1206, 1184, 1167, 1137, 1051, 1025, 990, 895, 820, 781, 736, 708, 693, 679, 654 cm^{-1}. HRMS calculated for $C_{16}H_{13}O_3F_3SI$ $[M]^+$ 468.9582; found 468.9594.

***7j**, (E)-(3-Hydroxy-2-(((trifluoromethyl)sulfonyl)oxy)prop-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate.*[6e] The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (99%, 340 mg, 358 μL) 2-propyn-1-ol; 1260 mg (2.26 mmol, 45% yield) off-white solid. MP: 101−105 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 4.51 (2H, d, *J* = 2.0 Hz, $H3_{x,y}$); 4.80 (1H, br. s, OH); 6.51 (1H, t, *J* = 2.0 Hz, H1); 7.57 (2H, m, H3′ + H5′), 7.75 (1H, m, H4′); 8.03 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 62.0 (C3); 90.4 (C1); 114.3 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 134.0 (C4′); 136.4 (C2′ + C6′); 151.3 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.1; −78.9. IR 1434, 1273, 1247, 1219, 1200, 1174, 1163, 1139, 1081, 1057, 1048, 1027, 992, 973, 899, 822, 800, 764, 742, 703, 680, 665, 654, cm^{-1}. HRMS calculated for $C_{10}H_9O_4F_3SI$ $[M]^+$ 408.9218; found 408.9219.

***7k**, (E)-(4-Hydroxy-2-(((trifluoromethyl)sulfonyl)oxy)but-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(4-Hydroxy-2-(((trifluoromethyl)sulfonyl)oxy)but-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (99%, 425 mg, 459 μL) 3-butyn-1-ol; 2043 mg (3.57 mmol, 71% yield, 85% *E*, 15% *Z*) white solid. MP: <25 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 3.00 (2H, t, *J* = 5.6 Hz, $H3_{x,y}$); 3.94 (2H, t, *J* = 5.6 Hz, $H4_{x,y}$); 4.65 (1H, br. s, OH); 6.95 (1H, s, H1); 7.56 (2H, m, H3′ + H5′); 7.62 (1H, m, H4′); 8.00 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 37.9 (C3); 59.8 (C4); 96.2 (C1); 113.8 (C1′); 118.9 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.6 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.0 (C3′ + C5′); 133.7 (C4′); 135.8 (C2′ + C6′); 157.0 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.4; −78.9. IR 1419, 1284, 1236, 1217, 1173, 1135, 1089, 1027, 990, 964, 925, 887, 846, 802, 779, 762, 740, 714, 695, 679 cm^{-1}. HRMS calculated for $C_{11}H_{11}O_4F_3SI$ $[M]^+$ 422.9375; found 422.9366.

***7l**, (E)-(3-Bromo-2-(((trifluoromethyl)sulfonyl)oxy)prop-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (97%, 736 mg, 551 μL) 3-bromo-1-propyne; 1239 mg (1.99 mmol, 40% yield) white solid. MP: 156−159 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 600 MHz), δ (ppm): 4.53 (2H, s, $H3_{x,y}$); 7.28 (1H, s, H1); 7.55 (2H, m, H3′ + H5′), 7.71 (1H, m, H4′); 8.08 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 150 MHz), δ (ppm): 27.9 (C3); 95.5 (C1); 114.1 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.1 (C3′ + C5′); 133.7 (C4′); 136.1 (C2′ + C6′); 156.4 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 565 MHz), δ (ppm): −73.0; −78.8. IR 1428, 1275, 1264, 1243, 1234, 1217, 1178, 1158, 1135, 1066, 1022, 988, 908, 822, 785, 757, 736, 708, 679, 665, 654 cm^{-1}. HRMS calculated for $C_{10}H_8O_3F_3SBrI$ $[M]^+$ 470.8374; found 470.8373. XRD: see in SI.

***7m**, (E)-(5-Chloro-2-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (96%, 641 mg, 657 μL) 5-chloro-1-pentyne; 1991 mg (3.29 mmol, 66% yield) white solid. MP: 84−89 °C (dec.). ^1H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 2.08 (2H, m, $H4_{x,y}$); 3.04 (2H, t, *J* = 7.4 Hz, $H3_{x,y}$); 3.61 (2H, t, *J* = 6.1 Hz, $H5_{x,y}$); 7.17 (1H, s, H1); 7.56 (2H, m, H3′ + H5′), 7.70 (1H, m, H4′); 8.03 (2H, m, H2′ + H6′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 29.0 (C4); 32.7 (C3); 43.9 (C5); 94.2 (C1); 114.3 (C1′); 118.0 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.1 (C3′ + C5′); 133.6 (C4′); 135.6 (C2′ + C6′); 161.3 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.5; −78.9. IR 1435, 1428, 1279, 1266, 1242, 1227, 1210, 1186, 1171, 1161, 1139, 1057, 1025, 992, 975, 900, 861, 816, 736, 686, 680 cm^{-1}. HRMS calculated for $C_{12}H_{12}O_3F_3SClI$ $[M]^+$ 454.9193; found 454.9200.

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***7n**, (E)-(5-Cyano-2-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate and (Z)-(5-Cyano-2-(((trifluoromethyl)sulfonyl)oxy)pent-1-en-1-yl)(phenyl)iodonium Trifluoromethanesulfonate.* The general procedure was followed starting from 5 mmol (98%, 1643 mg) (diacetoxyiodo)benzene and 6 mmol (98%, 570 mg, 641 μL) 5-cyano-1-pentyne; 2491 mg (4.18 mmol, 84% yield, 95% *E*, 5% *Z*) light yellow solid. MP: 70−75 °C (dec.). ^{1}H NMR (CD_2Cl_2, 25 °C, 400 MHz), δ (ppm): 2.00 (2H, m, $H4_{x,y}$) 2.52 (2H, t, J = 6.5 Hz, $H5_{x,y}$); 3.03 (2H, t, J = 7.0 Hz, $H3_{x,y}$); 7.20 (1H, s, H1); 7.56 (2H, m, H3′ + H5′), 7.73 (1H, m, H4′); 8.04 (2H, m, H2′ + H6′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C, 100 MHz), δ (ppm): 16.9 (C5); 22.4 (C4); 34.1 (C3); 94.5 (C1); 114.1 (C1′); 117.3 (CN); 118.0 (q, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 133.2 (C3′ + C5′); 133.7 (C4′); 135.6 (C2′ + C6′); 160.5 (C2). ^{19}F NMR (CD_2Cl_2, 25 °C, 376 MHz), δ (ppm): −73.3; −78.8. IR 1428, 1273, 1240, 1225, 1214, 1193, 1174, 1163, 1135, 1063, 1023, 992, 979, 910, 904, 876, 815, 738, 716, 679 cm^{-1}. HRMS calculated for $C_{13}H_{12}NO_3F_3SI$ $[M]^+$ 445.9535; found 445.9536.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00728.

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■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: tothb@zng.elte.hu. Phone: +36 1 372 2500 #1608 (B.L.T.).

*E-mail: novakz@elte.hu (Z.N.).

ORCID

András Stirling: 0000-0002-1696-7932

Zoltán Novák: 0000-0001-5525-3070

Notes

The authors declare no competing financial interest.

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(12) See details in Supporting Information.

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