Synthesis of Multifunctional Aryl(trifloxyalkenyl)iodonium Triflate Salts

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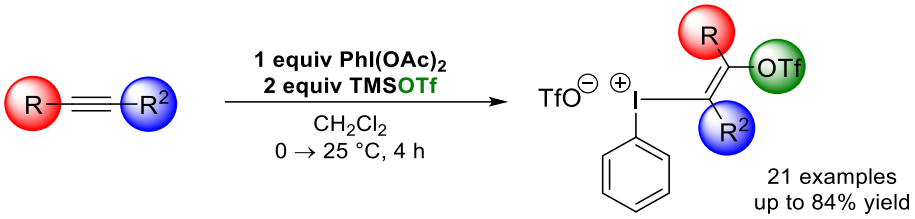


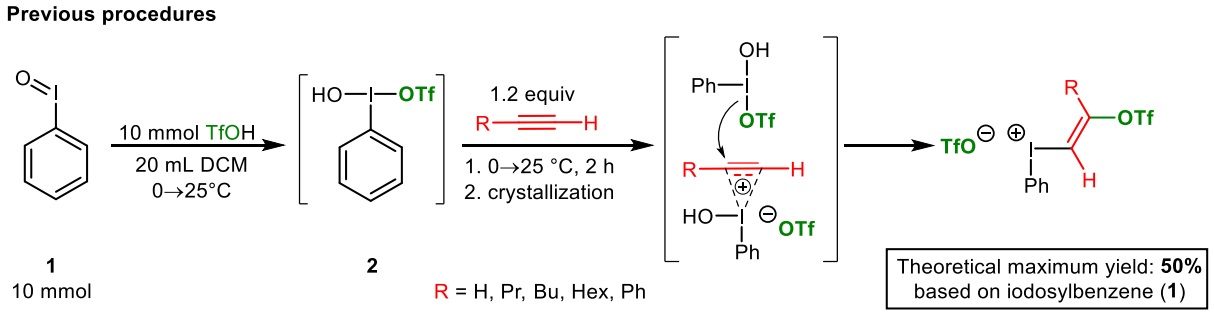
ABSTRACT: A convenient procedure for the synthesis of aryl(trifloxyalkenyl)iodonium triflate salts from commercially available (diacetoxyiodo)benzene, trimethylsilyl trifluoromethanesulfonate and acetylenes under mild conditions was developed. The obtained multifunctional hypervalent vinyliodonium salts 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 of the +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 important molecular motif in innumerable synthesis to the access of valuable chemical compounds.[4] Therefore, the design of direct alkenylation reactions and multifunctional alkenyl building blocks have great synthetic potential.[5] To fulfill this synthetic demand (trifloxyalkenyl)iodonium triflate salts[6] were designed and utilized in ligandum exchange reactions resulting various diaryliodonium species,[7] palladium catalyzed cross-coupling reactions[8] and also in metal-free substituted oxazole ring formation reaction.[9]

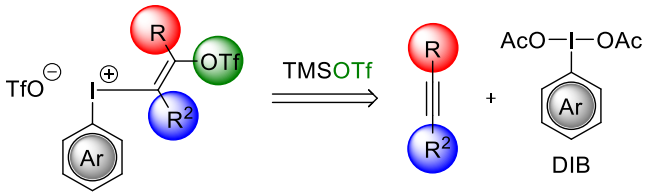
Although, the synthesis of aryl(trifloxyalkenyl)iodonium triflate salts can be achieved starting from iodosylbenzene, trifluoromethanesulfonic acid and acetylenes,[10] their synthesis is based on the utilization of less available I(III) species (prepared from DIB) and highly sensitive TfOH. Most importantly 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).



Scheme 1. Previous literature procedures, highlighting the formation of trifloxyalkenyl(aryl)iodonium triflates from two hypervalent iodine reagent.

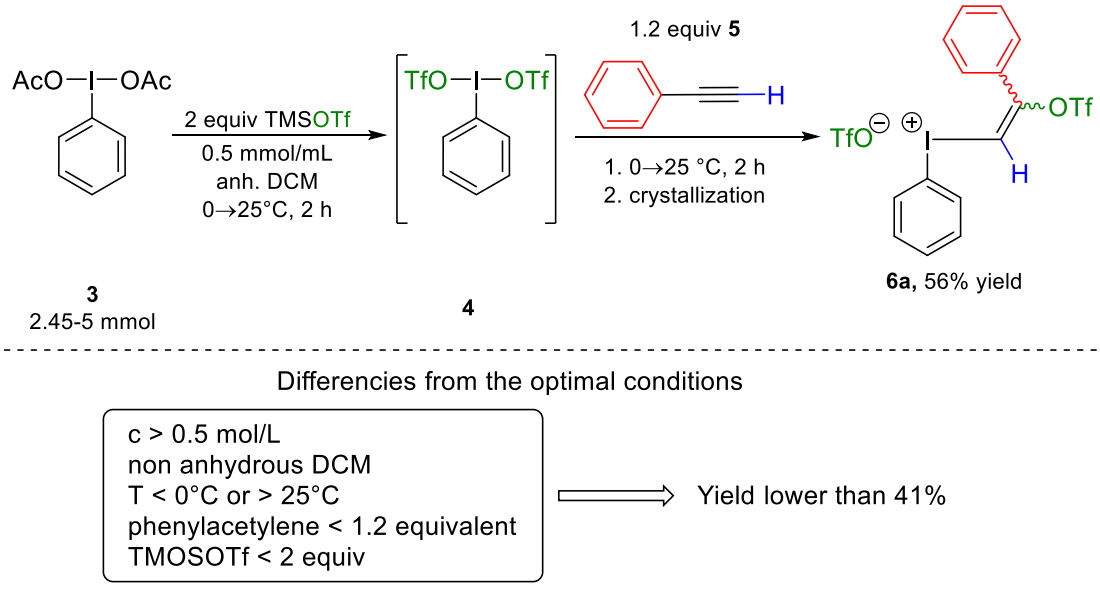
To overcome the limitations of existing procedures aforementioned and expand the chemical space of available alkenyl(aryl)iodonium salts we aimed to design new procedure and synthetic approach to the efficient synthesis of novel multifunctional alkenyl synthones with the use of less corrosive trimethylsilyl 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 or terminal acetylenes containing versatile

alkyl, aryl, hetaryl fragments equipped with various synthetically useful functional groups (OH, Br, Cl, CN).



Scheme 2. Retrosynthetic approach to the access of multifunctional aryl(trifloxyalkenyl)iodonium triflate salts.

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 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, less equivalent of added acetylene or TMSOTf (Scheme 3).

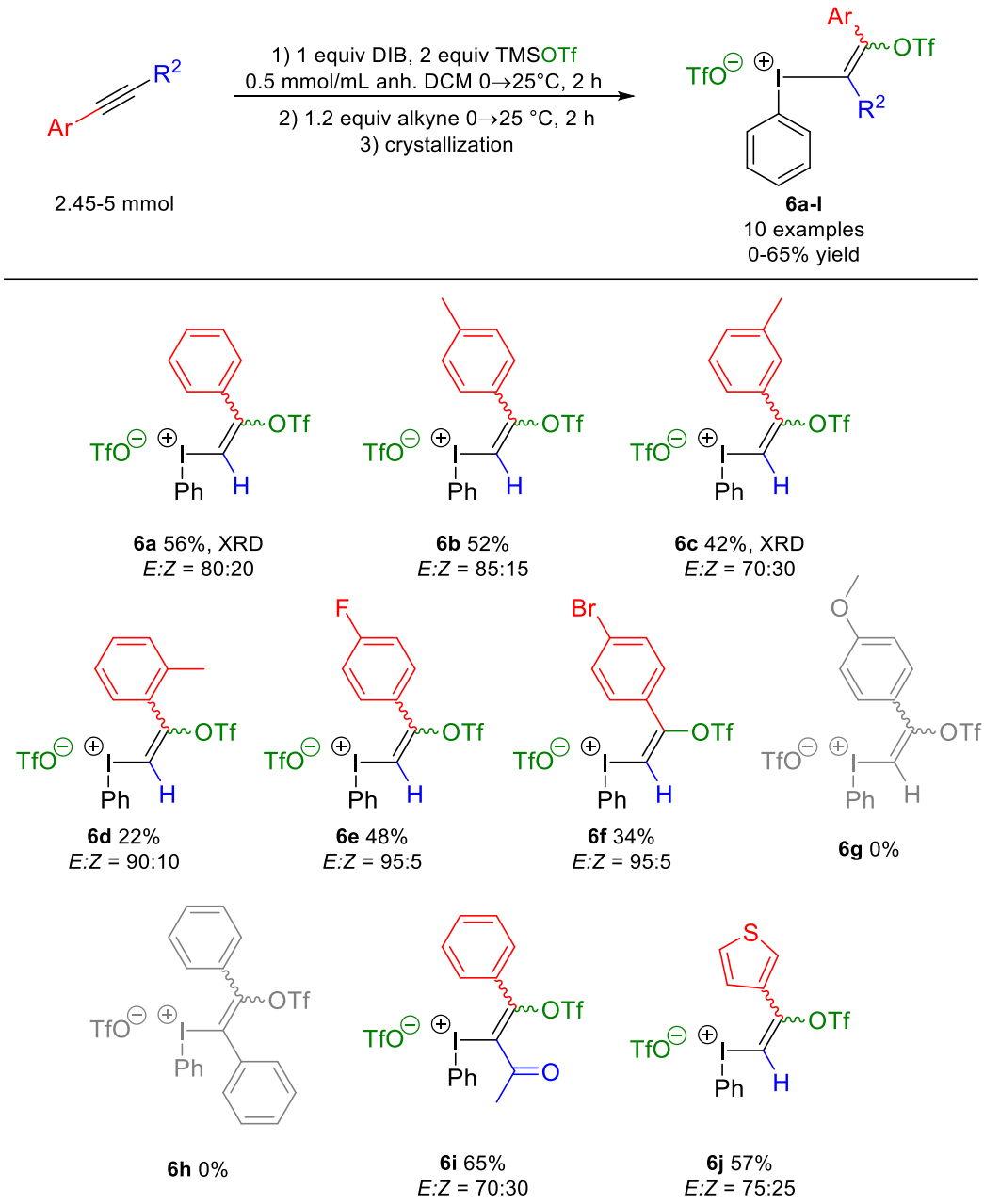


Scheme 3. Study of the conditions of the preparation of **6a**.

Additionally, increasing the amount of phenylacetylene up to 1.5 equivalents did not give the target product in higher yield. Drawing the lessons, we determined the best synthetic conditions to the access of the target compounds **6a**. To the anhydrous dichloromethane solution of DIB,

2 equivalents of trimethylsilyl trifluoromethanesulfonate has been added at 0 °C, and allowed to warm up to 25 °C. The colorless solution turns to yellow by forming the bis(trifloxy)iodobenzene (**4**).[11] The solution cooled again to 0 °C and the acetylene derivative 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% of yield.

In general, the reaction took place in a similar manner, resulting 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 has been synthesized.



Scheme 4. Scope of aryl substituted phenyl(vinyltrifloxy)iodonium triflate salts.

The methyl group in *para* position has no significant effect on the reaction and gave **6b** with 52% of yield, but the preparation of **6c** *meta* or **6d** *ortho* methyl product yielded 42% and 22%, respectively. However, the presence of methyl group lowered the yields, under the reaction conditions the formation of *E* product gained advantage over *Z* isomer. The structure of the *E*-**6a** and *E*-**6c** product has been determined also by X-ray crystallography (Figure 1).[12]

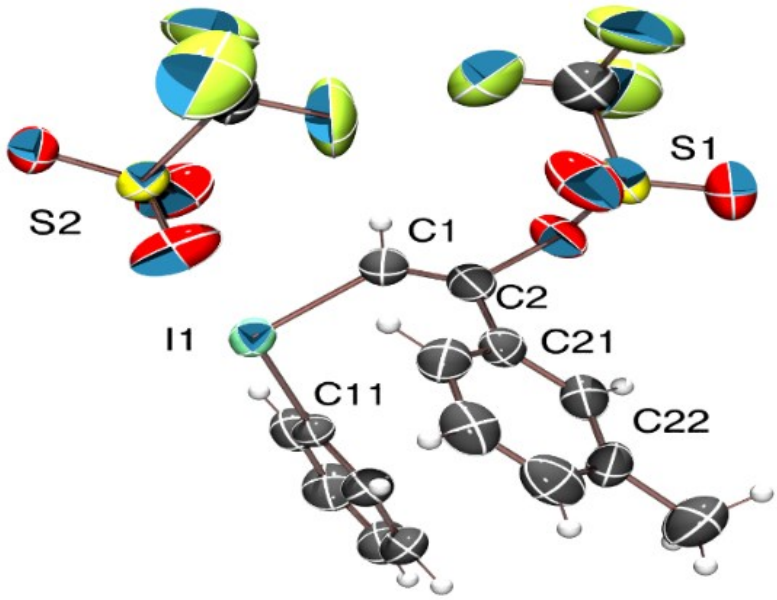


Figure 1. ORTEP view of **6c** at 50% probability level with partial numbering scheme. Selected bond distance [Å] and bond angle [°] data: I1-C1 2.091 (9) ; C1-C2 1.298 (14) ; I1-C11 2.112 (7); C2-C21 1.472 (13) ; I1-C1-C2 121.6 (7) ; C1-C2-C21 132.0 (9) ; C1-I1-C11 97.0 (3).

The *para*-fluoro **6e** and bromo substituted **6f** aryl derivative was synthetized in 48% and 34% yield. Pushing the limits further, we have experienced similar consequences in 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 synthetized the 3-ethynylthiophene to the corresponding **6j** product with 57% efficiency.

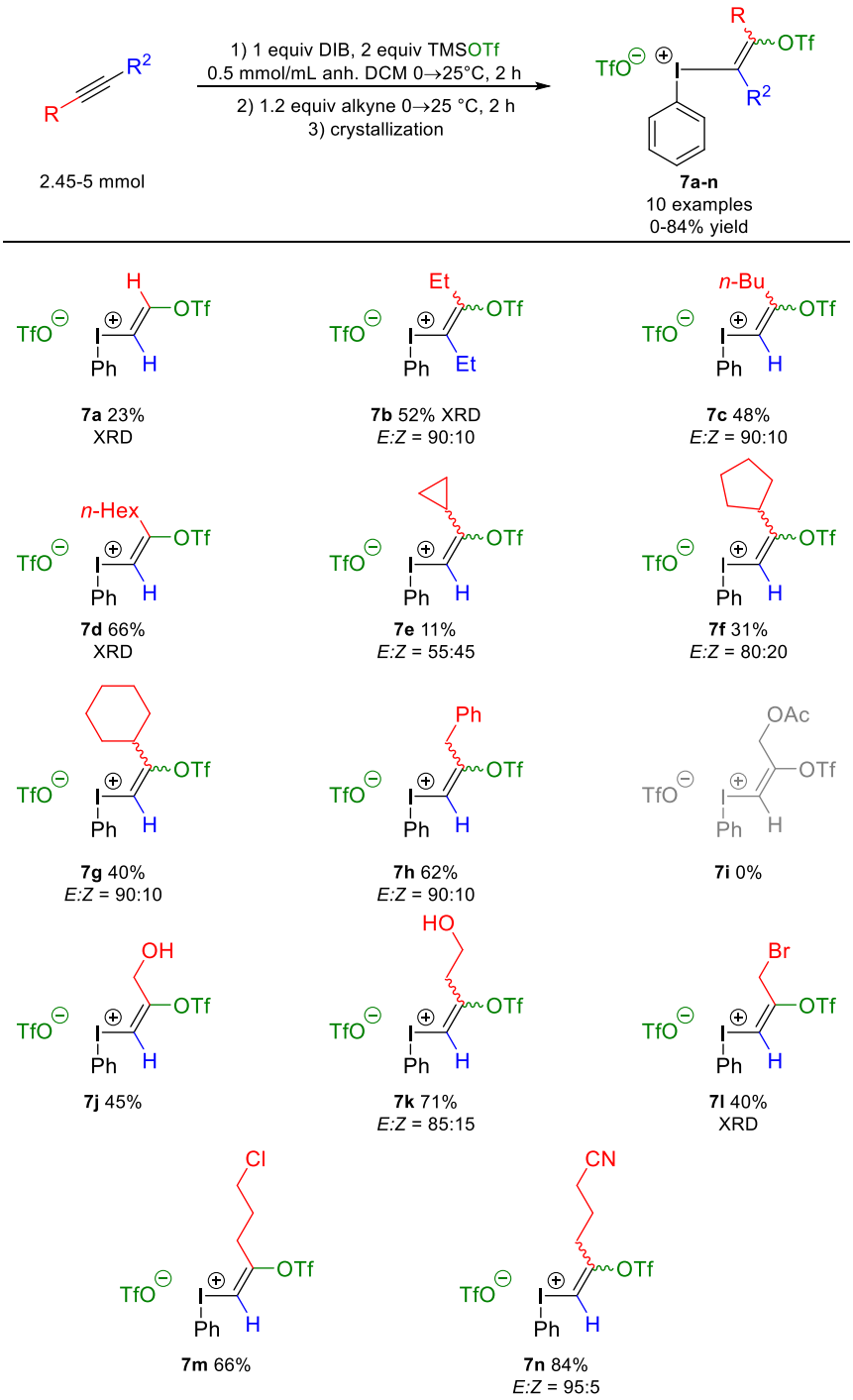
Fortunately, the reaction was not limited to the aromatic acetylenes, therefore we investigated the synthesis of phenyl(alkenyltrifloxy)iodonium triflate salts utilizing alkyl acetylene reactants. With the best reaction conditions in hand we started to examine the effect of structural diversity based on acetylene derivatives (Scheme 5). First, we synthetized the simplest and unsubstituted phenyl(vinyltrifloxy)iodonium triflate salt (**7a**) by bubbling acetylene gas into the reaction mixture, which yielded the vinyl salt with 23%. The low yield is understandable, since

the product (**7a**) is highly soluble in most of organic solvent and decomposes quickly. Increasing the length of side chains on vinyl moiety by the application of different terminal alkylacetylenes resulted higher stability, lower solubility and better yields. The transformation of the hex-3-yne, hex-1-yne and oct-1-yne yielded the desired product with 52% (**7b**), 48% (**7c**) and 66% (**7d**), 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 structure 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 in the 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 the benzyl (**7h**, 62%) derivatives resulted higher yields.

Moving forward to the synthesis of more challenging multifunctional alkenyl iodonium salts, we studied the synthetic applicability of different terminal alkyl acetylenes 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% and **7k** in 71% yield. Interestingly, we observed diminished stability at 25 °C in 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]



Scheme 5. Scope of alkyl substituted phenyl(vinyltrifloxy)iodonium triflate salts.

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

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 in the presence of an alkyl or aryl group in (vinyltrifloxy)iodonium moiety favored in *E* position. The separation of *Z* and *E* product is not feasible by crystallization.

CONCLUSION

In summary, we developed new synthetic method for the preparation of substituted trifloxyvinyliodonium triflates using commercially available, easy-to-handle starting materials such as acetylenes, (diacetoxyiodo)benzene and trimethylsilyl triflate. The synthesis of the target compounds was performed under mild reaction conditions and the procedure ensures 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 pre-coated 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), 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 x 1.5 m Fiber (Silver Halide), MCT detector. The in-situ reactions were followed with following setup: **s**ampling interval: 15 sec., 2500-650 cm^{-1} (resolution 8 cm^{-1}) Scan option: AutoSelect; Gain: 1x. 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 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: 4000V; sheath gas flow and temperature: 325 °C and 7.5 l/min; TOFMS parameters: fragmentor voltage: 120 V; skimmer potential: 120V; OCT 1 RF Vpp:750 V. Full-scan mass spectra were acquired over the m/z range 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 5 mmol *(diacetoxyiodo)benzene*, equipped with a stirring bar then sealed with a cap. The reaction atmosphere changed to argon by 3 consecutive evacuation

and argon backfillation process. Then 10 mL absolute dichloromethane was added by syringe and started to stir at 25 °C for 5 minutes. The solution was cooled to 0 °C and stirred vigorously for 10 minutes. 10 mmol of *trimethylsilyl trifluoromethanesulfonate* added dropwise in 1 minute. The solution turned to a clear yellow solution. The reaction mixture allowed to warm up to 25 °C and stirred for 2 hours. Then the solution was cooled to 0 °C and 1.2 equivalent *acetylene derivative* was added dropwise by syringe in 2 minutes during vigorous stirring. The reaction mixture allowed to warm up to 25 °C. The yellow solution turned to dark colored mixture. After 2 hours the solvent was evaporated, and cold diethyl ether and pentane were added and cooled in the 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 dried quickly in high vacuum at 25 °C, capped tightly and stored in freezer at -20 °C. In these conditions, the salts remained usable for more than a half of year.

6a, (*E*)-phenyl(2-phenyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium trifluoromethanesulfonate[8,9,10] **and (*Z*)-phenyl(2-phenyl-2-(((trifluoromethyl)sulfonyl)oxy)vinyl)iodonium trifluoromethanesulfonate**

The general procedure was followed starting from 5 mmol (diacetoxyiodo)benzene and 6 mmol 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 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 (diacetoxyiodo)benzene and 6 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 100 MHz), δ (ppm): 22.0 (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, 25ºC, 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 (diacetoxyiodo)benzene and 6 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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 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 (diacetoxyiodo)benzene and 4.18 mmol 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 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 (diacetoxyiodo)benzene and 4 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, 25ºC, 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 (diacetoxyiodo)benzene and 3 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, 25ºC, 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 (diacetoxyiodo)benzene and 6 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, 25ºC, 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 (diacetoxyiodo)benzene and 4.62 mmol 3-ethynyl-tiophene. 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 100 MHz), δ (ppm): 93.2 (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); 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 NMR** (CD_2Cl_2, 25°C, 100 MHz), δ (ppm): 89.2 (C1); 114.1 (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); 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 (diacetoxyiodo)benzene. The acetylene gas was generated from 6 mmol CaC_2. 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 NMR** (CD_2Cl_2, 25°C, 100 MHz), δ (ppm): 91.3 (C1); 113.1 (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); 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 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 (diacetoxyiodo)benzene and 6 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, 25ºC, 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 SI.

7c, (*E*)-phenyl(2-(((trifluoromethyl)sulfonyl)oxy)hex-1-en-1-yl)iodonium trifluoromethanesulfonate[6a,6e,6f,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 (diacetoxyiodo)benzene and 6 mmol 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, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, 25ºC, 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 (diacetoxyiodo)benzene and 6 mmol 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 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, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.6 (q, $^{1}J_{C,F}$ = 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 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 (diacetoxyiodo)benzene and 6 mmol 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 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, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^{1}J_{C,F}$ = 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 (diacetoxyiodo)benzene and 4.8 mmol 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, 25ºC, 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'); 7.98 (2H, m, H2' + H6'). **^{13}C NMR** (CD_2Cl_2, 25ºC, 100 MHz), δ (ppm): 26.5 (C3" + C4"); 31.0 (C2" + C5"); 45.1 (C1"); 89.9 (C1); 114.6 (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); 133.0 (C3' + C5'); 133.4 (C4'); 135.3 (C2' + C6'); 165.3 (C2). **^{19}F NMR** (CD_2Cl_2, 25ºC, 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 (diacetoxyiodo)benzene and 4.5 mmol cyclohexylacetylene. 910 mg (1.49 mmol, 40% yield, 90% *E,* 10% *Z*) off-white solid. **MP**: 153-156 °C (dec.). **^{1}H NMR** (CD_2Cl_2, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 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, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^{1}J_{C,F}$ = 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 (diacetoxyiodo)benzene and 4.08 mmol 3-phenyl-1-propyne. 1310 mg (2.12 mmol, 62% yield, 90% *E,* 10% *Z*) white solid. **MP**: 133-139 °C (dec.). **^{1}H 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 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 (diacetoxyiodo)benzene and 6 mmol 2-propyn-1-ol. 1260 mg (2.26 mmol, 45% yield) off-white solid. **MP**: 101-105 °C (dec.). **^{1}H 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 NMR** (CD_2Cl_2, 25°C, 100 MHz), δ (ppm): 62.0 (C3); 90.4 (C1); 114.3 (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); 133.0 (C3' + C5'); 134.0 (C4'); 136.4 (C2' + C6'); 151.3 (C2). **^{19}F NMR** (CD_2Cl_2, 25ºC, 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 (diacetoxyiodo)benzene and 6 mmol 3-butyn-1-ol. 2043 mg (3.57 mmol, 71% yield, 85% *E,* 15% *Z*) white solid. **MP**: <25 °C (dec.). **^{1}H NMR** (CD_2Cl_2, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 100 MHz), δ (ppm): 37.9 (C3); 59.8 (C4); 96.2 (C1); 113.8 (C1'); 118.9 (q, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.6 (q, $^{1}J_{C,F}$ = 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, 25ºC, 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 (diacetoxyiodo)benzene and 6 mmol 3-bromo-1-propyne. 1239 mg (1.99 mmol, 40% yield) white solid. **MP**: 156-159 °C (dec.). **^{1}H NMR** (CD_2Cl_2, 25ºC, 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 NMR** (CD_2Cl_2, 25ºC, 150 MHz),

δ (ppm): 27.9 (C3); 95.5 (C1); 114.1 (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); 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 (diacetoxyiodo)benzene and 6 mmol 5-chloro-1-pentyne. 1991 mg (3.29 mmol, 66% yield) white solid. **MP**: 84-89 °C (dec.). **^{1}H 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 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, $^{1}J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^{1}J_{C,F}$ = 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.

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 (diacetoxyiodo)benzene and 6 mmol 5-cyano-1-pentyne. 2491 mg (4.18 mmol, 84% yield, 95% *E,* 5% *Z*) slightly 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 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, $^1J_{C,F}$ = 320.0 Hz, CF_3); 120.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3); 133.2 (C3' + C5'); 133.7 (C4'); 135.6 (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.

CCDC numbers 1879587-1879592 for structures 7a, 7b, 7d, 7l, 6a, 6c, respectively.

Experimental procedures and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(12) See detailed in Supporting Information.