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# New One-Pot Method for the Stereoselective Synthesis of (E)-[β-(Trifluoromethylsulfonyloxy)-Alkenyl](Aryl) Iodonium Triflates.

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***Abstract:*** The reactions of reagent **1** with acetylenes leading to the alkenyl(aryl)iodonium triflates have been investigated. The results indicate that the very simple and efficient one-pot conversion of terminal alkynes into alkenyl(aryl)iodonium triflates described in this paper presents several advantages over the previously described procedure. The stereoselectivity of these reactions is discussed on the basis of physico-chemical evidence including IR, NMR spectroscopy and X-ray analysis. It is shown that these reactions are accompanied with anti-addition to afford (E)-[β-(trifyloxy)alkenyl](aryl) iodonium triflates in moderate to excellent yields. A possible mechanism is also discussed.


Presently there is considerable current interest in organo hypervalent iodine reagents because of their versatile use in organic synthesis.[1,2] Particularly, the highly reactive sulfonate iodosoderivatives are of special interest since they are used for bifunctionialization of alkenes,[3] formation of new carbon-carbon bonds[4] as well as for the synthesis of stable iodonium compounds[5] due to their high electrophilic properties.The reactions of these reagents with acetylenes leading to alkenyl-, alkynyl- and bis(alkynyl)iodonium salts are most promising.[6]

Hydroxy(tosyloxy)iodobenzene [PhI(OH)OTs] was shown by Koser et al.,[6a,b;7] to react with acetylenes to yield a mixture of (E)- and (Z)-[β-(tosyloxy)vinyl](phenyl) iodonium tosylates and/or alkynyl(phenyl)iodonium salts. Another iodonium triflate, namely phenyl(cyano)iodonium triflate [$PhI^{+}$-CN $^{-}OTf$] is the most convenient reagent for preparation of alkynyl iodonium triflates starting from a large variety of β-functionalized alkynylstannanes.[8] The importance of the reaction of iodosyltriflate with trimethylsilylacetylenes giving rise to bis(alkynyliodonium)triflates cannot be overemphasized.[9]

Even though the reactions of [PhIO•HOTf] with acetylenes are characterized by high stereoselectivity as in the case of the alternative preparation of alkenyl- and alkynyliodonium salts,[6a,b;7] these techniques are two-

step processes the first stage being a generation of aryliodoso derivatives from appropriate iodoarenes.[10] However, to the best of our knowledge no direct synthesis of alkenyl(phenyl)iodonium salts from iodoarenes through transformation of the latter into an ionic intermediate is described. Quite recently a new approach was suggested for the one-pot generation of aryliodosoderivatives directly from iodoarenes.[11] The iodonium triflate with the general formula [$ArI^+$-F $^-OTf$] **1** is assumed to be formed as a result of the oxidation of iodoarenes upon treatment with xenon fluorotriflate.

The high reactivity of compound **1** suggested additional experiments with the aim of obtaining information about their structure. In view of the current interest in the preparation and in the synthetic utilizations of alkenyl(phenyl)iodonium salts we have explored the application of reagent **1** in reactions which, because of the very simple conditions required, could represent a substantial improvement on the other previously described methods. For this purpose the reactions of a series of differently substituted terminal alkynes have been investigated. This paper presents a new stereoselective method to synthesize β-functionally substituted alkenyl(aryl)iodonium triflates directly from aryl iodides without the preparation of aryliodoso derivatives.

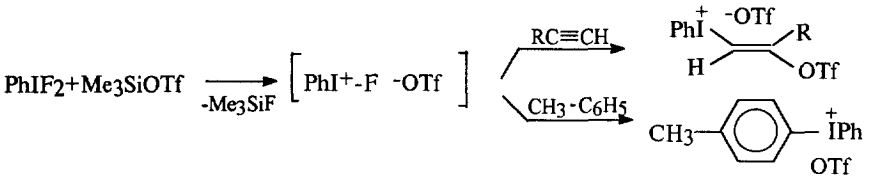
The reagents **1** were generated *in situ via* oxidation of aryl iodides with xenon fluorotriflate at -78° C in dichloromethane. The colored solutions of **1** were subsequently used in the reactions with a variety of differently substituted terminal acetylenes. Having established the general conditions required for successful reactions, a number of syntheses of alkenyliodonium structures were attempted. In every case, the conditions involved the use of methylene chloride as solvent. The expected triflates were the major products, isolated in 45-97 % yield.

It is worth emphasizing that the proposed intermediates **1** are particular cases of the general class of compounds with the formula [$ArI^+$-X $^-Z$], where X is a heteroatomic substituent and Z is a nucleofugic group. There are some well-known derivatives of these compounds with X = OH, Z = OTf ;[10] X = OH, Z = $FSO_3$;[11] X = OH, Z = $HSO_4$ ;[2c] X = OH, Z = $BF_4$;[4c] X = F, Z = $BF_4$.[12] In most cases the structure of these compounds was only postulated, but not actually substantiated. Part of the case for these compounds rests on the capture of such compounds by reactions with different substrates, i.e. the conclusions concerning the structure were made on the basis of the results of the subsequent chemical transformations, particularly, reactions with acetylenes, aromatic compounds and silyl enol esters to produce iodonium salts[6,7,11] and β-diketones [13] respectively.

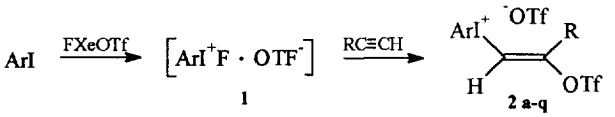
Experiments with phenyl(fluoro)iodonium triflate demonstrated that it reacts with excess iodobenzene affording phenyl(p-iodophenyl)iodonium triflate in the absence of more nucleophilic reagents as iododerivatives **1** are extremely reactive.

Several experiments were carried out starting from (difluoro)iodobenzene and trimethylsilyltriflate in order to obtain indirect evidence in relation to the structure of intermediates **1** and in every case the results

were successful. Addition of trimethylsilyltriflate to the pre-cooled (-78 °C) solution of difluoroiodobenzene in dicholoromethane leads to the desired reagent [PhI$^+$-F $^-$OTf] which is then introduced into reactions with parent acetylene, hexyne and toluene. The products are identical with the compounds synthesized by the reaction of reagent **1** generated from iodobenzene and xenon fluorotriflate .




Encouraged by these experiments on the structure of reagent **1** , we decided to investigate the reactions of **1** with acetylenes. It was shown that the normal and functionalized terminal acetylenes react with reagent [ArI$^+$-F $^-$OTf] prepared *in situ* from a 1:1 molar ratio of ArI and FXeOTf in dichloromethane under mild conditions. After removal of volatile components the products were isolated as white microcrystalline solids. All products reported herein were fully characterized by IR and multinuclear NMR spectroscopy, and the new compounds by elemental analysis. The structure of compound **2c** was unambiguously determined by X-ray diffraction studies.[14]




**a**: Ar = $C_6H_5$, R = H; **i**: Ar = $pCH_3C_6H_4$, R = $C_3H_7$;
**b**: Ar = $C_6H_5$, R = $C_3H_7$; **j**: Ar = $pCH_3C_6H_4$, R = $C_4H_9$;
**c**: Ar = $C_6H_5$, R = $C_4H_9$; **k**: Ar = $pCH_3C_6H_4$, R = $C_8H_1$;
**d**: Ar = $C_6H_5$, R = $C_8H_{17}$; **l**: Ar = $pCH_3C_6H_4$, R = $CH_2OCH_3$;
**e**: Ar = $C_6H_5$, R = $CH_2OCH_3$; **m**: Ar = $pCH_3C_6H_4$, R = $CH_2Cl$;
**f**: Ar = $C_6H_5$, R = $CH_2OH$; **n**: Ar = $oCH_3C_6H_4$, R = H;
**g**: Ar = $C_6H_5$, R = $CH_2Cl$; **o**: Ar = $oCH_3C_6H_4$, R = $C_3H_7$;
**h**: Ar = $pCH_3C_6H_4$, R = H; **p**: Ar = $oCH_3C_6H_4$, R = $CH_2OCH_3$;
**q**: Ar = $pNO_2C_6H_4$, R = H.

Spectral data match well with expectations. Specifically, the IR spectra show a C=C peak at 1620-1655 $cm^{-1}$ and absorption bands highly characteristic of triflates in addition to the aromatic C-H stretching. The $^1H$ NMR spectra display the typical patterns at low field for aromatic protons, with 2:1:2 ratio of signal intensity for compounds **2a-e** highly characteristic of the phenyl group in iodonium salts, AA'BB' system for compounds **2h-m, q** and ABCD system for compounds **2n-q**. Spectra exhibit AB system (compounds **2a, h, n, q**) or singlet for olefinic protons. $^1H$ chemical shifts of compounds under study are very sensitive to solvent. For example, the shielding of olefinic protons CH(COTf) of product **2a** decrease by *ca* 0.8 ppm in aceton-$d_6$ solution relatively $CD_2Cl_2$ solution.

The presence of the two different triflate groups was confirmed by $^{19}F$ NMR spectra where there are two peaks with a 1:1 ratio at about -73 and -78 ppm corresponding to the covalent and the ionic bonded. Most

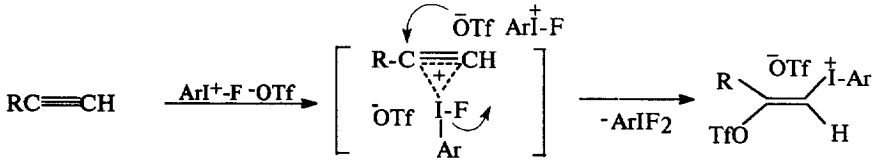
important, the NMR spectra were all consistent with the proposed structure. In particular, these spectra exhibit two quadruplets of $CF_3$ groups in the region 118-121 ppm with the $^{13}C$- $^{19}F$ spin-spin coupling constant $J_{CF} \cong$ 320 Hz.

It is customary to determine the stereochemistry around the C=C bond from coupling constants and nuclear Overhauser effects (NOE). The introduction of electronegative substituents into the molecule is accompanied by considerable decrease of the magnitude of the $^3J_{trans}$ and $^3J_{cis}$ in alkenes,[15] the values of $^3J$ = 12.2, 12.2, 12.1 and 11.9 Hz for compounds **2a, h, n, q**, respectively are well in accord with trans-configuration with respect to the carbon-carbon double bond. Unfortunately our NOE measurements gave ambiguous results even for degassed samples sealed under vacuum. Therefore, X-ray data for compound **2c**[14] and the vicinal spin-spin coupling constants of the AB-systems of vinylic protons were used in determining of (E)-configuration of the compounds.

That there is a trans-configuration around the double bond is indicated by physical evidence including infrared spectroscopy and X-ray analysis. It is interesting to note that in the infrared spectra the trans-configuration around the double bond is correlated with the appearance of a medium intensity absorption band near 990 $cm^{-1}$. The out-of-plane deformation of the =CH groups is generally quoted as absorbing in the range 970-960 $cm^{-1}$. The intensity pattern may be influenced by the presence of electrostatic effects which will contribute their own specific absorption in this region.

(E)-[(β-trifyloxy)alkenyl](phenyl) iodonium trifluoromethanesulfonates previously mentioned were prepared by the electrophilic addition of [PhIO•HOTf] to acetylenes.[10] This procedure was only used for the synthesis of the β-substituted vinyliodonium salts with phenyl fragment. Moreover it involves the preliminary transformation of iodobenzene into iodosobenzene and further activation of the latter by trifluoromethanesulfonic acid. However, use of xenon fluorotriflate already containing the triflate moiety allows the preparion of wide range of alkenyl(phenyl)iodonium salts in a one-pot synthesis from iodoarenes and alkynes. Furthermore, generated reagents [$ArI^+$-F $^-$OTf] are more reactive than hydroxy(trifyloxy)iodobenzene towards terminal alkynes and the reactions of **1** proceed even at -70° C.

In light of these observations it can be suggested that in the present case an electrophilic addition mechanism, provides the pathway for the above described conversion of terminal alkynes into vinyliodonium salts. Due to the excellent leaving property of the triflate group the iodine atom is considerably ionized. Subsequent electrophilic attack of iodonium cation on the triple bond of the alkynes resulting in cyclic cationoid intermediate occurs. The ring opening from the rear side by triflate ion of another molecule of the reagent leads to formation of products with (E) - geometry. Therefore, the reaction of [$ArI^+$-F $^-$OTf] with alkynes proceeds with highly stereospecific *anti* addition compared with Koser's reagent which provides a mixture of (E) and (Z) isomers.



In conclusion, we have found that aryl(fluoro)iodonium triflates generated from aryliodides and xenon fluorotriflate can be used as convenient intermediates for stereoselective synthesis of β-[(trifyloxy)alkenyl](aryl) iodonium triflates. These may serve as highly reactive substrates in vinylic nucleophilic substitution reactions because of the excellent leaving group ability of aryliodonium moiety, and as a synthon of vinyl cations.

**Acknowledgement** This work was supported by FIRCA of NIH ( RO3TW00437).

## EXPERIMENTAL SECTION

***General methods:***

Melting points are determined in cappillaries by means of a micro melting point apparatus and uncorrected, (d) indicates that the compound decomposed on melting. Infrared spectra were obtained with UR-20 IR spectrophotometer and peak position are reported in wavenumbers ($cm^{-1}$ ).

$^1H$ NMR spectra were recorded on a Varian VXR-400 spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to the proton resonance due to the residual protons of the deuteriated corresponding solvents. $^1H$ NMR splitting patterns are designated as s, d, t, q or m which indicate singlet, doublet, triplet, quartet or multiplet, respectively, even when spectra are non first-order; only vicinal couplings are taken to account for aromatic protons.

$^{13}C$ NMR spectra were obtained on a Varian VXR-400 spectrometer. Analysis of the carbon spectra was carried out using monoresonance mode, off-resonance decoupling and DEPT technique.[16] Assignments of $^{13}C$ NMR employ the abbreviations s', d', t' and q', which refer respectively to zero, one, two and three attached protons or in the case of q' to fluorine atoms too. $^{19}F$ NMR spectra were recorded on a Bruker CXP-200 spectrometer, $CF_3COOH$ being employed as an external standard.$^{13}C$ and $^{19}F$ chemical shifts are expressed in ppm in δ scale. Coupling constants are given in hertz .

Dichloromethane was distilled from calcium hydride and then from $P_2O_5$, and was stored over molecular sieves under argon atmosphere. All other solvents were dried and distilled according to the literature procedures[17] immediately prior to use. Commercially available xenon difluoride was used as received. The details of the preparation of FXeOTf have been described.[18] Starting $PhIF_2$ was prepared according to known procedure by oxidation of iodobenzene with $XeF_2$.[19]

Reactions were performed in a standard three-necked quartz flask maintained under a positive pressure of argon with magnetic stirring.

***General procedure for the preparation of (E)-[β-(trifluoromethylsulfonyloxy)alkenyl](aryl)iodonium triflates :***

To a solution of FXeOTf ( 4.72 mmol ) in dry $CH_2Cl_2$ ( 15 mL ) was slowly added dropwise at -78° C a solution of iodoarene ( 4.72 mmol ) in dry $CH_2Cl_2$ (5 mL) and then the mixture was stirred at -70° C for 0,5 h. A large excess of

the corresponding acetylenes ( 5.67 mmol ) was added to the obtained suspension at -70° C. The resulting mixture was allowed to warm to room temperature and stirring was continued for 1-3h after removal of the cooling bath until the yellow suspension dissolved to yield a clear yellow solution. The volatile materials were then removed on the rotary evaporator under reduced pressure to give an oily residue which was taken up in dry ether or hexane. The mixture was shaken vigorously for several minutes to precipitate slightly colored crystals. The solids were collected by filtration, and purified by washing with dry ether. Analytically pure samples were obtained by recrystallization from dichloromethane or acetone to yield white microcrystalline solids which were then dried in *vacuo*.

**[2-(Trifluoromethylsulfonyloxy)ethenyl](phenyl)iodonium trifluoromethylsulfonate 2a**: yield 72%; m.p.155-157° C( lit.[10] m.p. 156-157° C); $^1$H NMR (acetone-$d_6$), δ: 7.615 (t, $J$ = 8Hz, 2H, $H_{meta}$), 7.772 (t, $J$ = 8 Hz, 1H, $H_{para}$), 7.939 (d, $J$ = 12.2 Hz, 1H, =CH), 8.227 (d, $J$ = 12.2 Hz, 1H, =CH), 8.309 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}$C NMR (acetone-$d_6$), δ: 94.12 (d', =CH), 117.12 (s', $C_{ipso}$), 118.30 (q', $J_{CF}$ = 320 Hz, $CF_3$), 120.40 (q', $J_{CF}$ = 319Hz, $CF_3$), 132.90 (d', $C_{meta}$), 133.67 (d', $C_{para}$), 136.58 (d', $C_{ortho}$), 150.84 (s', =COTf); $^{19}$F NMR (acetone-$d_6$), δ: -76.7 (s, $CF_3SO_3^-$), -71.8 (s, $CF_3SO_3$).

**[2-(Trifluoromethylsulfonyloxy)1-pentenyl](phenyl)iodonium trifluoromethylsulfonate 2b**: yield 84% , m.p.129-130° C( lit.[10] m.p. 129-132° C); IR ($CCl_4$), cm$^{-1}$: 3070; 1630; 1225; 1185; 1035; 995; 830; $^1$H NMR (acetone-$d_6$), δ: 0.990 (t, $J$ = 6.9 Hz, 3H, $CH_3$), 1.645 (m, 2H, $CH_3$), 3.053 (t, $J$ = 6.9 Hz, 2H, $CH_2$-allylic), 7.640 (t, $J$ = 8 Hz, 2H, $H_{meta}$), 7.787 (t, $J$ = 8 Hz, 1H, $H_{para}$), 7.842 (s, 1H, =CH), 8.319 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}$C NMR (acetone-$d_6$), δ: 13.28 (q', $CH_3$), 20.29 (t', $CH_2$), 36.88 (t', $CH_2$- allylic), 95.87 (d', =CH), 115.60 (s', $C_{ipso}$), 118.5 (q', $J_{CF}$ = 319Hz, $CF_3$), 119.30 (q', $J_{CF}$ = 319Hz, $CF_3$), 133.04 (d', $C_{meta}$), 133.71 (d', $C_{para}$), 133.36 (d', $C_{ortho}$), 162.79(s', =COTf); $^{19}$F NMR (acetone-$d_6$), δ: -76.7 (s, $CF_3SO_3^-$), -71.6 (s, $CF_3SO_3$).

**[2-(Trifluoromethylsulfonyloxy)-1-hexenyl](phenyl)iodonium trifluoromethylsulfonate 2c**: yield 93%, m.p.127-128° C (lit.[10] m.p. 125-128° C); IR ($CCl_4$), cm$^{-1}$ : 3100; 1650; 1220; 1178; 1035; 990; $^1$H NMR ($CD_2Cl_2$), δ: 0.910 (t, $J$ = 7.0 Hz, 3H, $CH_3$), 1.380 (m, 2H, $CH_2$), 1.495 (m, 2H, $CH_2$), 2.825 (t, $J$ = 6.9 Hz, 2H, $CH_2$-allylic), 7.234 (s, 1H, =CH), 7.516 (t, $J$ = 8 Hz, 2H, $H_{meta}$), 7.673 (t, $J$ = 8 Hz, 1H, $H_{para}$), 8.020 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}$C NMR ($CD_2Cl_2$), δ: 13.75 (q', $CH_3$), 22.39 (t', $CH_2$), 28.41 (t', $CH_2$), 34.97 (t', $CH_2$-allylic), 93.27 (d', =CH), 114.28(s', $C_{ipso}$), 118.14(q', $J_{CF}$ = 320Hz, $CF_3$), 119.56 (q', $J_{CF}$ = 319 Hz, $CF_3$), 132.67(d', $C_{ortho}$), 133.13 (d', $C_{para}$), 135.36(d', $C_{meta}$), 163.00(s', =COTf); $^{19}$F NMR ($CD_2Cl_2$), δ: -78.2 (s, $CF_3SO_3^-$), -73.3 (s, $CF_3SO_3$).

**[2-(Trifluoromethylsulfonyloxy)-1-decenyl](phenyl)iodonium trifluoromethylsulfonate 2d**: yield 97%; m.p. 86-88° C(d); IR ($CCl_4$), cm$^{-1}$: 3090; 1645; 1220; 1185; 1035; 980; 830; $^1$H NMR ($CD_2Cl_2$), δ: 0.882 (t, $J$ =7.0 Hz, 3H, $CH_3$), 1.23 (m, 10H, 5 $CH_2$), 1.46 (m, 2H, $CH_2$), 2.774 (t, $J$ = 6.9 Hz, 2H, $CH_2$-allylic), 7.244 (s, 1H, =CH), 7.453(t, $J$ = 8 Hz, 2H, $H_{meta}$), 7.602 (t, $J$ = 8 Hz, 1H, $H_{para}$), 8.005 (d, $J$ = 8Hz, 2H, $H_{ortho}$); $^{13}$C NMR ($CD_2Cl_2$), δ: 13.99 (q',

$CH_3$), 22.57 (d', $CH_2$), 25.94 (d', $CH_2$), 28.78 (d', $CH_2$), 29.92 (d', $CH_2$), 29.06 (d', $CH_2$), 31.66 (d', $CH_2$), 34.82 (d', $CH_2$), 93.21 (d', =CH), 113.92 (s', $C_{ipso}$), 118.25 (q', $J_{CF}$ = 320 Hz, $CF_3$), 119.95 (q', $J_{CF}$ = 319 Hz, $CF_3$ ), 132.15 (d', $C_{meta}$), 132.57 (d', $C_{para}$), 134.93 (d', $C_{ortho}$), 162.51 (s', =COTf); $^{19}F$ NMR ($CD_2Cl_2$), δ: -78.0 (s', $CF_3SO_3^-$), -72.2 (s', $CF_3SO_3$); Anal. Calcd. for $C_{18}H_{23}IF_6O_6S_2$: C, 33.76; H,3.62; Found: C, 33.64; H, 3.79.

**[2-(Trifluoromethylsulfonyloxy)-3-methoxy-1-propenyl](phenyl)iodonium trifluoromethylsulfonate 2e**: yield 72%; m.p.73-74° C(d); IR ($CCl_4$), $cm^{-1}$ : 3090; 1645; 1225; 1180; 1030; 990; 825; $^1H$ NMR ($CDCl_3$), δ: 3.649(s, 3H, $CH_3$), 4.317 (d, 2H, $J$ = 1.7 Hz, $CH_2$), 6.551 (t, $J$ = 1.7 Hz, 1H, =CH), 7.533 (t, 2H, $H_{meta}$), 7.684 (t, $J$ = 8 Hz, 1H, $H_{para}$), 8.022 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR ( $CD_2Cl_2$), δ: 60.07 (q', $CH_3$), 70.30 (t', $CH_2$), 92.68 (d', =CH), 113.99 (s', $C_{ipso}$), 118.29 (q', $J_{CF}$ = 321 Hz, $CF_3$), 120.20 (q', $J_{CF}$ = 320 Hz, $CF_3$), 132.42 (d', $C_{meta}$), 133.15 (d', $C_{para}$), 135.56 (d', $C_{ortho}$), 148.78 (s', =COTf); $^{19}F$ NMR ($CDCl_3$), δ: -78.2 (s', $CF_3SO_3^-$), -72.5 (s', $CF_3SO_3$), Anal. Calcd. for $C_{12}H_{11}IF_6O_7S_2$: C, 25.19; H, 1.94; Found: C, 25.41; H, 2.12.

**[2-(Trifluoromethylsulfonyloxy)-3-hydroxy-1-propenyl](phenyl)iodonium trifluoromethylsulfonate 2f**: yield 45%; m.p. 76-77° C(d); $^1H$ NMR (acetone-$d_6$), δ: 4.469 (s, 2H, $CH_2$), 6.813 (s, 1H, =CH), 7.510 (t, $J$ = 8 Hz, 2H, $H_{meta}$), 7.642 (t, $J$ = 8 Hz, 1H, $H_{para}$), 8.056 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{19}F$ NMR (acetone-$d_6$), δ: -76.7 (s', $CF_3SO_3^-$), -71.7(s', $CF_3SO_3$); Anal. Calcd. for $C_{11}H_9IF_6O_7S_2$ : C, 23.67; H, 1.63; Found C, 23.90; H, 1.84.

**[2-(Trifluoromethylsulfonyloxy)-3-chloro-1-propenyl](phenyl)iodonium trifluoromethylsulfonate 2g**: yield 68%; m.p. 138-139° C(d); IR ($CCl_4$), $cm^{-1}$: 3100; 1640; 1230; 1185; 1030; 990; 815; $^1H$ NMR, (acetone-$d_6$), δ: 5.080 (s, 2H, $CH_2$), 7.665 (t, $J$ = 8 Hz, 2H, $H_{meta}$), 7.810 (t, $J$ = 8 Hz, 1H, $H_{para}$), 8.135 (s, 1H, =CH), 8.330 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR ($CDCl_3$), δ: 42.52 (t',$CH_2$), 94.91 (d', =CH), 113.29 (s', $C_{ipso}$), 118.95 (q', $J_{CF}$ = 319 Hz, $CF_3$), 120.04 (q', $J_{CF}$ = 319Hz, $CF_3$), 132.60 (d', $C_{meta}$), 133.15 (d', $C_{para}$), 135.38 (d', $C_{ortho}$), 155.64 (s', =COTf); $^{19}F$ NMR ($CDCl_3$), δ: -78.2 (s', $CF_3SO_3^-$), -72.5 (s', $CF_3SO_3$), Anal. Calcd. for $C_{11}H_8ClIF_6O_6S_2$: C, 22.91; H, 1.40; Found: C, 23,23; H, 1.44.

**[2-(Trifluoromethylsulfonyloxy)-ethenyl](p-tolyl)iodonium trifluoromethylsulfonate 2h**: yield 91%; m.p.119-120 °C(d); IR ($CCl_4$) $cm^{-1}$: 3100; 1640; 1240; 1180; 1030; 995; $^1H$ NMR ($CDCl_3$), δ: 2.320 (s, 3H, $CH_3$), 6.972 (d, $J$ = 12.2 Hz, 1H, =CH), 7.188 (d, $J$ = 8 Hz , 2H, $H_{meta}$), 7,499 (d, $J$ = 12.2 Hz, 1H, =CH), 7.789 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR, ($CDCl_3$), δ: 21.41 (q', $CH_3$), 93.59 (d', =CH), 110.30 (s', $C_{ipso}$), 118.50 (q', $J_{CF}$ = 320 Hz, $CF_3$), 119.65 (q', $J_{CF}$ = 320 Hz, $CF_3$), 132.89 (d', $C_{meta}$), 135.16 (d', $C_{ortho}$), 143.79 (s', $C_{para}$), 147.73 (s', =COTf); $^{19}F$ NMR, ($CDCl_3$), δ: -78.1 (s', $CF_3SO_3^-$), -72.1 (s' , $CF_3SO_3$); Anal. Calcd. for $C_{11}H_9IF_6O_6S_2$: C, 24.37; H, 1.67; Found: C, 24.66; H, 1.85.

**[2-(Trifluoromethylsulfonyloxy)-1-pentenyl](p-tolyl)iodonium trifluoromethylsulfonate 2i**: yield 95%; m.p. 113-114° C; IR ($CCl_4$), $cm^{-1}$: 3090; 1645; 1250; 1220; 1165; 1035; 995; 815; $^1H$ NMR (acetone-$d_6$), δ: 0.986 (t, $J$ = 7.1 Hz, 3H, $CH_3$), 1.648 (m, 2H, $CH_2$), 2.432 (s, 3H, $CH_3$), 3.043 (t, $J$ = 7 Hz, 2H, $CH_2$-allylic), 7.441 (d, $J$ = 8 Hz, 2H, $H_{meta}$), 7.796 (s, 1H, =CH), 8.170 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR (acetone-$d_6$), δ: 13.29 (q', $CH_3$), 20.28 (t', $CH_2$), 21.23 (q', $CH_3$-Ar), 36.84 (t', $CH_2$-allylic), 95.93 (d', =CH), 111.14 (s', $C_{ipso}$), 118.40 (q', $J_{CF}$ = 321 Hz, $CF_3$), 120.10 (q', $J_{CF}$ = 320 Hz, $CF_3$), 133.69 (d', $C_{meta}$), 136.36 (d', $C_{ortho}$), 144.80 (d', $C_{para}$), 162.54 (s', =COTf); Anal. Calcd. for $C_{14}H_{15}IF_6O_6S_2$: C, 28.77; H, 2.59; Found C, 28.69; H, 2.74.

**[2-(Trifluoromethylsulfonyloxy)-1-hexenyl](p-tolyl)iodonium trifluoromethylsulfonate 2j**: 88%; m.p. 122-123° C; IR ($CCl_4$) $cm^{-1}$: 3080; 1645; 1230; 1180; 1030; 980; 820; $^1H$ NMR ($CDCl_3$), δ: 0.90 (t, $J$ = 7 Hz, 3H, $CH_3$), 1.35 (m, 2H, $CH_2$), 1.39 (m, 2H, $CH_2$), 2.42 (s, 3H, $CH_3$), 2.77 (t, $J$ = 7 Hz, 2H, $CH_2$-allylic), 7.43 (s, 1H, =CH), 7.27 (d, $J$ = 8 Hz, 2H, $H_{meta}$), 7.84 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR ($CDCl_3$), δ: 13.61 (q', $CH_3$), 21.40 (q', $CH_3$-Ar), 22.25 (t', $CH_2$), 28.27 (t', $CH_2$), 34.83 (t', $CH_2$-allylic), 94.62 (d', =CH), 111.23 (s', $C_{ipso}$),, 119.04 (q', $J_{CF}$ = 319 Hz, $CF_3$), 121.12 (q', $J_{CF}$ = 319 Hz, $CF_3$), 133.32(d', $C_{meta}$), 135.80 (d' $C_{ortho}$), 143.92 (s', C $_{para}$), 160.08 (s', =COTf); Anal. Calcd. for $C_{15}H_{17}IF_6O_6S_2$: C, 30.11; H, 2.86; Found : C, 30.42; H, 2.98

**[2-(Trifluoromethylsulfonyloxy)-1-decenyl](p-tolyl)iodonium trifluoromethylsulfonate 2k**: yield 90%; m.p. 106-108° C; IR ($CCl_4$), $cm^{-1}$: 3100; 1655; 1230; 1155; 1040; 990; $^1H$ NMR ($CDCl_3$), δ: 0.881 (t, $J$ = 7.1 Hz, 3H, $CH_3$), 1.25 (m, 10H, $5CH_2$), 1.495 (m, 2H, $CH_2$), 2.413 (s, 3H, $CH_3$), 2.776 (t, $J$ = 7 Hz, 2H, $CH_2$-allylic), 7.147 (s, 1H, =CH), 7.262 (d, $J$ = 8 Hz, 2H, $H_{meta}$), 7.845 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR ($CDCl_3$), δ: 14.08 (q', $CH_3$), 21.44 (q', $CH_3$-Ar), 22.64 (t', $CH_2$), 25.97 (t', $CH_2$), 28.86 (t', $CH_2$), 29.01 (t', $CH_2$), 29.14 (t', $CH_2$), 31.72 (t', $CH_2$), 34.79 (t', $CH_2$), 37.22(t', $CH_2$-allylic), 93.17(d', =CH), 110.07 (s', $C_{ipso}$),, 119.84 (q', $J_{CF}$ = 319 Hz, $CF_3$), 121.50 (q', $J_{CF}$ = 319 Hz, $CF_3$), 133.10 (d', $C_{meta}$), 134.82 (d', $C_{ortho}$), 143.65(s', $C_{para}$), 162.16 (s', =COTf); $^{19}F$ NMR ($CDCl_3$), δ: -78.1 (s', $CF_3SO_3^-$), -73.0 (s', $CF_3SO_3$); Anal. Calcd. for $C_{19}H_{25}IF_6O_6S_2$: C, 34.87; H, 3.85; Found : C, 35.14; H, 4.08.

**[2-(Trifluoromethylsulfonyloxy)-3-methoxy-1-propenyl](p-tolyl)iodonium trifluoromethylsulfonate 2l**: yield 62%; m.p. 100-102° C; $^1H$ NMR ($CDCl_3$), δ: 2.323 (s, 3H, $CH_3$-Ar), 3.418 (s, 3H, $CH_3O$), 4.185 (s, 2H, $CH_2$), 6.520 (s, 1H, =CH), 7.244 (d, $J$ = 8 Hz, 2H, $H_{meta}$), 7.821 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{19}F$ NMR ($CDCl_3$), δ: -78.1 (s', $CF_3SO_3^-$), -72.1 (s', $CF_3SO_3$); Anal. Calcd. for $C_{13}H_{13}IF_6O_7S_2$: C, 26.63; H, 2.24; Found : C, 26.97; H, 2.46.

**[2-(Trifluoromethylsulfonyloxy)-3-chloro-1-propenyl](p-tolyl)iodonium trifluoromethylsulfonate 2m**: yield 88%; m.p. 179-180° C; IR ($CCl_4$), $cm^{-1}$: 3100; 1640; 1230; 1185; 1035; 990; 820; $^1H$ NMR (acetone-$d_6$), δ: 2.422 (s, 3H, $CH_3$), 4.880 (s, 2H, $CH_2$), 7.372 (d, $J$ = 8 Hz, 2H, $H_{meta}$), 7.855 (s, 1H, =CH), 8.075 (d, $J$ = 8 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR (acetone-$d_6$), δ: 21.44 (q', $CH_3$), 42.52 (t',$CH_2$), 98.09 (d', =CH), 110.47 (s', $C_{ipso}$), 118.88 (q', $J_{CF}$ = 319 Hz,

$CF_3$), 120.12 (q', $J_{CF}$ = 320 Hz, $CF_3$), 133.37 (d', $C_{meta}$), 136.09 (d', $C_{ortho}$), 144.40 (d', $C_{para}$), 154.98(s', =COTf); $^{19}F$ NMR (acetone-$d_6$), δ: -77.0 (s', $CF_3SO_3^-$), 73.0 (s', $CF_3SO_3$); Anal. Calcd. for $C_{12}H_{10}IF_6O_6S_2$: C, 24.40; H, 1.71; Found : C, 24.75; H, 2.02.

**[2-(Trifluoromethylsulfonyloxy)-ethenyl](o-tolyl) iodonium trifluoromethylsulfonate 2n**: yield 86%; m.p. 146-147 °C; $^1H$ NMR (DMSO-$d_6$/$CDCl_3$), δ: 2.48(s, 3H, $CH_3$), 6.933 (d, $J$ = 12.1 Hz, 1H, =CH), 7.133 (dd, $J$ = 8 Hz, 1H, $H^5_{ar}$), 7.366 (d, $J$ =8 Hz, 1H, $H^3_{ar}$), 7,391 (d, $J$ = 12.1 Hz, 1H, =CH), 7.433 (dd, 1H, $H^4_{ar}$), 7.988 (d, $J$ = 8 Hz, 1H, $H^6_{ar}$); $^{13}C$ NMR, (DMSO-$d_6$/$CDCl_3$), δ: 25.35 (q', $CH_3$), 92.91 (d', =CH), 119.01(s', $C_{ipso}$), 119.31(q', $J_{CF}$ = 320 Hz, $CF_3$), 120.31(q', $J_{CF}$ = 320 Hz, $CF_3$), 129.69 (d', $C^5_{ar}$), 131.81 (d', $C^3_{ar}$), 133.54 (d', $C^4_{ar}$), 137.33(d', $C^6_{ar}$), 140.98(s', $C^2_{ar}$), 147.28 (s',=COTf); $^{19}F$ NMR ($CDCl_3$), δ: -78.3 (s', $CF_3SO_3^-$), 72.7 (s', $CF_3SO_3$); Anal. Calcd. for $C_{11}H_9IF_6O_6S_2$ : C, 24.37, H, 1.67; Found: C, 24.02; H, 1.94.

**[2-(Trifluoromethylsulfonyloxy)-1-pentenyl](o-tolyl) iodonium trifluoromethylsulfonate 2o**: yield 73%; m.p.164-165°C; IR ($CCl_4$), $cm^{-1}$: 3060; 1650; 1230; 1165; 1030; 1000; 830; $^1H$ NMR (DMSO-$d_6$/$CDCl_3$), δ: 0.671 (t, $J$ = 7.2 Hz, 3H, $CH_3$), 1.254 (m, 2H, $CH_2$), 2.368 (s, 3H, $CH_3$), 2.485 (t, $J$ = 7.0 Hz), 6.930 (s, 1H, =CH), 7.027 (t, $J$ = 8 Hz, 1H, $H^5_{ar}$), 7.253 (d, $J$ = 8 Hz, 1H, $H^3_{ar}$); 7.318 (d, $J$ = 8 Hz, 1H, $H^4_{ar}$), 7.856 (d, $J$ = 8 Hz, 1H, $H^6_{ar}$); $^{13}C$ NMR, (DMSO-$d_6$/$CDCl_3$), δ: 13.03 (q', $CH_3$), 19.22 (t', $CH_2$), 25.19 (q', $CH_3$-Ar), 35.95 (t', $CH_2$-allylic), 94.67 (d', =CH), 118.01 (q', $J_{CF}$ = 320Hz, $CF_3$), 119.01 (s', $C_{ipso}$), 119.89(q', $J_{CF}$ = 320 Hz, $CF_3$), 129.45 (d', $C^5_{ar}$), 131.83 (d', $C^3_{ar}$), 133.23 (d', $C^4_{ar}$), 136.95 (d',$C^6_{ar}$), 140.52 (s', $C^2_{ar}$), 150.17 (s' =COTf); $^{19}F$ NMR (DMSO-$d_6$/$CDCl_3$), δ: -77.9 (s', $CF_3SO_3^-$), -72.3 (s', $CF_3SO_3$); Anal. Calcd. for $C_{14}H_{15}IF_6O_6S_2$ : C, 28.77, H, 2.59; Found: C, 28.94; H, 2.72.

**[2-(Trifluoromethylsulfonyloxy)-3-methoxy-1-propenyl](o-tolyl) iodonium trifluoromethylsulfonate 2p**: yield 68%; m.p. 179-180° C; $^1H$ NMR, (acetone-$d_6$), δ: 2.710 (s, 3H, $CH_3$-Ar), 3.642 (s, 3H, $CH_3O$), 4.615 (s, 2H, $CH_2$), 7.373 (d, $J$ = 8 Hz, $H^5_{ar}$), 7.598 (s, 1H, =CH), 7.67(m, 2H, $H^{3,4}_{ar}$), 8.316 (d, $J$ = 8 Hz, $H^6_{ar}$); $^{13}C$ NMR, (acetone-$d_6$), δ: 25.58 (q', $CH_3$-Ar), 59.95 (q', $CH_3O$), 70.96 (t', $CH_2O$), 94.97 (d', =CH), 118.50 (q', $CF_3$), 119.50 (q', $CF_3$), 119.64 (s', $C_{ipso}$), 130.33 (d', $C^5_{ar}$), 132.66 (d', $C^3_{ar}$), 134.64 (d', $C^4_{ar}$), 138.84 (d', $C^6_{ar}$), 142.79 (s, $C^2_{ar}$), 151.29 (s', =COTf); Anal. Calcd. for $C_{13}H_{13}IF_6O_7S_2$: C, 26.63; H, 2.24; Found : C, 26.72; H, 2.40

**[2-(Trifluoromethylsulfonyloxy)-ethenyl](p-nitrophenyl) iodonium trifluoromethylsulfonate 2q**: yield 57%; m.p. 158-159° C; $^1H$ NMR, (acetone-$d_6$), δ: 7.987 (d, $J$ = 11.9 Hz, 1H, =CH), 8.371 (d, $J$ = 11.9 Hz, 1H, =CH ), 8.4214 (d, $J$ = 8.5 Hz, 2H, $H_{meta}$), 8.633 (d, $J$ = 8.5 Hz, 2H, $H_{ortho}$); $^{13}C$ NMR, (acetone-$d_6$), δ: 94.42 (d', =CH), 120.07 (s', Cipso), 127.17(d', $C_{meta}$), 137.92 (d', $C_{ortho}$), 151.25(s', $C_{para}$-$NO_2$),152.01 (s', =COTf)); Anal. Calcd. for $C_{13}H_{13}IF_6NO_7S_2$: C, 20.96; H, 1.06; Found : C, 21.34; H, 1.27.

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