Synthesis of β-Dimethylsulfonium- and β-Methylthio-Substituted Vinyl Triflates by Reaction of Acetylenes with Dimethyl Sulfide Ditriflate

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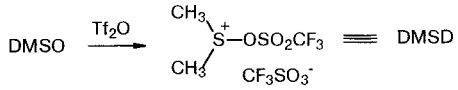
A one-pot synthesis of β-dimethylsulfonium-substituted vinyl triflates by the reaction of dimethyl sulfide ditriflate with acetylenes is described. β-Dimethylsulfonium-substituted vinyl triflates were found to exhibit unusual reactivity towards nucleophiles resulting in demethylation of sulfonium salts, but not substitution of triflate. Demethylation of these sulfonium salts with diethylamine gave the corresponding β-methylthio-substituted vinyl triflates. The possibility of thiophene derivative synthesis via triflic anhydride promoted cyclization of sulfoxide was studied.

Vinyl triflates play an important role in modern organic synthesis.[1] They are effective precursors of vinyl cations,[2] alkylidene carbenes (primary vinyl triflates),[3-5] acetylenes and allenes (secondary vinyl triflates).[6,7] There is significant current interest in the cross-coupling reactions of vinyl triflates catalyzed with low-valent platinum, palladium and nickel.[8-10] There are several methods of preparation of vinyl triflates, but elaboration of novel techniques, particularly for functionally substituted derivatives, is both a theoretical and synthetic goal.

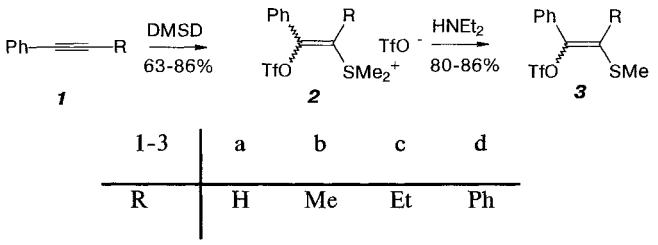
Now we report a synthesis of β-dimethylsulfonium- and methylthio-substituted vinyl triflates by reaction of acetylenes with dimethyl sulfide ditriflate. Quite recently, very similar types of vinyl triflates, alkenyl sulfoxides with a trifluoromethylsulfonyloxy group on the β-carbon, were obtained from α-alkyl β-oxo sulfoxides.[11] Ligand exchange reactions of these triflates to give acetylenes and allenes were studied.[11]

Dimethyl sulfide ditriflate [DMSD, dimethyl(trifluoromethylsulfonyloxy)sulfonium trifluoromethanesulfonate] is obtained by reaction of triflic anhydride with dimethyl sulfoxide (Scheme 1). Earlier this reagent was used for the oxidation of alcohols to the corresponding carbonyl compounds and for the conversion of aromatic amines to their sulfilimines.[12-14] Recently we have found that dimethyl sulfide ditriflate functions as a highly reactive S-electrophile in the reaction with various aromatic compounds including less active aromatics, such as benzene and toluene. This reaction permits one-pot synthesis of dimethylarylsulfonium salts in high yield.[15] Reaction of DMSD with acetylenes has not been described earlier.



Scheme 1

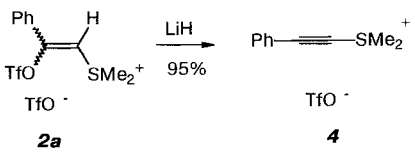
We investigated the reaction of dimethyl sulfide ditriflate with different acetylenes having both terminal and internal triple bonds. Reaction with phenyl-substituted alkynes **1a–d** proceeds under mild conditions as a conjugate addition of electrophile (dimethylsulfonium moiety) and nucleophile (triflate group). This reaction opens a convenient route to a new type of vinyl triflates having in the β-position at the double bond a powerful electron-withdrawing group, the dimethylsulfonium group **2a–d** (Scheme 2).



Scheme 2

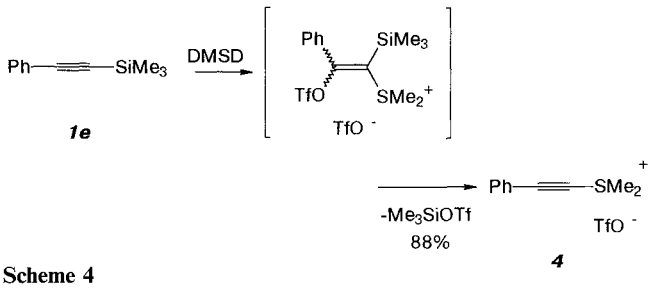
We have studied the stereochemistry of the addition of DMSD to triple bonds. In the case of 1-phenylprop-1-yne **(1b)** the reaction gave a mixture of *E* and *Z* isomers in 1:5 ratio. In the case of phenylacetylene **(1a)** and 1-phenylbut-1-yne **(1c)** only the *Z* isomer was formed, contrary to the case of diphenylacetylene **(1d)** in which only the *E* isomer was isolated. We explain the reaction stereochemistry by steric reasons. Molecular model analysis shows that for vinyl triflates **2a–d** in the case of *cis* orientation of dimethylsulfonium and CF_3SO_3 groups van der Waals' interactions are minimal, but in the case of reaction with diphenylacetylene **(1d)** the stereochemistry of DMSD addition to the triple bond is controlled possibly by *trans* arrangement of the more bulky phenyl moieties. The configurations of the products were established by NOE experiments.

In the reaction of DMSD with phenylacetylene **(1a)**, phenylacetylene contains a terminal triple bond and correspondingly the acetylenic proton gives rise to a mixture of the corresponding vinyl triflate **2a** and ethynylsulfonium salt **4** in 2:3 ratio. We believe that the compound **2a** is prone to transformation to the corresponding ethynylsulfonim salt **4** via spontaneous elimination of triflic acid to give a mixture of **2a** and **4**. We succeeded in converting this mixture to pure **4** under mild conditions using a base such as LiH (Scheme 3). Lithium hydride, due to very low reactivity, is rarely used as a base in contrast to sodium and potassium hydride.[16] However in the case of **2a** LiH is rather appropriate; other organic and inorganic bases induce undesirable reactions and the yield of target product **4** is lower.



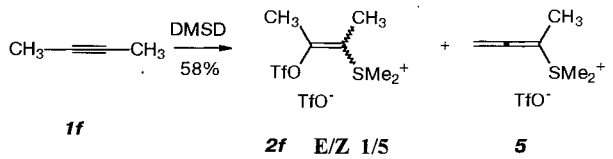
Scheme 3

The sulfonium salt **4** was also obtained in good yield by reaction of DMSD with phenyl(trimethylsilyl)acetylene (**1e**). The primary product of the reaction is evidently unstable and rapidly decomposes to form **4** and trimethylsilyl triflate (Scheme 4).



Scheme 4

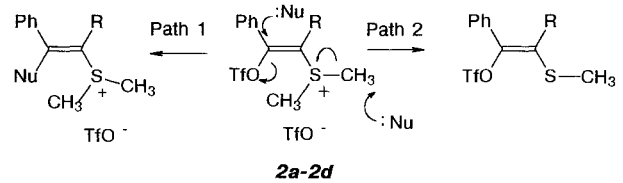
We have also investigated the reaction of DMSD with acetylenes with an alkyl- and a dialkyl-substituted triple bond. Reaction of dimethyl sulfide ditriflate with but-2-yne (**1f**) gave a mixture of sulfonium salts **2f** and **5** in ~1:2 ratio (Scheme 5). The major product of the reaction is allene **5** which is the product of elimination of triflic acid (as in the case of phenylacetylene) from **2f**. Sulfonium salt **2f** which is the product of conjugate addition of dimethylsulfonium and triflate groups is formed as a mixture of *E*/*Z* isomers in ratio 1:5.



Scheme 5

In the case of terminal aliphatic acetylenes such as hex-1-yne (**1g**) and hept-1-yne (**1h**) reaction with DMSD proceeds more complicatedly to give mixtures of sulfonium salts of unidentified structure.

We have investigated the reaction of vinyl triflates **2a–d** with different nucleophiles. Vinyl triflates **2a–d** have a number of reaction centers and the nucleophile can react with the triflate center (path 1) or with the sulfonium group (path 2) (Scheme 6).



Scheme 6

The reaction with different amines does not proceed as substitution of the triflate group, only demethylation of sulfonium salts take place (Path 2). Earlier, when we investigated the reaction of β-trifluoroacetyl-substituted vinyl sulfonium salts with nucleophiles, we also found that demethylation was the principal reaction,[17] and the most appropriate nucleophile for demethylation was dimethyl sulfide. However, the reaction of vinyl triflates **2a–d** with dimethyl sulfide proceeds very slowly. Obviously this is due to the weaker electron-withdrawing action of the triflate moiety compared to the trifluoroacetyl group. We have found that the demethylation of sulfonium salts proceeds in good yield using diethylamine, other amines give lower yields. Resulting compounds do not enter in the reaction with amines obviously due to the influence of the methylthio group. It is also possible to carry out a one-pot reaction to give methylthio-substituted vinyl triflates **3b–d** without isolation of sulfonium salts **2b–d**.

In the case of products of the reaction of DMSD with phenylacetylene, treatment with diethylamine gave the corresponding methylthioacetylene **6** without formation of corresponding vinyl triflate as in the cases of **2b–d**.

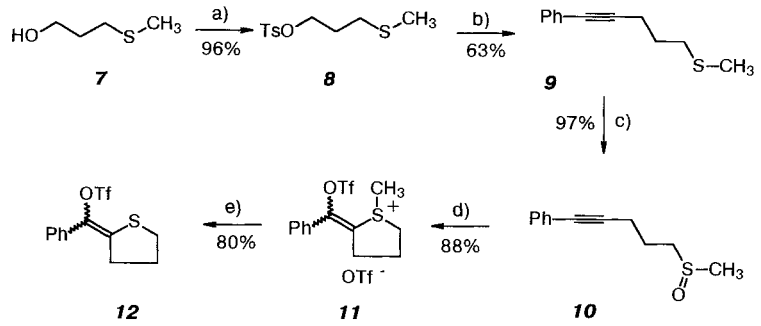
We have also investigated the intramolecular version of reaction of sulfoxide activated by triflic anhydride with acetylene. For this purpose the corresponding sulfoxide **10** was prepared according to Scheme 7 via alkylation of sodium phenylacetylenide by the corresponding tosylate **8** easily prepared from commercially available 3-(methylthio)propan-1-ol (**7**).

The cyclization of sulfoxide **10** by treatment with triflic anhydride gave the corresponding sulfonium salt **11** as a mixture of *E*- and *Z*-isomers 2:3. The reaction proceeds according to the Markovnikov and Baldwin rules as exo-cyclization. As in the case of the reaction of DMSD with acetylenes **1a–d** the *Z*-isomer of **11** was formed as the major isomer. Successive treatment with diethylamine resulted in the formation of the corresponding alkylidene thiophene **12** (mixture *E*/*Z* 2:3), dealkylation proceeds selectively as demethylation without thiophene ring cleavage. Recently a compound of similar structure, thiolenol triflate (the derivative of dihydrothiophene containing a triflate group in the α-position to sulfur), was used for synthesis of thionucleosides which display antiviral and anti-HIV activity.[18,19]

Thus, DMSD is a highly reactive S-electrophile in the reaction of electrophilic addition to acetylenes. The reaction proceeds as conjugate addition of dimethylsulfonium and triflate groups to a triple bond to give the corresponding vinyl triflates containing in the β-position a dimethylsulfonium group. Reaction with nucleophiles proceeds as demethylation of sulfonium salt, but not substitution of triflate group. Reaction with amines gives rise to selective demethylation to form the corresponding β-thioalkyl-substituted vinyl triflates.

Mps were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian VXR-400, Bruker AM 400C and Bruker AC 200P spectrometers with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer. Column chromatography was performed on silica gel (63–200 mesh, Merck). All solvents used were dried and distilled according to standard procedures. Triflic anhydride was prepared according to literature procedure[1] from trifluoromethanesulfonic acid (Merck).

Reaction of DMSD with Acetylenes; General Procedure:
To a well-stirred solution of DMSO (0.36 mL, 5 mmol, 1 equiv) in CH_2Cl_2 (20 mL) was added Tf_2O (0.84 mL, 5 mmol, 1 equiv) at



Reagents: a) TsCl, Py; b) DMSO, NaH, phenylacetylene; c) H_2O_2; d) Tf_2O; e) $HNEt_2$

Scheme 7

−30 °C. A solution of the corresponding acetylene (5 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added dropwise. The reaction mixture was allowed to react at −15 °C overnight. The solvents were removed in vacuo, followed by addition of Et_2O. The crude product was precipitated and the solution was decanted. The crude product crystallized from $Et_2O/CHCl_3$. If the product was isolated as an oil it was purified three times by dissolving in CH_2Cl_2 followed by reprecipitation with Et_2O.

Dimethyl[(Z)-2-phenyl-2-trifluoromethylsulfonyloxyvinyl]sulfonium Trifluoromethanesulfonate **(2a)**: (mixture with **4** 2:3);

yield: 63 %; white crystalline solid; mp 86–91 °C (dec.).

IR (Nujol): ν = 1670 (C=C), 1300–1100 (CF_3), 1040 (SO_3) cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ = 7.80–7.46 (m, 6 H, CH and Ph), 3.30 (s, 6 H, $(CH_3)_2S$).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.47 (C-2), 134.19 (Ph), 129.81 (2 C, Ph), 129.19 (C-q, Ph), 127.80 (2 C, Ph), 119.29 (q, CF_3, ^1J = 320.8 Hz), 107.19 (CH-1), 28.67 ($(CH_3)_2S$).

Dimethyl[(E/Z)-1-methyl-2-phenyl-2-trifluoromethylsulfonyloxyvinyl]sulfonium Trifluoromethanesulfonate **(2b)**: *E*/*Z* 1:5; yield: 71 %; white crystalline solid; mp 145–146 °C (dec.).

IR (Nujol): ν = 1660 (C=C), 1300–1120 (CF_3), 1040 (SO_3) cm^{-1}.

^1H NMR (400 MHz, CD_3COCD_3): *major isomer* δ = 7.76–7.58 (m, 5 H, Ph), 3.45 (s, 6 H, $(CH_3)_2S$), 2.47 (s, 3 H, CH_3); *minor isomer* δ = 7.76–7.58 (m, 5 H, Ph), 3.37 (s, 6 H, $(CH_3)_2S$), 2.58 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, CD_3COCD_3): *major isomer* δ = 154.12 (C-1), 133.19 (Ph), 130.43 (2 C, Ph), 130.21 (C-q, Ph), 129.84 (2 C, Ph), 119.52 (C-2), 118.85 (q, CF_3, ^1J = 320.1 Hz), 25.43 ($(CH_3)_2S$), 12.78 (CH_3); *minor isomer* δ = 156.43 (C-1), 133.38 (Ph), 131.05 (2 C, Ph), 130.73 (C-q, Ph), 129.97 (2 C, Ph), 121.94 (C-2), 118.85 (q, CF_3, ^1J = 320.1 Hz), 25.93 ($(CH_3)_2S$), 11.18 (CH_3).

Anal. $C_{13}H_{14}F_6O_6S_3$: Calcd C 32.77, H 2.96. Found: C 33.18, H 2.67.

[(Z)-1-Ethyl-2-phenyl-2-trifluoromethylsulfonyloxyvinyl]dimethylsulfonium Trifluoromethanesulfonate **(2c)**: yield: 86 %; white crystalline solid; mp 150–151 °C (dec.).

IR (Nujol): ν = 1650 (C=C), 1300–1140 (CF_3), 1040 (SO_3) cm^{-1}.

^1H NMR (200 MHz, CD_3COCD_3): δ = 7.80–7.64 (m, 5 H, Ph), 3.50 (s, 6 H, $(CH_3)_2S$), 2.93 (q, 2 H, CH_2, ^3J = 7.2 Hz), 1.15 (t, 3 H, CH_3, ^3J = 7.2 Hz).

^{13}C NMR (50 MHz, CD_3COCD_3): δ = 155.28 (C-1), 132.91 (Ph), 130.96 (C-q, Ph), 129.74 (4 C, Ph), 124.34 (C-2), 118.49 (q, CF_3, ^1J = 319.6 Hz), 25.58 ($(CH_3)_2S$), 20.45 (CH_2), 13.51 (CH_3).

Anal: $C_{14}H_{16}F_6O_6S_3$: Calcd C 34.29, H 3.29. Found: C 34.01, H 3.17.

Dimethyl[(E)-1,2-diphenyl-1-trifluoromethylsulfonyloxyvinyl]sulfonium Trifluoromethanesulfonate **(2d)**: yield: 81 %; pale yellow crystalline solid; mp 142–144 °C (dec.).

IR (Nujol): ν = 1670 (C=C), 1320–1140 (CF_3), 1050 (SO_3) cm^{-1}.

^1H NMR (400 MHz, CD_3COCD_3): δ = 7.71–7.67 (m, 2 H, 2Ph), 7.59–7.43 (m, 6 H, 2Ph), 7.37 (t, 2 H, 2Ph, ^3J = 8.0 Hz), 3.22 (s, 6 H, $(CH_3)_2S$).

^{13}C NMR (100 MHz, CD_3COCD_3): δ = 156.93 (C-2), 133.05 (2 C, Ph), 132.98 (Ph), 132.15 (Ph), 130.57 (C-q, Ph), 130.51 (2 C, Ph), 130.35 (2 C, Ph), 129.37 (2 C, Ph), 125.91 (C-q, Ph), 121.75 (C-1), 118.96 (q, CF_3, ^1J = 320.5 Hz), 26.78 ($(CH_3)_2S$).

Anal: $C_{18}H_{16}F_6O_6S_3$: Calcd C 40.15, H 2.99. Found: C 39.83, H 2.64.

Dimethyl(phenylethynyl)sulfonium Trifluoromethanesulfonate (4):
To a stirred solution of **2a** and **4** (1 g, 2.7 mmol) in CH_2Cl_2 (20 mL), powdered LiH (0.2 g, 27 mmol) was added. The reaction mixture was allowed to react for 40 h followed by filtration and crystallization of the product from Et_2O/CH_2Cl_2 mixture; yield: 95 %.

Compound **4** was also obtained according to the general procedure from phenyl(trimethylsilyl)acetylene in 88 % yield; white crystalline solid mp 103–105 °C (dec.).

IR (Nujol): ν = 2210 (C≡C), 1320–1100 (CF_3), 1040 (SO_3) cm^{-1}.

^1H NMR (200 MHz, CD_2Cl_2): δ = 7.62–7.38 (m, 5 H, 2Ph), 3.41 (s, 6 H, $(CH_3)_2S$).

^{13}C NMR (50 MHz, CD_2Cl_2): δ = 133.89 (2 C, Ph), 133.19 (Ph), 129.66 (2 C, Ph), 120.35 (q, CF_3, ^1J = 320.3 Hz), 118.15 (C-q, Ph), 105.95 (C-1), 66.68 (C-2), 33.31 ($(CH_3)_2S$).

Anal: $C_{11}H_{11}F_3O_3S_2$: Calcd C 42.30, H 3.55. Found: C 42.01, H 3.67.

Dimethyl[(*E*/*Z*)-1,2-dimethyl-2-trifluoromethylsulfonyloxyvinyl]sulfonium Trifluoromethanesulfonate (2f) and Dimethyl(1-methylpropa-1,2-dienylsulfonium Trifluoromethanesulfonate (5):
Using the general procedure for DMSD; mixture *E*-**2f**/*Z*-**2f**/**5** 1:5:10; yield 58 %; oil.

IR (Nujol): ν = 1320–1120 (CF_3); 1040 (SO_3) cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): *allene signals* δ = 5.56 (q, 2 H, CH_2=, ^5J = 3.2 Hz), 2.90 (s, 6 H, $(CH_3)_2S$), 2.11 (t, 3 H, CH_3, ^5J = 3.2 Hz); *signals of vinyltriflates: major isomer* δ = 3.04 (s, 6 H, $(CH_3)_2S$), 2.43 (q, 3 H, CH_3, ^5J = 1.6 Hz), 2.15 (q, 3 H, CH_3, ^5J = 1.6 Hz); *minor isomer* δ = 3.13 (s, 6 H, $(CH_3)_2S$), 2.48 (q, 3 H, CH_3, ^5J = 1.5 Hz), 2.17 (q, 3 H, CH_3, ^5J = 1.5 Hz).

^{13}C NMR (100 MHz, CD_2Cl_2): *allene signals* δ = 207.70 (C-3), 93.84 (C-2), 86.69 (C-4), 121.11 (q, CF_3, ^1J = 320.0 Hz), 26.79 ($(CH_3)_2S$), 14.94 (CH_3); *signals of vinyltriflates*: *major isomer* δ = 157.53 (C-3), 121.11 (q, CF_3, ^1J = 320.0 Hz), 118.72 (C-2), 25.96 ($(CH_3)_2S$), 19.53 and 10.4 (2 CH_3); *minor isomer* δ = 155.87 (C-3), 121.11 (q, CF_3, ^1J = 320.0 Hz), 118.72 (C-2), 25.43 ($(CH_3)_2S$), 19.45 and 13.4 (2 CH_3).

Sulfonium Salt Demethylation; General Procedure:
The sulfonium salt (5 mmol, 1 equiv) obtained as above described was dissolved in CH_2Cl_2 (20 mL). $HNEt_2$ (30 mmol, 6 equiv) was added to this solution or to reaction mixture without sulfonium salt separation. In 30 min the reaction mixture was evaporated in vacuo. The residue was mixed with Et_2O (20 mL) and passed through a short silica-gel column followed by evaporation to give pure sulfide.

(Z)-2-Methylthio-1-phenyl-1-trifluoromethylsulfonyloxyprop-1-ene **(3b)**: yield: 82%; pale yellow oil.

IR (neat): ν = 1250–1140 (CF_3), 1040 (CF_3SO_3) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.37 (m, 5H, Ph), 2.36 (s, 3H, CH_3S), 2.06 (s, 3H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.61 (C-1), 132.09 and 131.36 (C-2 and (C-q, Ph)), 129.50 (Ph), 129.38 (2C, Ph), 128.36 (2C, Ph), 118.04 (q, CF_3, ^1J = 320.6 Hz), 17.42 (CH_3S), 13.88 (CH_3).

Anal: $C_{11}H_{11}F_3O_3S_2$: Calcd C 42.30, H 3.55. Found: C 41.86, H 3.37.

(Z)-2-Methylthio-1-phenyl-1-trifluoromethylsulfonyloxybut-1-ene **(3c)**: yield: 80%, pale yellow oil.

IR (neat): ν = 1260–1120 (CF_3), 1060, 1040 (CF_3SO_3) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.31 (m, 5H, Ph), 2.36 (q, 2H, CH_2), 2.33 (s, 3H, SCH_3), 1.11 (t, 3H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.80 (C-1), 135.76 and 132.21 (C-2 and (C-q, Ph)), 129.73 (Ph), 129.28 (2C, Ph), 128.49 (2C, Ph), 118.05 (q, CF_3, ^1J = 319.6 Hz), 23.43 (CH_2), 13.94 and 13.42 (CH_3S and CH_3).

Anal: $C_{12}H_{13}F_3O_3S_2$: Calcd C 44.17, H 4.01. Found: C 43.72, H 3.84.

2-Methylthio-1,2-diphenyl-1-trifluoromethylsulfonyloxyethene **(3d)**: yield: 80%, pale yellow crystalline solid; mp 82–83°C (dec.).

IR (Nujol): ν = 1250, 1130 (OSO_2CF_3), 1210 (CF_3) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.11 (m, 10H, 2Ph), 1.98 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.05 (C-1), 135.07, 133.68, 132.70 (C-2, 2(C-q, Ph)), 130.18 (2C, Ph), 129.17 (2C, Ph), 128.97 (C, Ph), 128.63 (2C, Ph), 128.56 (C, Ph), 128.01 (2C, Ph), 118.18 (q, CF_3, ^1J = 318.2 Hz) 15.14 (CH_3S).

Anal: $C_{16}H_{13}F_3O_3S_2$: Calcd C 51.33, H 3.50. Found: C 51.00, H 3.27.

Methyl Phenylethynyl Sulfide **(6)**: yield: 76%.

IR and ^1H NMR spectra were identical to Lit[20].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 131.56 (2C, Ph), 128.45 (2C, Ph), 128.19 (C, Ph), 123.60 (C-q, Ph), 92.08 (C-2), 81.31 (C-1), 19.47 (CH_3S).

3-Methylthiopropyl Tosylate (8):
To a well-stirred solution of 3-(methylthio)propan-1-ol (21.2 g, 0.2 mol, 1 equiv) and TsCl (36.1 g, 0.19 mol, 0.95 equiv) in CH_2Cl_2 (100 mL) at −20°C was added dropwise pyridine (39.5 g, 0.5 mol, 2.5 equiv). The reaction mixture was allowed to react at −20°C overnight and then at r.t. for 2 h. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 (3 × 100 mL), washed with H_2O and dried (Na_2SO_4). Solvents were removed in vacuo. The crude product was mixed with CH_2Cl_2 (20 mL) followed by precipitation with hexane (100 mL). The resulting oil was decanted and solvents were removed in vacuo to yield 50 g (96%) of title compound as a colorless oil.

IR (neat) ν = 1380 (SO_2), 1180 (SO_2) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (m, 2H, 2CH-*o*, Ar), 7.30 (m, 2H, 2CH-*m*, Ar), 4.09 (t, 2H, CH_2O, ^3J = 6.3 Hz), 2.44 (t, 2H, CH_2S, ^3J = 7.0 Hz), 2.38 (s, 3H, CH_3Ar), 1.96 (s, 3H, CH_3S), 1.85 (m, 2H, CH_2, ^3J = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.88 (CSO_2), 132.92 (CCH_3), 129.91 and 127.80 (Ar), 68.93 (OCH_2), 29.50 (SCH_2), 28.27 (CH_2), 21.57 (CH_3Ar), 15.27 (CH_3S).

Anal: $C_{11}H_{16}O_3S_2$: Calcd C 50.74, H 6.19. Found: C 51.00, H 3.27.

Methyl (5-Phenylpent-4-ynyl) Sulfide (9):
A solution of dimesylsodium (0.2 mol) in DMSO (100 mL) was obtained according to literature procedure.[21] Then THF (50 mL) was added and stirred reaction mixture was cooled to −20°C under Ar. A solution of phenylacetylene (0.23 mol) in 50 mL of THF was added dropwise. Reaction mixture was allowed to warm to r.t. and stirred for 1 h. Then reaction mixture was cooled to −30°C and the solution of tosylate **8** (50 g, 0.19 mol) in THF (50 mL) was added dropwise. Reaction mixture was allowed to react at this temperature for 1 h then the temperature was raised to 20°C and reaction mixture was stirred for 3 h. The reaction mixture was quenched with water, extracted with Et_2O (3 × 100 mL) and dried (Na_2SO_4). The organic solvents were removed in vacuo. The rectification under reduced pressure gave 21.9 g (63%) of desired product; n_D^{19} 1.5665; bp 132–133°C/2 Torr.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.35 (m, 2H, 2CH-Ph), 7.27–7.22 (m, 3H, 3CH-Ph), 2.62 and 2.50 (2t, 2H, CH_2S and CCH_2, ^3J = 7.0 Hz), 2.07 (s, 3H, CH_3S), 1.85 (m, 2H, CH_2, ^3J = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.37 (2C, Ph), 128.39 (C-q, Ph), 128.03 (2C, Ph), 127.44 (Ph), 89.01 ($C_{acet.}$-4), 81.09 ($C_{acet.}$-5), 33.06 (SCH_2), 27.98 (CH_2-2), 18.28 (CH_2-3), 15.31 (CH_3S).

Anal: $C_{12}H_{14}S$: Calcd C 75.74, H 7.41. Found: C 75.25, H 7.57.

Methyl (5-Phenylpent-4-ynyl) Sulfoxide (10):
To a solution of methyl (5-phenylpent-4-ynyl) sulfide (**9**, 1.9 g, 0.01 mol) in HOAc (20 mL) was added 15.6% H_2O_2 (2.2 mL, 0.01 mol). The reaction mixture was stirred for 1 h and then water was added. The product was extracted with CH_2Cl_2 (3 × 20 mL) and stirred for 30 min over $NaHCO_3$. The organic fraction was separated and dried (Na_2SO_4). The organic solvents were removed in vacuo to give 2.0 g of pure sulfoxide as colorless oil (yield 97%).

IR (Nujol): ν = 1060 (SO) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.09 (m, 5H, Ph), 2.71 (m, 2H, CH_2S), 2.45 (m, 2H, CCH_2), 2.42 (s, 3H, CH_3S), 1.90 (m, 2H, CH_2-2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.49 (2C, Ph), 127.30 (2C, Ph), 126.88 (Ph), 122.44 (C-q, Ph), 87.35 ($C_{acet.}$-4), 80.88 ($C_{acet.}$-5), 52.01 (SCH_2), 37.37 (CH_3S), 20.85 (CH_2-2), 17.56 (CH_2-3).

Anal: $C_{12}H_{14}OS$: Calcd C 69.86, H 6.84. Found: C 70.12, H 6.82.

(*E,Z*)-1-Methyl-2-[phenyl(trifluoromethylsulfonyloxy)methylene]tetrahydrothiophenium Trifluoromethanesulfonate (11):
Using the procedure in **2**; *E*/*Z* 2:3; yield; 88%; brown oil.

IR (Nujol): ν = 1680 (C=C), 1320–1120 (CF_3), 1040, 1000 (CF_3SO_3) cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ = *major isomer* 7.66–7.50 (m, 5H, Ph), 4.06 (m, 2H, SCH_2), 3.18 (s, 3H, SCH_3), 3.11 (m, 2H, CCH_2), 2.57 (m, 2H, CH_2); *minor isomer* 7.66–7.50 (m, 5H, Ph), 4.06 (t, 2H, SCH_2), 3.11 (m, 2H, CCH_2), 2.72 (s, 2H, SCH_3), 2.57 (m, 2H, CH_2).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = *major isomer* 150.59 (C-1), 133.05 (Ph), 129.69 (C-q, Ph), 129.50 (2C, Ph), 129.04 (2C, Ph), 122.39 (C-2), 118.45 (q, CF_3, ^1J = 319.1 Hz), 46.54 (CH_2S), 33.10 (CH_2C), 27.67 (CH_3S), 26.37 (CH_2); *minor isomer* 151.21 (C-1), 133.34 (Ph), 132.41 (C-q, Ph), 130.24 (2C, Ph), 128.87 (2C, Ph), 119.22 (C-2), 118.45 (q, CF_3, ^1J = 319.1 Hz), 47.49 (CH_2S), 32.85 (CH_2C), 27.67 (CH_3S), 26.65 (CH_2).

Anal: $C_{14}H_{14}F_6O_6S_3$: Calcd C 34.43, H 2.89. Found: C 34.10, H 3.06.

(*E,Z*)-2-[Phenyl(trifluoromethylsulfonyloxy)methylene]tetrahydrothiophene (12):
Using the sulfonium salt demethylation general procedure; *E*/*Z* 2:3; yield: 80%; pale yellow oil.

IR (neat): ν = 1250–1120 (CF_3), 1030, 1040 (CF_3SO_3) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = *major isomer* 7.44–7.18 (m, 5H, Ph), 3.04 (t, 2H, SCH_2, ^3J = 6.4 Hz), 2.65 (t, 2H, CH_2, ^3J = 6.8 Hz), 2.03 (m, 2H, CH_2, ^3J = 6.4; 6.8 Hz); *minor isomer* 7.44–7.18 (m, 5H, Ph), 3.02 (t, 2H, SCH_2, ^3J = 6.2 Hz), 2.87 (t, 2H, CH_2, ^3J = 7.0 Hz), 2.03 (m, 2H, CH_2, ^3J = 6.2, 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = *major isomer* 140.31 (C-1), 135.60 and 133.24 (C-2 and (C-q, Ph)), 128.32 (2 C, Ph), 127.76 (2 C, Ph), 127.20 (C, Ph), 118.28 (q, CF_3, ^1J = 319.8 Hz), 34.80 and 34.32 (CH_2S and CH_2C), 30.81 (CH_2); *minor isomer* 140.65 (C-1), 133.54 and 132.92 (C-2 and C-q, Ph), 128.83 (2 C, Ph), 128.32 (C-Ph), 128.30 (2 C, Ph), 118.28 (q, CF_3, ^1J = 319.8 Hz), 35.43 and 35.12 (CH_2S and CH_2C), 29.26 (CH_2).

Anal: $C_{12}H_{11}F_3O_3S_2$: Calcd C 44.44, H 3.42. Found: C 44.03, H 3.20.

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