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Addition of Trifluoromethanethio- and Trifluoromethaneseleno-Sulfonates to Olefins. Synthesis of Vinyl Triflones.

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Abstract *: Trifluoromethanethio- and trifluoromethaneselenosulfonates are strong electrophilic reagents which add rapidly to olefins to deliver β-sulfenyl and β-selenyl triflones. These products are converted in high yields to vinyl triflones by different techniques under mild conditions. This two-step procedure is an efficient route to vinyl triflones from non-functionalized olefins.* © 1999 Elsevier Science Ltd. All rights reserved.

The addition of selenyl or sulfenyl halides to olefins has been proven to be of synthetic utility for the incorporation of selenium- and sulfur-containing moieties into unsatured systems, in order to allow their further functionalization.[1] Especially, selenosulfonates ($RSeSO_2R'$) are useful reagents to introduce, in one step, two versatile functionalities on an unsatured substrate.[2] To our knowledge, thiosulfonates ($RSSO_2R'$) have not been used for this purpose since they are 10^5 less reactive than their seleno-analogs.[2d]

We recently described a simple access to trifluoromethanethio- or selenosulfonates[3] which, because of the strong electron-withdrawing power of the CF_3SO_2 group, could be considered as powerful electrophilic reagents. Because of this enhanced reactivity, we therefore examined their addition to olefins to prepare β-sulfenyl- or β-selenyl-trifluoromethylsulfones (Scheme 1).

In this paper, we also describe further reactions which provide a two-step route, from non-functionalized olefins, to vinyl trifluoromethylsulfones ("triflones") which are more reactive than vinyl sulfones[4] and would be of value, for example as dienophiles or Michael acceptors. It must also be kept in mind that the trifluoromethanesulfonyl ("triflyl") group is present in some agrochemicals and drugs.[5]

Results and discussion

The reaction of non-fluorinated selenosulfonates with olefins is usually very sluggish at room temperature and requires addition of boron trifluoride, heating or irradiation to proceed.[2] However, we observed that trifluoromethaneselenosulfonates were much more reactive : their reaction with olefins was usually complete within 2 hours at room temperature even with cyclopentenone as substrate. This fact illustrates the strong electrophilicity of CF_3SO_2SePh. In contrast, trifluoromethanethiosulfonates failed to react under these conditions. To obtain β-sulfenyl triflones, trifluoromethanethiosulfonates and olefins must be heated at 80 °C in the absence of solvent (Table 1).

The exclusive formation of *trans*-adducts (**1-5** and **7**) from cyclic olefins indicates that selenosulfonylation proceeds via an *anti*-addition involving episelenonium or episulfonium salts as intermediates (Scheme 1).

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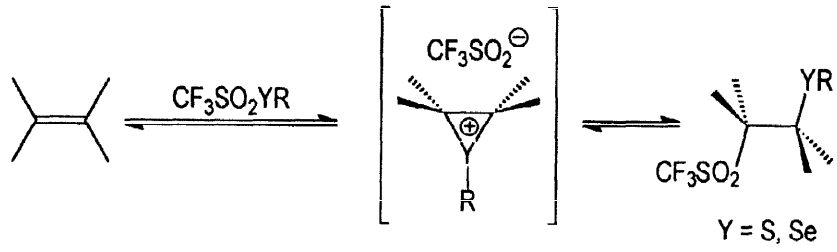
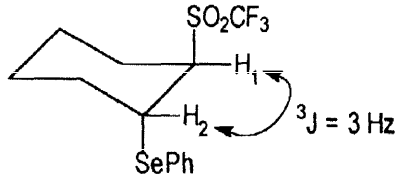
PII: S0040-4020(99)00421-4



Scheme 1

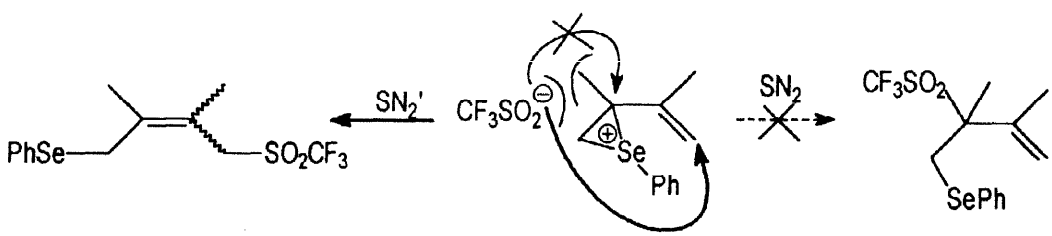
NMR spectra of compounds **2a-e** showed a coupling constant of about 3 Hz between protons H-1 and H-2, a typical value for an equatorial-equatorial coupling constant (Scheme 2). This conformation (CF_3SO_2 and YR groups in axial positions), similar to those already observed for the adducts between cyclohexene and p-tolueneselenosulfonates,[6] could be explained by an electrostatic repulsion through space between the lone-pairs of p-electrons belonging to the fluorine atoms and those belonging to the chalcogen atom.



Scheme 2

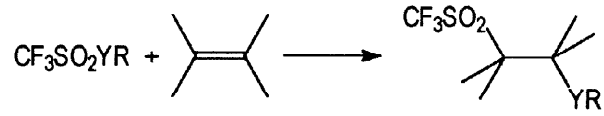
Concerning the regioselectivity, Markovnikov adducts (**4**, **5** and **7**) were only obtained from unsymmetrical cyclic olefins whereas a mixture of regioisomers (**6a** and **6b**) was obtained from a terminal olefin like 1-undecene. In this latter case, the Markovnikov-type opening of the episelenonium cation by $CF_3SO_2^-$ could be partly disfavoured by the bulkiness of this anion. Steric factors could also explain the absence of the expected products from an internal olefin like (E)-5-decene.

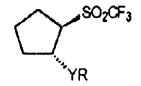
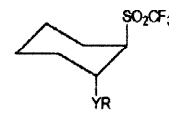
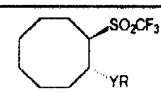
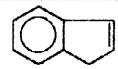
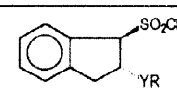
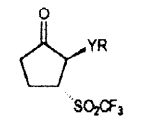
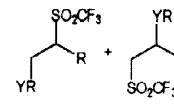
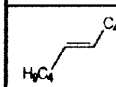
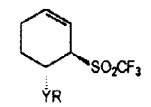
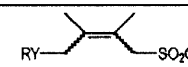
Concerning the addition on dienes, it was observed that the selenosulfonylation of 1,3-cyclohexadiene was completely regioselective (1,2-adduct) and stereoselective (*trans*-adduct) whereas 1,4-addition was only obtained from 2,3-dimethyl-1,3-butadiene, but without any stereoselectivity (Z/ E = 60/40). This difference could be related to the bulkiness of the triflinate anion : when formed, the episelenonium cation should be more easily opened by the $CF_3SO_2^-$ anion through a SN_2' process rather than through a SN_2 process, because of the steric hindrance due to the methyl group (Scheme 3).



Scheme 3

It can be noticed that the regioselectivities observed for **4**, **5** and **7** have been deduced unambiguously from ^1H and ^{13}C NMR spectra (H-H coupling patterns, deshielding effect of the CF_3SO_2 group, small C-Se coupling patterns ($^1J_{C\text{-}Se}$= 70 Hz) and C-H or H-H 2D correlations).



Olefin	Product	YR [a]	Yield (%)
		SePh (**1a**)	85
		SPh (**1b**)	85
		SePh (**2a**)	81
		SPh (**2b**)	75
		$SCH_2CH_2CO_2Et$ (**2c**)	75
		S-nC_8H_{17} (**2d**)	75
		S-C_6H_4-NO_2(p) (**2e**)	75
		SePh (**3a**)	90 [b]
		SPh (**3b**)	25
		SePh (**4**)	85 [b]
		SePh (**5**)	90
	 **6a** **6b**	SePh	93 [c] (6a/6b :60/40)
	Complex mixture	SePh	
		SePh (**7**)	90
	 Z : **8a** E : **8b**	SePh	80 (Z/E : 60/40)

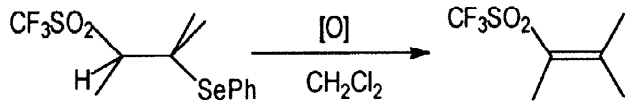
[a] : Y = S : 80°C / 3h / Neat ; Y = Se : 20°C / 2h / CH_2Cl_2

[b] : after 24h [c] : 40°C / 24h / CH_2Cl_2

Table 1

β-selenenyl and β-sulfenyl triflones, thus obtained, were converted to vinyl triflones, in excellent yields, by two different methods. The first one, especially suited to seleno compounds, involved the oxidation of the chalcogen atom, followed by spontaneous elimination of benzeneselenenic acid (Table 2). Because of the disproportionation of the latter compound, an excess of oxydant was advantageously used to oxidize also the residues into seleninic acid, easier to remove.[2c]

It can be noticed that, as expected from the literature[2c], the oxidation of **6b** led exclusively to the E isomer.



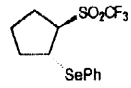
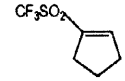
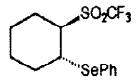
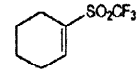
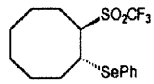
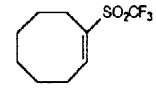
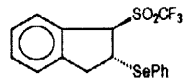
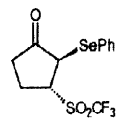
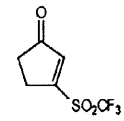
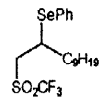
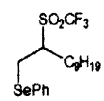
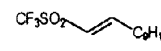
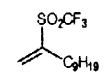
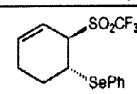
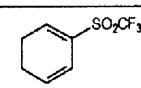
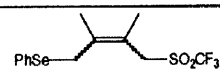
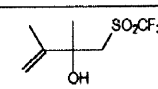
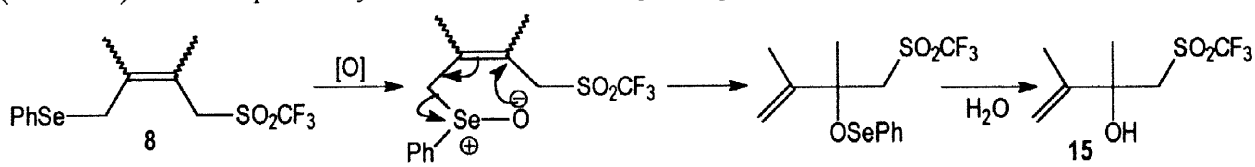
β-seleno Triflones	[O]	Product	Yield (%)
 **1a**	mCPBA H_2O_2	 **9**	87 80
 **2a**	mCPBA	 **10**	75
 **3a**	H_2O_2	 **13**	75
 **4**	H_2O_2 mCPBA	decomposition	
 **5**	mCPBA H_2O_2	 **12**	50 60
 **6b** (40)  **6a** (60)	H_2O_2	 **14b** (40)  **14a** (60)	77
 7	mCPBA H_2O_2	 **11**	91 87
 **8a + 8b**	H_2O_2 mCPBA	 **15**	65 60

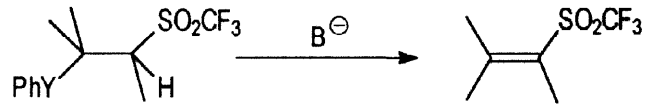
Table 2

On the other hand, oxidation of **8** (E + Z) did not deliver the expected dienic triflone but the allylic alcohol **15** which resulted from the sigmatropic [2,3] rearrangement of an intermediate allyl selenoxide[7] (Scheme 4). No attempt to dehydrate **15** into the corresponding diene has been done.



Scheme 4

As hydrogen atoms in α-position of a triflyl groups are very acidic,[8] the second access to vinyl triflones lay on the elimination, with a base, of thiolates or selenolates, from **1a-b**, **2b** and **3b**, through a E1cB process. This method is especially suited to β-sulfenyl triflones (Table 3).

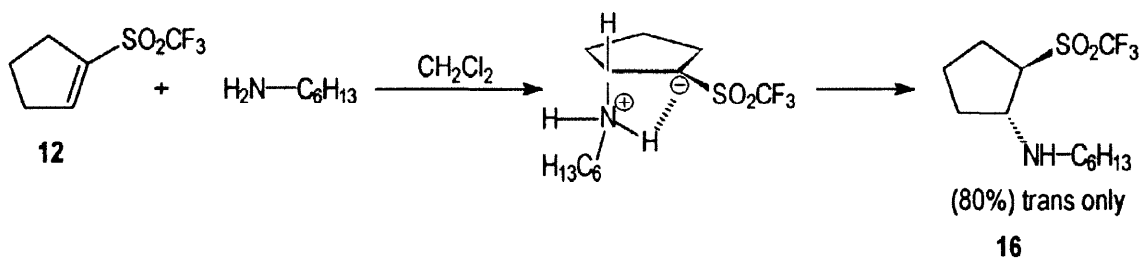


β-thio or β-seleno triflones	Base	Product	Yield (%)
1a (Y = Se)	DBU NaOH (50%)	**9**	89 75
1b (Y = S)	DBU	**9**	83
2b (Y = S)	DBU	**10**	85
3b (Y = S)	DBU	**13**	90

DBU : 1,8-diazabicyclo[5.4.0]-7-undecene

Table 3

In conclusion, trifluoromethanethio (or seleno) sulfonates, easily obtained from readily available sodium trifluoromethanesulfinate, are efficient reagents to prepare β-sulfenyl or β-selenenyl triflones from olefins in one step under mild conditions. These compounds are precursors of vinyl triflones which, in such a way, are prepared in two steps from non-functionalized olefins, without using very agressive and hygroscopic triflic anhydride. Vinyl triflones are probably potent synthetic tools which are under study in our laboratory. For example, we already used them as Michael acceptors towards amines : β-(trifluoromethanesulfonyl)amines were thus obtained in a completely diastereoselective way (Scheme 5).



Scheme 5

Experimental Section

Dichloromethane was distilled prior use and stored over 4 Å molecular sieves. Other reagents were used as received. Trifluoromethanethiosulfonates were synthesized as described in reference 3. Phenyl trifluoromethaneselenosulfonate was synthesized *in situ*, just before the reaction, from sodium trifluoromethanesulfinate and benzeneselenyl chloride.[3] Unless stated otherwise, ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300, 188 and 75 MHz, respectively.

Chemical shifts are given in ppm relative to TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F), used as internal references. Coupling constants are given in hertz. Mass spectrometry was performed at 70 eV after coupling with gas chromatography (except for **3a**, **4**, **5**, **7** and **12** which were unstable under GC conditions). Flash chromatographies were carried out on silica gel MERCK Geduran SI 60.

Reaction of Trifluoromethanethiosulfonates with Olefins. General Procedure.
In a screw-topped flask which was then hermetically closed, 1 mmol of trifluoromethanethiosulfonate and 1 mmol of olefin were introduced. The mixture was heated at 80°C for 3 hours. The resulting product was purified by flash chromatography.

Reaction of Phenyl Trifluoromethaneselenosulfonate with Olefins. General Procedure.
A solution of phenylselenenyl chloride (1 mmol) in dichloromethane (1 mL) was dropped, at room temperature, on a suspension of sodium triflinate (1 mmol) in dichloromethane (2 mL). The resulting mixture was stirred for 5 min. Then, the olefin (1 mmol) was added and the mixture was stirred for the time and at the temperature indicated in Table 1. The reaction medium was then filtered and the filtrate evaporated at room temperature under reduced pressure. The crude β-seleno triflones thus obtained were usually pure enough to be used in further reactions. Nevertheless, they can be purified by flash chromatography.

1-Trifluoromethanesulfonyl-2-(phenylseleno)cyclopentane (1a).
Yellow liquid which can be purified by flash chromatography with petroleum ether/ether (9/1) as eluent. ^{1}H NMR : 7.2-7.6 (m ; 5H) 4.18 (m ; 1H ; ΣJ = 12.5 Hz) 3.69 (ddd ; 1H ; ^{3}J = 2.8 Hz ; ^{3}J = 5.6 Hz ; ^{3}J = 7.8 Hz) 2.1-2.4 (m ; 3H) 1.8-2.0 (m ; 3H). ^{13}C NMR : 135.6 ; 129.49 ; 128.89 ; 127.82 ; 119.72 (q ; $^1J_{C\text{-}F}$ = 329 Hz) ; 66.04 ; 39.22 ; 33.87 ; 26.1 ; 24.54. ^{19}F NMR : -76.18. GC/MS : *m/z* = 358 ($M^{+\bullet}$^{80}Se) ; 225 ; 157 ; 77 ; 69 ; 67 ; 41 ; 30. Anal. Calcd for $C_{12}H_{13}F_3O_2SSe$: C (40.34 %) H (3.67 %) S (8.98 %) Se (22.10 %). Found : C (40.32 %) H (3.75 %) S (8.66 %) Se (21.75 %).

1-Trifluoromethanesulfonyl-2-(phenylthio)cyclopentane (1b).
Yellow liquid after purification by flash chromatography with petroleum ether/ether (6/1) as eluent. ^{1}H NMR : 7.2-7.5 (m ; 5H) 4.17 (m ; 1H ; ΣJ = 12.5 Hz) 3.64 (dt ; 1H ; ^{3}J = 2.8 Hz ; ^{3}J = 6.9 Hz) 2.15-2.37 (m ; 3H) 1.87-2.01 (m ; 3H). ^{13}C NMR : 133 ; 132.87 ; 129.26 ; 128.34 ; 119.65 (q ; $^1J_{C\text{-}F}$ = 328.8 Hz) 65.09 ; 47.45 ; 33.37 ; 26.1 ; 24.2. ^{19}F NMR : -76.23. GC/MS : *m/z* = 310 ($M^{+\bullet}$) ; 177 ; 109 ; 77 ; 69 ; 67 ; 41. Anal. Calcd for $C_{12}H_{13}F_3O_2S_2$: C (46.44 %) H (4.22 %) S (20.66 %). Found : C (46.61 %) H (4.33 %) S (20.61 %).

1-Trifluoromethanesulfonyl-2-(phenylseleno)cyclohexane (2a).
Yellow liquid which can be purified by flash chromatography with petroleum ether/ether (9/1) as eluent. ^{1}H NMR (CD_2Cl_2) : 7.28-7.59 (m ; 5H) 4.08 (m ; 1H ; 1/2 width = 9.0 Hz) 3.47 (m ; 1H ; 1/2 width = 10.5 Hz) 1.6-2.42 (m ; 8H). ^{13}C NMR : 134.99 ; 129.61 ; 128.75 ; 128.02 ; 119.56 (q ; $^1J_{C\text{-}F}$ = 330 Hz) ; 60.43 ; 38.60 ; 28.21 ; 21.70 ; 21.38 ; 20.76. ^{19}F NMR : -76.68. GC/MS : *m/z* = 372 ($M^{+\bullet}$^{80}Se) ; 239 ; 157 ; 81 ; 69 ; 41 ; 39. Anal. Calcd for $C_{13}H_{15}F_3O_2SSe$: C (42.05 %) H (4.04 %). Found : C (42.13 %) H (4.14 %).

1-Trifluoromethanesulfonyl-2-(phenylthio)cyclohexane (2b).
White solid after purification by flash chromatography with petroleum ether/ether (9/1) as eluent. ^{1}H NMR : 7.2-7.5 (m ; 5H) 4.05 (m ; 1H ; 1/2 width = 11.3 Hz) 3.43 (m ; 1H ; 1/2 width = 11.5 Hz) 2.45-1.6 (m ; 8H). ^{13}C NMR : 132.85 ; 132.71 ; 129.53 ; 128.42 ; 119.64 (q ; $^1J_{C\text{-}F}$ = 330 Hz) ; 59.18 ; 43.14 ; 27.69 ; 21.58 ; 20.40 ; 20.36. ^{19}F NMR : -76.68. GC/MS : *m/z* = 324 ($M^{+\bullet}$) ; 191 ; 123 ; 110 ; 109 ; 81 ; 69. Anal. Calcd for $C_{13}H_{15}F_3O_2S_2$: C (48.14 %) H (4.66 %) S (19.77 %). Found : C (48.07 %) H (4.42 %) S (19.76 %)

1-Trifluoromethanesulfonyl-2-[2'-(ethoxycarbonyl) ethylthio]cyclohexane (2c).
Yellow liquid after purification by flash chromatography with petroleum ether/ether (6/1) as eluent. ^{1}H NMR (200 MHz) : 4.17 (q ; 2H ; ^{3}J = 7.13 Hz) 3.6 (m ; 2H) 2.85 (t ; 2H ; ^{3}J = 6.7 Hz) 2.61 (t ; 2H ; ^{3}J = 6.7 Hz) 1.4-2.4 (m ; 8H) 1.27 (t ; 3H). ^{13}C NMR (50 MHz) : 171.5 ; 119.94 (q ; $^1J_{C\text{-}F}$ = 330.1 Hz) ; 61.14 ; 60.9 ; 40.53 ; 34.49 ; 29.19 ; 27.52 ; 21.55 ; 21.46 ; 20.7 ; 14.2. ^{19}F NMR : -76.15. GC/MS : *m/z* = 348 ($M^{+\bullet}$) 303 ; 275 ; 215 ; 169 ; 133 ; 113 ; 81 ; 73 ; 69 ; 41 ; 29. Anal. Calcd for $C_{12}H_{19}F_3O_4S_2$: C (41.38 %) H (5.46 %) S (18.39 %). Found : C (41.54 %) H (5.58 %) S (18.81 %)

1-Trifluoromethanesulfonyl-2-(*n*-octylthio)cyclohexane (2d).

Yellow liquid after purification by flash chromatography with petroleum ether/ether (9/1) as eluent. ^{1}H NMR (200 MHz) : 3.55 (m ; 2H) 2.56 (t ; 2H ; ^{3}J = 7.2 Hz) 1.28-2.28 (m ; 20 H) 0.88 (t ; 3H ; ^{3}J = 6.7 Hz). ^{13}C NMR (50 MHz) : 119.99 (q ; $^1J_{C\text{-}F}$ = 330.2 Hz) ; 61.22 ; 40.14 ; 31.82 ; 29.47 ; 29.17 ; 29.00 ; 28.87 ; 24.09 ; 23.58 ; 22.67 ; 21.57 ; 21.29 ; 20.62 ; 14.09. ^{19}F NMR : -76.35. GC/MS : *m/z* = 360 ($M^{+\bullet}$) ; 227 ; 145 ; 81 ; 69 ; 57 ; 55 ; 43 ; 41 ; 29. Anal. Calcd for $C_{15}H_{27}F_3O_2S_2$: C (49.98 %) H (7.55 %). Found : C (50.01 %) H (7.42 %) .

1-Trifluoromethanesulfonyl-2-(4-nitrophenylthio)cyclohexane (2e).

Brown solid after purification by flash chromatography with CH_2Cl_2 as eluent and recristallization in petroleum ether.

^{1}H NMR : 8.0-8.2 (m ; 2H) 7.3-7.5 (m ; 2H) 4.35 (m ; 1H ; 1/2 width = 8.8 Hz) 3.54 (m ; 1H ; 1/2 width = 8.8 Hz) 1.5-2.4 (m ; 8H). ^{13}C NMR : 146.21 ; 143.16 ; 128.84 ; 124.25 ; 119.58 (q ; $^1J_{C\text{-}F}$ = 330 Hz) ; 59.58 ; 40.92 ; 28.30 ; 21.33 ; 20.97 ; 20.52. ^{19}F NMR : -76.52. GC/MS : *m/z* = 369 ($M^{+\bullet}$) 236 ; 190 ; 155 ; 109 ; 81. Anal. Calcd for $C_{13}H_{14}F_3NO_4S_2$: C (42.27 %) H (3.82 %) S (17.36 %). Found : C (42.43 %) H (3.82 %) S (17.00 %)

1-Trifluoromethanesulfonyl-2-(phenylseleno)cyclooctane (3a).

Yellow liquid after purification by flash chromatography with petroleum ether/ether (20/1) as eluent. ^{1}H NMR : 7.2-7.7 (m ; 5H) 4.15 (ddd ; 1H ; ^{3}J = 3.9 Hz ; ^{3}J = 2.8 Hz ; ^{3}J = 6.0 Hz) 3.63 (ddd ; 1H ; ^{3}J = 3.9 Hz ; ^{3}J = 2.7 Hz ; ^{3}J = 7.6 Hz) 1.4-2.4 (m ; 12H). ^{13}C NMR : 135.5 ; 129.5 ; 128.8 ; 128.4 ; 119.66 (q ; $^1J_{C\text{-}F}$ = 330.8 Hz) 66.17 ; 41.8 ; 28.9 ; 26.5 ; 25.97 ; 25.11 ; 24.18 ; 22.26. ^{19}F NMR : -75.36. Anal. Calcd for $C_{15}H_{19}F_3O_2SSe$: C (45.12 %) H (4.80 %) Se (19.77 %). Found : C (47.02 %) H (4.93 %) Se (19.48 %).

1-Trifluoromethanesulfonyl-2-(phenylthio)cyclooctane (3b).

Yellow liquid after purification by flash chromatography with petroleum ether/ether (30/1) as eluent. ^{1}H NMR : 7.2-7.5 (m ; 5H) 4.05 (m ; 1H ; ΣJ = 14.0 Hz) 3.5 (ddd ; 1H ; ^{3}J = 5.2 Hz ; ^{3}J = 8.1 Hz ; ^{3}J = 2.3 Hz) 1.2-2.6 (m ; 12H). ^{13}C NMR : 133.41 ; 133.16 ; 129.26 ; 128.31 ; 119.79 (q ; $^1J_{C\text{-}F}$ = 330.5 Hz) 65.87 ; 46.58 ; 28.27 ; 25.85 ; 25.77 ; 25.39 ; 23.56 ; 22.35. ^{19}F NMR : -74.81. GC/MS : *m/z* = 352 ($M^{+\bullet}$) 219 ; 190 ; 123 ; 110 ; 109 ; 69 ; 67 ; 41 ; 29. Anal. Calcd for $C_{15}H_{19}F_3O_2S_2$: C (51.12 %) H (5.43 %). Found : C (50.96 %) H (5.47 %).

1-Trifluoromethanesulfonyl-2-(phenylseleno)indane (4).

Unstable brown solid (shelf life < 24h)

^{1}H NMR : 7.25-7.8 (m ; 9H) 4.83 (s ; 1H) 4.57 (d ; 1H ; ^{3}J = 7.0 Hz) 3.86 (dd ; 1H ; ^{2}J = 17.5 Hz ; ^{3}J = 7.0 Hz) 3.08 (d ; 1H ; ^{2}J = 17.5 Hz). ^{13}C NMR : 144.64 ; 133.95 ; 130.87 ; 129.5 ; 129.2 ; 128.55 ; 128.29 ; 127.66 ; 127.04 ; 125.63 ; 119.95 (q ; $^1J_{C\text{-}F}$ = 330.5 Hz) ; 73.31 ; 39.71 ; 39.29. ^{19}F NMR : -74.79.

3-Trifluoromethanesulfonyl-2-(phenylseleno)cylopentan-1-one (5).

Unstable yellow liquid (shelf life < 24h)

^{1}H NMR : 7.23-7.65 (m ; 5H) 4.2 (broad s ; 1H) 3.86 (ddd ; 1H ; ^{3}J = 2.4 Hz ; ^{3}J = 2.9 Hz ; ^{3}J = 7.6 Hz) 2.2-2.8 (m ; 4H). ^{13}C NMR : 208.1 ; 136.63 ; 130.25 ; 129.93 ; 125.19 ; 119.57 (t ; $^1J_{C\text{-}F}$ = 329.0 Hz) 62.86 ; 42.58 ; 34.30 ; 20.62. ^{19}F NMR : -75.38

2-Trifluoromethanesulfonyl-1-phenylseleno undecane (6a)

1-Trifluoromethanesulfonyl-2-phenylseleno undecane (6b)

Yellow liquid (mixture of the two isomers).

^{1}H NMR (200 MHz) : 7.5-7.6 (m ; 2H) 7.2-7.4 (m ; 3H) 2.9-3.7 (m ; 2H) 1.2-2.12 (m ; 16H) 0.89 (t ; 3H ; ^{3}J = 6.7 Hz). ^{13}C NMR (50 MHz) : 135.75 ; 134.02 ; 129.62 ; 129.00 ; 128.46 ; 127.82 ; 126.57 ; 120.05 (q ; $^1J_{C\text{-}F}$ = 325.0 Hz) ; 119.80 (q ; $^1J_{C\text{-}F}$ = 325.0 Hz) ; 61.73 ; 55.35 ; 35.38 ; 34.12 ; 31.89 ; 31.87 ; 29.60 ; 29.50 ; 29.43 ; 29.38 ; 29.30 ; 29.25 ; 29.13 ; 29.00 ; 27.39 ; 26.89 ; 26.04 ; 25.83 ; 24.30 ; 22.69 ; 14.12. ^{19}F NMR : -75.4 (60 %) and -79.16 (40 %). GC-MS : *First isomer* : *m/z* = 444 ($M^{+\bullet\,80}$Se) 311 ; 158 ; 157 ; 83 ; 77 ; 69 ; 55 ; 43 ; 41 ; 29. *Second isomer* : *m/z* = 444 ($M^{+\bullet\,80}$Se) 311 ; 158 ; 157 ; 83 ; 77 ; 69 ;

55 ; 43 ; 41 ; 29 Anal. Calcd for $C_{18}H_{27}F_3O_2SSe$: C (48.75 %) H (6.14 %) Se (17.81 %). Found : C (48.92 %) H (6.18 %) Se (17.75 %).

3-Trifluoromethanesulfonyl-4-(phenylseleno)-1-cyclohexene (7).

Yellow liquid.

^{1}H NMR : 7.2-7.6 (m ; 5H) 6.43 (m ; 1H ; 1/2 width = 20.0 Hz) 5.72 (m ; 1H ; 1/2 width = 20.0 Hz) 4.15 (m ; 1H ; 1/2 width = 7.5 Hz) 4.11 (m ; 1H ; 1/2 width = 9.0 Hz) 2.2-2.4 (m ; 3H) 2.0-2.1 (m ; 1H). ^{13}C NMR : 138.62 ; 135.28 ; 129.61 ; 128.84 ; 127.36 ; 119.96 (q ; $^1J_{C\text{-}F}$ = 330.7 Hz) ; 112.36 ; 61.5 ; 35.4 ; 23.49 ; 21.6. ^{19}F NMR : -75.55. Anal. Calcd for $C_{13}H_{13}F_3O_2SSe$: C (42.29 %) H (3.55 %). Found : C (42.37 %) H (3.58 %)

1-Trifluoromethanesulfonyl-2,3-dimethyl-4-(phenylseleno)-2-butene (Z+E) (8a+8b).

Yellow liquid (mixture of the two isomers).

^{1}H NMR (200 MHz) : 7.2-7.6 (massif ; 10H) 3.94 (s ; 2H) 3.59 (s ; 2H) 3.57 (s ; 2H) 3.36 (s ; 2H) 1.93 (s; 6H) 1.83 (s ; 3H) 1.55 (s ; 3H). ^{13}C NMR (50 MHz) : 139.75 ; 139.34 ; 135.6 ; 135.21 ; 129.07 ; 129.05 ; 128.36 ; 128.04 ; 119.68 (q ; $^1J_{C\text{-}F}$ = 328.5 Hz) ; 119.56 (q ; $^1J_{C\text{-}F}$ = 328.6 Hz) ; 115.24 ; 114.82 ; 54.94 ; 53.38 ; 32.94 ; 32.71 ; 20.22 ; 19.57 ; 19.44 ; 19.37. ^{19}F NMR : -78.88. GC-MS : *First isomer* : *m/z* = 372 ($M^{+\bullet}$^{80}Se) ; 239 ; 157 ; 81 ; 79 ; 77 ; 69 ; 57 ; 41 ; 39 *Second isomer* : *m/z* = 372 ($M^{+\bullet}$^{80}Se) ; 239 ; 157 ; 81 ; 79 ; 77 ; 69 ; 57 ; 41 ; 39. Anal. Calcd for $C_{13}H_{15}F_3O_2SSe$: C (42.05 %) H (4.07 %) S (8.64 %) Se (21.27 %). Found : C (42.23 %) H (4.06 %) S (8.24 %) Se (21.54 %).

Oxidation of β-Selenenyl Triflones with mCPBA. General Procedure.

A 70 % aqueous solution of mCPBA (2.5 mmol) in dichloromethane (40 mL) was dropped on a solution of β-selenyl triflone (1 mmol) dissolved in dichloromethane (4 mL). A yellow color developped initially and was discharged during further addition of the peracid. The mixture was washed with a 5% aqueous solution of Na_2CO_3 (2x20mL), then dried over anhydrous $MgSO_4$ and evaporated at room temperature under reduced pressure.

Oxidation of β-Selenenyl Triflones with H_2O_2. General Procedure.

A mixture of 30 % aqueous solution of H_2O_2 (2.5 mmol) and dichloromethane (1 mL) was dropped on a solution of β-selenyl triflone (1 mmol) in dichloromethane (2 mL). An initial yellow color developped which vanished with further addition of H_2O_2. The mixture was washed three times with water, dried over anhydrous $CaCl_2$ and evaporated at room temperature under reduced pressure.

Treatment of β-Thio(or Seleno) Triflones with DBU (1,8-diazabicyclo[5.4.0]-7-undecene). General Procedure.

DBU (1 mmol) was added to a solution of β-thio(or seleno) triflone (1 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 40 min, then the solvent was evaporated under reduced pressure. The product was purified by flash chromatography with petroleum ether/dichloromethane (95/5) as eluent.

Treatment of β-Thio(or Seleno) Triflones with 50% aqueous NaOH. General Procedure.

A solution of β-thio(or seleno) triflone (1 mmol) in ether (2 mL) was added to 50 % aqueous NaOH (730 mg, 9 mmol). The reaction mixture was stirred vigorously at room temperature for 1 hour, then washed with brine. The aqueous layer was extracted with ether. The combined organic layers were washed with water then dried over anhydrous $CaCl_2$. The solvent was evaporated at room temperature under reduced pressure.

1-(Trifluoromethanesulfonyl)-1-cyclopentene (9).

Yellow liquid.

^{1}H NMR : 7.17 (pseudo quint ; 1H ; ^3J = ^4J = 2.1 Hz) 2.6-2.8 (m ; 4H) 2.16 (quint ; 2H ; ^3J = 7.6 Hz). ^{13}C NMR : 156.5 ; 136.8 ; 119.9 (q ; $^1J_{C\text{-}F}$ = 325.9 Hz) ; 34.06 ; 31.53 ; 23.85. ^{19}F NMR : -78.85. GC/MS : *m/z* = 200 ($M^{+\bullet}$) ; 131 ; 67 ; 41 ; 39 ; 27. Anal. Calcd for $C_6H_7F_3O_2S$: C (36.00 %) H (3.52 %). Found : C (36.30 %) H (3.59 %).

1-(Trifluoromethanesulfonyl)-1-cyclohexene (10).

Yellow liquid.

^{1}H NMR : 7.3 (tt ; 1H ; ^{4}J = 1.8 Hz ; ^{3}J = 3.7 Hz) 2.3-2.5 (m ; 4H) 1.65-1.83 (m ; 4H). ^{13}C NMR : 150.88 ; 133.45 ; 120.1 (q ; $^1J_{C\text{-}F}$ = 327 Hz) ; 26.64 ; 23.77 ; 21.81 ; 20.35. ^{19}F NMR : -78.15. GC/MS : *m/z* = 214 ($M^{+\bullet}$) ; 145 ; 81 ; 69 ; 41 ; 39 ; 27. Anal. Calcd for $C_7H_9F_3O_2S$: C (39.25 %) H (4.23 %). Found : C (39.48 %) H (4.33 %).

2-(Trifluoromethanesulfonyl)-1,3-cyclohexadiene (11).

Yellow liquid.

^{1}H NMR (200 MHz) : 7.2 (broad t; 1H ; ^{3}J = 4.5 Hz) 6.0-6.2 (m ; 2H) 2.5-2.7 (m ; 2H) 2.2-2.4 (m ; 2H). ^{13}C NMR (50 MHz) : 146.29 ; 131.71 ; 130.88 ; 119.22 (q ; $^1J_{C\text{-}F}$ = 326.2 Hz) ; 117.68; 23.29 ; 20.26. ^{19}F NMR : -78.80. GC/MS : *m/z* = 212 ($M^{+\bullet}$) ; 143 ; 79 ; 77. Anal. Calcd for $C_7H_7F_3O_2S$: C (39.62 %) H (3.33 %). Found : C (39.57 %) H (3.33 %).

3-(Trifluoromethanesulfonyl)-2-cyclopenten-1-one (12).

Unstable yellow liquid (shelf life < 4h).

^{1}H NMR : 7.14 (t ; 1H ; ^{4}J = 2.1 Hz) 3.08 (m ; 2H) 2.78 (m ; 2H). ^{13}C NMR : 203.24 ; 163.74 ; 145.1 ; 119.33 (q ; $^1J_{C\text{-}F}$ = 326.6 Hz) ; 36.40 ; 27.30. ^{19}F NMR : -77.18

1-(Trifluoromethanesulfonyl)-1-cyclooctene (13).

Yellow liquid.

^{1}H NMR : 7.28 (t ; 1H ; ^{3}J = 8.4 Hz) 2.63 (t ; 2H ; ^{3}J = 6.2 Hz) 2.45 (dt ; 2H ; ^{3}J = 6.4 Hz ; ^{3}J = 8.4 Hz) 1.2-1.7 (massif ; 8H). ^{13}C NMR : 153.75 ; 135.7 ; 119.96 (q ; $^1J_{C\text{-}F}$ = 327.0 Hz) ; 29.24 (q ; $^5J_{C\text{-}F}$ = 0.5 Hz) ; 27.74 ; 27.7 ; 25.73 ; 25.45 (q ; $^4J_{C\text{-}F}$ = 1.0 Hz) ; 25.23. ^{19}F NMR : -78.11. GC/MS : *m/z* = 242 ($M^{+\bullet}$) ; 173 ; 109 ; 79 ; 67 ; 55 ; 41 ; 27. Anal. Calcd for $C_9H_{13}F_3O_2S$: C (44.62 %) H (5.41 %). Found : C (44.85 %) H (5.46 %).

1-(Trifluoromethanesulfonyl)-1-undecene et 2-(Trifluoromethanesulfonyl)-1-undecene (14b / 14a).

Yellow liquid mixture of the two isomers.

^{1}H NMR : 7.3 (dt ; 1H ; ^{3}J = 15.2 Hz ; ^{3}J = 6.8 Hz) 6.56 (d ; 1H ; ^{2}J = 1.2 Hz) 6.32 (d ; 1H ; ^{3}J = 15.2 Hz) 6.21 (d ; 1H ; ^{2}J = 1.2 Hz) 2.35-2.49 (m ; 4H) 1.47-1.64 (m ; 4H) 1.25 (m ; 24H) 0.86 (t ; 6H ; ^{3}J = 7 Hz). ^{13}C NMR : 160.72 ; 144.93 ; 133.26 ; 121.10 ; 119.88 (q ; $^1J_{C\text{-}F}$ = 327.4 Hz) ; 119.64 (q ; $^1J_{C\text{-}F}$ = 325.02 Hz) ; 32.5 to 22.6 (CH_2) 14.05. ^{19}F NMR : -77.8 (60%) and -79.76 (40%). GC-MS : *First isomer* : *m/z* = 287 ($M^{+\bullet}$+1) ; 187 ; 123 ; 109 ; 97 ; 83 ; 69 ; 55 ; 43 ; 41 ; 29. *Second isomer* : *m/z* = 287 ($M^{+\bullet}$+1) ; 123 ; 109 ; 96 ; 82 ; 69 ; 55 ; 43 ; 41 ; 47. Anal. Calcd for $C_{12}H_{21}F_3O_2S$: C (50.33 %) H (7.39 %). Found : C (50.38 %) H (7.22 %).

1-(Trifluoromethanesulfonyl)-2,3-dimethyl-3-buten-2-ol (15).

Yellow liquid.

^{1}H NMR : 5.21 (s ; 1H) 5.02 (s ; 1H) 3.62 (d ; 1H ; ^{2}J = 14.0 Hz) 3.49 (d ; 1H ; ^{2}J = 14.0 Hz) 3.15 (broad s ; 1H) 1.87 (s ; 3H) 1.59 (s ; 3H). ^{13}C NMR : 146.88 ; 119.01 (q ; $^1J_{C\text{-}F}$ = 327.4 Hz) ; 112.48 ; 74.14 ; 57.87 ; 27.85 ; 19.03. ^{19}F NMR : -80.23. GC/MS : *m/z* = 217 ($M^{+\bullet}$-CH_3) ; 214 ; 191 ; 85 ; 81 ; 69 ; 57 ; 43 ; 39. Anal. Calcd for $C_7H_{11}F_3O_3S$: C (36.20 %) H (4.77 %). Found : C (36.47 %) H (4.49 %).

1-trifluoromethanesulfonyl-2-(*n*-hexylamino)cyclopentane (16)

n-Hexylamine (130 µL ; 1 mmol) was added to a solution of 1-(trifluoromethanesulfonyl)-1-cyclopentene (**12** ; 206 mg ; 1 mmol) in dichloromethane (1 mL). The reaction mixture was stirred at room temperature for 1.5 h, then directly deposited at the top of a chromatography column and eluted with petroleum ether/ether (4/1). Yellow liquid.

^{1}H NMR : 3.67 (dt ; 1H ; ^{3}J = 6.4 Hz ; ^{3}J = 5.9 Hz) 3.39 (dt ; 1H ; ^{3}J = 7.3 Hz ; ^{3}J = 5.7 Hz) 2.52 (m ; 2H) 1.2-2.1 (massif ; 14H) 0.79 (t ; 3H ; ^{3}J = 6.6 Hz). ^{13}C NMR : 119.74 (q ; $^1J_{C\text{-}F}$ = 328.2 Hz) ; 64.88 ; 59.52 ; 47.81 ; 33.3 ; 31.62 ; 29.9 ; 26.81 ; 26.77 ; 23.97 ; 22.5 ; 13.85. ^{19}F NMR : -76.8. GC/MS : *m/z* = 301 ($M^{+\bullet}$) ; 230 ; 168 ; 140 ; 112 ; 70 ; 69 ; 67 ; 56 ; 43 ; 41 ; 30.

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