Pergamon

Tetrahedron, Vol. 52, No. 12, pp. 4383-4396, 1996

0040-4020/96 \$15.00 + 0.00

S0040-4020(96)00082-8

2-Phenylthio-3,3,3-Trifluoropropene, its Sulfoxide and Sulfone : Synthesis and Reactivity in 1,3-Dipolar Cycloadditions.

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Dedicated to Professor H. Vorbrüggen on the Occasion of his 65th Birthday

Abstract : Derivatives of 3,3,3-trifluoropropene **1** : α-sulfide **2**, sulfoxide **3**, sulfone **4** and bromide **6** are useful trifluoromethylated synthons. On reaction with diazo compounds, these derivatives can afford trifluoromethyl substituted pyrazolines, pyrazoles, cyclopropanes or allylsulfones in fair to excellent yields. 1,3-Dipolar cycloaddition of trifluoropropene derivatives **2-4** with N-benzyl-azomethine ylide provides disubstituted 3-trifluoromethyl-pyrrolidines.

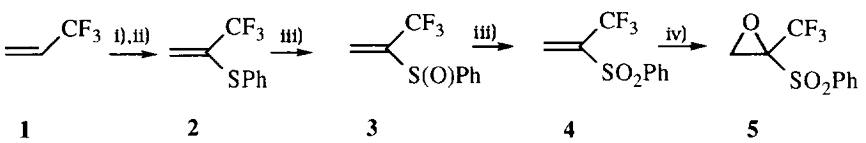
Introduction

The growing number of biologically active organic compounds with CF_3-substitution is not only indicative of their unique chemistry and biochemistry[1,2] but it also presents a challenge for the development of trifluoromethylated synthons. The simplest of such CF_3-reagents (C_1) are trifluoromethyl radicals or ions (*e.g.* trifluoromethyl metals)[3]. C_2-reagents containing the trifluoromethyl group are typically derived from trifluoroacetic acid, the corresponding aldehyde or trifluoroethanol[4]. Trifluoromethyl-based C_3-reagents include trifluoroacetone, trifluoropropionic and trifluoropyruvic acids[5], 3,3,3-trifluoropropene **1** and its derivatives[6]. Title trifluoropropenes **2-4** merit particular attention because of their non gaseous nature and tunable reactivity by virtue of the degree of S-oxidation.

Results and Discussion

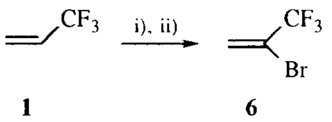
We have found that the α-sulfide **2**[7], sulfoxide **3**, sulfone **4**[8], epoxy-sulfone **5** and bromo **6**[9] derivatives of commercial 3,3,3-trifluoropropene **1** (schemes 1 and 2) are useful building blocks for the preparation of trifluoromethylated compounds.

From a practical point of view it is interesting to note that compounds **2-5** are easier to handle than gaseous 3,3,3-trifluoropropene **1** or 3,3,3-trifluoropropyne. More importantly, their differences in reactivity are useful in selective synthesis. Furthermore, compound **6** is a cheap and reactive synthon, which can be prepared on a large scale.



i) PhSCl, CH_2Cl_2, 70°C, 15 h, 86%; ii) KOH, MeOH, -40°C to -10°C, 30 min., 96%;
iii) *m*-CPBA, CH_2Cl_2, -40°C to 20°C, 3 h, 78-90%; iv) *m*-CPBA, 0.1 eq $NaHCO_3$,CH_2Cl_2, 20°C, from **2** to **5** : 82%.

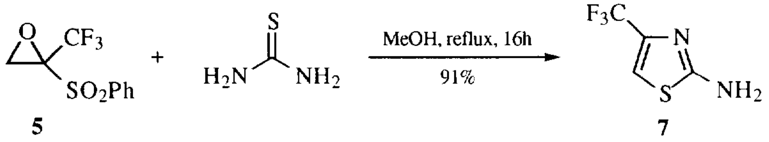
Scheme 1



i) Br_2, CCl_4, hν, 100%; ii) NEt_3, CCl_4, 90%.

Scheme 2

We have recently reported on the useful application of the epoxy-sulfone **5** with bis-nucleophiles in heterocyclisations[10]; thus for example, the known thiazole **7** was isolated in a much higher yield when epoxy-sulfone **5** rather than bromotrifluoroacetone[11] was employed (scheme 3).

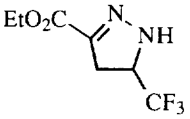
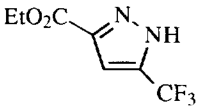


Scheme 3

We now report 1,3-dipolar cycloadditions of trifluoromethylated olefins with diazo compounds. This study was carried out using compounds **2**-**4** and, for the purpose of comparison, olefins **1** and **6**. The products, experimental conditions and yields of these cycloadditions are collected in tables 1-5.

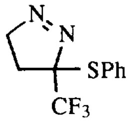
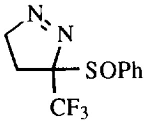
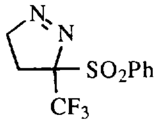
Cycloaddition of ethyl diazoacetate with 3,3,3-trifluoropropene **1** was carried out smoothly at room temperature for 10 hours. The Δ^1-pyrazoline was formed initially and was recognized by NMR spectroscopy without isolation. Subsequent isomerization affords the Δ^2-isomer **8**. Olefins **2**-**4** and **6**, as equivalents of 3,3,3-trifluoropropyne, provided regiospecifically the known[12] pyrazole derivative **9**, by elimination of the α-substituent in refluxing solvent (benzene for **2**; ether for **3**, **4** and **6**) (table 1).

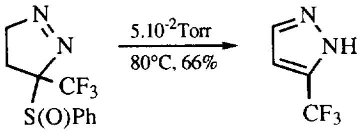
Table 1. Cycloadditions of ethyl diazoacetate with trifluoropropenes **1**-**6**.

Dipolarophile	Conditions	Products	Yield (%)
1	20°C, Et_2O, 10 h	 **8**	75
2	1) 20°C, 15 min 2) 50°C, 45 min 3) benzene, reflux, 16h	 **9**	≈100
3	1) 20°C, 1h30 2) Et_2O, reflux, 3 h	**9**	76
4	1) 0°C to 20°C, 30 min 2) Et_2O, reflux, 3 h	**9**	88
6	1) 0°C to 20°C 2) Et_2O, reflux, 2 h	**9**	86

Cycloadditions of diazomethane with trifluoropropenes **2**-**4** at room temperature in ether afforded, quantitatively and regiospecifically, the isolable Δ^1-pyrazolines **10a**-**c** (table 2) which differ in thermal stability depending on the nature of sulfur substituents. The pyrazoline-thioether **10a** is so stable that it could be purified by distillation at 100°C/0.1 Torr. In contrast, the pyrazoline **10b** underwent elimination of phenylsulfenate on thermolysis at 80°C, affording the known 3-trifluoromethyl-pyrazole **11**[12,13] (scheme 4). The sulfonylated pyrazoline **10c** could be isolated, but thermolysis led to a complex mixture of products. While our research was underway, this pyrazole **11** was independently synthesized by Yang *et al* [13b] from **6** by cycloaddition with diazomethane and subsequent elimination of hydrogen bromide with triethylamine.

Table 2. Cycloadditions of Diazomethane with Trifluoropropenes **2**-**4**.

Dipolarophile	Conditions	Products	Yield (%)
2	Et_2O, 20°C, 2h30	 **10a**	≈100
3	Et_2O, 0 to 20°C, 1h30	 **10b**	≈100
4	Et_2O, 0 to 20°C, 2h	 **10c**	≈100

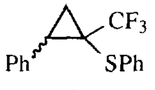
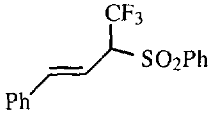


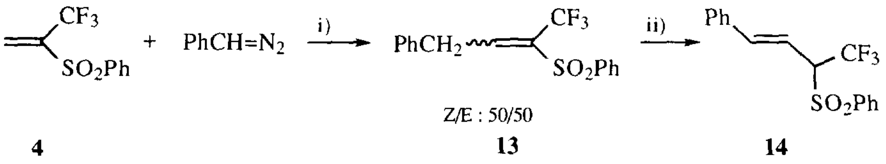
10b **11**

Scheme 4

Cycloadditions with phenyldiazomethane occured with N_2 elimination (table 3). Thus, the cyclopropane **12** was formed from **2**, in almost quantitative yield, as a mixture of *Z*- and *E*- isomers in a ratio of 56/44 (as determined from ^1H and ^{19}F-NMR analysis). In contrast, the vinyl sulfone **4** gave the benzyl derivative **13** (scheme 5), formally as the result of a C-H insertion. The product could be characterised by NMR analysis, but attempted purification led to variable amounts of the rearranged allylic isomer **14**. This rearrangement proceeded quantitatively in ethyl acetate at reflux in the presence of silica gel, and NMR analysis supports the *trans*-configuration ($^3J_{(H-H)}$=15.8 Hz) for **14**. The reaction with sulfoxide **3** was not selective, leading to a mixture of the corresponding cyclopropane, pyrazole and benzylated derivatives.

Table 3. Reactions with phenyldiazomethane

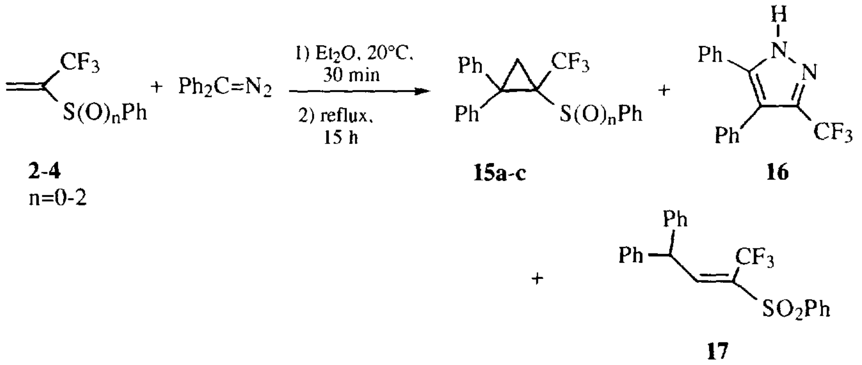
Dipolarophile	Conditions	Products	Yields (%)
2	20 to 50°C, C_6H_6	 **12**	≈100 (Z/E = 56/44)
4	1) 20°C, Et_2O 2) reflux, 15 min 3) silica gel, AcOEt, reflux	 **14**	76



i) Et_2O, 20°C to reflux, 15 min. ; ii) AcOEt, reflux, silica gel

Scheme 5

Cycloadditions with diphenyldiazomethane proceeded smoothly in ether providing the cyclopropane derivatives **15a-c** as the major components, accompanied by the pyrazole **16** (from **3**) or the allyl isomer **17** (from **4**) (scheme 6, table 4).



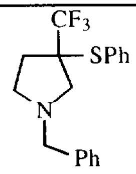
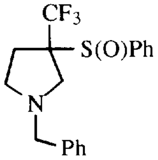
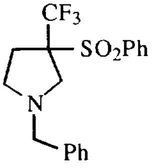
Scheme 6

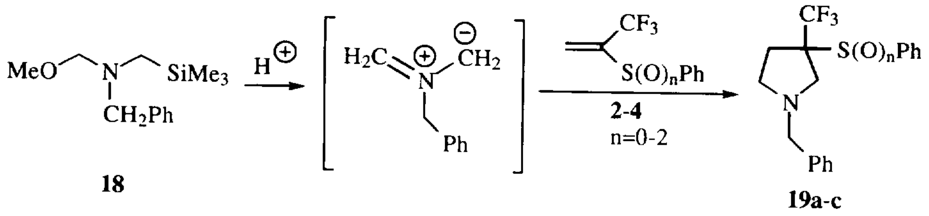
Table 4

n	Dipolarophile	Products (%)	
0	**2**	**15a** (76)	
1	**3**	**15b** (49)	**16** (24)
2	**4**	**15c** (52)	**17** (26)

Cycloaddition of N-benzyl-azomethine ylide with trifluoropropene derivatives **2-4** were also investigated. The ylide was generated from the precursor **18**[14] based on the procedure described by Achiwa (1% CF_3CO_2H in CH_2Cl_2) (scheme 7)[15]. The cycloadditions proceeded readily at room temperature with activated olefins **3** and **4**, or in refluxing dichloromethane with **2**, to give the corresponding pyrrolidines **19a-c** (table 5) in good yields (65-84 %).

Table 5. Cycloadditions of the azomethine ylide with trifluoropropenes **2-4**

Dipolarophile	Conditions	Products	Yields (%)
2	CH_2Cl_2, CF_3CO_2H, reflux	 **19a**	84
3	CH_2Cl_2, CF_3CO_2H, 20°C	 **19b**	65
4	CH_2Cl_2, CF_3CO_2H, 20°C	 **19c**	71



Scheme 7

These results constitute a valuable complement for existing procedures. Indeed, it has been reported recently that ethylenic compounds activated by a trifluoromethyl group could undergo 1,3-dipolar cycloadditions with non-stabilized azomethine ylides to provide polysubstituted 3-trifluoromethyl-pyrrolidines in good yields (30-80%), while non-fluorinated parent alkenes were in most cases unreactive [16].

In conclusion, 3,3,3-trifluoropropene **1**, the α-thioether **2**, the corresponding sulfoxide **3**, sulfone **4** and the α-bromo derivative **6** are useful trifluoromethylated C_3-reagents for dipolar cycloadditions with diazo compounds and with an azomethine ylide.

Acknowledgements

M. Redon thanks Rhône-Poulenc (Lyon) for a grant. H.G. Viehe and Z. Janousek are grateful to SPPS (Belgium) for the financial support.

Experimental

Melting points were taken in sealed capillaries using a Dr. Tottoli apparatus and are uncorrected. IR (ν_{max} in cm^{-1}) and mass spectra were measured on a Varian Matt 445 and Finnigan Mat TSQ 70 apparatus by electronic ionisation (70 eV). ^1H, ^{19}F and ^{13}C-NMR spectra were recorded in $CDCl_3$ solutions on a Varian VXR or Gemini 200 spectrometers using TMS as the internal reference for ^1H and ^{13}C spectra and $CFCl_3$ for ^{19}F spectra. Chemical shifts are expressed in ppm on the δ scale and coupling constants J are given in Hz. The following abbreviations are used : br s broad singlet, s singlet, d doublet, t triplet, q quartet, quint quintuplet and m multiplet; δ' indicates the chemical shifts of the other diastereoisomer.

2-Phenylthio-1,1,1-trifluoropropene (2) (improved preparation based on reference 7)

A 500 ml pressure vessel was charged with 45.6 g (0.32 mole) of freshly distilled phenylsulfenyl chloride and 100 ml of methylene chloride. The vessel was closed, cooled in dry ice/acetone, evacuated and 39.5 g (0.41 mole) of 3,3,3-trifluoropropene **1** were condensed. The mixture was heated overnight at 70°C. The vessel was cooled to room temperature and vented to atmospheric pressure. The contents were concentrated on a rotary evaporator to afford a dark oil. Distillation through a short-path still gave 66.0 g (86%) of 1-(trifluoromethyl)-2-chloroethyl phenyl sulfide.

Bp : 63-65°C/0.4 Torr; **^{1}H-NMR** : $\delta = 3.58$ (dq, J = 7.7-5.0, 2H), 3.83-3.95 (m,1H), 7.29-7.61 (m, 5H); **^{19}F-NMR** : $\delta = -69.00$ (d, J = 8.0).

A mixture of 13.2 g (0.24 mole) of potassium hydroxide pellets and 50 ml of dry methanol was stirred under argon atmosphere until the KOH dissolved. The mixture was cooled in a dry ice/acetone bath to -40°C. To this vigorously stirred solution were added 37.8 g (0.16 mole) of 1-(trifluoromethyl)-2-chloroethyl phenyl sulfide in one portion. The resulting mixture was stirred for 30 min at -10°C and then poured into 100 ml of ice water containing 2 ml of concentrated HCl. The aqueous mixture was extracted with ether (3 x 20 ml). The combined extracts were washed with water, dried ($MgSO_4$) and concentrated on a rotary evaporator to give 30.7 g (96%) of **2** as a colorless oil after Kugelrohr distillation.
Bp : 41-43°C/0.5 Torr; **^{1}H-NMR** : δ = 5.40 (quint, J = 1.3, 1H), 6.03 (quint, J = 1.3, 1H), 7.32-7.51 (m, 5H); **^{19}F-NMR** : δ = -65.97 (s).

1,1,1-Trifluoropropenes 3-4

A mixture of 10 g (0.05 mole) of sulfide **2** and 100 ml of dry CH_2Cl_2 was cooled in a dry ice/acetone bath to -40°C. To this vigorously stirred solution was added *m*-CPBA in several portions (1 equivalent for the synthesis of sulfoxide **3** or 2 equivalents for the synthesis of sulfone **4**). The resulting mixture was stirred for 5 hours at room temperature and then filtered through alkaline Al_2O_3. The combined extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator to give sulfoxide **3** and sulfone **4**, respectively, after purification by Kugelrohr distillation.

2-Phenylsulfinyl-1,1,1-trifluoropropene (3)

Yield : 78%

Bp : 60-65°C/0.15 Torr; **IR** (neat) : 2950, 1650, 1280-1140, 1170-1050, 1080, 990, 720, 675; **MS** : 220 (100%), 204, 187, 172, 151, 141, 125, 109, 97, 77, 69; **^{1}H-NMR** : δ = 6.47 (m, 1H), 6.67 (quint, J = 0.9, 1H), 7.43-7.70 (m, 5H); **^{19}F-NMR** : δ = -60.99 (d, J = 6.3); **^{13}C-NMR** : δ = 121.15 (qdd, $^{1}J_{C-F}$ = 277.3 - $^{3}J_{C-H}$ = 13.0-6.3), 123.74 (tq, $^{1}J_{C-H}$ = 166.4 - $^{3}J_{C-F}$ = 4.5), 125.60 (dt, $^{1}J_{C-H}$ = 165.2 - $^{3}J_{C-H}$ = 6.9), 141.51 (s), 146.12 (q, $^{2}J_{C-F}$ = 31.6); **Analysis** : calculated for $C_9H_7F_3OS$: C (49.09), H (3.20), S (14.56) - found C (49.73), H (3.09), S (13.93) %.

2-Phenylsulfonyl-1,1,1-trifluoropropene (4) [8]

Yield : 88%

Bp : 70-75°C/0.15 Torr; **IR** (neat) : 2950, 1650, 1390-1185, 1160-1025, 1340-1290, 1160-1090, 990-850, 730, 670; **MS** : 236, 220, 187, 172, 141, 125, 93, 77 (100%), 69, 65; **^{1}H-NMR** : δ = 6.67 (dq, J = 3.1 - $^{4}J_{H-F}$ = 1.3, 1H), 6.99 (quint, $^{4}J_{H-F}$ = 1.3, 1H), 7.53-7.95 (m, 5H); **^{19}F-NMR** : δ = -61.99 (s); **^{13}C-NMR** : δ = 119.41 (qdd, $^{1}J_{C-F}$ = 274.7 - $^{3}J_{C-H}$ = 12.6-6.4), 128.36 (ddd, $^{1}J_{C-H}$ = 162.9 - $^{3}J_{C-H}$ = 7.7-5.4), 129.29 (dd, $^{1}J_{C-H}$ = 165.9 - $^{3}J_{C-H}$ = 7.2), 133.22 (ddq, $^{1}J_{C-H}$ = 166.4-168.8 - $^{3}J_{C-F}$ = 4.3), 134.38 (dt, $^{1}J_{C-H}$ = 162.9 - $^{1}J_{C-H}$ = 7.2), 138.43 (t, $^{3}J_{C-H}$ = 8.6), 141.99 (q, $^{2}J_{C-F}$ = 33.5).

Ethyl 5-trifluoromethyl-pyrazoline-3-carboxylate (8)

A Carius tube was charged with 1.65 g (0.015 mole) of ethyl diazoacetate and 5 ml of dry ether. The tube was cooled in dry ice/acetone, evacuated and charged with 6 ml of 3,3,3-trifluoropropene **1**. The tube was sealed under vacuum and maintained at room temperature for 10 hours. The tube was then opened and vented to atmospheric pressure. To the resulting mixture was added 5 ml of diluted HCl. The aqueous layer was extracted with ether (3 x 10 ml). The combined extracts were washed with water, dried ($MgSO_4$) and concentrated on a rotary evaporator. Purification was performed by Kugelrohr distillation (20°C/0.05 Torr) to give **8** as a yellow powder (75%).

Mp : 64-65°C; **IR** (KBr) : 3250, 1750, 1560, 1380-1260, 1175-1110, 750; **MS** : 210, 196, 183, 165, 163, 153, 141, 95 (100%), 89, 69; **^{1}H-NMR** : δ = 1.37 (t, J = 7.1, 3H), 3.15 (dd, J = 18.1-8.5, 1H), 3.26 (dd, J = 18.1-12.1, 1H), 4.33 (q, J = 7.1, 2H), 4.45 (m, 1H), 6.49 (br s, 1H); **^{19}F-NMR** : δ = -77.78 (d, J = 6.8); **^{13}C-NMR** : δ = 13.91 (qt, $^{1}J_{C-H}$ = 127.3 - $^{2}J_{C-H}$ = 2.5), 32.05 (t, $^{1}J_{C-H}$ = 138.3), 61.02 (dq, $^{1}J_{C-H}$ = 179.5 - $^{2}J_{C-F}$ = 31.4), 61.36 (tq, $^{1}J_{C-H}$ = 148.2 - $^{2}J_{C-H}$ = 4.4), 124.32 (qdt, $^{1}J_{C-F}$ = 279.4 - $^{2}J_{C-H}$ = 7.8 - $^{3}J_{C-H}$ = 3.0), 142.06 (s), 161.50 (t, J = 3.0); **Analysis** : calculated for $C_7H_9F_3N_2O_2$: C (40.00), H (4.32), S (13.33) - found C (40.50), H (4.51), S (13.12) %.

Ethyl 5-trifluoromethyl-pyrazole-3-carboxylate (9) [12]

a- from sulfide 2 : Ethyl diazoacetate (0.30 g, 1.2 eq.) was added to the vinyl sulfide **2** in 4 ml of benzene. After 15 minutes at 20°C, the mixture was heated for 45 minutes at 50°C and then at reflux for 16 hours. The solvent was then evaporated under vacuum. The compound **9** was distilled using the Kugelrohr apparatus (85°C/0.05 Torr) and recrystallizated from hexane (yield ≈ 100%).

Mp : 94°C; **IR** (KBr) : 3258, 3254, 1712, 1700, 1568, 1318, 1174, 1155, 1136, 975; **MS** : 208, 196, 180, 163, 151, 136, 123, 109, 77, 65; **^{1}H-NMR** : δ = 1.39 (t, J = 7.1, 3H), 4.43 (q, 2H), 7.10 (s, 1H), 12.85 (s, 1H); **^{19}F-NMR** : δ = -62.85 (d, J = 1.8); **^{13}C-NMR** : δ = 13.96 (q, $^{1}J_{C-H}$ = 127.5), 62.30 (t, $^{1}J_{C-H}$ = 149.0), 107.31 (d, $^{1}J_{C-H}$ = 184.8), 120.44 (q, $^{1}J_{C-F}$ = 268.8), 135.70 (s), 143.38 (q, $^{2}J_{C-F}$ = 39.2), 158.79 (s); **Analysis** : calculated for $C_7H_7F_3N_2O_2$: C (40.39), H (3.39), N (13.46) - found C (40.34), H (3.22), N (13.29) %.

b- from sulfoxide 3 : Ethyl diazoacetate (0.30 g, 1.3 eq) in 4 ml of ether was added to a solution of vinyl sulfoxide **3** in 1 ml of ether. The mixture was stirred 1h30 at 20°C and then refluxed for 3 hours. Purification was performed as for **a-**. Yield = 76%.

c- from sulfone 4 : Ethyl diazoacetate (0.30 g, 1.4 eq) in 2 ml of ether was added dropwise to a solution of vinyl sulfone **4** in 3 ml of ether at 0°C. The temperature was allowed to reach 20°C. After 30 min, the mixture was refluxed for 3 hours. After recrystallization from hexane, the pyrazole was obtained in 88% yield.

d- from bromopropene 6 : Ethyl diazoacetate (1.30 g, 1.5 eq.) in 3 ml of ether was added dropwise to a solution of bromopropene **6** in 2 ml of ether at 0°C. The temperature was allowed to reach 20°C and the solution was then heated 2 hours under reflux. Purification proceeds as described for **a-** and recrystallization from hexane yielded **9** (86%).

3-Trifluoromethyl-Δ^{1}-pyrazolines 10a-c

A solution of diazomethane (0.01-0.015 mol) in 25 ml ether was added dropwise to the trifluoromethylated olefins **2-4** at 0°C. The temperature was then allowed to reach 20°C. The mixture was stirred during the time indicated in table 2. Excess of CH_2N_2 was removed by a few drops of glacial HOAc and the solvent was evaporated under vacuum.

a. 3-Trifluoromethyl-3-phenylthio-Δ^{1}-pyrazoline (10a)

0.70 g of vinyl thioether **2** were used. After purification by Kugelrohr distillation (105°C/0.1 Torr), pyrazoline **10a** was obtained in quantitative yield.
MS : 248, 247, 234, 218, 197, 185, 165, 149, 136 (100%), 134, 117, 109, 105, 91, 77; **^{1}H-NMR** : δ = 1.78 (ddd, J = 14.2-9.1-7.8, 1H), 2.00 (ddd, J = 14.2-9.5-3.7, 1H), 3.81 (ddd, J = 18.4-9.1-7.8, 1H), 4.62 (ddd, J = 18.4-9.5-3.7, 1H), 7.2-7.6 (m, 5H); **^{19}F-NMR** : δ = -72.31 (s); **^{13}C-NMR** : δ = 24.48 (dd, $^{1}J_{C-H}$ = 138.5-135.5), 77.37 (dd, $^{1}J_{C-H}$ = 145.2-143.6), 98.73 (q, $^{2}J_{C-F}$ = 26.7), 123.92 (q, $^{1}J_{C-F}$ = 281.7), 126.56 (m), 128.97 (dd, $^{1}J_{C-H}$ = 162.5), 130.20 (dt, $^{1}J_{C-H}$ = 161.9 - $^{3}J_{C-H}$ = 7.4), 137.05 (dt, $^{1}J_{C-H}$ = 164.4 - $^{3}J_{C-H}$ = 6.4).

b. 3-Trifluoromethyl-3-phenylsulfoxy-Δ^{1}-pyrazoline (10b)

0.25 g of the vinyl sulfoxide **3** were used to obtain quantitatively the Δ^{1}-pyrazoline **10b**.
^{1}H-NMR : δ = 1.66 (ddd, J = 14.6-9.1-6.1, 1H), 2.26 (ddd, J = 14.6-9.1-5.6, 1H), 4.63 (ddd, J = 18.7-9.1-6.1, 1H), 4.63 (ddd, J = 18.7-9.1-5.6, 1H), 7.3-7.7 (m, 5H); **^{19}F-NMR** : δ = -66.87 (s, 65%), δ' = -62.06 (s, 35%); **^{13}C-NMR** : δ = 15.31 (t, $^{1}J_{C-H}$ = 137.5), 79.74 (t, $^{1}J_{C-H}$ = 145.0), 112.94 (q, $^{2}J_{C-F}$ = 24.4), 121.86 (q, $^{1}J_{C-F}$ = 282.4), 125.51 (dt, $^{1}J_{C-H}$ = 166.3 - $^{3}J_{C-H}$ = 6.2), 128.83 (dd, $^{1}J_{C-H}$ = 164.8 - $^{3}J_{C-H}$ = 6.8), 132.74 (dt, $^{1}J_{C-H}$ = 162.7 - $^{3}J_{C-H}$ = 7.2), 136.71 (t, $^{3}J_{C-H}$ = 7.5).

c- 3-Trifluoromethyl-3-phenylsulfonyl-Δ^{1}-pyrazoline (10c)

0.70 g of the vinyl sulfone **4** were employed to obtain quantitatively the Δ^{1}-pyrazoline **10c**.
^{1}H-NMR : δ = 2.05 (ddd, J = 15.0-9.1-7.3, 1H), 2.72 (ddd, J = 15.0-8.8-5.1, 1H), 4.90 (ddd, J = 19.1-8.8-7.3, 1H), 5.02 (ddd, J = 19.1-9.1-5.1, 1H), 7.3-8.0 (m, 5H); **^{19}F-NMR** : δ = -69.14 (s); **^{13}C-NMR** : δ = 19.88 (t, $^{1}J_{C-H}$ = 138.7), 80.32 (t, $^{1}J_{C-H}$ = 145.6), 111.40 (qt, $^{2}J_{C-F}$ = 26.8 - $^{2}J_{C-H}$ = 3.1), 115.79 (q, $^{1}J_{C-F}$ = 282.7), 128.97 (dd, $^{1}J_{C-H}$ = 166.3 - $^{3}J_{C-H}$ = 7.3), 130.37 (dt, $^{1}J_{C-H}$ = 169.3 - $^{3}J_{C-H}$ = 6.5), 135.17 (dt, $^{1}J_{C-H}$ = 163.2 - $^{3}J_{C-H}$ = 7.4), 135.33 (t, $^{3}J_{C-H}$ = 9.0).

5-Trifluoromethyl-pyrazole (11)[12, 13]

Δ^{1}-pyrazoline **10b** was heated in a Kugelrohr distillation apparatus (80°C/5.10^{-2} Torr). The trifluoromethylated pyrazole **11** sublimes as white crystals in 66% yield. **Mp** : 47°C; **^{1}H-NMR** : δ = 6.64 (s, 1H), 7.70 (s, 1H), 13.2-13.5 (br s, 1H); **^{19}F-NMR** : δ = -62.06 (s).

1-Trifluoromethyl-1-phenylthio-2-phenylcyclopropane (12)

A solution of vinylthioether **2** (0.50 g) and phenyldiazomethane (0.32 g, 1 eq.) in 4 ml of benzene was first stirred for 15 min at 20°C and then for 45 min at 50°C (until disappearance of the red color). The mixture was then refluxed for 45 min. The solvent was removed by evaporation under vacuum. The cyclopropane **12** was obtained quantitatively as a mixture of two isomers which could be separated by chromatography on silicagel (eluant : petroleum ether - ethyl acetate, 8-2).
Z-isomer : R_f = 0.70 (56%), *E*-isomer : R_f' = 0.61 (44%)
IR : 3063, 3031, 1584, 1499, 1478, 1450, 1440, 1384, 1344, 1297, 1220, 1199, 1151; **MS** : 296, 295, 294 (100%), 261, 215, 185, 183, 165, 147, 115, 109, 77; **^{1}H-NMR** : δ = 1.56 (ddq, J = 7.9-6.3 - $^{4}J_{H-F}$ = 1.6, 1H), 1.87 (dd, J = 9.7-6.3, 1H), 2.96 (m, 1H), 7.05-7.65 (m, 5H); δ' = 1.65 (tq, J = 9.7-6.1 - $^{4}J_{H-F}$ = 1.9, 1H), 2.00 (dd, J = 6.1-7.9, 1H), 2.96 (m, 1H), 7.05-7.65 (m, 5H); **^{19}F-NMR** : δ = -69.49 (s), δ' = -63.21 (s); **^{13}C-NMR** : δ = 17.31 (dd, $^{1}J_{C-H}$ = 166.0-164.4), 29.53 (d, $^{1}J_{C-H}$ = 161.8), 34.51 (qm, $^{2}J_{C-F}$ = 35.1), 125.96 (q, $^{1}J_{C-F}$ =

275.3), 127.21 (dt, $^1J_{C-H}$ = 161.2), 127.35 (dt, $^1J_{C-H}$ = 160.8 - $^3J_{C-H}$ = 7.2), 128.03 (dd, $^1J_{C-H}$ = 160.0 - $^3J_{C-H}$ = 6.8), 128.25 (d, $^1J_{C-H}$ = 161.6), 128.99 (dt, $^1J_{C-H}$ = 160.4 - $^3J_{C-H}$ = 6.4), 131.17 (d, $^1J_{C-H}$ = 162.4), 133.36 (s), 133.76 (s); δ' = 18.15 (dd, $^1J_{C-H}$ = 169.1-161.4), 33.51 (d, $^1J_{C-H}$ = 162.4), 35.19 (q, $^2J_{C-F}$ = 33.5), 126.13 (q, $^1J_{C-F}$ = 274.3), 127.29 (d, $^1J_{C-H}$ = 161.3), 127.35 (dt, $^1J_{C-H}$ = 160.8 - $^3J_{C-H}$ = 7.2), 128.07 (d, $^1J_{C-H}$ = 159.8), 128.65 (d, $^1J_{C-H}$ = 161.4), 129.16 (dd, $^1J_{C-H}$ = 160.8 - $^3J_{C-H}$ = 6.2), 132.71 (d, $^1J_{C-H}$ = 162.5), 133.46 (s), 134.27 (s).

4,4,4-Trifluoro-1-phenyl-3-phenylsulfonyl-1-butene (14)

Phenyldiazomethane (0.27 g, 1.08 eq.) in 4 ml of benzene was added dropwise to vinylsulfone **4** in 1 ml of ether. The mixture was then refluxed until disappearance of the red color (15 min). The solvent was removed and ethyl acetate (5 ml) and silicagel (1 g) were added to the crude adduct. This mixture was then refluxed for 15 hours. After filtration, ethyl acetate was evaporated under vacuum. White crystals were obtained by chromatography on silicagel (eluant : petroleum ether - ethyl acetate, 9-1). Rf = 0.70 , yield : 76%.

IR (KBr) : 2959, 1448, 1327, 1252, 1201, 1164, 1147, 1116, 1081, 971; **MS** : 326, 185 (100%), 165, 145, 125, 115, 77; **^{1}H-NMR** : δ = 4.40 (dq, J = 9.8 - $^3J_{H-F}$ = 7.8, 1H), 5.99 (dd, J = 15.8-9.8, 1H), 6.30 (d, J = 15.8, 1H), 7.33 (m, 5H), 7.50-7.72 (m, 3H), 7.88 (s, 1H), 7.92 (s, 1H); **^{19}F-NMR** : δ = -64.38 (dd, $^3J_{F-H}$ = 8.0 - J = 2.9); **^{13}C-NMR** : δ = 71.51 (dqdd, $^1J_{C-H}$ = 139.8 - $^2J_{C-F}$ = 28.9 - J = 6.6-2.3), 112.02 (dq, $^1J_{C-H}$ = 163), 119.84 (qdd, $^1J_{C-F}$ = 281.5 - $^2J_{C-H}$ = 6.9 - J = 2.3), 126.94 (d), 128.76 (dd), 129.11 (dd), 129.35 (d), 129.55 (d), 134.64 (dt), 134.67 (m), 135.15 (t, $^3J_{C-H}$ = 8.5), 142.56 (d); **Analysis** : calculated for $C_{16}H_{13}F_3S$: C (58.89), H (4.02), S (9.82) - found C (58.80), H (3.91), S (9.72) %.

Reactions with diphenyl diazomethane

Diphenyl diazomethane (2.5 mmoles) in 4 ml of ether was added dropwise to the trifluoromethylated olefines **2-4** in 1 ml of ether. The solution was stirred for 30 minutes at 20°C and then for 17 hours at reflux. The excess of diphenyl-diazomethane was removed by addition of a few drops of glacial AcOH. The mixture was washed with water (20 ml) and extracted with CH_2Cl_2. The dried extract was evaporated and the residue was purified as indicated below.

1-Trifluoromethyl-2,2-diphenyl-1-phenylthio-cyclopropane (15a)

0.52 g of vinylthioether **2** are used. The cyclopropane **15a** was obtained in 76% yield after recrystallization from ether.

IR (KBr) : 3084, 3073, 3059, 3030, 1598, 1493, 1475, 1448, 1337, 1255, 1133, 1093, 1085, 1067, 1011; **MS** : 370, 292, 262, 260 (100%), 239, 221, 192, 191, 183, 178, 165, 163, 152, 111, 109, 91, 77; **^{1}H-NMR** : δ = 1.89 (dq, J = 6.2 - $^4J_{H-F}$ = 1.5, 1H), 2.30 (d, J = 6.2, 1H), 7.1-7.5 (m, 15H); **^{19}F-NMR** : δ = -62.15 (s); **^{13}C-NMR** : δ = 23.46 (t, $^1J_{C-H}$ = 164.1), 39.70 (q, $^2J_{C-F}$ = 34.0), 46.86 (s), 126.17 (q, $^1J_{C-F}$ = 275.2), 127.12 (dt, $^1J_{C-H}$ = 160.8 - $^3J_{C-H}$ = 7.3), 127.86 (d), 128.47 (dd, $^1J_{C-H}$ = 160.4 - $^3J_{C-H}$ = 7.6), 128.79 (d, $^1J_{C-H}$ = 163.8), 129.29 (dt, $^1J_{C-H}$ = 157.6 - $^3J_{C-H}$ = 6.8), 132.57 (d), 133.37 (s), 140.56 (s), 141.41 (s); **Analysis** : calculated for $C_{22}H_{21}F_3S$: C (71.33), H (4.63), S (8.65) - found C (71.48), H (4.88), S (8.50) %.

1-Trifluoromethyl-2,2-diphenyl-1-phenylsulfoxy-cyclopropane (15b) and 3,4-diphenyl-5-trifluoromethyl-pyrazole (16)

0.60 g of vinylsulfoxide **4** were used. The purification was realised by chromatography on silicagel (eluant : petroleum ether - ethyl acetate, 8-2) followed by recrystallization in ether-petroleum ether. The cyclopropane

15b and the pyrazole **16** were obtained in 49% and 24% yield respectively.

Cyclopropane 15b . Rf : 0.15; **Mp** : 92°C; **IR** (KBr) : 3084-3013, 1495, 1447, 1335, 1317, 1247, 1167, 1147-1050, 757, 749, 708, 698, 689; **MS** : 386, 260, 259 (100%), 241, 221, 204, 192, 191, 183, 165, 127, 97, 91, 77; **^{1}H-NMR** : δ = 2.38 (d, J = 7.1, 1H), 2.86 (dq, J = 7.1 - $^4J_{H\text{-}F}$ = 1.3, 1H), 7.1-7.8 (m, 15H); **^{19}F-NMR** : δ = -58.86 (s); **^{13}C-NMR** : δ = 19.13 (t, $^1J_{C\text{-}H}$ = 165.9), 45.34 (s), 54.68 (q, $^2J_{C\text{-}F}$ = 29.9), 124.27 (q, $^1J_{C\text{-}F}$ = 279.4), 125.32 (d), 125.36 (d), 127.40 (dt), 127.70 (dt), 128.44 (d), 128.50 (d), 128.53 (d), 128.56 (d), 128.66 (d), 128.70 (d), 128.72 (d), 128.75 (d), 129.01 (d), 129.04 (dt), 131.45 (dt), 138.33 (s), 139.44 (s), 139.95 (s); **Analysis** : calculated for $C_{22}H_{17}F_3OS$: C (68.38), H (4.43), S (8.30) - found C (68.19), H (4.16), S (8.32) %.

Pyrazole 16 . Rf : 0.24; **Mp** : 188°C; **IR** (KBr) : 3200-2700, 1480, 1175, 1160, 1144, 1136, 1095, 988, 697; **MS** : 288 (100%), 273, 267, 239, 238, 219, 218, 190, 189, 163; **^{1}H-NMR** : δ = 7.25-7.37 (m, 10H), 10.8-11.0 (br s, 1H); **^{19}F-NMR** : δ = -60.19 (s); **^{13}C-NMR** : δ = 118.24 (s), 45.34 (s), 121.35 (q, $^1J_{C\text{-}F}$ = 270.0), 127.49 (d), 127.84 (d), 128.01 (s), 128.42 (d), 128.90 (d), 129.07 (d), 130.25 (d), 130.33 (s), 141.12 (q, $^2J_{C\text{-}F}$ = 36.6), 142.43 (s). Its structure was confirmed by **X-ray analysis**[17].

1-Trifluoromethyl-2,2-diphenyl-1-phenylsulfonyl-cyclopropane (15c) and 1,1,1-trifluoro-4,4-diphenyl-1-phenylsulfonyl-2-butene (17)

0.60 g of vinylsulfone **4** were employed. The purification was realised by chromatography on silicagel (eluant : petroleum ether - ethyl acetate, 8-2) followed by recrystallization from ether. The cyclopropane **15c** (52% yield) and the butene **17** (26% yield) were obtained.

Cyclopropane 15c. Rf : 0.24; **Mp** : 206°C; **IR** (KBr) : 3087, 3060, 3031, 1584, 1495, 1450, 1341, 1327, 1255, 1188, 1166, 1152; **MS** : 403, 362, 261, 260, 240, 238, 221, 220, 191, 183, 165, 77; **^{1}H-NMR** : δ = 2.42 (d, J = 6.3, 1H), 2.84 (dq, J = 6.3 - $^4J_{H\text{-}F}$ = 1.5, 1H), 7.1-7.9 (m, 15H); **^{19}F-NMR** : δ = -56.06 (s); **^{13}C-NMR** : δ = 21.50 (t, $^1J_{C\text{-}H}$ = 164.1), 46.55 (s), 53.87 (q, $^2J_{C\text{-}F}$ = 31.30), 122.92 (q, $^1J_{C\text{-}F}$ = 278.2), 127.37 (dt), 128.09 (d), 128.36 (dd), 128.61 (dd), 128.85 (d), 133.91 (dt), 139.00 (s), 140.04 (s), 140.94 (s); **Analysis** : calculated for $C_{22}H_{17}F_3O_2S$: C (65.66), H (4.26), S (7.97) - found C (65.40), H (4.17), S (7.85) %.

Butene 17. Rf : 0.36; **Mp** : 133°C; **IR** (KBr) : 3085-3007, 1634, 1494, 1446, 1333, 1312, 1216, 1171-1132, 1086, 1063, 779, 760; **MS** : 402, 382, 363, 362, 261, 260, 241, 238, 221, 220, 191, 183, 166, 165, 152, 77; **^{1}H-NMR** : δ = 5.33 (d, J = 11.8, 1H), 7.1-7.9 (m, 15 H), 8.01 (dq, J = 11.8 - $^4J_{H\text{-}F}$ = 1.1, 1 H); **^{19}F-NMR** : δ = -54.99 (s); **^{13}C-NMR** : δ = 49.38 (d, $^1J_{C\text{-}H}$ = 133.1), 120.99 (qd, $^1J_{C\text{-}F}$ = 276.5 - J = 12.7), 127.65 (dt), 128.03 (d), 129.09 (d), 129.25 (d), 132.60 (q, $^2J_{C\text{-}F}$ = 32.9), 133.98 (d), 139.09 (t, $^3J_{C\text{-}H}$ = 8.3), 139.59 (s), 153.03 (d, $^1J_{C\text{-}H}$ = 163.5); **Analysis** : calculated for $C_{22}H_{17}F_3O_2S$: C (65.66), H (4.26), S (8.18) - found C (65.55), H (4.15), S (8.18) %.

3-Trifluoromethyl-pyrrolidines 19a-c

To a mixture of 2 mmoles of trifluoromethylated olefines **2-4** in 4 ml of dry methylene chloride cooled to 0°C, was added dropwise 0.64 g (3 mmoles) of N-benzyl-N-(methoxymethyl)-trimethylsilylmethylamine diluted in 5 ml of CH_2Cl_2. The mixture was treated with a few drops of trifluoroacetic acid. The reaction was exothermic and led to refluxing. The consumption of the olefin was followed by TLC. It was sometimes necessary to add an additional 2 drops of trifluoroacetic acid and to heat in refluxing solvent (15 min, for **2** only) to complete the reaction. The mixture was then washed with a saturated solution of sodium bicarbonate, with brine and then dried over $MgSO_4$. After evaporation of solvent, the residual oil was chromatographed on silica gel using petroleum ether-diethyl ether (95-5) as eluant to afford the pure pyrrolidines **19a-c** as colorless oils, which must be stored at ± 0°C. Therefore satisfactory elemental analysis could be obtained only for **19c**.

3-Trifluoromethyl-3-phenylthio-pyrrolidine (19a)

Yield : 84%; **IR** (neat) : 2804, 1703, 1475, 1440, 1320, 1292, 1182, 1146, 1072, 752, 699, 693; **MS** : 337, 259, 227, 205, 135, 133, 109, 91 (100%), 77, 69; **^{1}H-NMR** : δ = 2.02 (dt, J = 13.7-6.9, 1H), 2.21 (ddd, J = 13.7-7.4-5.9, 1H), 2.61 (dt, J = 14.9-7.4, 1H), 2.76 (dt, J = 14.9-6.9, 1H), 2.97 (s, 2H), 3.55 (d, J = 13.1, 1H), 3.70 (d, J = 13.1, 1H), 7.16-7.56 (m, 10H); **^{19}F-NMR** : δ = -71.97 (s); **^{13}C-NMR** : δ = 33.25 (t, $^{1}J_{C\text{-}H}$ = 133.7), 53.12 (t, $^{1}J_{C\text{-}H}$ = 137.2), 53.20 (t, $^{1}J_{C\text{-}H}$ = 133.1), 59.02 (q, $^{2}J_{C\text{-}F}$ = 27.3), 59.29 (t, $^{1}J_{C\text{-}H}$ = 132.9), 127.37 (q, $^{1}J_{C\text{-}F}$ = 279.7), 127.06 (dt, $^{1}J_{C\text{-}H}$ = 160.3 - $^{3}J_{C\text{-}H}$ = 6.6), 128.23 (dt, $^{1}J_{C\text{-}H}$ = 158.0 - $^{3}J_{C\text{-}H}$ = 6.3), 128.49 (dd, $^{1}J_{C\text{-}H}$ = 161.9 - $^{3}J_{C\text{-}H}$ = 7.6), 128.59 (dd, $^{1}J_{C\text{-}H}$ = 162.3 - $^{3}J_{C\text{-}H}$ = 7.2), 129.63 (dt, $^{1}J_{C\text{-}H}$ = 164.6 - $^{3}J_{C\text{-}H}$ = 6.3), 138.34 (t, $^{3}J_{C\text{-}H}$ = 4.4).

3-Trifluoromethyl-3-phenylsulfoxy-pyrrolidine (19b)

Yield : 65%; **IR** (neat) : 2900, 1350-1250, 1090, 900, 750; **MS** : 353, 276, 242, 220, 125, 105, 91 (100%), 77, 69; **^{1}H-NMR** : δ = 2.15 (dt, J = 13.6-6.9, 1H), 2.63 (ddd, J = 13.6-7.4-6.0, 1H), 2.70 (t, J = 7.4, 2H), 2.88 (d, J = 11.6, 1H), 3.15 (d, J = 11.6, 1H), 3.65 (s, 2H), 7.30 (m, 5H), 7.70 (m, 5H); **^{19}F-NMR** : δ = -70.05 (s); **^{13}C-NMR** : δ = 30.52 (t, $^{1}J_{C\text{-}H}$ = 134.5), 53.08 (t, $^{1}J_{C\text{-}H}$ = 139.2), 54.55 (t, $^{1}J_{C\text{-}H}$ = 137.4), 58.78 (t, $^{1}J_{C\text{-}H}$ = 132.8), 63.50 (q, $^{2}J_{C\text{-}F}$ = 26.9), 124.79 (q, $^{1}J_{C\text{-}F}$ = 280.2), 127.01 (dd, $^{1}J_{C\text{-}H}$ = 158.6 - $^{3}J_{C\text{-}H}$ = 6.2), 128.16 (dd, $^{1}J_{C\text{-}H}$ = 158.0 - $^{3}J_{C\text{-}H}$ = 6.0), 128.47 (dt, $^{1}J_{C\text{-}H}$ = 160.2 - $^{3}J_{C\text{-}H}$ = 6.1), 128.75 (dt, $^{1}J_{C\text{-}H}$ = 165.0 - $^{3}J_{C\text{-}H}$ = 5.8), 130.02 (dt, $^{1}J_{C\text{-}H}$ = 162.9 - $^{3}J_{C\text{-}H}$ = 7.2), 132.64 (dt, $^{1}J_{C\text{-}H}$ = 163.4 - $^{3}J_{C\text{-}H}$ = 7.0), 136.50 (t, $^{3}J_{C\text{-}H}$ = 9.1), 137.84 (t, $^{3}J_{C\text{-}H}$ = 5.0).

3-Trifluoromethyl-3-phenylsulfonyl-pyrrolidine (19c)

Yield : 71%; **IR** (neat) : 2831-2817, 1449, 1331, 1313, 1291, 1187-1152, 1074, 734, 699, 689, 594, 558; **MS** : 369, 318, 292, 258, 236, 227, 205, 141, 125, 105, 91 (100%), 77, 69, 65; **^{1}H-NMR** : δ = 2.27 (dt, J = 13.6 -7.1, 1H), 2.68 (dt, J = 13.6-5.8, 1H), 2.74 (t, J = 7.1, 1H), 2.83 (t, J = 5.1, 2H), 2.97 (d, J = 11.6, 1H), 3.27 (d, J = 11.6, 1H), 3.67 (s, 2H), 7.28 (m, 5H), 7.73 (m, 5H); **^{19}F-NMR** : δ = -68.64 (s); **^{13}C-NMR** : δ = 29.71 (t, $^{1}J_{C\text{-}H}$ = 136.2), 53.01 (t, $^{1}J_{C\text{-}H}$ = 139.1), 55.41 (t, $^{1}J_{C\text{-}H}$ = 141.7), 58.62 (t, $^{1}J_{C\text{-}H}$ = 132.9), 74.86 (q, $^{2}J_{C\text{-}F}$ = 25.9), 124.60 (q, $^{1}J_{C\text{-}F}$ = 282.1), 127.05 (dd, $^{1}J_{C\text{-}H}$ = 145.3 - $^{3}J_{C\text{-}H}$ = 5.6), 128.14 (dd, $^{1}J_{C\text{-}H}$ = 158.8 - $^{3}J_{C\text{-}H}$ = 6.8), 128.18 (dt, $^{1}J_{C\text{-}H}$ = 160.1 - $^{3}J_{C\text{-}H}$ = 6.8), 128.87 (dt, $^{1}J_{C\text{-}H}$ = 165.0 - $^{3}J_{C\text{-}H}$ = 6.5), 130.16 (dt, $^{1}J_{C\text{-}H}$ = 169.1 - $^{3}J_{C\text{-}H}$ = 6.1), 134.38 (dt, $^{1}J_{C\text{-}H}$ = 162.7 - $^{3}J_{C\text{-}H}$ = 7.1), 136.55 (t, $^{3}J_{C\text{-}H}$ = 8.1); **Analysis** : calculated for $C_{18}H_{18}F_{3}NO_{2}S$: C (58.53), H (4.91), N (3.79), S (8.68) - found C (58.25), H (4.79), N (3.49), S (8.15) %.

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17. We thank Dr. B. Tinant for the X-ray analysis.

(Received in Belgium 6 *September* 1995; *accepted* 17 *January* 1996)