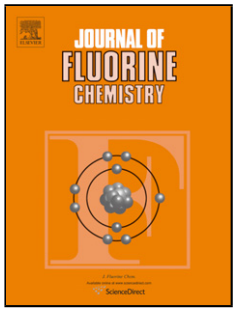

Title: Do Reactions of 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane Require Fluoride Anion Catalysis?

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Do Reactions of 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane Require Fluoride Anion Catalysis?

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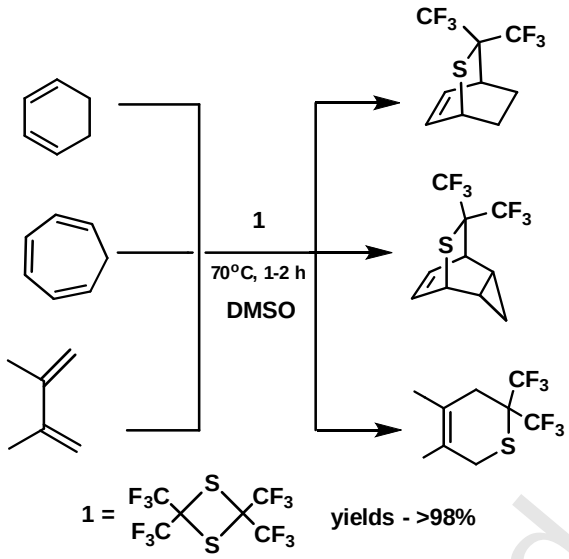

Graphical Abstract

Do Reactions of 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane Require Fluoride Anion Catalysis?

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Abstract

*2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (cyclic dimer of hexafluorothioacetone (**1**)) was shown to react with a variety of organic substrates in the absence of metal fluoride catalyst at elevated temperature in DMSO or DMF solvents. While the reactions of vinyl ethers, phenyl vinyl sulfide, dienes and anthracenes under these conditions led to the formation of expected cycloadducts, the reaction of 1,5-cyclooctadiene resulted in the formation of the product derived from an ene reaction with hexafluorothioacetone (HFTA). In contrast to results reported for the CsF catalysed process, 2-vinylnaphthalene reacted with **1** to produce a compound that resulted from reaction with two molecules of HFTA. The structure of this adduct was established using single crystal X-ray diffraction. The formation of similar products was also observed in non-catalysed reactions of styrene and 2-methylstyrene with **1**. Interestingly, no product of this type was observed in reaction of 4-MeO-styrene with **1**, which instead led to the high yield formation of the corresponding thietane. The reaction of **1** with 1,3-cyclohexadiene was carried out in various organic solvents: the reaction in DMSO and DMF was significantly faster than in acetonitrile, tetrahydrofurane or hexane.*

[≠] Publication # 2015-1179

Keywords: Reactions of cyclic dimer hexafluorothioacetone; 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane;

Research Highlights.

- The reaction of hexafluorothioacetone dimer does not require MF catalyst
- It can be carried out in DMSO or DMF solvent at 20-70 ^{o}C
- These reactions are as efficient as catalyzed processes

1. Introduction.

The cyclic dimer of hexafluorothioacetone (2,2,4,4-terakis(trifluoromethyl)-1,3-dithietane (**1**)) is a valuable synthon which has been used to prepare a variety of fluorine-containing martials. It has been shown to react to give hexafluorothioacetone (HFTA) cycloaddition products with vinyl ethers [1-3] vinyl sulfides [2], vinyl amides [4], various dienes [5-7], styrenes [5, 8], fluoroolefins [2, 9]. It has also been shown to give the product of HFTA insertion into allylic C-H bond with certain hydrocarbon olefins [10-12]. Most of these reactions were carried out in the presence of an alkali metal fluoride catalyst (either KF or CsF), since in earlier publications [1, 5, 9] it was suggested that the catalyst was required to induce the equilibrium between **1** and monomeric hexafluorothioacetone.

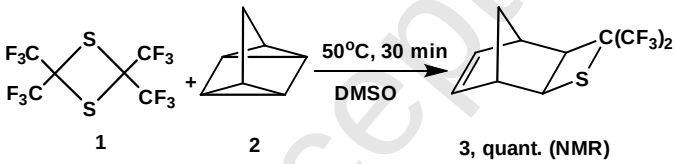
In contrast, a significant number of reactions of **1** have been reported that did *not* contain metal fluoride catalyst, including substrates such as phosphorous, arsenic, germanium and silicon cyanides [13-

15], thiourea, dithiooxamide and cyanoformamidines[16-18], 1,1-dimethoxyethylene [3], *N*-vinylamides [4], azoles [19], *N*-alkyl(aryl)imidazoles [20].

In order to further elucidate the chemical behavior of **1**, we undertook a separate study of its reported reactions, but in the *absence* of alkali metal fluoride catalysts. The observed results demonstrate that when using a polar *nucleophilic* solvent, the majority of the reactions involving **1** *do not* require the catalyst.

2. Results and Discussion.

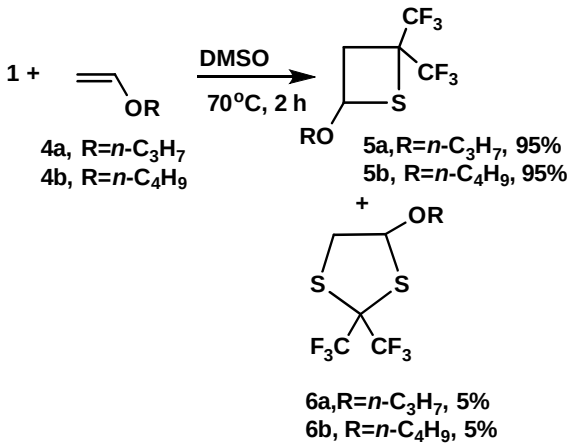
Previously [7] we reported that the reaction of **1** with quadricyclane (**2**) carried out in diglyme in the presence of CsF catalyst resulted in rapid formation of the corresponding cycloadduct **3**. Interestingly, the formation of the same product, albeit at a significantly slower rate, was observed when this reaction was carried out at ambient temperature *in the absence* of either catalyst or solvent [7]. Intrigued by this result, we repeated the reaction of **1** with **2** in the absence of catalyst, but using a polar aprotic solvent - dimethylsulfoxide (DMSO). Surprisingly, at 50^{o}C, the reaction was complete (by ^{19}F NMR) after 10 min. to give a high yield of **3** (Eq.1).



(1)

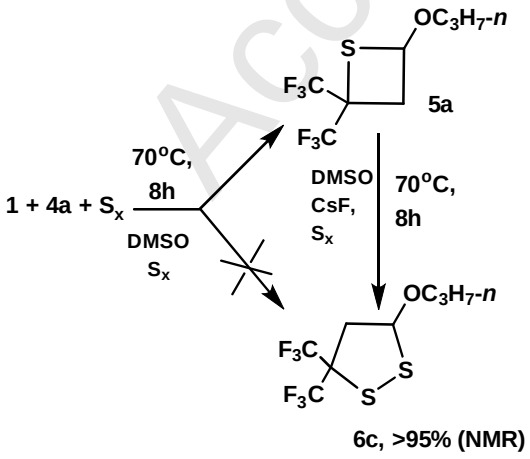
We also examined other previously reported KF or CsF catalyzed reactions of **1** by running the reactions in the absence of catalyst. To our surprise, the majority of these reactions *did not* require metal fluoride catalysis, as long as the reaction was carried out in a polar solvent such as DMSO or DMF.

One example, the reaction of alkylvinyl ethers **4a,b** with **1** in DMSO (70 °C, 2 h) led to high yields of previously reported [2] thietanes **5a** and **5b,** along with smaller amounts of 1,3-dithiolanes **6a** and **6b** (Eq.2, Table 2).



(2)

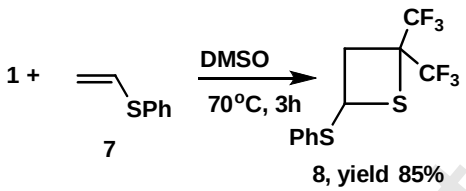
When one equivalent of sulfur was included in this reaction (DMSO, 70 °C, 24 h) the major product was compound **5a** (and trace amount of **6a**), rather than the expected 1,2-dithiolane **6c** [2]. However, when dry CsF catalyst was added to the existing reaction mixture, complete conversion of **5a** into **6c** was observed within 8 h at 70 °C. (Eq.3)



(3)

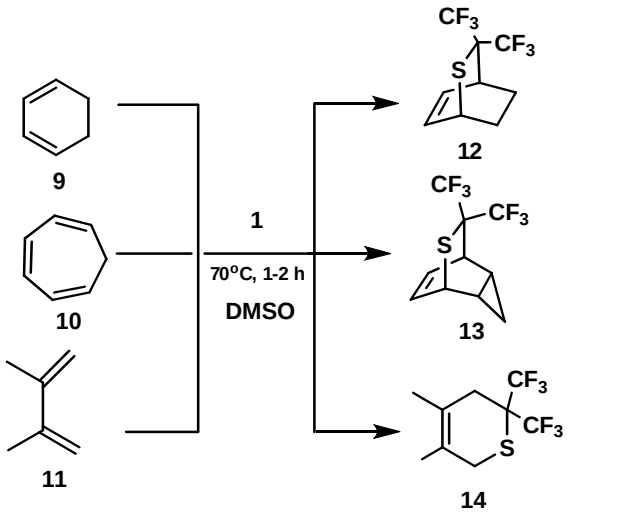
This experiment demonstrated that while the formation of thietane **5a** does not require catalyst, the ring-expansion process leading to **6c** is catalyzed by CsF. It is likely that in this case CsF reacts with elemental sulfur (rather than **5a**), converting it into an anionic species that is then able to react with **5a**.

Phenylvinyl sulfide (**7**), under similar reaction conditions, was completely consumed after 3 h at 70 ^{o}C to give thietane **8** in 85 % isolated yield (Eq.4). The structure of this material was established by single crystal X-ray diffraction.



(4)

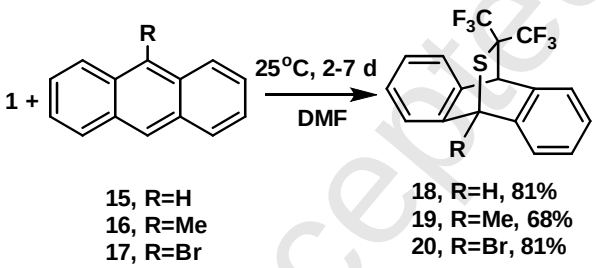
1,3-Cyclohexadine (**9**), 1,3,5-cycloheptatriene (**10**) and 2,3-dimethyl-1,3-butadiene (**11**) all readily reacted with **1** at elevated temperature in DMSO to produce the corresponding cycloadducts **12-14** in nearly quantitative yields.



12,13,14 - yields - >98% (NMR)

(5)

The reaction of anthracenes **15-17** with **1** were carried out at ambient temperature in DMF. Although these reactions were relatively slow (2 -7 days), the corresponding cycloadducts **18-20** were isolated in 68-81 % yield.



15, R=H
16, R=Me
17, R=Br

18, R=H, 81%
19, R=Me, 68%
20, R=Br, 81%

(6)

In the case of substituted anthracenes **16** and **17,** the formation of only one regioisomer was observed. The structures of products **18-20** were established by single crystal X-ray diffraction. Compounds **19** and **20** both were shown to exist as the isomer in which sulfur was connected to the carbon bearing the R-group (Fig. 1).

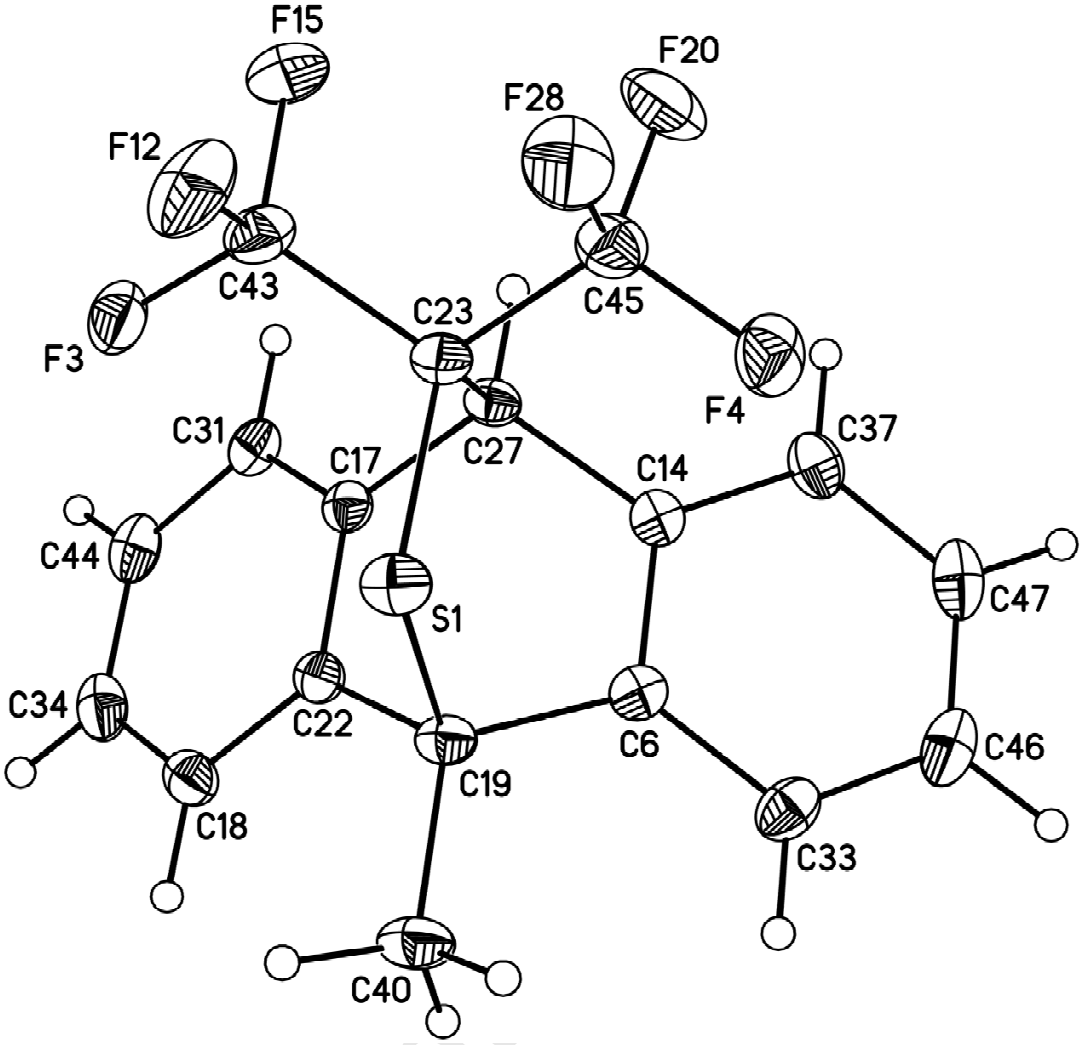
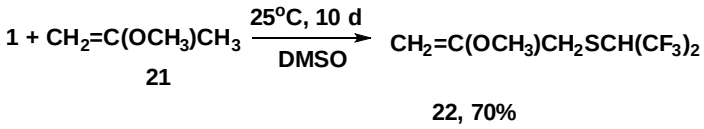


Fig.1 Single Crystal Structure for **19** with thermal ellipsoids drawn to the 30% probability level.

Ene reactions involving HFTA were first reported by Middleton [21], but later it was found, that **1** in the presence of KF catalyst, can be used for preparation of variety of allyl hexafluoro-*i*-propyl sulfides [5, 11, 22]. We found that **1** produced ene- product in the reaction with 2-methoxypropene (**21**) in DMSO in the absence of CsF catalyst. Indeed, the agitation of the mixture of **1** and an excess of **21** (two layers due to limited solubility of **1** in DMSO) led to the homogenization of the reaction mixture and formation of compound **22** as major product (Eq.7), along with smaller amounts of bis- and tris-

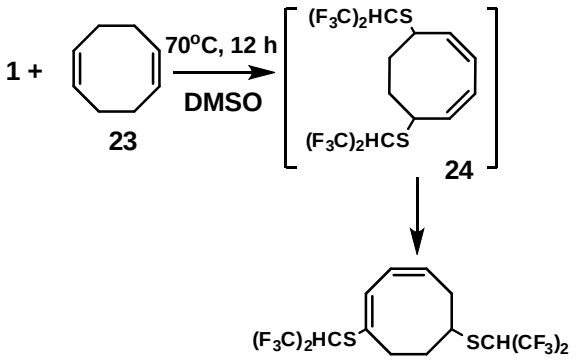
substituted adducts (Eq.7). Compound **22** was not isolated, but it was characterized in reaction mixture by NMR and GC/MS.



(7)

The ene reaction was previously found to play an important role in the CsF catalyzed reaction of non-conjugated dienes (such as 1,4-cyclohexadiene and 1,5-cyclooctadiene (**23**)) with **1**. In both cases the initial step was insertion of HFTA into the allylic C-H bond of the diene (leading to the formation of cycloadducts with conjugated double bonds) followed by Diels-Alder reaction involving a second mole of HFTA [6].

The outcome of the non-catalyzed reaction of 1,5-cyclooctadiene (**23**) with **1** was found to be different from the result reported for catalyzed process [6]. At 70 ^{o}C in DMSO, **23** was consumed within 3 h, but ^{1}H and ^{19}F NMR spectra of the reaction mixture revealed the presence of at least two isomeric species resulting in significant broadening of the NMR signals. A longer reaction time (12 h) led to simplification of the NMR spectra of the crude reaction mixture, from which compound **25** (the isomer of **24** reported to form in the catalyzed process [6]), was isolated in 51% yield.



25, yield 51%

(8)

The structure of **25** was established by single crystal X-ray diffraction (Fig. 2).

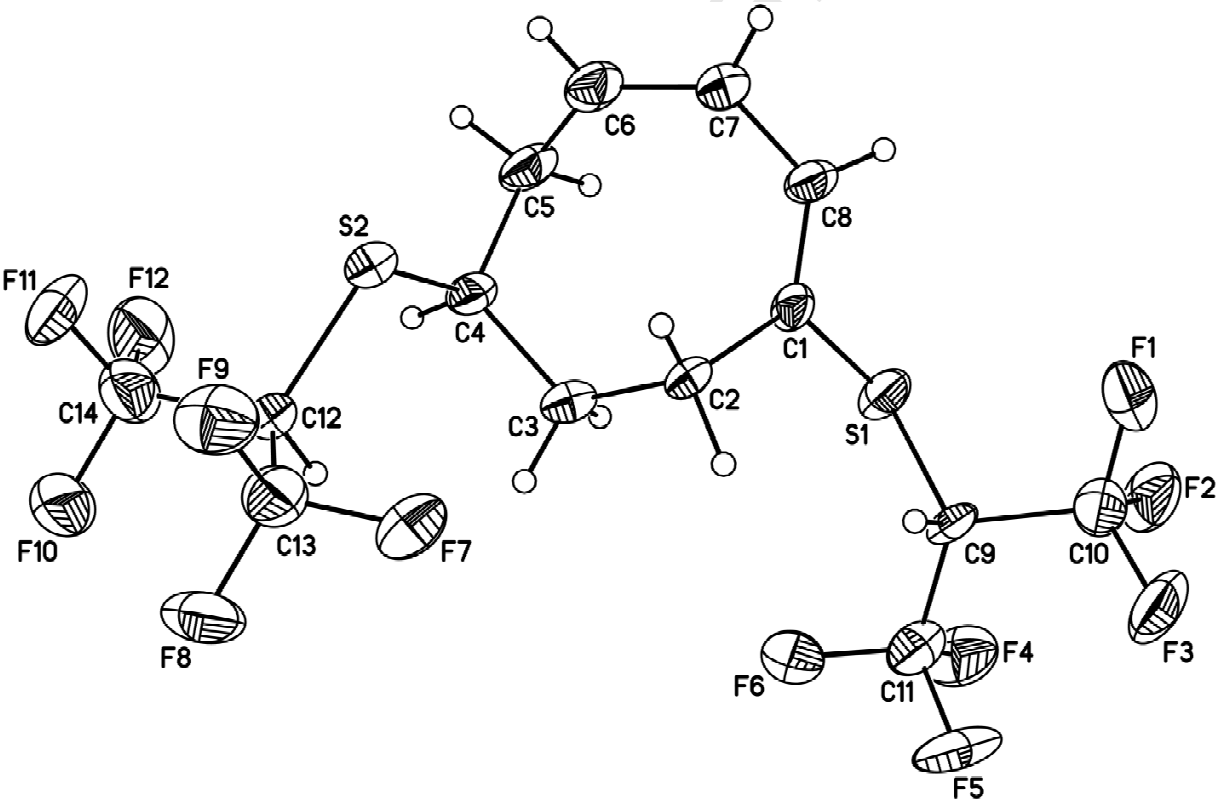
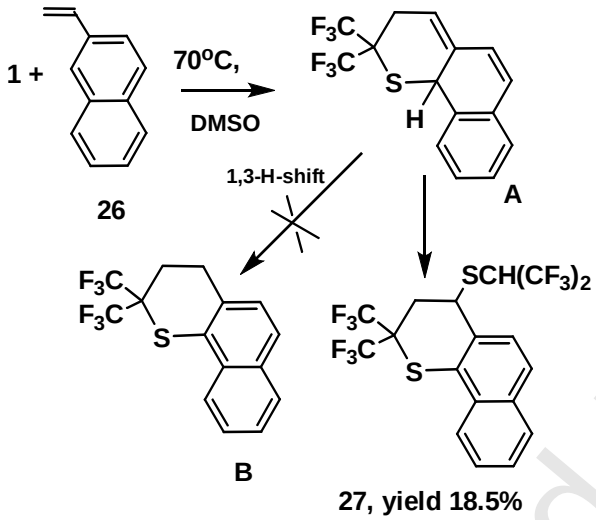


Fig.2. Single Crystal Structure for **25** with thermal ellipsoids drawn to the 30% probability level.

Obviously, the formation of **25** involved isomerization of isomer **24** [6] by the migration of both C=C bonds under the reaction conditions.

The ene reaction was also found to play an important role in non-catalyzed reactions of **1** with styrenes. For example, the reaction of 2-vinylnaphthalene (**26**) with excess **1** rapidly and selectively led to the formation of bis-adduct **27** (NMR yield > 95%) rather than expected mono-adduct **B** [8] (Eq.9).



(9)

Although the isolated yield of **27** was low (the isolation protocol was not optimized), its structure was established by single crystal X-ray diffraction.

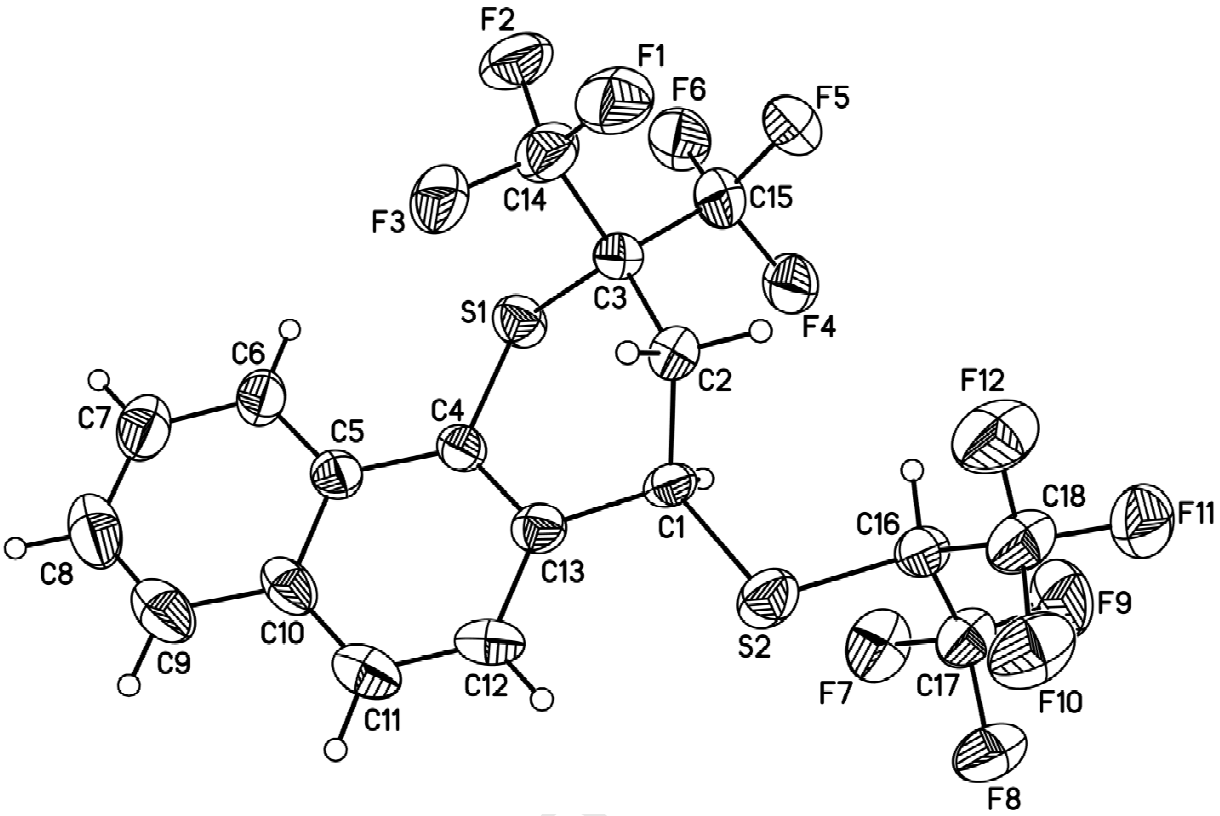
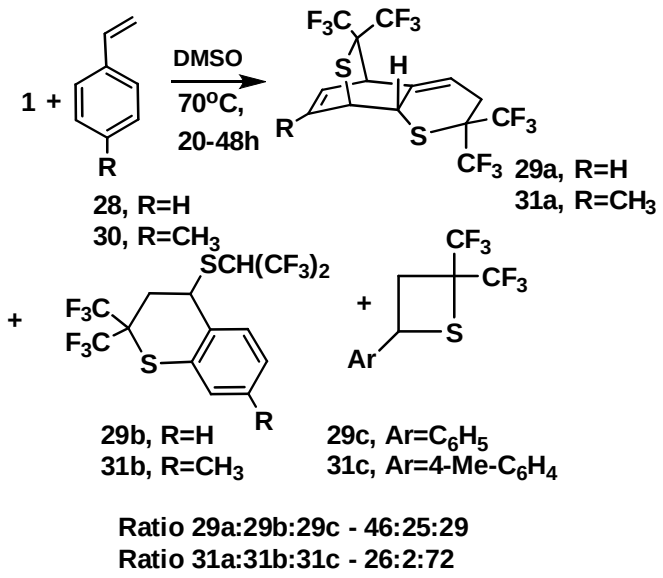


Fig. 3 Single Crystal Structure for **27** with thermal ellipsoids drawn to the 30% probability level.

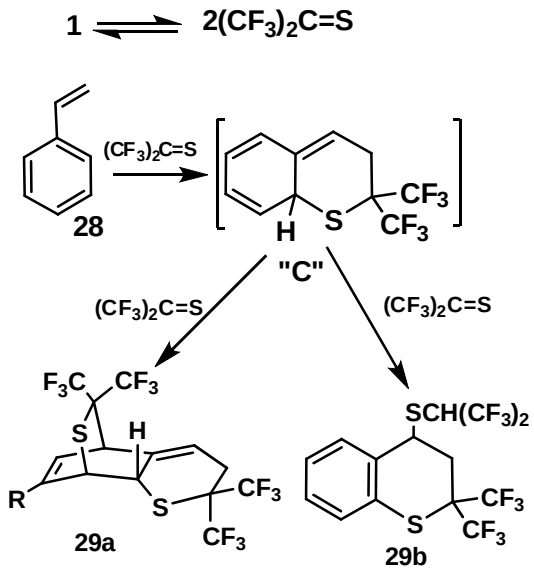
An initial Diels-Alder reaction produced compound A, which then underwent an ene reaction [8] with a second mole of HFTA to give **27**. The transient formation of **A** was clearly seen in NMR spectra taken throughout the reaction: after 1 h at 65 ^{o}C, the reaction mixture contained **A** and **27** in a ratio of 59:41, while after 12 h only compound **27** was observed.

Interestingly, the formation of adducts similar to **27** was also observed in the reactions of **1** with styrene (**28**) and 4-methylstyrene (**30**). In both cases, the reaction was not as selective, leading to the formation of three products in each case – **29a-c** and **31a-c**, respectively.



(10)

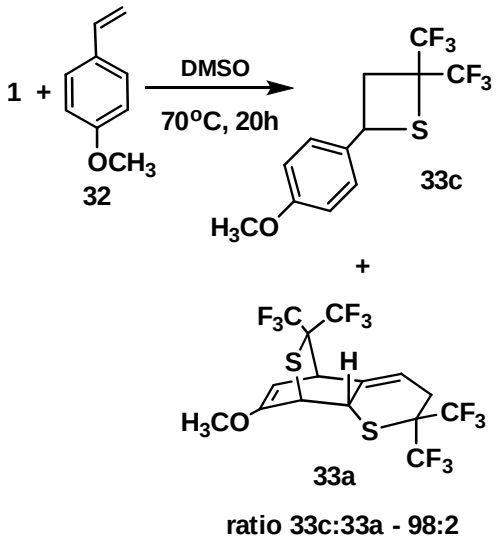
As shown in Eq. 10, a decrease in the amount of products **29b** and **31b** (29% for X=H *vs.* 2 % for X=CH_3) and increase in the amounts of thietanes **29c** and **31c** (25% for X=H vs. 72% for X=CH_3) correlates well with an increase in the electron-donating properties of the substituent on the phenyl ring. While no formation of product **29b** was observed in the CsF catalyzed reaction of **1** with styrene [8], in the reaction of monomeric HFTA with styrene reported by W. Middleton [23], the formation of two isomeric 2:1 adducts was observed. According to Middleton, the structure of **29a** was assigned to the major isomer, while the structure of the second adduct was not established [23]. Based on the data obtained in this present work, it is reasonable to assume that the second isomer reported by Middleton had the structure **29b**. Mechanistically, both isomers **29a** and **29b** formed from the same Diels-Alder intermediate **C** (Eq.11) by reaction with a second mole of HFTA through either a second Diels-Alder reaction leading to **29a**, or an ene- reaction (driven by aromatization) leading to the formation of isomer **29b**.



(Eq. 11)

The absence of product **29b** in the CsF catalyzed reaction of **1** with **28** [8] is likely the result of the instability of **29b** in the presence of fluoride anion. Indeed, when dry CsF was added to the reaction mixture obtained by the non-catalyzed process (the ratio of **29a:b:c** - 46:29:25), the complete disappearance of the signals of **29b** was observed in the ^{19}F NMR spectrum after 8 h at 65 ^{o}C, resulting in a reaction mixture containing only **29a** and **29c** (ratio 63:37, see Experimental Section).

In the case of the reaction between p-methoxystyrene (**32**) and **1**, the formation of products analogous to **29b** or **31b** was not observed, and the reaction led to predominant formation of thietane **33c** along with a small amount of adduct **33a** (Eq. 12). Due to its higher selectivity, this reaction to make **33c** is preferred over the CsF catalyzed reaction.



(12)

3. Mechanistic Considerations.

The fact that **1** is able to react with a variety of organic substrates *in the absence of the catalyst* strongly suggests that in polar solvents with high *nucleophilicity,* such as DMSO or DMF, compound **1** may exist in equilibrium with monomeric HFTA. In order to check this hypothesis we carried out a series of small scale (0.01 mol) experiments involving the reaction of **1** (10 mol % excess) with 1,3-cyclohexadiene (**9**) in different solvents, and compared the conversion of **9** to cycloadduct **10** (see Eq. 5) after 45 min at 65 ^{o}C. While the reaction in DMSO and DMF under these conditions resulted in 98 and 87% conversion of **9** to **10** (respectively), the reaction in acetonitrile (ACN) was significantly slower, resulting in only 0.7 % conversion (see Table 1). This result was comparable to the value obtained for the reaction in DMSO at ambient temperature (0.5%). The reaction in less polar tetrahydrofuran (THF) was even slower, and gave only 0.1 % conversion (45 min, 65 ^{o}C). Virtually no formation of compound **10** was observed in nonpolar hexane under the same conditions. Data summarized in Table 1 suggest that

although the polarity of the solvent strongly influences the rate of the reaction, the obtained results cannot be explained only by solvent polarity since the value of the dipole moment (μ as a reflection of polarity of the reaction media) of ACN (3.92 D) is close to that of both DMF (3.82 D) and DMSO (3.96 D, Table 1) [24].

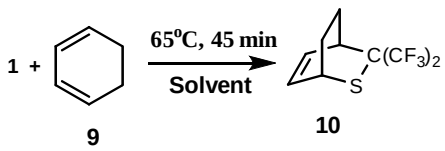


Table 1. Reaction of 9 with **1** in different solvents [a]

Solvent	Dipole moment (μ, D)	Conversion of **9** (%)
DMSO	3.96[b,c]	98
DMF	3.82[d]	87
ACN	3.92[e]	0.7
THF	1.75[f]	<0.1
Hexane	0[g]	no rxn

[a] 0.01 mol scale, 15 mL solvent, 10 mol % excess of **1**, 65 °C, 45 min.

[b] ref. [24], p.193

[c] same reaction in DMSO at 25 °C; conversion of **9** = 0.5 % after 45 min and 2.8% after 5h

[d] ref. [24], p.178

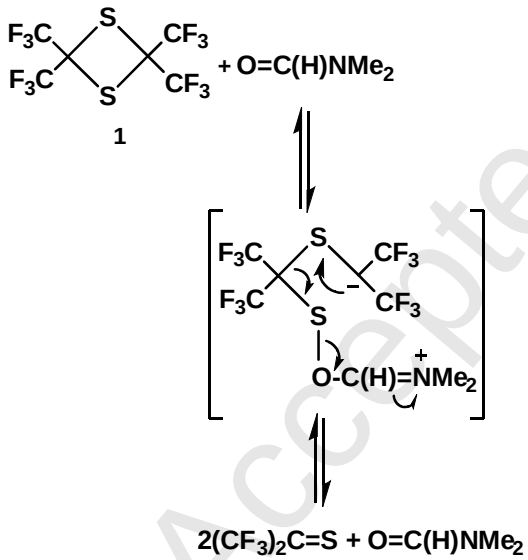
[e] ref. [24], p.7

[f] ref. [24], p.434

[g] ref. [24], p. 262

Such difference in reaction rates can, however, be explained based on the *nucleophilicity* of these solvents. Indeed, while DMSO and DMF are both relatively nucleophilic, ACN has significantly lower nucleophilicity, which is reflected in the much higher resistance of ACN towards action of electrophiles. As an example, DMF was reported to react at ambient temperature with relatively weak electrophile as $(CF_3)_2C=CF_2$, resulting in formation of $(CF_3)_2C=CHN(CH_3)_2$ [25, 26] and the formation of same product was observed in the reaction of **1** and DMF at elevated temperature (70^{o}C) [8], while such reactions are not reported for ACN. The proposed mechanism for both reactions involves the initial attack of DMF on the electron-poor double bond of either $(CF_3)_2=CF_2$ [25, 26] or HFTA [8].

It is thus reasonable to propose that the mechanism of dissociation of **1** in polar solvents, such as DMF, which involves nucleophilic attack of DMF on sulfur leading to the final formation of two moles of HFTA monomer (Eq. 13).



(13)

A similar mechanism can be used for the dissociation of **1** in DMSO as well, since in this molecule the S=O bond is strongly polarized and oxygen atom bears substantial negative charge.

Acknowledgement.

Authors are grateful to Dr. C. Junk for helpful discussion and suggestions and Joe Buriak for technical support.

4. Experimental

^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker DRX-500 (499.87 MHz) instrument using $CFCl_3$ or TMS as an internal standards. Unless stated otherwise, $CDCl_3$ was used as a lock solvent. GC and GC/MS analyses were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) and mass selective (GS/MS) detectors, respectively. Dry DMF, THF, ACN and DMSO (Aldrich) and all hydrocarbon starting materials were obtained from commercial sources and used without further purification. Compound **1** was prepared according modified procedure using CsF as a catalyst [2]. For most experiments **1** having purity ~96-98% (reminder DMF) was used. For experiments involving the reaction of **1** with **9** in different solvents (see below), compound **1** with purity 99.3 % (containing 0.55% of 3,3,5,5-tetrakis(trifluoromethyl)-1,2,4-trithiolane and 0.15 % of DMF) was used. Due to a high ratio of sulfur to fluorine, elemental analysis were not attempted for new materials, and the purity of all isolated compounds was established by GC and NMR spectroscopy to be at least 98%.

4.1.Crystallography:

X-ray data for **19, 25, 27, 20, 18** and **8** were collected at -100˚C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structures were solved and refined using the Shelxtl [27] software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #1043351 to #1043353 and #1043357 to #1043359 . Copies of the data can be obtained, free of charge, on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

*4.2. Reaction of **1** with substrates* **2,4,7,9-11,21,23,28,30,32** *(typical procedure).*

A mixture of 12-35 mmol of **1** (~10-20% excess), 10-30 mmol of the corresponding substrate , in 15 mL dry DMSO or DMF was agitated at 65-70 ^{o}C for period of time specified in Table 2. The reaction mixtures were analyzed by GC and NMR. Compounds **3** [7]**, 5a,5b,6a-c** [2]**, 12-14** [6]**, 29a, 29c, 31a, 31c, 33a, 33c [8]** were identified in reaction mixture by comparison of NMR data with values reported in the literature. Reaction conditions, ratio of reagents, and conversions are given in Table 2. ^{1}H, ^{13}C, ^{19}F NMR and mass-spectrometry data are given in Table 3.

*4.3. Preparation of compounds **8** and **25**.*

A mixture of 25-35 mmol of **1** (~10-15 % excess), 20-30 mmol of the corresponding substrate in 15 mL dry DMSO was agitated at 70 ^{o}C for 3-12 h (see Table 2). The reaction mixtures were monitored by GC. The reaction mixture was diluted with 200-300 mL of water, extracted by hexane (50 mL x 3), and combined organics washed by water (100 mL x 2), dried over $MgSO_4$ and hexane was removed under reduced pressure to give crude product of 96-98 % purity. Pure samples (~99%) of **8** and **25** were obtained by recrystallization from hexane. Reaction conditions, ratio of reagents, yields, melting (boiling) points and data of mass-spectrometry for products are given in Table 2. ^{1}H, ^{13}C, ^{19}F NMR and mass-spectroscopy data are given in Table 3.

*4.4. Preparation of compounds **18-20**.*

A mixture of 30 mmol of **1** (~10-15 % excess), 20 mmol of the corresponding anthracene in 15 mL dry DMF was agitated at 25 ^{o}C for 2-7 days (see Table 2). The reaction mixtures were monitored by GC. The reaction mixture was diluted with 200-300 mL of water, extracted by hexane (50 mL x 3), and combined organics washed by water (100 mL x 2), dried over $MgSO_4$ and hexane was removed under reduced pressure to give crude product of 96-98 % purity. Pure samples (~99%) of **8** and **25** were obtained by recrystallization from hexane. Reaction conditions, ratio of reagents, yields, melting points and data of mass-spectrometry for products are given in Table 2. ^{1}H, ^{13}C, ^{19}F NMR and mass-spectroscopy data are given in Table 3.

*4.5 Isomerization of the mixture **29a-c**.*

An agitated mixture of 1.1 g (0.01 mmol) **28**, 3.8 g (0.052 mol) of **1** and 12 mL of DMSO was kept at 65 ^{o}C for 24 h in a closed 20 mL glass vial. According to ^{19}F NMR at this point the reaction mixture contained products **2a-c** in ratio 46:25:29, respectively (^{1}H, ^{19}F NMR). The reaction mixture was placed inside a dry box and 0.4 g (0.0026 mol) of dry CsF was added and the heating was resumed. An aliquot of the reaction mixture was analyzed by NMR after 8 h at 65 ^{o}C which showed the reaction mixture contained compounds **29a** and **29c** in the ratio 75:25.

*4.6 Relative rates of the reaction of **1** and **9** in different solvents.*

To a 20 mL glass sample vial equipped with magnetic stir bar was added dry solvent (15 mL, Table 1), compound **9** (0.8 g, 0.01 mol, 98%, Aldrich), and compound **1** (2.0 g, 0.055 mol, 99.3%). Sealed sample vials were kept in a heating block (65 ^{o}C) with agitation. An aliquot of the reaction mixture was taken after 45 min. and analyzed by GC/MS and ^{1}H and ^{19}F NMR. Conversions and values of dipole moments of solvents are given in Table 1.

Table 2. Reaction of **1** with Different Substrates in the Absence of Metal Fluoride Catalyst. [a]

Entry No	**Reagent (mols)**	**Solv. (mL)**	**Temp. (Time, h)**	**Conv. (%)[b]**	**Selectivity (%) [c]**	**Product(s) (ratio, m.p ^{o}C) [c]**
1	**2** (0.01)	DMSO (15)	50^{o}C (30 min)	Quan t.	100	**3**
2	**4a** (0.01)	DMSO (15)	70 (2h)	100	95	**5a, 6a** (95:5)
3	**4b** (0.01)	DMSO (15)	70 (2h)	100	95	**5b, 6b** (95:5)

4	**5c** (0.01) S_x (0.015) CsF (0.001)	DMSO (15)	70 (8h)	100	95	**6c**
5	**7** (0.037)	DMSO (30)	70 (3h)	100	>95[d]	**8** (85%,[e] m.p.=35.5-36.5C)
6	**9** (0.01)	DMSO (15)	70 (2h)	100	>99	**12**
7	**10**	DMSO (15)	70 (2h)	100	>99	**13**
8	**11**	DMSO (15)	70 (2h)	100	>99	**14**
9	**15**(0.02)	DMF (15)	25C, (48h)	100	>99	**18** (80.6%,[e] m.p. 123-124^o C)
10	**16**(0.02)	DMF (15)	25C, (48h)	100	>99	(67.5%,[e] m.p. 142-143^{o}C)
11	**17**(0.02)	DMF (15)	25C, (1 week)	100	>99	**18**(80.6%,[e] m.p. 163-165^o C)
12	**21**[f] **(0.06)**	DMSO(15)	25C, (10days)	100	~70[g]	**22** (major)
13	**23**(0.02)	DMSO (15)	70 (12h)	100	>99	**25** (51%[e, h])

14	**26**(0.02)	DMSO (15)	65 (12h)	100	>95	**27**(18.5%[e], m.p. 53-55)
15	**28** (0.01)	DMSO (15)	70 (48h)	100	30[i]	**29a, 29b, 29c** (50:30:20)[c]
16	**30** (0.01)	DMSO (15)	70 (20h)	100	3.5[j]	**31a,31b,31c** (70:3.5:26.5)[c]
17	**32**(0.01)	DMSO (15)	70 (20h)	100		**33a, 33c** (2:98)

[a] reactions were carried out using 0.01-0.02 mol of organic substrate and 10 mol % excess of **1** in 15 ml of DMSO or DMF solvent

[b] conversion of organic substrate, NMR

[c] NMR data

[d] crude product contained ~ 5 % of unknown material (likely to be the corresponding 1,3-dithiolane), structure of which was not established.

[e] isolated yield

[f] three mol excess of **21**

[g] reaction mixture also contained ~ 30 % of unsaturated products containing two and three $-SCH(CF_3)_2$ groups

[h] purity 98%

[i] selectivity for **29b**

[j] selectivity for **31b**

Table 3. NMR and Mas-spectroscopy Data for New Materials [a]

Compound No	^{1}H NMR (δ, ppm, J, Hz)	^{19}F NMR (δ, ppm, J, Hz)	^{13}C NMR[b] (δ, ppm, J, Hz)	MS (*m/z*, M^+)
8	3.28(2H, m),	-73.43(3F, q, 9.6),	35.23, 43.71,	318 (M^+,$C_{11}H_8F_6S_2^+$)

	5.08(1H, t, 7.1), 7.40(3H,m), 7.45(2H, m)	-74.26(3F, q, 9.6)	47.80(sept., 32.2), 122.88(q, 278.0), 124.46(q, 282.2), 129.07, 129.34, 130.64	
18	5.12(1H,s), 5.23(1H,s), 7.20 (4H,m), 7.34(2H,d), 7.39(2H,d)	-64.56(s)	46.58, 47.53, 66.89(sept., 25.6), 122.46, 124.16(q, 286.0), 126.52, 126.84, 127.39, 138.40, 142.39	362(M^+, $C_{17}H_{12}F_6S^+$)
19	2.25(3H,s), 5.04(1H,s), 7.12 (2H, t), 7.18(2H,t), 7.26(2H,d), 7.33(2H,d)	-64.86(s)	16.35, 47.69, 50.31 68.30(sept., 25.3), 119.49, 124.20(q, 288.0), 126.35, 126.52, 127.17, 138.76, 144.91	376 (M^+,$C_{18}H_{14}F_6S^+$)
20	5.16(1H,s), 7.27 (4H, m), 7.39(2H,d), 7.73(2H,d)	-64.64(s)	47.82, 62.84 70.22(sept., 25.5), 122.95 123.80 (q, 288.0), 126.02, 127.74, 136.89, 142.76	441 (M^+, $C_{17}H_{11}BrF_6S^+$)
22	3.41(3H,s), 3.55(2H, s), 3.90(1H, sept, 7.7), 4.05(1H,d, 2.4), 4.15(1H, d, 2.4)	-66.90(d, 7.7)		254 (M^+,$C_7H_8F_6OS^+$)
27	2.33(1H,dd, 14.8, 10.5), 3.04(1H,dd, 14.7, 3.8), 3.75(1H, sept., 8.0), 4.47(1H,dd, 10.5, 3.5), 7.61(2H,m), 7.87(3H,m), 8.34(1H, d, 8.3)	-65.99(3F, sept, 8.9), -66.54(3F, sept., 8.9), -71.09(3F,q, 11.0), -71.43(3F, q, 11.0)	35.74,46.02, 51.68(sept. 31.2), 58.28(sept. 28.3), 122.67(q, 2777.5), 122.94(q, 278.5)' 123.28, 123.64,	518 (M^+, $C_{18}H_{10}F_{12}S_2^+$)

			123.91(q,280.0), 126.52, 127.15, 127.67, 128.23, 128.65, 131.83, 132.20, 133.60	
29b	3.29(2H,m), 3.86(1H, sept., 7.5), 4.22(1H, dd, 10.5, 3.5) 7.31(1H,m), 7.39(1H,m), 7.46(1H,d, 7.2), 7.67(1H, d, 7.2)	-66.11(3F, sept., 8.8), -66.73(3F, sept., 8.8), -71.35(3F, q, 10.2), -71.62(3F, q, 10.2)		
31b		-66.11(3F, sept., 9.2), -66.66(3F, sept., 9.2), -71.26(3F, q, 10.1), -71.58(3F, q, 10.1)		

[a] in $CDCl_3$

[b] {H} ^{13}C NMR spectrum

[1] T. Kitazume, T. Otaka, R. Takei, N. Ishikawa, Bull. Chem. Soc. Jpn. 49 (1976) 2491-2494.

[2] V.A. Petrov, W. Marshall, J. Fluorine Chem. 131 (2010) 1144-1155.

[3] V.A. Petrov, W. Marshall, J. Fluorine Chem. 143 (2012) 220-225.

[4] V.A. Petrov, W. Marshall, Beilstein J. Org. Chem. 9 (2013) 2615-2626-2619.

[5] T. Kitazume, N. Ishikawa, Lett. No. 3 (1973) 267-268.

[6] V. Petrov, W. Marshall, J. Fluorine Chem. 128 (2007) 729-735.

[7] V.A. Petrov, C.G. Krespan, W. Marshall, J. Fluorine Chem. 126 (2005) 1332-1341.

[8] V.A. Petrov, W. Marshall, J. Fluorine Chem. 132 (2011) 783-791.

[9] S.A. Postovoi, I.M. Vol'pin, N.I. Delyagina, M.V. Galakhov, Y.V. Zeifman, L.S. German, Izv. Akad. Nauk SSSR, Ser. Khim. (1989) 1380-1383.

[10] B.B. Snider, L. Fuzesi, Tetrahedron Lett. (1978) 877-880.

[11] D.J. Burton, Y. Inouye, J. Fluorine Chem. 18 (1981) 459-473.

[12] D.J. Burton, Y. Inouye, Tetrahedron Lett. (1979) 3397-3400.

[13] K. Burger, E. Huber, Chem.Ztg. 110 (1986) 211-213.

[14] H.W. Roesky, K.S. Dhathathreyan, J. Chem. Soc., Chem. Commun. (1984) 1053-1054.

[15] H.W. Roesky, K.S. Dhathathreyan, M. Noltemeyer, G.M. Sheldrick, Z. Naturforsch., B Anorg. Chem., Org. Chem. 40B (1985) 240-246.

[16] H. Gruetzmacher, N. Keweloh, H.W. Roesky, M. Noltemeyer, G.M. Sheldrick, J. Fluorine Chem. 37 (1987) 279-287.

[17] G. Rabe, H.W. Roesky, R. Bohra, H.G. Schmidt, M. Noltemeyer, J. Fluorine Chem. 52 (1991) 235-244.

[18] G. Rabe, J. Sundermeyer, H.W. Roesky, H.G. Schmidt, M. Noltemeyer, Chem. Ber. 123 (1990) 691-696.

[19] V.A. Petrov, W. Marshall, J. Fluorine Chem. 156 (2013) 262-267.

[20] V.A. Petrov, W. Marshall, R. Dooley, J. Fluorine Chem. (2014) Ahead of Print.

[21] W.J. Middleton, J. Org. Chem. (1965) 1395-1398.

[22] Y. Inouye, Burton D., J. Fluorine Chem. 14 (1979) 89-92.

[23] W.J. Middleton, J. Org. Chem. (1965) 1390-1394.

[24] R.D. Lide, Handbook of Organic Solvents, CRC Press, London, 1995.

[25] K. Cheburkov Yu.A., I.L., Izv. AN USSR. Ser. Khim. (1967) 346.

[26] M.N. Cheburkov Yu.A., Aronov Y.E., Knunyants, I.L., Izv. AN USSR. Ser. Khim. (1965) 1478.

[27] G. Sheldrick, (SHELXTL Sofware Suite, v. 6.0, Bruker Axes Corp., Madison WI, 1996.