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ANODIC FLUORINATION OF VINYL SULFIDES - SYNTHESIS OF α-FLUORO-β-THIO-α,β-UNSATURATED CARBONYL COMPOUNDS

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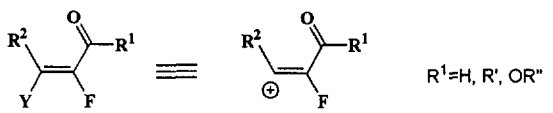
Key Words : anodic oxidation; electrofluorination; vinyl sulfides; enol thioethers; fluoro vinyl sulfides; α-fluoro enals; α-fluoro enones; α-fluoro alkenoates; dehydrofluorination.

Abstract : A series of new title compounds **3** was synthesised in moderate to excellent yield, by anodic fluorination of their corresponding hydrogenated homologues **1** in $Et_3N,3HF/CH_3CN$, followed by a chemical dehydrofluorination step. From vinyl sulfides, we showed that anodically generated vicinal difluoro adducts **2** were easily dehydrofluorinated by an E1cB mechanism, leading to **3** with high stereoselectivity in most cases. In contrast, the anodic behaviour of a thio flavone in the same media was slightly different, giving rise to the formation of vinylic fluoride **3** during the anodic fluorination.

INTRODUCTION

Many new synthetic methods have been developed during the last decade for the preparation of α-fluoro-α,β-unsaturated carbonyl compounds, e.g. reacting anions of α-substituted-α-fluoro acetates with carbonyl compounds [1,2,3] and alkylating agents [4], or using organometallic species [5] and fluoro carbenoid reagents [6].

α-fluoro-α,β-unsaturated carbonyl compounds bearing a leaving group Y in the β-position can be considered as cation equivalents (see below) and are therefore of particular interest. Addition-elimination reactions well demonstrated in the case of unfluorinated analogues [7], would lead to a wide variety of fluoro acrylates. Furthermore, such synthons have been used as precursors of fluoroheterocycles [8].

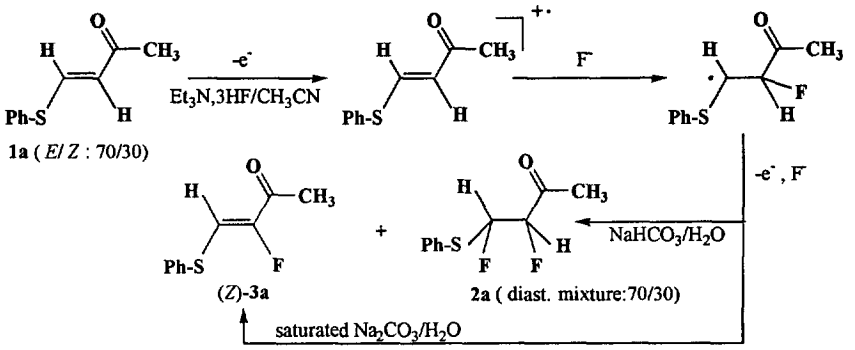


α-Fluoro-β-halogeno derivatives (Y=F, Br) have received much attention due to their use as intermediates in the synthesis of fluoro enynes and fluoro retinal analogues [9]. They can be obtained by palladium catalysed condensation of vicinal difluoro vinyl zinc reagents with acid halide or ethyl chloroformate[10], but also by the reaction of diethylamino sulfur trifluoride (DAST) and β-ketoesters [11].

α-Fluoro-β-alkoxy enones or acrylates (Y=OR) have been synthesised using [:CClF] carbene [12]. Due to the leaving group ability of the alkoxy substituent, catalytic acidic condition was employed to convert α-fluoro-β-methoxy acrylamide to 3-fluoro quinoline [13].

Recently, Pirrung *et al.* [14] described a new route to α-fluoro acrylate compounds involving the versatile reactivity of 3,3-bis(methylthio)-2-fluoro propenal (R^1=H, Y=R^2=S-Me) which was itself prepared from fluoro acetonitrile as the fluorinated precursor.

Previously we have reported [15] the selective nucleophilic anodic fluorination ($EC_{Nu}EC_{Nu}$ mechanism) of the β-phenylthio-α,β-unsaturated ketone **1a** in $Et_3N,3HF/CH_3CN$ (Scheme 1). After treatment with NH_4OH or $NaHCO_3$ (pH=7-8) a mixture of vicinal difluoro sulfide **2a** (29 %) and corresponding fluoro vinyl sulfide (*Z*)-**3a** (19 %) was obtained. Dehydrofluorination [16] can be completed if a more alkaline work-up (saturated Na_2CO_3 solution) is employed.



Scheme 1

In this paper we try to elaborate the generality of this new process for the preparation of α-fluoro-β-thio enals, -enones or -acrylates **3**.

RESULTS and DISCUSSION

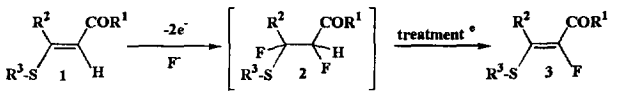
Aldehydes and Ketones:

In an initial study, acyclic vinyl sulfides **1** bearing a carbonyl group (R^1=H, alkyl, phenyl) were synthesised [17]. Sulfides **1a-c** were easily prepared by reaction between the thiol and commercially available 3-butyn-2-one [18], while **1d-i** were prepared by nucleophilic addition-elimination reaction of the appropriate thiolate anion with the corresponding β-chloro enones [19] and β-chloro enals [20], respectively. Their electrofluorination was then carried out using a known procedure [15].

Examination of the results given in Table 1 shows that the dehydrofluorination of difluoro adducts **2** obtained from unsaturated ketones **1b-c**, **1f** and aldehydes **1g-i** occurred smoothly on work-up of the electrolytic solution with a saturated aqueous solution of Na_2CO_3 as demonstrated for **1a**.

On the other hand, the dehydrohalogenation of α,β-difluoro ketones **2d-e** required more drastic conditions due probably to steric hindrance. Thus, we found that to obtain dehydrofluorination basic alumina [21] in refluxing diethyl ether was better suited than DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in dichloromethane [9c]: **3d** and **3e** were isolated in 63 % and 69 % yield respectively using these conditions. With the exception of aldehydic derivatives, this method allows easy preparation of **3** in reasonable isolated yields which seem not to be dependant on the type of R^3-S used (arylthio or alkylthio). However, we noticed a reduction in stability of these compounds (e.g. **3a** goinging to **3c**). The yields were also unaffected by the presence of an alkyl R^2 substituent, the low isolated yield observed for **3f** was probably due to the high potential of oxidation of the corresponding starting sulfide **1f**. We then expected that the reported instability of α-fluoro aldehydes in acidic media [22] could be used to explain the modest yields observed for the conversion of aldehydes **1g-i** (corresponding α,β-difluoro-β-thio aldehydes **2g-i** were generated in weakly acidic media during the anodic step). It is also worth noting that reductive desulfurisation of starting material was only observed for aldehydic vinyl sulfide **1i**, giving cinnamaldehyde (30 %) as the major product. A divided cell was used in an attempt to suppress the formation of this undesired product, but without success.

Table 1: Preparation of fluoro ketones and aldehydes 3 from 1 [a]



n°	Vinyl sulfides 1 CO-R^1	R^2	R^3	E_p^{ox} (V) [b]	Adducts 2 % yield [c] (M/m) [d]	treatment [e]	Fluoro vinyl sulfides 3 (% yield) [f]	*E/Z*
1a	CO-Me	H	Ph	1.43	undetected	no	**3a** (75)	0/100
1b	CO-Me	H	*p*-ClPh	1.58	undetected	no	**3b** (63)	0/100
1c	CO-Me	H	Et	1.51	undetected	no	**3c** (59)	0/100
1d	CO-Me	Me	Ph	1.43	**2d** 68 (68/32)	DBU/CH_2Cl_2	**3d** (56)	60/40
						Al_2O_3/Et_2O	**3d** (63)	50/50
1e	CO-Ph	Me	Ph	1.40	**2e** 72 (50/50)	DBU/CH_2Cl_2	**3e** (30)	50/50
						Al_2O_3/Et_2O	**3e** (69)	60/40
1f	CO-Ph	CF_3	Et	1.87	undetected	no	**3f** (20)	100/0 [g]
1g	CO-H	Me	Ph	1.50	undetected	no	**3g** (47)	32/68
1h	CO-H	*t*-Bu	Ph	1.44	undetected	no	**3h** (22)	78/22
1i	CO-H	Ph	Ph	1.51	undetected	no	**3i** (20) [h]	15/85 [g]

[a] ~3F/mol was commonly passed through 5 mmol of **1**. [b] First anodic peak observed by cyclic voltammetry of **1**[15] *vs* Pleskov electrode ($Ag/AgNO_3$ 10^{-2}M). [c] Yield calculated by ^{19}F NMR of crude electrolysis with $PhOCF_3$ as internal standard. [d] Major/minor. [e] After the neutralisation of the electrolytic solution with a saturated aqueous solution of Na_2CO_3 up to pH 9-10. [f] Isolated yields from **1**. [g] Major isomer unknown. [h] Other identified product from **1i** : cinnamaldehyde (~30 %).

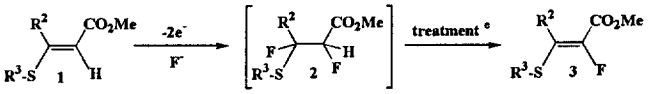
Esters

From a synthetic point of view, fluoro vinyl esters **3** (R^1=OMe) would be also promising fluoro compounds and one of them was recently synthesised [23] in several chemical steps. The derivatives **3j-k, 3m-n** were also obtained from their hydrogenated analogues [18] using our methodology, in satisfactory isolated yields (Table 2). Dehydrofluorination of corresponding difluoro sulfides **2** was achieved using DBU/CH_2Cl_2 as base.

Stereoselectivity

The relative configuration of trisubstituted fluoro olefins **3a-c, 3j-k** (R^2=H) was easily assigned from their ^1H NMR spectra which showed a characteristic *trans* $^3J_{H-F}$ coupling constant (28Hz < $^3J_{H-F}$ < 34Hz). The configuration of tetrasubstituted fluoro vinyl sulfides were more difficult to establish [24]. Stereochemistry was unambiguously determined for compounds **3d-e, 3g-h** for which each isomer was isolated as a pure compound, using both their ^1H-{^1H} NOE difference spectra and ^{13}C NMR spectral data (simultaneous upfield shift, by γ effects, observed on carbon of the carbonyl group and the saturated allylic carbon of R^2 in *cis* position in *Z*

Table 2: Preparation of fluoro esters 3 from 1 [a]

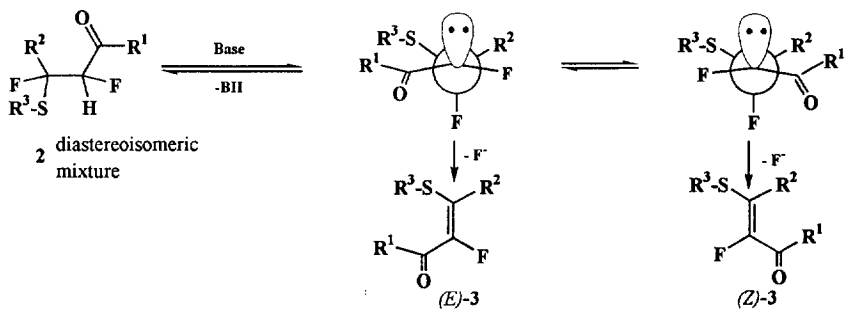


n°	Vinyl sulfides 1 R^2	R^3	E_p^{ox} (V) [b]	Adducts 2 % yield [c] (M/m) [d]	treatment [e]	Fluoro vinyl sulfides 3 (% yield) [f]	E/Z
1j	H	Ph	1.56	**2j** 78 (59/41)	DBU/CH_2Cl_2	**3j** (62)	0/100
1k	H	*p*-Cl-Ph	1.57	**2k** 75 (51/49)	DBU/CH_2Cl_2	**3k** (66)	0/100
1m	CO_2Me	*n*-Bu	1.73	**2m** 56 [f] (56/44)	DBU/CH_2Cl_2	**3m** (45)	100/0 [g]
1n	CO_2Me	Ph	1.53	**2n** 33 [f] (67/33)	DBU/CH_2Cl_2	**3n** (21)	100/0 [g]

[a] ~3F/mol was commonly passed through 5 mmol of **1**. [b] First anodic peak observed by cyclic voltammetry of **1**[15] *vs* Pleskov electrode ($Ag/AgNO_3$ 10^{-2}M). [c] Yield calculated by ^{19}F NMR of crude electrolysis with $PhOCF_3$ as internal standard. [d] Major/minor. [e] After the neutralisation of the electrolytic solution with a saturated aqueous solution of Na_2CO_3 up to pH 9-10. [f] Isolated yields from **1**. [g] Major isomer unknown.

stereoisomer: see experimental part: Table 5B). However this determination was uncertain for compounds **3f**, **3i**, **3m-n** which were formed as a single stereoisomer or a mixture consisting largely of a single compound. Isomerisation was not observed unlike some examples from the literature [25].

The results could be best explained by assuming an E1cB mechanism for the dehydrofluorination step: fast and reversible deprotonation of **2** forming a carbanion [26], followed by slow rate determining elimination of the fluoride anion as a poor leaving group (Scheme 2). Thus the carbanion can equilibrate to their most stable configuration. This explains the stereoselective formation of *Z*-**3** in cases where R^2=H even though the intermediates **2** are formed as mixtures of diastereoisomers.

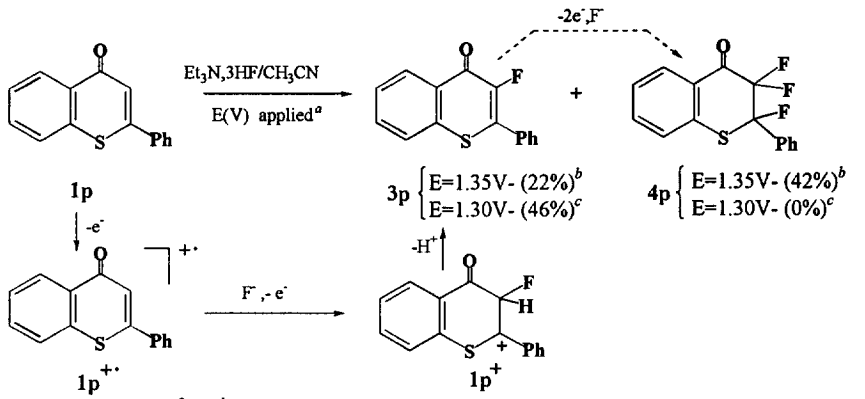


Scheme 2

The stereoisomeric ratio of **3h** (*E*/*Z*: 78/22), resulting from the dehalogenation of **1h** (R^1=H, R^2=*t*-Bu, R^3=Ph) also agreed with this mechanistic pathway since steric interaction between the *t*-butyl group and the carbonyl function became stronger in the carbanionic intermediate leading to *Z* geometry. Finally, dehydrofluorination of **2d** and **2e** furnished approximately a 1/1 isomeric ratio of **3d** and **3e** respectively, due to equal steric bulk of R^2 and the thio group (S-R^3) in carbanionic intermediates.

Application to heterocycles

To extend the scope of our methodology we examined the anodic fluorination of α,β-unsaturated cyclic sulfides, compounds of potential biological activity [27]. Several groups have reported that anodic fluorination of heterocycles was particularly advantageous over classical chemical approaches to the preparation of their fluorinated analogues [28]. We initially attempted to convert the commercially available thio flavone **1p** (Scheme 3). Surprisingly, the major isolated product, after anodic oxidation and neutralisation with Na_2CO_3/H_2O was the trifluorinated heterocycle **4p** (42 %), easy to separate from the minor 3-fluoro thio flavone **3p** (22 %).

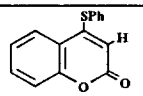
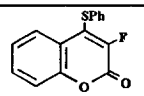


[a] *vs* Ag/AgNO3 (10^{-2}M). [b] Conversion rate 67%-2.2 F/mol. [c] Conversion rate 24%-3.1 F/mol.

Scheme 3

In contrast to the reaction of acyclic vinyl sulfides (e.g. **1e**), 3-fluoro thio flavone **3p** is present in the reaction mixture prior to neutralisation and can therefore be electrolytically reoxidised forming the trifluorinated sulfide [29] **4p**. On the other hand, the competitive oxidation of **3p** with respect to **1p** was less surprising since the value of their respective first anodic potential peak, established by cyclic voltammetry in the same condition, was practically identical (~ 1.75V). However, electrofluorination of **1p** at very low potential (1.30V) gave selectively **3p** in modest yield (46 %). This technique was then successfully applied to cyclic vinyl sulfides [30] **1q** and **1r**, allowing the isolation of their corresponding fluorinated analogues **3q** and **3r**, respectively (Table 3).

Table 3: Electrofluorination of cyclic vinyl sulfides

Vinyl sulfides 1	E_p^{ox} (V) [a]	Treatment [b]	Product % yield [c]
 **1q** [d]	1.80	no	 **3q (47%)**
 **1r** [e]	1.73	no	 **3r (28%)**

[a] vs Pleskov electrode (Ag/$AgNO_3$ 10^{-2}M). [b] After the neutralisation of the electrolytic solution with a saturated aqueous solution of Na_2CO_3 up to pH 9-10. [c] Isolated yields. [d] Electrofluorination carried out on 2.70 mmol of **1q** (conversion rate: 55 %-3.0F/mol). [e] Electrofluorination carried out on 4.72.mmol of **1r** (conversion rate:64 %-2.3F/mol) in CH_3CN/CH_2Cl_2: 4/1

CONCLUSION

We have shown that this electrofluorination-dehydrofluorination of vinyl sulfides is a versatile method to prepare α-fluoro-β-thio-α,β-unsaturated carbonyl compounds. The intermediate difluoro adducts **2** could not be obtained by using other reagents (e.g. F-TEDA-BF_4+Pyr.10HF) [31]. The corresponding vinyl sulfoxides were the only isolated products of the reaction. The study of the reactivity of **3** is currently under investigation; especially, their usefulness as Michael acceptors or as precursors of fluoroheterocycles is in progress.

EXPERIMENTAL SECTION

1 Generalities

a) - Analyses : ^1H NMR spectra (TMS, $CDCl_3$, ppm, Hz) were carried out on a BRUKER AC 200 (200MHz). The $^1H\{^1H\}$ NOE difference spectra were obtained on a AM 300 BRUKER (300MHz). ^{13}C NMR spectra (TMS, $CDCl_3$) were measured at 50.3 MHz on a BRUKER AC 200 whilst ^{19}F NMR ($CFCl_3$, $CDCl_3$) were registered on the same apparatus at 188.2 MHz (Ortho, meta, para and ipso carbons of aromatic ring are noticed by the following abbreviations, respectively: C_o, C_m, C_p, C_i. Uncorrected melting points were measured using a capillary tube in a Buchi instrument. Acetonitrile (chromasol quality) was stored over 3Å molecular sieves. Elemental analyses were performed by Service of Microanalyses of CNRS (Solaise - France).

b) - Preparative electrolysis : As previously described [15], all vinyl sulfides **1** have been studied in analytical conditions (cyclic voltammetry technique) to determine their working anodic potential range. Then, except where otherwise stated, selective anodic fluorination of **1** was carried out as previously, using an undivided glass cell (100 mL) and the same electric equipment. Each electrolysis was monitored by coulometry (3 faraday/mol had commonly been passed) and thin layer chromatography (TLC aluminum sheets - Silica gel 60 F_{254}) until the starting material was consumed. The electrolytic solution was neutralised by an iced cooled saturated aqueous solution of Na_2CO_3 up to pH=9-10. After the final work-up [15], ^{19}F NMR ($PhOCF_3$ as internal standard) analysis of the crude product was taken to determine the percentage of **2** and/or **3**. If necessary, an additive dehydrofluorinative treatment was then directly performed on the crude, using the convenient basic media (*vide infra*). The final crude product was purified by chromatography (Silica gel MERCK 60-petroleum ether/Et_2O: 95/5). Fine separations of olefins stereoisomers were obtained by medium pressure liquid chromatography (MPLC) on a 10-M20/25 Partisil column (Whatman).

c) - Dehydrofluorination with DBU: Typical procedure used for the dehydrofluorination of **2m**: 1 equivalent of DBU (0.56 mmol-82 µl) was slowly added (2 h) at 0°C to a stirred solution of pure **2m** (0.15 g-0.56 mmol) in 10 mL of dry CH_2Cl_2. The reaction was then monitored by TLC (petroleum ether/acetone: 90/10) and stirring was continued during 2.5 hours at 0°C. CH_2Cl_2 was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/acetone: 99/1) to give 0.11 g of **3m** (79 % yield from **2m**).

d) - Dehydrofluorination with Al_2O_3/Et_2O: Typical procedure used for the dehydrofluorination of **2e**: After electrolysis of 1.58 g (6.22 mmol) of **1e**, the oily residue (1.58 g) was dissolved in 50 mL of dry Et_2O and 6 g of basic Al_2O_3 (Merck-activity stage 1) was added. The resulting heterogeneous solution was stirred under reflux for 4 hours, until disappearance of **2e** was noted (the reaction was monitored by semicapillary GLC using a Varian 3300 chromatograph on a 15m x 0.53mm-OV1 column). The solution was then filtered and the filtrate was evaporated to dryness to give 1.35 g of crude product which was purified by column chromatography.

2) Table 4: Selected spectroscopic data of starting vinyl sulfides 1

Sulfide 1 [a]	mp °C	*E/Z*	^1H NMR ($CDCl_3$, TMS) δ, *J* (Hz)
Ketone			
1b	oil	*40/60*	2.20 (s, 1.2H, CH_3), 2.27 (s, 1.8H, CH_3), 5.98 (d, 0.4H, $^3J_{trans}$=15.3), 6.40 (d, 0.6H, $^3J_{cis}$= 9.6), 7.16 (d, 0.6H, $^3J_{cis}$ = 9.6), 7.29-7.43 (m, 4H, pClPhS), 7.63 (d, 0.4H, $^3J_{trans}$= 15.3).
1c	oil	*60/40*	1.33 (t, 3H, CH_3, ^3J= 7.0), 2.80 (m, 2H, S-CH_2), 6.17 (d, 0.6H, $^3J_{trans}$= 16.0), 6.37 (d, 0.4H, $^3J_{cis}$= 10.0), 7.18 (d, 0.4H, $^3J_{cis}$= 10.0), 7.70 (d, 0.6H, $^3J_{trans}$= 16.0).

Table 4 (Continued)

Sulfide 1 [a]	mp °C	*E/Z*	^{1}H NMR ($CDCl_3$, TMS) δ, *J* (Hz)
Aldehyde			
1g [b]	oil	*70/30*	2.04 (d, 0.9H, CH_3, ^4J = 1.1), 2.44 (d, 2.1H, CH_3, ^4J = 1.0), 5.48 (dd, 0.7H, =CH-, ^1J = 7.8, ^4J= 1.0), 6.15 (dd, 0.3H, =CH-, ^3J = 6.3, ^4J = 1.1), 7.45 (m, 5H, SPh), 9.79 (d, 0.7H, CHO, ^3J = 7.8), 10.06 (d, 0.3H, CHO, ^3J = 6.3).
(*E*)-1h [c]	77-78 [d]		1.53 (s, 9H, *t*-Bu), 5.30 (d, 1H, =CH-, ^3J = 8.0), 7.42 (s, 5H, SPh), 10.13 (d, 1H, CHO, ^3J = 8.0).
(*Z*)-1h [c]	oil		1.26 (s, 9H, *t*-Bu), 6.38 (d, 1H, =CH-, ^3J = 6.9), 7.09-7.41 (m, 5H, SPh), 9.96 (d, 1H, CHO, ^3J = 6.9).
(*E*)-1i [c]	50-51 [d]		5.67 (d, 1H, =CH-, ^3J = 8.0), 7.23 (m, 2H, Ph), 7.47 (m, 8H, Ph), 9.27 (d, 1H, CHO, ^3J = 8.0).
(*Z*)-1i [c]	oil		6.56 (d, 1H, =CH-, ^3J= 7.1), 7.10-7.60 (m, 10H, Ph+SPh), 10.33 (d, 1H, CHO, ^3J=7.1).
Ester			
1k	oil	*40/60*	3.71 (s, 1.2H, CH_3), 3.80 (s, 1.8H, CH_3), 5.65 (d, 0.4H, $^3J_{trans}$ = 15.0), 5.95 (d, 0.6H, $^3J_{cis}$ = 9.9), 7.20 (d, 0.6H, $^3J_{cis}$ = 9.9), 7.25-7.45 (m, 4H, *p*-ClPhS), 7.74 (d, 0.4H, $^3J_{trans}$ = 15.0).
1m	oil	*70/30* [e]	0.90 (t, 2.1H, CH_3, ^3J = 7.2), 0.94 (t, 0.9H, CH_3, ^3J = 7.1), 1.35-1.74 (m, 4H), 2.78-2.87 (m, 2H), 3.71 (s, 0.9H, CH_3), 3.76 (s, 2.1H, CH_3), 3.86 (s, 2.1H, CH_3), 3.88 (s, 0.9H, CH_3), 5.72 (s, 0.3H, =CH-), 6.32 (s, 0.7H, =CH-).
1n	oil	*70/30* [e]	3.33 (s, 2.1H, CH_3), 3.66 (s, 0.9H, CH_3), 3.72 (s, 0.9H, CH_3), 3.80 (s, 2.1H, CH_3), 5.50 (s, 0.3H, =CH-), 6.37 (s, 0.7H, =CH-), 7.28-7.56 (m, 5H, SPh).
Heterocycle			
1q	oil		4.75 (d, 2H, CH_2, ^4J = 1.5), 5.50 (t, 1H, =CH-, ^4J = 1.5), 7.43-7.59 (m, 5H, SPh).
1r	oil		5.63 (s, 1H, =CH-), 7.30-7.45 (m, 3H$_{arom}$), 7.50-7.60 (m, 5H$_{arom}$), 7.84 (d, 1H, ^3J = 7.6).

[a] ^{1}H NMR data of (*E/Z:70/30*)-**1a** and (*E/Z:30/70*)-**1j** have been previously given [15]. (*E/Z:60/40*)-**1e** and (*E/Z:90/10*)-**1d**: after separation of their respective stereoisomeric mixture (petroleum ether/Et_2O), ^{1}H and ^{13}C NMR data of (*E*)-**1d** (oil), (*Z*)-**1d** (mp 63-64°C-Et_2O) and (*E*)-**1e** (mp 40-42°C-unrecrystallised), (*Z*)-**1e** (mp 95-96°C-petroleum ether/Et_2O) were identical with those previously published [32]. ^{1}H NMR and ^{19}F NMR data of (*E/Z: 20/80*)-**1f** were identical with those previously published [33]. [b] Configuration proved by ^{1}H-{^{1}H} NOE experiment: irradiation of signal of CH_3 (2.04 ppm) underwent an enhancement (+7.5 %) of signal of vinylic proton (6.15 ppm), while irradiation of signal of CH_3 (2.44 ppm) gave an enhancement (+7.5 %) of signal of aldehydic proton (9.79 ppm). [c] After separation of stereoisomeric mixture by column chromatography (petroleum ether/Et_2O:95/5). [d] Et_2O. [e] Major isomer unknown.

3) Table 5A-C: Electrofluorination-dehydrofluorination of starting vinyl sulfides 1

Table 5A: Experimental conditions, physical and ^{19}F NMR data of fluoro vinyl sulfides 3

(*E/Z*)-1 [a] (x g, y mmol)	E^{ox}_w (V) [b]	Crude product[c] (x g)	(*E/Z*)-3 (mp °C, x isolated g, chem. yield %) [d]	^{19}F NMR ($CDCl_3$, $CFCl_3$) δ, *J* (Hz)
Ketone				
(*70/30*)-**1a** (1.12, 6.4)	1.30	(1.30)	(*Z*)-**3a** (oil, 0.94, 75)	-125.4 ($^3J_{HF}$ = 32.6)
(*40/60*)-**1b** (1.20, 5.2)	1.30	(1.21)	(*Z*)-**3b** (62-64°C, 0.59 , 63) [e,f]	-121.3 (d, $^3J_{HF}$ = 32.3)
(*60/40*)-**1c** (1.30, 10.0)	1.35	(1.40)	(*Z*)-**3c** (oil, 0.81, 59) [f]	-125.4 (qd, $^3J_{HF}$ = 33.0, $^4J_{HF}$ = 3.4)
(*60/40*)-**1d** (1.62, 8.4)	1.40	(1.07)	(*70/30*)-**3d** (oil, 1.07, 63)	
			(*E*)-**3d** (oil) [g]	-123.0 (broad s)
			(*Z*)-**3d** (oil) [g]	-114.4 (broad s)
(*90/10*)-**1e** (1.58, 6.2)	1.35	(1.35)	(*60/40*)-**3e** (oil, 1.17, 69)	
			(*E*)-**3e** (oil) [g]	-108.6 (broad s)
			(*Z*)-**3e** (36-40°C) [g,h]	-117.2 (broad m)
(*20/80*)-**1f** (1.00, 3.8)	1.65	(0.90)	(*100/0*)-**3f** (oil, 0.22, 20) [i]	-60.8 (d, 3F, CF_3, $^4J_{CF}$ = 22.7), -77.4 (q, 1F, $^4J_{CF}$ = 22.7)
Aldehyde				
(*70/30*)-**1g** (0.70, 3.9)	1.35	(0.80)	(*32/68*)-**3g** (oil, 0.37, 47)	
			(*E*)-**3g** (oil) [g]	-124.9 (dq, $^3J_{HF}$=19.0, $^4J_{HF}$ = 4)
			(*Z*)-**3g** (59-60°C) [e,g]	-121.8 (dq, $^3J_{HF}$=16.8, $^4J_{HF}$=3.0)
(*12/88*)-**1h** (1.10, 5.0)	1.35	(0.80)	(*78/22*)-**3h** (oil, 0.37, 22)	

Table 5A (continued)

(*E*/*Z*)-1 [a] (x g, y mmol)	E_w^{ox} (V) [b]	Crude product [c] (x g)	(*E*/*Z*)-3 (mp °C, x isolated g, chem. yield %) [d]	^{19}F NMR ($CDCl_3$, $CFCl_3$) δ, *J* (Hz)
			(*E*)-**3h** (oil)	-103.7 (d, $^3J_{HF}$ = 15.3)
			(*Z*)-**3h** (70-72°C) [g,h]	-106.7 (d, $^3J_{HF}$ = 17.3)
(*76*/*24*)-**1i** (1.20, 5.0)	1.30	(1.20)	(**85**/**15**)-**3i** (oil, 0.26, 20) [i,j]	
			(*Major*)-**3i** (103-104°C) [e,k]	-123.6 (d, $^3J_{HF}$ = 18.8)
			(*Minor*)-**3i**	-118.6 (d, $^3J_{HF}$ = 17.7) [l]
Ester				
(*30*/*70*)-**1j** (1.03, 5.3)	1.35	(1.25)	(Z)-**3j** (oil, 0.70, 62)	-124.7 (d, $^3J_{HF}$ = 31.6)
(*40*/*60*)-**1k** (0.50, 2.2)	1.35	(0.44)	(Z)-**3k** (oil, 0.32, 66)[f]	-123.6 (d, $^3J_{HF}$ = 31.2)
(*70*/*30*)-**1m** (1.16, 5.0)	1.50	(1.20) [m]	(*100*/*0*)-**3m** (oil, 0.11, 45) [i,n]	-123.0 (s)
(*70*/*30*)-**1n** (2.25, 8.9) [i]	1.45	(1.20) [m]	(*100*/*0*)-**3n** (oil, 0.48, 21) [i,p]	-122.4 (s)
Heterocycle				
1p (1.00, 4.2)	1.35	(0.96)	**3p** (oil, 0.16, 22)[f]	-126.4 (s)
			4p (oil, 0.35, 42)	-110.0 (ddd, $^2J_{FF}$ = 267.3, $^3J_{FF}$ = 7.6), -132.6 (ddd, $^2J_{FF}$ = 267.3, $^3J_{FF}$ =14.7), -150.9 (dd, $^3J_{FF}$=14.7, $^3J_{FF}$=7.6)
1q (0.52, 2.7)	1.50	(0.59)	**3q**, (oil, 0.15, 47)	-148.6 (t, $^4J_{HF}$ = 5.2)
1r (1.20, 4.7) [q]	1.45	(1.10)	**3r**, (oil, 0.15, 28)[f]	-121.7 (s)

[a] Except where otherwise stated electrofluorination of x g (y mmol) of **1** was performed as previously described [15]. [b] Working potential *vs* Pleskov electrode (Ag/$AgNO_3$ 10^{-2}M). [c] After all treatments. [d] Chemical yield of isolated **3** from the converted sulfide **1**. [e] Recrystallisation in petroleum ether-Et_2O. [f] Conversion rate: 78 % from **1b**, 92 % from **1c**, 86 % from **1k**, 67 % from **1p**, 55 % from **1q**, 64% from **1r**. [g] Isolated after separation of the stereoisomeric mixture by MPLC (petroleum ether/acetone:95/5). [h] Unrecrystallised. [i] Configuration unknown. [j] Other identified product from 1i: cinnamaldehyde (0.20 g, ~30 %). [k] Obtained by crystallisation (petroleum ether-Et_2O) from the stereoisomeric mixture. [l] Deduced from ^{19}F NMR of the stereoisomeric mixture. [m] Before treatment with DBU. [n] Purification of the crude product (1.20 g) by column chromatography afforded 0.76 g of **2m** (diast. mixture: *56*/*44*, 56 %); the dehydrofluorination of 0.15 g (0.55mmol) of **2m** with DBU gave 0.11 g of **3m** after purification by column chromatography (petroleum ether/acetone: 99/1). [p] Purification of the crude product (1.20 g) by column chromatography afforded 0.85 g of **2n** (diast. mixture: *77*/*23*, 33 %); dehydrofluorination of 0.76 g of **2m** with DBU gave 0.48 g of **3n** after purification by column chromatography (petroleum ether/acetone: 99/1). [q] Electrofluorination carried out in CH_3CN/CH_2Cl_2: 4/1.

Table 5B: ^{1}H and ^{13}C NMR data of fluoro vinyl sulfides 3

(*E*/*Z*)-3	^{1}H NMR ($CDCl_3$, TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$, TMS) δ, J_{CF} (Hz)
Ketone		
(*Z*)-**3a** [a]	see Ref 15	25.3 (C_1), 120.8 (d,C_4, $^2J_{CF}$ = 14.3), 128.6 (C_p), 129.7 ($2CH_{o/m}$), 130.7 ($2CH_{o/m}$), 132.3 (C_i), 152.2 (d, C_3, $^1J_{CF}$ = 259.1), 188.6 (d, C_2=O, $^2J_{CF}$= 30.0).
(*Z*)-**3b** [a]	2.30 (d, 3H, CH_3, $^4J_{HF}$ = 3.3), 6.95 (d, 1H, =CH-, $^3J_{HF}$ = 32.3), 7.32-7.43 ($m,4H_{arom}$).	25.2 (C_1), 119.7 (d, C_4, $^2J_{CF}$ = 14.3), 129.7 ($2CH_{o/m}$), 130.8 (C_i), 132.3 ($2CH_{o/m}$), 134.9 (C_p), 152.4 (d, C_3, $^1J_{CF}$ = 260.4), 188.4 (d, C_2=O, $^2J_{CF}$ = 30.3).
(*Z*)-**3c**	1.38 (t, 3H, CH_3, $^3J_{HH}$ = 7.4), 2.27 (d, 3H, CH_3, $^4J_{HF}$ = 3.4), 2.86 (q, 2H, CH_2, $^3J_{HH}$ = 7.4), 6.87 (d, 1H, =CH-, $^3J_{HF}$ = 33.0).	15.6 ($C_{2'}$), 28.2 (d, C_1, $^3J_{CF}$ = 1.1), 28.3 ($C_{1'}$), 121.2 (d, C_4, $^2J_{CF}$= 15.0), 152.8 (d, C_3, $^1J_{CF}$= 255.9), 188.0 (d, C_2=O, $^2J_{CF}$= 30.1).
(*E*)-**3d** [b]	1.77 (d, 3H, CH_3, $^4J_{HF}$ = 4.6), 2.32 (d, 3H, CH_3, $^4J_{HF}$ = 4.7), 7.45 (m, 5H, Sph).	16.2 (d, C_5, $^3J_{CF}$ = 8.0), 26.5 (d, C_1, $^3J_{CF}$ = 3.1), 129.6 ($2CH_{o/m}$), 129.9(C_p), 130.2 (C_i), 133.9 (d, C_4, $^2J_{CF}$ = 19.1), 135.8 ($2CH_{o/m}$), 148.0 (d, C_3, $^1J_{CF}$= 246.8), 191.7 (d, C_2=O, $^2J_{CF}$= 35.2).
(*Z*)-**3d** [b]	2.06 (d, 3H, CH_3, $^4J_{HF}$ = 3.6), 2.30 (d, 3H, CH_3, $^4J_{HF}$ = 5.2), 7.52 (m, 5H, SPh).	16.1 (C_5), 27.7 (d, C_1, $^3J_{CF}$ = 1.9), 129.2 (C_i), 129.3 ($2CH_{o/m}$), 129.6 (C_p), 133.0 (d, C_4, $^2J_{CF}$ = 14.9), 135.8 ($2CH_{o/m}$), 148.8 (d, C_3, $^1J_{CF}$ = 246.8), 191.1 (d, C_2=O, $^2J_{CF}$=38.0).

Table 5B (continued)

(*E*/*Z*)-3	^{1}H NMR ($CDCl_3$, TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$, TMS) δ, J_{CF} (Hz)
(*E*)-3e [b,c]	2.07 (d, 3H, CH_3, $^4J_{HF}$=3.6), 7.25-7.66 (m, 8H, Ph+SPh), 7.84-7.97 (m, 2H, PhCO).	16.4 (C_4), 128.3 ($2CH_{o/m}$), 129.1 ($2CH_{o/m}$), 129.2 (C_p), 129.3 ($2CH_{o/m}$), 131.0 (C_i), 132.7 (C_p), 135.1 ($2CH_{o/m}$), 135.5 (d, C_3, $^2J_{CF}$= 17), 136.3 (d, Ci, J_{CF} = 5.3), 149.4 (d, C_2, $^1J_{CF}$ =259.5), 185.7 (d, C_1=O, $^2J_{CF}$= 31.8).
(*Z*)-3e [a,b,c]	1.91 (d, 3H, CH_3, $^4J_{HF}$= 4.8), 7.26-7.61 (m, 8H), 7.93-7.99 (m, 2H, PhCO).	16.7 (C_4), 128.3 ($2CH_{o/m}$), 128.9 (d, C_i, $^4J_{CF}$ = 3.6)), 129.2 ($2CH_{o/m}$), 129.3 ($2CH_{o/m}$), 129.5 (C_p), 132.8 (C_p), 133.7 (d, C_3, $^2J_{CF}$ = 14.6), 135.6 ($2CH_{o/m}$), 137.0(d, C_i, $^3J_{CF}$ = 4.9), 153.8 (d, C_2, $^1J_{CF}$ = 251.2), 185.7 (d, C_1=O, $^2J_{CF}$= 33.8).
(*100/0*)-3f	1.16 (t, 3H, CH_3, $^3J_{HH}$ = 7.5), 2.71 (q, 2H, CH_2, $^3J_{HH}$ = 7.5), 7.51-7.73 (m, 3H, Ph), 7.88-7.95 (m, 2H, Ph).	13.8 (CH_3), 29.8 (CH_2), 108.9 (qd, C_3, $^2J_{CF}$= 35.7, $^2J_{CF}$= 29.2), 122.2 (q, C_4, $^1J_{CF}$= 274.5), 129.2 ($2CH_{o/m}$), 129.5 ($2CH_{o/m}$), 133.7 (C_i), 135.2(C_p), 159.6 (d, C_2, $^1J_{CF}$= 311.3), 185.1 (d, $^2J_{CF}$= 28.3).
Aldehyde		
(*E*)-3g [e]	2.02 (d, 3H, CH_3, $^4J_{HF}$= 4), 7.43 (s, 5H, SPh), 10.21 (d, 1H, CHO, $^3J_{HF}$= 19.0).	17.1 (d, C_4, $^3J_{CF}$ = 4.4), 128.9 (C_p), 129.2 (C_i), 129.6 ($2CH_{o/m}$), 132.5 ($2CH_{o/m}$), 136.5 (d, C_3, $^2J_{CF}$= 21.4), 154.1 (d, C_2, $^1J_{CF}$= 261.6), 180.6 (d, C_1=O, $^2J_{CF}$= 24.7).
(*Z*)-3g [c,e]	2.00 (d, 3H, CH_3, $^4J_{HF}$= 3), 7.52 (s, 5H, SPh), 9.65 (d, 1H, CHO, $^3J_{HF}$= 16.8.	14.5 (C_4), 127.6 (d, C_i, $^4J_{CF}$ = 3.0), 129.6 ($2CH_{o/m}$), 130.3 (C_p), 136.1 ($2CH_{o/m}$), 141.2 (d, C_3, $^2J_{CF}$= 13.7), 149.7 (d, C_2, $^1J_{CF}$= 242.8), 177.6 (d, C_1=O, $^2J_{CF}$= 26.9).
(*E*)-3h [c,e]	1.25 (d, 9H, *t*-Bu, $^5J_{HF}$= 1.5), 7.29 (m, 5H, SPh), 10.12 (d, 1H, CHO, $^3J_{HF}$= 15.3).	29.3 (d, $3CH_3$, $^4J_{CF}$= 4.1), 39.3 (d, C_4, $^3J_{CF}$= 3.4), 127.0 (C_p), 128.0 (d, $2CH_{o/m}$, J_{CF}= 0.7), 129.5 ($2CH_{o/m}$), 135.7 (d, C_i, $^4J_{CF}$= 3.2), 142.0 (d, C_3, $^2J_{CF}$= 12.8), 158.3 (d, C_2, $^1J_{CF}$= 277.0), 184.2 (d, C_1=O, $^2J_{CF}$= 25.6).
(*Z*)-3h [c,e]	1.52 (d, 9H, *t*-Bu, $^5J_{HF}$= 1.5), 7.23-7.38 (m, 5H, SPh), 9.92 (d, 1H, CHO, $^3J_{HF}$= 17.3).	32.0 (d, $3CH_3$, $^4J_{CF}$ = 1.9), 37.8 (C_4), 127.7 (C_p), 128.6 (C_i), 129.1 ($2CH_{o/m}$), 130.4 (d, $2CH_{o/m}$, J_{CF}= 1.7), 151.4 (d, C_3, $^2J_{CF}$= 23.0), 153.2 (d, C_2, $^1J_{CF}$= 253.6), 180.2 (d, C_1=O, $^2J_{CF}$= 26.8).
(*Major*)-3i [a,d]	7.08-7.27 (m, 10H, Ph+SPh), 9.01 (d, 1H, CHO, $^3J_{HF}$= 18.8).	128.2 ($2CH_{o/m}$), 128.5 (d, C_i, $^4J_{CF}$ = 2.4), 128.8 ($2CH_{o/m}$), 129.1 (C_p), 129.7 (C_p), 129.9 (d, C_i, $^3J_{CF}$= 3.6), 130.9 (d, $2CH_{o/m}$, J_{CF}= 2.9), 134.9 ($2CH_{o/m}$), 145.5 (d, C_3, $^2J_{CF}$= 15.0), 150.8 (d, C_2, $^1J_{CF}$= 256.3), 179.8 (d, C_1=O, $^2J_{CF}$= 21.0).
(*Minor*)-3i [d]	7.08-7.27 (m, 10H, Ph+SPh), 10.34 (d, 1H, CHO, $^3J_{HF}$= 17.7).	
Ester		
(Z)-3j	3.81 (s, 3H, CH_3), 7.07 (d, 1H, =CH-, $^3J_{HF}$= 31.6), 7.34-7.64 (m, 5H, SPh).	52.4 (O-CH_3), 121.5 (d, C_3, $^2J_{CF}$ = 13.3), 128.5 (C_p), 129.6 ($2CH_{o/m}$), 130.9 ($2CH_{o/m}$), 132.5 (C_i), 144.5 (d, C_2, $^1J_{CF}$ = 253.6), 159.6 (d, C_1=O, $^2J_{CF}$= 32.6).
(Z)-3k	3.83 (s, 3H, CH_3), 6.99 (d, 1H, =CH-, $^3J_{HF}$= 31.2), 7.32-7.43 (m, 5H, SPh).	52.6 (O-CH_3), 120.6 (d, C_3, $^2J_{CF}$ = 13.3), 129.8 ($2CH_{o/m}$), 131.0 (C_i), 132.3 ($2CH_{o/m}$), 134.8 (C_p), 144.9 (d, C_2, $^1J_{CF}$= 255.3), 159.6 (d, C_1=O, $^2J_{CF}$= 32.6).
(*100/0*)-3m [d]	0.92 (t, 3H, CH_3, $^3J_{HH}$ = 7.2), 1.33-1.50 (m, 2H), 1.51-1.70 (m, 2H), 2.75 (t, 2H, $^3J_{HH}$ = 7.2), 3.83 (s, 3H, CH_3), 3.89 (s, 3H, CH_3).	13.5 (CH_3), 21.7 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 53.2 (CH_3), 53.6 (CH_3), 127.2 (d, C_2, $^2J_{CF}$= 18.4), 143.7 (d, C_3, $^1J_{CF}$= 264.4,), 159.1 (d, CO, $^2J_{CF}$ = 32.1), 163.3 (d, CO, $^3J_{CF}$= 10.1).
(*100/0*)-3n [d]	3.38 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 7.32-7.58 (m, 5H, SPh).	52.7 (CH_3), 52.8 (CH_3), 128.3 (d, C_2, $^2J_{CF}$=18.0), 129.2 ($2CH_{o/m}$), 130.3 (C_p), 132.5 (C_i), 135.8 ($2CH_{o/m}$), 142.2 (d, C_3, $^1J_{CF}$=264.8), 158.8 (d, Co, $^2J_{CF}$=31.9), 162.0 (d, Co, $^3J_{CF}$=10.1)
Heterocycle		
3p [f]	7.26-7.71 (m, 8H), 8.60 (d, 1H, *J* = 7.9).	125.9 (1CH), 127.3 (1CH), 129.0 (5CH), 130.6 (1CH), 131.0 (C_q), 131.8 (1CH), 132.8 (d, C_q, $^3J_{CF}$ = 6.9), 134.1 (d, C_2, $^2J_{CF}$ = 21.0), 136.7 (C_q), 147.9 (d, C_3, $^1J_{CF}$= 240.8), 173.0 (d, C_4=O, $^2J_{CF}$= 19.7).
3q	4.48 (d, 2H, CH_2, $^4J_{HF}$= 5.2), 7.33 (m, 3H, SPh), 7.53-7.60 (m, 2H, SPh).	67.1 (d, CH_2, $^3J_{CF}$ = 5.2), 125.5 (C_i), 130.0 ($2CH_{o/m}$), 130.7 (C_p), 134.8 ($2CH_{o/m}$), 136.2 (d, C_3, $^2J_{CF}$ = 7.6), 141.7 (d, C_2, $^1J_{CF}$ = 269.6), 163.7 (d, C_1=O, $^2J_{CF}$= 29.2).
3r	7.29-7.65 (m, 8H), 7.90 (d, 1H, J_{HH}=8.0	116.9 (d, 1CH, J_{CF}= 1.3), 118.8 (C_q), 125.1 (1CH), 126.2 (d, 1CH, J_{CF}= 6.6), 128.7 (1CH), 129.5 (2CH), 130.5 (d, C_q, J_{CF}= 3.1), 131.1 (d, 1CH, J_{CF} = 2.7), 131.4 (d, C_q, J_{CF}= 1.3), 131.7 (d, 2CH, J_{CF}= 1.2), 146.1 (d, C_3, $^1J_{CF}$= 258.6), 149.7 (d, C_4, $^2J_{CF}$= 2.9), 154.1 (d, C_2=O, $^2J_{CF}$= 30.1).

[a] Anal. Calc for **3a** $C_{10}H_9SOF$: C, 61.21; H, 4.62; S, 16.34; F, 9.68. Found: C, 61.54; H, 4.78; S, 16.20; F, 10.03; **3b** $C_{10}H_8SOClF$: C, 52.07; H, 3.50; S, 13.90, F, 8.24. Found: C, 52.10; H, 3.50; S, 12.61, F, 7.96; **(Z)-3e**: $C_{16}H_{13}SOF$: C, 70.57; H,

4.82; S, 11.75; F, 6.98. Found: C, 70.83; H, 4.73; S, 11.79; F, 6.85; (***Major* 3i**): $C_{15}H_{11}SOF$: C, 69.75; H, 4.29; S, 12.41. Found: C, 70.30; H, 4.65; S, 13.53; **(Z)-3k**: $C_{10}H_8SO_2ClF$: C, 48.69; H, 3.27; S, 13.00; F, 7.70. Found: C, 48.50; H, 3.24; S, 12.85; F, 7.45. [b] Isolated after separation of the stereoisomeric mixture by MPLC (petroleum ether/acetone: 95/5). [c] Configurations proved by ^1H-{^1H} NOE experiments: **(*E*)-3e and (*Z*)-3e**: irradiation of CH_3 (2.07 ppm, ***E***) had no effect on two ortho hydrogens of PhCO, while irradiation of CH_3 (1.91 ppm, ***Z***) underwent an enhancement (+3.5 %) of two ortho hydrogens of PhCO; **(Z)-3g**: irradiation of methyl (2.00 ppm) underwent an enhancement (+4.2 %) of aldehydic proton (9.65 ppm); **(*E*)-3h** and **(*Z*)-3h**: irradiation of *t*-Bu (1.25 ppm, ***E***) had no effect on aldehydic hydrogen (10.12 ppm, ***E***) while irradiation of *t*-Bu (1.53 ppm, ***Z***) underwent an enhancement (+2 %) of aldehydic hydrogen (9.92 ppm, ***Z***); [d] Configuration unknown. [e] Isolated after separation by a second column chromatography. [f] **4p**: ^1H NMR: δ 7.21-7.72 (m, 8H), 8.15 (d, 1H, J = 7.9); ^{13}C NMR: 105.2 (ddd, C_2, $^1J_{CF}$ = 220.1, $^2J_{CF}$ = 25.9, $^2J_{CF}$ = 27.9), 118.2 (ddd, C_3, $^1J_{CF}$ = 267.3, $^1J_{CF}$ = 249.6, $^2J_{CF}$ = 47.9), 126.2 (1CH), 126.3 (1CH), 126.9 (2CH), 127.4 (d, C_q, J_{CF} = 2.7), 128.8 (2CH), 130.8 (2CH), 131.3 (C_q), 135.8 (1CH), 136.1 (C_q), 182.0 (t, C_4=O, $^2J_{CF}$ = 51.9).

Table 5C: Characterization of intermediate Difluoro sulfides 2

(M/m)[a] -Difluoro sulfide 2	Yield % [b]	^{19}F NMR ($CDCl_3$, $CFCl_3$) δ, J (Hz)
Ketone		
(*68/32*)-**2d**	68	(***Major***)-**2d**: -127.6 (m, 1F, $^3J_{FF}$ = 21.7), -190.8 (dd, 1F, $^2J_{HF}$ = 48.7, $^3J_{FF}$ = 21.7). (***Minor***)-**2d**: -124.9 (m, 1F, $^3J_{FF}$ = 18.6), -188.6 (dd, 1F, $^2J_{HF}$ = 48.7, $^3J_{FF}$ = 18.6).
Ester		
(*50/50*)-**2e**	72	(***diast. mixture***): -121.6 (m, 0.5F, $^3J_{FF}$ = 19.6), -122.7 (m, 0.5F, $^3J_{FF}$ = 23.3), -188.2 (dd, 0.5F, $^3J_{FF}$ = 19.6, $^2J_{HF}$ = 47.1), -190.4 (dd, 0.5F, $^3J_{FF}$ = 23.3, $^2J_{HF}$ = 47.6).
(*59/41*)-**2j**	78	see Ref. 15
(*51/49*)-**2k**	75	(***Major***)-**2k**: -157.6 (ddd, 1F, $^2J_{HF}$ = 42.7, $^3J_{HF}$ = 10.8, $^3J_{FF}$ = 23.2), -198.0 (ddd, 1F, $^2J_{HF}$ = 46.1, $^3J_{HF}$ = 20.8, $^3J_{FF}$ = 23.2). (***Minor***)-**2k**: -162.8 (ddd, 1F, $^2J_{HF}$ = 45.4, $^3J_{HF}$ = 21.4, $^3J_{FF}$ = 17.8), -200.9 (ddd, 1F, $^2J_{HF}$ = 43.6, $^3J_{HF}$ = 22.6, $^3J_{FF}$ = 17.8).
(*56/44*)-**2m**	56 [c]	(***Major***)-**2m** [d]: -151.7 (t, 1F, $^3J_{HF}$ = $^3J_{FF}$ = 23.6), -201.9 (dd, 1F, $^2J_{HF}$ = 46.3, $^3J_{FF}$ = 23.6). (***Minor***)-**2m** [e]: -149.5 (t, 1F, $^3J_{HF}$ = $^3J_{FF}$ = 20.0), -190.7 (dd, 1F, $^2J_{HF}$ = 45.8, $^3J_{FF}$ = 20.0).
(*67/33*)-**2n**	33 [c]	(***Major***)-**2n** [f]: -145.2 (dd, 1F, $^3J_{HF}$ = 23.5, $^3J_{FF}$ = 17.8), -202.8 (dd, 1F, $^2J_{HF}$ = 46.2, $^3J_{FF}$ = 17.8). (***Minor***)-**2n** [g]: -146.7 (t, 1F, $^3J_{HF}$ = $^3J_{FF}$ = 19.9), -189.4 (dd, 1F, $^2J_{HF}$ = 45.5, $^3J_{FF}$ = 19.9).

[a] (Major/Minor). [b] Evaluated yield by ^{19}F NMR of crude electrolysis with $PhOCF_3$ as internal standard. [c] Isolated yield. [d] **(*Major*)-2m**: oil, ^1H NMR: δ 0.91 (t, 3H, CH_3, $^3J_{HH}$ = 7.2), 1.34-1.62 (m, 4H, 2 CH_2), 2.56-2.82 (m, 2H, CH_2), 3.84 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 5.47 (dd, 1H, $^2J_{HF}$ = 46.3, $^3J_{HF}$ = 23.6); 13.5 (CH_3), 21.9 (CH_2), 29.1 (CH_2), 31.2 (CH_2), 53.1 (CH_3), 53.2 (CH_3), 89.9 (dd, C_3, $^1J_{CF}$ = 201.8, $^2J_{CF}$ = 24.5), 101.6 (dd, C_2, $^1J_{CF}$ = 241.1, $^2J_{CF}$ = 20.8), 164.9 (dd, CO, $^2J_{CF}$ = 24.8, $^3J_{CF}$ = 2.4), 165.3 (dd, CO, $^2J_{CF}$ = 30.3, $^3J_{CF}$ = 6.4); Anal. Calc for $C_{10}H_{16}SO_4F_2$: C, 44.44; H, 5.97; S, 11.86; F, 14.06. Found: C, 44.60; H, 5.96; S, 11.84; F, 13.70. [e] **(*Minor*)-2m**: oil, ^1H NMR: δ 0.91 (t, 3H, CH_3, $^3J_{HH}$ = 7.2), 1.34-1.63 (m, 4H, 2 CH_2), 2.57-2.80 (m, 2H, CH_2), 3.89 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 5.37 (dd, 1H, $^2J_{HF}$ = 45.8, $^3J_{HF}$ = 20.0); ^{13}C NMR: δ 13.4 (CH_3), 21.8 (CH_2), 29.4 (CH_2), 31.0 (CH_2), 53.0 (CH_3), 53.6 (CH_3), 89.0 (dd, C_3, $^1J_{CF}$ = 199.8, $^2J_{CF}$ = 24.1), 100.7 (dd, C_2, $^1J_{CF}$ = 241.4, $^2J_{CF}$ = 23.2), 164.5 (dd, CO, $^2J_{CF}$ = 24.8, $^3J_{CF}$ = 1.7), 165.4 (dd, CO, $^2J_{CF}$ = 32.8, $^3J_{CF}$ = 3.9). [f] **(*Major*)-2n**: oil; ^1H NMR: δ 3.49 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 5.64 (dd, 1H, $^2J_{HF}$ = 46.2, $^3J_{HF}$ = 23.5), 7.26-7.47 (m, 3H, SPh), 7.47-7.60 (m, 2H, SPh); ^{13}C NMR: δ 53.1 (CH_3), 53.2 (CH_3), 89.8 (dd, C_3, $^1J_{CF}$ = 200.8, $^2J_{CF}$ = 24.8), 104.2 (dd, C_2, $^1J_{CF}$ = 245.1, $^2J_{CF}$ = 20.2), 126.8 (C_i), 129.2 ($2CH_{o/m}$), 130.6 (C_p), 136.5 (d, $2CH_{o/m}$, J_{CF} = 1.3), 164.1 (dd, CO, $^2J_{CF}$ = 30.8, $^3J_{CF}$ = 6.8), 164.6 (dd, CO, $^2J_{CF}$ = 24.8, $^3J_{CF}$ = 2.1). [g] **(*Minor*)-2n**: oil; ^1H NMR: δ 3.41 (s, 3H, CH_3), 3.94 (s, 3H, CH_3), 5.50 (dd, 1H, $^2J_{HF}$ = 45.5, $^3J_{HF}$ = 19.9), 7.32-7.48 (m, 3H, SPh), 7.49-7.63 (m, 2H, SPh).

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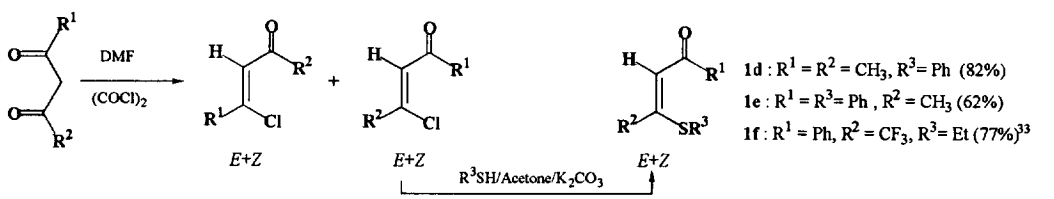

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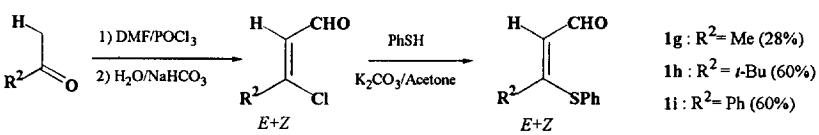

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