

β -Chlorovinylaldehydes as intermediates in the synthesis of new functionalized β -fluoroalkoxyvinyl aldehydes and corresponding alcohols

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Abstract

*A convenient synthesis of a series of new β -fluoroalkoxyvinyl aldehydes (9-30) and their corresponding alcohols (31-37) from β -chloro- α,β -unsaturated aldehydes (1-8) was developed. The etherification reaction and the carbonyl reduction were successfully achieved, affording the desired products in good yields. The mechanism of the nucleophilic vinylic substitution reaction of the β -chlorovinylaldehyde **3** has been studied using DFT methods. IRC analysis shows the presence of a hidden intermediate, in agreement with one kinetic step two-stage process. The isomerization of intermediate **3-Z** into intermediate **3-E** was explained in terms of the small energy gap difference between the two intermediates Int_Z and Int_E and the thermodynamic stability of compound **3-E** compared to **3-Z**.*

Key words : β -chlorovinylaldehydes, nucleophilic vinylic substitution, β -fluoroalkoxyvinyl aldehydes, isomerization, DFT.

Introduction

It is generally known that the vinyl ether compounds are of considerable interest due to their potential applications in a wide array of chemical transformations¹⁻⁴. They are also important raw materials used as easily degradable vinyl polymer materials⁵, precursors of active pharmaceutical compounds⁶ and efficient intermediates in several reactions⁷⁻⁸. More interestingly, in the last decades, vinyl ethers bearing fluorine atoms have attracted much attention owing to their beneficial effects on the metabolic stability and lipophilicity of biologically active alkyl ethers^{9,10}. Therefore, a variety of methods have been reported for the synthesis of vinyl ethers, including modified transesterification¹¹, addition-elimination

reactions¹², carbonyl olefinations¹³, additions of alcohol to triple bonds¹⁴ and metal-catalyzed coupling or transfer reactions¹⁵. However, classical synthesis of vinyl ethers has shown serious limitations, such as the use of strong acids or bases^{16,17}, expensive catalyse metals¹⁸ and high temperatures¹⁹. Therefore, the need to implement new inexpensive and easy methodologies to produce functional vinyl ethers remains challenging. For instance, the nucleophilic substitution of the vinylic chlorine atom was largely described in the literature¹². It was successfully carried out with several nucleophiles such as ΦS^- , MeS^{22} , R_2NH^{20} , ΦO^- ^{20,12} and MeO^- ²⁰. Highly functionalized alkenes and interesting cyclic and heterocyclic compounds were obtained in this way²². Meanwhile, the fluorinated alkyl vinyl ethers were rarely reported. Furthermore, R_fCH_2OH or $R_fCH_2O^-$ have not been always considered as nucleophiles; they are rather described as high ionizing power, acidic agents, strong high bond donors and very weak nucleophiles²³. Nevertheless, aromatic nucleophilic substitution was reported by Novack *et al.*²⁴ for the synthesis of the trifluoroethoxylated pharmaceuticals, but rarely used without metal catalysts or high temperatures²⁴. It was shown that only activated aryl chlorides underwent trifluoroethoxylation with strong electron withdrawing groups^{25,26}. In our previous works, we have explored the reactivity of the β -chlorovinyl aldehydes as precursors for highly substituted benzenes²⁷, phosphonates²⁸, phosphoramidates²⁹ and phosphates³⁰. We have also investigated their coordinating chemistry towards tin tetrachloride and showed that the C-Cl carbon was a strong electrophilic site, due to the conjugated carbonyl group effect upon coordination to the tin metal center³¹. As an extension of our work, we report herein a further experimental and theoretical reactivity investigation of β -chlorovinyl aldehydes for the synthesis of new variously substituted β -fluoroalkoxyvinyl aldehydes and corresponding alcohols. All these new compounds were obtained in mild conditions with good to excellent yields and were fully characterized by multinuclear (1H , ^{13}C and ^{19}F) NMR, IR spectroscopies and HRMS.

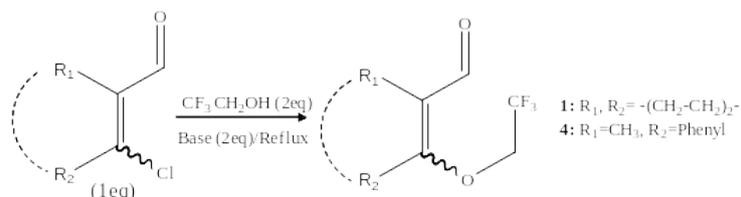
Results and discussion

Synthesis

The starting substrates **1-8** were synthesized from corresponding α -methylene ketones using the Vilsmeier-Haack reaction according to literature procedures³². The synthesis of the new β -fluoroalkoxy- α,β -unsaturated aldehydes (**9-30**) was performed by fluoroalkoxy-etherification of the β -chloro- α,β -unsaturated aldehydes (**1-8**) in a mild basic medium.

Several tests were attempted to optimize the reaction of the cyclic and acyclic substrates namely, the β -chlorovinylaldehydes **1** and **4**, with trifluoroethanol in the presence of several basic agents. (Table 1).

Table 1. Optimized reactions of β -chlorovinylaldehydes **1** and **4** with trifluoroethanol in the presence of several basic agents



Entry	Compounds (Z/E)	Base (eq)	t(h)/ T(°C)	Solvent	% Conversion ^[a]
1		Et ₃ N	24/78	THF	0
2		K ₂ CO ₃	24/78	THF	15
3		KOH	12/78	THF	100
4	1	KOH	8/50	neat	100
5	(100/0)	NaOH	12/78	THF	100
6		NaOH	12/50	neat	94
7		Cs ₂ CO ₃	8/40	neat	100
8		Et ₃ N	48/70	neat	0
9		KF	42/78	THF	0
10		K ₂ CO ₃	48/78	THF	61
11	4	KOH	24/50	neat	95
12	(05/95)	NaOH	8/50	neat	100
13		Cs ₂ CO ₃	24/50	neat	69

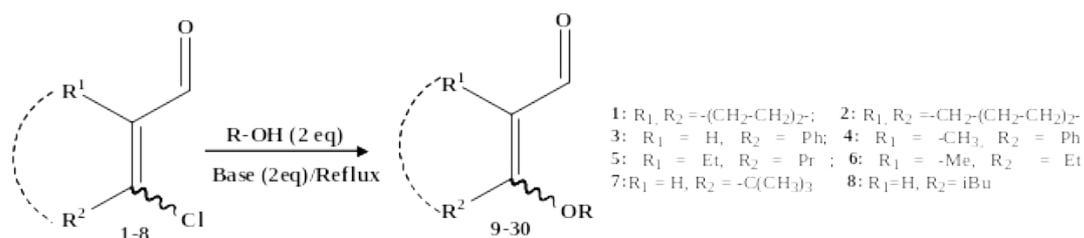
[a] The conversion was monitored by ¹H NMR spectroscopy

When Et₃N or KF were used, no reaction was observed and the starting β -chloro- α,β -unsaturated aldehydes **1** and **4** were recovered as deduced by thin layer chromatography (entries 1, 8 and 9). Although K₂CO₃ in dry THF, reacted to give low or moderate yields of the

expected products and the reactions were not completed, even for several hours at refluxing temperature of THF (entries 2 and 10). The action of NaOH or KOH in neat conditions led to the expected products with good to excellent yields (entries 3-6, 11, 12). The reaction with Cs₂CO₃ in neat conditions at 40°C for 8h gave the expected product in an excellent yield for the cyclic compound **7** (entry 7). When generalizing the reaction to other fluoroalcohols, the bases KOH and NaOH gave good to excellent results with acyclic starting aldehydes **3-8**, however it did not yield the satisfactory results when applied on the cyclic aldehydes **1** and **2**. In these cases, the better results were achieved with Cs₂CO₃ as basic reagent in neat conditions as shown in Table 2.

It is worth to note that the aliphatic chlorovinylaldehydes **5-8** reacted with the fluoroalcohols and gave the expected products **26-30** in moderate yields. However, it was difficult to isolate them due to their volatility. On the other hand, the non-fluorinated homologous alcohols such as methanol, ethanol, isopropanol and allylic alcohol reacted with the chlorovinyl aldehydes **1,2** and **4** and gave several products with lack of the aldehydic signal in ¹H NMR spectra. Only the expected product **25**, starting from CH₂=CH-CH₂-OH and aldehyde **4**, was obtained in a good yield. All the results are gathered in Table 2.

Table 2. Optimized synthesis of β -fluoroalkoxy- α,β -unsaturated aldehydes (**9-30**).



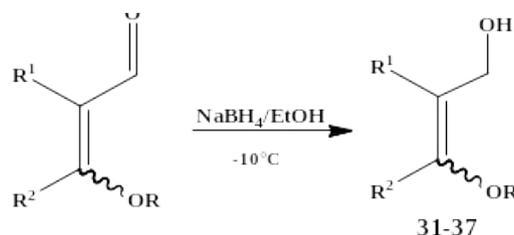
compound s	R_1	R_2	-OR	Base	T°C(t(h))	Yields
						(Z/E)(%) ^b
(Z/E)(%) ^a						
9			-OCH ₂ CF ₃	Cs ₂ CO ₃	40(8)	100 (100/0)
10			-OCH ₂ CF ₂ CF ₃	Cs ₂ CO ₃	80(3)	92 (100/0)
11		-(CH ₂ -CH ₂) ₂ -	-OCH(CF ₃) ₂	Cs ₂ CO ₃	58(3)	90 (100/0)
12		(100/0)	-OCH ₂ CF ₂ CHF ₂ ^b	KOH	100(18)	58(100/0)
13			-OCH ₂ CF ₃	Cs ₂ CO ₃	45(12)	99 (100/0)
14		-(CH ₂ -CH ₂) ₂ -CH ₂ -	-OCH ₂ CF ₂ CF ₃	Cs ₂ CO ₃	80(12)	99 (100/0)
15		(100/0)	-OCH(CF ₃) ₂	Cs ₂ CO ₃	58(3)	94 (100/0)
16			-OC(CF ₃) ₂ CHCH=CH ₂ ^b	NaOH	100(8)	74 (100/0)
17			-OCH ₂ CF ₃	KOH	50(24)	98 (7/93)
18	H	Ph	-OCH ₂ CF ₂ CF ₃	Cs ₂ CO ₃	80(12)	78 (9/91)
19		(95/5)	-OCH(CF ₃) ₂ ^c	KOH	58(24)	72(29/71)
20			-OC(CF ₃) ₂ CHCH=CH ₂ ^b	NaOH	80(24)	91 (63/37)
21			-OCH ₂ CF ₃	NaOH	50(8)	99(9/91)
22			-OCH ₂ CF ₂ CF ₃	Cs ₂ CO ₃	80(36)	82 (8/92)
23	CH ₃	Ph	-OCH(CF ₃) ₂ ^c	NaOH	58(12)	98(7/93)
24		(0/95)	-OC(CF ₃) ₂ CHCH=CH ₂ ^b	KOH	80(14)	94 (4/96)
25			-OCH ₂ CH=CH ₂	KOH	97(12)	82 (9/91)
26	H	C(CH ₃) ₃	-OCH ₂ CF ₃	KOH	25(48)	100(49/51)
		(100/0)				

27	H	CH ₂ CH(CH ₃) ₂ (72/28)	-OCH ₂ CF ₃	KOH	25(24)	83(0/100)
28	CH ₂ CH ₃	CH ₃ (26/74)	-OCH ₂ CF ₃	KOH	25(24)	100(23/77)
29	CH ₃ CH ₂	CH ₂ CH ₂ CH ₃ (22/78)	-OCH ₂ CF ₃	KOH	25(48)	96(21/79)
30	CH ₃ CH ₂	CH ₂ CH ₂ CH ₃	-OCH(CF ₃) ₂	KOH	58(48)	93(24/76)

^a: Isomer percentages measured in crude products from ¹H NMR spectra ^b: Isomer percentages measured in crude products by ¹⁹F NMR spectra ^c: in dry THF

To explore the reactivity of the β-fluoroalkoxy-α,β-unsaturated aldehydes **9–30**, further treatment of these compounds with NaBH₄ as a reducing agent in absolute ethanol at (-10°C), afforded successfully the corresponding new β-fluoroalkoxyallyl alcohols **31–37** in 76–99% yields (Table 2).

Table 2: Synthesis of β-fluoroalkoxyallyl alcohols **31–37**.



Product	R ¹	R ²	-OR	t(h)	Yields ^a (Z/E) ^b
31	-(CH ₂ -CH ₂) ₂ - (100/0)		-OCH(CF ₃) ₂	12	89(100/0)
32	-(CH ₂ -CH ₂) ₂ -CH ₂ - (100/0)		-OCH ₂ CF ₃	8	77(100/0)
33	-(CH ₂ -CH ₂) ₂ -CH ₂ - (100/0)		-OCH ₂ CF ₂ CF ₃	12	95(100/0)
34	-(CH ₂ -CH ₂) ₂ -CH ₂ - (100/0)		-OC(CF ₃) ₂ CHCH=CH ₂	12	91(100/0)
35	CH ₃	Ph	-OCH ₂ CF ₃	12	76(5/95)

		(9/91)			
36	H	Ph	-OCH ₂ CF ₃	15	49(5/95)
		(7/93)			
37	H	Ph	-OC(CF ₃) ₂ CHCH=CH ₂	1	85(57/43)
		(63/37)			

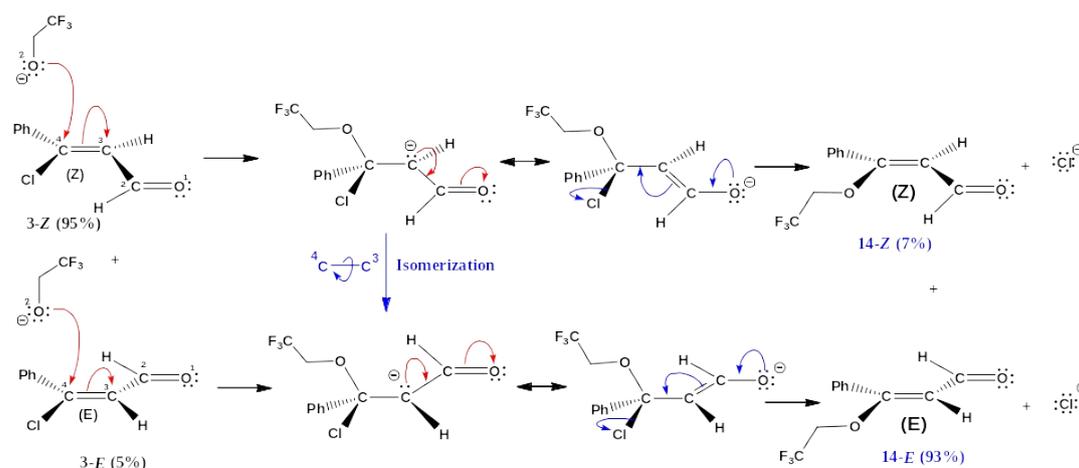
^a: Yields measured from crude products ^b: Isomer percentages measured from ¹⁹F NMR spectra of crude products.

All the reactions were monitored by TLC and NMR. The products **9-30** were obtained as orange or yellow viscous oils that are soluble in both CHCl₃ and DMSO. Alcohols **31-37** were stable at room temperature and obtained as yellow liquids soluble in CHCl₃. All the new compounds were identified by NMR (¹H, ¹³C and ¹⁹F), IR spectroscopies and HRMS. All the spectra are in agreement with proposed molecular structures and the percentages were calculated using ¹H-NMR spectra of the crude reaction mixtures.

In the course of our investigation and as shown in Table 1, the *Z* and *E* isomer ratios are in the same order as those of starting substrates, except for the α -unsubstituted aldehydes **17-20**, **26** and **27**. Remarkably, in these cases, a partial or complete stereoconversion has occurred; the percentage of the *Z*-isomer decreases in favor of the *E*-isomer. Additional experiments were carried out and the stereoconversion was found to be not affected if the reaction of the chlorovinylaldehyde **3** with TFE/KOH is realized in solvents with different polarities such as THF, CH₂Cl₂, CHCl₃, toluene or DMF. The same proportions of *Z/E* (7/93) isomers of the product **17** are observed implying that the solvent polarity is not involved in the observed stereoconversion. However, this latter is dramatically affected with bulkier substituents belonging to either the substrate (compounds **26** and **27**) or to the alcohol fluorinated alkyl group of the nucleophiles (compounds **18-20**). By reducing the aldehyde group of the compound **3** to alcohol, the resulting product Cl(Ph)C=CH-CH₂OH (**3'**) does not react with trifluoroethanol in basic mild even at high temperatures and long reaction times. This suggests that the resonative electron-withdrawing aldehydic group is necessary to the nucleophilic vinylic substitution reaction in these β -chloro- α,β -unsaturated aldehydes.

There are literature reports, in which the products stereochemistry issued from nucleophilic vinylic substitution reaction is directly related to the nature of the reaction mechanism. The stereochemical outcome would be retention of configuration, partial or total stereoconversion depending on whether the reaction takes place into a concerted process or stepwise^{12, 33, 34}. The most common reaction route for similar highly activated systems is an addition-elimination

mechanism that is initiated by nucleophilic attack perpendicular to the π -bond^{12,35, 36} as proposed in Scheme 2.



Scheme 2. Proposed mechanism of the etherification reaction of compound **3**

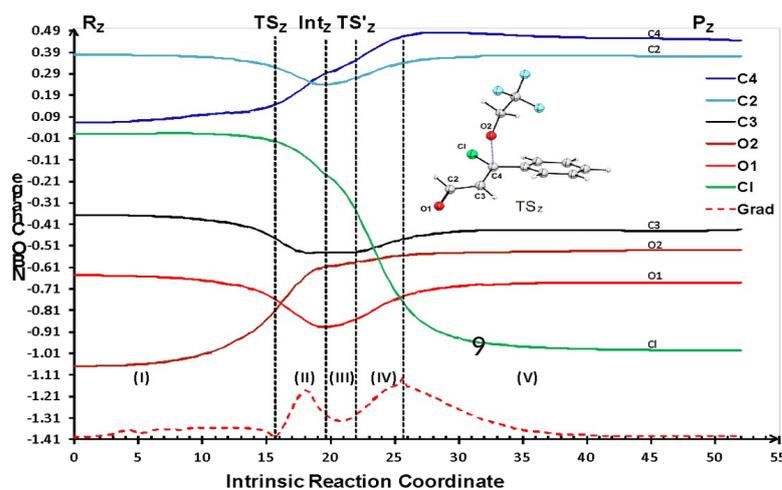
Theoretical calculations

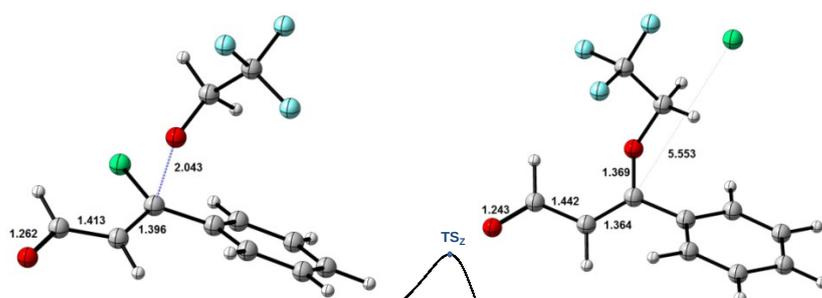
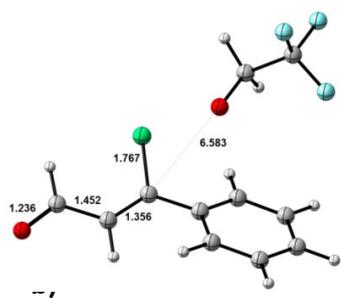
To get more insight into the experimentally observed stereoconvergence, theoretical B3LYP/6-31+G(d,p) calculations have been carried out using the implicit SMD model to simulate 2,2,2-trifluoroethanol solvent mainly on compound **3**, which showed a high stereoselectivity. . Therefore, it was necessary to study the nucleophilic vinylic substitution mechanism and extract the structure of the reaction intermediate corresponding to the *Z* stereoisomer (IntZ) from the IRC calculation in order to evaluate the rotational energy barrier allowing the passage of IntZ \rightarrow IntE and consequently the *Z* \rightarrow *E* isomerization of the reaction products. The geometry configurations and frequencies of all reactants R_Z and R_E , transition states TS_Z , TS'_Z , TS_E and TS'_E and products **3-Z** and **3-E** involved in the mechanism of the reaction were optimized, as well as Natural Bond Orbital (NBO) charge analysis and bond length changes along the intrinsic coordinate of the reaction were calculated. (Fig.2). R_Z , TS_Z and P_Z optimized geometries are given in Figure 2a. All the relative data of the stereoisomer *E* are given in the supplementary materials.

The kinetic study through the reaction coordinate from R_Z by IRC computations shows an interesting behavior, whereby the product formation showed a shoulder revealing the presence of a so-called hidden intermediate (Figure 2b)⁴¹ and the reaction is pseudo-first order. However, the calculations performed on the compound **3'** show only a single step without any intermediate (Fig. 2b'), supporting the role of the aldehydic group in the carbanion intermediate formation. On the other hand, the applied RMS gradient norm on the

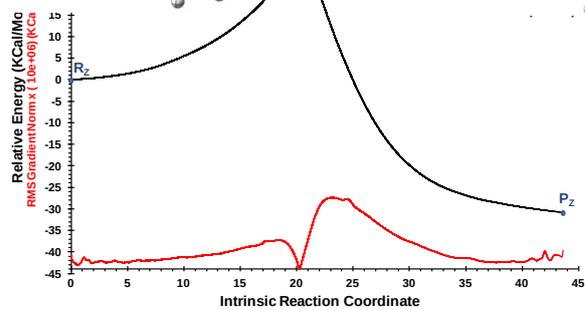
IRC plot of compound **3** showed five different zones (Fig. 2c). The zone I describes the nucleophile ($\text{CF}_3\text{CH}_2\text{O}^-$) orientation and approach from the electrophilic site C_4 of the aldehyde **3** forming the activated complex TS_Z . The NBO charge and the bond length along the IRC plots (Fig. 2e, 2d and 2d') and Table 3 show that there is a charge transfer from O_2 to C_3 and O_1 atoms, while the $\text{C}_3\text{-C}_4$ and $\text{C}_2\text{-O}_1$ bond lengths increase and $\text{C}_2\text{-C}_3$ bond decreases. The zone II corresponds to the enolate intermediate (Int_Z) formation. There is addition of the nucleophile on the C_4 atom, which goes from *pseudo* sp^2 to sp^3 hybridization while the $\text{O}_2\text{-C}_4$ bond is formed. At this stage, an electronic charge transfer is observed from O_2 and C_4 atoms to C_2 , C_3 and O_1 atoms. The $\text{O}_2\text{-C}_4$ and $\text{C}_2\text{-C}_3$ bonds decrease in length ; $\text{C}_3\text{-C}_4$, $\text{C}_2\text{-O}_1$ and $\text{C}_4\text{-Cl}$ bond lengths increase and the maximum charge transfer to O_1 in IRC plot is $q_{\text{max}}(\text{O}_1) = -0.887$. The zones IV and V reflect the elimination step: there are both electronic and geometrical reorganizations. The maximum of the zone IV represents the second transition state TS'_Z of the reaction with an increase in bond lengths of $\text{C}_4\text{-Cl}$ and $\text{C}_2\text{-C}_3$ and a decrease in those of $\text{O}_2\text{-C}_4$, $\text{C}_3\text{-C}_4$ and $\text{O}_1\text{-C}_2$. Then there is molecular reorganization and sp^2 hybridization recovery of C_4 with Cl^- elimination accompanied by $\text{C}_2\text{-C}_3$ bond length increasing and $\text{C}_3\text{-C}_4$ and $\text{O}_1\text{-C}_2$ bond lengths decreasing. At the end of the reaction, the transfer charge occurs from O_1 to C_2 to C_3 to C_4 to Cl atoms. These observations are in good agreement with the assumption of the addition-elimination mechanism.

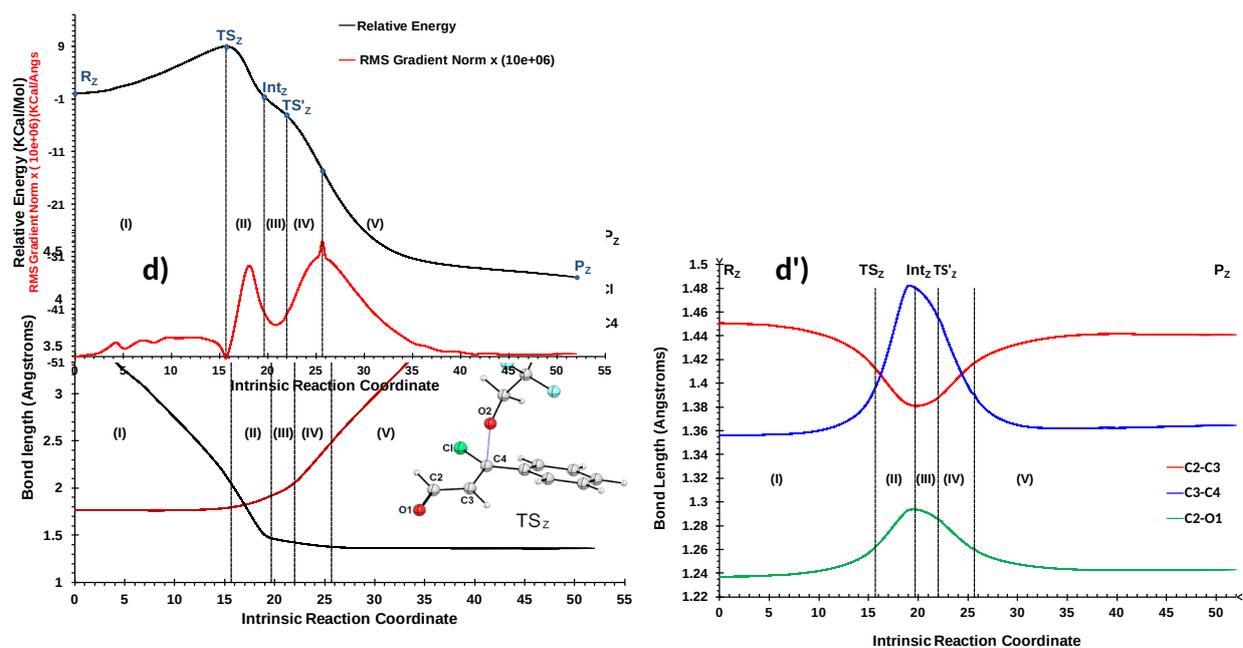
a)





c)





e)

Figure 2 (a) Reactant, transition state and product geometries of 3-Z, (b) energy profile of 3, (b') energy profile of 3' (c) associated RMS gradient norm, (d) and (d') bond length evolution along IRC computed at the B3LYP/6-31+G(d,p)/SMD (2,2,2-trifluoroethanol) level. (e) NBO charges along the reaction pathway for compound 3-Z

Table 3: NBO charges and bond length values Evolution.

Zon e	NBO Charge evolution					Bond Lenth evolution (Å)					
	C ₄	C ₃	C ₂	O ₁	O ₂	Cl	O ₂ -C ₄	C ₄ -Cl	C ₃ -C ₄	C ₂ -C ₃	C ₂ -O ₁
R _Z	0.063	-0.367	0.377	-0.646	-1.069	0.011	3.593	1.766	1.356	1.451	1.237
I TS _z	0.143	-0.477	0.319	-0.760	-0.815	-0.026	2.043	1.797	1.396	1.413	1.262
II Int _z	0.289	-0.540	0.239	-0.887	-0.608	-0.180	1.467	1.92	1.481	1.381	1.294
III TS' _z	0.349	-0.539	0.267	-0.855	-0.588	-0.343	1.423	2.056	1.455	1.388	1.285
IV V	0.463	-0.480	0.338	-0.749	-0.554	-0.772	1.376	2.482	1.39	1.417	1.26
P _Z	0.445	-0.436	0.371	-0.680	-0.531	-0.996	1.361	4.55	1.365	1.441	1.243

Further more, the activation energy value in the reaction pathway from R_Z to P_Z is less than in the reaction from R_E to P_E and P_E isomer is more stable then P_Z by 1.36 kcal.mol⁻¹ as shown in Fig. 3 and Table 4. The calculations performed on the activation energy of the non-reactive compound **3'** toward trifluoroethanol, rise to a value of $\Delta G^{\ddagger} = 29.65$ kcal.mol⁻¹ supporting the effective contribution of the aldehydic group in the nucleophilic vinylic substitution reaction by reducing the energy barrier. The reaction of both compounds **3** and **3'** are thermodynamically favored and exothermic with insignificant change in enthalpy. All parameters of the reaction calculated with 6 31+G (d,p) basis sets are gathered in table 4.

Table 4 : Theoretical parameters of the reactions of compounds **3** and **3'** with 6 31+G (d, p) basis in kcal.mol⁻¹

			$\Delta_r E$	$\Delta_r (E+ZPE)^{\ddagger}$	$\Delta_r H^0$	$\Delta_r G^0$	$\Delta_r S^0$
Reaction energies	Aldehyde 3	E → E	-36.40	-34.67	-34.84	-35.27	1.43
		Z → Z	-36.86	-34.76	-35.15	-32.18	-9.95
	Alcohol 3'	E → E	-32.20	-30.25	-30.51	-30.95	1.48
		Z → Z	-33.23	-31.27	-30.92	-34.39	11.63
			ΔE^{\ddagger}	$\Delta (E+ZPE)^{\ddagger}$	ΔH^{\ddagger}	ΔG^{\ddagger}	ΔS^{\ddagger}
Activation energies	Aldehyde 3	E → E	10.45	10.30	9.46	13.58	-13.82
		Z → Z	9.70	9.90	8.92	14.94	-20.20
	Alcohol 3'	E → E	29.25	28.59	28.48	30.17	5.69
		Z → Z	27.71	27.39	27.11	29.65	8.54

In order to relate the stereoconversion ratios to the structure of the molecules involved in the reaction, some internal rotation barrier key values have been calculated. It was found that the internal barrier rotation from the conformer Int_Z to the conformer Int_E is only 3.7 kcal.mol⁻¹,

similar to those of the simple molecules as ethane (2.9 kcal.mol⁻¹) and propane (3.4 kcal.mol⁻¹) and much lower than the value of the activation energy of compound **3'** (Fig. 4).

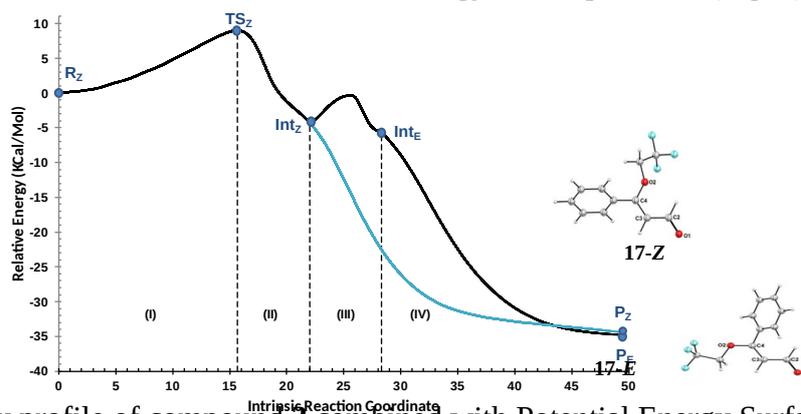


Figure 4. Energy profile of compound **3** combined with Potential Energy Surface (PES) scan isomerization from IntZ to IntE

The compound **27** have the lowest barrier rotation leading to a total conversion. However, in the compound **29**, due to the bulky substituents, the relative high rotational barrier (6 kcal.mol⁻¹) leads to configuration retention. It is worthnoting that the bulkiness of the alcohol alkyl group in compound **19** affect the barrier rotation inhibiting the stereoconversion ratio.

Table 4 barrier rotation values

aldehydes	-OR	Ea (Kcal.mol ⁻¹)	Z/E(%)
17	-OCH ₂ CF ₃	3.69	7/93
19	-OCH(CF ₃) ₂	4.75	29/71
27	-OCH ₂ CF ₃	3.48	0/100
30	-OCH ₂ CF ₃	6.09	21/79*

*Retention of configuration

Thus, the carbanion intermediate stability, in consequent relationship with the steric hindrance of the substituents including those of the nucleophiles, is the driving force of the vinylic substitution reaction feasibility on the various β -chloro- α,β -unsaturated aldehydes, as well as the stereoconversion rates. Particularly, The α -position substituents of the substrate do affect dramatically the barrier rotation due to hyperconjugation between C-H bond in α -position of the carbonyle and the carbanion intermediate. This latter is destabilized and, due to its reduced lifetime, the internal rotation is prevented leading to retention of configuration. On

the other hand, the unsubstituted α -position favors the fast rotation leading to inversion of configuration.

Conclusion

A series of new functionalized β -fluoroalkoxyvinyl aldehydes and corresponding alcohols have been synthesized from α -methylene ketones using a facile and efficient method in neat conditions in most cases. The major advantage of this green transformation is the non-use of metal catalysts or high temperatures. We have shown that the driving force of this reaction is the resonative electron-withdrawing aldehydic group effect. The theoretical DFT investigations of the nucleophilic vinylic substitution mechanism showed the charge transfers in the stabilized hidden intermediate enolate. Isomerization of the intermediate **3-Z** into the most stable intermediate **3-E**, was justified by the very low energy accompanying the internal rotation of the carbanion intermediate. The new functionalized β -fluoroalkoxyvinyl aldehydes can be used as building blocks of new fluorinated compounds that are synthetically attractive in biological active molecules and advanced materials. Further works to explore the synthetic applications of these new intermediates are in progress in our laboratory as well as their biological activity and coordination chemistry.

EXPERIMENTAL SECTION

General Information

The usual solvents and reagents were purchased from commercial sources and use without further purification. TLC was performed on silica gel, 60F-250 (0.26mm thickness) plates. The plates were visualized with UV light (254 nm). NMR spectra were performed on an Ultrafield AVANCE 300 MHz (^1H , 300 MHz; ^{13}C , 75 MHz) or Bruker ARX 200 (^{19}F , 188MHz) spectrometers. Chemical shifts $^{\text{TM}}$ are in parts per million (ppm) and the following abbreviations are used: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quadruplet (q), quintet (quint) and multiplet (m). High resolution mass spectra were obtained using a Bruker Esquire electrospray ionization apparatus at the SAMM (Faculty of Pharmacy at Chatenay-Malabry). All solvents were dried, distilled and stored over molecular sieves (4 Å) using standard techniques. The starting aldehydes were prepared using Vilsmeier–Haack reaction⁷⁰⁻⁷³.

General procedure for the preparation of β -O-F-alkyl vinyl ethers (9-30)

Alcohols (2mmol) was added to an oven-dried flask under argon with base (2mmol), The mixture was stirred for 2h at reflux. The aldehyde (1mmol) was added at 0°C, and the reaction was stirred at reflux. The progress of the reaction was monitored by TLC. Until the conversion of β -chloro- α,β -unsaturated aldehydes was completed. Then, water (50mL) was added to the mixture, the products were extracted with diethyl ether. (3*30mL) and washed by 10mL of NaCl. The solvent (diethyl ether) was evaporated, and the crude product was purified by short-column chromatography using cyclohexane–diethylether as eluent (8/2).

2-(2,2,2-trifluoroethoxy)cyclohex-1-ene-1-carbaldehyde (9)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 10.19 (s, 1H, CHO), 4.30 (q, 2H, CH_2CF_3 , $^3J_{\text{H-F}}=8\text{Hz}$), 2.37-2.33 (m, 2H, $\text{CH}_{2\text{cyc}}$), 2.22- 2.18 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.80-1.76 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.60-1.56 (m, 2H, $\text{CH}_{2\text{cyc}}$). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ :** 189.83 (CHO), 167.54($\text{C}=\text{CO}$), 122.97 (q, CF_3 , $^1J_{\text{C-F}}=277\text{Hz}$), 120.64 ($\text{C}=\text{C-CHO}$), 64.28 (q, CH_2CF_3 , $^2J_{\text{F-C}}=35\text{Hz}$), 25.51, 22.13, 21.00 and 20.71 (4C_{cyc}). **$^{19}\text{F NMR}$ (188 MHz, CDCl_3) δ :** -73.77 (t, $^3J_{\text{F-H}}=8\text{Hz}$). HRMS calcd for $[\text{M}+\text{H}]^+$ $[\text{C}_9\text{H}_{11}\text{F}_3\text{O}_2\text{H}]^+$ 208.0789 found 208.0785.

2-(2,2,3,3,3-pentafluoropropoxy)cyclohex-1-ene-1-carbaldehyde (10)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 10.14 (s, 1H, CHO), 4.37 (t, 2H, CH_2CF_2 , $^3J_{\text{H-F}}=12\text{Hz}$), 2.37-2.33 (m, 2H, $\text{CH}_{2\text{cyc}}$), 2.19-2.15 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.78-1.74 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.57-1.53 (m, 2H, $\text{CH}_{2\text{cyc}}$). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ :** 189.60 (CHO), 167.33 ($\text{C}=\text{C-O}$), 120.19 ($\text{C}=\text{C-CHO}$), 118.39 (tq, $\text{CF}_3\text{-CF}_2$, $^1J_{\text{C-F}}=286\text{Hz}$, $^2J_{\text{C-F}}=35\text{Hz}$), 112.33 (qt, $\text{CF}_2\text{-CF}_3$, $^1J_{\text{C-F}}=258\text{Hz}$, $^2J_{\text{C-F}}=37\text{Hz}$), 63.32 (t, CH_2CF_2 , $^2J_{\text{C-F}}=27\text{Hz}$), 25.38, 22.09, 20.91 and 20.67 (4C_{cyc}). **$^{19}\text{F NMR}$ (188 MHz, CDCl_3) δ :** -83.49 (s, CF_3), -123.63(t, 2F, CH_2CF_2 , $^2J_{\text{F-H}}=12\text{Hz}$). HRMS calcd for $[\text{M}+\text{H}]^+$ $[\text{C}_9\text{H}_{11}\text{F}_5\text{O}_2\text{H}]^+$ 359.0757 found 359.075.

2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)cyclohex-1-ene-1-carbaldehyde (11)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 10.17 (s, CHO), 4.97 (sept, $\text{CH}(\text{CF}_3)_2$), 2.37-2.33 (m, $\text{CH}_{2\text{cyc}}$), 2.22-2.18 (m, $\text{CH}_{2\text{cyc}}$), 1.82-1.78 (m, $\text{CH}_{2\text{cyc}}$), 1.60-1.56 (m, $\text{CH}_{2\text{cyc}}$). **$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ :** 189.33 (CHO), 165.19 ($\text{C}=\text{C-O}$), 122.49 ($\text{C}=\text{C-CHO}$), 120.65 (q, CF_3 , $^1J_{\text{C-F}}=283.347\text{Hz}$), 71.10 (m, $\text{CH}(\text{CF}_3)_2$), 24.85, 22.07, 20.77 and 20.75 (4C_{cyc}). **$^{19}\text{F NMR}$ (188 MHz, CDCl_3) δ :** -73.35 (d, 6F, $\text{CH}(\text{CF}_3)_2$, $^3J_{\text{F-H}}=5\text{Hz}$). HRMS calcd for $[\text{M}+\text{H}]^+$ $[\text{C}_{11}\text{H}_{12}\text{F}_6\text{O}_2\text{H}]^+$ 277.0663 found 277.0658.

2-(2,2,3,4,4,4-hexafluorobutoxy)cyclohex-1-ene-1-carbaldehyde (12)

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 10.14(s,1H, CHO), 5.19-4.92 (m, 1H, $\text{CF}_2\text{CHFCF}_3$), 4.37-4.19 (m, 2H, $\text{CH}_2\text{CF}_2\text{CHFCF}_3$), 2.38-2.34 (m, 2H, $\text{CH}_{2\text{cyc}}$), 2.19-2.15 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.80-

1.72 (m, 2H, CH_{2Cyc}), 1.59-1.51 (m, 2H, CH_{2Cyc}). ¹³C NMR (75 MHz, CDCl₃) δ: 189.03(C=O), 167.63(C=C-O), 120.21(C=C-CHO), 126.24-107.38 (m, CF₃CFHCF₂), 86.34-76.57 (m, CF₂CFHCF₃), 64.69 (td, CH₂CF₂CF, ²J_{C-F}= 31Hz, ³J_{C-F}= 26.49Hz), 25.58, 22.06, 20.89 and 20.70(4C_{cycl}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -74.19 (m, 3F, CF₃CFHCF₂), -118.32 (qd, 2F, CF₂CFHCF₃), -213.13 (m, 1F, CF₂CFHCF₃). HRMS calcd for [M+H]⁺ [C₁₁H₁₂F₆O₂H]⁺ 291.0820 found 291.0835.

2-(2,2,2-trifluoroethoxy)cyclohept-1-ene-1-carbaldehyde (13)

¹H NMR (300 MHz, CDCl₃) δ: 10.12 (s, 1H, CHO), 4.24 (q, 2H, CH₂CF₃, ³J_{H-F}= 8Hz), 2.55-2.52 (m, 2H, CH_{2Cyc}), 2.39-2.35 (m, 2H, CH_{2Cyc}), 1.79-1.46 (m, 6H, CH₂CH₂CH_{2Cyc}). ¹³C NMR (75 MHz, CDCl₃) δ: 189.21 (CHO), 173.30 (C=C-O), 123.02 (q, CF₃, ¹J_{C-F}= 277Hz), 127.84 (C=C-CHO), 65.55 (q, 3F, CH₂CF₃, ²J_{C-F}=35 Hz), 31.52, 30.41, 25.93, 24.68 and 21.49 (5C_{cycl}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -73.76 (t, ³J_{F-H}= 8Hz). HRMS calcd for [M+H]⁺ [C₁₀H₁₃F₃O₂H]⁺ 223.0946 found 223.0940.

2-(2,2,3,3,3-pentafluoropropoxy)cyclohept-1-ene-1-carbaldehyde (14)

¹H NMR (300 MHz, CDCl₃) δ: 10.09 (s, 1H, CHO), 4.30 (t, 2H, CH₂CF₂, ³J_{H-F}=12Hz), 2.55-2.52 (m, 2H, CH_{2Cyc}), 2.37-2.33 (m, 2H, CH_{2Cyc}), 1.77-1.46 (m, 6H, CH₂CH₂CH_{2Cyc}). ¹³C NMR (75 MHz, CDCl₃) δ: 188.94 (CHO), 173.30 (C=C-O), 127.32 (C=C-CHO), 118.38 (tq, CF₃CF₂, ¹J_{C-F}= 286Hz, ²J_{C-F}= 34Hz), 112.29 (tq, CF₂CF₃, ¹J_{C-F}=256 Hz, ²J_{C-F}= 38Hz), 64.62 (t, CH₂CF₂, ²J_{C-F}= 26 Hz), 31.38, 30.05, 25.84, 24.54 and 21.35 (5C_{cycl}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -83.69 (s, CF₃), -123.61 (t, CF₂CH₂, ³J_{F-H}=12Hz). HRMS calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 273.0914 found 273.0914.

2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)cyclohept-1-ene-1-carbaldehyde (15)

¹H NMR (300 MHz, CDCl₃) δ: 10.08 (s, 1H, CHO), 4.82 (sept, 1H, CH(CF₃)₂), 2.56-2.52 (m, 2H, CH_{2Cyc}), 2.37-2.34 (m, 2H, CH_{2Cyc}), 1.77-1.43 (m, 6H, CH_{2Cyc}). ¹³C NMR (75 MHz, CDCl₃) δ: 188.78 (CHO), 170.73(C=C-O), 128.78 (C=C-CHO), 120.73 (q, ¹J_{C-F}= 283Hz, CF₃), 72.05 (sept, CH(CF₃)₂), 31.27, 29.82, 25.49, 24.46 and 21.45 (5C_{cycl}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -73.85 (d, 6F, (CF₃)₂, ³J_{F-H}= 5Hz). HRMS calcd for [M+H]⁺ [C₁₀H₁₀F₆O₂H]⁺ 291.0820 found 291.0823.

2-((1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)oxy)cyclohept-1-ene-1-carbaldehyde (16)

¹H NMR (300 MHz, CDCl₃) δ : 9.98 (s, 1H, CHO), 5.79-5.68 (m, 1H, CH₂CH=CH₂), 5.21-5.15 (m, 2H, CH₂CH=CH₂), 2.79 (d, 2H, CH₂-CH=CH₂, ³J_{H-H}= 6Hz), 2.51-2.48 (m, 2H, CH_{2Cyc}), 2.34-2.31 (m, 2H, CH_{2Cyc}), 1.70-1.39 (m, 6H, CH₂CH₂CH_{2Cyc}). ¹³C NMR (75 MHz,

CDCl₃ δ : 189.78 (CHO), 169.91 (C=C-O), 134.06 (CH₂CH=CH₂), 127.22 (CH₂CH=CH₂), 122.25 (q, 6F, (CF₃)₂, ¹J_{C-F}= 288Hz), 121.61 (C=C-CHO), 82.65 (m, C(CF₃)₂), 34.60 (CH₂-CH=CH₂), 34.08, 31.28, 25.12, 24.62 and 22.27 (5C_{cycl}). **¹⁹F NMR (188 MHz, CDCl₃) δ** : -71.83 (s, 6F, (CF₃)₂). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 331.1133 found 331.1126.

3-phenyl-3-(2,2,2-trifluoroethoxy)acrylaldehyde (17)

¹H NMR (300 MHz, CDCl₃) δ : (**Z**) 10.17 (d, 1H, CHO, ³J_{H-H}= 7Hz), 5.81 (d, 1H, CH, ³J_{H-H}= 7Hz), 4.27 (d, 2H, CH₂CF₃, ³J_{H-F}= 8Hz). (**E**) 9.51 (d, 1H, CHO, ³J_{H-H}= 7Hz), 7.59-7.47 (m, H_{am}), 5.64 (d, 1H, CH, ³J_{H-H}= 7Hz), 4.37 (d, 2H, CH₂CF₃, ³J_{H-F}= 7Hz). **¹³C NMR (75 MHz, CDCl₃) δ** : (**Z**) 189.76 (CHO), 169.99 (C=C-O), 115.23 (C=C-CHO), 67.74 (q, 3F, CH₂-CF₃, ²J_{C-F}= 36Hz). (**E**) 191.83 (CHO), 174.41(C=C-O), 131.67-128.58 (C_{am}), 122.47 (q, 3F, CF₃, ¹J_{C-F}= 267Hz), 107.05 (C=C-CHO), 65.89 (q, 3F, CH₂-CF₃, ²J_{C-F}= 36Hz). **¹⁹F NMR (188 MHz, CDCl₃) δ** : (**Z**): -73.76 (t, 3F, CF₃-CH₂, ³J_{F-H}= 8Hz), (**E**) -73.48 (t, 3F, CF₃-CH₂, ³J_{F-H}= 7Hz). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 231.0633 found 231.0631.

3-(2,2,3,3,3-pentafluoropropoxy)-3-phenylacrylaldehyde (18)

¹H NMR (300 MHz, CDCl₃) δ : (**Z**) 10.16 (d, 1H, CHO, ³J_{H-H}= 6Hz), 5.78 (d, 1H, CH, ³J_{H-H}= 6Hz), 4.32 (t, 2H, CH₂CF₂, ³J_{F-H}= 12Hz). (**E**) 9.51 (d, 1H, CHO, ³J_{H-H}=6Hz), 7.57-7.45 (m, H_{am}), 5.61(d, 1H, CH, ³J_{H-H}=6Hz), 4.44 (t, 2H, CH₂CF₂, ³J_{F-H}= 12Hz). **¹³C NMR (75 MHz, CDCl₃) δ** : (**Z**) 189.59 (CHO), 169.92 (C=C-O), 114.97 (C=C-CHO), 66.87 (t, CH₂, 2F, ²J_{C-F}= 26.87Hz). (**E**) 191.71(CHO), 174.34 (C=C-O), 131.61-128.57 (C_{am}), 118.41 (tq, CF₃CF₂, ¹J_{C-F}= 286Hz, ²J_{C-F}=36Hz), 112.16 (qt, CF₂CF₃, ¹J_{C-F}= 256Hz, ²J_{C-F}= 38Hz), 107.03 (C=C-CHO), 64.92 (t, CH₂, 2F, ²J_{C-F}= 28Hz). **¹⁹F NMR (188 MHz, CDCl₃) δ** : (**Z**) -83.56 (s, CF₃), -123.59 (t, 2F, CF₂CH₂, ³J_{F-H}= 12.84Hz). (**E**) -83.37 (s, CF₃), -122.99 (t, 2F, CF₂CH₂, ³J_{F-H}= 12Hz). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 281.0501 found 281.0576.

3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-3-phenylacrylaldehyde (19)

¹H NMR (300 MHz, CDCl₃) δ : (**Z**) 10.16 (d, 1H, CHO, ³J_{H-H}= 7Hz), 5.75 (d, 1H, CH-CHO, ³J_{H-H}= 7Hz), 4.82-4.76 (sept, 1H, CH(CF₃)₂). (**E**) 9.45 (d, 1H, CH, ³J_{H-H}= 7Hz), 7.61-7.48 (m, 5H, C_{am}), 5.96 (d, 1H, CH, ³J_{H-H}= 7Hz), 5.12 (sept, 1H, CH(CF₃)₂). **¹³C NMR (75 MHz, CDCl₃) δ** : (**Z**) 189.02 (CHO), 167.76 (C=C-O), 116.62 (C=C-CHO), 74.10-71.42(sept, CH(CF₃)₂). (**E**) 191.63(CHO), 173.53 (C=C-O), 132.07-128.01 (C_{am}), 120.55 (q, 6F, (CF₃)₂, ¹J_{C-F}= 284Hz), 110.19 (C=C-CHO), 72.75 (sept, 6F, CH-(CF₃)₂). **¹⁹F NMR (188 MHz, CDCl₃) δ** : (**Z**) -72.44 (d, 6F, (CF₃)₂, ³J_{F-H}= 5Hz). (**E**) -72.91 (d, 6F, (CF₃)₂, ³J_{F-H}= 5Hz) **HRMS** calcd for [M+H]⁺ [C₁₂H₈F₆O₂H]⁺ 299.0507 found 299.0504.

3-phenyl-3-((1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)oxy)acrylaldehyde (20)

¹H NMR (300 MHz, CDCl₃) δ: (**Z**) 10.11 (d, 1H, CHO, ³J_{H-H}= 7Hz), 5.95 (d, 1H, CH, ³J_{H-H}= 7Hz), 7.57-7.44 (m, 5H, H_{arm}), 5.78-5.68 (m, 1H, CH₂CH=CH₂), 5.29-5.05 (m, 2H, CH₂CH=CH₂), 2.64 (d, 2H, CH₂-CH=CH₂, ³J_{H-H}= 7Hz). (**E**) 9.50 (d, 1H, CHO, ³J_{H-H}= 7Hz), 6.10 (d, 1H, CH, ³J_{H-H}= 7Hz), 2.99 (d, 2H, CH₂CH=CH₂, ³J_{H-H}= 7Hz). **¹³C NMR (75 MHz, CDCl₃) δ:** (**Z**) 191.91 (CHO), 165.24 (C=C-O), 135.58 (CH₂C=CH₂), 132.71-126.73(C_{arm}), 122.09 (q, CF₃, ¹J_{C-F}= 288Hz), 122.52 (CH₂CH=CH₂), 117.22 (C=C-CHO), 83.85 (Sept, C(CF₃)₂), 34.10 (CH₂-CH=CH₂). (**E**) 189.67 (CHO), 169.86 (C=C-O), 132.71 (CH₂CH=CH₂), 122.00 (CH₂CH=CH₂), 120.17 (C=C-CHO), 31.93 (CH₂CH=CH₂). **¹⁹F NMR (188 MHz, CDCl₃) δ:** (**Z**) -71.64 (s, 6F, (CF₃)₂), (**E**) -71.93 (s, 6F, (CF₃)₂). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 339.0820 found 339.0803.

2-methyl-3-phenyl-3-(2,2,2-trifluoroethoxy)acrylaldehyde (21)

¹H NMR (300 MHz, CDCl₃) δ: (**Z**) 10.35 (s,1H, CHO), 3.98 (q, 2H, CH₂CF₃, ³J_{H-F}= 8Hz), 1.64 (s, 3H, CH₃). (**E**) 9.26 (s, 1H, CHO), 7.51-7.33 (m, H_{arm}), 4.00 (q, 2H, CH₂CF₃, ³J_{H-F}= 8Hz), 1.88 (s, 3H, CH₃). **¹³C NMR (75 MHz, CDCl₃) δ:** (**Z**) 190.89 (CHO), 166.21 (C=C-O), 121.30 (C=C-CHO), 66,57 (q, CH₂CF₃, ²J_{C-F}= 35Hz), 10.68 (CH₃). (**E**) 192.85 (CHO), 170.46 (C=C-O), 130.91-124.98 (C_{arm}), 122.15 (C=C-CHO), 121.15 (q, CH₂CF₃, ¹J_{C-F}= 257Hz), 65.39 (q, CH₂CF₃, ²J_{C-F}= 35Hz), 7.92 (CH₃). **¹⁹F NMR (188 MHz, CDCl₃) δ:** (**Z**) -73.60 (t, 3F, CH₂CF₃, ³J_{F-H}= 8H), (**E**) -74.35 (t, 3F, CH₂CF₃, ³J_{F-H}= 8Hz). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 245.0789 found 245.0788.

2-methyl-3-(2,2,3,3,3-pentafluoropropoxy)-3-phenylacrylaldehyde (22)

¹H NMR (300 MHz, CDCl₃) δ: (**Z**) 10.38 (s, 1H, CHO), 4.04 (t, 2H, CH₂, ³J_{H-F}= 12Hz), 1.66 (s, 3H, CH₃). (**E**) 9.28 (s, 1H, CHO), 7.56-7.35 (m, H_{arm}), 4.07 (t, 2H, CH₂, ³J_{H-F}= 12Hz), 1.90 (s, 3H, CH₃). **¹³C NMR (75 MHz, CDCl₃) δ:** (**Z**) 190.88 (CHO), 166.09 (C=C-O), 121.08 (C=C-CHO), 65.57 (t, CH₂, ²J_{C-F}= 27Hz), 10.72 (CH₃). (**E**) 192.86 (CHO), 170.33 (C=C-O), 130.96-129.07(C_{arm}), 121.98 (C=C-CHO), 118.38 (tq, CF₂CF₃, ¹J_{C-F}= 286Hz, ²J_{C-F}= 35Hz), 112.22(qt, CF₂CF₃, ¹J_{C-F}= 255Hz, ²J_{C-F}= 37Hz), 64.54 (t, CH₂, ²J_{C-F}= 27Hz), 7.80 (CH₃). **¹⁹F NMR (188 MHz, CDCl₃) δ:** (**Z**) -83.73 (s, CF₃), -123.49 (t, 2F, CF₂, ³J_{F-H}= 12Hz). (**E**) -83.58 (s, CF₃), -123.71 (t, 2F,CF₂, ³J_{F-H}= 12Hz). **HRMS** calcd for [M+H]⁺ [C₉H₁₁F₃O₂H]⁺ 295.0757 found 295.0749.

3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-2-methyl-3-phenylacrylaldehyde (23)

¹H NMR (300 MHz, CDCl₃) δ: (**Z**) 10.24 (s, 1H, CHO), 1.52 (s, 3H, CH₃). (**E**) 9.14 (s, 1H, CHO), 7.47-7.26 (m, H_{arm}), 4.39 (sept, CH(CF₃)₂), 1.82 (s, 3H, CH₃). **¹³C NMR (75 MHz, CDCl₃) δ:** (**Z**) 190.02 (CHO), 163.90(C=C-O), 122.55(C=C-CHO), 10.69(CH₃). (**E**) 192.42

(CHO), 168.36 (C=C-O), 131.50-127.80 (C_{arm}), 123.65 (C=C-CHO), 120.66 (q, CF₃, ¹J_{C-F}= 281Hz), 71.72 (m, C(CF₃)₂), 7.7(CH₃). ¹⁹F NMR (188 MHz, CDCl₃) δ: (Z) -72.93 (d, 6F, (CF₃)₂, ³J_{F-H}=5Hz). (E) -73.64 (d, 6F, (CF₃)₂, ³J_{F-H}= 5Hz). HRMS calcd for [M+H]⁺ [C₁₃H₁₀F₆O₂H]⁺ 313.0663 found 313.0666.

2-methyl-3-phenyl-3-((1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)oxy)acrylaldehyde (24)

¹H NMR (300 MHz, CDCl₃) δ: (E) 9.47 (s, 1H, CHO), 7.46-7.43 (m, 5H, H_{arm}), 5.94-5.80 (m, 1H, CH=CH₂), 5.33-5.27 (m, 2H, CH=CH₂), 2.73 (d, 2H, CH₂CH=CH₂, ³J_{H-H}= 6Hz), 2.10 (s, 3H, CH₃). (Z) 10.40 (s, 1H, CHO), 1.86 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ: (E) 190.58 (CHO), 154.83 (C=C-O), 136.25 (CH₂CH=CH₂), 135.73-128.42 (C_{arm}), 123.02 (q, 6F, CH(CF₃)₂, ¹J_{C-F}= 286.12Hz), 121.95 (C=C-CHO), 75.41 (m, C(CF₃)₂), 34.98 (CH₂CH=CH₂), 13.10 (CH₃). (Z) 192.30 (CHO), 148.07(C=C-O), 13.86 (CH₃). ¹⁹F NMR (188 MHz, CDCl₃) δ: (E) -76.35 (s, 6F, (CF₃)₂), (Z) -71.81 (s, 6F, (CF₃)₂).

3-(allyloxy)-2-methyl-3-phenylacrylaldehyde (25)

¹H NMR (300 MHz, CDCl₃) δ: (Z) 10.28 (s, 1H, CHO), 7.39-7.22 (m, H_{arm}), 5.88-5.68 (m, 1H, CH₂CH=CH₂), 5.16-5.07 (m, 2H, CH₂CH=CH₂), 4.07 (dt, 2H, CH₂CH=CH₂, ³J_{H-H}= 5Hz), 1.55 (s, 3H, CH₃). (E) 9.11 (s, 1H, CHO), 7.39-7.22 (m, H_{arm}), 5.88-5.68 (m, 1H, CH₂CH=CH₂), 5.16-5.07 (m, 2H, CH₂CH=CH₂), 4.12 (dt, 2H, CH₂CH=CH₂, ³J_{H-H}= 5Hz), 1.80 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ: (Z) 191.51 (CHO), 168.77 (C=C-O), 134.69-128.43 (C_{arm}), 130.02 (C=C-CHO), 118.54 (CH₂CH=CH₂), 116.49 (CH₂CH=CH₂), 66.70 (CH₂CH=CH₂), 10.71 (CH₃). (E) 193.07 (CHO), 173.05 (C=C-O), 134.69-128.43 (C_{arm}), 130.29 (C=C-CHO), 120.25 (CH₂CH=CH₂), 117.61 (CH₂CH=CH₂), 69.97 (CH₂CH=CH₂), 8.04(CH₃).

4,4-dimethyl-3-(2,2,2-trifluoroethoxy)pent-2-enal (26)

¹H NMR (200 MHz, CDCl₃) δ: (Z) 10.15 (d, 1H, CHO, ³J_{H-H}= 7Hz), 5.14 (d, 1H, CH, ³J_{H-H}= 7Hz), 4.07 (q, 2H, CH₂CH₃, ³J_{H-H}= 7Hz), 1.33 (s, 3H, (CH₃)₃). (E) 9.70 (d, 1H, CHO, ³J_{H-H}= 6Hz), 5.53 (d, 1H, CH, ³J_{H-H}= 6Hz), 4.48 (q, 2H, CH₂CF₃, ³J_{H-H}= 8Hz), 1.13 (s, 3H, (CH₃)₃). ¹³C NMR (75 MHz, CDCl₃) δ: (Z) 190.07 (CHO), 181.96 (C=C-O), 122.65 (q, CF₃, ¹J_{C-F}= 277Hz), 105.56, (C=C-CHO), 65.41 (q, CH₂CF₃, ³J_{C-F}= 36Hz), 38.35 (C(CH₃)₂), 30.15(C(CH₃)₂). (E) 188.28 (CHO), 181.04 (C=C-O), 122.51 (q, CF₃, ¹J_{C-F}= 278Hz), 106.28 (C=C-CHO), 72.35 (q, CH₂CF₃, ³J_{C-F}= 35Hz), 39.25 (C(CH₃)₂), 27.77 (C(CH₃)₂). ¹⁹F NMR (188 MHz, CDCl₃) δ: (Z) -73.94 (t, CH₂CF₃, ³J_{F-H}= 7Hz), (E)-74.88 (t, CH₂CF₃, ³J_{F-H}= 8Hz).

5-methyl-3-(2,2,2-trifluoroethoxy)hex-2-enal (27)

¹H NMR (300 MHz, CDCl₃) δ: 9.81 (d, 1H, CHO, ³J_{H-H} = 7Hz), 5.37 (d, 1H, CH, ³J_{H-H} = 7Hz), 4.15 (q, 2H, CH₂CF₃, ³J_{H-F} = 7Hz), 2.55 (d, 2H, CH₂CH, ³J_{H-H} = 7Hz), 2.12-1.98 (m, CH₂CH(CH₃)₂), 0.98 (d, 6H, CH(CH₃)₂, ³J_{H-H} = 6Hz). **¹³C NMR (75 MHz, CDCl₃) δ:** 189.82 (CHO), 176.69 (C=C-O), 122.65 (q, CF₃, ¹J_{C-F} = 277Hz), 106.50 (C=C-CHO), 65.06 (q, CH₂CF₃, ³J_{C-F} = 36Hz), 39.63 (CH₂CH(CH₃)₂), 29.74 (CH₂CH(CH₃)₂), 22.19 (CH₂CH(CH₃)₂). **¹⁹F NMR (282 MHz, CDCl₃) δ:** -73.64 (t, 3F, ³J_{F-H} = 7Hz).

2-methyl-3-(2,2,2-trifluoroethoxy)pent-2-enal (28)

¹H NMR (200 MHz, CDCl₃) δ: (*Z*) 10.16 (s, 1H, CHO), 4.23 (q, 2H, CH₂CF₃, ³J_{H-F} = 8Hz), 2.45 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.67 (s, 3H, CH₃), 1.15 (t, 3H, CH₃CH₂, ³J_{H-H} = 7Hz). (*E*) 9.90 (s, 1H, CHO), 4.33 (q, 2H, CH₂CF₃, ³J_{H-F} = 8Hz), 1.70 (s, 3H, CH₃), 2.65 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.20 (t, 3H, CH₃CH₂, ³J_{H-H} = 7Hz). **¹³C NMR (75 MHz, CDCl₃) δ:** (*Z*) 190.24 (CHO), 167.67 (C=C-O), 125.95 (C=C-CHO), 122.84 (q, CF₃, ¹J_{C-F} = 278Hz), 63.90 (q, CH₂CF₃, ²J_{C-F} = 39Hz), 29.62 (CH₂CH₃), 15.84(CH₃), 12.76 (CH₂CH₃). (*E*) 190.16 (CHO), 166.22 (C=C-O), 123(q, CF₃, ¹J_{C-F} = 278Hz), 125.79 (C=C-CHO), 64.95 (CH₂CF₃, ²J_{C-F} = 35Hz), 37.01 (CH₂CH₃), 17.42 (CH₃), 13.37 (CH₂CH₃). **¹⁹F NMR (188 MHz, CDCl₃) δ:** (*Z*) -74.11 (t, 3F, CH₂CF₃, ³J_{F-H} = 8Hz), (*E*) -74.62 (t, 3F, CH₂CF₃, ³J_{F-H} = 8Hz).

2-ethyl-3-(2,2,2-trifluoroethoxy)hex-2-enal (29)

¹H NMR (300 MHz, CDCl₃) δ: (*Z*) 10.18 (s, 1H, CHO), 4.27 (q, 2H, CH₂CF₃, ³J_{H-F} = 8Hz), 2.45 (t, 2H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 2.18 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.68-1.56 (m, 2H, CH₂CH₂CH₃), 1.03 (t, 3H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 0.99 (t, 3H, CH₂CH₃, ³J_{H-H} = 7Hz). (*E*) 9.89 (s, 1H, CHO), 4.38, (q, 2H, CH₂CF₃, ³J_{H-F} = 8Hz), 2.72 (t, 2H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 2.30 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.68-1.56 (m, 2H, CH₂CH₂CH₃), 1.01 (t, 3H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 0.92 (t, 3H, CH₂CH₃, ³J_{H-H} = 7Hz). **¹³C NMR (75 MHz, CDCl₃) δ:** (*Z*) 190.58 (CHO), 169.46 (C=C-O), 127.55 (C=C-CHO), 123.37 (q, CF₃, ¹J_{C-F} = 280Hz), 65.72 (q, CH₂CF₃, ²J_{C-F} = 35Hz), 29.78 (CH₂CH₂CH₃), 20.64 (CH₂CH₂CH₃), 17.71 (CH₂CH₃), 14.11 (CH₂CH₂CH₃), 13.29 (CH₂CH₃). (*E*) 190.14 (CHO), 170.91 (C=C-O), 127.41 (C=C-CHO), 123.26 (q, CF₃, ¹J_{C-F} = 278Hz), 64.48 (q, CH₂CF₃, ²J_{C-F} = 35Hz), 27.24 (CH₂CH₂CH₃), 22.00 (CH₂CH₂CH₃), 16.18 (CH₂CH₃), 13.80 (CH₂CH₂CH₃), 13.20 (CH₂CH₃). **¹⁹F NMR (282 MHz, CDCl₃) δ:** (*Z*) -74.20 (t, 3F, CF₃, ³J_{F-H} = 8Hz), (*E*) -74.63 (t, 3F, CF₃, ³J_{F-H} = 8Hz).

2-ethyl-3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)hex-2-enal (30)

¹H NMR (300 MHz, CDCl₃) δ: (*Z*) 10.17 (s, 1H, CHO), 4.81-4.70 (m, 1H, CH(CF₃)₂), 2.44 (t, 2H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 2.20 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.04 (t, 3H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 0.97 (t, 3H, CH₂CH₃, ³J_{H-H} = 7Hz). (*E*) 9.90 (s, 1H, CHO), 4.95-4.84 (m, 1H, CH(CF₃)₂), 2.72 (t, 2H, CH₂CH₂CH₃, ³J_{H-H} = 7Hz), 2.34 (q, 2H, CH₂CH₃, ³J_{H-H} = 7Hz), 1.65-

1.57 (m, 2H, CH₂CH₂CH₃), 1.01 (t, 3H, CH₂CH₂CH₃, ³J_{H-H}= 7Hz), 0.94 (t, 3H, CH₂CH₃, ³J_{H-H}= 7Hz). ¹³C NMR (75 MHz, CDCl₃) δ: (Z) 190.21 (C=O), 166.51 (C=C-O), 128.61 (C=C-CHO), 120.72 (q, (CF₃)₂, ¹J_{C-F}= 284Hz), 72.87-70.22 (m, CH(CF₃)₂), 28.96 (CH₂CH₂CH₃), 20.61 (CH₂CH₂CH₃), 17.92 (CH₂CH₃), 13.87 (CH₂CH₂CH₃), 13.78 (CH₂CH₃). (E) 190.14 (C=O), 168.11 (C=C-O), 128.61 (C=C-CHO), 120.72 (q, (CF₃)₂, ¹J_{C-F}= 284Hz), 72.87-70.22 (m, CH(CF₃)₂, ²J_{C-F}= 35Hz), 26.34 (CH₂CH₂CH₃), 21.57 (CH₂CH₂CH₃), 16.31 (CH₂CH₃), 13.19 (CH₂CH₂CH₃), 12.84 (CH₂CH₃). ¹⁹F NMR (282 MHz, CDCl₃) δ: (Z) -72.80 (d, 6F, CH(CF₃)₂, ³J_{F-H}= 5.49Hz), (E) -73.40 (d, 6F, CH(CF₃)₂, ³J_{F-H}= 5.41Hz).

General procedure for the preparation of β-O-F-alkyl allyl alcohols (31-37).

The β-O-F-alkyl vinyl ethers (1mmol) was stirred at -10°C in absolute ethanol with (0.25 mmol) of NaBH₄. The progress of the reaction was monitored by TLC (by dissolving the sample in ether) using cyclohexane: diethylether (8:2).until the conversion of β-O-F-alkyl vinyl aldehydes was completed. Then, water (100mL) was added to the mixture, the products were extracted with diethyl ether. (3*30mL) and washed 2 times by 10 ml of NaCl. The solvent (diethyl ether) was evaporated, and the crude product was purified by short-column chromatography using cyclohexane–diethylether as eluent (8/2).

(2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)cyclohex-1-en-1-yl)methanol (31)

¹H NMR (300 MHz, CDCl₃) δ: 4.52 (m, 1H, CH(CF₃)₂), 4.12 (s, 2H, CH₂OH), 2.12-2.03 (m, 2H, CH₂cyc), 1.98 (s, 1H, CH₂OH), 1.71-1.64 (m, 2H, CH₂cyc), 1.56-1.48 (m, 2H, CH₂cyc). ¹³C NMR (75 MHz, CDCl₃) δ: 146.43 (C=C-O), 121.36 (C=C-CHO), 121.14 (q, CF₃, ¹J_{C-F}= 282Hz), 71.46 (sept, CH(CF₃)₂), 59.42 (CH₂OH), 25.71, 24.01, 22.79 and 21.86 (4C_{cyc}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -73.84 (d, 6F, CH(CF₃)₂, ³J_{F-H}= 6Hz).

(2-(2,2,2-trifluoroethoxy)cyclohept-1-en-1-yl)methanol (32)

¹H NMR (300 MHz, CDCl₃) δ: 4.19 (s, 2H, CH₂OH), 3.99 (q, 2H, CH₂CF₃, ³J_{H-F}= 8Hz), 2.34-2.31 (m, 2H, CH₂cyc), 2.22-2.18 (m, 2H, CH₂cyc), 1.78-1.52 (m, 6H, CH₂CH₂CH₂cyc). ¹³C NMR (75 MHz, CDCl₃) δ: 153.98 (C=C-O), 123.58 (q, CF₃, ¹J_{C-F}= 277Hz), 126.20 (C=C-CHO), 66.20 (q, 3F, CH₂CF₃, ²J_{C-F}= 35Hz), 61.53 (CH₂OH), 31.49, 30.00, 28.75, 26.65 and 25.52 (5C_{cyc}). ¹⁹F NMR (188 MHz, CDCl₃) δ: -74.25 (t, 3F, CH₂CF₃, ³J_{F-H}= 8.54Hz).

(2-(2,2,3,3,3-pentafluoropropoxy)cyclohept-1-en-1-yl)methanol (33)

¹H NMR (300 MHz, CDCl₃) δ: 4.18 (s, 2H, CH₂OH), 4.05 (t, 2H, CH₂CF₂, ³J_{H-F}= 13Hz), 2.35-2.31 (m, 2H, CH₂cyc), 2.22-2.18 (m, 2H, CH₂cyc), 1.76- 1.52 (m, 6H, CH₂CH₂CH₂cyc). ¹³C NMR (75 MHz, CDCl₃) δ: 154.11 (C=C-O), 126.28 (C=C-CHO), 118.61 (tq, CF₂CF₃, ¹J_{C-F}= 286Hz, ²J_{C-F}= 35Hz), 112.70 (qt, CF₂CF₃, ¹J_{C-F}= 255Hz, ²J_{C-F}= 37Hz), 65.52 (t, CH₂CF₂, ²J_{C-F}=

26Hz), 61.43 ($\underline{\text{C}}\text{H}_2\text{OH}$), 31.41, 29.89, 28.73, 26.60 and 25.48 (5C_{cyc}). ^{19}F NMR (188 MHz, CDCl_3) δ : -83.65 (s, 3F, $\underline{\text{C}}\text{F}_3\text{CF}_2$), -124.03 (t, 2F, $\text{CH}_2\text{CF}_2\text{CF}_3$, $^3\text{J}_{\text{F-H}}=13\text{Hz}$).

(2-((1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)oxy)cyclohept-1-en-1-yl)methanol
(34)

^1H NMR (300 MHz, CDCl_3) δ : 5.89-5.75 (m, 1H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 5.25-5.20 (m, 2H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 4.16 (s, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$), 2.79 (d, 2H, $\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$, $^3\text{J}_{\text{H-H}}=6\text{Hz}$), 1.83 (s, 1H, $\underline{\text{C}}\text{H}_2\text{OH}$), 2.38-2.34 (m, 2H, $\text{CH}_{2\text{cyc}}$), 2.27-2.23 (m, 2H, $\text{CH}_{2\text{cyc}}$), 1.77-1.53 (m, 6H, $\text{CH}_2\text{CH}_2\text{CH}_{2\text{cyc}}$). ^{13}C NMR (75 MHz, CDCl_3) δ : 150.01 ($\text{C}=\underline{\text{C}}\text{-O}$), 132.32 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 128.29 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 122.61 (q, 6F, $(\underline{\text{C}}\text{F}_3)_2$, $^1\text{J}_{\text{C-F}}=286\text{Hz}$), 120.68 ($\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 81.58 (m, $\underline{\text{C}}(\text{CF}_3)_2$), 60.88 ($\underline{\text{C}}\text{H}_2\text{OH}$), 33.55 ($\underline{\text{C}}\text{H}_2\text{-CH}=\text{CH}_2$), 33.17, 31.28, 28.82, 25.85 and 25.13 (5C_{cyc}). ^{19}F NMR (188 MHz, CDCl_3) δ : -72.24 (s, $(\text{CF}_3)_2$).

2-methyl-3-phenyl-3-(2,2,2-trifluoroethoxy)prop-2-en-1-ol (35)

^1H NMR (300 MHz, CDCl_3) δ : (*Z*) 4.21 (s, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$), 3.79 (q, 2H, $\underline{\text{C}}\text{H}_2\text{CF}_3$, $^3\text{J}_{\text{H-F}}=8.46\text{Hz}$), 1.76 (s, 3H, $\underline{\text{C}}\text{H}_3$). (*E*) 7.43-7.33 (m, 5H, H_{arm}), 4.04 (s, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$), 3.79 (q, 2H, $\underline{\text{C}}\text{H}_2\text{CF}_3$, $^3\text{J}_{\text{H-F}}=8.46\text{Hz}$), 1.99 (s, 3H, $\underline{\text{C}}\text{H}_3$). ^{13}C NMR (75 MHz, CDCl_3) δ : (*Z*) 146.09 ($\text{C}=\underline{\text{C}}\text{-O}$), 118.12 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 61.53 ($\underline{\text{C}}\text{H}_2\text{OH}$), 15.75 ($\underline{\text{C}}\text{H}_3$). (*E*) 150.56 ($\text{C}=\underline{\text{C}}\text{-O}$), 132.66-128.56 (C_{arm}), 123.46 (q, CF_3 , $^1\text{J}_{\text{C-F}}=2771\text{Hz}$), 119.71 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 65.55 (q, CH_2CF_3 , $^2\text{J}_{\text{CF}}=34\text{Hz}$), 63.76 ($\underline{\text{C}}\text{H}_2\text{OH}$), 13.28 ($\underline{\text{C}}\text{H}_3$). ^{19}F NMR (188 MHz, CDCl_3) δ : (*Z*) -73.60 (t, 3F, $^3\text{J}_{\text{F-H}}=8\text{Hz}$). (*E*) : -74.34 (t, 3F, $^3\text{J}_{\text{F-H}}=8\text{Hz}$).

3-phenyl-3-(2,2,2-trifluoroethoxy)prop-2-en-1-ol (36)

^1H NMR (300 MHz, CDCl_3) δ : (*Z*) 4.97 (t, 1H, $\underline{\text{C}}\text{H}$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 4.42 (d, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 4.10 (q, H, CH_2CF_3 , $^3\text{J}_{\text{H-F}}=7\text{Hz}$). (*E*) 7.43-7.38 (m, 5H, H_{arm}), 5.07 (t, 1H, $\underline{\text{C}}\text{H}$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 4.15 (q, H, CH_2CF_3 , $^3\text{J}_{\text{H-F}}=8\text{Hz}$), 4.18 (d, 2H, CH_2OH , $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 1.68 (s, 1H, OH). ^{13}C NMR (75 MHz, CDCl_3) δ : (*E*) 157.20 ($\text{C}=\underline{\text{C}}\text{-O}$), 133.52-128.29 (C_{arm}), 123.22 (q, CF_3 , $^1\text{J}_{\text{C-F}}=277\text{Hz}$), 102.48 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 65.30 (q, CH_2CF_3 , $^1\text{J}_{\text{C-F}}=35\text{Hz}$), 59.22 ($\underline{\text{C}}\text{H}_2\text{OH}$). ^{19}F NMR (282 MHz, CDCl_3) δ : -73.71 (t, 3F, $^3\text{J}_{\text{F-H}}=8\text{Hz}$).

3-phenyl-3-((1,1,1-trifluoro-2-(trifluoromethyl)pent-4-en-2-yl)oxy)prop-2-en-1-ol (37)

^1H NMR (300 MHz, CDCl_3) δ : (*Z*) 7.42-7.32 (m, 5H, H_{arm}), 5.74-5.62 (m, 1H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 5.57 (t, 1H, $\underline{\text{C}}\text{H}$, $^3\text{J}_{\text{H-H}}=6\text{Hz}$), 5.13-5.07 (m, 2H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 4.40 (d, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$, $^3\text{J}_{\text{H-H}}=6\text{Hz}$), 2.59 (d, 2H, $\underline{\text{C}}\text{H}_2\text{CH}=\text{CH}_2$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 2.13 (s, 1H, OH). (*E*) 5.84 (t, 1H, $\underline{\text{C}}\text{H}$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 5.74-5.62 (m, 1H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 5.04-5.02 (m, 2H, $\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 4.20 (d, 2H, $\underline{\text{C}}\text{H}_2\text{OH}$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$), 2.64 (d, 2H, $\underline{\text{C}}\text{H}_2\text{CH}=\text{CH}_2$, $^3\text{J}_{\text{H-H}}=7\text{Hz}$). ^{13}C NMR (75 MHz, CDCl_3) δ : (*Z*) 150.18 ($\underline{\text{C}}\text{HO}$), 137.76 ($\text{C}=\underline{\text{C}}\text{-O}$), 129.35-128.28 (C_{arm}), 126.82 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 122.64 (q, CF_3 , $^1\text{J}_{\text{C-F}}=273\text{Hz}$), 120.86 ($\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 83.11-81.62 (m, $\underline{\text{C}}(\text{C}(\text{CF}_3)_2)$), 58.91

($\underline{\text{C}}\text{H}_2\text{OH}$), 33.95 ($\underline{\text{C}}\text{H}_2\text{CH}=\text{CH}_2$). (**E**) 151.06 ($\underline{\text{C}}\text{HO}$), 134.79 ($\text{C}=\underline{\text{C}}\text{-O}$), 129.35-128.28 (C_{arm}), 122.83 ($\text{C}=\underline{\text{C}}\text{-CHO}$), 122.64 (q, CF_3 , $^1\text{J}_{\text{C-F}} = 273\text{Hz}$), 120.67 ($\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$), 83.11-81.62 (m, $\underline{\text{C}}(\text{C}(\text{CF}_3)_2)$, 57.40($\underline{\text{C}}\text{H}_2\text{OH}$), 33.29 ($\underline{\text{C}}\text{H}_2\text{CH}=\text{CH}_2$). ^{19}F NMR (282 MHz, CDCl_3) δ : (**Z**) : -72.18 (s, 6F, $(\text{CH}_3)_2$), (**E**) -72.70 (s, 6F, $(\text{CH}_3)_2$).

Theoretical calculations

Full geometry optimizations were performed with GAUSSIAN 09W³⁷ program package, in 2,2,2-trifluoroethanol as solvent, modeled by universal solvation model (SMD)³⁸ using B3LYP method³⁹ with 6-31+G(d,p) basis set⁴⁰. From transition states (TSs), reaction paths were traced by the intrinsic reaction coordinate (IRC) method [22,23] to obtain the energy-minimum geometries. The relaxed Potential Energy Surface (PES) scan was performed with geometry optimization at each point. The energies of the optimized structures were evaluated by freezing the distances $\text{C}_4\text{-Cl} = 1.890\text{\AA}$ and $\text{C}_4\text{-O}_2 = 1.501\text{\AA}$ for each value of the dihedral angle ($\text{Cl-C}_4\text{-C}_3\text{-C}_2$).

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