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Reactions of ethyl triphenylphosphoranylideneacetate with fluorinated β-ketoaldehyde derivatives

Ivan S. Kondratov,* Igor I. Gerus, Marina V. Furmanova, Sergey I. Vdovenko and Valery P. Kukhar

Institute of Bioorganic Chemistry and Petrochemistry, National Ukrainian Academy of Science, Murmanska 1, Kiev-94, 02660, Ukraine

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Abstract—The reactions of fluorinated β-ketoaldehyde derivatives: β-alkoxyvinyl polyfluoroalkyl ketones **1** and fluorinated β-ketoacetals **2** with ethyl triphenylphosphoranylideneacetate **3** are described. In the case of ketones **1** the result of the reaction is a mixture of products: fluorinated alkoxydienes **5** (Wittig reaction product) and polyfluoroacyl vinyl ylides **7** (Michael addition product). The reaction with fluorinated β-ketoacetals **2** leads to a mixture of *E*- and *Z*-isomers of polyfluoroalkyl acrylates **8** and **9**, respectively. The influence of the nature of fluorinated substituent and solvent or other factors on the outcome of the reactions are discussed.
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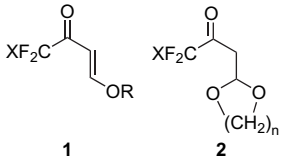
1. Introduction

The growing interest in fluorine-containing compounds as pharmaceuticals, agrochemicals, and tools for modern biochemistry stimulates the development of synthetic methods, which lead to fluoroorganic molecules.[1] While direct introduction of fluorine atoms or polyfluoroalkyl groups is a very popular route to fluorinated molecules, the methods based on available fluorine-containing building blocks are useful too. In the last case, the reactions leading to C–C bond formation play an important role for further transformations.

Among various C–C bond formation reactions Wittig reactions belong to the most popular organic synthesis.[2] It is also widely used for obtaining fluorinated compounds.[3,4] For example, Wittig reaction was one of the key stages in synthesis of fluorine-containing isopentenyl pyrophosphate,[3a] cephalosporine,[3b] retinal,[3c] juvenile hormones,[3d] pyrethroids,[3e] aconiates,[3f] and 3-isopropyl malate,[3g] hexafluorovaline,[3h] and trifluoroisoleucine,[3i] chiral ferroelectric liquid crystals.[3j] Various types of fluorine-containing molecules such as polyfluoroalkyl aliphatic and aromatic ketones, α,β-unsaturated ketones, β-diketones, and β-ketoesters were introduced in Wittig reactions.[3,4] However there are no reports on the interaction between Wittig reagents and fluorinated β-ketoaldehydes or their derivatives in spite of the high synthetic potential of these fluorinated building blocks.

The easily available and well-known fluorinated β-ketoaldehyde derivatives are β-alkoxyvinyl polyfluoroalkyl ketones **1** (Fig. 1).[5] These compounds can be considered both as β-ketoaldehyde derivatives with a protected aldehyde group and α,β-unsaturated ketones. The reactions of nucleophiles with compounds **1** lead to products of 1,2 or/and 1,4-addition depending on the nature of the nucleophile and reaction conditions used for the synthesis of various fluorine-containing products such as fluorinated enaminoketones, protected amino acids, heterocycles, cyanine dyes, and others.[6] Nevertheless the reaction of enones **1** with phosphorus ylides has not been previously studied yet, in general, there are just a few publications concerning the reaction of enones **1** with phosphorus-containing reagents.[7]

Recently we have reported an approach to other fluorinated β-ketoaldehyde derivatives—fluorinated β-ketoacetals **2** (Fig. 1, X=F).[8] In contrast to enones **1** these compounds have just one electrophilic center (the carbonyl carbon



1 **2**

X = H, F, Cl, CF_3, C_2F_5
R = alkyl, n = 2, 3

Figure 1. Fluorinated β-ketoaldehyde derivatives.

Keywords: Wittig reaction; Stabilized ylides; Fluorinated building blocks; Polyfluoroalkyl ketones; β-Ketoacetals; β-Alkoxy enones.
* Corresponding author. Tel.: +380 44 573 2598; fax: +380 44 573 2552; e-mail: vanya_ko@mail.ru

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atom). Therefore ketoacetals **2** can be used in reactions instead of enones **1** if it is necessary to avoid an undesirable 1,4-addition.[8]

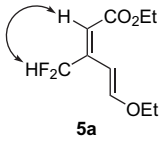
In the course of our research on the use of enones **1** for the synthesis of bioactive compounds, in the present paper, we report our investigations on the Wittig reaction between ethyl triphenylphosphoranylideneacetate **3** and fluorinated β-ketoaldehyde derivatives **1** and **2**.

2. Results and discussion

We have found that enones **1a–e** react with ylide **3** and a mixture of two products **5a–d** and **7a–e** is formed (Scheme 1) in complete conversion and high yields, moreover, the products can be easily and effectively separated.

Compounds **5** are 'normal' products of the Wittig reaction, which are formed due to initial ylide addition to carbonyl group (intermediate **4**) with the following triphenylphosphine oxide elimination. At the same time products **7** are formed due to initial ylide attack at the β-position of enone **1** (intermediate **6**) with subsequent ethanol elimination. The latter direction of the reaction is unusual for α,β-unsaturated carbonyl compounds. It should be mentioned that there are just a few examples when the addition of a phosphorus ylide to the β-position of α,β-unsaturated ketones or esters has been observed.[9] The formation of stable ylides with structures similar to compounds **7** was observed only for cases when two electron withdrawing groups (EWG) were attached to the double bond (C=C(EWG)$_2$).[9b,c] Additionally some highly stabilized ylides (including fluorinated) have been obtained by synthetic methods,[10] which are different from those mentioned above.[9b,c] Nevertheless there are no literature reports on the concurrent formation of 1,2- and 1,4-addition products from α,β-unsaturated carbonyl compounds under Wittig reaction conditions. At the same time such dual reactivity was observed for β-alkoxyvinyl polyfluoroalkyl ketones **1** in addition reactions with nucleophilic reagents such as sodium borohydride,[8] trimethylsilyl cyanide,[11] and tris(trimethylsilyl) phosphite.[7c]

It is noteworthy that only one stereoisomer of the products **5a–d** and **7a–e** was formed (demonstrated by NMR, IR spectroscopy, and X-ray analysis for compound **7b**). It was



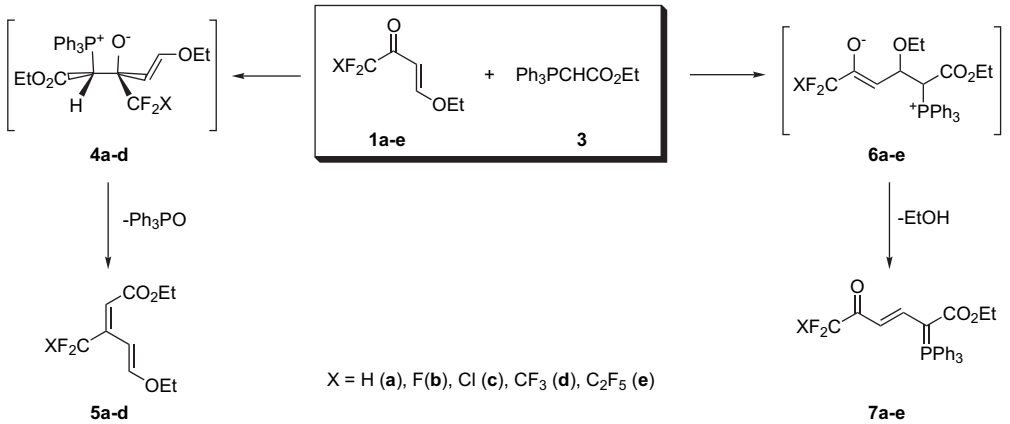
5a

Figure 2. NOE observation in product **5a**.

shown that the C=C double bond (CH=CHOEt fragment) in products **5a–d** retains the 4*E*-configuration (J_{HH} 13.5–13.7 Hz) of the starting enones **1**. The 2*E*-configuration of the formed C=C double bond of products **5a–d** (C=CHCO$_2$Et fragment) was confirmed by NOE experiments for product **5a** (Fig. 2). According to the literature[3,4] for the Wittig reaction of polyfluoroalkyl ketones the formation of the *E*-stereoisomer is favorable because an interaction between the largest vicinal polyfluoroalkyl and ethoxycarbonyl groups is minimal in the intermediate betaine **4**. Since compound **5a** is formed from enone **1a**, bearing the least hindered polyfluoroalkyl group (CHF$_2$) in comparison with other β-alkoxyvinyl polyfluoroalkyl ketones **1b–e** (CF$_3$, CF$_2$Cl, and C$_2$F$_5$), there is no doubt that products **5b–d** also have 2*E*-configuration, especially as the spectral data of compounds **5a–d** are very similar.

We have also found that the C=C double bond of compounds **7a–e** has the *E*-configuration (J_{HH} 13.4–13.8 Hz). Additionally the structure of product **7b** was proven by X-ray analysis (Fig. 3).[12] It should be noted that the C=P (1.765(1) Å) is longer than the same bond in similar ylides (1.727 Å/1.747 Å).[13]

The ratio of the products **5** and **7** depends on the nature of substituent X (Table 1). Its influence could result from either steric changes (the increase of polyfluoroalkyl group volume in series CHF$_2$<<CF$_3$<CF$_2$Cl<C$_2$F$_5$<C$_3$F$_7$) or electronic changes (the increase of electron withdrawing effect in series CHF$_2$<<CF$_3$≈CF$_2$Cl<C$_2$F$_5$<C$_3$F$_7$). Whereas the influence of sterical factors is obvious (the increase of substituent X size leads to increasing hindrance to ylide attack on carbonyl group) and electronic effects caused by substituent X influence are not so clear. Thus we used ^{13}C NMR spectroscopic data from enones **1a–e** in order to find possible differences of electronic density distribution of the conjugated systems and to elucidate their reactivity. The ^{13}C NMR data of starting enones **1** do not point to considerable



Scheme 1. Reaction between β-alkoxyvinyl polyfluoroalkyl ketones **1** and ethyl triphenylphosphoranylideneacetate **3** (CH$_2$Cl$_2$, rt, overnight, 100% conversion).

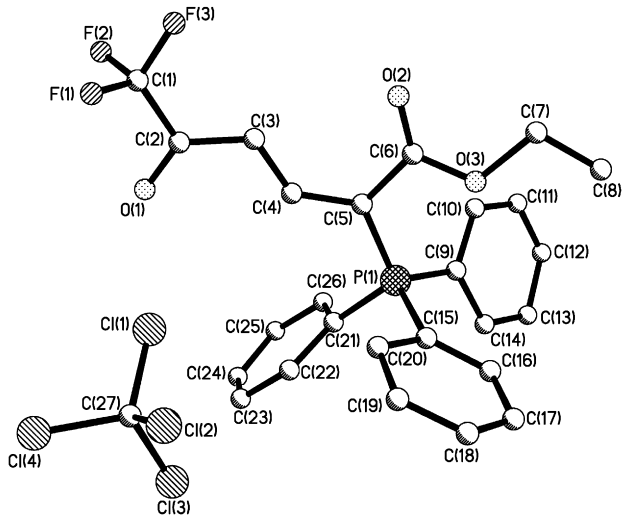


Figure 3. X-ray structure of compound **7b** (as a solvate with CCl_4).

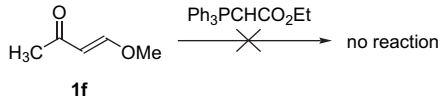
Table 1. Product ratios in the reaction mixture and isolated yields in the reaction between enones **1a–e** and ylide **3**

Starting enone **1**	Substituent X	Product ratios[a] in reaction mixture (isolated yields) (%)	
		5	**7**
1a	H	48 (32)	52 (41)
1b	F	16 (11)	84 (78)
1c	Cl	14 (9)	86 (81)
1d	CF_3	5[b] (0)	95 (78)
1e	C_2F_5	0	100 (89)

[a] Ratios were obtained from the ^{19}F NMR spectra of reaction mixtures of **1** (2 mmol) and **3** (2.2 mmol) after overnight stirring at rt in 1 mL of CH_2Cl_2.

[b] Product **6d** was observed by ^{19}F NMR spectroscopy in reaction mixture but not isolated.

difference in the electronic structure of enones **1b–e**: the signals of the carbonyl carbon appear at 180–182 ppm and the signals of the β-carbon atom at about 168 ppm (in $CDCl_3$). At the same time the corresponding signals in the ^{13}C NMR spectrum of enone **1a** have different values of chemical shifts in comparison with enones **1b–e**: the signal of carbonyl carbon atom appears at 187.8 ppm and the signal of β-carbon atom at 166.4 ppm (in $CDCl_3$). The facts demonstrate a significant electronic structure difference between enone **1a** and enones **1b–e**. Therefore it can be concluded that the main factor, which exerts influence on the ratio of the products **5** and **7** is steric hindrance in enones **1a–e** produced by polyfluoroalkyl groups, and that electronic changes are minor factors, which can only explain the difference of reactivity between enone **1a** and enones **1b–e**. Furthermore, even greater changes in the electronic structure can be observed for the nonfluorinated enone **1f** (^{13}C NMR spectroscopy data: the signals of C=O and β-carbon atoms appear at 196.9 and 163.0 ppm, correspondingly (in $CDCl_3$)) that results in no reaction between enone **1f** and ylide **3** even after 6 days under reflux in CH_2Cl_2 (Scheme 2).



1f

Scheme 2. Attempted reaction between enone **1f** and ylide **3** (CH_2Cl_2, reflux, 6 days, 0% conversion).

Table 2. Product ratios of the reaction between enone **1b** and ylide **3** in various solvents

Solvent	Product ratios[a] (%)	
	5b	**7b**
CCl_4	27	73
Benzene	23	77
Toluene	23	77
$CHCl_3$	18	82
CH_2Cl_2	16	84
THF	14	86
CH_3CN	16	84
DMF	12	88

[a] Ratios were obtained from ^{19}F NMR spectra of reaction mixtures of **1b** (20 mg) and **3** (45 mg) after overnight stirring in 1 mL of the corresponding solvent at rt.

The outcome of the Wittig reaction often depends on the nature of solvent.[14] Thus, we investigated the influence of solvents on the reaction between ylide **3** and enone **1b** by ^{19}F NMR spectroscopy method (Table 2). The percentage of the product **5b** decreases mostly with increasing solvent polarity that can be explained by the changes of electronic structure of enone **1b** as a result of specific solvatation. This assumption is confirmed by the IR[15] and ^{13}C NMR spectral data[16] of enone **1b** in various solvents: the increasing solvent polarity results in a decrease of electrophilicity at carbonyl carbon atom, whereas the reactivity of the β-position of enone **1b** increases.

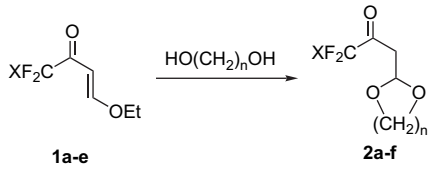
It should be mentioned that the data here represents the first example of a strong dependence between the ratio of products of 1,2- and 1,4-additions of nucleophiles to enones **1** and the nature of a solvent. Moreover, using the data of Table 2 (exact percentage of the products were used, see Supplementary data) we determined that the product ratio depends linearly on solvent parameters (Kamlet–Taft multiparameter linear solvatation energy correlation)[17] and the high correlation coefficient (R=0.981) demonstrates the strong sensitivity of the reaction to the nature of the solvents. The dependence of percentage of **5b** and **7b** is evaluated by Eqs. 1 and 2, respectively:

$$\omega\ (\%) = 29.150 - 16.062\pi^* - 14.219\alpha - 14.817\beta + 4.511\delta_H^2/100 \quad (1)$$

$$\omega\ (\%) = 70.850 + 16.062\pi^* + 14.219\alpha + 14.817\beta - 4.511\delta_H^2/100 \quad (2)$$

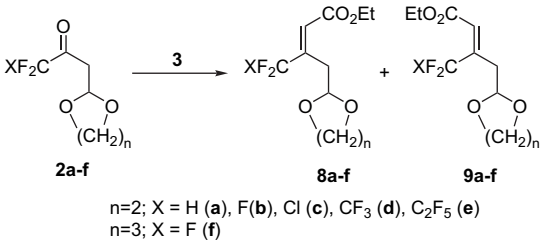
where π^*—index of solvent dipolarity/polarizability, α—measure of the solvent hydrogen bond donor acidity, β—measure of the solvent hydrogen bond acceptor basicity, δ_H—discontinuous polarizability correction term for polychlorine substituted aliphatic solvents. Equations show that in addition to polarity (polarizability) of solvent (regression coefficient of π^*), the role of solvent acidity/basicity is also important (regression coefficients of α and β) and the growth of solvent acidity (basicity) leads to increase of ylide product **7b** (from signs of coefficients of α and β).

Products **5** can be considered as polyfluoroalkyl-containing dienoates and are of interest both as powerful synthons for further conversions, due to the considerable quantity of functional groups in such a compact molecule, and as potential biologically active agents.[18] But a serious disadvantage to the wide usage of dienes **5** is their low yields. In order to obtain compounds with a similar carbon skeleton and functionality we studied the Wittig reaction of other fluorinated ketoaldehyde derivatives—ketoacetals **2a–f**, which afford only 'normal' Wittig products with ylide **3**. Recently we have reported practical synthetic methods for the preparation of ketoacetals **2b**,**f** from enone **1b**[8]. Thus, the new compounds **2a**,**c–e** were obtained by the same way in 56–75% yields (Scheme 3).



Scheme 3. Synthesis of ketoacetals **2a–f** (benzene, PTSA, reflux, 2–5 h, 56–75% yield).

The reaction of ketoacetals **2a–f** with ylide **3** leads to a mixture of isomeric *E*- and *Z*-acrylates **8a–f** and **9a–f**, respectively (Scheme 4). The reaction proceeds in high conversion and yields and the isomeric acrylates were separated by column chromatography.



Scheme 4. Wittig reaction between ketoacetals **2a–f** and ylide **3** (CH_2Cl_2, rt, overnight, 100% conversion).

The structure of compounds **8a–f** and **9a–f** was inferred by NMR and IR spectroscopy. The configuration of the C=C double bond of the products **8a–f** and **9a–f** was confirmed by NOE-experiments (Fig. 4): both isomers **8a–f** and **9a–f** demonstrate changes of integral intensity of the =CH

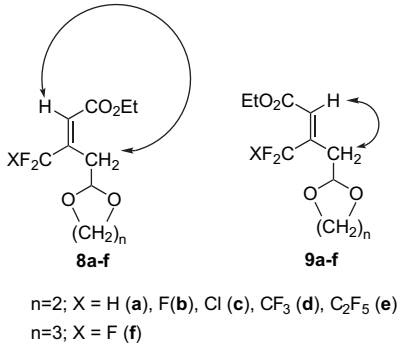


Figure 4. NOE-observation in products **8a–f** and **9a–f**.

Table 3. Product ratios of stereoisomeric products **8a–f** and **9a–f** in Wittig reaction of ketoacetals **2a–f**

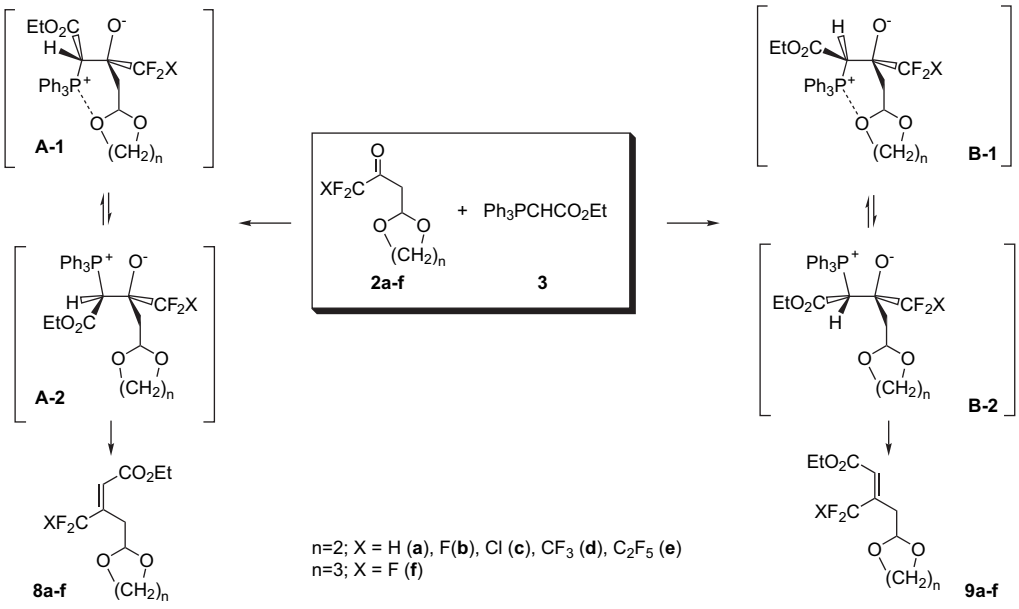
Compound	Substituent X	Product ratios[a] in reaction mixture (isolated yields) (%)	
		E-Isomer (**8**)	*Z*-Isomer (**9**)
2a	H	48 (39)	52 (45)
2b	F	73 (69)	27 (23)
2c	Cl	66 (64)	34 (24)
2d	CF_3	45 (34)	55 (39)
2e	C_2F_5	38 (29)	62 (58)
2f	F	41 (34)	59 (46)

[a] Ratio were obtained from ^{19}F NMR spectra of reaction mixtures of **2** (2 mmol) and **3** (2.2 mmol) after overnight stirring at rt in 1 mL of CH_2Cl_2.

proton signals under the irradiation of the CH_2 proton signals but the NOE-effect in compounds **9a–f** was much higher in comparison with **8a–f**.

The ratio of the products **8a–f** and **9a–f** was obtained from ^1H and ^{19}F NMR spectra of the crude reaction mixture (Table 3) and two interesting observations can be seen. On the one hand, the reaction results in a low stereoselectivity in the C=C double bond formation (38–73% of E-isomer) that is quite unusual for Wittig reaction between other fluorinated ketones and stabilized ylides: generally E-olefins are obtained in high percentage (>90%).[3,4] On the other hand, the increase of the stereoselectivity (a growing percentage of *E*-isomer) can be expected with the enlargement of polyfluoroalkyl substituent volume. However, one can see that the increase of the *E*-isomer percentage occurs only under conversion from **2a** to **2b** (from X=H to X=F, correspondingly), whereas further increase in the polyfluoroalkyl substituent volume in the starting ketoacetals **2b–e** (from X=F to X=C_2F_5) leads to an increase in the percentage of 'less favorable' *Z*-isomer. These data can be explained by the additional participation of acetal oxygen atoms in stabilization of the 'less stable' conformer of the intermediate betaines. The fact, that the stereoselectivity depends significantly on acetal cycle size (compare the reactions with ketoacetals **2b** and **2f**) and is not sensitive to the nature of solvents, confirms this assumption indirectly. It should be mentioned that the participation of oxygen-containing substituents (at β-position to carbonyl group) in the stabilization of Wittig reaction intermediates was earlier proposed to explain abnormal stereoselectivity in the Wittig reaction of some carbohydrate derivatives.[14c] Nevertheless, the same effect with the participation of fluorinated carbonyl compounds was not described earlier.

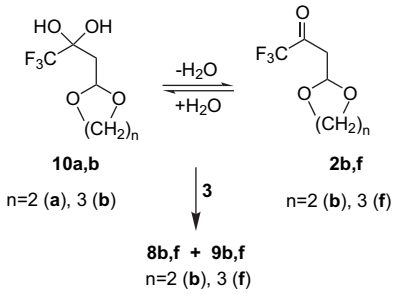
In order to explain the ratios of the products **8a–f** and **9a–f** we propose the following scheme: the addition of ylide **3** to the carbonyl group of ketoacetals **2a–f** leads to intermediate rotamers A-**1** and A-**2** (responsible for *E*-products) and rotamers B-**1** and B-**2** (responsible for *Z*-products) (Scheme 5). In the absence of additional stabilizing factors the stereochemical outcome of Wittig reaction is usually determined by favorable formation of the intermediate A-**2**, where interaction between the largest vicinal polyfluoroalkyl and ethoxycarbonyl groups is minimal. In our case, the stability of intermediates A-**1** and B-**1** is enhanced by additional stabilizing interactions between the phosphorus and acetal oxygen atoms, but conformer **A-1** is less stable than **B-1**



Scheme 5. The stabilizing effect of the acetal oxygen atoms in the Wittig reaction of ketoacetals **2a–f**.

(owing to steric interactions between vicinal polyfluoroalkyl and esters groups). So, the stabilizing participation of the acetal oxygen atom can explain both the high percentage of *Z*-products and the observed change of the stereoselectivity with the increase of polyfluoroalkyl substituent volume. At the same time the Wittig reaction of ketoacetal **2a** (bearing the smallest difluoromethyl group among other polyfluoroalkyl ones) results in a mixture of the products with an unexpectedly high percentage of *Z*-isomer **9a** (see Table 3). This probably results from a decrease of the electron withdrawing power of the difluoromethyl group that suppresses the influence of steric factors only.

Earlier the similar participation of the acetal oxygen atom was also observed in an intramolecular hydrogen bond formation in *gem*-diols **10** (which are easily formed from ketoacetals **2** and water).[8] However *gem*-diols **10** and ketoacetals **2** exist in equilibrium in solution and the equilibrium position depends on the nature of the solvent. We questioned whether the stereochemical outcome of the Wittig reaction changes if *gem*-diols **10** are used instead of ketoacetals **2**. We found that the yields and *Z*- and *E*-isomers ratio of the Wittig reaction between hydrates **10a**,**b** and ylide **3** are the same as in the case of ketoacetals **2b**,**f** (Scheme 6).



Scheme 6. *gem*-Diols **10** in Wittig reaction (CH_2Cl_2, rt, overnight, 100% conversion).

3. Conclusion

The Wittig reaction of fluorinated ketoacetaldehyde derivatives **1a–e** and **2a–f** with ethyl triphenylphosphoranylideneacetates **3** is useful for the synthesis of novel stabilized fluorinated ylides **5a–e** (as a result of ylide attack at the β-position of enones **1a–e**) and acrylates **7a–d**, **8a–f**, and **9a–f** (as a result of ylide attack at the carbonyl group of compounds **1a–d** and **2a–f**). The direction of the reaction depends on many factors such as the nature of solvent and fluoroalkyl group. Moreover in the case of ketoacetals **2a–f** the additional participation of the acetal oxygen atoms in intermediate betaine stabilization and its influences on the ratio of isomeric products **8a–f** and **9a–f** is observed. The compounds obtained are of interest as fluorinated polyfunctional building blocks for synthesis of products with potential biological activity, particularly fluorinated mevalonates.

4. Experimental

4.1. General

IR spectra were recorded on Specord M-80. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian VXR instrument at 300 MHz, Varian Unian Plus at 400 MHz, and Bruker Avance DRX at 500 MHz in $CDCl_3$ solutions. Chemical shifts were reported in parts per million (ppm). TMS and CCl_3F were used as internal standards for ^{1}H (^{13}C) and ^{19}F, respectively. ^{31}P spectra are referenced to 85% H_3PO_4. The conversion of reactions was monitored by TLC-plates (silica gel 60 F_{254}, Merck). Column chromatography was carried out on silica gel 60 (Merck no. 109385, particle size 0.040–0.063). Starting materials were commercially available (Aldrich, Fluka, and Merck). All solvents and liquid reagents were distilled before using. Starting enones **1a**,**d**,**e**,[6a] **1b**,[5a] and **1c**;[19] ketoacetals **2b**,**f**;[8] and hydrates **10a**,**b**[8] were prepared according to the literature procedures.

4.1.1. General procedure for the Wittig reaction with enones 1a–e. To a solution of ylide **3** (2.2 mmol) in 5 mL of CH_2Cl_2 the corresponding enones **1a–f** (2.0 mmol) were added under stirring. After 8–12 h monitored by TLC and NMR the solvent was evaporated and the residue was crystallized from an appropriate solvent to give the corresponding ylide **7a–e**. The filtrate after crystallization was evaporated and the residue was purified by column chromatography using an appropriate eluent to give the corresponding alkoxydiene **5a–c** (alkoxydiene **5d** was not isolated) in ~95% purity. The yields of compounds **5a–c** and **7a–f** as well as their percentage in the reaction mixture are presented in Table 1.

4.1.1.1. Ethyl (2*E*,4*E*)-3-(difluoromethyl)-5-ethoxy-2,4-pentadienoate (5a). Purified by column chromatography. CH_2Cl_2 (with few drops of Et_3N) was used as an eluent; colorless oil [Found: C, 54.7; H, 6.5. $C_{10}H_{14}F_2O_3$ requires C, 54.54; H, 6.41%]; R_f (CH_2Cl_2) 0.74; ν_{max} (CH_2Cl_2) 3060, 2960, 2928, 2872, 1712, 1632, 1519, 1455, 1381, 1307, 1240, 1189, 1133, 1096, 1033 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 1.36 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.96 (2H, q, J_{HH} 7.1 Hz, CH_2), 4.20 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 5.75 (1H, s, =C*H*–CO_2Et), 6.17 (1H, t, J_{HF} 54.8 Hz, C*H*F_2), 6.92 (1H, d, J_{HH} 13.5 Hz, C–C*H*=), 7.22 (1H, d, J_{HH} 13.5 Hz, O–C*H*=); δ_C (126 MHz, $CDCl_3$) 14.2, 14.5, 60.2, 65.7, 98.7, 113.7 (t, J_{CF} 10.1 Hz), 115.2 (t, J_{CF} 242.6 Hz), 144.3 (t, J_{CF} 20.2 Hz), 155.8 (t, J_{CF} 2.8 Hz), 165.9; δ_F (470.5 MHz, $CDCl_3$) −113.86 (d, J_{HF} 54.8, CHF_2).

4.1.1.2. Ethyl (*E*)-6,6-difluoro-5-oxo-2-(triphenylphosphoranylidene)-3-hexenoate (7a). Crystallized from toluene/hexane (1:2); light yellow needles, mp 163–164 °C [Found: C, 69.2; H, 5.0. $C_{26}H_{23}F_2O_3P$ requires C, 69.02; H, 5.12%]; ν_{max} (CH_2Cl_2) 3060, 2984, 1677, 1632, 1516, 1440, 1400, 1368, 1303, 1186, 1153, 1104, 1043, 1000 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.85 (3H, t, J_{HH} 6.9 Hz, *Me*), 3.97 (2H, q, J_{HH} 6.9 Hz, C*H*$_2$), 5.70 (1H, t, J_{HF} 55.4 Hz, C*H*F_2), 6.96–7.85 (17H, m, Ph and C*H*=C*H*); δ_C (126 MHz, $CDCl_3$) 14.0, 59.4, 67.8 (d, J_{CP} 115.5 Hz), 103.1, 111.7 (t, J_{CF} 252.6 Hz), 124.0 (d, J_{CP} 92.4 Hz), 129.2 (d, J_{CP} 12.6 Hz), 133.1 (d, J_{CP} 2.7 Hz), 133.7 (J_{CP} 9.2 Hz), 150.6 (d, J_{CP} 13.5 Hz), 167.3 (d, J_{CP} 15.3 Hz), 184.9 (t, J_{CF} 22.4 Hz); δ_F (470.5 MHz, $CDCl_3$) −125.98 (br s, CHF_2); δ_P (202 MHz, $CDCl_3$) 30.04 (br s, *P*Ph_3).

4.1.1.3. Ethyl (2*E*,4*E*)-5-ethoxy-3-(trifluoromethyl)-2,4-pentadienoate (5b). Purified by column chromatography. CH_2Cl_2 (with few drops of Et_3N) was used as an eluent; colorless oil [Found: C, 50.2; H, 5.6. $C_{10}H_{13}F_3O_3$ requires C, 50.42; H, 5.50%]; R_f (CH_2Cl_2) 0.81; ν_{max} (CH_2Cl_2) 3060, 2984, 2927, 2872, 1728, 1628, 1448, 1372, 1308, 1260, 1190, 1135, 1031 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.31 (3H, t, J_{HH} 7.1 Hz, *Me*), 1.35 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.97 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 4.21 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 5.97 (1H, s, =C*H*–CO_2Et), 6.96 (1H, d, J_{HH} 13.7 Hz, C–C*H*=), 7.16 (1H, d, J_{HH} 13.7 Hz, O–C*H*=); δ_C (126 MHz, $CDCl_3$) 14.2, 14.5, 60.5, 66.0, 97.8, 113.9 (q, J_{CF} 6.5 Hz), 122.7 (q, J_{CF} 276.5 Hz), 140.3 (q, J_{CF} 29.7 Hz), 156.4 (q, J_{CF} 3.4 Hz), 165.5; δ_F (470.5 MHz, $CDCl_3$) −64.21 (s, CF_3).

4.1.1.4. Ethyl (*E*)-6,6,6-trifluoro-5-oxo-2-(triphenylphosphoranylidene)-3-hexenoate (7b). Crystallized from toluene/hexane (1:1) or CCl_4; light yellow needles, mp 162–164 °C [Found: C, 66.2; H, 4.6. $C_{26}H_{22}F_3O_3P$ requires C, 66.38; H, 4.71%]; ν_{max} (CH_2Cl_2) 3052, 2984, 1680, 1632, 1522, 1440, 1400, 1368, 1320, 1260, 1190, 1163, 1136, 1102, 1000 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.87 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.98 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 7.07 (1H, d, J_{HH} 13.8 Hz, COC*H*=), 7.35–7.72 (16H, m, Ph and C*H*–C=PPh_3); δ_C (126 MHz, $CDCl_3$) 13.8, 59.5, 70.1 (d, J_{CP} 112.6 Hz), 101.5, 118.2 (q, J_{CF} 291.3 Hz), 123.5 (d, J_{CP} 92.1 Hz), 129.2 (d, J_{CP} 12.6 Hz), 133.2 (d, J_{CP} 3.1 Hz), 133.6 (d, J_{CP} 9.7 Hz), 152.3 (d, J_{CP} 14.5 Hz), 167.0 (d, J_{CP} 14.5 Hz), 177.4 (q, J_{CF} 30.9 Hz); δ_F (470.5 MHz, $CDCl_3$) −78.31 (br s, CF_3); δ_P (202 MHz, $CDCl_3$) 30.11 (br s, *P*Ph_3).

4.1.1.5. Ethyl (2*E*,4*E*)-3-[chloro(difluoro)methyl]-5-ethoxy-2,4-pentadienoate (5c). Purified by column chromatography. CH_2Cl_2 (with few drops of Et_3N) was used as an eluent; colorless oil [Found: C, 47.3; H, 5.2. $C_{10}H_{13}ClF_2O_3$ requires C, 47.16; H, 5.15%]; R_f (CH_2Cl_2) 0.81; ν_{max} (CH_2Cl_2) 3060, 2985, 2935, 1732, 1560, 1448, 1376, 1132 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.31 (3H, t, J_{HH} 7.1 Hz, *Me*), 1.36 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.98 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 4.21 (2H, q, J_{HH} 7.1 Hz, C*H*$_2$), 5.95 (1H, s, =C*H*–CO_2Et), 6.92 (1H, d, J_{HH} 13.6 Hz, C–C*H*=), 7.28 (1H, d, J_{HH} 13.6 Hz, O–C*H*=); δ_C (126 MHz, $CDCl_3$) 14.2, 14.6, 60.6, 65.9, 97.2, 112.3 (t, J_{CF} 8.1 Hz), 124.6 (t, J_{CF} 293.5 Hz), 145.3 (t, J_{CF} 23.6 Hz), 156.8 (t, J_{CF} 3.8 Hz), 165.7; δ_F (470.5 MHz, $CDCl_3$) −51.69 (s, CF_2Cl).

4.1.1.6. Ethyl (*E*)-6-chloro-6,6-difluoro-5-oxo-2-(triphenylphosphoranylidene)-3-hexenoate (7c). Crystallized from diethyl ether/CCl_4 (1:2); light yellow needles, mp 151–152 °C [Found: C, 63.9; H, 4.5. $C_{26}H_{22}ClF_2O_3P$ requires C, 64.14; H, 4.55%]; ν_{max} (CH_2Cl_2) 3048, 2990, 1680, 1634, 1513, 1440, 1424, 1392, 1312, 1216, 1163, 1104, 1040, 1000, 947 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, J_{HH} 6.9 Hz, *Me*), 3.97 (2H, q, J_{HH} 6.9 Hz, C*H*$_2$), 7.08 (1H, d, J_{HH} 13.4 Hz, COC*H*=), 7.34–7.75 (16H, m, Ph and C*H*–C=PPh_3); δ_C (126 MHz, $CDCl_3$) 13.9, 59.6, 70.3 (d, J_{CP} 115.7 Hz), 100.2, 122.5 (t, J_{CF} 295.0 Hz), 123.6 (d, J_{CP} 92.3 Hz), 129.3 (d, J_{CP} 12.5 Hz), 133.2 (d, J_{CP} 2.5 Hz), 133.8 (d, J_{CP} 9.8 Hz), 152.7 (d, J_{CP} 13.9 Hz), 167.1 (d, J_{CP} 14.8 Hz), 179.2 (t, J_{CF} 24.7 Hz); δ_F (470.5 MHz, $CDCl_3$) −64.70 (br s, CF_2Cl); δ_P (202 MHz, $CDCl_3$) 30.05 (br s, *P*Ph_3).

4.1.1.7. Ethyl (*E*)-6,6,7,7,7-pentafluoro-5-oxo-2-(triphenylphosphoranylidene)-3-heptenoate (7d). Crystallized from diethyl ether/CCl_4 (1:2); light yellow needles, mp 160–162 °C [Found: C, 62.4; H, 4.3. $C_{27}H_{22}F_5O_3P$ requires C, 62.31; H, 4.26%]; ν_{max} (CH_2Cl_2) 3052, 2985, 1682, 1633, 1515, 1440, 1394, 1368, 1311, 1192, 1164, 1104, 1058, 992 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.85 (3H, t, J_{HH} 6.8 Hz, *Me*), 3.97 (2H, q, J_{HH} 6.8 Hz, C*H*$_2$), 7.16 (1H, d, J_{HH} 13.4 Hz, COC*H*=), 7.41–7.86 (16H, m, Ph and C*H*–C=PPh_3); δ_C (126 MHz, $CDCl_3$) 13.9, 59.7, 71.0 (d, J_{CP} 115.0 Hz), 102.3, 123.5 (d, J_{CP} 92.7 Hz), 129.3 (d, J_{CP} 12.4 Hz), 133.3 (d, J_{CP} 2.3 Hz), 133.7 (d, J_{CP} 9.9 Hz), 152.2 (d, J_{CP} 13.8 Hz), 167.0 (d, J_{CP} 13.8 Hz), 178.1 (t, J_{CF} 23.2 Hz), low intensity and high multiplicity signals of carbon atoms of C_2F_5-fragment overlapped in the area of

110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −123.32 (2F, br s, CF_2), −82.78 (3F, s, CF_3); δ_P (202 MHz, $CDCl_3$) 30.20 (br s, PPh_3).

4.1.1.8. Ethyl (*E*)-6,6,7,7,8,8,8-heptafluoro-5-oxo-2-(triphenylphosphoranylidene)-3-octenoate (7e). Crystallized from diethyl ether/CCl_4 (1:2); light yellow needles, mp 136–138 °C [Found: C, 59.3; H, 3.8. $C_{28}H_{22}F_7O_3P$ requires C, 58.96; H, 3.89%]; ν_{max} (CH_2Cl_2) 3060, 2984, 1681, 1632, 1513, 1440, 1394, 1312, 1228, 1168, 1104, 1046, 1000, 952 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.86 (3H, t, J_{HH} 6.8 Hz, *Me*), 3.98 (2H, q, J_{HH} 6.8 Hz, CH_2), 7.15 (1H, d, J_{HH} 13.4 Hz, COC*H*=), 7.42–8.04 (16H, m, Ph and C*H*–C=PPh_3); δ_C (126 MHz, $CDCl_3$) 13.7, 59.5, 70.8 (d, J_{CP} 115.5 Hz), 102.6, 123.4 (d, J_{CP} 91.8 Hz), 129.2 (d, J_{CP} 12.7 Hz), 133.2 (d, J_{CP} 2.6 Hz), 133.6 (d, J_{CP} 9.4 Hz), 152.1 (d, J_{CP} 13.7 Hz), 167.1 (d, J_{CP} 14.1 Hz), 178.1 (t, J_{CF} 23.2 Hz), low intensity and high multiplicity signals of carbon atoms of C_3F_7-fragment overlapped in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −127.12 (2F, s, CF_3CF_2), −121.03 (2F, br s, CF_2CO), −81.14 (3F, t, J_{FF} 8.8 Hz, CF_3CF_2); δ_P (202 MHz, $CDCl_3$) 30.17 (br s, PPh_3).

4.1.2. General procedure for synthesis of ketoacetals 2a,c–e. A mixture of the corresponding enone (1 equiv) **1a**,**c**–**e**, ethylene glycol (1.2 equiv), 20 mL of benzene, and catalytic amount of *p*-toluenesulfonic acid (10 mg) was refluxed with the simultaneous distillation of an ethanol/benzene azeotrope. The conversion was monitored by NMR and, if necessary, additional portion of benzene (10 mL) was added until enones **1a**,**c**–**e** disappeared by NMR. Then benzene was removed and the residue was distilled in vacuum giving corresponding products **2a**,**c**–**e**.

4.1.2.1. 3-(1,3-Dioxolan-2-yl)-1,1-difluoroacetone (2a). From 2.5 g of enone **1a** and 1.14 g of ethylene glycol; yield: 1.88 g (68%); light yellow liquid, bp 58–59 °C (20 Torr) [Found: C, 43.4; H, 4.9. $C_6H_8F_2O_3$ requires C, 43.38; H, 4.85%]; ν_{max} (CH_2Cl_2) 3060, 2984, 2895, 1752, 1592, 1424, 1392, 1248, 1216, 1135, 1083, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.04 (2H, d, J_{HH} 5.0 Hz, COCH_2), 3.80–4.12 (4H, m, OCH_2CH_2O), 5.31 (1H, t, J_{HH} 5.0 Hz, CH_2C*H*), 5.76 (1H, t, J_{HF} 54.0 Hz, C*H*F_2); δ_C (126 MHz, $CDCl_3$) 41.5, 65.0, 99.8, 109.5 (t, J_{CF} 252.2 Hz), 195.8 (t, J_{CF} 26.7 Hz); δ_F (470.5 MHz, $CDCl_3$) −128.89 (d, J_{HF} 54.0 Hz, C*H*F_2).

4.1.2.2. 1-Chloro-3-(1,3-dioxolan-2-yl)-1,1-difluoroacetone (2c). From 5 g of enone **1c** and 1.68 g of ethylene glycol; yield: 4.09 g (75%); light yellow liquid, bp 65–66 °C (12 Torr) [Found: C, 36.1; H, 3.4. $C_6H_7F_2ClO_3$ requires C, 35.93; H, 3.52%]; ν_{max} (CH_2Cl_2) 3052, 2986, 2895, 1760, 1597, 1416, 1221, 1136, 1072, 1016, 920 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.09 (2H, d, J_{HH} 4.9 Hz, COCH_2), 3.82–4.05 (4H, m, OCH_2CH_2O), 5.34 (1H, t, J_{HH} 4.9 Hz, CH_2C*H*); δ_C (126 MHz, $CDCl_3$) 40.3, 65.1, 99.7, 119.3 (t, J_{CF} 306.0 Hz), 187.8 (t, J_{CF} 30.5 Hz); δ_F (470.5 MHz, $CDCl_3$) −69.60 (s, CF_2Cl).

4.1.2.3. 1-(1,3-Dioxolan-2-yl)-3,3,4,4,4-pentafluoro-2-butanone (2d). From 3 g of enone **1d** and 0.90 g of ethylene glycol; yield: 1.80 g (56%); light yellow liquid, bp 49–51 °C (10 Torr) [Found: C, 36.1; H, 2.9. $C_7H_7F_5O_3$ requires C, 35.91; H, 3.01%]; ν_{max} (CH_2Cl_2) 3060, 2962, 2896, 1760, 1592, 1416, 1392, 1335, 1200, 1140, 1032, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.10 (2H, d, J_{HH} 4.8 Hz, COCH_2), 3.84–4.03 (4H, m, OCH_2CH_2O), 5.36 (1H, t, J_{HH} 4.8 Hz, CH_2C*H*); δ_C (126 MHz, $CDCl_3$) 42.4, 65.1, 99.5, 119.3 (t, J_{CF} 306.0 Hz), 190.5 (t, J_{CF} 27.4 Hz), low intensity and high multiplicity signals, which belong to carbon atoms of C_2F_5-fragment overlapped in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −124.25 (2F, s, CF_2), −82.40 (3F, s, CF_3).

4.1.2.4. 1-(1,3-Dioxolan-2-yl)-3,3,4,4,5,5,5-heptafluoro-2-pentanone (2e). From 3 g of enone **1e** and 0.76 g of ethylene glycol; yield: 1.82 g (57%); light yellow liquid, bp 59–60 °C (10 Torr) [Found: C, 33.6; H, 2.4. $C_8H_7F_7O_3$ requires C, 33.82; H, 2.48%]; ν_{max} (CH_2Cl_2) 3060, 2960, 2894, 1760, 1608, 1592, 1421, 1392, 1352, 1327, 1236, 1123, 1016, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 3.10 (2H, d, J_{HH} 4.9 Hz, COCH_2), 3.85–4.06 (4H, m, OCH_2CH_2O), 5.36 (1H, t, J_{HH} 4.9 Hz, CH_2C*H*); δ_C (126 MHz, $CDCl_3$) 42.9, 65.1, 99.5, 119.3 (t, J_{CF} 306.0 Hz), 190.3 (t, J_{CF} 26.6 Hz), low intensity and high multiplicity signals, which belong to carbon atoms of C_3F_7-fragment overlapped in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −127.06 (2F, s, CF_3CF_2), −121.96 (2F, q, J_{FF} 8.7 Hz, CF_2CO), −81.10 (3F, t, J_{FF} 8.7 Hz, CF_3).

4.1.3. General procedure for the Wittig reaction with ketoacetals 2a–f or hydrates 10a,b. To a solution of ylide **3** (2.2 mmol) in 5 mL of CH_2Cl_2 the corresponding ketoacetals **2a**–**f** or *gem*-diols **10a**,**b** (2 mmol) was added under stirring. After 8–12 h (the reaction monitored by TLC or ^{19}F NMR) the solvent was evaporated and isomers **8a**–**f** and **9a**–**f** were separated by column chromatography using an appropriate eluent. The yields of compounds **8a**–**f** and **9a**–**f** as well as their percentage in the reaction mixture are presented in Table 3.

4.1.3.1. Ethyl (*E*)-3-(1,3-dioxolan-2-ylmethyl)-4,4-difluoro-2-butenoate (8a). CH_2Cl_2 was used as an eluent; colorless oil [Found: C, 50.7; H, 6.0. $C_{10}H_{14}F_2O_4$ requires C, 50.85; H, 5.97%]; R_f (CH_2Cl_2) 0.40; ν_{max} (CH_2Cl_2) 3060, 2987, 2893, 1722, 1671, 1442, 1391, 1368, 1336, 1248, 1195, 1162, 1130, 1093, 1034, 968, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.07 (2H, d, J_{HH} 4.8 Hz, CH_2CH), 3.82–4.01 (4H, m, OCH_2CH_2O), 4.22 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.11 (1H, t, J_{HH} 4.8 Hz, CH_2C*H*), 6.23 (1H, t, J_{HF} 55.7 Hz, C*H*F_2), 6.25 (1H, s, C*H*=); δ_C (126 MHz, $CDCl_3$) 14.1, 31.6, 60.7, 64.9, 102.9, 114.1 (t, J_{CF} 242.2 Hz), 122.4 (t, J_{CF} 9.7 Hz), 144.6 (t, J_{CF} 19.2 Hz), 165.2; δ_F (470.5 MHz, $CDCl_3$) −121.51 (d, J_{HF} 55.7 Hz, C*H*F_2).

4.1.3.2. Ethyl (*Z*)-3-(1,3-dioxolan-2-ylmethyl)-4,4-difluoro-2-butenoate (9a). CH_2Cl_2 was used as an eluent; colorless oil [Found: C, 50.7; H, 6.0. $C_{10}H_{14}F_2O_4$ requires C, 50.85; H, 5.97%]; R_f (CH_2Cl_2) 0.46; ν_{max} (CH_2Cl_2) 3060, 2985, 2893, 1718, 1664, 1472, 1396, 1338, 1246, 1155, 1096, 1028, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.65 (2H, d, J_{HH} 4.8 Hz, CH_2CH), 3.85–4.05 (4H, m, OCH_2CH_2O), 4.21 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.09 (1H, t, J_{HH} 4.8 Hz, CH_2C*H*), 6.17 (1H, s, C*H*=), 7.40 (1H, t, J_{HF} 55.7 Hz, C*H*F_2); δ_C (126 MHz,

$CDCl_3$) 14.1, 31.5, 61.0, 65.0, 102.1, 110.2 (t, J_{CF} 235.9 Hz), 125.8 (t, J_{CF} 8.2 Hz), 145.2 (t, J_{CF} 23.6 Hz), 164.3; δ_F (470.5 MHz, $CDCl_3$) −120.44 (d, J_{HF} 55.7 Hz, CHF_2).

4.1.3.3. Ethyl (*E*)-3-(1,3-dioxolan-2-ylmethyl)-4,4,4-trifluoro-2-butenoate (8b). EtOAc/hexane (1:5) was used as an eluent; colorless oil [Found: C, 47.4; H, 5.2. $C_{10}H_{13}F_3O_4$ requires C, 47.25; H, 5.15%]; R_f (EtOAc/hexane, 1:5) 0.56; ν_{max} (CH_2Cl_2) 3060, 2984, 2894, 1726, 1672, 1472, 1444, 1376, 1360, 1311, 1183, 1133, 1080, 1035, 900 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.32 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.08 (2H, d, J_{HH} 4.9 Hz, CH_2CH), 3.82–4.01 (4H, m, OCH_2CH_2O), 4.24 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.18 (1H, t, J_{HH} 4.9 Hz, CH_2CH), 6.45 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 14.0, 31.3, 61.0, 64.9, 102.3, 123.1 (q, J_{CF} 275.4 Hz), 125.3 (q, J_{CF} 6.0 Hz), 139.4 (q, J_{CF} 30.5 Hz), 164.5; δ_F (470.5 MHz, $CDCl_3$) −69.81 (s, CF_3).

4.1.3.4. Ethyl (*Z*)-3-(1,3-dioxolan-2-ylmethyl)-4,4,4-trifluoro-2-butenoate (9b). EtOAc/hexane (1:5) was used as an eluent; colorless oil [Found: C, 47.3; H, 5.2. $C_{10}H_{13}F_3O_4$ requires C, 47.25; H, 5.15]; R_f (EtOAc/hexane, 1:5) 0.37; ν_{max} (CH_2Cl_2) 3060, 2985, 2892, 1735, 1669, 1384, 1260, 1176, 1136, 1098, 1032, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.60 (2H, d, J_{HH} 4.6 Hz, CH_2CH), 3.85–4.04 (4H, m, OCH_2CH_2O), 4.24 (2H, q, J_{HH} 7.1 Hz, OCH_2CH_3), 5.06 (1H, t, J_{HH} 4.6 Hz, CH_2CH), 6.30 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 13.9, 35.7 (q, J_{CF} 1.8 Hz), 61.4, 65.1, 101.7, 122.3 (q, J_{CF} 275.5 Hz), 128.5 (q, J_{CF} 3.7 Hz), 132.8 (q, J_{CF} 32.1 Hz), 164.3; δ_F (470.5 MHz, $CDCl_3$) −64.63 (s, CF_3).

4.1.3.5. Ethyl (*E*)-4-chloro-3-(1,3-dioxolan-2-ylmethyl)-4,4-difluoro-2-butenoate (8c). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 44.3; H, 4.9. $C_{10}H_{13}ClF_2O_4$ requires C, 44.38; H, 4.84%]; R_f (EtOAc/hexane, 1:4) 0.59; ν_{max} (CH_2Cl_2) 3060, 2985, 2894, 1726, 1664, 1472, 1437, 1376, 1352, 1260, 1200, 1125, 1072, 1037, 968 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.32 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.13 (2H, d, J_{HH} 4.9 Hz, CH_2CH), 3.82–4.02 (4H, m, OCH_2CH_2O), 4.24 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.23 (1H, t, J_{HH} 4.9 Hz, CH_2CH), 6.41 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 14.1, 31.9, 61.0, 64.9, 102.4, 123.1 (t, J_{CF} 7.5 Hz), 125.9 (t, J_{CF} 292.7 Hz), 144.1 (t, J_{CF} 24.4 Hz), 164.8; δ_F (470.5 MHz, $CDCl_3$) −56.47 (s, CF_2Cl).

4.1.3.6. Ethyl (*Z*)-4-chloro-3-(1,3-dioxolan-2-ylmethyl)-4,4-difluoro-2-butenoate (9c). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 44.3; H, 4.9. $C_{10}H_{13}ClF_2O_4$ requires C, 44.38; H, 4.84%]; R_f (EtOAc/hexane, 1:4) 0.40; ν_{max} (CH_2Cl_2) 3060, 2984, 2894, 1733, 1664, 1472, 1424, 1375, 1248, 1123, 1088, 1032, 936 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.61 (2H, d, J_{HH} 4.8 Hz, CH_2CH), 3.84–4.06 (4H, m, OCH_2CH_2O), 4.23 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.07 (1H, t, J_{HH} 4.8 Hz, CH_2CH), 6.20 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 13.9, 35.4, 61.4, 65.4, 101.8, 124.5 (t, J_{CF} 292.5 Hz), 125.1 (t, J_{CF} 3.9 Hz), 136.8 (t, J_{CF} 25.7 Hz), 164.8; δ_F (470.5 MHz, $CDCl_3$) −52.76 (s, CF_2Cl).

4.1.3.7. Ethyl (*E*)-3-(1,3-dioxolan-2-ylmethyl)-4,4,5,5,5-pentafluoro-2-pentenoate (8d). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 43.5; H, 4.4. $C_{11}H_{13}F_5O_4$ requires C, 43.43; H, 4.31%]; R_f (EtOAc/hexane, 1:4) 0.52; ν_{max} (CH_2Cl_2) 3060, 2992, 2895, 1726, 1662, 1448, 1376, 1328, 1220, 1092, 1034, 900 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.31 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.06 (2H, d, J_{HH} 4.9 Hz, CH_2CH), 3.80–4.00 (4H, m, OCH_2CH_2O), 4.23 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.16 (1H, t, CH_2CH, J_{HH} 4.8 Hz), 6.41 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 14.0, 31.7, 61.1, 64.9, 102.5, 128.1 (t, J_{CF} 8.3 Hz), 139.0 (t, J_{CF} 21.6 Hz), 164.3, low intensity and high multiplicity signals, which belong to carbon atoms of C_2F_5-fragment are in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −117.00 (2F, s, CF_2), −83.92 (3F, s, CF_3).

4.1.3.8. Ethyl (*Z*)-3-(1,3-dioxolan-2-ylmethyl)-4,4,5,5,5-pentafluoro-2-pentenoate (9d). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 43.5; H, 4.4. $C_{11}H_{13}F_5O_4$ requires C, 43.43; H, 4.31%]; R_f (EtOAc/hexane, 1:4) 0.39; ν_{max} (CH_2Cl_2) 3060, 2986, 2894, 1737, 1664, 1446, 1376, 1328, 1248, 1194, 1136, 1104, 1032, 944 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.27 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.55 (2H, d, J_{HH} 4.7 Hz, CH_2CH), 3.83–4.02 (4H, m, OCH_2CH_2O), 4.21 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.02 (1H, t, J_{HH} 4.7 Hz, CH_2CH), 6.55 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 13.8, 34.8, 61.4, 65.0, 102.0, 129.5 (t, J_{CF} 22.0 Hz), 131.2 (t, J_{CF} 5.3 Hz), 164.7, low intensity and high multiplicity signals, which belong to carbon atoms of C_2F_5-fragment are in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −114.02 (2F, s, CF_2), −82.93 (3F, s, CF_3).

4.1.3.9. (*E*)-4-(1,3-Dioxolan-2-ylmethyl)-5,5,6,6,7,7,7-heptafluoro-1-methoxy-3-hepten-2-one (8e). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 40.8; H, 3.8. $C_{12}H_{13}F_7O_4$ requires C, 40.69; H, 3.70%]; R_f (EtOAc/hexane, 1:4) 0.54; ν_{max} (CH_2Cl_2) 3060, 2984, 1729, 1660, 1376, 1344, 1232, 1120, 1037, 992, 962 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.31 (3H, t, J_{HH} 7.1 Hz, *Me*), 3.06 (2H, d, J_{HH} 4.8 Hz, CH_2CH), 3.80–3.99 (4H, m, OCH_2CH_2O), 4.24 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 5.16 (1H, t, J_{HH} 4.8 Hz, CH_2CH), 6.40 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 14.0, 31.9, 61.1, 64.9, 102.6, 128.5 (t, J_{CF} 8.6 Hz), 139.2 (t, J_{CF} 21.7 Hz), 164.3, low intensity and high multiplicity signals of C_3F_7-fragment C atoms are in the area of 110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −126.41 (2F, s, CF_3CF_2), −114.13 (2F, q, J_{FF} 9.7 Hz, CF_2CO), −80.73 (3F, t, J_{FF} 9.7 Hz, CF_3CF_2).

4.1.3.10. (*Z*)-4-(1,3-Dioxolan-2-ylmethyl)-5,5,6,6,7,7,7-heptafluoro-1-methoxy-3-hepten-2-one (9e). EtOAc/hexane (1:4) was used as an eluent; colorless oil [Found: C, 40.8; H, 3.8. $C_{12}H_{13}F_7O_4$ requires C, 40.69; H, 3.70%]; R_f (EtOAc/hexane, 1:4) 0.41; ν_{max} (CH_2Cl_2) 3060, 2992, 2896, 1738, 1663, 1447, 1374, 1343, 1247, 1119, 1032, 946, 912 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.26 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.55 (2H, d, J_{HH} 4.5 Hz, CH_2CH), 3.82–4.01 (4H, m, OCH_2CH_2O), 4.20 (2H, q, OCH_2Me, J_{HH} 7.1 Hz), 5.02 (1H, t, J_{HH} 4.5 Hz, CH_2CH), 6.57 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 13.7, 34.9 (t, J_{CF} 2.1 Hz), 61.4, 65.0, 102.1, 129.6 (t, J_{CF} 22.7 Hz), 131.4 (t, J_{CF} 5.3 Hz), 164.6, low intensity and high multiplicity signals, which belong to carbon atoms of C_3F_7-fragment are in the area of

110–130 ppm; δ_F (470.5 MHz, $CDCl_3$) −124.74 (2F, s, CF_3CF_2), −110.98 (2F, q, J_{FF} 9.7 Hz, CF_2CO), −81.01 (3F, t, J_{FF} 9.7 Hz, CF_3CF_2).

4.1.3.11. Ethyl (*E*)-3-(1,3-dioxan-2-ylmethyl)-4,4,4-trifluoro-2-butenoate (8f). EtOAc/hexane (1:5) was used as an eluent (R_f 0.42); colorless oil [Found: C, 49.1; H, 5.7. $C_{11}H_{15}F_3O_4$ requires C, 49.26; H, 5.64%]; ν_{max} (CH_2Cl_2) 3060, 2984, 2932, 1726, 1673, 1470, 1428, 1376, 1360, 1312, 1240, 1203, 1136, 1080, 1033, 900 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.31 (1H, dtt, J_{HH} 13.6, 2.5, 1.1 Hz, $OCH_2CH_aH_bCH_2O$), 1.32 (3H, t, J_{HH} 7.1 Hz, *Me*), 2.08 (1H, dtt, J_{HH} 13.6, 12.6, 5.0 Hz, $OCH_2CH_aH_b$-CH_2O), 3.03 (2H, d, J_{HH} 5.5 Hz, CH_2CH), 3.73 (2H, ddd, J_{HH} 12.6, 11.8, 2.5 Hz, $OCH_aH_bCH_2CH_aH_bO$), 4.08 (2H, ddd, J_{HH} 11.8, 5.0, 1.1 Hz, $OCH_aH_bCH_2CH_aH_bO$), 4.25 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 4.73 (1H, t, J_{HH} 5.5 Hz, CH_2CH), 6.42 (1H, s, CH=); δ_C (126 MHz, $CDCl_3$) 14.0, 25.5, 32.1, 61.0, 66.9, 99.9, 123.1 (q, J_{CF} 275.4 Hz), 125.3 (q, J_{CF} 6.0 Hz), 139.1 (q, J_{CF} 30.2 Hz), 164.5; δ_F (470.5 MHz, $CDCl_3$) −69.49 (s, CF_3).

4.1.3.12. Ethyl (*Z*)-3-(1,3-dioxan-2-ylmethyl)-4,4,4-trifluoro-2-butenoate (9f). EtOAc/hexane (1:5) was used as an eluent (R_f 0.27); colorless oil [Found: C, 49.1; H, 5.7. $C_{11}H_{15}F_3O_4$ requires C, 49.26; H, 5.64%]; ν_{max} (CH_2Cl_2) 3060, 2983, 2930, 1734, 1672, 1469, 1432, 1381, 1284, 1179, 1132, 1100, 1034, 928, 912 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.30 (3H, t, J_{HH} 7.1 Hz, *Me*), 1.36 (1H, dtt, J_{HH} 13.6, 2.5, 1.3 Hz, $OCH_2CH_aH_bCH_2O$), 2.08 (1H, dtt, J_{HH} 13.6, 12.6, 4.6 Hz, $OCH_2CH_aH_bCH_2O$), 2.54 (2H, dd, J_{HH} 5.2, 1.1 Hz, CH_2CH), 3.78 (2H, ddd, J_{HH} 12.6, 10.8, 2.5 Hz, $OCH_aH_bCH_2CH_aH_bO$), 4.11 (2H, ddd, J_{HH} 10.8, 4.6, 1.3 Hz, $OCH_aH_bCH_2CH_aH_bO$), 4.24 (2H, q, J_{HH} 7.1 Hz, OCH_2Me), 4.69 (1H, t, J_{HH} 5.2 Hz, CH_2CH), 6.25 (1H, d, J_{HH} 1.1 Hz, CH=); δ_C (126 MHz, $CDCl_3$) 13.8, 25.5, 36.9 (q, J_{CF} 1.8 Hz), 61.3, 66.9, 99.2, 122.4 (q, J_{CF} 275.5 Hz), 128.3 (q, J_{CF} 3.7 Hz), 132.6 (q, J_{CF} 31.9 Hz), 164.4; δ_F (470.5 MHz, $CDCl_3$) −64.52 (s, CF_3).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.102.

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