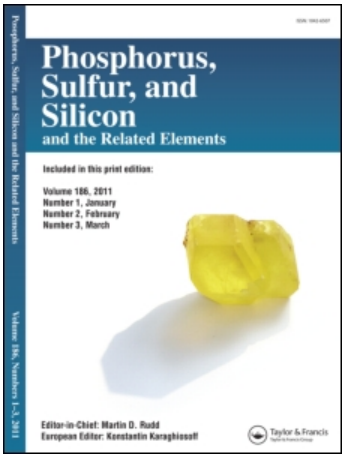

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SYNTHESIS OF PHENYL AND ESTER SUBSTITUTED VINYL FLUORIDES VIA REDUCTION AND OLEFINATION OF ESTERS

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SYNTHESIS OF PHENYL AND ESTER SUBSTITUTED VINYL FLUORIDES VIA REDUCTION AND OLEFINATION OF ESTERS

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A reduction-olefination sequence has been used to convert ethyl pentafluoropropanoate **6** to 1-fluoro-1-phenyl-2-pentafluoroethyl ethene **7** and ethyl 2,4,4,5,5,5-hexafluoro-**2**-pentenoate **8.** Addition of lithium diethyl α-fluorobenzylphosphonate $[(EtO)_2P(O)CFPh]^- Li^+$ **4** or lithium fluorocarboethoxymethylene dialkylphosphonate $[(RO)_2P(O)CFCO_2Et]^- Li^+$ **5** (R = Et, i-Pr) to a THF solution of fluorinated aldehydes prepared *in situ* from **6** and diisobutylaluminum hydride (DIBAL) affords the vinyl fluorides $C_2F_5CH{=}CFPh$ **7** and $C_2F_5CH{=}CFCO_2Et$ **8** in good yields. However, yields of the final products **7** and **8** are low when *in situ* reduction of **6** to aldehyde was performed in the presence of lithium salts of **4** or **5.**

Keywords: reduction-olefination; fluorinated ester; fluorophosphonate; vinyl fluoride

INTRODUCTION

Vinyl fluorides of defined stereochemistry are useful building blocks in the preparation of biologically active 12-fluororetinal,[1] fluorinated mimics of insect sex pheromones,[2] and in the field of pyrethroids.[3] The methods reported for the preparation of β-poly-fluoroalkyl phenyl or ester-substituted vinyl fluorides include the reaction of (bromodifluoromethyl)phenyl acetylene with tetrabutylammonium fluoride to obtain an E and Z mixture of 1,3,3,3-tetrafluoro- 1-phenylpropene.[4] Reaction of 1-phenylpentafluoropropene with lithium aluminum hydride in ethylene glycol dimethyl ether gives 1,3,3,3-tetrafluoro-1-phenylpropene[5] in more

than 93% E-selectivity. The Wittig reaction of fluorocarboethoxymethylene tri-n-butylphosphorane with per- and poly-fluoroalkyl-substituted carboxylic acid esters furnished the corresponding enol ethers $R_f(OEt)C{=}CFCO_2Et$.[6] Although many methods offer a convenient route to introduce a fluorine atom at the α-position with concomitant elongation of the chain by two carbon atoms,[7,8,9] the generality of these methods depends upon the availability of the carbonyl compounds. All of the reported unsaturated esters were derived from fluorine-free aldehydes, and the reaction of fluorinated aldehydes with lithium fluorocarboethoxymethylene diisopropylphosphonate $[(i\text{-}PrO)_2P(O)CFCO_2Et]^-Li^+$ has not been reported.[10] The lack of a general synthetic method to prepare fluorinated aldehydes may be the main reason for this scarcity. Fluorine-substituted aldehydes are usually protected either as an acetal or as a hemiacetal and prior deprotection is required. This paper describes a general synthesis of 1 -fluoro-1-phenyl –2-pentafluoroethyl ethene $C_2F_5CH{=}CFPh$ and of ethyl 2,4,4,5,5,5-hexafluoro-2-pentenoate $C_2F_5CH{=}CFCO_2Et$ via the reactions of the anions generated from α-fluorobenzylphosphonate $(EtO)_2P(O)CFHPh$ or fluorocarboethoxymethylene dialkylphosphonate $(RO)_2P(O)CFCO_2Et$ with fluorinated aldehydes produced in situ from fluorinated ester ethyl pentafluoropropanoate.

RESULTS AND DISCUSSION

Sodium methoxide-catalyzed condensation of diethyl phosphite with benzaldehyde at room temperature,[11] or thermal non-catalyzed addition of diethylphosphite to benzaldehyde[12] at 110°C gives the diethyl α-hydroxyphosphonate $(EtO)_2P(O)CH(OH)Ph$ **1** in 52% yield. The signal at 5.2 ppm in the ^1H NMR spectrum disappeared after H-D exchange reaction and could be attached to the aldehyde function. The ^{31}P NMR spectrum of diethyl α-hydroxybenzylphosphonate $(EtO)_2P(O)CH(OH)Ph$ consists of a doublet of pentets at 21.6 ppm ($^2J_{PCH}$ = 10 Hz, $^3J_{POCH}$ = 7 Hz). The conversion of the α-hydroxy group into fluorine was achieved by the reaction of **1** with diethylaminosulphur trifluoride (DAST) in dichloromethane solution[13] to give in 53% yield of diethyl α-fluorobenzylphosphonate $(EtO)_2P(O)CFHPh$ **2** (Equation (1)).

$$(EtO)_2P(O)H+PhCHO \xrightarrow[\text{or satd. } CH_3ONa,\ RT]{100-110^\circ C} (EtO)_2P(O)CH(OH)Ph$$

1

$$\xrightarrow[2)\ EtOH/Py]{1)\ (C_2H_5)_2NSF_3/CH_2Cl_2} (EtO)_2P(O)CFHPh \quad (1)$$

2

The Michaelis-Arbuzov reaction of triethyl phosphite or triisopropyl phosphite with ethyl bromofluoroacetate, prepared from the hydrolysis of 1-ethoxy-1,2,2-trifluoro-2-bromoethane $EtOCF_2CFHBr$ with concentrated sulfuric acid, gives diethyl (fluorocarbethoxymethyl) phosphonate $(EtO)_2P(O)CFHCO_2Et$ **3a** and diisopropyl(fluorocarbethoxymethyl)phosphonate $(i\text{-}PrO)_2P(O)CFHCO_2Et$ **3b** in 75% and 71% isolated yields, respectively (Equation (2)).[14]

$$F_2C=CFBr \xrightarrow[RT]{EtONa/EtOH} EtOCF_2CFHBr \xrightarrow[0^\circ C]{H_3O^+} CFHBrCO_2Et$$

$$(RO)_3P+CFHBrCO_2Et \xrightarrow{140-150^\circ C} (RO)_2P(O)CFHCO_2Et+EtBr$$

3

3a : R = Et 75%

3b : R = i–Pr 71% (2)

The deprotonation at the carbon atom in phosphonates $(EtO)_2P(O)CFHPh$ **2,** $(EtO)_2P(O)CFHCO_2Et$ **3a** or $(i\text{-}PrO)_2P(O)CFHCO_2Et$ **3b** was conveniently carried out at -78°C in THF with organolithium reagents such as n-butyllithium (n-BuLi),[15] t-butyllithium (t-BuLi), lithium bis(trimethylsilyl)amide ($LiN(TMS)_2$), and lithium diisopropylamide (LDA).[16] For example, when n-butyllithium was employed as proton abstractor, deprotonation of $(EtO)_2P(O)CFHCO_2Et$ **3a** to $[(EtO)_2P(O)CFCO_2Et]^-Li^+$ **5a** causes an upfield chemical shift from –211 to –230 ppm in the ^{19}F NMR spectrum, and a shift from 10.0 ppm to 24.5 ppm in the ^{31}P NMR spectrum (Equation (3)).

$$(RO)_2P(O)CFHR' + \text{Base} \xrightarrow{THF/-78^\circ C} [(RO)_2P(O)CFR']^-Li^+$$

2 or **3a**, **3b** — **4** or **5a**, **5b**

Base = n–BuLi, t–BuLi, $LiN(TMS)_2$, LDA

R = Et, i–Pr and R′ = Ph, CO_2Et (3)

Addition of lithium diethyl α-fluorobenzylphosphonate $[(EtO)_2P(O)CFPh]^-Li^+$ **4** or lithium fluorocarboethoxymethylene dialkylphosphonate $[(RO)_2P(O)CFCO_2Et]^-Li^+$ **5** (R = Et, i-Pr) to a THF solution of fluorinated aldehydes prepared *in situ* from ethyl pentafluoropropanoate **6** and diisobutylaluminum hydride (DIBAL) achieve the vinyl fluoride compounds $C_2F_5CH{=}CFPh$ **7** and $C_2F_5CH{=}CFCO_2Et$ **8** in good yields (Method A, Equation (4)).[10,16] For example, for the preparation of $(C_2F_5)CH{=}CFPh$ **7**, the lithium salt $[(EtO)_2P(O)CFPh]^-Li^+$ **4** was generated independently from the phosphonate $(EtO)_2P(O)CFHPh$ **2** and n-BuLi in THF at −78°C. In another flask, ethyl pentafluoropropanoate **6** was allowed to react with DIBAL in THF at −78°C, followed by dropwise addition of the lithium salt **4** which was generated in the first flask. The resultant mixture was then allowed to warm to room temperature to give the product $(C_2F_5)CH{=}CFPh$ **7.**

$$C_2F_5CO_2Et \xrightarrow[2)\,[(RO)_2P(O)CFR']^-Li^+\ \textbf{4 or 5a, 5b}}{1)\ DIBAL/CH_2Cl_2, THF, -78^\circ C} (C_2F_5)CH{=}CFR' \text{ (Method A)}$$

6 — **7** or **8**

$-78^\circ C$ to RT

R = Et, i–Pr and R′ = Ph, CO^2Et (4)

In contrast, when *in situ* reduction of ethyl pentafluoropropanoate $C_2F_5CO_2Et$ **6** to the aldehyde was performed in the presence of lithium diethyl α-fluorobenzylphosphonate $[(EtO)_2P(O)CFPh]^-Li^+$ **4** or lithium fluorocarboethoxymethylene dialkylphosphonate $[(RO)_2P(O)CFCO_2Et]^-Li^+$ **5** (R =Et, i-Pr), only 31–38% of the ester **6** was converted to $C_2F_5CH{=}CFPh$ **7** and $C_2F_5CH{=}CFCO_2Et$ **8** according to the ^{19}F NMR spectrum of the reaction mixture (Method B, Equation (5)). Excess DIBAL and prolonged stirring of the reaction mixture at room temperature did not improve the yield. The reason for the low yield is not clear.

$$[(RO)_2P(O)CFR']^-Li^+ \xrightarrow[2)\ DIBAL/CH_2Cl_2]{1)\ C_2F_5CO_2Et\ \mathbf{6},\ THF,\ -78°C}$$

4 or **5a**, **5b**

$$(C_2F_5)CH = CFR' \text{ (Method B)}$$

7 or **8**

$$R = Et,\ i\text{–}Pr \text{ and } R' = Ph,\ CO_2Et \qquad (5)$$

The results for the preparation of 1 -fluoro-1-phenyl –2-pentafluoroethyl ethene $C_2F_5CH{=}CFPh$ **7,** and ethyl 2,4,4,5,5,5-hexafluoro –2-pentenoate $C_2F_5CH{=}CFCO_2Et$ **8** from ethyl pentafluoropropanoate $C_2F_5CO_2Et$ **6** and $[(RO)_2P(O)CFR']^-Li^+$ (R = Et, i-Pr and R′ = Ph, CO_2Et) using different methods are summarized in Table I.

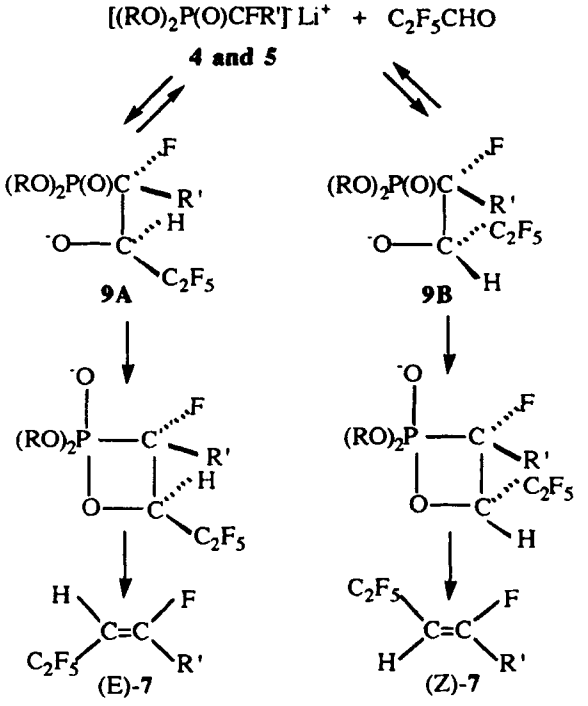
TABLE I Preparation of the phenyl- and ester-substituted vinyl fluorides **7** and **8** from **6** and $[(RO)_2P(O)CFR']^-Li^+$

Products	*R*	*R′*	*E/Z*[b]	*Method*	*Isolated yields (%)*[a]
7	Et	Ph	1/99	A	71[d]
7	Et	Ph	1/99	B	38[c]
8	Et	CO_2Et	80/20	A	42[e]
8	Et	CO_2Et	78/22	B	31[c]
8	i-Pr	CO_2Et	82/18	A	50
8	i-Pr	CO_2Et	81/19	B	35[c]

[a] The isolated yields are based on ethyl pentafluoropropanoate $C_2F_5CO_2Et$.
[b] The E/Z ratio was determined by ^{19}F NMR integration of the vinyl fluorine signals.
[c] The ^{19}F NMR yields vs $C_6H_5CF_3$ as an internal standard.
[d] See reference 16.
[e] See reference 10.

A high degree of Z-stereoselectivity of $C_2F_5CH{=}CFPh$ **7** was observed in the reaction of **4** with ethyl pentafluoropropanoate **6.** However, the E-isomer was the major product in the preparation of $C_2F_5CH{=}CFCO_2Et$ **8** from the reaction of **3** with ethyl pentafluoropropanoate. Change of the lithium diethyl(carboethoxyfluoromethyl) phosphonate $[(EtO)_2P(O)CFCO_2Et]^-Li^+$ **5a** to the lithium diisopropyl(carboethoxyfluoromethyl) phosphonate $[(i\text{-}PrO)_2P(O)CFCO_2Et]^-Li^+$ **5b** did not alter the E/Z ratio of the product $C_2F_5CH{=}CFCO_2Et$ **8.** The formation of the intermediate **9** from **4** or **5** with ethyl pentafluoropropanoate is reversible[10,17], and the

intermediate can exist in two diastereoisomeric forms **9A** and **9B** (Scheme 1). The irreversible decomposition of **9A** and **9B** isomers gives the specific E and Z isomers. The relative rates of formation and decomposition of the intermediates will determine the E/Z ratio. The greater steric hindrance between the phenyl and the C_2F_5 group in **9A** compared to **9B** leads to the Z isomer as the major product.



SCHEME 1

In conclusion, in the presence of diisobutyl aluminum hydride, ethyl 2,4,4,5,5,5-hexafluoro-2-pentenoate is reduced to the aldehydes that react *in situ* with $[(EtO)_2P(O)CFPh]^-Li^+$ or $[(RO)_2P(O)CFCO_2Et]^-Li^+$ to form the vinyl fluoride compounds $C_2F_5C{=}CFPh$ and $C_2F_5C{=}CFCO_2Et$ in good yields. In this work, readily available esters are used as substrates in the olefination reaction. It is very useful in fluorocarbon chemistry, because

the stable and easily distillable fluorine-substituted esters can be employed as synthons for fluorinated aldehydes in organic synthesis.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Bruker MSL-300 multinuclear spectrometer and were referenced against internal $CFCl_3$. ^{31}P NMR spectra were recorded on a Bruker AM-300WB multinuclear spectrometer, and are referenced against external 85% H_3PO_4. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM360X spectrometer, and were referenced against internal $(CH_3)_4Si$. The mass spectral analyses were performed on a FININGAN MAT TSQ-46C instrument. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. FT-IR spectra were recorded on a Bomen DA instrument in CCl_4 solutions, using a solution cell with 0.1 cm path length. Triethyl phosphite, triisopropyl phosphite and diethyl phosphite were distilled from sodium metal at reduced pressure. Ethyl bromofluoroacetate was prepared similar to the reported preparation of ethyl chlorofluoroacetate.[18] Diethyl(carboethoxyfluoromethyl)phosphonate $(EtO)_2P(O)CFHCO_2Et$ and diisopropyl (carboethoxyfluoromethyl)phosphonate $(i\text{-}PrO)_2P(O)CFHCO_2Et$ were prepared by the reaction of ethyl chlorofluoroacetate with triethyl phosphite and triisopropyl phosphite, respectively.[14] The normality of a 2.5 M n-hexane solution of n-butyllithium was determined by the method of Duhamel.[19] Tetrahydrofuran, absolute ethanol, diethyl ether, dichloromethane, ethyl pentafluoropropanoate and benzaldehyde were distilled prior to use.[20] Ethyl acetate, n-hexane, pyridine, t-Butyllithium (t-BuLi), lithium diisopropylamide (LDA), lithium bis(tri-methylsilyl)amide ($LiN(TMS)_2$), diisopropyl aluminum hydride (DIBAL, 1.0 M dichloromethane solution) and diethylaminosulphur trifluoride (DAST) were used without further purification.

Preparation of diethyl-α-hydroxybenzylphosphonate $(EtO)_2P(O)CH(OH)Ph$ 1, non-catalyzed

A 250 mL two-necked flask equipped with a septum port, a Teflon-coated magnetic stirring bar, and a water condenser topped with a nitrogen T tube, leading to a source of nitrogen and a mineral oil bubbler, was charged sequentially with 0.2 mol (27.6 g, 26 mL) of diethyl phosphite and

0.25 mol (26.6 g, 26 mL) of freshly distilled benzaldehyde. The contents of the flask were heated at 100–110°C (oil bath temperature) for 10 hours, then filtered through a funnel to give 16 g (52%) of $(EtO)_2P(O)CH(OH)Ph$. mp = 82–84°C. ^{31}P NMR : 21.6 (d, d, J_{PCH}= 10 Hz, J_{POCH} = 7 Hz); ^{1}H NMR : 7.49 (m, 2H), 7.35 (m, 3H), 5.23 (1H), 5.03 (d, 1H, J = 10 Hz), 4.16 (q, 4H, J = 7 Hz), 1.32 (t, 6H, J = 7 Hz); ^{13}C NMR : 128.2–127.0, 70.7 (d, J_{CP}= 158 Hz), 63.4, 63.1, 16.3, 16.2; GC-MS m/z (relative intensity): 245(M^++1, 0.17), 244(M^+, 1.83), 215(M^+-Et, 0.81), 199(M^+-OEt, 0.64), 138(M^+-PhCOH or $(EtO)_2P(O)$+H, 23.33), 111(41.43), 106(29.52), 105(34.72), 82(24.64), 79(13.93), 77(C_6H_5+); FT-IR spectrum (CCl_4 solution): 3300(broad, OH), 3065(m), 3033(m, Ar-H), 2983(m), 2930(m), 2909(m, C-H), 1392(s, C-F), 1255(m), 1235(m, P=O), 1221(m), 1081(m), 1049(m), 1040(s), 1034(m, P-O-C) cm^{-1}.

Preparation of $(EtO)_2P(O)CH(OH)Ph$ 1 catalyzed by sodium methoxide

Diethyl phosphite (0.2 mol, 27.6 g, 26 mL) and freshly distilled benzaldehyde (0.2 mol, 21.2 g, 21 mL) were placed into a 250 mL two-necked flask under nitrogen. To the solution, a few drops of a saturated solution of CH_3ONa in methanol were added to this mixture. The contents of the flask were stirred at room temperature for 3 hours, then filtered through a funnel to give 16 g of $(EtO)_2P(O)CH(OH)Ph$.

Preparation of diethyl-α-fluorobenzylphosphonate $(EtO)_2P(O)CFHPh$ 2

A solution of 19.2 mmol (3.12 g, 2.4 mL) of diethylaminosulphur trifluoride (DAST) in 20 mL of dichloromethane was cooled to –78°C via a dry ice/isopropyl alcohol slush bath under nitrogen. To the cooled solution, 16.4 mmol (4.0 g) of diethyl α-hydroxybenzylphosphonate in 40 mL of dichlonomethane was added dropwise via a syringe over 1 hour. The mixture was allowed to warm to room temperature and stirred for a further 2 hours, then the reaction was quenched by pouring the reaction mixture into a solution of pyridine (5 mL) in ethanol (120 mL). After 1 hour, this mixture was poured into ice water (400 mL) and extracted with dichloromethane (3 × 150 mL). The combined extracts were washed with dilute hydrochloric acid (2 × 80 mL) and water (2 × 60 mL), dried with anhy-

drous $MgSO_4$, filtered, and evaporated under reduced pressure to obtain the crude product (4.0 g) as a mobile yellow oil. This crude product was distilled under reduced pressure at 100–102°C and 0.3 mmHg to give 2.2 g (53%) of the pure compound. GLPC purity : 99%. ^{19}F NMR : –200.4 (d, d, J_{FCP}=84 Hz, J_{FCH} = 45 Hz) ; ^{31}P NMR : 16.4 (d, d, J_{PCF} = 84 Hz, J_{PCH} = 8 Hz, J_{POCH} = 7 Hz); ^{1}H NMR : 7.48 (m, 2H), 7.36 (m, 3H), 5.68 (d, d, 1H, J_{HCF} = 45 Hz, J_{HCP} = 8 Hz), 4.07 (m, 4H), 1.25 (t, 3H, J = 7 Hz), 1.24 (t, 3H, J = 7 Hz); ^{13}C NMR : 133.1–126.8, 89.4 (d, d, J_{CF} = 183 Hz, J_{CP}= 169 Hz), 63.7, 63.6, 16.4, 16.3; GC-MS m/z (relative intensity): 248(M^++2, 0.01), 247(M^++1, 0.10), 246(M^+, 0.86), 218(M^+-CH_2=CH_2, 3.35), 217(M^+-Et, 5.19), 169(M^+-$(EtO)_2P(O)$, 100), 110(9.36), 109(100.00), 81(15.90), 77($C_6H_5^+$, 2.04); FT-IR spectrum (CCl_4 solution): 3092(m), 3067(m), 3051(w), 3035(m, Ar-H), 2983(m), 2931(m), 2910(m, C-H), 2868(m), 2785(w), 1454(m), 1392(s, C-F), 1264(m, P=O), 1190(w), 1029(m, P-O-C) cm^{-1}.

Preparation of (Z)-(C_2F_5)CH=CFPh 7 and of C_2F_5CH=CFCO_2Et 8 from ethyl pentafluoropropanoate $C_2F_5CO_2Et$ 6 and $[(RO)_2P(O)CFR']^-Li^+$

Method A

A solution of 16.0 mmol (3.9 g) of $(EtO)_2P(O)CFHPh$ in 30 mL of dry THF was cooled and stirred at –78°C, as 16.0 mmol (6.4 mL) of a 2.5 M solution of n-butyllithium in n-hexane was added dropwise via a syringe. In another flask, a solution of 16.0 mmol (3.0 g) of $C_2F_5CO_2Et$ in 20 mL of dry THF was stirred and cooled to –78°C while 16 mmol (16 mL) of a 1.0 M dichloromethane solution of DIBAL-H was added dropwise via a syringe. The resultant mixture was stirred at –78°C, for 30 min, and then the cold solution in the first flask was added dropwise via a syringe to the aldehyde. The resulting mixture was stirred at –78°C for 1 h, and was allowed to warm to room temperature over 4 h. The reaction mixture was poured into water (40 mL), the organic layer was separated, washed successively with brine (30 mL) and water (30 mL), and was subjected to steam distillation. The water layer of the steam distillate was extracted with diethyl ether (2 × 25 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. Removal of the solvents via distillation at atmospheric pressure gave a yellow residue that was redistilled through a

six-inch Vigreaux column at 58–60°C and 3.8 mmHg to obtain 2.95 g (71%) of the pure compound. GLPC purity : 94%. ^{19}F NMR: −86.4(d, $^{3}J_{F,F}$= 3.5 Hz), −100.8 (d,t, $^{3}J_{F,H(trans)}$ = 33.5 Hz, $^{4}J_{F,F}$= 22.8 Hz), − 110.8 (d,d,q, $^{4}J_{F,F}$= 22.8 Hz, $^{3}J_{F,H}$= 13.9 Hz, $^{3}J_{F,F}$= 3.5 Hz); ^{1}H NMR: 7.60–7.49 (m, 2H), 7.48–7.41 (m, 3H), 5.54 (d,t, 1H, $^{3}J_{H,F(trans)}$=33.5 Hz, $^{3}J_{H,F}$ = 13.9 Hz); ^{13}C NMR: 164.6 (d,t, $^{1}J_{C,F}$= 272 Hz, $^{3}J_{C,F}$= 6 Hz), 131.6, 128.9, 125.4 (d, $^{2}J_{C,F}$= 8 Hz), 118.8 (d,t, $^{1}J_{C,F}$ = 285 Hz, $^{3}J_{C,F}$= 38 Hz), 93. (d,t, $^{2}J_{C,F}$ = 25 Hz, $^{2}J_{C,F}$ = 10 Hz) ; GC-MS m/z (relative intensity): 240 (M^{+}, 36.30), 221 (4.43), 171 (93.15), 152 (9.59), 151(100.00), 102 (9.85), 69 (8.99). FT-IR 3095 (m), 3067 (m), 2982 (m), 2934 (m), 1683 (m), 1341 (m), 1287 (m), 1216 (s), 1206 (s), 1119 (m) cm^{-1}.

Method B

A solution of 16.0 mmol (3.9 g) of $(EtO)_2P(O)CFHPh$ in 30 mL of dry THF was cooled and stirred at −78°C, as 16.0 mmol (6.4 mL) of a 2.5 M n-hexane solution of n-butyllithium were added dropwise via a syringe. The resultant bright yellow solution was stirred at −78°C for 20 minutes and then 16.0 mmol (3.0 g) of ethyl pyruvate were added dropwise via a syringe. After the bath temperature was equilibrated to −78°C, 16 mmol (16 mL) of a 1.0 M dichloromethane solution of DIBAL-H were added dropwise via a syringe. The resultant mixture was stirred at −78°C for one hour, allowed to warm to room temperature over 5 hours, and then quenched with 25 mL of 6M HCl. The organic layer was separated, washed successively with brine (30 mL) and water (30 mL), dried over anhydrous $MgSO_4$ to give the pure compound in 38% yield. (^{19}F NMR ; $C_6H_5CF_3$ as internal standard). ^{19}F NMR of the product : −86.4 (d, $^{3}J_{F,F}$ = 3.5 Hz), −100.8 (d,t, $^{3}J_{F,H(trans)}$= 33.5 Hz, $^{4}J_{F,F}$= 22.8 Hz) and −110.8 (d,d,q, $^{4}J_{F,F}$= 22.8 Hz, $^{3}J_{F,H}$ = 13.9 Hz, $^{3}J_{F,F}$ = 3.5 Hz).

Preparation of (E, Z)-$(C_2F_5)CH=CFCO_2Et$ 8

Yield: 3. 1 g (42%). ^{19}F NMR : E/Z = 80/20, (E)-isomer : − 110.6 (d, $^{3}J_{F,H}$ = 13.8 Hz), -99.5 (d, t, $^{3}J_{F,H(cis)}$ = 17.8 Hz, $^{4}J_{F,F}$= 4.5 Hz), −86.1 (s); (Z)-isomer: −113.5 (d, q, $^{3}J_{F,H}$ = 14.5 Hz, $^{3}J_{F,F}$ = 2.3 Hz), −109.0 (d, t, $^{3}J_{F,H(trans)}$ = 27.9 Hz, $^{4}J_{F,F}$= 22.7 Hz), -85.5 (s); ^{1}H NMR : 5.84 (d, t, 1H, $^{3}J_{H,F(cis)}$= 17.6 Hz, $^{3}J_{H,F}$ = 13.7 Hz), 4.37 (q, 2H, $^{3}J_{H,H}$ = 7.14 Hz), 1.36 (t, 3H, $^{3}J_{H,H}$= 7.14 Hz); ^{13}C NMR : 158.5 (d, $^{2}J_{C,F}$= 34 Hz), 155.9 (d, t, $^{2}J_{C,F}$ = 272 Hz, $^{3}J_{C,F}$ = 5 Hz), 120.1 (t, d, $^{1}J_{C,F}$ = 286 Hz, $^{3}J_{C,F}$ = 36 Hz),

104.5 (d, t, $^2J_{C,F}$= 29 Hz, $^2J_{C,F}$ = 25 Hz), 63.2 (s), 13.7(s); GC-MS m/z (relative intensity): 237 (M^++1, 0.1), 235 (M^+-1, 0.1), 191 (53,4), 163 (36.6), 113 (53.8), 94 (46.9), 69 (100.0); FT-IR spectrum (CCl_4 solution): 1758 (s, C=O), 1695 (m, C=C), 1337 (s), 1211 (s), 1184 (s, C-F) cm^{-1},

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