

# A convenient synthesis of perfluoroalkylated enamines and vinyl phosphonates

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## Abstract

The reaction of fluoroalkynes with ammonia and benzylamine gave perfluoroalkylated enamines predominantly as the *Z* isomer, which were hydrogenated with palladium on carbon to afford perfluoroalkylated  $\beta$ -amino acids in good yield. The reaction of fluoroalkynes with diethyl phosphite afforded perfluoroalkylated vinyl phosphonates in moderate yield.

**Keywords:** Synthesis; Perfluoroalkylated enamines; Vinyl phosphonates; NMR spectroscopy; IR spectroscopy; Mass spectrometry

## 1. Introduction

Fluoroalkynes have been found to be good dipolarophiles and dienophiles in the synthesis of fluorinated heterocyclic compounds [1], as exemplified by the reaction of aromatic nitrile oxides and methyl perfluoro-2-alkynoate [2]. They are also useful intermediates in the synthesis of fluorinated heterocyclic compounds [3] and can be conveniently synthesized by an intramolecular Wittig reaction [4,5].

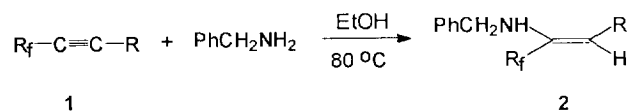
Enamines are important intermediates in synthetic organic chemistry. The reaction products initiated from enamines exist widely in natural products and heterocyclic compounds. As a fluorine-containing building block, fluorine-containing enamines can be used both for the synthesis of various new fluorine-containing heterocyclic compounds and for the introduction of fluorinated groups into natural products. Hence the preparation of fluorine-containing enamines has attracted much interest in recent years [6,7].

## 2. Results and discussion

Fluorinated enamines can be synthesized by the reaction of fluoroalkynes with amines or ammonia in alcoholic solution. After chromatography on silica gel, the products were obtained in good yield (Scheme 1).

No imine tautomer was detected in the product, the enamine being the unique tautomer. The configuration of the products was identified from  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR data compared with those reported in the literature [7–9]. When  $\text{R}_f$  is *cis* with respect to the vinyl hydrogen, the  $^{19}\text{F}$  chemical shift is upfield and the enamines **2** are the *Z* isomers. The ratio of the *Z* and *E* isomers in **2e** was 53:47. The reaction results are summarized in Table 1.

Fluoroalkynes were dropped into a freshly prepared saturated methanolic ammonia solution and allowed to stir at room temperature for 4 h, to give fluorinated enamines. In this reaction, owing to the strong electron-withdrawing action of the perfluoroalkyl group  $\text{R}_f$ , nucleophilic attack took place only on the alkyne carbon atom bound to the perfluoroalkyl group and did not lead to aminolysis of the carboxylic acid derivatives [10] (Scheme 2). Similar to the above reaction, the reaction of fluoroalkynes with ammonia also gave enamines exclusively as the *Z* isomer. Because of the greater electron-donor ability of  $\text{NH}_2$  on the vinyl carbon bound to the perfluoroalkyl group relative to  $\text{PhCH}_2\text{NH}$ , the  $^{19}\text{F}$  chem-



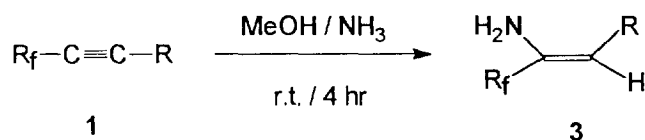
(a):  $\text{R}_f = \text{CF}_3$ ,  $\text{R} = \text{CO}_2\text{Et}$ ; (b):  $\text{R}_f = n\text{-C}_3\text{F}_7$ ,  $\text{R} = \text{CO}_2\text{Et}$ ; (c):  $\text{R}_f = \text{CF}_3$ ,  $\text{R} = \text{CONEt}_2$ ; (d):  $\text{R}_f = n\text{-C}_3\text{F}_7$ ,  $\text{R} = \text{CONEt}_2$ ; (e):  $\text{R}_f = n\text{-C}_3\text{F}_7$ ,  $\text{R} = \text{CN}$

Scheme 1.

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Table 1  
Preparation of compounds 2

Compound	R <sub>f</sub>	R	B.p. (°C/mmHg)	Yield (%)	Z/E
2a	CF <sub>3</sub>	CO <sub>2</sub> Et	71/2	60	100:0
2b	n-C <sub>3</sub> F <sub>7</sub>	CO <sub>2</sub> Et	118/2	65	100:0
2c	CF <sub>3</sub>	CONEt <sub>2</sub>	92/2	76	100:0
2d	n-C <sub>3</sub> F <sub>7</sub>	CONEt <sub>2</sub>	51 (m.p.)	71	100:0
2e	n-C <sub>3</sub> F <sub>7</sub>	CN	86/2	53	53:47

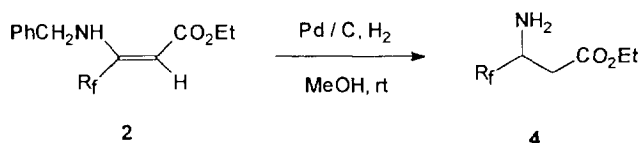


(a): R<sub>f</sub> = CF<sub>3</sub>, R = CO<sub>2</sub>Et; (b): R<sub>f</sub> = n-C<sub>3</sub>F<sub>7</sub>, R = CO<sub>2</sub>Et; (c): R<sub>f</sub> = CF<sub>3</sub>, R = CONEt<sub>2</sub>; (d): R<sub>f</sub> = n-C<sub>3</sub>F<sub>7</sub>, R = CONEt<sub>2</sub>

Scheme 2.

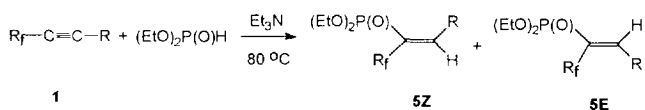
Table 2  
Preparation of compounds 3

Compound	R <sub>f</sub>	R	B.p. (°C/mmHg)	Yield (%)
3a	CF <sub>3</sub>	CO <sub>2</sub> Et	83/15	42
3b	n-C <sub>3</sub> F <sub>7</sub>	CO <sub>2</sub> Et	71/8	48
3c	CF <sub>3</sub>	CONEt <sub>2</sub>	69 (m.p.)	61
3d	n-C <sub>3</sub> F <sub>7</sub>	CONEt <sub>2</sub>	68/2	72



(a): R<sub>f</sub> = CF<sub>3</sub>, yield 71%; (b): R<sub>f</sub> = n-C<sub>3</sub>F<sub>7</sub>, yield 76%

Scheme 3.



(a): R<sub>f</sub> = CF<sub>3</sub>, R = CO<sub>2</sub>Et; (b): R<sub>f</sub> = n-C<sub>3</sub>F<sub>7</sub>, R = CO<sub>2</sub>Et; (c): R<sub>f</sub> = CF<sub>3</sub>, R = CONEt<sub>2</sub>; (d): R<sub>f</sub> = n-C<sub>3</sub>F<sub>7</sub>, R = CONEt<sub>2</sub>

Scheme 4.

Table 3  
Preparation of compounds 5

Compound	R <sub>f</sub>	R	B.p. (°C/mmHg)	Yield (%)	Z/E
5a	CF <sub>3</sub>	CO <sub>2</sub> Et	64/2	46	46:54
5b	n-C <sub>3</sub> F <sub>7</sub>	CO <sub>2</sub> Et	78/2	42	95:5
5c	CF <sub>3</sub>	CONEt <sub>2</sub>	76/2	44	67:33
5d	n-C <sub>3</sub> F <sub>7</sub>	CONEt <sub>2</sub>	90/2	48	81:19

ical shifts of the perfluoroalkyl groups of compounds 3 were moved upfield compared with compounds 2. The reaction results are summarized in Table 2.

β-Amino acids are an important class of compounds since they are the precursors of β-lactams found in antibiotics and also used for peptide modifications. Some of these compounds occur naturally and are also present in biologically active peptides [11]. Fluorine-containing β-amino acids are new. The introduction of fluorine atoms into such amino acids modifies the bonding ability of the peptide and increases the resistance to hydrolysis by peptidases. Hence, peptides containing fluoroalkyl amino acids show strong biological activity and can act as enzyme inhibitors in analgesic and antitumor medicine [12].

As a practical application of fluorine-containing enamines, compounds 2 were hydrogenated with palladium on carbon at room temperature to give the precursor of fluoroalkylated β-amino acids, i.e. fluoroalkyl-substituted β-amino acid ester 4, in good yield (Scheme 3).

Perfluoroalkylated vinylphosphonates are of interest and are attracting increasing attention. The presence in the same molecule of a fluoroalkyl group, a C=C double bond and a P(O)(OR)<sub>2</sub> group gives these compounds a unique reactivity and they possess wide practical value. They have been proposed as monomers for making cation-exchange resins, impregnating agents for textiles and paper, extraction agents for heavy metal ions, intermediates in the synthesis of insecticides and incombustible polymers [13]. For their preparation, a mixture of fluoroalkyne, diethyl phosphite and 10% triethylamine was warmed to 80 °C and stirred for 2 h. After chromatography on silica gel, perfluoroalkylated vinyl phosphonates were obtained in moderate yield (Scheme 4). The ratio of Z and E isomers was estimated by NMR spectroscopy and compared with that reported in the literature [14]. The amount of Z isomer in the products increased with the size of the R<sub>f</sub> group and the reaction results are summarized in Table 3.

### 3. Experimental details

All boiling points and melting points were uncorrected. IR spectra of products as films were obtained on a Perkin-Elmer 983 spectrometer. NMR spectra (CDCl<sub>3</sub> as solvent, chemical shifts in ppm from TMS for <sup>1</sup>H NMR, from external TFA for <sup>19</sup>F NMR and from external 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR, positive for downfield shifts) were determined on a Varian EM-360 (60 MHz) or JEOL FX-90Q (90 MHz) spectrometer. Mass spectra were recorded on a HP 5989A spectrometer.

Fluoroalkynes 1 were prepared according to literature methods [4].

#### 3.1. Typical procedure for the preparation of compounds 2

Benzylamine (10 mmol) was added dropwise into a stirred mixture of 10 mmol of ethyl 4,4,4-trifluorobutanoate (1a) and 5 ml of ethanol. After addition, the mixture was allowed to warm to 80 °C and stirred for 1 h. <sup>19</sup>F NMR spectra showed that the reaction was complete. Removal of the solvent gave

the crude product which was purified by chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5) to afford 1.65 g of a pale yellow liquid identified as **2a**.

Ethyl 4,4,4-trifluoro-3-benzylamino-2-butenolate (**2a**): yield 60%, b.p. 71 °C/2 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3280 (m); 1670 (s); 1630 (s); 1210 (s).  $^1\text{H}$  NMR  $\delta$ : 1.22 (t,  $J=7$  Hz, 3H); 4.10 (q,  $J=7$  Hz, 2H); 4.41 (d,  $J=6$  Hz, 2H); 5.14 (s, 1H); 7.10~7.40 (m, 5H); 8.43 (br, 1H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 10.4 (s, 3F) ppm. MS  $m/e$ : 273 ( $\text{M}^+$ ); 244 ( $\text{M}^+ - \text{C}_2\text{H}_5$ ); 92 ( $\text{PhC}^+\text{H}_3$ , base). Analysis: calc. for  $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}_2$ : C, 57.14; H, 5.13; N, 5.13%. Found: 56.91; H, 5.16; N, 5.22%.

Ethyl 4,4,5,5,6,6,6-heptafluoro-3-benzylamino-2-hexenoate (**2b**): yield 65%, b.p. 118 °C/5 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3280 (m); 1670 (s); 1620 (s); 1200 (s).  $^1\text{H}$  NMR  $\delta$ : 1.23 (t,  $J=7$  Hz, 3H); 4.10 (q,  $J=7$  Hz, 2H); 4.40 (d,  $J=6$  Hz, 2H); 5.09 (s, 1H); 7.10~7.40 (m, 5H); 8.56 (br, 1H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -3.4 (s, 3F); -34.1 (s, 2F); -48.2 (s, 2F) ppm. MS  $m/e$ : 373 ( $\text{M}^+$ ); 344 ( $\text{M}^+ - \text{C}_2\text{H}_5$ ); 91 ( $\text{PhC}^+\text{H}_2$ , base). Analysis: calc. for  $\text{C}_{15}\text{H}_{14}\text{F}_7\text{NO}_2$ : C, 48.26; H, 3.75; N, 3.75%. Found: C, 48.27; H, 3.80; N, 3.97%.

*N,N*-Diethyl 4,4,4-trifluoro-3-benzylamino-2-butenamide (**2c**): yield 76%, b.p. 92 °C/2 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3280 (m); 1680 (s); 1600 (s); 1420 (s); 1190 (s).  $^1\text{H}$  NMR  $\delta$ : 1.14 (t,  $J=7$  Hz, 6H); 3.32 (q,  $J=7$  Hz, 4 Hz); 4.41 (d,  $J=6$  Hz, 2H); 5.27 (s, 1H); 7.10~7.37 (m, 5H); 9.46 (br, 1H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 10.8 (s, 3F) ppm. MS  $m/e$ : 300 ( $\text{M}^+$ ); 288 ( $\text{M}^+ - \text{NEt}_2$ ); 91 ( $\text{PhC}^+\text{H}_2$ , base); 72 ( $^+\text{NEt}_2$ ). Analysis: calc. for  $\text{C}_{15}\text{H}_{19}\text{F}_3\text{N}_2\text{O}$ : C, 60.00; H, 6.33; N, 9.33%. Found: C, 59.67; H, 6.44; N, 9.60%.

*N,N*-Diethyl 4,4,5,5,6,6,6-heptafluoro-3-benzylamino-2-hexenoamide (**2d**): yield 71%, m.p. 51 °C. IR (film) ( $\text{cm}^{-1}$ ): 3280 (m); 1630 (s); 1610 (s); 1420 (s); 1240 (s).  $^1\text{H}$  NMR  $\delta$ : 1.13 (t,  $J=7$  Hz, 6H); 3.32 (q,  $J=7$  Hz, 4H); 4.36 (d,  $J=6$  Hz, 2H); 5.19 (s, 1H); 7.20~7.40 (m, 5H); 9.50 (br, 1H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -3.3 (s, 3F); -34.3 (s, 2F); -48.9 (s, 2F) ppm. MS  $m/e$ : 400 ( $\text{M}^+$ ); 328 ( $\text{M}^+ - \text{NEt}_2$ ); 91 ( $\text{PhC}^+\text{H}_2$ , base); 72 ( $^+\text{NEt}_2$ ). Analysis: calc. for  $\text{C}_{17}\text{H}_{19}\text{F}_7\text{N}_2\text{O}$ : C, 51.00; H, 4.75; N, 7.00%. Found: C, 50.65; H, 4.59; N, 6.82%.

4,4,5,5,6,6,6-Heptafluoro-3-benzylamino-2-hexenitrile (**2e**): yield 53%, b.p. 86 °C/2 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3310 (s); 2210 (s); 1620 (s); 1540 (s); 1230 (s).  $^1\text{H}$  NMR  $\delta$ : 4.20 (d,  $J=6$  Hz) and 4.52 (d,  $J=6$  Hz) ( $Z+E$ , 2H); 4.70 (s) and 4.80 (s) ( $Z+E$ , 1H); 5.26 (br) and 5.56 (br) ( $Z+E$ , 1H); 7.10~7.40 (m,  $Z+E$ , 5H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -3.5 (s) and -3.6 (s) ( $Z+E$ , 3F); -38.7 (s) and -40.9 (s) ( $Z+E$ , 2F); -49.2 (s) and -49.5 (s) ( $Z+E$ , 2F) ppm. MS  $m/e$ : 326 ( $\text{M}^+$ ); 91 ( $\text{PhC}^+\text{H}_2$ , base). Analysis: calc. for  $\text{C}_{13}\text{H}_9\text{F}_7\text{N}_2$ : C, 47.85; H, 2.76; N, 8.59%. Found: C, 48.20; H, 2.88; N, 8.68%.

### 3.2. Typical procedure for the preparation of compounds 3

Ethyl 4,4,4-trifluorobutyrate (**1a**) (5 mmol) was added dropwise into a freshly prepared saturated methanolic ammo-

nia solution (10 ml) and the reaction mixture allowed to stir at room temperature for 4 h. Evaporation of the solvent in vacuo gave crude products which were purified by chromatography on silica gel eluting with petroleum ether/ethyl acetate (95:5) to give 0.38 g of a colourless liquid identified as **3a**.

Ethyl 4,4,4-trifluoro-3-amino-2-butenolate (**3a**): yield 42%, b.p. 83 °C/13 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3450 (s); 3350 (s); 1690 (s); 1650 (s); 1220 (s).  $^1\text{H}$  NMR  $\delta$ : 1.28 (t,  $J=7$  Hz, 3H); 4.16 (q,  $J=7$  Hz, 2H); 5.09 (s, 1H); 6.28 (br, 2H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 5.0 (s, 3F) ppm. MS  $m/e$ : 183 ( $\text{M}^+$ ); 155 ( $\text{M}^+ - \text{C}_2\text{H}_4$ ); 138 ( $\text{M}^+ - \text{OC}_2\text{H}_5$ , base); 111 ( $\text{M}^+ - \text{CO}_2\text{C}_2\text{H}_4$ ). Analysis: calc. for  $\text{C}_6\text{H}_8\text{F}_3\text{NO}_2$ : C, 39.34; H, 4.37; N, 7.65%. Found: C, 39.18; H, 4.48; N, 7.74%.

Ethyl 4,4,5,5,6,6,6-heptafluoro-3-amino-2-hexenoate (**3b**): yield 48%, b.p. 71 °C/8 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3450 (s); 3350 (s); 1690 (s); 1640 (s); 1220 (s).  $^1\text{H}$  NMR  $\delta$ : 1.27 (t,  $J=7$  Hz, 3H); 4.16 (q,  $J=7$  Hz, 2H); 5.05 (s, 1H); 6.30 (br, 2H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -3.1 (s, 3F); -42.5 (s, 2F); -49.6 (s, 2F) ppm. MS  $m/e$ : 283 ( $\text{M}^+$ ); 255 ( $\text{M}^+ - \text{C}_2\text{H}_4$ ); 238 ( $\text{M}^+ - \text{OC}_2\text{H}_5$ , base); 211 ( $\text{M}^+ - \text{CO}_2\text{C}_2\text{H}_4$ ). Analysis: calc. for  $\text{C}_8\text{H}_8\text{F}_7\text{NO}_2$ : C, 33.92; H, 2.83; N, 4.95%. Found: C, 33.75; H, 2.59; N, 4.66%.

*N,N*-Diethyl 4,4,4-trifluoro-3-amino-2-butenamide (**3c**): yield 61%, m.p. 69 °C. IR (film) ( $\text{cm}^{-1}$ ): 3380 (s); 3300 (s); 1650 (s); 1640 (s); 1240 (s).  $^1\text{H}$  NMR  $\delta$ : 1.13 (t,  $J=7$  Hz, 6H); 3.34 (q,  $J=7$  Hz, 4H); 5.20 (s, 1H); 6.50 (br, 2H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : 5.2 (s, 3F) ppm. MS  $m/e$ : 210 ( $\text{M}^+$ ); 141 ( $\text{M}^+ - \text{CF}_3$ ); 137 ( $\text{M}^+ - \text{NEt}_2\text{H}$ , base). Analysis: calc. for  $\text{C}_8\text{H}_{13}\text{F}_3\text{N}_2\text{O}$ : C, 45.71; H, 6.19; N, 13.33%. Found: C, 45.51; H, 6.45; N, 13.61%.

*N,N*-Diethyl 4,4,5,5,6,6,6-heptafluoro-3-amino-2-hexenoamide (**3d**): yield 72%, b.p. 68 °C/2 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3400 (s); 3300 (s); 1650 (s); 1640 (s); 1240 (s).  $^1\text{H}$  NMR  $\delta$ : 1.13 (t,  $J=7$  Hz, 6H); 3.33 (q,  $J=7$  Hz, 4H); 5.13 (s, 1H); 6.57 (br, 2H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -3.0 (s, 3F); -42.2 (s, 2F); -49.5 (s, 2F) ppm. MS  $m/e$ : 310 ( $\text{M}^+$ ); 238 ( $\text{M}^+ - \text{NEt}_2$ , base); 141 ( $\text{M}^+ - \text{C}_3\text{F}_7$ ). Analysis: calc. for  $\text{C}_{10}\text{H}_{13}\text{F}_7\text{N}_2\text{O}$ : C, 38.71; H, 4.19; N, 9.03%. Found: C, 38.46; H, 3.85; N, 8.80%.

### 3.3. Typical procedure for the preparation of compounds 4

A suspension of 10% palladium on carbon (0.40 g) and **2a** (0.82 g, 3 mmol) in methanol (30 ml) was hydrogenated at atmospheric pressure and the mixture stirred for 24 h at room temperature. The catalyst was removed by filtration and the methanolic filtrate evaporated under reduced pressure to give the crude product as a liquid, which was purified by microdistillation to afford 0.39 g of **4a**.

Ethyl 4,4,4-trifluoro-3-amino-butyrate (**4a**): yield 71%, b.p. 47 °C/5 mmHg. IR (film) ( $\text{cm}^{-1}$ ): 3410 (s); 3350 (s); 1740 (s); 1170 (s); 1120 (s).  $^1\text{H}$  NMR  $\delta$ : 1.26 (t,  $J=7$  Hz, 3H); 1.61 (s, 2H); 2.57 (m, 2H); 3.72 (m, 1H); 4.17 (q,  $J=7$  Hz, 2H) ppm.  $^{19}\text{F}$  NMR  $\delta$ : -1.3 (s) ppm. MS  $m/e$ : 186 ( $\text{M}^+ + 1$ , base); 165 ( $\text{M}^+ - \text{HF}$ ); 140 ( $\text{M}^+ - \text{OC}_2\text{H}_5$ );

116 ( $M^+ - CF_3$ ); 98 ( $M^+ - CH_2CO_2Et$ ). Analysis: calc. for  $C_6H_{10}F_3NO_2$ : C, 38.92; H, 5.41; N, 7.57%. Found: C, 38.99; H, 5.40; N, 7.73%.

Ethyl 4,4,5,5,6,6,6-heptafluoro-3-amino-2-hexanoate (**4b**): yield 76%, b.p. 73 °C/8 mmHg. IR (film) ( $cm^{-1}$ ): 3420 (s); 3360 (s); 1740 (s); 1220 (s); 1120 (s).  $^1H$  NMR  $\delta$ : 1.24 (t,  $J=7$  Hz, 3H); 1.53 (s, 2H); 2.60 (m, 2H); 3.70 (m, 1H); 4.18 (q,  $J=7$  Hz, 2H) ppm.  $^{19}F$  NMR  $\delta$ : -4.2 (s); -42.6 and -48.1 (AB,  $J_{AB}=280$  Hz, 2F); -48.0 (s) ppm. MS  $m/e$ : 286 ( $M^+ + 1$ , base); 265 ( $M^+ - HF$ ); 240 ( $M^+ - OC_2H_5$ ); 198 ( $M^+ - CH_2CO_2Et$ ); 116 ( $M^+ - C_3F_7$ ). Analysis: calc. for  $C_8H_{10}F_7NO_2$ : C, 33.68; H, 3.51; N, 4.91%. Found: C, 33.83; H, 3.55; N, 5.18%.

### 3.4. Typical procedure for the preparation of compounds 5

Diethyl phosphite (4 mmol) was added dropwise into a stirred mixture consisting of 4 mmol of ethyl 4,4,4-trifluorobutynoate (**1a**) and 0.4 mmol of triethylamine. The mixture was allowed to warm to 80 °C and stirred for 2 h. After chromatography on silica gel eluting with petroleum ether/ethyl acetate (9:1), 0.71 g of **5a** was obtained.

Ethyl 4,4,4-trifluoro-3-diethylphosphoryl-2-butenate (**5a**): yield 46%, b.p. 64 °C/2 mmHg. IR (film) ( $cm^{-1}$ ): 2980 (s); 1740 (s); 1640 (m); 1270 (s).  $^1H$  NMR  $\delta$ : 1.33 (t,  $J=7$  Hz, 9H); 4.00~4.40 (m, 6H); 7.10 (d,  $J=39$  Hz, Z, 1H); 7.22 (d,  $J=23$  Hz, E, 1H) ppm.  $^{19}F$  NMR  $\delta$ : 15.0 (s, Z, 3F); 19.0 (s, E, 3F) ppm.  $^{31}P$  NMR  $\delta$ : 6.1 (s, Z); 9.1 (s, E) ppm. MS  $m/e$ : 305 ( $M^+ + 1$ ); 259 ( $M^+ - OC_2H_5$ ); 231 ( $M^+ - OC_2H_5 - C_2H_4$ ); 203 ( $M^+ - OC_2H_5 - 2C_2H_4$ , base). Analysis: calc. for  $C_{10}H_{16}F_3O_5P$ : C, 39.47; H, 5.26%. Found: C, 39.44; H, 5.33%.

Ethyl 4,4,5,5,6,6,6-heptafluoro-3-diethylphosphoryl-2-hexenoate (**5b**): yield 42%, b.p. 78 °C/2 mmHg. IR (film) ( $cm^{-1}$ ): 2980 (s); 1740 (s); 1640 (m); 1240 (s).  $^1H$  NMR  $\delta$ : 1.26 (t,  $J=7$  Hz, 9H); 3.80~4.40 (m, 6H); 6.96 (d,  $J=39$  Hz, Z, 1H) ppm.  $^{19}F$  NMR  $\delta$ : -3.3 (s, Z, 3F); -29.3 (s, Z, 2F); -47.7 (s, Z, 2F) ppm.  $^{31}P$  NMR  $\delta$ : 6.2 (s, Z) ppm. MS  $m/e$ : 404 ( $M^+$ ); 359 ( $M^+ - OC_2H_5$ ); 331 ( $M^+ - OC_2H_5 - C_2H_4$ ); 303 ( $M^+ - OC_2H_5 - 2C_2H_4$ , base). Analysis: calc. for  $C_{12}H_{16}F_7O_5P$ : C, 35.64; H, 3.96%. Found: C, 35.30; H, 4.00%.

*N,N*-Diethyl 4,4,4-trifluoro-3-diethylphosphoryl-2-butenamide (**5c**): yield 44%, b.p. 76 °C/2 mmHg. IR (film) ( $cm^{-1}$ ): 2980 (s); 1640 (s); 1460 (s), 1270 (s).  $^1H$  NMR

$\delta$ : 1.18 (t,  $J=7$  Hz, 6H); 1.32 (t,  $J=7$  Hz, 6H); 3.36 (m, 4H); 4.18 (m, 4H); 7.29 (d,  $J=40$  Hz, Z, 1H) ppm.  $^{19}F$  NMR  $\delta$ : 14.5 (s, Z, 3F) ppm.  $^{31}P$  NMR  $\delta$ : 6.4 (s, Z) ppm. MS  $m/e$ : 332 ( $M^+ + 1$ ); 260 ( $M^+ + 1 - NEt_2$ ); 203 ( $M^+ - NEt_2 - 2C_2H_4$ ); 72 ( $^+NEt_2$ , base). Analysis: calc. for  $C_{12}H_{21}F_3NO_4P$ : C, 43.50; H, 6.34; N, 4.23%. Found: C, 43.55; H, 6.60; N, 4.31%.

*N,N*-Diethyl 4,4,5,5,6,6,6-heptafluoro-3-diethylphosphoryl-2-hexenoamide (**5d**): yield 48%, b.p. 90 °C/2 mmHg. IR (film) ( $cm^{-1}$ ): 2980 (s); 1640 (s); 1460 (s); 1240 (s).  $^1H$  NMR  $\delta$ : 1.20 (t,  $J=7$  Hz, 6H); 1.34 (t,  $J=7$  Hz, 6H); 3.14~3.56 (m, 4H); 4.02~4.35 (m, 4H); 7.19 (d,  $J=41$  Hz, Z, 1H) ppm.  $^{19}F$  NMR  $\delta$ : -3.4 (s, Z, 3F); -29.1 (s, Z, 2F); -47.7 (s, Z, 2F) ppm.  $^{31}P$  NMR  $\delta$ : 6.7 (s, Z) ppm. MS  $m/e$ : 432 ( $M^+ + 1$ ); 360 ( $M^+ + 1 - NEt_2$ ); 302 ( $M^+ - 1 - NEt_2 - 2C_2H_4$ , base). Analysis: calc. for  $C_{14}H_{21}F_7NO_4P$ : C, 38.98; H, 4.87; N, 3.25%. Found: C, 38.91; H, 5.06; N, 3.30%.

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