Stereoselective Synthesis of (*Z*)-Methyl 3-Perfluoroalkyl-4-substituted-phenylbutenoates

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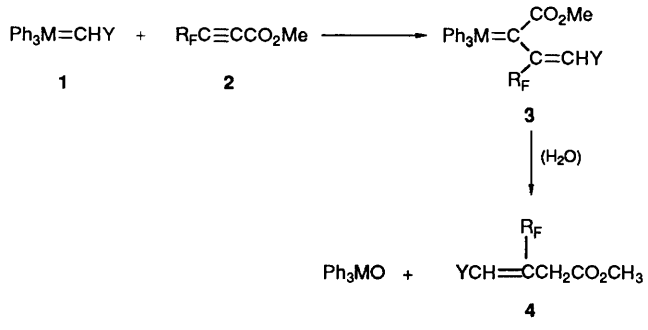
The stereoselective synthesis of (*Z*)-methyl 3-perfluoroalkyl-4-substituted-phenylbut-3-enoates **8a–o** has been investigated. The reaction of substituted benzyltriphenylphosphonium bromides **5a–e** with methyl 2-perfluoroalkylnoates **2a–c** in the presence of K_2CO_3 at room temp. gives two adducts, methyl 3-perfluoroalkyl-4-substituted-phenyl-2-triphenylphosphoranylidenebut-3-enoates, **6a–o** and methyl 3-perfluoroalkyl-4-substituted-phenyl-4-triphenylphosphoranylidenebut-2-enoates, **7a–o**. Compounds **6a–o** exists as pairs of *E*/*Z* isomers, the ratios are 2:1 for $R_F = CF_3$, and 3:1 for $R_F = C_2F_5$ or C_3F_7. Compounds **7a–o** are transformed into **6a–o** when heated. (*Z*)-Methyl 3-perfluoroalkyl-4-substituted-phenylbut-3-enoates **8a–o** can be obtained stereoselectively in high yield when an aqueous methanol solution of mixed **6a–o** and **7a–o** was heated for 10–20 h.

Although stereospecific trisubstituted alkenes are important organic intermediates, isomerically pure products are difficult to obtain and, therefore, their stereoselectively synthesis is still of interest.

We have reported the stereoselective synthesis of methyl 4-cyano-3-perfluoroalkylbuten-3-oates **4a** (Y = CN, *Z*:*E* = 95:5),[1] (*Z*)-dimethyl 3-perfluoroalkylpentenedioates **4b** (Y = CO_2Me)[2] and (*Z*)-methyl 4-*p*-nitrophenyl-3-perfluoroalkylbuten-3-oates **4c** (Y = $C_6H_4NO_2$-*p*)[3] through hydrolysis of the corresponding arsenic or phosphonic adduct **3**. The latter is the reaction product of the corresponding arsorane **1a** (M = As) or phosphorane **1b** (M = P) with methyl 2-perfluoroalkynoates **2** ($R_F = CF_3$, C_2F_5 or C_3H_7) (Scheme 1).



Scheme 1

As a continuation of this study, we report here the stereoselective synthesis of (*Z*)-methyl 3-perfluoroalkyl-4-substituted-phenylbuten-3-oates **8a–o** (Scheme 2). This method is a simple and high yield process for synthesis of stereoselective trisubstituted (*Z*)-alkenes.

Results and Discussion

Reaction of the Phosphonium Bromides **5a–e** *with the Methyl 2-Perfluoroalkynoates* **2a–c** *in the Presence of* K_2CO_3.—Substituted-benzyltriphenylphosphonium bromides **5a–e** reacted with methyl 2-perfluoroalkynoates **2a–c** in anhydrous dimethoxyethane in the presence of K_2CO_3 at room temp. MS and elemental analytical data suggest that the reaction products are adducts of **2a–c** and the phosphorane derived from the phosphonium bromides **5a–e**. The ^1H and ^{19}F NMR spectra show it is a mixture of three components, *i.e.* *Z*-**6a–o**, *E*-**6a–o** and **7a–o**, as discussed in the previous paper.[3] The *E*/*Z* ratio of **6a–o** is 2:1 as ($R_F = CF_3$) and 3:1 ($R_F = C_2F_5$ or C_3F_7). The total yield of **6a–o** and **7a–o** is almost quantitative. This mixture cannot be separated by column chromatography, but when heated at 110–130 °C, **7a–o** is completely transformed to **6a–o**.

From the ^1H NMR spectra the proton shifts appearing at 3.20, 3.70 and 3.50 ppm are assigned to the methoxy protons of *Z*-**6**, *E*-**6** and **7** respectively. The upfield chemical shift of methoxy protons in *Z*-**6** is caused by the shield of π-electrons of the benzene ring. The chemical shift of two protons at abnormal upfield shifts (*ca.* 6.7–6.8 ppm) can be recognized as the two *ortho* hydrogens in the benzene ring which connect to the ylidic carbon atom of **7**.

It was suggested that the reaction mechanism was similar to that mentioned in the previous paper.[3] First, the phosphorane derived from **5** attacks the β-C of **2** giving rise to a betaine **A**, it then either undergoes a four-membered ring rearrangement to form **6**, or a 1,3-H shift to form **7**.

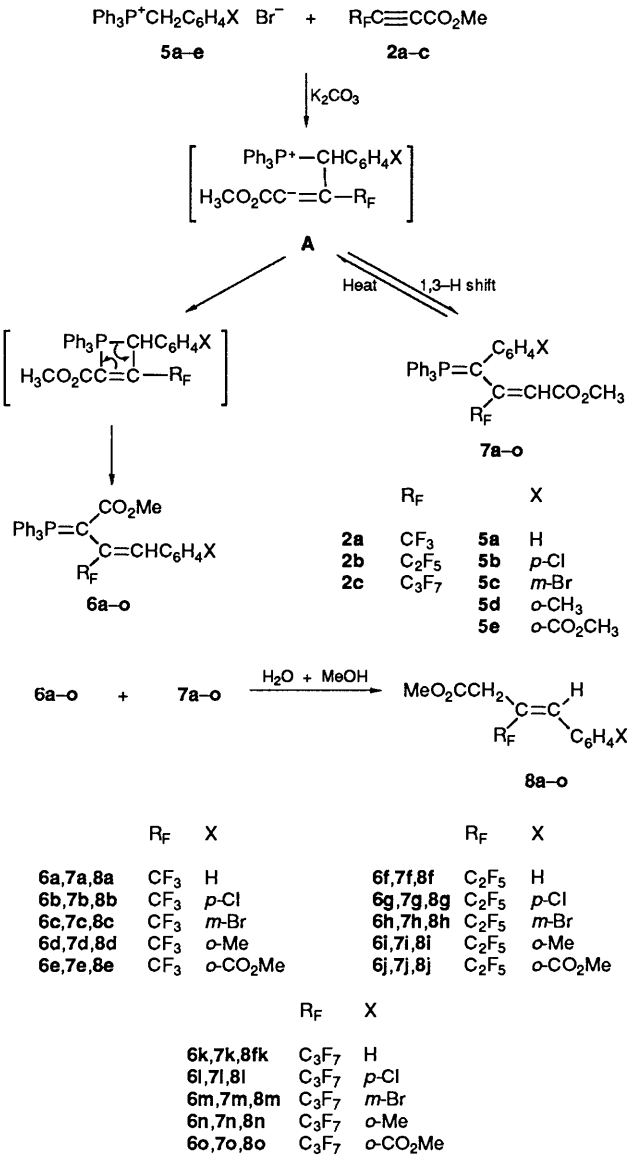
Stereoselective Synthesis of (Z)-*Methyl* 3-*Perfluoroalkyl*-4-*substituted-phenylbut*-3-*enoates* **8a–o**.—(*Z*)-Methyl 3-perfluoroalkyl-4-substituted-phenylbut-3-enoates **8a–o** were formed in high yield when a mixture of **6a–o** and **7a–o** in aqueous methanol was heated in a sealed tube at 150–160 °C for 10–20 h. The structures of **8a–o** were confirmed by IR, ^1H and ^{19}F NMR spectroscopy, MS, and elemental analyses. Since in the MS there are fragments of M − $CH_2CO_2CH_3$ and $CH_2CO_2CH_3$, and an IR ester carbonyl absorption at 1745 cm^{-1}, it is believed the structure of product should be **8** rather than **9**.

^1H and ^{19}F NMR spectra of the products **8a–o** show there is only one geometrical isomer and its (*Z*) configuration is confirmed by the chemical shift of the methoxy protons[3] and also by the empirical formula suggested by U. E. Matter *et al.*[4]

Table 1 Calculation of the chemical shift of olefinic hydrogen: $\delta_H = 5.25 + Z_{gem} + Z_{trans} + Z_{cis}$ ($R_F = CF_3$)

	Z_{gem}	Z_{trans}	Z_{cis}	δ_H
Z-**8**	1.38 (Ar)	0.32 (CF_3)	−0.08 (CH_2CO)	6.87
E-**8**	1.38 (Ar)	−0.06 (CH_2CO)	0.61 (CF_3)	7.18
Z-**9**	0.80 (CO_2R)	0.32 (CF_3)	−0.29 (CH_2Ar)	6.08
E-**9**	0.80 (CO_2R)	−0.32 (CH_2Ar)	0.61 (CF_3)	6.34

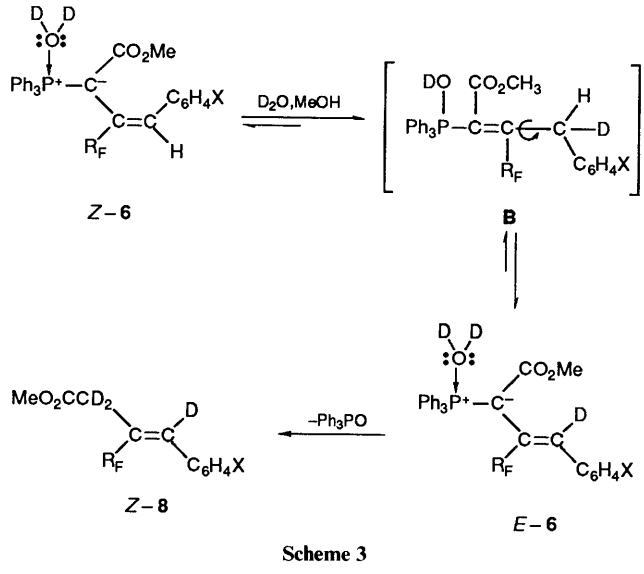
This paper is the 16th report on the studies of Chemistry and Application of Phosphonium and Arsonium Ylides.



Scheme 2

(Table 1). The experimental chemical shift values of olefinic hydrogens of **8a–d** (R_F = CF_3) were in the range of 6.88–6.97 ppm coinciding with the calculated value of *Z*-**8**. But the δ_H value of the olefinic hydrogen of **8e**, **8j** and **8o** (8.02–8.04 ppm) was more downfield than that of **8a–d** and this might be caused by the conjugated position of the olefinic hydrogen and the methoxycarbonyl group of the aromatic ring; its *Z* configuration was further confirmed by NOE spectroscopy.

Compound **7** is transformed into compound **6** when heated. When the hydrolysis of **6** is carried out in methanolic deuteroxide, the methylenic and ethylenic hydrogen atoms of product **8** are partially displaced by deuterium atoms. It can be inferred from this that there is an equilibrium between *E*-**6** and *Z*-**6** *via* intermediate **B** when the phosphorane is attacked by water. Owing to the bulkiness of the phenyl group, *E*-**6** exists as the stereo-preferable configuration; thus *Z*-**8** is produced by the cleavage of P–C bond of *E*-**6** on hydrolysis. According to



Scheme 3

the above experimental evidence, the mechanism of this stereoselective formation of *Z*-**8** shown in Scheme 3 is acceptable.

Experimental

M.p.s and b.p.s are uncorrected. IR spectra were recorded on a 7400 spectrometer made in China as KBr discs or liquid films. NMR spectra were determined with an AC-100SC spectrometer in $CDCl_3$ with TMS (tetramethylsilane) as the internal standard for ^1H NMR, or TFA (trifluoroacetic acid) as the external reference for ^{19}F NMR. *J* Values are given in Hz. Mass spectra were run on a Finnigan-Mat 4510 spectrometer.

p-Chlorobenzyl bromide,[5] *m*-bromobenzyl bromide (NBS is used instead of Br_2),[6] *o*-methylbenzyl bromide,[7] methyl *o*-bromomethylbenzoate,[8] benzyltriphenylphosphonium bromide **5a**,[9] *p*-chlorobenzyltriphenylphosphonium bromide **5b**,[10] *o*-methylbenzyltriphenylphosphonium bromide **5d**[11] and methyl 2-perfluoroalkynoates **2a–c**[2,12] were prepared according to the literature.

m-*Bromobenzyltriphenylphosphonium Bromide* **5c**.—A mixture of *m*-bromobenzyl bromide (2.5 g, 10 mmol) and triphenylphosphine (3.0 g, 11.5 mmol) in anhydrous benzene (40 cm^3) was stirred under reflux for 12 h. The resulting precipitate was filtered off and recrystallized from methanol–ether to give **5c** (5.0 g, 98%); m.p. >295 °C (Found: C, 58.35; H, 4.0. $C_{25}H_{21}Br_2P$ requires C, 58.62; H, 4.13%).

o-*Methoxycarbonylbenzyltriphenylphosphonium Bromide* **5e**.—A solution of triphenylphosphine (5.24 g, 20 mmol) and methyl *o*-bromomethylbenzoate (5.04 g, 22 mmol) dissolved in anhydrous DMF (dimethylformamide) was stirred for 12 h at 50–60 °C. After cooling, the reaction mixture was diluted with ethyl acetate to give the *product*, **5e**, as a white precipitate (9.45 g, 96%); m.p. (recrystallized from chloroform–ethyl acetate) 232–233 °C (Found: C, 66.2; H, 4.95. $C_{27}H_{24}BrO_2P$ requires C, 66.00; H, 4.92%).

Reaction of Phosphonium Bromides **5a–e** *with Methyl 2-Perfluoroalkynoates* **2a–c** *in the Presence of* K_2CO_3.—*General procedure*. To substituted benzyltriphenylphosphonium bromide **5a–e** (2.0 mmol) and K_2CO_3 (0.5 g) in anhydrous dimethoxyethane (DME) (15 cm^3), was added methyl 2-perfluoroalkynoate **2a–c** (2.2 mmol) and the mixture was stirred at 15–25 °C under nitrogen for 48 h. The insoluble residue was filtered off and washed with EtOAc (2 × 10 cm^3) (when

$R_F = C_2F_5$ or C_3F_7) or with CH_2Cl_2 (2 × 10 cm^3) (when $R_F = CF_3$). The combined organic extracts were distilled under reduced pressure and the residue was purified on silica gel G column with EtOAc–light petroleum (b.p. 60–90 °C) (1:1) as eluent to give a mixture of **6a–o** and **7a–o** quantitatively, as a yellow solid. Recrystallization from benzene–hexane or chloroform–hexane gave colourless or light yellow crystals. Efforts to separate **6a–o** and **7a–o** were unsuccessful.

Mixture of methyl 3-perfluoromethyl-4-phenyl-2-triphenylphosphoranylidenebut-3-enoate **6a** *and methyl 3-perfluoromethyl-4-phenyl-4-triphenylphosphoranylidenebut-2-enoate* **7a**. (100%) m.p. 210–211 °C (Found: C, 71.9; H, 4.75. $C_{30}H_{24}F_3O_2P$ requires C, 71.43; H, 4.80%); ν_{max}/cm^{-1} 1614 (CO), 1445, 1435, 1314, 1247, 1150 and 1105; δ_H (**6a**) 3.19 (3 H, s, OCH_3, *Z*-isomer), 3.67 (3 H, s, OCH_3, *E*-isomer) and 6.8–7.8 (21 H, m, 3 × Ph + ArH + C=CH), (**7a**) 3.50 (3 H, s, OCH_3), 6.60 (1 H, s, C=CH), 6.85 (2 H, m, *o*-aryl H), 7.14 (3 H, m, *m*- and *p*-aryl H) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (**6a**) −10.3 (3 F, s, CF_3) and δ_F (**7a**) −18.6 (3 F, s, CF_3); *m/z* 504 (M^+, 28%), 262 (100), 187 (35), 183 (47) and 108 (72).

Mixture of methyl 4-(p-chlorophenyl)-3-perfluoromethyl-2-triphenylphosphoranylidenebut-3-enoate **6b** *and 4-(p-chlorophenyl)-3-perfluoromethyl-4-triphenylphosphoranylidenebut-2-enoate* **7b**. (100%) m.p. 224–225 °C (Found: C, 66.6; H, 3.95. $C_{30}H_{23}ClF_3O_2P$ requires C, 66.86; H, 4.30%); ν_{max}/cm^{-1} 1611 (CO), 1445, 1320, 1242, 1157 and 1112; δ_H (**6b**) 3.19 (3 H, s, OCH_3, *Z*-isomer), 3.65 (3 H, s, OCH_3, *E*-isomer) and 6.9–7.8 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7b**) 3.49 (3 H, s, OCH_3), 6.46 (1 H, s, C=CH), 6.71 (2 H, d, *J* 8.2, *o*-aryl H), 7.13 (2 H, d, *J* 8.2, *m*-aryl H) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (**6b**) −10.2 (3 F, s, CF_3); δ_F (**7b**) −18.6 (3 F, s, CF_3); *m/z* 538 (M^+, 1.5%). 540 [(M + 2) 0.69], 298 (27), 296 (38), 262 (67), 183 (66) and 108 (100).

Mixture of methyl 4-(m-bromophenyl)-3-perfluoromethyl-2-triphenylphosphoranylidenebut-3-enoate **6c** *and methyl 4-(m-bromophenyl)-3-perfluoromethyl-4-triphenylphosphoranylidenebut-2-enoate* **7c**. (100%) m.p. 205–206 °C (Found: C, 62.0; H, 3.75. $C_{30}H_{23}BrF_3O_2P$ requires C, 61.77; H, 3.97%) ν_{max}/cm^{-1} 1612 (CO), 1435, 1320, 1270, 1237, 1150 and 1105; δ_H (**6c**) 3.19 (3 H, s, OCH_3, *Z*-isomer), 3.68 (3 H, s, OCH_3, *E*-isomer) and 6.9–7.8 (21 H, m, 3 × Ph + ArH + C=CH); δ_H (**7c**) 3.50 (3 H, s, OCH_3), 6.42 (1 H, s, C=CH), 6.78–7.15 (4 H, m, ArH) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (**6c**) −10.1 (3 F, s, CF_3, *E*-isomer) and −10.0 (3 F, s, CF_3, *Z*-isomer); δ_F (**7c**) −18.7 (3 F, s, CF_3); *m/z* 582 (M^+, 19%), 584 [(M + 2) 26], 342 (12), 262 (53), 183 (78) and 108 (100).

Mixture of methyl 3-perfluoromethyl-4-(o-tolyl)-2-triphenylphosphoranylidenebut-3-enoate **6d** *and methyl 3-perfluoromethyl-4-(o-tolyl)-4-triphenylphosphoranylidenebut-2-enate* **7d**. (100%) m.p. 137–138 °C (Found: C, 71.5; H, 5.35. $C_{31}H_{26}F_3O_2P$ requires C, 71.81; H, 5.05%); ν_{max}/cm^{-1} 1612 (CO), 1440, 1320, 1245, 1150 and 1101; δ_H (**6d**) 2.05 (3 H, s, $ArCH_3$), 3.10 (3 H, s, OCH_3, *Z*-isomer), 3.69 (3 H, s, OCH_3, *E*-isomer) and 7.0–7.8 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7d**) 2.13 (3 H, s, $ArCH_3$), 3.48 (3 H, s, OCH_3), 6.43 (1 H, br, C=CH), 6.73–7.10 (4 H, m, ArH) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (**6d**) −10.5 (3 F, s, CF_3, *Z*-isomer) and −10.8 (3 F, s, CF_3, *E*-isomer); δ_F (**7d**) −17.4 (3 F, s, CF_3); *m/z* 518 (M^+, 12%), 262 (100), 183 (28) and 108 (33).

Mixture of methyl 4-(o-methoxycarbonylphenyl)-3-perfluoromethyl-2-triphenylphosphoranylidenebut-3-enoate **6e** *and methyl 4-(o-methoxycarbonylphenyl)-3-perfluoromethyl-4-triphenylphosphoranylidenebut-3-enoate* **7e**. (94%) m.p. 171–172 °C (Found: C, 67.85; H, 4.6. $C_{32}H_{26}F_3O_4P$ requires C, 68.33; H, 4.66%); ν_{max}/cm^{-1} 1732 (ArCO), 1612 (CO), 1445, 1243, 1106 and 1079; δ_H (**6e**) 3.13 (3 H, s, OCH_3, *Z*-isomer), 3.66 (3 H, s, OCH_3, *E*-isomer), 3.70 (3 H, s, $ArCO_2CH_3$) and 7.2–7.8 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7e**) 3.53 (3 H, s, OCH_3), 3.89 (3 H, s, $ArCO_2CH_3$), 6.39 (1 H, br, C=CH) and 7.2–7.9 (19 H, m, 3 × Ph + ArH); δ_F (**6e**) −10.5 (3 F, s, CF_3, *E*-isomer) and −10.3 (3 F, s, CF_3, *Z*-isomer); δ_F (**7e**) −17.9 (3 F, s, CF_3); *m/z* 562 (M^+, 13%), 262 (100), 187 (27), 183 (59), 108 (64) and 59 (26).

Mixture of methyl 3-perfluoroethyl-4-phenyl-2-triphenylphosphoranylidenebut-3-enoate **6f** *and methyl 3-perfluoroethyl-4-phenyl-4-triphenylphosphoranylidenebut-2-enoate* **7f**. (93%) m.p. 182–183 °C (Found: C, 67.15; H, 4.35. $C_{31}H_{24}F_5O_2P$ requires C, 67.15; H, 4.36%); ν_{max}/cm^{-1} 1615 (CO), 1606 (CO), 1446, 1440, 1315, 1235, 1212, 1150, 1095 and 1025; δ_H (**6f**) 3.18 (3 H, s, OCH_3, *Z*-isomer), 3.59 (3 H, s, OCH_3, *E*-isomer) and 7.1–7.8 (21 H, m, 3 × Ph + ArH + C=CH); δ_H (**7f**) 3.47 (3 H, s, OCH_3), 6.7–6.9 (3 H, m, C=CH + *o*-aryl H), 7.1–7.2 (3 H, *m*, *m*- and *p*-aryl H) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (**6f**) 5.5 (3 F, s, CF_3, *Z*-isomer), 5.8 (3 F, s, CF_3, *E*-isomer) and 34.7 (2 F, s, CF_2); δ_F (**7f**) 4.8 (3 F, s, CF_3), 27.5(s) and 27.8(s) (2 F, unequal CF_2); *m/z* 554 (M^+, 2.2%), 262 (100), 183 (27) and 108 (30).

Mixture of methyl 4-(p-chlorophenyl)-3-perfluoroethyl-2-triphenylphosphoranylidenebut-3-enoate **6g** *and methyl 4-(p-chlorophenyl)-3-perfluoroethyl-4-triphenylphosphoranylidenebut-2-enoate* **7g**. (97.4%) m.p. 205–206 °C (Found: C, 63.3; H, 3.85. $C_{31}H_{23}ClF_5O_2P$ requires C, 63.22; H, 3.94%); ν_{max}/cm^{-1} 1610 (CO), 1446, 1440, 1305, 1232, 1090 and 1022; δ_H (**6g**) 3.17 (3 H, s, OCH_3, *Z*-isomer), 3.57 (3 H, s, OCH_3, *E*-isomer) and 7.1–7.8 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7g**) 3.45 (3 H, s, OCH_3), 6.69 (2 H, d, *J* 8.1, *o*-aryl H), 6.95 (1 H, s, C=CH), 7.14 (2 H, d, *J* 8,1, *m*-aryl H) and 7.1–7.8 (15 H, m, 3 × Ph); δ_F (**6g**) 5.5 (3 F, s, CF_3, *Z*-isomer), 5.9 (3 F, s, CF_3, *E*-isomer), 34.3 (2 F, s, CF_2, *Z*-isomer), 34.9 (2 F, s, CF_2, *E*-isomer); δ_F (**7g**) 4.8 (3 F, s, CF_3), 27.5(s) and 27.8(s) (2 F, unequal CF_2); *m/z* 588 (M^+, 9%), 590 (M + 2, 3.6), 262 (100), 183 (49) and 108 (65).

Mixture of methyl 4-(m-bromophenyl)-3-perfluoroethyl-2-triphenylphosphoranylidenebut-3-enoate **6h** *and methyl 4-(m-bromophenyl)-3-perfluoroethyl-4-triphenylphosphoranylidenebut-2-enoate* **7h**. (100%) m.p. 141–143 °C (Found: C, 58.7; H, 3.8. $C_{31}H_{23}BrF_5O_2P$ requires C, 58.79; H, 3.66%); ν_{max}/cm^{-1} 1624 (CO), 1620 (CO), 1448, 1441, 1330, 1310, 1236, 1194, 1189 and 1020; δ_H (**6h**) 3.16 (3 H, s, OCH_3, *Z*-isomer), 3.62 (3 H, s, OCH_3, *E*-isomer), 6.92 (1 H, s, C=CH, *E*-isomer), 7.02 (1 H, s, C=CH, *Z*-isomer) and 7.08–7.7 (19 H, m, 3 × Ph + ArH); δ_H (**7h**) 3.46 (3 H, s, OCH_3), 6.7–7.1 (5 H, m, C=CH + ArH) and 7.1–7.7 (15 H, m, 3 × Ph); δ_F (**6h**) 5.4 (3 F, s, CF_3, *Z*-isomer), 5.7 (3 F, s, CF_3, *E*-isomer), 34.1(s) and 34.3(s) (2 F, unequal CF_2, *Z*-isomer) and 34.6 (2 F, s, CF_2, *E*-isomer); δ_F (**7h**) 4.8 (3 F, s, CF_3) and 27.5 (2 F, br, CF_2); *m/z* 632 (M^+, 4%), 634 [(M^+ + 2) 3.8], 342 (30), 340 (31), 262 (100), 183 (53) and 108 (58).

Mixture of methyl 3-perfluoroethyl-4-(o-tolyl)-2-triphenylphosphoranylidenebut-3-enoate **6i** *and methyl 3-perfluoroethyl-4-(o-tolyl)-4-triphenylphosphoranylidenebut-2-enoate* **7i**. (100%) m.p. 159–160 °C (Found: C, 67.85; H, 4.55. $C_{32}H_{26}F_5O_2P$ requires C, 67.71; H, 4.61%); ν_{max}/cm^{-1} 1650 (CO), 1620 (CO), 1447, 1442, 1330, 1313, 1240, 1220, 1200, 1105 and 1022; δ_H (**6i**) 2.04 (3 H, s, $ArCH_3$), 3.15 (3 H, s, OCH_3, *Z*-isomer), 3.61 (3 H, s, OCH_3, *E*-isomer), 6.9–7.8 (20 H, m, 3 × Ph + ArH + C=H); δ_H (**7i**) 2.13 (3 H, s, $ArCH_3$), 3.51 (3 H, s, OCH_3), 6.5 (1 H, br, C=CH) and 6.9–7.8 (19 H, m, 3 × Ph + ArH); δ_F (**6i**) 5.6 (3 F, s, CF_3, *Z*-isomer), 6.1 (3 F, s, CF_3, *E*-isomer), 33.5(s) and 33.8(s) (2 F, unequal CF_2, *Z*-isomer), 339(s) and 34.1(s) (2 F, unequal CF_2, *E*-isomer); δ_F (**7i**) 6.0 (3 F, s, CF_3), 29.1(s) and 29.8(s) (2 F, unequal (CF_2); *m/z* 568 (M^+, 0.32%), 262 (100), 183 (18) and 108 (14).

Mixture of methyl 4-(o-methoxycarbonylphenyl)-3-perfluoroethyl-2-triphenylphosphoranylidenebut-3-enoate **6j** *and methyl 4-(o-methoxycarbonylphenyl)-3-perfluoroethyl-4-triphenylphosphoranylidenebut-2-enoate* **7j**. (100%) m.p. 163.5–164.5 °C

(Found: C, 64.65; H, 4.25. $C_{33}H_{26}F_5O_4P$ requires C, 64.71; H, 4.28%); ν_{max}/cm^{-1} 1727 (ArCO), 1625 (CO), 1449, 1445, 1437, 1330, 1315, 1235, 1217, 1195 and 1022; δ_H (**6j**) 3.09 (3 H, s, OCH_3, *Z*-isomer), 3.62 (3 H, s, OCH_3, *E*-isomer), 3.67 (3 H, s, $ArCO_2CH_3$) and 7.2–8.0 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7j**) 3.51 (3 H, s, OCH_3), 3.90 (3 H, s, $ArCO_2CH_3$), 6.4 (1 H, s, C=CH), 7.1–8.0 (19 H, m, 3 × Ph + ArH); δ_F (**6j**) 5.4 (3 F, s, CF_3, *Z*-isomer), 5.9 (3 F, s, CF_3, *E*-isomer), 33.0(s) and 33.5(s) (2 F, unequal CF_2, *Z*-isomer), 33.5(s) and 33.8(s) (2 F, unequal CF_2, *E*-isomer); δ_F (**7j**) 5.5 (3 F, s, CF_3), 29.2(s) and 29.5(s) (2 F, unequal CF_2); *m/z* 612 (M^+, 0.22%), 262 (100), 187 (5.5), 183 (18) and 108 (15).

Mixture of methyl 3-*perfluoropropyl*-4-*phenyl*-2-*triphenylphosphoranylidenebut*-3-*enoate* **6k** *and methyl* 3-*perfluoropropyl*-4-*phenyl*-4-*triphenylphosphoranylidenebut*-2-*enoate* **7k**. (100%) m.p. 159–160 °C (Found: C, 63.7; H, 4.15. $C_{32}H_{24}F_7O_2P$ requires C, 63.59; H, 4.00%); ν_{max}/cm^{-1} 1615 (CO), 1442, 1314, 1231 and 1107; δ_H (**6k**) 3.14 (3 H, s, OCH_3, *Z*-isomer), 3.58 (3 H, s, OCH_3, *E*-isomer), 6.9–7.7 (21 H, m, 3 × Ph + ArH + C=CH); δ_H (**7k**) 3.51 (3 H, s, OCH_3), 6.82 (1 H, s, C=CH), 7.1–7.8 (20 H, m, 3 × Ph + ArH); δ_F (*E*-**6k**) 3.9 (3 F, t, *J* 11, CF_3), 31.5 (2 F, q, *J* 11, $C=CCF_2$), 49.0(s) and 49.3(s) (2 F, unequal CF_3CF_2), (*Z*-**6k**) 3.8 (3 F, t, *J* 11, CF_3), 31.5 (2 F, q, *J* 11, $C=CCF_2$), 48.3(2) and 48.7(s) (2 F, unequal CF_3CF_2); δ_F (**7k**) 4.3 (3 F, t, *J* 11, CF_3), 24.1 (2 F, m, $C=CCF_2$), 46.9(s) and 47.4(s) (2 F, unequal CF_3CF_2); *m/z* 604 (M^+, 16%), 435 (14), 262 (100), 183 (23) and 108 (3).

Mixture of methyl 4-(p-*chlorophenyl*)-3-*perfluoropropyl*-2-*triphenylphosphoranylidenebut*-3-*enoate* **6l** *and methyl* 4-(p-*chlorophenyl*)-3-*perfluoropropyl*-4-*triphenylphosphoranylidenebut*-3-*enoate* **7l**. (93.2%) m.p. 157.5–159 °C (Found: C, 60.25; H, 3.8. $C_{32}H_{23}ClF_7O_2P$ requires C, 60.16; H, 3.63%); ν_{max}/cm^{-1} 1615 (CO), 1446, 1312, 1232, 1193, 1115 and 1090; δ_H (*Z*-**6l**) 3.14 (3 H, s, OCH_3), 7.00 (1 H, s, C=CH) and 7.0–7.4 (19 H, m, 3 × Ph + ArH); δ_H (*E*-**6l**) 3.56 (3 H, s, OCH_3), 6.89 (1 H, s, C=CH) and 7.0–7.4 (19 H, m, 3 × Ph + ArH); δ_H (**7l**) 3.43 (3 H, s, OCH_3), 6.68 (2 H, d, *J* 8.4, *o*-aryl H), 7.04 (1 H, s, C=CH), 7.13 (2 H, d, *J* 8.4, *m*-aryl H) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (*Z*-**6l**) 3.8 (3 F, t, *J* 11, CF_3), 31.8 (2 F, q, *J* 11, $C=CCF_2$), 484(s) and 48.7(s) (2 F, unequal CF_3CF_2); δ_F (*E*-**6l**) 3.9 (3 F, t, *J* 11, CF_3), 31.8 (2 F, q, *J* 11, $C=CCF_2$), 49.0(s) and 49.3(s) (2 F, unequal CF_3CF_2); δ_F (**7l**) 4.3 (3 F, t, *J* 11, CF_3), 24.1 (2 F, m, $C=CCF_2$), 46.6(s) and 47.3(s) (2 F, unequal CF_3CF_2); *m/z* 638 (M^+, 8%), 640 [(M + 2) 3], 298 (22), 296 (58), 262 (100), 183 (20) and 108 (12).

Mixture of methyl 4-(m-*bromophenyl*)-3-*perfluoropropyl*-2-*triphenylphosphoranylidenebut*-3-*enoate* **6m** *and methyl* 4-(m-*bromophenyl*)-3-*perfluoropropyl*-4-*triphenylphosphoranylidenebut*-2-*enoate* **7m**. (99.3%) m.p. 155–156 °C (Found: C, 56.0; H, 3.55. $C_{32}H_{23}BrF_7O_2P$ requires C, 56.24; H, 3.39%); ν_{max}/cm^{-1} 1627 (CO), 1595, 1449, 1442, 1354, 1308, 1235, 1190 and 1105; δ_H (*Z*-**6m**) 3.14 (3 H, s, OCH_3), 6.96 (1 H, s, C=CH) and 7.0–7.6 (19 H, m, 3 × Ph + ArH); δ_H (*E*-**6m**) 3.61 (3 H, s, OCH_3), 6.85 (1 H, s, C=CH) and 7.0–7.6 (19 H, m, 3 × Ph + ArH); δ_H (**7m**) 3.44 (3 H, s, OCH_3), 6.7–7.2 (5 H, m, C=CH + ArH) and 7.2–7.8 (15 H, m, 3 × Ph); δ_F (*Z*-**6m**) 3.8 (3 F, t, *J* 11, CF_3), 31.4 (2 F, q, *J* 11, $C=CCF_2$), 48.3(s) and 48.7(s) (2 F, unequal CF_2CF_3); δ_F (*E*-**6m**) 3.9 (3 F, t, *J* 11, CF_3), 31.4 (2 F, q, *J* 11, $C=CCF_2$), 48.9(s) and 49.2(s) (2 F, unequal CF_3CF_2); δ_F (**7m**) 4.2 (3 F, t, *J* 11, CF_3), 24.2 (2 F, q, *J* 11, $C=CCF_2$), 46.6(s) and 47.3(s) (2 F, unequal CF_3CF_2); *m/z* 682 (M^+, 5.1%), 684 (M + 2, 5.8), 342 (42), 340 (42), 262 (100), 183 (24) and 108 (12).

Mixture of methyl 3-*perfluoropropyl*-4-(o-*tolyl*)-2-*triphenylphosphoranylidenebut*-3-*enoate* **6n** *and methyl* 3-*perfluoropropyl*-4-(o-*tolyl*)-4-*triphenylphosphoranylidenebut*-2-*enoate* **7n**. (100%) m.p. 155–157.5 °C (Found: C, 64.1; H, 4.3. $C_{33}H_{26}F_7O_2P$ requires C, 64.08; H, 4.34%); ν_{max}/cm^{-1} 1620 (CO), 1445, 1314, 1228 and 1113; δ_H (**6n**) 2.16 (3 H, s, $ArCH_3$), 3.10 (3 H, s, OCH_3, *Z*-isomer), 3.61 (3 H, s, OCH_3, *E*-isomer) and 6.9–7.8 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7n**) 2.15 (3 H, s, $ArCH_3$), 3.47 (3 H, s, OCH_3), 6.57 (1 H, s, C=CH) and 6.9–7.8 (19 H, m, 3 × Ph + ArH); δ_F (*Z*-**6n**) 3.8 (3 F, t, *J* 11, CF_3), 30.3 (2 F, q, *J* 11, $C=CCF_2$), 49.8(s) and 49.9(s) (2 F, unequal CF_3CF_2); δ_F (*E*-**6n**) 3.9 (3 F, t, *J* 11, CF_3), 30.3 (2 F, q, *J* 11, $C=CCF_2$), 48.7(s) and 49.0(s) (2 F, unequal CF_3CF_2); δ_F (**7n**) 4.3 (3 F, t, *J* 11, CF_3), 25.1 (2 F, m, $C=CCF_2$), 48.2(s) and 48.4(s) (2 F, unequal CF_3CF_2); *m/z* 618 (M^+, 5%), 262 (100), 183 (18) and 108 (10).

Mixture of methyl 4-(o-*methoxycarbonylphenyl*)-3-*perfluoropropyl*-2-*triphenylphosphoranylidenebut*-3-*enoate* **6o** *and methyl* 4-(o-*methoxycarbonylphenyl*)-3- *perfluoropropyl*-4-*triphenylphosporanylidenebut*-2-*enoate* **7o**. (96.7%) m.p. 131–132 °C (Found: C, 61.6; H, 4.05. $C_{34}H_{26}F_7O_4P$ requires C, 61.64; H, 3.95%); ν_{max}/cm^{-1} 173.0 (ArCO), 1660 (CO), 1620 (CO), 1445, 1305, 1268, 1232, 1190, 1109 and 1085; δ_H (**6o**) 3.07 (3 H, s, OCH_3, *Z*-isomer), 3.62 (3 H, s, OCH_3, *E*-isomer), 3.66 (3 H, s, $ArCH_3$) and 7.2–8.0 (20 H, m, 3 × Ph + ArH + C=CH); δ_H (**7o**) 3.49 (3 H, s, OCH_3), 3.90 (3 H, s, $ArCH_3$), 6.39 (1 H, s, C=CH) and 7.2–8.0 (19 H, m, 3 × Ph + ArH); δ_F (*Z*-**6o**) 3.8 (3 F, t, *J* 11, CF_3), 29.6–30.0 (2 F, m, $C=CCF_2$), 48.0(s) and 48.3(s) (2 F, unequal CF_3CF_2); δ_F (*E*-**6o**) 3.9 (3 F, t, *J* 11, CF_3), 30.0–30.4 (2 F, m, $C=CCF_2$), 48.6(s) and 48.8(s) (2 F, unequal CF_3CF_2); δ_F (**7o**) 4.4 (3 F, t, *J* 11, CF_3), 24.9–25.0 (2 F, m, $C=CCF_2$), 47.3(s) and 47.5(s) (2 F, unequal CF_3CF_2); *m/z* 662 (M^+, 8%), 262 (100), 187 (9), 183 (26) and 108 (16).

(*Z*)-*Methyl* 3-*Perfluoroalkyl*-4-*substituted-phenylbut*-3-*enoates* **8a–o**.—*General procedure.* The mixture of **6** and **7** (2 mmol) was dissolved in methanol (8 cm^3) and water (2 cm^3) in a sealed tube and heated at 150–160 °C for 10–20 h. The solvent was evaporated under reduced pressure and the residue was passed through a plug of silica gel G eluting with EtOAc–light petroleum (60–90 °C) (1:3) to remove the unchanged reactant and triphenylphosphine oxide. Further purification by molecular distillation gave the title compound *Z*-**8a–o** as a colourless viscous oil; **8l** and **8m** solidified with time.

Methyl 3-*perfluoromethyl*-4-*phenylbut*-3-*enoate* **8a**. (92.4%) b.p. 130–145 °C/1333 Pa* (Found: C, 58.9; H, 4.2. $C_{12}H_{11}F_3O_2$ requires C, 59.02; H, 4.54%); ν_{max}/cm^{-1} 1740 (CO), 1647, 1485, 1430, 1350, 1240, 1160, 1120, 745 and 695; δ_H 3.28 (2 H, s, CH_2), 3.67 (3 H, s, OCH_3), 6.88 (1 H, s, C=CH), 7.26 (5 H, br, ArH); δ_F −17.0 (3 F, s, CF_3); *m/z* 244 (M^+, 59%), 185 (M − CO_2CH_3, 100), 165 (77), 115 (83) and 59 (CO_2CH_3, 95).

Methyl 4-(p-*chlorophenyl*)-3-*perfluoromethylbut*-3-*enoate* **8b**. (66%) b.p. 100–150 °C/1333 Pa* (Found: C, 51.85; H, 3.4. $C_{12}H_{10}ClF_3O_2$ requires C, 51.72; H, 3.62%); ν_{max}/cm^{-1} 1737 (CO), 1650, 1587, 1485, 1430, 1235, 1160, 1122, 1010 and 815; δ_H 3.36 (2 H, s, CH_2), 3.75 (3 H, s, OCH_3), 6.89 (1 H, s, C=CH), 7.25–7.47 (4 H, m, ArH); δ_F −16.9 (3 F, s, CF_3); *m/z* 278 (M^+, 31%), 280 (M + 2, 15), 219 (51), 199 (15), 183 (19), 164 (39), 115 (58) and 59 (100).

Methyl 4-(m-*bromophenyl*)-3-*perfluoromethylbut*-3-*enoate* **8c**. (57.3%) b.p. 120–150 °C/1333 Pa* (Found: C, 44.85; H, 3.0. $C_{12}H_{10}BrF_3O_2$ requires C, 44.61; H, 3.12%); ν_{max}/cm^{-1} 1740 (CO), 1650, 1590, 1555, 1467, 1434, 1232, 1165, 1125, 995 and 785; δ_H 3.36 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3), 6.89 (1 H, s, C=CH) and 7.15–7.45 (4 H, m, ArH); δ_F −17.0 (3 F, s, CF_3); *m/z* 322 (M^+, 15%), 324 (M + 2, 16), 263 (8), 199 (11), 184 (70), 164 (15), 133 (14), 115 (83), 63 (16) and 59 (100).

Methyl m-*perfluoromethyl*-4-(o-*tolyl*)*but*-3-*enoate* **8d**. (77.5%) b.p. 150–160 °C/1333 Pa* (Found: C, 60.0; H, 4.8. $C_{13}H_{13}F_3O_2$ requires C, 40.46; H, 5.07%); ν_{max}/cm^{-1} 1745 (CO), 1668, 1600,

* Oil bath temperature.

1435, 1335, 1245, 1165, 1125 and 750; δ_H 2.26 (3 H, s, $ArCH_3$), 3.36 (2 H, s, CH_2), 3.75 (3 H, s, OCH_3), 6.97 (1 H, s, C=CH) and 7.15–7.30 (4 H, m, ArH); δ_F −16.0 (3 F, s, CF_3); *m/z* 258 (M^+, 47%), 238 (16), 226 (21), 199 (100), 179 (80), 164 (53), 159 (40), 129 (79), 115 (68) and 59 (76).

Methyl 4-(o-*methoxycarbonylphenyl*)-3-*perfluoromethylbut*-3-*enoate* **8e** (87%) b.p. 175–176 °C/3999 Pa* (Found: C, 55.7; H, 4.4. $C_{14}H_{13}F_3O_4$ requires C, 55.63; H, 4.34%); ν_{max}/cm^{-1} 1745 (CO), 1725 (ArCO), 1595, 1575, 1440, 1340, 1275, 1170 and 1130; δ_H 3.40 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3), 3.87 (3 H, s, $ArCO_2CH_3$), 7.36–7.53 (4 H, m, ArH) and 8.04 (1 H, br, C=CH); δ_F −17.2 (3 F, s, CF_3); *m/z* 302 (M^+, 21%), 243 (15), 233 (39), 226 (13), 115 (22) and 59 (100).

Methyl 3-*perfluoroethyl*-4-*phenylbut*-3-*enoate* **8f**. (83.4%) b.p. 120–140 °C/1333 Pa* (Found: C, 52.8; H, 3.6. $C_{13}H_{11}F_5O_2$ requires C, 53.07; H, 3.77%); ν_{max}/cm^{-1} 1745 (CO), 1655, 1495, 1440, 1335, 1210, 1135, 1105, 995 and 715; δ_H 3.32 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3), 7.13 (1 H, s, C=CH) and 7.2–7.4 (5 H, m, ArH); δ_F 7.2 (3 F, s, CF_3) and 33.6 (2 F, s, CF_2); *m/z* 294 (M^+, 44%), 235 (81), 215 (11), 195 (20), 165 (22), 146 (40), 131 (24), 116 (100) and 59 (83).

Methyl 4-(p-*chlorophenyl*)-3-*perfluoroethylbut*-3-*enoate* **8g**. (67.3%) b.p. 150–160 °C/1333 Pa* (Found: C, 47.35; H, 2.9. $C_{13}H_{10}ClF_5O_2$ requires C, 47.51; H, 3.07); ν_{max}/cm^{-1} 1745 (CO), 1595, 1492, 1437, 1335, 1210, 1140, 1095, 1015 and 817; δ_H 3.33 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3), 7.19 (1 H, s, C=CH) and 7.2–7.3 (4 H, m, ArH); δ_F 7.0 (3 F, s, CF_3) and 33.4 (2 F, s, CF_2); *m/z* 328 (M^+, 26%), 330 [(M + 2) 9.4], 269 (46), 164 (22), 150 (25), 115 (56) and 59 (100).

Methyl 4-(m-*bromophenyl*)-3-*perfluoroethylbut*-3-*enoate* **8h**. (82%) b.p. 150–170 °C/1333 Pa* (Found: C, 41.8; H, 2.6. $C_{13}H_{10}BrF_5O_2$ requires C, 41.85; H, 2.70%); ν_{max}/cm^{-1} 1750 (CO), 1565, 1435, 1350, 1210, 1140, 1107, 1020 and 790; δ_H 3.33 (2 H, s, CH_2), 3.77 (3 H, s, OCH_3) and 6.9–7.5 (5 H, m, ArH + C=CH); δ_F 7.0 (3 F, s, CF_3) and 33.6 (2 F, s, CF_2); *m/z* 372 (M^+, 9.5%), 374 [(M + 2) 10], 234 (31), 165 (66), 115 (46) and 59 (100).

Methyl 3-*perfluoroethyl*-4-(o-*tolyl*)*but*-3-*enoate* **8i**. (59%) b.p. 105–140 °C/1333 Pa* (Found: C, 54.4; H, 4.15. $C_{14}H_{13}F_5O_2$ requires C, 54.55; H, 4.22%); ν_{max}/cm^{-1} 1745 (CO), 1650, 1477, 1434, 1325, 1200, 1125, 1095, 1010 and 748; δ_H 2.19 (3 H, s, $ArCH_3$), 3.26 (2 H, s, CH_2), 3.68 (3 H, s, OCH_3) and 7.0–7.1 (5 H, m, ArH + C=CH); δ_F 7.3 (3 F, s, CF_3) and 34.7 (2 F, s, CF_2); *m/z* 308 (M^+, 31%), 276 (13), 249 (100), 229 (19), 209 (18), 179 (29), 165 (17), 130 (85), 115 (45) and 59 (70).

Methyl 4-(o-*methoxycarbonylphenyl*)-3-*perfluoroethylbut*-3-*enoate* **8j**. (90%) b.p. 188–189 °C/3999 Pa* (Found: C, 51.2; H, 3.75. $C_{15}H_{13}F_5O_4$ requires C, 51.15; H, 3.72%); ν_{max}/cm^{-1} 1745 (CO), 1725 (ArCO), 1600, 1572, 1440, 1270, 1210 and 1135; δ_H 3.38 (2 H, s, CH_2), 3.78 (3 H, s, OCH_3), 3.89 (3 H, s, $ArCO_2CH_3$), 7.44 (4 H, m, ArH) and 8.02 (1 H, br, C=CH); δ_F 7.1 (3 F, s, CF_3) and 33.3 (2 F, s, CF_2); *m/z* 352 (M^+, 12%), 293 (12), 233 (92), 115 (12) and 59 (100).

Methyl 3-*perfluoropropyl*-4-*phenylbut*-3-*enoate* **8k**. (76.3%) b.p. 150–160 °C/1333 Pa* (Found: C, 48.9; H, 3.0. $C_{14}H_{11}F_7O_2$ requires C, 48.85; H, 3.22%); ν_{max}/cm^{-1} 1755 (CO), 1436, 1345, 1235, 1185, 1115 and 702; δ_H 3.34 (2 H, s, CH_2), 3.76 (3 H, s, OCH_3) and 7.2–7.4 (6 H, m, ArH + C=CH); δ_F 4.2 (3 F, t, *J* 10, CF_3), 30.1 (2 F, q, *J* 10, $C=CCF_2$) and 48.7 (2 F, s, CF_3CF_2); *m/z* 344 (M^+, 27%), 285 (42), 165 (25), 146 (48), 131 (20), 116 (100) and 59 (95).

Methyl 4-(p-*chlorophenyl*)-3-*perfluoropropylbut*-3-*enoate* **8l**. (89.5%) m.p. 49–50 °C (from MeOH) (Found: C, 44.5; H, 2.45. $C_{14}H_{10}ClF_7O_2$ requires C, 44.41; H, 2.66%); ν_{max}/cm^{-1} 1738 (CO), 1490, 1420, 1350, 1240, 1185, 1112 and 755; δ_H 3.33 (2 H, s, CH_2), 3.77 (3 H, s, OCH_3) and 7.1–7.4 (5 H, m, ArH + C=CH); δ_F 4.1 (3 F, t, *J* 10, CF_3), 30.2 (2 F, q, *J* 10, $C=CCF_2$) and 48.7 (2 F, s, CF_3CF_2); *m/z* 378 (M^+, 31%), 380 [(M + 2), 11], 319 (54), 166 (57), 151 (29), 115 (7) and 59 (100).

Methyl 4-(m-*bromophenyl*)-3-*perfluoropropylbut*-3-*enoate* **8m**. (94%) m.p. 32–33 °C (from MeOH) (Found: C, 40.15; H, 2.15. $C_{14}H_{10}BrF_7O_2$ requires C, 39.74; H, 2.38%); ν_{max}/cm^{-1} 1750 (CO), 1590, 1506, 1435, 1340, 1225, 1115, 915 and 705; δ_H 3.33 (2 H, s, CH_2), 3.77 (3 H, s, OCH_3) and 7.1–7.5 (5 H, m, ArH + C=CHO); δ_F 4.1 (3 F, t, *J* 10, CF_3), 30.4 (2 F, q, *J* 10, $C=CCF_2$) and 48.7 (2 F, s, CF_3CF_2); *m/z* 422 (M^+, 8%), 424 [(M + 2) 9], 284 (16), 165 (70), 115 (27) and 59 (100).

Methyl 3-*perfluoropropyl*-4-(o-*tolyl*)-*but*-3-*enoate* **8n**. (73%) b.p. 105–140 °C/1333 Pa* (Found: C, 49.7; H, 3.6. $C_{15}H_{13}F_7O_2$ requires C, 50.29; H, 3.66%); ν_{max}/cm^{-1} 1745 (CO), 1650, 1432, 1335, 1225, 1110, 914 and 755; δ_H 2.27 (3 H, s, $ArCH_3$), 3.36 (2 H, s, CH_2), 3.77 (3 H, s, OCH_3) and 7.1–7.3 (5 H, m, ArH + C=CH); δ_F 3.7 (3 F, t, *J* 10, CF_3), 30.9 (2 F, q, *J* 10, $C=CCF_2$) and 48.5 (2 F, s, CF_3CF_2); *m/z* 358 (M^+, 24%), 299 (81), 179 (53), 165 (22), 159 (31), 130 (100), 115 (49) and 59 (89).

Methyl 4-(o-*methoxycarbonylphenyl*)-3-*perfluoropropylbut*-3-*enoate* **8o**. (92%) b.p. 182–183 °C/3999 Pa* (Found: C, 47.8; H, 3.3. $C_{16}H_{13}F_7O_4$ requires C, 47.77; H, 3.26%); ν_{max}/cm^{-1} 1750 (CO), 1730 (ArCO), 1600, 1573, 1450, 1345, 1275, 1230, 1170 and 1120; δ_H 3.39 (2 H, s, CH_2), 3.78 (3 H, s, OCH_3), 3.88 (3 H, s, $ArCO_2CH_3$), 7.37–7.54 (4 H, m, ArH) and 8.03 (1 H, br, C=CH); δ_F 4.1 (3 F, t, *J* 10, CF_3), 30.0 (2 F, q, *J* 10, $C=CCF_2$) and 49.2 (2 F, s, CF_3CF_2); *m/z* 402 (M^+, 11%), 343 (13), 233 (99), 115 (10) and 59 (100).

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