

Simple Synthesis of Dimethyl 4-Methyl-6-perfluoroalkylisophthalates and Dimethyl 5-Perfluoroalkylbiphenyl-2,4-dicarboxylates *via* Acyclic Precursors†

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Reaction of methyl propynoate **2** with acetylmethylenetriphenylphosphorane **1a** or benzoylmethylenetriphenylphosphorane **1b** at 90 °C gives methyl 5-oxo-2-(triphenylphosphoranylidene)hex-3-enoate **4a** or methyl 4-benzoyl-2-(triphenylphosphoranylidene)but-3-enoate **4b** as the main product, respectively. Phosphoranes **4a** or **4b** can further react with methyl perfluoroalkynoates **5a** and **5b** to afford dimethyl 2-(3-oxo-1-perfluoroalkylbut-1-enyl)-4-(triphenylphosphoranylidene)pent-2-enedioates **6a** and **6b** or dimethyl 2-(2-benzoyl-1-perfluoroalkylvinyl)-4-(triphenylphosphoranylidene)pent-2-enedioates **6c** and **6d**, respectively. Dimethyl 4-methyl-6-perfluoroalkylisophthalates **7a** and **7b** or dimethyl 5-perfluoroalkylbiphenyl-2,4-dicarboxylates **7c** and **7d** were prepared in high yield *via* intramolecular Wittig reaction of phosphoranes **6a/6b** or **6c/6d** in benzene or methanol. The structures of compounds **4a**, **6a** and **7a** were confirmed by IR, MS and ¹H, ¹⁹F and ¹³C NMR spectroscopy and elemental analyses. Reaction mechanisms for the formation of compounds **4**, **6** and **7** are proposed.

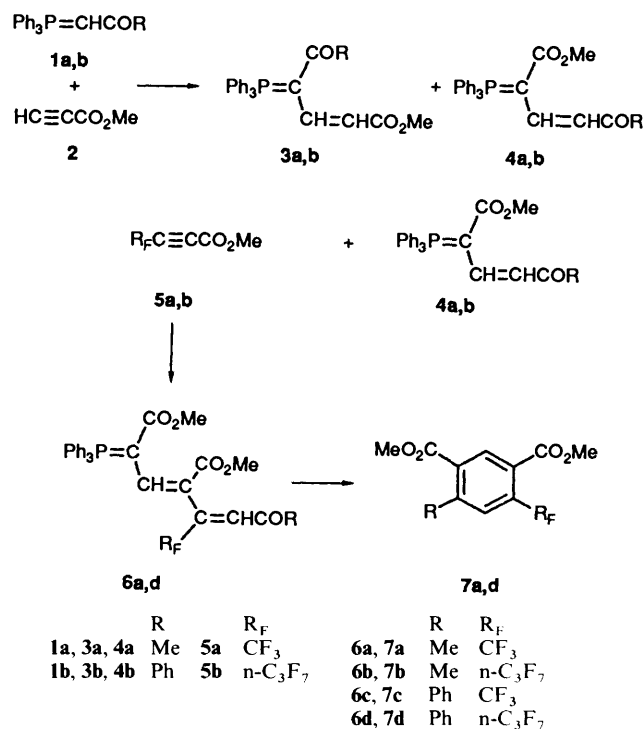
Polysubstituted arenes have been synthesized traditionally through substitution of aromatic ring compounds. However, this method suffered from long synthetic routes and the presence of complicated positional isomers. Therefore, to study the convenient and efficient syntheses of polysubstituted arenes is valuable in organic synthetic methodology. We have reported the syntheses of trisubstituted benzenes—methyl 2-perfluoroalkyl-6-methoxybenzoates,¹ methyl 1-alkoxy-3-perfluoroalkyl-2-naphthoates² and methyl 2,6-bis(perfluoroalkyl)benzoates³—*via* acyclic precursors. It is a preferable method, attributed to its simplicity and the production of only a sole product with definite positional functional groups.

As a continuation of this study, a simple synthesis of tetrasubstituted benzenes—dimethyl 4-methyl-6-perfluoroalkylisophthalates **7a** and **7b** and dimethyl 5-perfluoroalkylbiphenyl-2,4-dicarboxylates **7c** and **7d**—will be reported in this paper.

Results and Discussion

Synthesis of the Precursors 6a–d.—Reaction of acetylmethylenetriphenylphosphorane **1a** or benzoylmethylenetriphenylphosphorane **1b** with methyl propynoate **2** at room temperature afforded a mixture of compounds **3a** and **3b** and **4a** and **4b** (Scheme 1). Compounds **3** and compounds **4** were the products of 1,3-H migration and four-membered-ring rearrangement of the betaine A, respectively (Scheme 2). When the reaction was carried out at 90 °C compound **4a** or **4b** was the main product (Table 1). They could further react with methyl perfluoroalkynoates **5a** and **5b** at room temperature to produce compounds **6a–d**, a phosphorus ylide possessing a conjugated six-carbon main chain with a terminal acyl group. These latter are acyclic precursors in the synthesis of aromatic compounds through an intramolecular Wittig reaction.

Synthesis of Isophthalates 7a–d.—Phosphoranes **6a/b** or **6c/d** were heated in benzene in a sealed tube at 140–160 or 210–220 °C, respectively, whereupon an intramolecular Wittig reaction took place to form aromatic ring compounds **7a/b** or **7c/d** in high yield. The reaction temperature could be much



Scheme 1

lower and the reaction time much shorter if the reaction were to be carried out in methanolic solution. Interestingly, even when aq. methanol is used as solvent substrates **6** still undergo aromatic cyclization rather than hydrolysis of the P–C bond (Table 2).

Structural Confirmation of Compound 7a and the Reaction Mechanism.—According to spectral analyses of compound **7a**, it is a tetrasubstituted benzene. The four substituents are a methyl group, a trifluoromethyl group, and two methoxycarbonyl groups. Two aromatic hydrogens with chemical shifts δ 7.64 and 8.36 are situated *para* to each other. The relative positions of the four functional groups were ascertained by the following methods:

† This paper is the 19th report on our studies of the Chemistry and Application of Phosphonium and Arsonium Ylides.

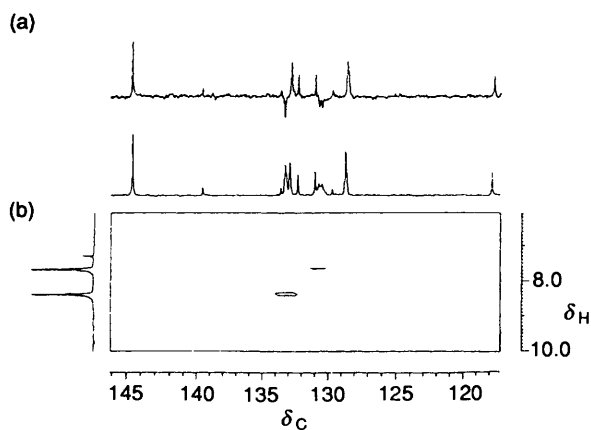
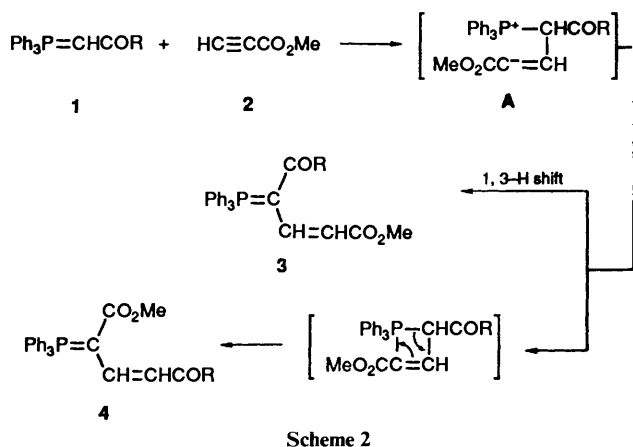


Fig. 1 (a) Heteronuclear J -modulated spin echo spectrum of compound **7a**. (b) ^{13}C - ^1H Shift correlation 2D-NMR spectrum of compound **7a**.

Table 1 Reaction of phosphoranes **1** with methyl propynoate **2**

Phosphorane	Conditions	Product	
		Yield (%)	3:4
1a	0–5 °C, CHCl_3	81	1:0.1
1a	r.t., ^a CH_2Cl_2	85	1:0.43
1a	90 °C, $\text{MeOCH}_2\text{CH}_2\text{OMe}$	82	1:4.6
1b	r.t., CH_2Cl_2	92	1:1.5
1b	90 °C, $\text{MeOCH}_2\text{CH}_2\text{OMe}$	82	1:8.5
1b	90 °C, CH_2Cl_2 , sealed tube	97	1:12

^a Room temperature.

(a) Through heteronuclear J -modulated spin echo spectroscopy (Fig. 1a), it appears that two aromatic carbons with chemical shifts δ_{C} 130.38 and 133.02 are bonded to two hydrogens. From a ^{13}C - ^1H shift-correlation 2D-NMR experiment (Fig. 1b), the carbon atom with chemical shift δ_{C} 130.38 is correlated to the hydrogen with chemical shift at δ 7.64, while the carbon at δ_{C} 133.02 is correlated to the hydrogen at δ 8.36. The former carbon appears as a quartet with coupling constant 5.48 Hz, this coincides with the $^3J_{\text{CF}}$ splitting (Fig. 2). Therefore the trifluoromethyl group is situated *ortho* to the hydrogen with δ 7.64.

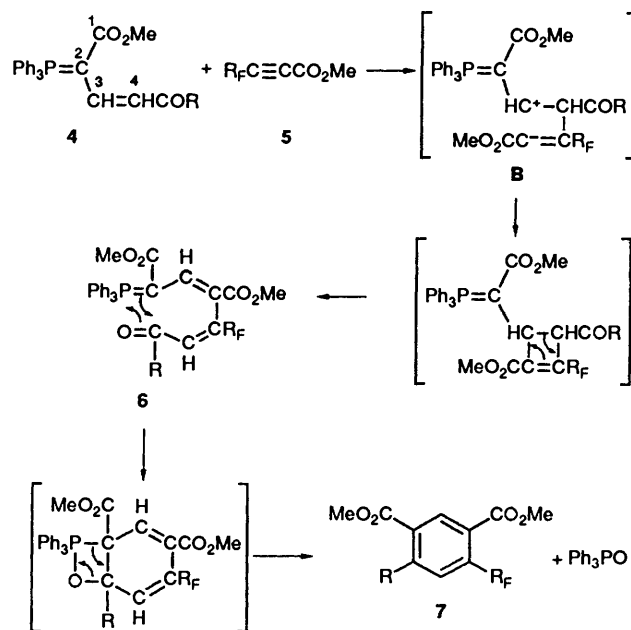
(b) From a ^1H COSYLR 2D-NMR spectrum (Fig. 3), the correlation between the methyl group with δ 2.70 and the aromatic proton at δ 7.64 is greater than that with the hydrogen at δ 8.36. Therefore the methyl group and the aromatic proton at δ 7.64 are *ortho* to each other.

Table 2 Preparation of **7a–d**

Reactant	Solvent	Temp. (T /°C)	Time (t /h)	Product	Yield (%)
6a	Benzene	165	30	7a	93
6a	MeOH–water (9:1)	140	30	7a	90
6a	MeOH	140	13	7a	95
6a	MeOH	120	3	7a	86
6b	Benzene	140	20	7b	98
6c	Benzene	220	8	7c	91
6c	MeOH–water (9:1)	160	9	7c	82
6d	Benzene	220	8	7d	90
6d	MeOH–water	160	9	7d	77

According to the above facts, it follows that compound **7a** is dimethyl 4-trifluoromethyl-6-methylisophthalate.

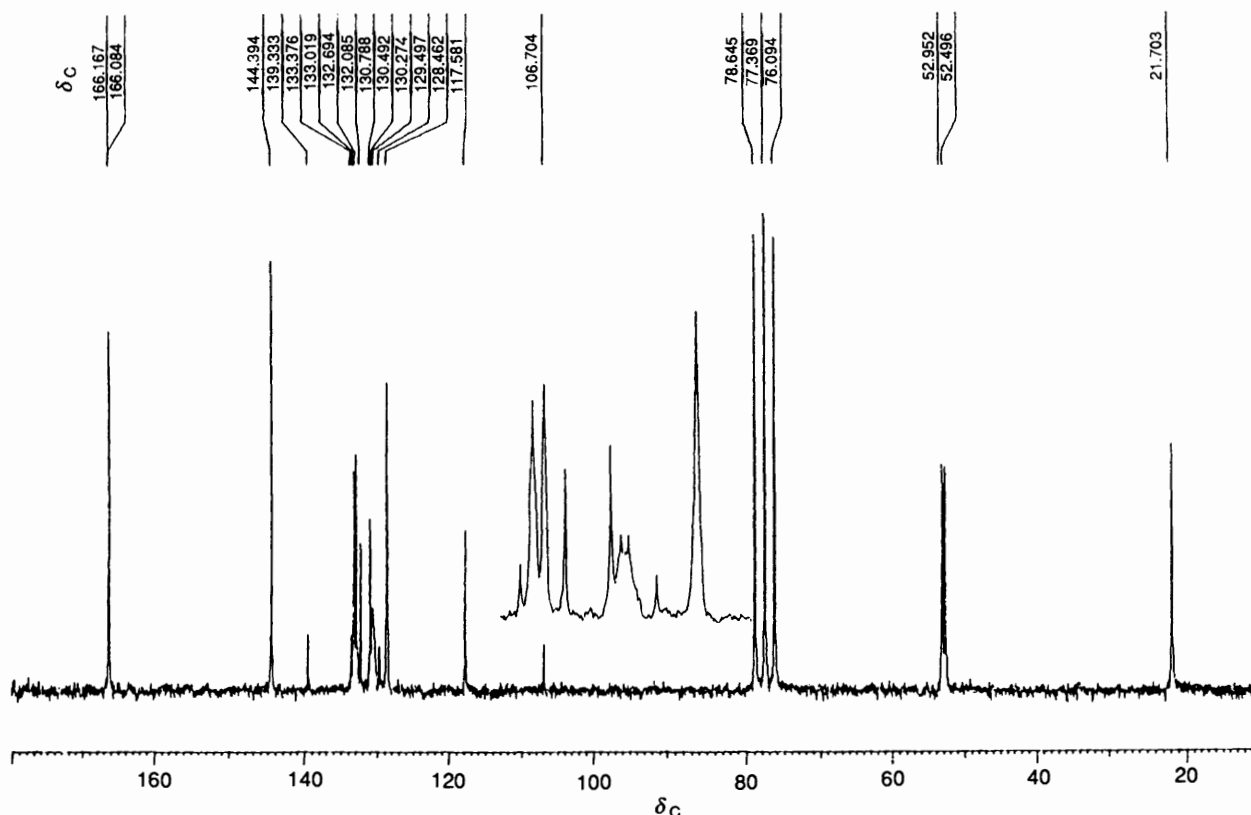
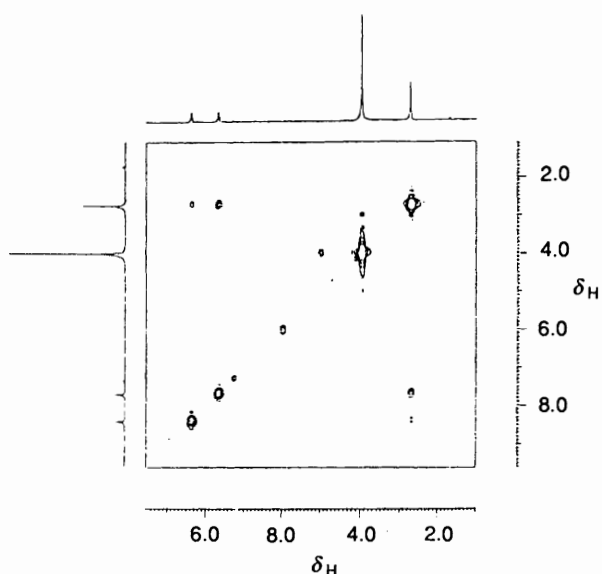
Compound **7** is formed through elimination of a molecular of Ph_3PO from compound **6**, therefore the structure of isophthalate **7a**, *i.e.* as dimethyl 2-(3-oxo-1-trifluoromethylbut-1-enyl)-2-(triphenylphosphoranylidene)pent-2-enedioate. The spectral data of **6a** are also in accord with the above proposition. Thus, the reaction mechanism of the formation of compounds **6** is suggested as follows: first, the C-4 of the phosphoranes **4** attacks C- β of esters **5** to give betaine **B**, which then undergoes a four-membered-ring rearrangement to form phosphorane **6** (Scheme 3).



Experimental

M.p.s and b.p.s are uncorrected. M.p.s. were measured with WRS-1 Digital Melting Point Apparatus made by Shanghai Physical Optical Instrument Factory (SPOIF), China. IR spectra were recorded on a 7400 spectrometer (Shanghai Analytical Instrument Factory, China) for samples as KBr discs or liquid films. NMR spectra were determined with an AC-100SC or an AMX-600 spectrometer for solutions in CDCl_3 with tetramethylsilane as internal standard for ^1H NMR, and 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.

Acetylmethylenetriphenylphosphorane **1a**,⁴ benzoylmethylenetriphenylphosphorane **1b**,⁴ methyl propynoate **2**⁵ and

Fig. 2 ^{13}C NMR spectrum of compound 7aFig. 3 ^1H COSYLR 2D-NMR spectrum of compound 7a

methyl perfluoroalk-2-ynoates **5a** and **5b**⁶ were prepared according to the respective literature method. Light petroleum refers to the fraction boiling in the range 60–90 °C.

Preparation of Methyl 5-Oxo-2-(triphenylphosphoranylidene)hex-3-enoate 4a.—To a solution of acetylmethylenetriphenylphosphorane **1a** (4 mmol) in anhydrous 1,2-dimethoxyethane (DME) (40 cm³) was added a solution of methyl propynoate **2** (4.4 mmol) in anhydrous DME (4 cm³) and the mixture was stirred at 90 °C for 4 h. The solvent was removed under reduced pressure and the residue was separated on a silica gel G column with EtOAc–light petroleum (1:1–2:1) as eluent

to give compound **3a** (0.23 g, 14.6%) and title compound **4a** (1.08 g, 67.4%). Further purification was by recrystallization from benzene–light petroleum.

Methyl 5-oxo-4-(triphenylphosphoranylidene)hex-2-enoate 3a had m.p. 211–213 °C (Found: C, 74.55; H, 5.8. C₂₅H₂₃O₃P requires C, 74.62; H, 5.76%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1680, 1578, 1567 and 1545; δ_{H} 2.40 (3 H, s, COMe), 3.57 (3 H, s, OMe), 5.13 (1 H, d, $^3J_{\text{HH}}$ 15.3, =CH) and 7.17–7.60 (16 H, m, ArH and =CH); δ_{C} 28.63 (d, $^3J_{\text{PC}}$ 8.19, COMe), 50.52 (s, CO₂Me), 77.45 (d, $^1J_{\text{PC}}$ 109.77, P=C), 100.50 (d, $^2J_{\text{PC}}$ 13.84, =C), 125.02 (d, $^1J_{\text{PC}}$ 91.37, Ar), 128.94 (d, $^3J_{\text{PC}}$ 12.28, Ar), 132.31 (d, $^4J_{\text{PC}}$ 2.37, Ar), 133.42 (d, $^2J_{\text{PC}}$ 9.84, Ar), 145.06 (d, $^3J_{\text{PC}}$ 16.09, =C), 169.67 (s, CO₂Me) and 193.17 (d, $^2J_{\text{PC}}$ 5.92, COMe); m/z 402 (M⁺, 19.21%), 387 (30), 371 (11), 359 (2), 343 (100) and 262 (6).

Methyl 5-oxo-2-(triphenylphosphoranylidene)hex-3-enoate 4a had m.p. 168–170 °C (Found: C, 74.6; H, 5.7%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1673, 1667, 1640, 1604, 1597, 1560, 1550, 1515 and 1510; δ_{H} 1.94 (3 H, s, COMe), 3.48 (3 H, s, OMe), 6.75 (1 H, d, $^3J_{\text{HH}}$ 14.7, =CH), 7.03 (1 H, dd, $^3J_{\text{HH}}$ 14.7, $^3J_{\text{PH}}$ 17.1, =CH) and 7.35–7.68 (15 H, m, ArH); δ_{C} 26.74 (s, COMe), 50.01 (s, CO₂Me), 60.05 (d, $^1J_{\text{PC}}$ 119.25, P=C), 113.58 (d, $^3J_{\text{PC}}$ 13.55, =C), 124.59 (d, $^1J_{\text{PC}}$ 97.25, Ar), 129.08 (d, $^3J_{\text{PC}}$ 12.31, Ar), 132.76 (d, $^4J_{\text{PC}}$ 2.59, Ar), 133.64 (d, $^2J_{\text{PC}}$ 9.82, Ar), 145.71 (d, $^2J_{\text{PC}}$ 14.81, =C), 168.35 (d, $^2J_{\text{PC}}$ 15.59, CO₂Me) and 196.44 (s, COMe); m/z 402 (M⁺, 11.23%), 387 (5), 370 (9), 359 (3), 343 (4) and 262 (100).

Preparation of Methyl 4-Benzoyl-2-(triphenylphosphoranylidene)but-3-enoate 4b.—To a solution of benzoylmethylenetriphenylphosphorane **1b** (0.38 g, 1 mmol) in anhydrous methylene dichloride (10 cm³) was added methyl propynoate **2** (0.084 g, 1 mmol) and the mixture was heated at 90 °C for 5 h in a sealed tube. The solvent was removed and the residue was separated on a silica gel G column with EtOAc–light petroleum (1:1–2:1) as eluent to give compound **3b** (0.034 g, 7.4%) and title compound **4b** (0.414 g, 89.2%). Further purification was by recrystallization from benzene–light petroleum.

Methyl 4-benzoyl-4-(triphenylphosphoranylidene)but-2-enoate **3b** had m.p. 219–220 °C (Found: C, 77.8; H, 5.4. C₃₀H₂₅O₃P requires C, 77.57; H, 5.42%); $\nu_{\max}/\text{cm}^{-1}$ 1693, 1689, 1583, 1577, 1542 and 1537; δ_{H} 3.46 (3 H, s, OMe), 4.47 (1 H, d, $^3J_{\text{HH}}$ 15.3, =CH) and 7.35–7.81 (21 H, m, ArH + =CH); δ_{C} 50.40 (s, Me), 75.65 (d, $^1J_{\text{PC}}$ 106.34, P=C), 101.50 (d, $^2J_{\text{PC}}$ 10.32, =C), 124.59 (d, $^1J_{\text{PC}}$ 90.70, Ar), 128.99 (d, $^3J_{\text{PC}}$ 12.64, Ar), 132.43 (d, $^4J_{\text{PC}}$ 2.69, Ar), 133.55 (d, $^2J_{\text{PC}}$ 9.67, Ar), 128.20 (d, $^4J_{\text{PC}}$ 4.51, Ar), 129.89 (s, Ar), 131.79 (s, Ar), 141.04 (d, $^3J_{\text{PC}}$ 9.44, Ar), 146.03 (d, $^3J_{\text{PC}}$ 13.37, =C), 169.30 (s, CO₂Me) and 191.93 (d, $^2J_{\text{PC}}$ 6.57, C(=O)Ph); m/z 464 (M⁺, 29.22%), 449 (45), 405 (100) and 262 (24).

Methyl 4-benzoyl-2-(triphenylphosphoranylidene)but-3-enoate **4b** had m.p. 197.8–198.8 °C (Found: C, 77.8; H, 5.2%); $\nu_{\max}/\text{cm}^{-1}$ 1674, 1516, 1508 and 1488; δ_{H} 3.47 (3 H, s, OMe) and 7.31–7.92 (22 H, m, ArH + =CH); m/z 464 (M⁺, 24.48%), 433 (6), 405 (5), 359 (4) and 262 (100).

Preparation of Dimethyl 2-(3-Oxo-1-perfluoroalkylbut-1-enyl)-4-(triphenylphosphoranylidene)pent-2-enedioates 6a/6b and Dimethyl 2-(2-Benzoyl-1-perfluoroalkylvinyl)-4-(triphenylphosphoranylidene)pent-2-enedioates 6c/6d.—General procedure. To a solution of compound **4a** or **4b** (1.0 mmol) in anhydrous methylene dichloride (15 cm³) was added a methyl perfluoroalkynoate **5a** or **5b** (1.5 mmol) and the mixture was stirred at room temperature under nitrogen for 48 h. The solvent was removed, and the residue was purified by column chromatography on silica gel and elution with EtOAc–light petroleum (2:1). Further purification by recrystallization from benzene–hexane or EtOAc–light petroleum gave compounds **6a–d**.

Dimethyl 2-[3-oxo-1-(trifluoromethyl)but-1-enyl]-4-(triphenylphosphoranylidene)pent-2-enedioate 6a. This compound (58%) had m.p. 187–188 °C (Found: C, 65.1; H, 5.0. C₃₀H₂₆F₃O₅P requires C, 64.98; H, 4.73%); $\nu_{\max}/\text{cm}^{-1}$ 1688, 1683, 1670, 1620, 1613 and 1543; δ_{H} 2.28 (3 H, s, COMe), 3.29 (3 H, s, CO₂Me), 3.49 (3 H, s, CO₂Me), 6.55 (1 H, s, =CH), 7.22 (1 H, d, $^3J_{\text{PH}}$ 19.2, =CH), 7.52–7.55 (6 H, m, ArH) and 7.60–7.65 (9 H, m, ArH); δ_{F} –11.35 (3 F, s, CF₃); δ_{C} 29.75 (s, COMe), 49.44 (s, CO₂Me), 51.26 (s, CO₂Me), 63.18 (d, $^1J_{\text{PC}}$ 123.89, P=C), 102.05 (q, =C), 124.47 (d, $^1J_{\text{PC}}$ 92.16, Ar), 124.39 (q, $^1J_{\text{CF}}$ 295.29, CF₃), 129.08 (s, Ar), 132.74 (d, =C), 133.66 (s, Ar), 133.71 (s, Ar), 139.60 (q, $^2J_{\text{CF}}$ 48.07, =C), 145.91 (q, $^3J_{\text{CF}}$ 16.62, =C), 167.16 (d, $^2J_{\text{PC}}$ 15.11, CO₂Me), 168.21 (s, CO₂Me) and 199.62 (s, COMe); m/z 554 (M⁺, 3%), 523 (2), 495 (100) and 59 (43).

Dimethyl 2-[1-(heptafluoropropyl)-3-oxobut-1-enyl]-4-(triphenylphosphoranylidene)pent-2-enedioate 6b. This compound (85%) had m.p. 147–148 °C (Found: C, 59.0; H, 4.2. C₃₂H₂₆F₇O₅P requires C, 58.74; H, 4.00%); $\nu_{\max}/\text{cm}^{-1}$ 1700, 1692, 1684, 1678, 1645, 1640, 1550 and 1537; δ_{H} 2.32 (3 H, s, COMe), 3.34 (3 H, s, OMe), 3.46 (3 H, s, OMe), 6.48 (1 H, br s, =CH) and 7.42–7.65 (16 H, m, ArH + =CH); δ_{F} 3.87 (3 F, t, J 11, CF₃), 33.25 and 39.02 (2 F, AB, J_{AB} 264.18, C|F₂CF₂CF₃) and 49.76 (s) and 50.03 (s), (2 F, unequal CF₂CF₃); m/z 654 (M⁺, 2%), 595 (49), 345 (39) and 51 (100).

Dimethyl 2-[2-benzoyl-1-(trifluoromethyl)vinyl]-4-(triphenylphosphoranylidene)pent-2-enedioate 6c. This compound (92%) had m.p. 170–172 °C (Found: C, 68.0; H, 4.9. C₃₅H₂₈F₃O₅P requires C, 68.2; H, 4.58%); $\nu_{\min}/\text{cm}^{-1}$ 1650, 1630, 1600 and 1550, δ_{H} 3.33 (3 H, s, OMe), 3.47 (3 H, s, OMe), 6.74 (1 H, s, =CH) and 7.26–7.52 (21 H, m, ArH + =CH); δ_{F} –13.62 (3 F, s, CF₃); m/z 616 (M⁺, 2%), 557 (22), 307 (100) and 278 (97).

Dimethyl 2-[2-benzoyl-1-(heptafluoropropyl)vinyl]-4-(triphenylphosphoranylidene)pent-2-enedioate 6d. This compound (97%) had m.p. 118–120 °C (Found: C, 62.2; H, 3.95. C₃₇H₂₈F₇O₅P requires C, 62.02; H, 3.94%); $\nu_{\max}/\text{cm}^{-1}$ 1680, 1670, 1650 and 1600; δ_{H} 3.28 (3 H, s, OMe), 3.37 (3 H, s, OMe) and 7.08–7.99 (22 H, m, ArH + =CH); δ_{F} 3.52 (3 F, t, J 11, CF₃), 32.71 and 39.64 (2 F, AB, J_{AB} 256.15, CF₂CF₂CF₃) and

49.21 (s) and 49.53 (s), (2 F, unequal CF₂CF₃); m/z 716 (M⁺, 4%), 658 (100) and 278 (1).

Syntheses of Dimethyl Perfluoroalkylisophthalates 7a, b or Dimethyl 5-(Perfluoroalkyl)biphenyl-2,4-dicarboxylates 7c, d.—Typical procedure. A solution of **6a** (1.5 mmol) in anhydrous benzene (5 cm³) was heated in a sealed tube at 165 °C for 30 h. After cooling, the solution was passed through a silica gel column and eluted with benzene to separate the product **7a** from triphenylphosphine oxide. The product **7a** was further purified by recrystallization from ethyl acetate–light petroleum. Compound **7b** was a liquid product, purified by molecular distillation. When aq. methanol or methanol was used as reaction medium, the reaction temperature and time were as recorded in Table 2.

Dimethyl 4-methyl-6-(trifluoromethyl)isophthalate 7a. This compound (93%) had m.p. 79–81 °C (Found: C, 52.15; H, 4.1. C₁₂H₁₁F₃O₄ requires C, 52.18; H, 4.01%); $\nu_{\max}/\text{cm}^{-1}$ 1745, 1716, 1620, 1585, 1560 and 1510; δ_{H} 2.70 (3 H, s, Me), 3.95 (6 H, s, 2 × OMe), 7.65 (1 H, s, ArH) and 8.36 (1 H, s, ArH); δ_{F} –16.35 (3 F, s, CF₃); δ_{C} 21.7 (s, Me), 52.50 (s, CO₂Me), 52.95 (s, CO₂Me), 123.02 (q, $^1J_{\text{CF}}$ 273.95, CF₃), 128.46 (m, Ar), 130.38 (q, $^3J_{\text{CF}}$ 5.48, Ar), 131.43 (q, $^2J_{\text{CF}}$ 32.65, Ar), 132.69 (s, Ar), 133.02 (s, Ar), 144.39 (s, Ar), 166.08 (s, CO₂Me) and 166.19 (s, CO₂Me); m/z 276 (M⁺, 54%), 245 (100), 217 (9) and 59 (13).

Dimethyl 4-heptafluoropropyl-6-methylisophthalate 7b. This compound (98%) had b.p. 145–165 °C/267 Pa (Found: C, 44.6; H, 2.7. C₁₄H₁₁F₇O₄ requires C, 44.70; H, 2.95%); $\nu_{\max}/\text{cm}^{-1}$ 1740; δ_{H} 2.70 (3 H, s, Me), 3.91 (3 H, s, OMe), 3.94 (3 H, s, OMe), 7.51 (1 H, s, ArH) and 8.19 (1 H, s, ArH); δ_{F} 4.17 (3 F, t, J 10, CF₃), 29.57 (2 F, m, CF₂CF₂CF₃) and 47.29 (2 F, s, CF₂CF₃); m/z 376 (M⁺, 34%), 345 (100), 317 (3) and 59 (5).

Dimethyl 5-(trifluoromethyl)-2,4-dicarboxylatebiphenyl 7c. This compound (91%) had m.p. 59–60 °C (Found: C, 60.3; H, 4.0. C₁₇H₁₃F₃O₄ requires C, 60.36; H, 3.87%); $\nu_{\max}/\text{cm}^{-1}$ 1745 and 1730; δ_{H} 3.72 (3 H, s, OMe), 3.98 (3 H, s, OMe), 7.40 (5 H, m, ArH), 7.78 (1 H, s, ArH) and 8.27 (1 H, s, ArH); δ_{F} –16.54 (3 F, s, CF₃); m/z 338 (M⁺, 62%), 307 (100) and 59 (27).

Dimethyl 5-(heptafluoropropyl)-2,4-dicarboxylatebiphenyl 7d. This compound (90%) had m.p. 80–82 °C (Found: C, 52.05; H, 3.0. C₁₉H₁₃F₇O₄ requires C, 52.07; H, 2.99%); $\nu_{\max}/\text{cm}^{-1}$ 1740 and 1725; δ_{H} 3.69 (3 H, s, OMe), 3.94 (3 H, s, OMe), 7.39 (5 H, m, ArH), 7.65 (1 H, s, ArH) and 8.08 (1 H, s, ArH); δ_{F} 3.75 (3 F, t, CF₃), 29.17 (2 F, m, CF₂CF₂CF₃) and 46.93 (2 F, s, CF₂CF₃); m/z 438 (M⁺, 77.5%), 407 (100) and 59 (15).

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* Oil-bath temperature.

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