Electron-rich heteroaroylphosphonates and their reaction with trimethyl phosphite

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Supplementary Data

Experimental

Additional general details

Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were taken on a Shimadzu FTIR-8300 instrument. Low resolution mass spectra were recorded on a ES Bruker Esquire 300 Plus Daltronics instrument with ES ionisation whilst most high resolution spectra were obtained from the mass spectrometry facility at Kings College, London. TLC was performed with alumina backed silica gel 60 F_{254} eluting with the solvent system used for the column chromatography unless otherwise stated and the plates were visualised under UV light or developed in an iodine tank. Column chromatography used silica gel with particle size 33–50 μm purchased from BDH. All other materials were purchased from Sigma-Aldrich Ltd. and used as received unless indicated otherwise.

Typical procedure for the *in situ* preparation of the carboxylic acid chloride precursors of the aroylphosphonates 1a-h and 2a-c

Thionyl chloride (30 cm^3) was added to the carboxylic acid (40 mmol) under an atmosphere of dry nitrogen and the mixture stirred for 12 h or until NMR spectroscopy indicated that the reaction was complete. The mixture was then warmed under reduced pressure to remove volatile components. Finally, dry toluene (5 cm^3) was added and then removed under reduced pressure to give the acid chloride free from thionyl chloride.

Dimethyl thiophene-2-carbonylphosphonate 1a.

Trimethyl phosphite (1.7 g, 13.7 mmol) was added dropwise over a period of 30 min to a stirred sample of thiophene-2-carbonyl chloride (2 g, 13.7 mmol) kept below 0 °C and under an atmosphere of dry nitrogen. The resulting mixture was stirred for 1 h at room temperature then purified by distillation *in vacuo*. The phosphonate **1a** was obtained as a pale yellow oil in essentially quantitative yield, bp 112 °C at 0.06 mmHg. (Found: C, 38.05; H, 4.0%; M^+, 220. $C_7H_9O_4PS$ requires C, 38.18; H, 4.12%; M^+, 220); δ_P(109.3 MHz, $CDCl_3$) 0.1; δ_H(270 MHz; $CDCl_3$) 3.91 (6 H, d, J_{PH} 10.8, POMe), 7.37 (1 H, m, 4-H), 7.67 (1 H, m, 3-H) and 8.85 (1 H, m, 5-H); δ_C(67.9 MHz; $CDCl_3$) 53.3 (x2)(d, J_{PC} 7, POMe) 128.3 (d, J_{PC} 1, C-4), 136.9 (C-5), 137.2 (d, J_{PC} 2, C-3), 142.1 (d, J_{PC} 81, C-2) and 188.6 (d, J_{PC} 182, C=O).

Dimethyl furan-2-carbonylphosphonate 1b

Trimethyl phosphite (4.27 g, 34 mmol) was added slowly to a cooled (-48 °C), stirred solution of furan-2-carbonyl chloride (4.5 g, 34 mmol) in dry toluene (8 cm^3) under an atmosphere of dry nitrogen. The resulting solution was allowed to warm to room temperature slowly and then stirred for 12 h. Distillation of the product *in vacuo* gave the phosphonate **1b** (4.0 g, 58%) as a pale yellow oil, bp 110 °C at 0.005 mmHg (Found: C, 41.2; H, 4.4; M^+, 204. $C_7H_9O_5P$ requires C, 41.19; H, 4.44%; M^+, 204); δ_P(109.3 MHz, $CDCl_3$) -0.1; δ_H(270 MHz; $CDCl_3$) 3.92 (6 H, d, J_{PH} 11, POMe), 6.64 (1 H, dd, J_{HH} 4 and 2, 4-H), 7.77 (1 H, dd, J_{HH} 2 and 1, J_{PH} 2, 3-H) and 7.88 (1 H, dd, J_{HH} 4 and 1, 5-H); δ_C(67.9 MHz; $CDCl_3$) 54.1 (x2)(d, J_{PC} 7, POMe), 113.0 (C-4), 125.3 (C-3), 149.5 (C-5), 151.7 (d, J_{PC} 89, C-2) and 183.7 (d, J_{PC} 190, C=O).

Dimethyl 3-benzylfuran-2-carbonylphosphonate1c

To a stirred solution of 3-benzylfuran-2-carbonyl chloride (1.4 g, 6.34 mmol) in dry toluene (30 cm^3), cooled to -78 ºC under an atmosphere of dry nitrogen was added trimethyl phosphite (0.79 g, 6.4 mmol). The mixture was then allowed to warm to room temperature and the progress of the reaction monitored by NMR spectroscopy. This showed the formation of the required phosphonate **1c**, together with a small quantity of the aldehyde **20c**, and an equivalent quantity of trimethyl phosphate. A sample of the pure phosphonate **1c** (1.2 g, 63%) was isolated as a pale yellow oil by chromatography on silica using ethyl acetate as the eluent; δ_P(109.3 MHz, $CDCl_3$) 0.9; δ_H(400 MHz, $CDCl_3$) 3.88 (6 H, d, J_{PH} 11, POMe), 4.12 (2 H, s, CH_2), 6.30 (1 H, br s, 4-H), 7.11-7.17 (3 H, m, 2'/6'-H and 4'-H), 7.17-7.24 (2 H, m, 3'/5'-H) and 7.52 (1 H, d, J_{HH} 2, 5-H); δ_C(67.9 MHz; $CDCl_3$) 31.9 (CH_2), 54.4 (x2)(d, J_{PC} 7, POMe), 115.4 (d, J_{PC} 3, C-4), 126.7 (C-4'), 128.7 (x2)(C-3'/5'), 128.9 (x2)(C-2'/6'), 138.4 (d, J_{PC} 9, C-3), 138.6 (C-1'), 148.0 (C-5), 148.1 (d, J_{PC} 60, C-2), and 186.2 (d, J_{PC} 186, C=O); *m/z* (EI) 317.0489 (M^+. $C_{14}H_{15}NaO_5P$ requires 317.0555).

Dimethyl 5-methylfuran-2-carbonylphosphonate 1d

5-Methylfuran-2-carbonyl chloride (5.64 g, 39 mmol) was dissolved in dry toluene (30 cm^3) and cooled to -78 ºC under an atmosphere of dry nitrogen. Trimethyl phosphite (4.83 g, 39 mmol) was added and the solution allowed to warm to room temperature. After 12 h the solvent was removed under reduced pressure and the residue distilled *in vacuo*. The phosphonate **1d**

(5.1 g, 60%) was obtained as a pale yellow oil, bp 147 ºC at 0.005 mmHg; δ_P(109.3 MHz, $CDCl_3$) 0.6; δ_H(270 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 3.91 (6 H, d, J_{PH} 10.4, POMe), 6.23 (1 H, d, J_{HH} 3.5, 4-H) and 7.86 (1 H, d, J_{HH} 3.5, 3-H); δ_C(67.9 MHz; $CDCl_3$) 14.1 (Me), 54.1 (x2)(d, J_{PC} 7, POMe), 110.3 (s, C-4), 128.2 (C-3), 151.1 (d, J_{PC} 91, C-2), 161.7 (C-5) and 182.3 (d, J_{PC} 189, C=O); *m/z* (ESI) 241.0236 ($M+Na^+$. $C_8H_{11}O_5PNa$ requires 241.0242).

Dimethyl 5-phenylfuran-2-carbonylphosphonate 1e

5-Phenylfuran-2-carbonyl chloride (0.34 g, 1.63 mmol) was dissolved in dry toluene (30 cm^3) and cooled to -78 ºC under an atmosphere of dry nitrogen. Trimethyl phosphite (0.20 g, 1.63 mmol) was then added and the solution was allowed to warm to room temperature over a period of 12 h. Removal of the solvent under reduced pressure (60 ºC at 0.005 mmHg) gave a residue which was purified by distillation *in vacuo*. The phosphonate **1e** (0.09 g, 20%) was isolated as a pale yellow oil, bp 130 ºC at 0.005 mmHg; δ_P(109.3 MHz, $CDCl_3$) 0.6; δ_H(400 MHz, $CDCl_3$) 3.91 (6 H, d, J_{PH} 10.8, POMe), 6.88 (1 H, d, J_{HH} 3.8, 4-H), 7.38-7.48 (3 H, m, 3'/5'-H and 4'-H) 7.84 (2 H, dd, J_{HH} 7.5 and 1.5, 2'/6'-H) and 8.00 (1 H, d, J_{HH} 3.8, 3-H); δ_C(67.9 MHz; $CDCl_3$) 54.5 (x2)(d, J_{PC} 7, POMe), 108.5 (C-4), 125.9 (C-2'/6'), 128.7 (C-4'), 129.1 (C-1'), 129.2 (C-3'/5'), 130.4 (C-3), 151.5(d, J_{PC} 92, C-2), 161.0 (C-5) and 183.0 (d, J_{PC} 189, C=O); *m/z* (ESI) 303.0393 ($M+Na^+$. $C_{13}H_{13}O_5PNa$ requires 303.0398.

Dimethyl 1-methylpyrrole-2-carbonylphosphonate 1f

To a suspension of 1-methylpyrrole-2-carboxylic acid (1.0 g, 8 mmol) in benzene (30 cm^3) under an atmosphere of dry nitrogen was added oxalyl chloride (2.03 g, 16 mmol) together with one drop of dimethylformamide. The mixture was then stirred at room temperature until all of the solid had dissolved (*ca.* 2 h). Volatile components were then removed under reduced pressure and the residue taken up into dry acetonitrile (30 cm^3) under an atmosphere of dry nitrogen. After cooling to -40 ºC trimethyl phosphite (0.99 g, 8 mmol) was added and the resulting mixture then allowed to warm to room temperature. After stirring for 48 h, volatile components were removed under reduced pressure and the residue distilled *in vacuo*. The phosphonate ester **1f** (1.04 g, 60%) was isolated as a pale yellow oil, bp 137 ºC at 0.005 mmHg; δ_P(109.3 MHz, $CDCl_3$) 2.5; δ_H(400 MHz, $CDCl_3$) 3.89 (6 H, d, J_{PH} 10.7, POMe), 3.94 (3 H, s, N-Me), 6.24 (1 H, dd, *J* 2.4 and 4.3, 4-H), 6.99 (1 H, m, 3-H) and 7.71 (1 H, dd, *J* 4.3 and 1.4, 5-H); δ_C(67.9 MHz; $CDCl_3$) 37.7 (NMe), 54.0 (x2)(d, J_{PC} 7, POMe), 110.1 (C-4), 126.5 (d, J_{PC} 2, C-3), 130.9 (d, J_{PC} 86, C-2), 134.5 (C-5) and 184.2 (d, J_{PC} 183, C=O); *m/z* (ESI) 240.0393 ($M+Na^+$. $C_8H_{12}NO_4PNa$ requires 240.0402).

Dimethyl 1-phenylpyrrole-2-carbonylphosphonate 1g

Trimethyl phosphite (1.025 g, 8.26 mmol) was added dropwise to a stirred solution of 1-phenylpyrrole-2-carbonyl chloride (1.7 g, 8.26 mmol) in dry toluene (10 cm^3) at room temperature under an atmosphere of dry nitrogen. The resulting solution was stirred for 48 h and then volatile components were removed *in vacuo* to give the desired phosphonate in a good state of purity. A pure sample of this material was obtained by chromatography on silica gel using hexane-ethyl acetate mixtures as the eluent; δ_P(109.3 MHz, $CDCl_3$) 2.1; δ_H(400 MHz, $CDCl_3$) 3.85 (6 H, d, J_{PH} 11, POMe), 6.41 (1 H, dd, J_{HH} 4.3 and 2.5, 4-H), 7.09-7.10 (1 H, m, 3-H), 7.23-7.27 (2 H, m, 2'/6'-H) , 7.39-7.43 (3 H, m, 3'/5'-H and 4'-H) and 7.89 (1 H, dd, *J* 4.3 and 1.7, 5-H); δ_C(100.63 MHz; $CDCl_3$) 54.1 (x2)(d, J_{PC} 7, POMe), 111.3 (C-4), 126.1 (x2)(C-2'/6'), 127.4 (d, J_{PC} 3, C-3), 128.3 (C-4') 128.9 (x2)(C-3'/5'), 131.0 (d, J_{PC} 88, C-2), 134.4 (C-5), 139.9 (C-1') and 183.6 (d, J_{PC} 184, C=O); *m/z* (ESI) 302.0552 ($M+Na^+$. $C_{13}H_{14}NO_4PNa$ requires 302.0558).

Dimethyl pyrrole-2-carbonylphosphonate 1h.

Due to problems associated with the preparation and subsequent reaction of pyrrole-2-carbonyl chloride,[1] it has so far proved difficult to obtain the phosphonate ester **1h** in sufficiently quantities and in a sufficiently pure state to carry out satisfactory further studies although its presence was clearly visible in the NMR spectra of the reaction product; δ_P(109.3 MHz, $CDCl_3$) 2.0; δ_H(270 MHz, $CDCl_3$) 3.90 (6 H, d, J_{PH} 11, POMe), 6.35 (1 H, m, 4-H), 7.24 (1 H, br s, 3-H), 7.55 (1 H, br s, 5-H), 11.20 (1 H, s, NH); δ_C(67.9 MHz; $CDCl_3$) 53.9 (x2)(d, J_{PC} 7, POMe), 111.9 (C-4), 122.5 (br s, C-5), 129.0 (C-3), 132.4 (d, J_{PC} 80, C-2), 182.9 (d, J_{PC} 184, C=O).

Dimethyl thiophene-3-carbonylphosphonate 2a

Trimethyl phosphite (3.4 g, 27.3 mmol) was added dropwise to a stirred sample of thiophene-3-carbonyl chloride (4 g, 27.3 mmol) at 0°C under an atmosphere of dry nitrogen. The resulting mixture was stirred for 3 h and then distilled under reduced pressure. The phosphonate **2a** was isolated in essentially quantitative yield as a pale yellow oil, bp 126 °C at 0.08 mmHg; δ_P(109.3 MHz, $CDCl_3$) 0.75; δ_H(270 MHz; $CDCl_3$) 3.85 (6 H, d, J_{PH} 11, POMe), 7.31 (1 H, m, 5-H), 7.63 (1 H, dm, J_{PH} 5, 4-H) and 8.81 (1 H, m, 2-H); δ_C (67.9 MHz; $CDCl_3$) 53.8 (x2)(d, J_{PC} 7, POMe), 126.6 (d, J_{PC} 1, C-5), 126.9 (d, J_{PC} 7, C-4), 138.4 (C-2), 140.5 (d, J_{PC} 67, C-3) and 191.0 (d, J_{PC} 178, C=O).

This compound was converted to its 2,4-dinitrophenylhydrazone derivative and recrystallised from ethanol to give a yellow solid, mp 113 °C (Found: C, 39.0; H, 3.2; N, 13.75. $C_{13}H_{13}N_4O_7PS$ requires C, 39.01; H, 3.27; N, 14.00%).

Dimethyl furan-3-carbonylphosphonate 2b

Trimethyl phosphite (11.2 g, 90 mmol) was added dropwise to a stirred sample of furan-3-carbonyl chloride (11.7 g, 90 mmol) at room temperature. The resulting solution was stirred for 12 h and then distilled under reduced pressure. The phosphonate **2b** (12.4

g, 68%) was obtained as a pale yellow oil, bp 103 °C at 0.04 mmHg (Found: C, 41.15; H, 4.5. $C_7H_9O_5P$ requires C, 41.19; H, 4.44%); δ_P(109.3 MHz, $CDCl_3$) -0.4; δ_H(270 MHz; $CDCl_3$) 3.92 (6 H, d, J_{PH} 10.8, POMe), 6.86 (1 H, m, 4-H), 7.57 (1 H, m, 5-H) and 8.74 (1 H, br s, 2-H); δ_C(67.9 MHz; $CDCl_3$) 53.9 (x2)(d, J_{PC} 6, POMe), 107.2 (d, J_{PC} 8, C-4), 127.2 (d, J_{PC} 71, C-3), 144.4 (C-5), 153.0 (d, J_{PC} 2, C-2) and 192.0 (d, J_{PC} 183, C=O); *m/z* (EI) 204.0182 (M^+ $C_7H_9O_5P$ requires 204.0188).

Dimethyl 2-(prop-2-ynyloxymethyl)furan-3-carbonyl-phosphonate 2c

2-(Prop-2-ynyloxymethyl)furan-3-carbonyl chloride (2.18 g, 11 mmol) was dissolved in dry toluene (30 cm^3) and trimethyl phosphite (1.36 g, 11 mmol) was added. The mixture was then stirred under an atmosphere of dry nitrogen for 12 h at room temperature. Volatile components were then removed under reduced pressure and the residue distilled *in vacuo*. The phosphonate ester **2c** was obtained as a pale yellow oil in essentially quantitative yield, bp 130 ºC at 0.005 mmHg; δ_P(109.3 MHz, $CDCl_3$) 0.2; δ_H(400 MHz, $CDCl_3$) 2.49 (1 H, t, J_{HH} 2.4, CCH), 3.90 (6 H, d, J_{PH} 10.8, POMe), 4.22 (2 H, d, J_{PH} 2.3, CH_2), 4.89 (2 H, s, CH_2), 6.71 (1 H, d, J_{HH} 1.8, 4-H) and 7.40 (1 H, d, J_{HH} 1.8, 5-H); δ_C(67.9 MHz; $CDCl_3$) 54.4 (x2)(d, J_{PC} 7, POMe), 58.5 (CH_2), 63.1 (CH_2Ar), 75.5 (CH), 79.4 (C), 111.4 (d, J_{PC} 2,C-4), 122.7 (d, J_{PC} 69, C-3), 142.9 (C-5), 158.4 (d, J_{PC} 15.6, C-2) and 193.9 (d, J_{PC} 185, C=O); *m/z* (ESI) 290.0792, ($M+NH_4^+$.[2] $C_{11}H_{17}NO_6P$ requires 290.0788.

Reaction of dimethyl furan-2-carbonylphosphonate 1b with triethyl phosphite

Triethyl phosphite (3.2 g, 20 mmol) was slowly added to a stirred sample of dimethyl furan-2-carbonylphosphonate **1b** (2.0 g, 10 mmol) at -40 °C under an atmosphere of dry nitrogen. The resulting solution was then allowed to warm slowly to room temperature. After a period of *ca.*12 h, volatile components were removed by warming under reduced pressure (50 °C at 0.005 mmHg)[3] to give *dimethyl 5-[(Z)-4-(dimethoxy-phosphoryl)-but-1-en-3-ynyl]-4-furan-2-yl-2,2,2-triethoxy-2λ^5-[1,3,2]dioxa-phospholan-4-yl-phosphonate* **19b'** in a good state of purity; δ_P(109.3 MHz, $CDCl_3$) 19.0 [d, J_{PP} 41, $P(O)(OMe)_2$], -3.4 [s, $CCP(O)(OMe)_2$] and -51.4 [d, J_{PP} 41, $P(OEt)_3$]; δ_C(67.9 MHz, $CDCl_3$) 16.4 (x3)(d, J_{PC} 9, Me), 53.5 (x2)(d, J_{PC} 5, POMe), 54.1 (d, J_{PC} 7, POMe), 54.4 (d, J_{PC} 7, POMe), 63.5 (x3)(d, J_{PC} 9, $POCH_2$), 70.2 (dd, J_{PC} 6 and 2, C-5), 75.8 (dd, J_{PC} 179 and 2, C-4), 82.4 (d, J_{PC} 298, C-4'), 95.2 (d, J_{PC} 53, C-3'), 110.2 (d, J_{PC} 4, C-3 furan), 110.6 (C-4 furan), 111.3 (d, J_{PC} 7, C-2'), 143.1 (s, C-5 furan), 144.2 (d, J_{PC} 14, C-1'), 148.6 (d, J_{PC} 7, C-2 furan). Efforts to purify the triphosphorus compound **19b'** by chromatography were unsuccessful leading to the formation of decomposition products.

Supplementary NMR Data

Tetramethyl thiophen-2-ylmethane-1,1-bisphosphonate **6a**; δ_P(109.3 MHz, $CDCl_3$) 19.7; δ_H(400 MHz, $CDCl_3$) 3.72 (6 H, d, J_{PC} 11.0, POMe), 3.82 (6 H, d, J_{PC} 11.0, POMe), 4.12 (1 H, t, J_{PC} 25.0, α-CH), 7.03 (1 H, dd, J_{HH} 3.6 and 5.1, 4-H) and 7.26–7.30 (2 H, m, 3-H and 5-H); δ_C(100.63 MHz, $CDCl_3$) 39.5 (t, J_{PC} 136, α-C), 53.7 (t, J_{PC} 6, POMe), 54.3 (t, J_{PC} 6, POMe), 126.0 (t, J_{PC} 3, C-4), 127.2 (t, J_{PC} 3, C-5), 129.2 (t, J_{PC} 7, C-3) and 129.6 (t, J_{PC} 10, C-2).

Tetramethyl 3-benzylfuran-2-ylmethane-1,1-bisphosphonate **6c**; δ_P(109.3 MHz, $CDCl_3$) 19.5; δ_H(400 MHz, $CDCl_3$) 3.73 (6 H, d, J_{PH} 11.3, POMe), 3.77 (2 H, br s, CH_2), 3.76 (6 H, d, J_{PH} 11.3, POMe), 4.03 (1 H, t, J_{PH} 25.7, α-H), 6.20 (1 H, br 's', 4-H), 7.17-7.22 (3 H, m, 2'/6'-H and 4'-H), 7.28 (2 H, tm, *J* 7.6, 3'/5'-H) and 7.40 (1 H, q, *J* 2, 5-H); δ_C(100.63 MHz, $CDCl_3$) 31.1 (CH_2), 37.5 (t, J_{PC} 136, α-CH), 53.8 (x2)(t, 'J'$_{PC}$ 3, POMe), 54.1 (x2)(t, 'J'$_{PC}$ 3, POMe), 113.0 (t, J_{PC} 3, C-4), 123.0, (t, J_{PC} 8.5, C-3), 126.5 (C-4'), 128.4 (x2)(C-3'/5'), 128.6 (x2)(C-2'/6'), 139.0 (t, J_{PC} 12, C-2), 139.7 (t, J_{PC} 2, C-1') and 142.6 (t, J_{PC} 3, C-5).

Tetramethyl 5-methylfuran-2-ylmethane-1,1-bisphosphonate **6d**; δ_P(109.3 MHz, $CDCl_3$) 19.0; δ_H(400 MHz, $CDCl_3$) 2.29 (3 H, s, Me), 3.74 (6 H, d, J_{PH} 10.9, POMe), 3.81 (6 H, d, J_{PH} 10.9, POMe), 4.04 (1 H, t, J_{PH} 25.2, α-CH), 5.98 (1 H, d, J_{PH} 3, 4-H) and 6.40 (1 H, dt, J_{HH} 3, J_{PH} 3, 3-H); δ_C(100.63 MHz, $CDCl_3$) 12.8 (Me), 37.7 (t, J_{PC} 136, α-CH), 53.1 (x2)(m, POMe), 53.1 (x2)(m, POMe), 106.6 (t, J_{PC} 2, C-4), 110.8, (t, J_{PC} 6, C-3), 139.8 (t, J_{PC} 8, C-2) and 151.8 (t, J_{PC} 3, C-5).

Tetramethyl 5-phenylfuran-2-ylmethane-1,1-bisphosphonate **6e**; δ_P(109.3 MHz, $CDCl_3$) 18.8; δ_H(400 MHz, $CDCl_3$) 3.77 (6 H, d, J_{PC} 11, POMe), 3.83 (6 H, d, J_{PC} 11, POMe), 4.16 (1 H, t, J_{PC} 25.5, α-CH), 6.61 (1 H, dt, J_{HH} 3.4, J_{PH} 3, 3-H), 6.65 (1 H, d, J_{HH} 3.4, 4-H), 7.26 (1 H, m, 4'-H), 7.40 (2 H, t, J_{HH} 7.5, 3'/5'-H), 7.65 (2 H, d, J_{HH} 7.5, 2'/6'-H); δ_C(100.63 MHz, $CDCl_3$) 38.9 (t, J_{PC} 136, α-CH), 54.0 (m, POMe), 54.5 (m, POMe), 106.6 (t, J_{PC} 3, C-4), 112.8 (t, J_{PC} 6, C-3), 123.8 (C-2'/6'), 127.7 (C-4'), 128.9 (C-3'/5'), 130.5 (C-1'), 142.2 (t, J_{PC} 8, C-2), 154.3 (t, J_{PC} 3, C-5).

Tetramethyl 1-methylpyrrole-2-ylmethane-1,1-bisphosphonate **6f**; δ_P(109.3 MHz, $CDCl_3$) 20.0; δ_H(270 MHz, $CDCl_3$) 3.59 (3 H, br s, NCH_3), 3.67 (6 H, d, J_{PH} 11, POMe), 3.77 (6 H, d, J_{PH} 11, POMe), 3.72 (1 H, br t, J_{PH} 25, α-CH), 6.09 (1 H, dd, *J* 3.8 and 2.8, 4-H), 6.48 (1 H, br s, 5-H) and 6.62 (1 H, m, 3-H); δ_C(100.63 MHz, $CDCl_3$) 33.9 (NCH_3), 36.1 (t, J_{PC} 133, α-C), 53.8 (x2)(t, 'J'$_{PC}$ 3.5, POMe), 54.4 (x2)(t, 'J'$_{PC}$ 3.5, POMe), 107.5 (t, J_{PC} 2, C-4), 111.4 (t, J_{PC} 4, C-3), 118.2 (t, J_{PC} 6, C-2) and 124.3 (t, J_{PC} 3, C-5).

Tetramethyl 1-phenylpyrrole-2-ylmethane-1,1-bisphosphonate **6g**; δ_P(109.3 MHz, $CDCl_3$) 20.1; δ_H(400 MHz, $CDCl_3$) 3.68 (6 H, d, J_{PC} 11.0, POMe), 3.71 (6 H, d, J_{PC} 11.0, POMe), 3.87 (1 H, t, J_{PC} 25.7, α-CH), 6.28 (1 H, t, 3.2, X-H), 6.65 (1 H, m, 3-H), 6.83 (1 H, m, 4-H), 7.31- 7.35 (2 H, m, 2'/6'-H), 7.38-7.43(1 H, m, 4'-H), 7.44-7.50 (2 H, m, 3'/5'-H); δ_C(100.63 MHz, $CDCl_3$) 35.9 (t,

J_{PC} 139, α-C), 53.7 (m, POMe), 54.4 (m, POMe), 108.91 (t, J_{PC} 2, C-4), 112.3 (t, J_{PC} 4, C-3), 119.2 (t, J_{PC} 6, C-2), 123.6 (t, J_{PC} 2, C-5), 126.9 (x2)(C-2'/6'), 128.2 (C-4'), 129.6 (x2)(C-3'/5') and 139.0 (C-1').

Dimethyl thiophen-2-ylmethylphosphonate **7a**; δ_P(109.3 MHz, $CDCl_3$) 27.3; δ_H(400 MHz, $CDCl_3$) 3.37 (2 H, d, J_{PH} 20.8, CH_2), 3.70 (6 H, d, J_{PH} 10.8, POMe), 6.94–7.12 (2 H, m, 4-H and 5-H) and 7.18 (1 H, ddd, J_{HH} 1.8 and 1.2, J_{PH} 5.0, 3-H); δ_C(100.63 MHz, $CDCl_3$) 27.1 (d, J_{PC} 144, CH_2), 53.1 (x2)(d, J_{PC} 7, POMe), 124.9 (d, J_{PC} 4, C-4), 127.2 (d, J_{PC} 4, C-5), 127.5 (d, J_{PC} 9, C-3) and 132.1 (d, J_{PC} 10, C-2).

Dimethyl 5-methylfuran-2-ylmethylphosphonate **7d**; δ_P(109.3 MHz, $CDCl_3$) 26.7; δ_H(400 MHz, $CDCl_3$) 2.26 (3 H, d, J_{PH} 2, Me), 3.21 (2 H, d, J_{PH} 20.8, CH_2), 3.69 (6 H, d, 10.9, POMe), 5.91 (1 H, d, J_{HH} 2.5, 3-H) and 6.11 (1 H, d, J_{HH} 3.5, 4-H); δ_C(100.63 MHz, $CDCl_3$) 13.4 (Me), 25.7 (d, J_{PC} 144, CH_2), 52.8 (x2)(d, J_{PC} 7, POMe), 106.7 (d, J_{PC} 2, C-4), 109.0 (d, J_{PC} 7, C-3), 143.0 (d, J_{PC} 10, C-2) and 151.6 (d, J_{PC} 3, C-5).

Dimethyl 5-phenylfuran-2-ylmethylphosphonate **7e**; δ_P(109.3 MHz, $CDCl_3$) 26.1; δ_H(400 MHz, $CDCl_3$) 3.33 (2 H, d, J_{PH} 21, CH_2), 3.76 (6 H, d, J_{PH} 10.9, POMe), 6.34 (1 H, t, J_{HH} 3.5, J_{PH} 3.5, 3-H) 6.60 (1 H, d, J_{HH} 3.5, 4-H), 7.24 (1 H, t, J_{HH} 7.4, 4'-H), 7.37 (2 H, t, J_{HH} 7.5, 3'/5'-H) and 7.64 (2 H, d, J_{HH} 7.5, 2'/6'-H); δ_C(100.63 MHz, $CDCl_3$) 26.1 (d, J_{PC} 144, CH_2), 53.2 (d, J_{PC} 7, POMe), 106.4 (d, J_{PC} 3.5, C-3), 110.7 (d, J_{PC} 8, C-4), 123.7 (C-2'/6'), 127.4 (C-4'), 128.8 (C-3'/5'), 129.1 (d, J_{PC} 3, C-1'), 145.0 (d, J_{PC} 10, C-2) and 153.7 (d, J_{PC} 3, C-5).

Dimethyl 1-methylpyrrol-2-ylmethylphosphonate **7f**; δ_P(109.3 MHz, $CDCl_3$) 27.4; δ_H(400 MHz, $CDCl_3$) 3.12 (2 H, d, J_{PH} 20, CH_2), 3.63 (3 H, s, NCH_3), 3.66 (6 H, d, J_{PH} 10.7, POMe), 6.0-6.05 (2 H, m, 3-H and 4-H) and 6.58 (1 H, dt, J_{PH} 2.2, J_{HH} 2.3, 5-H); δ_C(100.63 MHz, $CDCl_3$) 24.1 (d, J_{PC} 144, CH_2), 34.1 (s, NCH_3), 53.1 (x2)(d, J_{PC} 7, POMe), 107.3 (d, J_{PC} 3, C-4), 109.3 (d, J_{PC} 7, C-3), 121.5 (d, J_{PC} 9, C-2) and 122.8 (d, J_{PC} 3, C-5).

Dimethyl 5-(dimethoxyphosphorylmethyl)thiophen-2-yl-phosphonate **10**; δ_P(109.3 MHz, $CDCl_3$) 15.2 [d, J_{PP} 3, $P(O)(OMe)_2$] and 26.3 [d, J_{PP} 3, $CH_2P(O)(OMe)_2$]; δ_H(400 MHz, $CDCl_3$) 3.34 (2 H, d, J_{PC} 21.2, CH_2), 3.67 (6 H, d, J_{PC} 10.8, POMe), 3.69 (6 H, d, J_{PC} 11.4, POMe), 7.10 (1 H, dd, J_{HH} 3.6, J_{PC} 3.5, 4-H) and 7.44 (1 H, ddd, J_{HH} 3.6, J_{PC} 8.5 and 0.5, 3-H); δ_C(100.63 MHz, $CDCl_3$) 26.3 (d, J_{PC} 143, CH_2), 52.0 (x2)(d, J_{PC} 6, POMe), 52.1 (x2)(d, J_{PC} 7, POMe), 124.7 (dd, J_{PC} 211 and 4, C-2), 127.6 (dd, J_{PC} 17 and 8, C-3), 136.2 (dd, J_{PC} 11 and 4, C-4) and 140.7 (dd, J_{PC} 10 and 8, C-5).

T*etramethyl 1-(thiophen-3-yl)ethane-1,1-bisphosphonate* **15a**; δ_P(109.3 MHz, $CDCl_3$) 24.7; δ_H(270 MHz, $CDCl_3$) 1.86 (3 H, t, J_{PH} 16, Me), 3.56 (6 H, d, J_{PH} 11, POMe), 3.68 (6 H, d, J_{PH} 11, POMe), 7.25 (1 H, dd, *J* 5 and 3, 5-H) and 7.35-7.43 (2 H, m, 2-H and 4-H); δ_C(67.9 MHz, $CDCl_3$) 18.0 (t, J_{PC} 6, Me), 44.3 (t, J_{PC} 140, α-C), 53.9 (x2)(m, POMe), 54.4 (x2)(m, POMe), 124.2 (t, J_{PC} 8, C-2), 125.1 (t, J_{PC} 1, C-5), 129.0 (t, J_{PC} 4, C-4) and 134.0 (t, J_{PC} 8, C-3).

T*etramethyl 1-(furan-3-yl)ethane-1,1-bisphosphonate* **15b**; δ_P(109.3 MHz, $CDCl_3$) 24.6; δ_H(270 MHz, $CDCl_3$) 1.73 (3 H, t, J_{PH} 16, Me), 3.64 (6 H, d, J_{PH} 10.3, POMe), 3.71 (6 H, d, J_{PH} 10.3, POMe), 6.62 (1 H, m, 4-H), 7.35 (1 H, m, 5-H) and 7.45 (1 H, m, 2-H); δ_C(69.7 MHz, $CDCl_3$) 16.2 (t, J_{PC} 6, Me), 39.4 (t, J_{PC} 136, α-C), 52.9 (x2)(m, POMe), 53.3 (x2)(m, POMe), 110.5 (t, J_{PC} 4, C-4), 118.4 (t, J_{PC} 8, C-3), 140.5 (t, J_{PC} 9, C-2) and 141.7 (C-5).

Tetramethyl thiophen-3-ylmethane-1,1-bisphosphonate **16a**; δ_P(109.3 MHz, $CDCl_3$) 20.8; δ_H(400 MHz, $CDCl_3$) 3.67 (6 H, d, J_{PH} 11.0, POMe), 3.78 (6 H, d, J_{PH} 11.0, POMe), 4.02 (1 H, t, J_{PH} 24.7, α-CH), 7.18 (1 H, dm, J_{HH} 5, 4-H), 7.33 (1 H, dd, *J* 5 and 3, 5-H) and 7.40–7.43 (1 H, m, 2-H); δ_C(100.63 MHz, $CDCl_3$) 40.1 (t, J_{PC} 134, α-CH), 53.5 (m, POMe), 54.0 (m, POMe), 125.4 (t, J_{PC} 8, C-2), 126.1 (t, J_{PC} 1, C-5), 128.1 (t, J_{PC} 8, C-3) and 129.4 (t, J_{PC} 4, C-4).

Tetramethyl furan-3-ylmethane-1,1-bisphosphonate **16b**; δ_P(109.3 MHz, $CDCl_3$) 21.2; δ_H(400 MHz, $CDCl_3$) 3.73 (6 H, d, J_{PH} 11.0, POMe), 3.77 (1 H, t, J_{PH} ~24,[4] α-H), 3.79 (6 H, d, J_{PH} 11.0, POMe), 6.54 (1 H, br s, 4-H), 7.42 (1 H, br s, 5-H) and 7.55 (1 H, br t, J_{PH} 3, 2-H); δ_C(100.63 MHz, $CDCl_3$) 34.9 (t, J_{PC} 136, α-CH), 53.5 (x2)(m, POMe), 54.0 (x2)(m, POMe), 111.8 (t, J_{PC} 4, C-4), 112.9 (t, J_{PC} 9, C-3), 141.9 (t, J_{PC} 9, C-2) and 143.0 (C-5).

Tetramethyl 2-(prop-2-ynyloxymethyl)furan-3-ylmethane-1,1-bisphosphonate **16c** was isolated as a pale yellow oil; δ_P(109.3 MHz, $CDCl_3$) 21.2; δ_H(400 MHz, $CDCl_3$) 2.53 (1 H, t, J_{HH} 2.4, CCH), 3.78 (6 H, d, J_{PH} 11.0, POMe), 3.82 (6 H, d, J_{PH} 11.0, POMe), 3.97 (1 H, t, J_{PH} 24.6, α-H), 4.18 (2 H, d, J_{HH} 2.4, CH_2), 4.61 (2 H, t, J_{HH} 1.3, CH_2), 6.72 (1 H, d, J_{HH} 1.8, 4-H) and 7.42 (1 H, d, J_{HH} 1.8, 5-H); δ_C(100.63 MHz, $CDCl_3$) 34.9 (t, J_{PC} 136, α-CH), 53.7 (x2)(m, POMe), 53.8 (x2)(m, POMe), 57.1 (CH_2), 61.2 (CH_2), 75.4 (CH), 79.4 (C), 112.6 (C-4), 113.2 (t, J_{PC} 9, C-3), 142.7 (C-5) and 148.9 (t, J_{PC} 11, C-2).

Dimethyl thiophene-3-ylmethylphosphonate **17a**; δ_P(109.3 MHz, $CDCl_3$) 28.8; δ_H(400 MHz, $CDCl_3$) 3.22 (2 H, d, J_{PH} 20.9, CH_2), 3.68 (6 H, d, J_{PH} 10.7, POMe), 7.10 (1 H, dt, *J* 5 and 1.2, 4-H), 7.16-7.14 (1 H, m, 2-H) and 7.24 (1 H, dt, *J* 5 and 3.2, 5-H);

δ_C(100.63 MHz, $CDCl_3$) 27.3 (d, J_{PC} 141, CH_2), 52.8 (x2)(d, J_{PC} 7, POMe), 123.2 (d, J_{PC} 10, C-2), 125.8 (d, J_{PC} 2, C-5), 128.8 (d, J_{PC} 7, C-4) and 130.4 (d, J_{PC} 9, C-3).

Dimethyl 1-(dimethoxyphosphoryloxy)-1-(thiophen-3-yl)methyl-phosphonate **18a**; δ_P(109.3 MHz, $CDCl_3$) 2.0 (d, J_{PP} 32), 19.2 (d, J_{PP} 32); δ_H(400 MHz, $CDCl_3$) 3.55 (3 H, d, J_{PH} 11.2, POMe), 3.72 (3 H, d, J_{PH} 10.6, POMe), 3.77 (3 H, d, J_{PH} 11.2, POMe), 3.80 (3 H, d, J_{PH} 10.6, POMe), 5.72 (1 H, dd, J_{PH} 10 and 13, α-CH), 7.30 (1 H, dm, J 5, 4-H), 7.36 (1 H, dd, J 5 and 3, 5-H) and 7.52-7.55 (1 H, m, 2-H); δ_C(100.63 MHz, $CDCl_3$) 53.9 (d, J_{PC} 6, POMe), 54.0 (d, J_{PC} 6, POMe), 54.2 (d, J_{PC} 6, POMe), 54.5 (d, J_{PC} 6, POMe), 70.4 (dd, J_{PC} 176 and 7, α-C), 125.6 (d, J_{PC} 10, C-3), 126.6 (C-5), 127.0 (d, J_{PC} 3, C-4) and 133.7 (C-2).

Dimethyl 1-(dimethoxyphosphoryloxy)-1-(furan-3-yl)methyl-phosphonate **18b**; δ_P(109.3 MHz, $CDCl_3$) 1.7, (d, J_{PP} 33) and 19.3 (d, J_{PP} 33); δ_H(400 MHz, $CDCl_3$) 3.60 (3 H, d, 11.4, POMe), 3.77 (3 H, d, J_{PH} 10.6, POMe), 3.79 (3 H, d, J_{PH} 11.4, POMe), 3.83 (3 H, d, J_{PH} 10.6, POMe), 5.62 (1 H, dd, J_{PH} 13 and 10, α-CH), 6.64 (1 H, m, 4-H), 7.46 (1 H, t, J_{HH} 1.7, 5-H) and 7.67 (1 H, m, 2-H); δ_C(100.63 MHz, $CDCl_3$) 53.8 (d, J_{PC} 7, POMe), 53.9 (d, J_{PC} 7, POMe), 54.1 (d, J_{PC} 6, POMe), 54.3 (d, J_{PC} 6, POMe), 67.0 (dd, J_{PC} 180 and 6, α-C), 109.8 (d, J_{PC} 4, C-4), 118.3 (C-3), 142.3 (d, J_{PC} 11, C-2) and 142.6 (C-5).

Dimethyl 5-[(Z)-4-(dimethoxy-phosphoryl)-but-1-en-3-ynyl]-4-furan-2-yl-2,2,2-trimethoxy-2λ^5-[1,3,2]dioxaphospholan-4-yl-phosphonate **19b**; δ_P(109.3 MHz, $CDCl_3$) 19.0 [d, J_{PP} 41, $P(O)(OMe)_2$], -3.4 [s, $CCP(O)(OMe)_2$] and -48.3 [d, J_{PP} 41, $P(OMe)_3$]; δ_H(270 MHz, $CDCl_3$) 3.66 (6 H, d, J_{HH} 12.9, POMe), 3.77 (9 H, br d, J_{HH} 11, POMe), 3.84 (6 H, d, J_{HH} 11.7, POMe), 5.20 (1 H, dd, J_{HH} 9, J_{PH} 9.3, 5-H), 5.73 (1 H, dd, J_{HH} 11 and 9, 1'-H), 5.80 (1 H, dd, J_{HH} 11, J_{PH} 3.5, 2'-H), 6.41 (1 H, m, furan 4-H), 6.55 (1 H, m, furan 3-H), 7.47 (1 H, m, furan 5-H); δ_C(100.65 MHz, $CDCl_3$) 53.14 (m, POMe), 53.16 (m, POMe), 53.8 (d, J_{PC} 7, POMe), 54.1 (d, J_{PC} 7, POMe), 55.1 (x3)(d, J_{PC} 8, POMe), 70.1 (dd, J_{PC} 5 and 2, C-5), 75.6 (dd, J_{PC} 176 and 2, C-4), 82.4 (d, J_{PC} 298, C-4'), 94.9 (d, J_{PC} 52, C-3'), 110.0 (d, J_{PC} 4, C-3 furan), 110.3 (C-4 furan), 111.1 (d, J_{PC} 5, C-2'), 142.9 (d, J_{PC} 1, C-5 furan), 143.4 (d, J_{PC} 13, C-1'), 148.0 (d, J_{PC} 6, C-2 furan).

Dimethyl 5-[(Z)-4-(dimethoxy-phosphoryl)-but-1-en-3-ynyl]-4-furan-2-yl-2,2,2-triethoxy-2λ^5-[1,3,2]dioxaphospholan-4-yl-phosphonate **19b'**; δ_P(109.3 MHz, $CDCl_3$) 19.0 [d, J_{PP} 41, $P(O)(OMe)_2$], -3.4 [s, $CCP(O)(OMe)_2$] and -51.4 [d, J_{PP} 41, $P(OEt)_3$]; δ_C(67.9 MHz, $CDCl_3$) 16.4 (x3)(d, J_{PC} 9, Me), 53.5 (x2)(d, J_{PC} 5, POMe), 54.1 (d, J_{PC} 7, POMe), 54.4 (d, J_{PC} 7, POMe), 63.5 (x3)(d, J_{PC} 9, $POCH_2$), 70.2 (dd, J_{PC} 6 and 2, C-5), 75.8 (dd, J_{PC} 179 and 2, C-4), 82.4 (d, J_{PC} 298, C-4'), 95.2 (d, J_{PC} 53, C-3'), 110.2 (d, J_{PC} 4, C-3 furan), 110.6 (C-4 furan), 111.3 (d, J_{PC} 7, C-2'), 143.1 (s, C-5 furan), 144.2 (d, J_{PC} 14, C-1'), 148.6 (d, J_{PC} 7, C-2 furan).

The 2,4-dinitrophenylhydrazone derivative of dimethyl (Z)-5-oxo-pent-3-en-1-ynylphosphonate **20b**
Dimethyl (Z)-5-[(2,4-dinitrophenyl)hydrazono]pent-3-en-1-ynylphosphonate; δ_P(109.3 MHz, $CDCl_3$) -3.1; δ_H(400 MHz, $CDCl_3$) 2.11 (1 H, s, NH), 3.86 (6 H, d, J_{PH} 12.2, POMe), 6.04 (1 H, dd, J_{HH} 11.1 and 1, J_{PH} 4, 3-H), 6.93 (1 H, ddd, J_{HH} 11.1 and 9.7, J_{PH} 1.4, 4-H), 8.00 (1 H, d, J_{HH} 9.6, 6'-H), 8.31 (1 H, d, J_{HH} 9.7, 5-H), 8.36 (1 H, dd, J_{HH} 9.6, 2.6 and 0.5, 5'-H) and 9.13 (1 H, d, J_{HH} 2.6, 3'-H); δ_C(100.63 MHz, $CDCl_3$) 53.8 (x2)(d, J_{PC} 6, POMe), 86.2 (d, J_{PC} 299, C-1), 94.9 (d, J_{PC} 52, C-2), 112.6 (d, J_{PC} 6, C-3), 117.3 (C-6'), 123.4 (C-3'), 130.2 (C-5'), 130.6 (C-2'), 139.4 (C-4'), 141.2 (d, J_{PC} 3, C-4), 144.3 (C-1') and 144.9 (C-5).

Dimethyl (Z)-3-benzyl-5-oxo-pent-3-en-1-ynylphosphonate **20c**; δ_P(109.3 MHz, $CDCl_3$) -4.5; δ_H(400 MHz, $CDCl_3$) 3.72 (2 H, br d, J_{PH} 1, CH_2), 3.73 (6 H, d, J_{PH} 12, POMe), 6.34 (1 H, dq, J 8 and 1.2, CH=), 7.21 (2 H, dm, J_{HH} 8, 2'/6'-H), 7.27-7.32 (1 H, m, 4'-H), 7.35 (1 H, tm, J_{HH} 8, 3'/5'-H) and 10.05 (1 H, d, J_{HH} 8, CHO); δ_C(100.63 MHz, $CDCl_3$) 43.5 (d, J_{PC} 2, CH_2), 53.8 (d, J_{PC} 6, POMe), 54.5 (d, J_{PC} 6, POMe), 88.2 (d, J_{PC} 291, C-1), 94.1 (d, J_{PC} 50, C-2), 127.8 (C-4'), 129.1 (x2)(C-3'/5'), 129.4 (x2)(C-2'/6'), 135.2 (C-1'), 138.9 (d, J_{PC} 2, C-4), 141.3 (d, J_{PC} 6, C-3) and 191.1 (s, C-5).

Dimethyl (Z)-3-benzyl-5-(dimethoxyphosphoryloxy)penta-1,2,4-trienylphosphonate **23**; δ_P(109.3 MHz, $CDCl_3$) -1.9 and 17.3; δ_H(400 MHz, $CDCl_3$) 3.47 (2 H, br dt, J_{PH} 6.1, J_{HH} 2.7, CH_2), 3.57 (3 H, d, J_{PH} 11.3, POMe), 3.58 (3 H, d, J_{PH} 11.3, POMe), 3.67 (3 H, d, J_{PH} 11.4, POMe), 3.68 (3 H, d, J_{PH} 11.4, POMe), 4.82 (1 H, ddt, J_{HH} 6.4 and 1.6, J_{PH} 2.7, 4-H), 5.35 (1 H, tddd, J_{HH} 2.7, 1.6 and 1.6, J_{PH} 1.4, 1-H), 6.46 (1 H, dddd, J_{HH} 6.4 and 1.6, J_{PH} 6.6 and 3.2, 5-H),7.21 (1 H, m, 4'-H) and 7.15-7.22 (4 H, m, 2'/6'-H and 3'/5'-H); δ_C(100.63 MHz, $CDCl_3$) 38.9 (d, J_{PC} 7, CH_2), 52.9 (d, J_{PC} 6, POMe), 53.0 (d, J_{PC} 6, POMe), 55.0 (d, J_{PC} 6, POMe), 55.1 (d, J_{PC} 6, POMe), 80.0 (d, J_{PC} 199, C-1), 100.3 (d, J_{PC} 17.5, C-3), 107.1 (dd, J_{PC} 10.2 and 9.8, C-4), 126.9 (C-4'), 128.6, (x2)(C-3'/5'), 129.1 (x2)(C-2'/6'), 137.7 (dd, J_{PC} 5.3 and 5.1, C-5), 137.7 (d, J_{PC} 4, C-1') and 215.7 (d, J_{PC} 3, C-2).

Dimethyl 4-benzyl-5-(dimethoxyphosphorylmethyl)furan-2-ylphosphonate **25**; δ_P(109.3 MHz, $CDCl_3$) 7.6, (d, J_{PP} 4) and 25.1 (d, J_{PP} 4); δ_H(400 MHz, $CDCl_3$) 3.26 (2 H, d, J_{PH} 21, PCH_2), 3.72 (6 H, d, J_{PH} 11.0, POMe), 3.77 (6 H, d, J_{PH} 11.4, POMe), 3.78 (2 H, br d, J 2, CH_2), 6.95 (1 H, m, 3-H), 7.17 (2 H, dm, J_{HH} 7.5, 2'/6'-H), 7.22 (1 H, tt, J_{HH} 7.5 and 1.3, 4'-H) and 7.30 (2 H, tt, J_{HH} 7.5 and 1.3, 3'/5'-H); δ_C(100.63 MHz, $CDCl_3$) 25.0 (d, J_{PC} 143, PCH_2), 30.8 (d, J_{PC} 2, CH_2Ph), 53.1 (d, J_{PC} 7, POMe), 53.4 (d, J_{PC} 6, POMe), 122.8 (dd, J_{PC} 11 and 9, C-4), 126.4 (dd, J_{PC} 24 and 4, C-3), 126.6 (C-4'), 128.7 (x2)(C-3'/5'), 128.8 (x2)(C-2'/6'), 139.1 (s, C-1'), 141.6 (dd, J_{PC} 245 and 4, C-2) and 147.9 (dd, J_{PC} 13 and 10, C-5).

X-Ray crystallography

Data were collected at 120 K using a Nonius Kappa CCD area detector diffractometer mounted at the window of a molybdenum rotating anode (50 KV, 90 mA, λ=0.71069 Å). The crystal-to-detector distance was 30 mm and ϕ and Ω scans (1.0° increments, 20 s exposure time) were carried out to fill the Ewald sphere. Data collection and processing were carried out using COLLECT[5], DENZO[6] and maXus[7] and an empirical absorption correction was applied using SORTAV.[8] The structure was solved by direct-method using SHELXS-97[9] and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using the SHELXL-97[9] program. The H atoms were calculated geometrically and refined with a riding model.

Crystal data. $C_{13}H_{13}N_4O_7P$, M = 368.24, triclinic, a = 8.2246(2), b = 8.6176(2), c = 11.5999(3) Å, U = 767.27(3) Å^3, T = 120(2) K, space group P 1(no. 2), Z = 2, μ(Mo-Kα) = 0.228 mm^{-1}, 14406 reflections measured, 3510 unique (R_{int} = 0.0321) which were used in all calculations. The final $wR(F^2)$ was 0.1213 (all data).

Notes and references

1 K. S. Feldman, J. C. Saunders and M. L. Wrobleski, *J. Org. Chem.*, 2002, **67**, 7096.
2 Ammonium acetate used as the buffer.
3 Care – higher temperatures can cause charring and decomposition.
4 Signal partially obscured.
5 Data collection software, R. Hooft, Nonius B.V., 1998.
6 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C.W. Carter, Jr and R.M. Sweet, Academic Press, New York, 1997, vol. 276, part A, p. 307.
7 S. Mackay, C.J. Gilmore, C. Edwards, M. Tremayne, N. Stewart, K. Shankland. maXus: a computer program for the solution and refinement of crystal structures from diffraction data; University of Glasgow; Glasgow, U.K., Nonius BV , Delft, The Netherlands and MacScience Co. Ltd., Yokohama, Japan,1998.
8 R.H. Blessing, *Acta Cryst.*, 1995, **A51**, 33 and *J. Appl. Cryst.*, 1997, **30**, 421.
9 G. M. Sheldrick, SHELX-97, Release 97–2, Univ. Göttingen, Germany, 1998.