Synthesis of 2-Phosphono Pyrroles via a One-pot RCM/oxidation Sequence

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General

All ^1H NMR spectra were recorded at room temperature (22°C) using a 300 MHz spectrometer with CDCl_3 as a solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded at 75 MHz and ^{31}P NMR spectra at 121 MHz. IR spectra were measured as a film between NaCl plates for oils and as a KBr disk for solids. MS spectra were measured using electron spray ionisation (ESI, 4000 V). The MS spectrum of **10a** was measured using a GCMS with electron impact ionization (EI).

(*E*)-Cinnamaldehyde, (*E*)-2-methyl and (*E/Z*)-2-isoamyl cinnamaldehyde and (*E/Z*)-2-phenyl crotonaldehyde were commercially available. (*E*)-2-benzyl and (*E*)-2-phenylethyl crotonaldehyde were synthesized according to a literature procedure.¹ Dichloromethane was dried over CaH_2 and distilled before use. Other solvents were used as such.

Imines **1** were synthesized via a condensation reaction between the corresponding aldehyde and a slight excess of allylamine in dichloromethane with MgSO_4 as a drying agent. The reaction mixtures were stirred during an overnight period at room temperature. Formation of imine **1d** required reflux temperatures.

Experimental procedures and spectral data:

Synthesis of α -aminoalkenyl phosphonates **2**

15 Mmol of aldimine **1** is dissolved in 20 ml of MeOH in a round bottom flask. Then, 2 equivalents of dimethyl phosphite (DMP) is added and the mixture is refluxed for 3 – 4 hours. After removing the solvent under vacuum, the resulting oil is dissolved in 20 ml of diethyl ether and added to a separatory funnel containing 20 ml of 1 M $\text{HCl}_{(\text{aq})}$. Both phases are vigorously mixed and the organic phase is removed from the funnel. The aqueous phase is washed twice with 10 ml of diethyl ether, added to 20 ml of dichloromethane and then neutralized using 3 M $\text{NaOH}_{(\text{aq})}$ until slightly alkaline. Both phases are vigorously mixed and the organic phase is now collected. The aqueous phase is extracted twice more with 10 ml of dichloromethane and the combined organic phases are dried using MgSO_4 . The α -aminoalkenyl phosphonates **2** are obtained in pure form after filtration and evaporation of the solvent.

Dimethyl (2*E*)-1-(allylamino)-3-phenylprop-2-enylphosphonate (**2a**)

Spectral data are identical to those reported earlier.¹⁶

Dimethyl (2*E*)-1-(allylamino)-2-methyl-3-phenyl-propenylphosphonate (**2b**)

^1H NMR (300 MHz, ppm) δ : 1.90 (1H, s (br.)); 1.99 (3H, dd, $J_{\text{H-P}} = 3.3$ Hz, $J = 1.4$ Hz); 3.13 (1H, dd, $J_{\text{AB}} = 14.0$ Hz, $J = 6.9$ Hz); 3.33 (1H, dd, $J_{\text{AB}} = 13.8$ Hz, $J = 5.2$ Hz); 3.70 (1H, d, $J_{\text{H-P}} = 21.5$ Hz); 3.78

¹ Takabe, K.; Fujiwara, H.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 1237.

(3H, d, $J_{\text{H-P}} = 10.5$ Hz); 3.83 (3H, d, $J_{\text{H-P}} = 10.7$ Hz); 5.12-5.29 (2H, multiplet); 5.81-5.94 (1H, multiplet); 6.55 (1H, d, $J_{\text{H-P}} = 4.1$ Hz); 7.21-7.37 (5H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 15.4; 49.9 (d, $J_{\text{C-P}} = 18.5$ Hz); 53.5 (d, $J_{\text{C-P}} = 6.9$ Hz); 53.7 (d, $J_{\text{C-P}} = 8.1$ Hz); 63.0 (d, $J_{\text{C-P}} = 153.5$ Hz); 117.0; 126.8, 128.3, 129.1; 130.5 (d, $J_{\text{C-P}} = 12.7$ Hz); 132.7 (d, $J_{\text{C-P}} = 4.6$ Hz); 136.1; 137.3 (d, $J_{\text{C-P}} = 2.3$ Hz). **^{31}P NMR (121 MHz, ppm) δ :** 26.98. **IR ν_{max} (cm^{-1}):** 3470 (NH), 1248 (P=O), 1039 (br., P-O). **MS: m/z (%):** 296 (81, $[\text{M}+\text{H}]^+$); 186 (100, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Yield:** 90%.

Dimethyl (2*E*)-1-(allylamino)-2-benzyl-but-2-enylphosphonate (2c)

^1H NMR δ (300 MHz, ppm): 1.54 (1H, s (br.)); 1.87 (3H, dd, $J = 6.3$ Hz, $J = 5.8$ Hz); 2.68 (1H, dd, $J_{\text{AB}} = 14.0$ Hz, $J = 6.6$ Hz); 2.99 (1H, dd, $J_{\text{AB}} = 14.0$ Hz, $J = 5.5$ Hz); 3.34 – 3.40 (1H, multiplet); 3.41 (1H, d, $J_{\text{H-P}} = 21.7$ Hz); 3.68 – 3.82 (1H, multiplet); 3.73 (3H, d, $J_{\text{H-P}} = 10.5$ Hz); 3.78 (3H, d, $J_{\text{H-P}} = 10.5$ Hz); 4.75 – 7.90 (2H, multiplet); 5.49 – 5.63 (1H, multiplet); 5.81 (1H, ~quintet, $J \approx 6.3$ Hz); 7.15 – 7.30 (5H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 14.2; 35.2; 49.6 (d, $J_{\text{C-P}} = 16.2$ Hz); 53.1 (d, $J_{\text{C-P}} = 6.9$ Hz); 53.9 (d, $J_{\text{C-P}} = 6.9$ Hz); 58.9 (d, $J_{\text{C-P}} = 154.6$ Hz); 116.3; 124.9 (d, $J_{\text{C-P}} = 11.5$ Hz); 126.3; 128.5; 128.90; 133.3 (d, $J_{\text{C-P}} = 3.5$ Hz); 136.1; 139.4. **^{31}P NMR δ (121 MHz, ppm):** 27.40. **IR ν_{max} (cm^{-1}):** 3321 (NH); 1238 (P=O), 1074, 1026 (P-O). **MS m/z (%):** 310 (100, $[\text{M}+\text{H}]^+$), 200 (19, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Mp.:** 78-80°C. **Yield:** 27%.

Dimethyl 1-(allylamino)-2-isopentyl-3-phenyl-propenylphosphonate (2d)

Mixture of two isomers: 79% E and 21% Z.

Major and minor isomer are indicated as M and m respectively whenever possible.

^1H NMR (300 MHz, ppm) δ : 0.85-0.96 (2x3H, multiplet); 1.27-1.49 (2x5H, multiplet); 1.53-1.71 (2x1H, multiplet); 1.89 (2x1H, s (br.)); 2.11-2.20 (1H, multiplet); 2.22-2.37 (2H, multiplet); 2.50-2.60 (1H, multiplet); 2.84 (1H, dd, $J_{\text{AB}} = 13.8$ Hz, $J = 6.3$ Hz); 3.17 (1H, dd, $J_{\text{AB}} = 14.0$ Hz, $J = 5.5$ Hz); 3.13-3.20 (1H, multiplet); 3.40 (1H, dd, $J_{\text{AB}} = 13.8$ Hz, $J = 3.9$ Hz); 3.66 (1H, d, $J_{\text{H-P}} = 20.6$ Hz); 3.77 (2x3H, d, $J_{\text{H-P}} = 10.5$ Hz); 3.78 (3H, d, $J_{\text{H-P}} = 10.5$ Hz); 3.83 (3H, d, $J_{\text{H-P}} = 10.5$ Hz); 4.25 (1H, d, $J_{\text{H-P}} = 22.6$ Hz); 4.83-4.90 (2H, multiplet); 5.11-5.25 (2H, multiplet); 5.61-5.74 (1H, multiplet); 5.81-5.94 (1H, multiplet); 6.67 (1H, d, $J_{\text{H-P}} = 5.5$ Hz); 6.70 (1H, s (br.)); 7.20-7.36 (2x5H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 14.0 (M); 14.1 (m); 22.3 (M), 22.7 (m); 27.8 (d, $J_{\text{C-P}} = 2.3$ Hz); 28.1 (m); 30.6 (m); 30.9 (d, $J_{\text{C-P}} = 2.3$ Hz, M); 31.9 (m); 32.0 (M); 49.6 (d, $J_{\text{C-P}} = 16.2$ Hz, m); 49.8 (d, $J_{\text{C-P}} = 16.2$ Hz, M); 53.0 (d, $J_{\text{C-P}} = 6.9$ Hz, m); 53.3 (d, $J_{\text{C-P}} = 6.9$ Hz, M); 53.5 (d, $J_{\text{C-P}} = 6.9$ Hz, m); 53.9 (d, $J_{\text{C-P}} = 6.9$ Hz, M); 54.8 (d, $J_{\text{C-P}} = 156.9$ Hz, m); 59.7 (d, $J_{\text{C-P}} = 152.3$ Hz, M); 116.6; 126.6; 128.2; 128.2; 128.5; 128.6 (d, $J_{\text{C-P}} = 13.9$ Hz, M); 130.5 (d, $J_{\text{C-P}} = 13.9$ Hz, m); 135.8 (m); 136.2 (M); 136.4; 137.3; 137.4; 137.4; 137.5. **^{31}P NMR (121 MHz, ppm) δ :** 26.94 (M), 27.64 (m). **IR ν_{max} (cm^{-1}):** 3329 (NH), 1246 (P=O), 1052, 1035 (P-O). **MS: m/z (%):** 352 (53, $[\text{M}+\text{H}]^+$); 242 (100, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$, 100). **Yield:** 88%.

Dimethyl (2E)-1-(allylamino)-2-phenyl-but-2-enylphosphonate (E-(2e))

¹H NMR (300 MHz, ppm) δ: 1.66 (3H, dd, J = 6.6 Hz, J = 5.2 Hz); 1.84 (1H, s (br.)); 3.23 (1H, dd, J_{AB} = 13.8 Hz, J = 6.6 Hz); 3.44 (1H, dd, J_{AB} = 13.6 Hz, J = 5.2 Hz); 3.64 (3H, d, J_{H-P} = 10.5 Hz); 3.66 (3H, d, J_{H-P} = 10.7 Hz); 3.80 (1H, d, J_{H-P} = 22.6 Hz); 5.10-5.22 (2H, multiplet); 5.80-5.97 (2H, multiplet); 7.22-7.40 (5H, multiplet). **¹³C NMR (75 MHz, ppm) δ:** 14.8 (d, J_{C-P} = 2.3 Hz); 49.7 (d, J_{C-P} = 17.3 Hz); 52.9 (d, J_{C-P} = 6.9 Hz); 53.4 (d, J_{C-P} = 6.9 Hz); 60.8 (d, J_{C-P} = 156.9 Hz); 116.7; 127.9; 127.2 (d, J_{C-P} = 10.4 Hz); 128.0; 129.0; 135.7 (br.); 136.1; 138.8 (d, J_{C-P} = 3.5 Hz). **³¹P NMR (121 MHz, ppm) δ:** 26.87. **IR ν_{max} (cm⁻¹):** 3469 (NH), 1244 (P=O), 1039 (br., P-O). **MS: m/z (%):** 296.3 ([M+H]⁺, 100); 186.2 ([M+H-PO(OMe)₂]⁺, 84). **Chromatography:** Hex/EtOAc (2/8) R_f = 0.20. **Yield:** 52%.

Dimethyl (2Z)-1-(allylamino)-2-phenyl-but-2-enylphosphonate (Z-(2e))

¹H NMR (300 MHz, ppm) δ: 1.86 (3H, dd, J = 7.2 Hz, J = 4.7 Hz); 1.89 (1H, s (br.)); 3.00 (1H, dd, J_{AB} = 13.5 Hz, J = 6.9 Hz); 3.18 (1H, dd, J_{AB} = 13.8 Hz, J = 5.2 Hz); 3.73 (3H, d, J_{H-P} = 10.5 Hz); 3.79 (3H, d, J_{H-P} = 10.5 Hz); 4.29 (1H, d, J_{H-P} = 26.4 Hz); 5.05-5.12 (2H, multiplet); 5.71-5.84 (1H, multiplet); 5.97 (1H, dq, J = 7.2 Hz, J = 4.1 Hz); 7.20-7.36 (3H, multiplet); 7.55-7.59 (2H, multiplet). **¹³C NMR (75 MHz, ppm) δ:** 14.3; 50.2 (d, J_{C-P} = 18.5 Hz); 53.4 (d, J_{C-P} = 8.1 Hz); 53.8 (d, J_{C-P} = 6.9 Hz); 54.6 (d, J_{C-P} = 160.4 Hz); 117.1; 127.2; 127.3; 128.4; 130.6 (d, J_{C-P} = 11.5 Hz); 136.1; 136.8; 140.9. **³¹P NMR (121 MHz, ppm) δ:** 27.40. **IR ν_{max} (cm⁻¹):** 3469 (NH), 1246 (P=O), 1058, 1032 (br., P-O). **MS: m/z (%):** 296.3 ([M+H]⁺, 100); 186.2 ([M+H-PO(OMe)₂]⁺, 39). **Chromatography:** Hex/EtOAc (2/8) R_f = 0.24. **Yield:** 10%.

Dimethyl (2E)-1-(allylamino)-2-(2-phenylethyl)but-2-enylphosphonate (2f)

¹H NMR (300 MHz, ppm) δ: 1.71 (3H, t, J = 6.1 Hz); 1.76 (1H, s); 2.28-2.81 (4H, multiplet); 3.07 (1H, dd, J_{AB} = 14.1 Hz, J = 6.3 Hz); 3.27 (1H, dd, J_{AB} = 14.1 Hz, J = 5.1 Hz); 3.50 (1H, d, J_{H-P} = 21.5 Hz); 3.74 (3H, d, J_{H-P} = 10.5 Hz); 3.80 (3H, d, J_{H-P} = 10.2 Hz); 5.09-5.22 (2H, multiplet); 5.66 (1H, dq, J = 6.6 Hz, J = 6.2 Hz); 5.77-5.88 (1H, multiplet); 7.16-7.32 (5H, multiplet). **¹³C NMR (75 MHz, ppm) δ:** 13.4; 31.4; 34.4; 49.7 (d, J_{C-P} = 16.2 Hz); 52.9 (d, J_{C-P} = 6.9 Hz); 53.6 (d, J_{C-P} = 6.9 Hz); 60.2 (d, J_{C-P} = 154.6 Hz); 116.3; 125.2 (d, J_{C-P} = 11.5 Hz); 125.8; 128.3; 133.7 (d, J_{C-P} = 3.5 Hz); 136.3; 142.0. **³¹P NMR (121 MHz, ppm) δ:** 27.56 **IR ν_{max} (cm⁻¹):** 3324 (NH), 1246 (P=O), 1031 (P-O). **MS: m/z (%):** 324.2 (100, [M+H]⁺). **Elem. Anal.** Calc. for C₁₇H₂₆NO₃P: C63.14, H8.10, N4.33; found: C62.98, H7.92, N4.42. **Chromatography:** Hex/EtOAc (2/8) R_f = 0.32. **Yield:** 44%.

Dimethyl (2E)-1-[(2-methylprop-2-enyl)amino]-3-phenyl-prop-2-enylphosphonate (2g)

¹H NMR (300 MHz, ppm) δ: 1.75 (4H, s); 3.16 (1H, d, J_{AB} = 14.3 Hz); 3.29 (1H, d, J_{AB} = 14.3 Hz); 3.71 (1H, ddd, J_{H-P} = 19.5 Hz, J = 8.5 Hz, J = 0.8 Hz); 3.80 (3H, d, J_{H-P} = 9.6 Hz); 3.83 (3H, d, J_{H-P} = 9.6 Hz); 4.88 (1H, s); 4.90 (1H, s); 6.11 (1H, ddd, J = 15.8 Hz, J = 8.5 Hz, J_{H-P} = 5.6 Hz); 6.62 (1H, dd, J = 15.8 Hz, J_{H-P} = 4.5 Hz); 7.23-7.42 (5H, multiplet). **¹³C NMR (75 MHz, ppm) δ:** 20.7; 53.2 (d, J_{C-P} = 16.1 Hz); 53.5 (d, J_{C-P} = 6.9 Hz); 53.8 (d, J_{C-P} = 7.0 Hz); 57.5 (d, J_{C-P} = 156.9 Hz); 112.00; 124.0 (d, J_{C-P} = 6.9 Hz); 126.6; 128.1; 128.7; 134.6 (d, J_{C-P} = 13.8 Hz); 136.37; 143.03. **³¹P NMR (121 MHz, ppm) δ:** 26.9 **IR ν_{max} (cm⁻¹):** 3460 (NH), 1244 (P=O), 1057 (P-O). **MS: m/z (%):** 296.7 (100, [M+H]⁺). **Yield:** 74%.

Synthesis *N*-benzyl α-aminoalkenyl phosphonates 3

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-methyl-3-phenyl-prop-2-enylphosphonate (3b)

¹H NMR δ (300 MHz, ppm): 2.07 (3H, s); 3.25 (1H, dd, J_{AB} = 14.2 Hz, J = 7.4 Hz); 3.62-3.70 (1H, multiplet); 3.72 (3H, d, J_{H-P} = 10.5 Hz); 3.72-3.86 (2H, multiplet); 3.84 (3H, d, J_{H-P} = 10.5 Hz); 4.18 (1H, dd, J_{AB} = 13.8 Hz, J_{H-P} = 2.5 Hz); 5.15-5.26 (2H, multiplet); 5.79-5.92 (1H, multiplet); 6.66 (1H, s (br.)); 7.20-7.39 (10H, multiplet). **¹³C NMR δ (75 MHz, ppm):** 18.6 (d, J_{C-P} = 6.9 Hz); 52.9 (d, J_{C-P} = 8.1 Hz); 53.0 (d, J_{C-P} = 6.9 Hz); 63.9 (d, J_{C-P} = 153.5 Hz); 117.8; 126.8; 127.0; 128.2; 128.3; 128.9; 129.1; 132.00 (d, J_{C-P} = 4.6 Hz); 132.4 (d, J_{C-P} = 11.5 Hz); 136.5; 137.4; 139.8. **³¹P NMR δ (121 MHz, ppm):** 27.35. **IR ν_{max} (cm⁻¹):** 1247 (P=O); 1037 (br., P-O). **MS m/z (%):** 386 (100, [M+H]⁺). **Chromatography:** Hex/EtOAc (3/2) R_f = 0.26. **Yield:** 50%.

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-benzyl-but-2-enylphosphonate (3c)

¹H NMR δ (300 MHz, ppm): 1.83 (3H, d, J = 6.6 Hz); 3.20 (1H, d, J_{AB} = 14.9 Hz); 3.34 – 3.39 (2H, multiplet); 3.46 (3H, d, J_{H-P} = 10.5 Hz); 3.53 (1H, d, J_{H-P} = 20.6 Hz); 3.66 (3H, d, J_{H-P} = 10.5 Hz); 3.68 – 3.74 (1H, multiplet); 3.86 – 3.88 (2H, multiplet); 5.05 – 5.16 (2H, multiplet); 5.73 (1H, dxdxt, J_{trans} = 17.3 Hz, J_{cis} = 10.2 Hz, J = 6.5 Hz); 6.27 (1H, q, J = 6.6 Hz); 6.92 (2H, d, J = 6.6 Hz); 7.10 – 7.39 (8H, multiplet). **¹³C NMR δ (75 MHz, ppm):** 14.4; 35.7 (d, J_{C-P} = 11.5 Hz); 51.8 (d, J_{C-P} = 6.9 Hz); 52.7 (d, J_{C-P} = 6.9 Hz); 54.2 (d, J_{C-P} = 3.5 Hz); 54.9 (br.); 58.4 (d, J_{C-P} = 140.8 Hz); 117.6; 126.1; 127.0; 127.7 (d, J_{C-P} = 5.8 Hz); 128.3; 128.8; 129.2; 133.2 (d, J_{C-P} = 10.4 Hz); 137.2; 139.5; 140.3. **³¹P NMR δ (121 MHz, ppm):** 28.84. **IR ν_{max} (cm⁻¹):** 1236 (P=O); 1053, 1030 (P-O). **MS m/z (%):** 400 (100, [M+H]⁺). **Chromatography:** Hex/EtOAc (1/1) R_f = 0.45. **Yield:** 50%.

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-isopentyl-3-phenyl-prop-2-enylphosphonate (*E*-3d)

¹H NMR (300 MHz, ppm) δ: 0.83-0.88 (3H, multiplet); 1.12-1.35 (6H, multiplet); 2.05-2.17 (1H, multiplet); 2.40-2.49 (1H, multiplet); 3.42-3.57 (2H, multiplet); 3.75 (3H, d, J_{H-P} = 10.5 Hz); 3.83 (1H, d, J_{H-P} = 21.5 Hz); 3.87 (3H, d, J_{H-P} = 10.5 Hz); 3.96 (1H, d, J_{AB} = 13.5 Hz); 4.04 (1H, dd,

$J_{AB} = 13.8$ Hz, $J = 3.9$ Hz); 5.15-5.28 (2H, multiplet); 5.77-5.90 (1H, multiplet); 7.12 (1H, s (br.)); 7.21-7.35 (10H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 14.1; 22.4; 28.0; 31.3 (d, $J_{C-P} = 10.4$ Hz); 31.8; 52.1 (d, $J_{C-P} = 6.9$ Hz); 53.1 (d, $J_{C-P} = 6.9$ Hz); 54.3 (d, $J_{C-P} = 4.6$ Hz); 55.1 (d, $J_{C-P} = 4.6$ Hz); 58.7 (d, $J_{C-P} = 144.2$ Hz); 117.7; 126.7; 127.0; 128.2; 128.2; 128.7; 129.1; 131.4 (d, $J_{C-P} = 5.8$ Hz); 137.0; 137.2 (d, $J_{C-P} = 8.1$ Hz); 137.7; 140.0. **^{31}P NMR (121 MHz, ppm) δ :** 28.72 **IR $\nu_{\max}$ (cm^{-1}):** 1247 (P=O); 1058, 1029 (P-O), **MS: m/z (%):** 442 (100, $[\text{M}+\text{H}]^+$), 332 (32, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Chromatography:** Hex/EtOAc (1/1) $R_f = 0.50$. **Yield:** 34%.

Dimethyl (2Z)-1-(allyl(benzyl)amino)-2-isopentyl-3-phenyl-prop-2-enylphosphonate (Z-(3d))

^1H NMR (300 MHz, ppm) δ : 0.84-0.96 (3H, multiplet); 1.32-1.46 (4H, multiplet); 1.61-1.72 (2H, multiplet); 2.40-2.63 (2H, multiplet); 3.05 (1H, dd, $J_{AB} = 14.3$ Hz, $J = 7.4$ Hz); 3.47-3.57 (1H, multiplet); 3.55 (1H, d, $J_{AB} = 14.0$ Hz); 3.69 (3H, d, $J_{H-P} = 10.7$ Hz); 3.71 (3H, d, $J_{H-P} = 10.7$ Hz); 4.05 (1H, dd, $J_{AB} = 14.0$ Hz, $J_{H-P} = 1.9$ Hz); 4.54 (1H, d, $J_{H-P} = 24.8$ Hz); 4.71-4.87 (2H, multiplet); 5.52-5.65 (1H, multiplet); 6.70 (1H, s (br.)); 7.07-7.35 (10H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 14.2; 22.8; 28.6; 32.01 33.5; 52.6 (d, $J_{C-P} = 6.9$ Hz); 53.1 (d, $J_{C-P} = 6.9$ Hz); 54.7 (d, $J_{C-P} = 8.1$ Hz); 55.6 (d, $J_{C-P} = 8.1$ Hz); 56.8 (d, $J_{C-P} = 156.9$ Hz); 117.3; 126.7; 128.1; 128.37; 128.44; 128.9; 131.1 (d, $J_{C-P} = 13.9$ Hz); 135.8; 137.0; 137.9; 139.9. **^{31}P NMR (121 MHz, ppm) δ :** 27.79. **IR $\nu_{\max}$ (cm^{-1}):** 1249 (P=O); 1059, 1031 (P-O). **MS: m/z (%):** 442 (100, $[\text{M}+\text{H}]^+$), 332 (19, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Chromatography:** Hex/EtOAc (1/1) $R_f = 0.58$. **Yield:** 11%.

Dimethyl (2E)-1-(allyl(benzyl)amino)-2-phenyl-but-2-enylphosphonate (3e)

^1H NMR (300 MHz, ppm) δ : 1.69 (3H, d, $J = 6.3$ Hz); 2.95 (1H, dd, $J_{AB} = 13.9$ Hz, $J = 7.6$ Hz); 3.43 (1H, d, $J_{AB} = 13.5$ Hz); 3.44-3.51 (1H, multiplet); 3.70 (3H, d, $J_{H-P} = 10.5$ Hz); 3.82 (3H, d, $J_{H-P} = 10.7$ Hz); 4.03 (1H, d, $J_{H-P} = 24.5$ Hz); 4.02-4.08 (1H, multiplet); 4.84-5.01 (2H, multiplet); 5.60-5.74 (1H, multiplet); 6.41 (1H, qd, $J = 6.8$ Hz, $J_{H-P} = 1.7$ Hz); 7.04-7.36 (10H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 15.1; 52.6 (d, $J_{C-P} = 6.9$ Hz); 53.3 (d, $J_{C-P} = 6.9$ Hz); 54.4 (d, $J_{C-P} = 6.9$ Hz); 55.3 (d, $J_{C-P} = 6.9$ Hz); 60.8 (d, $J_{C-P} = 156.9$ Hz); 117.6; 126.8; 128.0; 128.1; 129.0; 129.1 (d, $J_{C-P} = 4.6$ Hz); 134.1 (d, $J_{C-P} = 8.1$ Hz); 136.5; 139.4; 141.5 (d, $J_{C-P} = 13.9$ Hz). **^{31}P NMR (121 MHz, ppm) δ :** 27.19. **IR (cm^{-1}) $\nu_{\max}$:** 1246 (P=O); 1057, 1036 (P-O). **MS: m/z (%):** 386 (100, $[\text{M}+\text{H}]^+$), 276 (10, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Chromatography:** Hex/EtOAc (1/1) $R_f = 0.30$. **Yield:** 25%. - The minor (2Z)-isomer could not be obtained in pure form.

Dimethyl (2E)-1-(allyl(benzyl)amino)-2-(2-phenylethyl)but-2-enylphosphonate (3f)

^1H NMR (300 MHz, ppm) δ : 1.64 (3H, d, $J = 6.8$ Hz); 2.23-2.33 (1H, multiplet); 2.47-2.57 (3H, multiplet); 3.32 (1H, dd, $J_{AB} = 13.8$ Hz, $J = 6.1$ Hz); 3.44 (1H, ddd, $J_{AB} = 13.8$ Hz, $J = 6.6$ Hz, $J = 4.3$ Hz); 3.65-3.81 (2H, multiplet); 3.68 (3H, d, $J_{H-P} = 10.6$ Hz); 3.83 (3H, d, $J_{H-P} = 10.7$ Hz); 3.92 (1H,

dd, J_{AB} = 13.8 Hz, J = 1.1 Hz); 5.11-5.25 (2H, multiplet); 5.79 (1H, ddt, J = 16.6 Hz, J = 10.5 Hz, J = 6.5 Hz); 6.05 (1H, q, J = 6.8 Hz); 7.10-7.38 (10H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 13.7; 33.0 (d, J_{C-P} = 10.7 Hz); 34.6; 52.1 (d, J_{C-P} = 8.1 Hz); 52.9 (d, J_{C-P} = 7.0 Hz); 54.1 (d, J_{C-P} = 4.6 Hz); 54.8 (d, J_{C-P} = 3.4 Hz); 59.2 (d, J_{C-P} = 143.1 Hz); 117.8; 125.9; 127.0; 127.4 (d, J_{C-P} = 5.8 Hz); 128.3; 128.4; 128.5; 129.1; 133.5 (d, J_{C-P} = 8.0 Hz); 137.1; 140.2; 142.0. **^{31}P NMR (121 MHz, ppm) δ :** 29.01 **IR ν_{max} (cm^{-1}):** 1241 (P=O), 1028 (P-O). **MS: m/z (%):** 414 (100, $[\text{M}+\text{H}]^+$). **Elem. Anal.** Calc. for $\text{C}_{24}\text{H}_{32}\text{NO}_3\text{P}$: C69.71, H7.80, N3.39; found: C69.85, H7.75, N3.28. **Chromatography:** Hex/EtOAc (4/6) R_f = 0.41. **Yield:** 92%.

Dimethyl (2*E*)-1-[benzyl(2-methylprop-2-enyl)amino]-3-phenylprop-2-enylphosphonate (3g)

^1H NMR (300 MHz, ppm) δ : 1.79 (3H, s), 3.02 (1H, d, J_{AB} = 12.7 Hz), 3.47 (1H, d, J_{AB} = 13.8 Hz), 3.51 (1H, d, J_{AB} = 12.7 Hz), 3.68 (3H, d, J_{H-P} = 10.5 Hz), 3.82 (3H, d, J_{H-P} = 10.7 Hz), 3.82 (1H, dd, J_{H-P} = 23.7 Hz, J = 9.8 Hz), 4.22 (1H, dd, J_{AB} = 13.8 Hz, J = 2.2 Hz), 4.91 (1H, s), 4.98 (1H, s), 6.38 (1H, ddd, J = 15.7 Hz, J = 9.8 Hz, J_{H-P} = 6.3 Hz), 6.70 (1H, dd, J_{H-P} = 3.0 Hz, J = 15.7 Hz), 7.22-7.45 (5H, multiplet). **^{13}C NMR (75 MHz, ppm) δ :** 20.6; 52.9 (d, J_{C-P} = 6.9 Hz); 53.3 (d, J_{C-P} = 6.9 Hz); 55.1 (d, J_{C-P} = 6.9 Hz); 57.8 (d, J_{C-P} = 8.1 Hz); 59.0 (d, J_{C-P} = 160.4 Hz); 113.6; 119.7; 126.8; 127.1; 128.2; 128.4; 128.8; 128.8; 136.4; 137.3 (d, J_{C-P} = 15.0 Hz); 139.6; 143.5. **^{31}P NMR (121 MHz, ppm) δ :** 27.48 **IR ν_{max} (cm^{-1}):** 1246 (P=O), 1029 (P-O). **MS: m/z (%):** 386 (100, $[\text{M}+\text{H}]^+$). **Chromatography:** Hex/EtOAc (4/6) R_f = 0.47. **Mp. ($^{\circ}\text{C}$):** 78.5. **Yield:** 86%.

Synthesis of 2-phosphono 3-pyrrolines 4

Dimethyl 1-benzyl-3-methyl-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (4b)

^1H NMR δ (300 MHz, ppm): 1.86 (3H, s (br.)); 3.19 - 3.47 (1H, multiplet); 3.63 (d, J_{AB} = 13.2 Hz); 3.63 - 3.74 (1H, multiplet); 3.82 (6H, d, J_{H-P} = 10.7 Hz); 3.92 (1H, multiplet); 4.28 (1H, d, J_{AB} = 13.2 Hz); 5.49 - 5.52 (1H, multiplet); 7.21 - 7.39 (5H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 14.8; 53.2 (d, J_{C-P} = 8.1 Hz); 53.4 (d, J_{C-P} = 6.9 Hz); 59.9 (d, J_{C-P} = 8.1 Hz); 60.6 (d, J_{C-P} = 5.8 Hz); 70.8 (d, J_{C-P} = 174.2 Hz); 124.8 (d, J_{C-P} = 12.7 Hz); 126.9; 128.3; 128.6; 133.4 (d, J_{C-P} = 4.6 Hz); 139.4. **^{31}P NMR δ (121 MHz, ppm):** 24.69. **IR ν_{max} (cm^{-1}):** 1249 (P=O); 1057, 1029 (P-O). **MS m/z (%):** 282 (100, $[\text{M}+\text{H}]^+$). **Yield:** 58%.

Dimethyl 1-benzyl-3-benzyl-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (4c)

^1H NMR δ (300 MHz, ppm): 3.20-3.34 (1H, multiplet); 3.43 (1H, d (br.), J_{AB} = 16.2 Hz); 3.60 (1H, d, J_{AB} = 13.2 Hz); 3.63-3.76 (2H, multiplet); 3.80 (3H, d, J_{H-P} = 10.5 Hz); 3.82 (3H, d, J_{H-P} = 10.5 Hz); 3.89-3.94 (1H, multiplet); 4.13 (1H, d, J_{AB} = 13.2 Hz); 5.43-5.48 (1H, multiplet); 7.20-7.34 (10H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 35.3; 53.3 (d, J_{C-P} = 6.9 Hz); 53.4 (d, J_{C-P} = 8.1 Hz); 59.9 (d,

$J_{C-P} = 6.9$ Hz); 60.7 (d, $J_{C-P} = 6.9$ Hz); 69.0 (d, $J_{C-P} = 173.1$ Hz); 125.8 (d, $J_{C-P} = 11.5$ Hz); 126.4; 127.1; 128.3; 128.5; 128.7; 129.2; 137.7 (d, $J_{C-P} = 4.6$ Hz); 138.9; 139.2. **^{31}P NMR δ (121 MHz, ppm):** 24.69. **IR ν_{max} (cm^{-1}):** 1245 (P=O); 1056, 1029 (P-O). **MS m/z (%):** 358 (100, $[\text{M}+\text{H}]^+$) 248 (34, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Yield:** 62%.

Dimethyl 1-benzyl-3-isopentyl-2,5-dihydro-1H-pyrrol-2-ylphosphonate (4d)

^1H NMR δ (300 MHz, ppm): 0.90 (3H, ~t, $J = 6.7$ Hz); 1.25-1.38 (4H, multiplet); 1.42-1.55 (2H, multiplet); 2.06-2.31 (2H, multiplet); 3.20-3.34 (1H, multiplet); 3.63 (1H, d, $J_{AB} = 13.2$ Hz); 3.65-3.78 (1H, multiplet); 3.80 (3H, d, $J_{H-P} = 10.2$ Hz); 3.81 (3H, d, $J_{H-P} = 10.2$ Hz); 3.93-3.99 (1H, multiplet); 4.24 (1H, d, $J_{AB} = 13.2$ Hz); 5.51 (1H, s (br.)); 7.21-7.38 (5H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 14.2; 22.6; 27.3; 28.8; 31.6; 53.4 (d, $J_{C-P} = 6.9$ Hz); 60.0 (d, $J_{C-P} = 8.1$ Hz); 60.8 (d, $J_{C-P} = 6.9$ Hz); 69.9 (d, $J_{C-P} = 174.2$ Hz); 123.3 (d, $J_{C-P} = 11.5$ Hz); 127.0; 128.3; 128.7; 138.3 (d, $J_{C-P} = 4.6$ Hz); 139.5. **^{31}P NMR δ (121 MHz, ppm):** 24.91. **IR ν_{max} (cm^{-1}):** 1249 (P=O); 1058, 1032 (P-O). **MS m/z (%):** 338 (100, $[\text{M}+\text{H}]^+$) 228 (17, $[\text{M}+\text{H}-\text{PO}(\text{OMe})_2]^+$). **Yield:** 70%.

Dimethyl 1-benzyl-3-phenyl-2,5-dihydro-1H-pyrrol-2-ylphosphonate (4e)

Could only be isolated together with small amounts of pyrrole **5e** because of spontaneous oxidation during the work-up procedure and product handling. Spectral data given below are determined from the mixture and are indicative.

^1H NMR δ (300 MHz, ppm): 3.51 (3H, d, $J_{H-P} = 10.5$ Hz); 3.52-3.60 (1H, multiplet); 3.64 (3H, d, $J_{H-P} = 10.5$ Hz); 3.82 (1H, d, $J_{AB} = 13.2$ Hz); 3.93-4.05 (1H, multiplet); 4.15 (1H, d, $J_{AB} = 13.2$ Hz); 4.54-4.59 (1H, multiplet); 6.17-6.19 (1H, multiplet); 7.19-7.45 (10H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 53.2 (d, $J_{C-P} = 6.9$ Hz); 60.6 (d, $J_{C-P} = 4.5$ Hz); 61.2 (d, $J_{C-P} = 9.2$ Hz, CH_2Ph); 68.7 (d, $J_{C-P} = 173.1$ Hz); 127.0 (d, $J_{C-P} = 11.5$ Hz); 127.1; 127.2; 127.9; 128.3; 128.4; 128.8; 134.1; 137.5 (d, $J_{C-P} = 3.5$ Hz); 139.1. **^{31}P NMR δ (121 MHz, ppm):** 24.64.

Synthesis of 2-phosphono pyrroles **5**

Dimethyl 1-benzyl-3-methyl-1H-pyrrol-2-ylphosphonate (5b)

^1H NMR δ (300 MHz, ppm): 2.29 (3H, d, $J = 1.4$ Hz); 3.53 (6H, d, $J_{H-P} = 11.7$ Hz); 5.38 (2H, s); 6.07-6.09 (1H, multiplet); 6.82 (1H, dd, $J_{H-P} = 5.0$ Hz, $J = 2.5$ Hz); 7.07-7.35 (5H, multiplet). **^{13}C NMR δ (75 MHz, ppm):** 12.9; 52.0 (d, $J_{C-P} = 4.6$ Hz); 52.5; 111.3 (d, $J_{C-P} = 15.0$ Hz); 113.5 (d, $J_{C-P} = 226.1$ Hz); 126.9; 127.4; 128.5 (d, $J_{C-P} = 12.7$ Hz); 128.5; 133.47 (d, $J_{C-P} = 18.5$ Hz); 138.6. **^{31}P NMR δ (121 MHz, ppm):** 14.82. **IR ν_{max} (cm^{-1}):** 1249 (P=O); 1025 (br., P-O). **MS m/z (%):** 280 (100, $[\text{M}+\text{H}]^+$). **Chromatography:** Hex/EtOAc (2/3) $R_f = 0.27$. **Yield:** 84%.

Dimethyl 1,3-dibenzyl-1*H*-pyrrol-2-ylphosphonate (5c)

¹H NMR δ (300 MHz, ppm): 3.47 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 4.11 (2H, s); 5.38 (2H, s); 6.02 (1H, dd, $J_{\text{H-P}} = 4.2$ Hz, $J = 2.5$ Hz); 6.84 (1H, dd, $J_{\text{H-P}} = 5.0$ Hz, $J = 2.5$ Hz); 7.07–7.35 (10H, multiplet). **¹³C NMR δ (75 MHz, ppm):** 33.1; 52.1 (d, $J_{\text{C-P}} = 5.8$ Hz); 52.5; 110.9 (d, $J_{\text{C-P}} = 16.2$ Hz); 113.5 (d, $J_{\text{C-P}} = 226.0$ Hz); 125.7; 126.9; 127.4; 128.2; 128.5; 128.7 (d, $J_{\text{C-P}} = 11.5$ Hz); 128.8; 137.2 (d, $J_{\text{C-P}} = 18.5$ Hz); 138.4; 141.8. **³¹P NMR δ (121 MHz, ppm):** 14.39. **IR ν_{max} (cm⁻¹):** 1240 (P=O); 1023 (br., P-O). **MS m/z (%):** 356 (100, [M+H]⁺). **Chromatography:** Hex/EtOAc (2/3) $R_f = 0.29$. **Yield:** 72%.

Dimethyl 1-benzyl-3-isopentyl-1*H*-pyrrol-2-ylphosphonate (5d)

¹H NMR δ (300 MHz, ppm): 0.87-0.92 (3H, multiplet); 1.28-1.40 (4H, multiplet); 1.54 – 1.64 (2H, multiplet); 2.69 (2H, t, $J = 7.8$ Hz); 3.52 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 5.38 (2H, s); 6.13 (1H, dd, $J_{\text{H-P}} = 4.1$ Hz, $J = 2.8$ Hz); 6.84 (1H, dd, $J_{\text{H-P}} = 5.1$ Hz, $J = 2.8$ Hz); 7.06–7.32 (5H, multiplet). **¹³C NMR δ (75 MHz, ppm):** 14.2; 22.7; 27.0; 31.0; 31.9; 52.1 (d, $J_{\text{C-P}} = 5.8$ Hz); 52.5; 109.9 (d, $J_{\text{C-P}} = 15.0$ Hz); 112.9 (d, $J_{\text{C-P}} = 226.1$ Hz); 127.0; 127.4; 128.6; 128.7 (d, $J_{\text{C-P}} = 12.7$ Hz); 138.8; 139.4 (d, $J_{\text{C-P}} = 19.6$ Hz). **³¹P NMR δ (121 MHz, ppm):** 14.87. **IR ν_{max} (cm⁻¹):** 1250 (P=O); 1025 (br.) (P-O). **MS m/z (%):** 336 (100, [M+H]⁺). **Chromatography:** Hex/EtOAc (2/3) $R_f = 0.46$. **Yield:** 70%.

Dimethyl 1-benzyl-3-phenyl-1*H*-pyrrol-2-ylphosphonate (5e)

¹H NMR δ (300 MHz, ppm): 3.36 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 5.57 (2H, s); 6.29 (1H, dd, $J_{\text{H-P}} = 4.0$ Hz, $J = 2.5$ Hz); 6.94 (1H, dd, $J_{\text{H-P}} = 5.0$ Hz, $J = 2.5$ Hz); 7.19–7.46 (10H, multiplet). **¹³C NMR δ (75 MHz, ppm):** 52.1 (d, $J_{\text{C-P}} = 5.8$ Hz); 53.0; 111.0 (d, $J_{\text{C-P}} = 13.9$ Hz); 113.8 (d, $J_{\text{C-P}} = 226.1$ Hz); 126.9; 127.3; 127.6; 128.6; 128.7 (d, $J_{\text{C-P}} = 12.7$ Hz); 129.5; 136.0; 137.5 (d, $J_{\text{C-P}} = 18.5$ Hz); 138.3. **³¹P NMR δ (121 MHz, ppm):** 13.77. **IR ν_{max} (cm⁻¹):** 1249 (P=O); 1053, 1028 (br., P-O). **MS m/z (%):** 342 (100, [M+H]⁺). **Chromatography:** Hex/EtOAc (2/3) $R_f = 0.30$. **Yield:** 75%.

Dimethyl 1-benzyl-3-(2-phenylethyl)-1*H*-pyrrol-2-ylphosphonate (5f)

¹H NMR (300 MHz, ppm) δ: 2.87-2.92 (2H, multiplet), 3.01-3.06 (2H, multiplet); 3.47 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 5.37 (2H, s); 6.13 (1H, dd, $J = 4.1$ Hz, $J = 2.5$ Hz); 6.84 (1H, dd, $J = 5.0$ Hz, $J = 2.5$ Hz); 7.03-7.35 (10H, multiplet). **¹³C NMR (75 MHz, ppm) δ:** 29.2; 37.9; 52.1 (d, $J_{\text{C-P}} = 5.8$ Hz); 52.5; 110.1 (d, $J_{\text{C-P}} = 16.2$ Hz); 113.3 (d, $J_{\text{C-P}} = 225.0$ Hz); 125.8; 126.8; 127.5; 128.3; 128.6; 128.6 (d, $J_{\text{C-P}} = 12.7$ Hz); 128.8; 138.2 (d, $J_{\text{C-P}} = 19.6$ Hz); 138.8; 142.3. **³¹P NMR (121 MHz, ppm) δ:** 14.52. **IR ν_{max} (cm⁻¹):** 1248 (P=O), 1025 (P-O). **MS: m/z (%):** 370.2 (100, [M+H]⁺). **Elem. Anal.** Calc. for C₂₁H₂₄NO₃P: C68.28, H6.55, N3.79; found: C68.43, H6.49, N3.54. **Chromatography:** Hex/EtOAc (6/4) $R_f = 0.27$. **Yield:** 71%.

Synthesis of 1H-pyrrol-2-ylphosphonates **11**

To an oven-dry round-bottom flask, 0.61 mmol of aminoalkenyl phosphonate **2** is added together with 6 ml of dry dichloromethane and 149 mg (0.61 mmol) of TCQ. The solution is stirred under a nitrogen atmosphere and 25.7 mg (5 mol%) of Grubbs' second generation catalyst **6** is added. The reaction mixture is then stirred 23 hours at reflux temperature. The course of the reaction is conveniently monitored via ^{31}P NMR spectra of samples directly from the reaction mixture. When complete conversion is obtained, the solvent is removed under reduced pressure. The pyrroles **11** are obtained in pure form as brownish oils using column chromatography on silica gel with hexane, ethyl acetate mixture as a mobile phase.

Dimethyl 1H-pyrrol-2-ylphosphonate (**11a**)

^1H -NMR δ (300 MHz, ppm): 3.73 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 6.29-6.33 (1H, multiplet); 6.73-6.76 (1H, multiplet); 7.07-7.10 (1H, multiplet). ^{13}C -NMR δ (75 MHz, ppm): 53.0 (d, $J_{\text{C-P}} = 5.8$ Hz); 109.9 (d, $J_{\text{C-P}} = 15.0$ Hz); 115.2 (d, $J_{\text{C-P}} = 230.8$ Hz); 118.7 (d, $J_{\text{C-P}} = 17.3$ Hz); 124.6 (d, $J_{\text{C-P}} = 12.7$ Hz). ^{31}P -NMR δ (121 MHz, ppm): 15.01. IR ν (cm^{-1}): 3199 (NH); 1244 (P=O); 1029 (br.) (P-O). MS^{ESI} m/z (%): 175 (100, M^+); 130 (30), 80 (87), 67 (47). Chromatography: EtOAc; $R_f = 0.20$. Yield: 39%.

Dimethyl 3-isopentyl-1H-pyrrol-2-ylphosphonate (**11d**)

^1H -NMR δ (300 MHz, ppm): 0.86-0.92 (3H, multiplet); 1.25-1.41 (4H, multiplet); 1.52-1.63 (2H, multiplet); 2.58 (2H, t, $J = 7.8$ Hz); 3.71 (6H, d, $J_{\text{H-P}} = 11.6$ Hz); 6.18-6.21 (1H, multiplet); 6.93-6.97 (1H, multiplet). ^{13}C -NMR δ (75 MHz, ppm): 14.0; 22.5; 26.3; 30.6; 31.7; 52.4 (d, $J_{\text{C-P}} = 5.8$ Hz); 110.8 (d, $J_{\text{C-P}} = 15.0$ Hz); 111.7 (d, $J_{\text{C-P}} = 229.6$ Hz); 123.4 (d, $J_{\text{C-P}} = 11.5$ Hz); 135.2 (d, $J_{\text{C-P}} = 18.5$ Hz). ^{31}P -NMR δ (121 MHz, ppm): 16.21. IR ν (cm^{-1}): 3215 (NH); 1245 (P=O); 1030, 1053 (P-O). MS m/z (%): 246 (100, $[\text{M}+\text{H}]^+$). Chromatography: Hex/EtOAc (2/3) $R_f = 0.23$. Yield: 27%. Purity: 90%.

Sample spectra

Dimethyl (2*E*)-1-(allylamino)-3-phenylprop-2-enylphosphonate (2a)

Dimethyl (2*E*)-1-(allylamino)-2-methyl-3-phenyl-propenylphosphonate (2b)

Dimethyl (2*E*)-1-(allylamino)-2-benzyl-but-2-enylphosphonate (2c)

Dimethyl 1-(allylamino)-2-isopentyl-3-phenyl-propenylphosphonate (2d)

Dimethyl (2*E*)-1-(allylamino)-2-phenyl-but-2-enylphosphonate (E-(2e))

Dimethyl (2Z)-1-(allylamino)-2-phenyl-but-2-enylphosphonate (Z-(2e))

Dimethyl (2*E*)-1-[(2-methylprop-2-enyl)amino]-3-phenylprop-2-enylphosphonate (2g)

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-3-phenylprop-2-enylphosphonate (3a)

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-methyl-3-phenyl-prop-2-enylphosphonate (3b)

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-benzyl-but-2-enylphosphonate (3c)

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-isopentyl-3-phenyl-prop-2-enylphosphonate (*E*-(3d))

Dimethyl (2Z)-1-(allyl(benzyl)amino)-2-isopentyl-3-phenyl-prop-2-enylphosphonate (Z-(3d))

Dimethyl (2*E*)-1-(allyl(benzyl)amino)-2-phenyl-but-2-enylphosphonate (3e)

Dimethyl (2*E*)-1-[benzyl(2-methylprop-2-enyl)amino]-3-phenylprop-2-enylphosphonate (3g)

Dimethyl 1-benzyl-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (4a)

Dimethyl 1-benzyl-3-methyl-2,5-dihydro-1H-pyrrol-2-ylphosphonate (4b)

Dimethyl 1-benzyl-3-benzyl-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (4c)

Dimethyl 1-benzyl-3-isopentyl-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (4d)

Dimethyl 1-benzyl-1H-pyrrol-2-ylphosphonate (5a)

Dimethyl 1-benzyl-3-methyl-1H-pyrrol-2-ylphosphonate (5b)

Dimethyl 1,3-dibenzyl-1H-pyrrol-2-ylphosphonate (5c)

Dimethyl 1-benzyl-3-isopentyl-1H-pyrrol-2-ylphosphonate (5d)

Dimethyl 1-benzyl-3-phenyl-1H-pyrrol-2-ylphosphonate (5e)

Dimethyl 1H-pyrrol-2-ylphosphonate (11a)