Supporting Information

Diastereotopic Differentiation on Phosphorus Templates via the Ring-Closing Metathesis Reaction

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Experimental Section

General Methods.

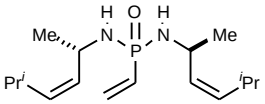
All reactions were carried out in flame-dried glassware under argon. CH_2Cl_2 was purified by passage through the Solv-Tek purification system employing activated Al_2O_3. Toluene and Et_3N and DME were distilled from CaH_2. Flash column chromatography was performed with Merck silica gel (EM-9385-9, 230-400 mesh). Thin layer chromatography was performed out on silica gel $60F_{254}$ plates (EM-5717, Merck). ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 100 MHz, and 162 MHz respectively. High resolution mass spectrometry (HRMS) and FAB spectra were obtained on a VG Instrument ZAB double-focusing mass spectrometer.

General procedure for formation of phosphonamides 1a-g, **2a-c** and phosphonate **3.** To a solution of the corresponding phosphonodichloridate in CH_2Cl_2[1] or toluene[2] was

(1) Compounds **1a**, **f** and **g** were prepared in CH_2Cl_2.
(2) Toluene was used for compounds **1b-e**, **2a-d** and **3**.

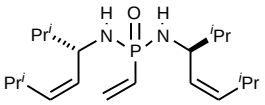
added Et_3N at 0 °C. After stirring for 20 min at RT the mixture was cooled to –50 °C and a solution of the amine or alcohol[3] in toluene or amine hydrochloride in CH_2Cl_2 was added via cannulae. The mixture was allowed to warm up slowly to -20 °C and was stirred at this temperature for 2-4 additional hours. The reaction mixture was quenched with brine, extracted with EtOAc and dried with Na_2SO_4. Removal of the solvent and chromatography afforded bisphosphonamides **1a-g**, **2a-c** and phosphonate **3.**

Vinylbisphosphonamide 1a (R^1=*Z*-^{i}Pr, R^2=Me)



Flash chromatography (EtOAc/2% MeOH) yielded 65.0% **1a**; $[\alpha]_D$ +86.0 (*c* 4.2, CH_2Cl_2); ^{1}H NMR δ 6.20-5.84 (m, 3H), 5.10-5.01 (m, 4H), 4.16-4.02 (m, 2H), 2.62-2.51 (m, 2H), 2.26-2.16 (m, 2H), 1.16 (d, *J* = 6.5 Hz), 1.14 (d, *J* = 6.5 Hz)(6H), 0.92 (d, *J* = 6.6 Hz), 0.88 (d, *J* = 6.5 Hz), 0.87 (d, *J* = 6.7 Hz), 0.85 (d, *J* = 6.7 Hz)(12H); ^{13}C NMR δ 136.5 (d), 136.3 (d), 132.7 (t), 131.8 (dd, J_p = 4.7), 131.5 (dd, J_p = 146.9), 131.4 (dd, J_p = 5.0), 44.0 (d), 43.9 (d), 26.72 (d), 26.69 (d), 25.1 (dq, J_p = 5.5), 25.0 (dd, J_p = 5.8), 23.22 (q), 23.19 (q), 22.9 (q), 22.8 (q); ^{31}P NMR δ 17.20; IR (neat) 3202, 2960, 2927, 2867, 1460, 1366, 1189, 1124, 1078, 994 cm^{-1}; Exact mass: calculated for $C_{16}H_{32}N_2OP$ (M+1) 299.2252; found 299.2233 (FAB).

Vinylbisphosphonamide 1b (R^1=*Z*-^{i}Pr, R^2=^{i}Pr)

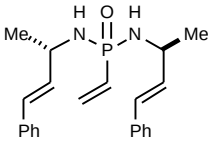


Flash chromatography (EtOAc/2% MeOH) yielded 60.5% **1b**; $[\alpha]_D$ +91.4 (*c* 3.7, CH_2Cl_2); ^{1}H NMR δ 6.26-5.88 (m, 3H), 5.22-5.15 (m, 2H), 5.08-5.00 (m, 2H), 3.90-3.70 (m, 2H), 2.61-2.54 (m, 2H), 2.17 (br. s, 2H), 1.71-1.62 (m, 2H), 0.98-0.86 (m, 24H); ^{13}C NMR δ 138.1 (d), 137.8 (d), 132.9 (t), 131.6 (dd, J_p = 147.6), 128.1 (dd, J_p = 3.1), 127.6 (dd, J_p = 3.5), 53.4 (d), 53.1 (d), 34.4 (dd, J_p = 5.6), 34.3 (dd, J_p = 6.2), 27.0 (d), 26.8 (d), 22.9 (q), 22.8 (q), 18.9 (q), 18.9 (q), 18.6 (q), 18.1 (q), 17.8 (q); ^{31}P NMR δ 17.60; IR (CH_2Cl_2)

(3) Catalitic amount of DMAP was used for the phosphonate **3**.

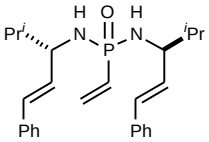
3392, 3052, 2958, 2930, 2870, 1465, 1420, 1395, 1265, 1201, 1132, 1054, 989, 896 cm^{-1}; Exact mass: calculated for $C_{20}H_{40}N_2OP$ (M+1) 355.2878; found 355.2870 (FAB).

Vinylbisphosphonamide 1c (R=*E*-Ph, R^2=Me)



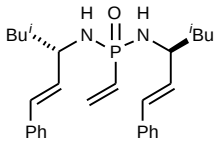
Flash chromatography (EtOAc/2% MeOH) yielded 65.3% **1c**; $[\alpha]_D$ –100.0 (*c* 1.2, CH_2Cl_2); ^{1}H NMR δ 7.32-7.18 (m, 10H), 6.48 (dd, *J* = 15.9, 0.8 Hz), 6.46 (dd, *J* = 15.9, 0.7 Hz)(2H), 6.33-6.11 (m, 4H), 6.00 (ddd, *J* = 44.9, 11.9, 2.8 Hz, 1H), 4.10-3.98 (m, 2H), 2.60-2.55 (m, 2H), 1.35 (d, *J* = 6.9 Hz), 1.34 (d, *J* = 6.3 Hz)(6H); ^{13}C NMR δ 136.6 (s), 136.5 (s), 133.7 (dd, J_p = 5.4), 133.6 (dd, J_p = 4.9), 133.1 (t), 131.1 (dd, J_p = 148.1), 128.4 (d), 127.3 (d), 127.26 (d), 126.18 (d), 126.1 (d), 48.2 (d), 47.9 (d), 23.9 (dq, J_p = 4.6), 23.8 (dq, J_p = 4.8); ^{31}P NMR δ 17.56; IR (CH_2Cl_2) 3390, 3020, 2880, 2773, 1679, 1601, 1493, 1195, 1089, 999, 967, 851 cm^{-1}; Exact mass: calculated for $C_{22}H_{28}N_2OP$ (M+1) 367.1939; found 367.1933 (FAB).

Vinylbisphosphonamide 1d (R^1=*E*-Ph, R^2=^{i}Pr)



Flash chromatography (EtOAc/4% MeOH) yielded 63.2% **1d**; $[\alpha]_D$ –64.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR δ 7.33-7.20 (m, 10H), 6.48 (d, *J* = 15.9 Hz, 2H), 6.31-5.90 (m, 5H), 3.80-3.63 (m, 2H), 2.56-2.47 (m, 2H), 1.89-1.81 (m, 2H), 0.95 (d, *J* = 6.7 Hz), 0.94 (d, *J* = 6.8 Hz), 0.92 (d, *J* = 6.7 Hz)(12H); ^{13}C NMR δ 136.8 (s), 136.7 (s), 133.3 (t), 131.2 (dd, J_p = 149.1), 130.8 (dd, J_p = 3.1), 130.6 (d), 130.5 (d), 128.5 (d), 128.4 (d), 127.3 (d), 126.3 (d), 126.2 (d), 58.6 (d), 58.1 (d), 34.2 (dd, J_p = 5.2), 34.1 (dd, J_p = 5.6), 18.6 (q), 18.4 (q), 18.3 (q), 18.2 (q); ^{31}P NMR δ 17.93; IR (neat) 3210, 3026, 2860, 1600, 1494, 1448, 1411, 1265, 1188, 1064, 966 cm^{-1}; Exact mass: calculated for $C_{26}H_{36}N_2OP$ (M+1) 423.2565; found 423.2567 (FAB).

Vinylbisphosphonamide 1e (R^1=*E*-Ph, R^2=^{i}Bu)



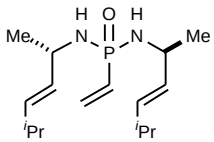
Flash chromatography (EtOAc/2% MeOH) yielded 60.0% **1e** as white solid; m.p. 118-119 ˚C; $[\alpha]_D$ –75.8 (*c* 2.0, CH_2Cl_2); ^{1}H NMR δ 7.33-7.20 (m, 10H), 6.47 (d, *J* = 15.7 Hz, 2H), 6.26-5.94 (m, 5H), 4.10-3.81 (m, 2H), 2.48-2.38 (m, 2H), 1.74-1.71 (m, 2H), 1.49-1.40 (m, 4H), 0.94-0.90 (m, 12H); ^{13}C NMR δ 136.7 (s), 136.6 (s), 133.1 (t), 132.9 (dd, J_p = 3.2), 132.7 (dd, J_p = 3.2), 131.5 (dd, J_p = 148.6), 129.4 (d), 129.3 (d), 128.4 (d), 127.3 (d), 126.2 (d), 126.1 (d), 51.5 (d), 51.1 (d), 47.2 (t), 47.1 (t), 24.5 (d), 22.70 (q), 22.67 (q), 22.28 (q), 22.25 (q); ^{31}P NMR δ 17.17; IR (CH_2Cl_2) 3389, 3018, 2904, 2773, 1600, 1369, 1197, 1085, 969, 839 cm^{-1}; Exact mass: calculated for $C_{28}H_{40}N_2OP$ (M+1) 451.2878; found 451.2853 (FAB).

Vinylbisphosphonamide 1f (R^1=*E*-^{i}Pr, R^2=Me)

Synthesis of the starting allylic amine

To a solution of N-trityl alaninal and the 1-phenyl-1-*H*-tetrazol-5-yl-sulfone (2 eq) in DME was added NaHMDS (1M solution in THF, 2 eq) at –55 ˚C over 20 min. The reaction mixture was stirred at this temperature for 3 hrs, quenched with water and extracted with ether. Flash chromatography (95% Hexanes/ EtOAc) yielded 70.4% (2*S*)(3*E*)-2-(N-Tritylamino)-5-methyl-3-hexene. Treatment of this compound with TFA in CH_2Cl_2, followed by formation of the hydrochloride gave 70% product as white solid; ^{1}H NMR δ 8.37 (br. s, 3H), 5.80 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.50 (dd, *J* =15.5, 6.8 Hz, 1H), 3.84-3.81 (m, 2H), 2.33-2.28 (m, 1H), 1.48 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 6.6 Hz), 0.98 (d, *J* = 6.7 Hz), (6H).

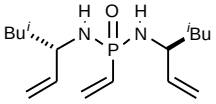
Data for vinylbisphosphonamide 1f



Flash chromatography (EtOAc/2% MeOH) yielded 62.9% **1f**; $[\alpha]_D$ –20.5 (*c* 4.2, CH_2Cl_2); ^{1}H NMR δ 6.20-6.59 (m, 2H), 5.90 (ddd, *J* = 44.6, 11.8, 3.0 Hz, 1H), 5.46-5.39 (m, 2H), 5.28 (dd, *J* = 15.5, 5.6 Hz, 2H), 3.76-3.66 (m, 2H), 2.24-2.13 (m, 4H), 1.15 (d, *J* = 6.6 Hz), 1.14 (d, *J* = 6.6 Hz)(6H), 0.89 (d, *J* = 6.7 Hz), 0.88 (d, *J* = 6.7 Hz)(12H); ^{13}C NMR δ

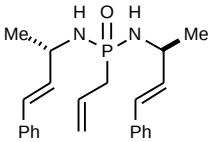
136.2 (d), 132.5 (t), 131.5 (dd, J_p = 148.3), 131.1 (dd, J_p = 5.1), 130.9 (dd, J_p = 5.0), 47.8 (d), 47.6 (d), 30.5 (d), 24.1 (dq, J_p = 3.4), 24.0 (dq, J_p = 3.6), 22.2 (q); ^{31}P NMR δ 17.35; IR (neat) 3213, 2982, 2869, 1680, 1431, 1177, 1080, 971 cm^{-1}; Exact mass: calculated for $C_{16}H_{32}N_2OP$ (M+1) 299.2252; found 299.2225 (FAB).

Vinylbisphosphonamide 1g (R^1=H, R^2= ^{i}Bu)



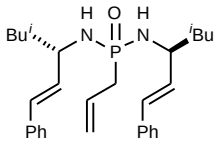
Flash chromatography (EtOAc/2% MeOH) yielded 77.2% **1g** as white solid; m.p. 42-44 ˚C; $[\alpha]_D$ +20.7 (*c* 4.1, CH_2Cl_2); ^{1}H NMR δ 6.30-5.94 (m, 3H), 5.81-5.69 (m, 2H), 5.15 (dd, *J* = 17.1, 1.2 Hz, 2H), 5.07-5.03 (m, 2H), 3.72-3.64 (m, 2H), 2.15 (br. s, 2H), 1.74-1.66 (m, 2H), 1.40-1.28 (m, 4H), 0.91 (d, *J* = 6.5 Hz), 0.90 (d, *J* = 6.5 Hz), 0.90 (d, *J* = 6.5 Hz), 0.89 (d, *J* = 6.5 Hz)(12H); ^{13}C NMR δ 141.3 (dd, J_p = 2.9), 141.1 (dd, J_p = 3.3), 132.5 (t), 131.2 (dd, J_p = 149.4), 113.49 (t), 113.46 (t), 51.4 (d), 51.1 (d), 46.6 (dt, J_p = 5.1), 46.5 (dt, J_p = 5.7), 24.1 (d), 22.4 (q), 22.3 (q), 22.1 (q); ^{31}P NMR δ 17.22; IR (CH_2Cl_2) 3395, 3040, 2955, 1641, 1607, 1395, 1200, 1067, 992, 928 cm^{-1}; Exact mass: calculated for $C_{16}H_{32}N_2OP$ (M+1) 299.2252; found 299.2249 (FAB).

Allylbisphosphonamide 2a (R^1=*E*-Ph, R^2=Me)



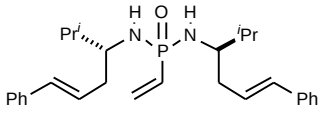
Flash chromatography (EtOAc/2% MeOH) yielded 57.3% **2a**; $[\alpha]_D$ –85.0 (c 0.2, CH_2Cl_2); ^{1}H NMR δ 7.33-7.19 (m, 10H), 6.52 (dd, *J* = 15.9, 0.8 Hz), 6.47 (dd, *J* = 15.9, 1.2 Hz)(2H), 6.20 (dd, *J* = 15.9, 6.0 Hz), 6.15 (dd, *J* = 15.9, 6.0 Hz)(2H), 5.96-5.87 (m, 1H), 5.20-5.14 (m, 2H), 4.13-4.03 (m, 2H), 2.62 (ddd, *J* = 19.4, 7.5, 1.3 Hz, 2H), 2.52-2.40 (m, 2H), 1.37 (d, *J* = 6.7 Hz), 1.34 (d, *J* = 6.7 Hz)(6H); ^{13}C NMR δ 136.6 (s), 136.5 (s), 133.8 (dd, J_p = 5.4), 133.7 (dd, J_p = 3.7), 129.7 (dd, J_p = 10.0), 128.5 (d), 128.46 (d), 127.5 (d), 1274 (d), 126.3 (d), 126.2 (d), 119.2 (dt, J_p = 13.2), 48.2 (d), 47.8 (d), 36.1 (dt, J_p = 109.0), 24.1 (dq, J_p = 4.1), 23.9 (dq, J_p = 5.2); ^{31}P NMR δ 25.30; IR (CH_2Cl_2) 3394, 3053, 2980, 1636, 1598, 1493, 1414, 1264, 1190, 1071, 968 cm^{-1}; Exact mass: calculated for $C_{23}H_{30}N_2OP$ (M+1) 381.2096; found 381.2086 (FAB).

Allylbisphosphonamide 2b (R^1=*E*-Ph, R^2= ^{i}Bu)



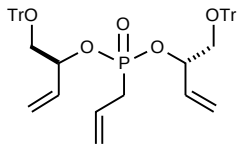
Flash chromatography (EtOAc/2% MeOH) yielded 43.3% **2b**; $[\alpha]_D$ –20.7 (c 4.0, CH_2Cl_2); ^{1}H NMR δ 7.34-7.19 (m, 10H), 6.52 (d, *J* = 16.2 Hz, 1H), 6.48 (d, *J* = 16.4 Hz, 1H), 6.09-6.00 (m, 2H), 5.90-5.82 (m, 1H), 5.15-5.07 (m, 2H), 4.01-3.91 (m, 2H), 2.62-2.49 (m, 2H), 2.38 (br. t, 1H), 2.29 (br. t, 1H), 1.74-1.65 (m, 2H), 1.54-1.32 (m, 4H), 0.93 (d, *J* = 6.3 Hz), 0.91 (d, *J* = 5.7 Hz), 0.88 (d, *J* = 6.6 Hz)(12H); ^{13}C NMR δ 136.8 (s), 136.6 (s), 133.0 (dd, J_p = 3.3), 132.8 (d), 130.2 (dd, J_p = 9.8), 129.7 (d), 129.5 (d), 128.6 (d), 128.5 (d), 127.5 (d), 127.4 (d), 126.3 (d), 119.0 (dt, J_p = 13.2), 51.6 (d), 50.9 (d), 47.3 (dt, J_p = 5.3), 47.11 (dt, J_p = 6.5), 36.4 (dt, J_p = 108.8), 24.7 (d), 22.9 (q), 22.8 (q), 22.3 (q), 22.2(q); ^{31}P NMR δ 24.58; IR (CH_2Cl_2) 3396, 3054, 2985, 1422, 1264, 1064, 967, 895 cm^{-1}; Exact mass: calculated for $C_{29}H_{42}N_2OP$ (M+1) 465.3035; found 465.3031 (FAB).

Vinylbisphosphonamide 2c (R^1=*E*-Ph, R^2=^{i}Pr)



Flash chromatography (EtOAc/1% MeOH) yielded 48.9% **2c**; $[\alpha]_D$ +17.9 (*c* 7.7, CH_2Cl_2); ^{1}H NMR δ 7.35-7.18 (m, 10H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.30-5.98 (m, 5H), 5.90 (ddd, *J* = 44.8, 12.2, 2.8 Hz, 1H), 3.17-3.07 (m, 2H), 2.37-2.22 (m, 3H), 2.17-2.05 (m, 3H), 1.75-1.70 (m, 2H), 0.91 (d, *J* = 6.8 Hz), 0.90 (d, *J* = 6.8 Hz), 0.86 (d, *J* = 6.8 Hz), 0.85 (d, *J* = 6.8 Hz) (12H); ^{13}C NMR δ 137.3 (s), 137.2 (s), 132.9 (t), 132.2 (d), 132.1 (dd, J_p = 150.4), 128.5 (d), 128.4 (d), 127.6 (d), 127.5 (d), 127.1 (d), 127.0 (d), 126.0 (d), 125.9 (d), 56.01 (d), 55.99 (d), 38.0 (dt, J_p = 3.1), 37.7 (dt, J_p = 3.7), 32.7 (dd, J_p = 4.1), 32.4 (dd, J_p = 4.8), 19.1 (q), 18.9 (q), 17.7 (q), 17.6 (q); ^{31}P NMR δ 16.75; IR (CH_2Cl_2) 3393, 3053, 2885, 2962, 1598, 1494, 1419, 1264, 1203, 1040, 968, 895 cm^{-1}; Exact mass: calculated for $C_{28}H_{40}N_2OP$ (M+1) 451.2878; found 451.2871 (FAB).

Allylbisphosphonate 3

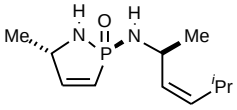


Flash chromatography (80% Hexanes/EtOAc yielded 65.2% **3a**; $[\alpha]_D$ –2.9 (*c* 3.4, CH_2Cl_2); ^{1}H NMR δ 7.46-7.30 (m, 12H), 7.29-7.17 (m, 18H), 5.94-5.84 (m, 1H), 5.81-5.66 (m, 2H), 5.36 (d, *J* = 17.2 Hz, 1H), 5.26-5.20 (m, 2H), 5.12-4.96 (m, 5H), 3.24-3.10 (m, 4H), 2.66 (dd, *J* = 22.3, 7.3 Hz, 2H); ^{13}C NMR δ 143.7 (s), 143.6 (s), 134.7 (dd, J_p = 2.7), 134.5 (dd, J_p = 2.9), 128.7 (d), 127.8 (d), 127.7 (d), 127.0 (d), 126.9 (d), 119.7 (dt, J_p = 14.9), 118.2 (t), 118.0 (t), 86.7 (s), 86.6 (s), 76.4 (dd, J_p = 6.4), 76.1 (dd, J_p = 6.5), 66.3 (dt, J_p = 5.6), 66.1 (dt, J_p = 5.8), 33.0 (dt, J_p = 140.9) ; ^{31}P NMR δ 27.98; IR (CH_2Cl_2) 3054, 2985, 1490, 1448, 1421, 1264, 1079, 986, 896 cm^{-1}.

General procedure for RCM of bisphosphonamides 1a-g, **2a-c** and phosphonate **3.**

To 0.01 M solution of the corresponding bisphosphonamide in CH_2Cl_2 was added catalyst **4** at RT. After completion of the reaction (TLC) the mixture was diluted with CH_2Cl_2, flushed with air and stirred overnight at RT. Removal of the solvent and chromatography afforded the cyclic phosphonamides **5a-g**, **6a-c** and phosphonate **7.**

Vinylbisphosphonamide 5a (R^1=*Z*-^{i}Pr, R^2=Me) major diastereoisomer



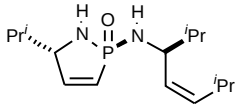
RCM reaction conditions: 3.0 h reflux, 3 mol% **4**. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 2.6:1. Flash chromatography (EtOAc/4% MeOH) yielded 63.6% **5a** as white solid; m.p. 137-39 ˚C; $[\alpha]_D$ +213.8 (*c* 5.2, CH_2Cl_2); ^{1}H NMR δ 6.75 (ddd, *J* = 41.9, 8.4, 1.4 Hz, 1H), 5.98 (dddd, *J* = 28.3, 8.4, 1.6, 1.5 Hz, 1H), 5.16-5.05 (m, 2H), 4.00-3.95 (m, 1H), 3.81-3.74 (m, 1H), 2.99 (br. d, *J* = 10.9 Hz, 1H), 2.58 (br. t, *J* = 8.3 Hz, 1H), 2.54-2.45 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz), 0.89 (d, *J* = 6.7 Hz) (6H); ^{13}C NMR δ 149.8 (dd, J_p = 16.3), 136.1 (d), 132.1 (dd, J_p = 3.4) 121.4 (dd, J_p = 142.9), 53.7 (dd, J_p = 20.0), 44.5 (d), 26.7 (d), 24.6 (dq, J_p = 7.2), 23.3 (q), 23.1 (q), 22.7 (q); ^{31}P NMR δ 38.68; IR (CH_2Cl_2) 3440, 3404, 3052, 2973, 2927, 2869, 1584, 1421, 1371, 1264, 1193, 1072, 1002, 895 cm^{-1}; Exact mass: calculated for $C_{11}H_{22}N_2OP$ (M+1) 229.1470; found 229.1465 (FAB).

Vinylbisphosphonamide 5a (R^1=*Z*-^{i}Pr, R^2=Me) minor diastereoisomer

Flash chromatography (EtOAc/10% MeOH) yielded 21.9% **5a**; ^{1}H NMR δ 6.70 (dddd, *J* = 42.3, 8.4, 1.4, 1.5 Hz, 1H), 5.95 (dddd, *J* = 28.5, 8.4, 1.8, 1.7 Hz, 1H), 5.14-5.03 (m,

2H), 4.14-4.11 (m, 1H), 3.86-3.82 (m, 1H), 3.11 (br. d, J = 9.6 Hz, 1H), 2.59 (br. t, J = 9.4 Hz, 1H), 2.48-2.43 (m, 1H), 1.25 (d, J = 6.7 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 0.90 (d, J = 6.7 Hz), 0.89 (d, J = 6.5 Hz) (6H); ^{13}C NMR δ 149.5 (dd, J_p = 15.3), 136.1 (d), 131.6 (dd, J_p = 4.4) 121.8 (dd, J_p = 142.0), 52.7 (dd, J_p = 20.2), 44.7 (d), 26.9 (d), 24.9 (dq, J_p = 5.5), 23.2 (q), 22.8 (q), 22.1 (dq, J_p = 4.1); ^{31}P NMR δ 39.84.

Vinylbisphosphonamide 5b (R^1=*Z*-^{i}Pr, R^2= ^{i}Pr) major diastereoisomer

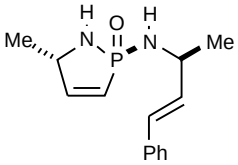


RCM reaction conditions: 2.5 h reflux, 3 mol% **4**. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 5.0:1. Flash chromatography (EtOAc/4% MeOH) yielded 79.8% **5b**; $[\alpha]_D$ +203.0 (*c* 2.3, CH_2Cl_2); ^{1}H NMR δ 6.80 (dddd, J = 42.5, 8.5, 1.7 Hz, 1H), 6.04 (dddd, J = 28.1, 8.5, 1.7 Hz, 1H), 5.19 (dd, J = 10.7, 10.4 Hz, 1H), 5.10 (dd, J = 10.9, 9.5 Hz, 1H), 3.79-3.74 (m, 1H), 3.33-3.24 (m, 1H), 2.84 (br. d, J = 11.0 Hz, 1H), 2.57-2.45 (m, **1**H), 1.82-1.76 (m, 1H), 1.58-1.50 (m, 1H),1.25-0.98 (m, 1H), 0.96-0.84 (m, 18H); ^{13}C NMR δ 147.1 (dd, J_p = 16.2), 136.9 (d), 129.2 (dd, J_p = 1.7), 122.6 (dd, J_p = 146.4), 64.0 (dd, J_p = 18.2), 54.1 (d), 34.1 (dd, J_p = 6.9), 32.9 (d), 26.8 (d), 23.2 (q), 22.9 (q), 18.9 (q), 18.8 (q), 18.4 (q), 17.6 (q); ^{31}P NMR δ 39.58; IR (neat) 3220, 2959, 2868, 1464, 1380, 1246, 1188, 1082, 1027, 929 cm^{-1}; Exact mass: calculated for $C_{15}H_{30}N_2OP$ (M+1) 285.2096; found 285.2082 (FAB).

Vinylbisphosphonamide 5b (R^1=*Z*-^{i}Pr, R^2= ^{i}Pr) minor diastereoisomer

Flash chromatography (EtOAc/4% MeOH) yielded 15.7% **5b**; ^{1}H NMR δ 6.82 (dd, J = 42.6, 8.5 Hz, 1H), 6.02 (dddd, J = 28.4, 8.5, 2.0, 1.6 Hz, 1H), 5.16 (dd, J = 10.5, 10.4 Hz, 1H), 5.07 (dd, J = 10.9, 9.5 Hz, 1H), 3.77 (br. d, J = 5.7 Hz, 1H) 3.61-3.53 (m, 1H), 2.97 (br. d, J = 7.8 Hz, 1H), 2.53 (br. t, J = 10.1 Hz, 1H), 2.45-2.39 (m, 1H), 1.72-1.59 (m, 2H), 1.00-0.89 (m, 18H); ^{13}C NMR δ 147.3 (dd, J_p = 14.6), 137.5 (d), 128.2 (dd, J_p = 3.3), 123.0 (dd, J_p = 141.3), 63.1 (dd, J_p = 18.2), 53.9 (d), 34.4 (dd, J_p = 5.4), 33.5 (dd, J_p = 4.6), 27.1 (q), 22.9 (q), 22.8 (q), 18.9 (q), 18.7 (q), 18.4 (q), 18.3 (q); ^{31}P NMR δ 40.69; Exact mass: calculated for $C_{15}H_{30}N_2OP$ (M+1) 285.2096; found 285.2081 (FAB).

Vinylbisphosphonamide 5c (R^1=*E*-Ph, R^2=Me), major diastereoisomer

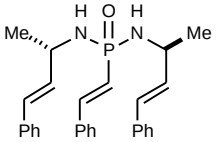


RCM reaction conditions: 24 h reflux, 6 mol% **4**[4]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 12:1. Flash chromatography (EtOAc/4% MeOH) yielded 68.7% **5c** as white solid; m.p. 160-61 ˚C**;** ; $[\alpha]_D$ +49.0 (*c* 2.0, CH_2Cl_2); ^{1}H NMR δ 7.35-7.19 (m, 5H), 6.77 (ddd, *J* = 42.1, 8.4, 2.0 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.99 (ddd, *J* = 28.5, 8.4, 1.8 Hz, 1H), 4.00-3.97 (m, 1H), 3.60-3.55 (m, 1H), 3.16 (br. d, *J* = 11.2 Hz, 1H), 2.76 (br. t, *J* = 9.2 Hz, 1H), 1.26 (d, *J* = 6.8 Hz), 1.24 (d, *J* = 6.8 Hz)(6H); ^{13}C NMR δ 150.0 (dd, J_p = 16.3), 136.7 (s), 134.0 (dd, J_p = 3.5), 128.5 (d), 127.9 (d), 127.4 (d), 126.2 (d), 121.0 (dd, J_p = 143.3), 53.7 (dd, J_p = 20.0), 48.8 (d), 23.7 (dq, J_p = 6.2), 22.6 (q); ^{31}P NMR δ 38.83; IR (CH_2Cl_2) 3423, 2890, 1594, 1493, 1372, 1192, 1069, 966, 855 cm^{-1}**;** Exact mass: calculated for $C_{14}H_{20}N_2OP$ (M+1) 263.1314; found 263.1286 (FAB).

Vinylbisphosphonamide 5c (R^1=*E*-Ph, R^2=Me), minor diastereoisomer

Flash chromatography (EtOAc/10% MeOH) yielded 6.0% **5c**; $[\alpha]_D$ –284.0 (*c* 0.44, CH_2Cl_2); ^{1}H NMR δ 7.35-7.21 (m, 5H), 6.71 (dd, *J* = 42.6, 8.4 Hz, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 5.5 Hz, 1H), 5.99 (dd, *J* = 28.4, 8.4 Hz, 1H), 4.16-14 (m, 1H), 3.76 (br.s, 1H), 3.09-3.07 (m, 1H), 2.68 (br. s, 1H), 1.32 (d, *J* = 6.7 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR δ 159.8 (dd, J_p = 21.5), 136.7 (s), 133.7 (dd, J_p = 3.8), 128.6 (d), 128.5 (d), 127.5 (d), 126.3 (d), 121.6 (dd, J_p = 143.4), 52.8 (dd, J_p = 20.2), 48.8 (d), 23.7 (dq, J_p = 5.2), 22.1 (dq, J_p = 3.6); ^{31}P NMR δ 39.79; MS 263 (M+1) (FAB).

Vinylbisphosphonamide 8c (R^1=*E*-Ph, R^2=Me)

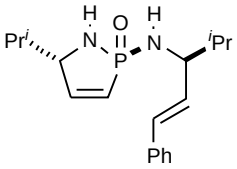


Flash chromatography (EtOAc/2% MeOH) yielded 17.2% **8a**; ^{1}H NMR δ 7.51 (dd, *J* = 20.8, 17.3 Hz, 1H), 7.41-7.18 (m, 15H), 6.50 (d, *J* = 15.9 Hz, 2H), 6.39 (dd, *J* = 19.3, 17.3 Hz, 1H), 6.24-6.17 (m, 2H), 4.17-4.05 (m, 2H), 2.54-2.47 (m, 2H), 1.39 (d, *J* = 6.7

(4) Catalyst **4** was added in sequential portions of 3 mol%.

Hz), 1.38 (d, J = 6.7 Hz)(3H); ^{13}C NMR δ 146.8 (dd, J_p = 5.4), 136.7 (s), 136.6 (s), 135.4 (ds, J_p = 20.5), 133.9 (dd, J_p = 5.2), 129.6 (d), 128.7 (d), 128.5 (d), 127.5 (d), 127.4 (d), 126.3 (d), 119.5 (dd, J_p = 153.9), 48.5 (d), 48.4 (d), 24.1 (q), 24.0 (q); ^{31}P NMR δ 18.90; Exact mass: calculated for $C_{28}H_{32}N_2OP$ (M+1) 443.2252; found 443.2258 (FAB).

Vinylbisphosphonamide 5d (R^1=*E*-Ph, R^2=^{i}Pr) major diastereoisomer

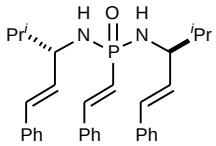


RCM reaction conditions: 8 h reflux, 3 mol% **4**. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 15:1. Flash chromatography (EtOAc/4% MeOH) yielded 66.3% **5d**; $[\alpha]_D$ +36.8 (*c* 2.2, CH_2Cl_2); ^{1}H NMR δ 7.36-7.20 (m, 5H), 6.78 (dd, J = 42.5, 8.5 Hz, 1H), 6.51 (d, J = 15.9 Hz, 1H), 6.15 (dd, J = 15.9, 6.1 Hz, 1H), 6.04 (dd, J = 28.3, 8.5 Hz, 1H), 3.78-3.74 (m, 1H), 3.22-3.17 (m, 1H), 2.93 (br. d, J = 11.3 Hz, 1H), 2.77 (br. t, J = 9.4 Hz, 1H), 1.79-1.72 (m, 2H), 0.90 (d, J = 6.9 Hz), 0.89 (d, J = 6.6 Hz), 0.87 (d, J = 8.0 Hz), 0.86 (d, J = 6.9 Hz)(12H); ^{13}C NMR δ 147.2 (dd, J_p = 16.0), 136.7 (s), 131.8 (d), 129.4 (d), 128.6 (d), 127.4 (d), 126.2 (d), 122.4 (dd, J_p = 146.5), 63.8 (dd, J_p = 18.2), 58.8 (d), 33.7 (dd, J_p = 6.4), 32.8 (d), 19.1 (q), 18.6 (q), 17.9 (q), 17.7 (q); ^{31}P NMR δ 39.84; IR (CH_2Cl_2) 3441, 3410, 3018, 2896, 1585, 1476, 1360, 1190, 1050, 967, 879, 843 cm^{-1}; Exact mass: calculated for $C_{18}H_{28}N_2OP$ (M+1) 319.1939; found 319.1944 (FAB).

Vinylbisphosphonamide 5d (R^1=*E*-Ph, R^2=^{i}Pr) minor diastereoisomer

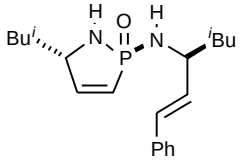
Flash chromatography (EtOAc/10% MeOH) yielded 4.7% **5b**; ^{1}H NMR δ 7.36-7.21 (m, 5H), 6.81 (dd, J = 42.9, 8.6 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9, 6.1 Hz, 1H), 6.03 (dd, J = 28.5, 8.5 Hz, 1H), 3.79 (br. d, J = 4.8 Hz, 1H), 3.57-3.52 (m, 1H), 3.01 (br. d, J = 7.3 Hz, 1H), 2.71 (br. t, J = 10.2 Hz, 1H), 1.80-1.71 (m, 2H), 1.00 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H); ^{31}P NMR δ 41.15; MS 319 (M+1) (FAB).

Vinylbisphosphonamide 8d (R^1=*E*-Ph, R^2=^{i}Pr)



Flash chromatography (EtOAc/2% MeOH) yielded 14.5% **8b**; ^{1}H NMR δ 7.48 (dd, *J* = 20.7, 17.4 Hz, 1H), 7.34-7.19 (m, 15H), 6.50 (d, *J* = 15.9 Hz), 6.48 (d, *J* = 15.8 Hz)(2H), 6.35 (dd, *J* = 19.0, 17.4 Hz, 1H), 6.14-6.07 (m, 2H), 3.80-3.68 (m, 2H), 2.55 (br. s, 2H), 1.91-1.83 (m, 2H), 0.97-0.94 (m, 12H); ^{13}C NMR δ 146.7 (dd, J_p = 5.5), 136.82 (s), 136.79 (s), 135.1 (ds, J_p = 20.6), 131.1 (dd, J_p = 2.9), 130.8 (dd, J_p = 3.5), 129.9 (d), 128.9 (d), 127.9 (d), 127.83 (d), 127.81 (d), 126.79 (d), 126.77 (d), 119.7 (dd, J_p = 156.2), 58.9 (d), 58.7 (d), 34.3 (dd, J_p = 5.5), 34.1 (dd, J_p = 6.1), 18.8 (q), 18.53 (q), 18.50 (q), 18.3 (q); ^{31}P NMR δ 19.56; Exact mass: calculated for $C_{32}H_{40}N_2OP$ (M+1) 499.2878; found 499.2876 (FAB).

Vinylbisphosphonamide 5e (R^1=*E*-Ph, R^2=^{i}Bu) major diastereoisomer



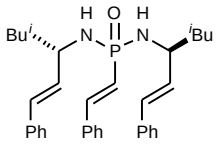
RCM reaction conditions: 20 h reflux, 6 mol% **4**[3]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 15:1. Flash chromatography (EtOAc/4% MeOH) yielded 63.4% **5e**; $[\alpha]_D$ +51.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR δ 7.34-7.18 (m, 5H), 6.80 (dd, *J* = 44.2, 8.4 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.10 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.98 (ddd, *J* = 28.4, 8.4, 1.5 Hz, 1H), 3.94-3.87 (m, 1H), 3.46-3.40 (m, 1H), 3.08 (br. d, *J* = 10.9 Hz, 1H), 2.70 (t, *J* = 8.9 Hz, 1H), 1.73-1.61 (m, 2H), 1.37-1.33 (m, 4H), 1.37-1.33 (m, 12H); ^{13}C NMR δ 149.3 (dd, J_p = 16.5), 136.6 (s), 133.5 (dd, J_p = 1.7), 128.5 (d), 128.3 (d), 127.4 (d), 126.2 (d), 121.0 (dd, J_p = 144.5), 56.2 ((dd, J_p = 19.3), 51.8 (d), 46.7 ((dt, J_p = 7.4), 45.6 (t), 25.3 (d), 24.4 (d), 23.1 (q), 22.7 (q), 22.3 (q), 21.7 (q); ^{31}P NMR δ **39.25**; IR (neat) 3221, 3018, 2904, 1580, 1414, 1180, 1069, 967 cm^{-1}; Exact mass: calculated for $C_{20}H_{32}N_2OP$ (M+1) 347.2247; found 347.2252 (FAB).

Vinylbisphosphonamide 5e (R^1=*E*-Ph, R^2=^{i}Bu) minor diastereoisomer (contaminared with $Cy_3P(O)$)

Flash chromatography (EtOAc/4% MeOH) yielded 5.0% **5e**; ^{1}H NMR δ 7.34-7.21 (m, 5H), 6.72 (dd, *J* = 44.7, 8.4 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.07 (dd, *J* = 15.8, 6.4 Hz,

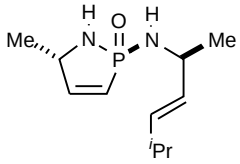
1H), 5.96 (dd, *J* = 28.8, 8.4, 1H), 4.11-4.07 (m, 1H), 3.64-3.57 (m, 1H), 3.04 (br.d, *J* = 8.6 Hz, 1H), 2.61 (t, *J* = 9.9 Hz, 1H), 1.73-1.61 (m, 2H), 1.37-1.33 (m, 4H), 0.99-0.91 (m, 12H); ^{31}P NMR δ 40.46.

Vinylbisphosphonamide 8e (R^1=*E*-Ph, R^2=^{i}Bu)



Flash chromatography (EtOAc/2% MeOH) yielded 13.2% **8c**; ^{1}H NMR δ 7.46 (dd, *J* = 20.7, 17.3 Hz, 1H), 7.32-7.17 (m, 15H), 6.50 (d, *J* = 15.8 Hz), 6.48 (d, *J* = 15.8 Hz)(2H), 6.34 (dd, *J* = 19.3, 17.3 Hz, 1H), 6.12-6.04 (m, 2H), 4.00-3.88 (m, 2H), 2.45-2.37 (m, 2H), 1.78-1.72 (m, 2H), 1.55-1.39 (m, 4H), 0.95-0.90 (m, 12H); ^{13}C NMR δ 146.6 (dd, J_p = 5.4), 136.8 (s), 136.7 (s), 135.5 (ds, J_p = 20.8), 133.3 (dd, J_p = 2.8), 132.8 (dd, J_p = 3.3), 129.8 (d), 129.6 (d), 129.4 (d), 128.6 (d), 128.5 (d), 128.4 (d), 127.42 (d), 127.37 (d), 126.34 (d), 126.32 (d), 120.0 (dd, J_p = 154.4), 51.8 (d), 51.7 (d), 47.3 (dt, J_p = 5.8), 47.2 (dd, J_p = 6.4), 24.7 (d), 22.8 (q), 22.7 (q), 22.5 (q), 22.4 (q); ^{31}P NMR δ 18.72; MS 527 (M+1) (FAB).

Vinylbisphosphonamide 5f (R^1=*E*-^{i}Pr, R^2=Me) major diastereoisomer

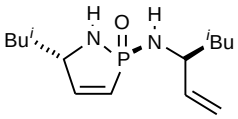


RCM reaction conditions: 3.0 h reflux, 3 mol% **4**. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 3.9:1. Flash chromatography (EtOAc/4% MeOH) yielded 63.6% **5f** as white solid; m.p. 135-37 ˚C; $[\alpha]_D$ +189.2 (*c* 4.46, CH_2Cl_2); ^{1}H NMR δ 6.73 (dddd, *J* = 42.0, 8.4, 1.5, 1.5 Hz, 1H), 5.97 (dddd, *J* = 28.3, 8.4, 1.6, 1.6 Hz, 1H), 5.47 (ddd, *J* = 15.5, 6.5, 1.2 Hz, 1H), 5.31 (ddd, *J* = 15.5, 5.6, 0.9 Hz, 1H), 4.01-3.97 (m, 1H), 3.37-3.31 (m, 1H), 2.97 (br. d, *J* = 10.8 Hz, 1H), 2.50 (br. t, *J* = 9.2 Hz, 1H), 2.26-2.19 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR δ 149.6 (dd, J_p = 16.3), 136.0 (d), 131.2 (dd, J_p = 3.6), 121.4 (dd, J_p = 143.2), 53.5 (dd, J_p = 20.0), 48.5 (d), 30.4 (d), 23.9 (dq, J_p = 6.0), 22.6 (q), 22.4 (q), 22.3 (q); ^{31}P NMR δ 38.83; IR (CH_2Cl_2) 3432, 3405, 2925, 2869, 1586, 1465, 1372, 1190, 1069, 1004, 966, 862 cm^{-1}; Exact mass: calculated for $C_{11}H_{22}N_2OP$ (M+1) 229.1470; found 229.1458 (FAB).

Vinylbisphosphonamide 5f (R^1=*E*-^{i}Pr, R^2=Me) minor diastereoisomer

Flash chromatography (EtOAc/10% MeOH) yielded 5.4% **5d**; ^{1}H NMR δ 6.70 (dddd, *J* = 42.3, 8.4, 1.5 Hz, 1H), 5.95 (dddd, *J* = 28.3, 8.4, 1.8, 1.8 Hz, 1H), 5.43 (ddd, *J* = 15.5, 6.5, 1.1 Hz, 1H), 5.30 (dd, *J* = 15.5, 5.6 Hz, 1H), 4.14-4.10 (m, 1H), 3.52-3.48 (m, 1H), 3.00 (br. d, *J* = 9.9 Hz, 1H), 2.51 (br. t, *J* = 9.4 Hz, 1H), 2.26-2.21 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz), 0.94 (d, *J* = 6.7 Hz)(6H); ^{13}C NMR δ 149.4 (dd, J_p = 15.4), 136.5 (d), 130.9 (dd, J_p = 4.0), 122.2 (dd, J_p = 142.8), 53.7 (dd, J_p = 20.0), 48.5 (d), 30.6 (d), 23.8 (dq, J_p = 5.6), 22.4 (q), 22.3 (q), 22.0 (dd, J_p = 4.0); ^{31}P NMR δ 38.78; MS 229 (M+1) (FAB).

Vinylbisphosphonamide 5g (R^1=H, R^2=^{i}Bu) major diastereoisomer



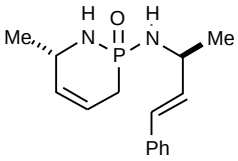
RCM reaction conditions: 72 h reflux, 18 mol% **4**[3]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 2.3:1. RCM reaction conditions: 72 h RT, 18 mol% **4**[1]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 2.4:1. Flash chromatography (EtOAc/4% MeOH) yielded 47.7% **5g**; $[\alpha]_D$ +196.4 (*c* 1.12, CH_2Cl_2); ^{1}H NMR δ 6.79 (dd, *J* = 42.3, 8.3 Hz, 1H), 5.95 (dd, *J* = 28.3, 8.3 Hz, 1H), 5.75 (ddd, *J* = 16.7, 10.6, 6.3 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.91-3.89 (m, 1H), 3.24-3.19 (m, 1H), 3.02 (br. d, *J* = 10.6 Hz, 1H), 2.52 (br. t, *J* = 8.9 Hz, 1H), 1.72-1.63 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 2H), 0.90 (d, *J* = 6.4 Hz), 0.88 (d, *J* = 6.4 Hz), 0.83 (d, *J* = 6.7 Hz), 0.82 (d, *J* = 6.7 Hz)(12H); ^{13}C NMR δ 149.2 (dd, J_p = 16.7), 142.2 (d), 120.9 (dd, J_p = 145.3), 112.9 (t), 56.2 (dd, J_p = 19.4), 52.0 (d), 46.4 (dt, J_p = 7.3), 45.7 (t), 25.4 (d), 23.4 (d), 23.1 (q), 22.7 (q), 22.1 (q), 21.8 (q); ^{31}P NMR δ 39.49; IR (neat) 3217, 2955, 2868, 1640, 1583, 1468, 1412, 1285, 1185, 1053, 931, 732 cm^{-1}; Exact mass: calculated for $C_{14}H_{28}N_2OP$ (M+1) 271.1939; found 271.1921 (FAB).

Vinylbisphosphonamide 5g (R^1=H, R^2=^{i}Bu) minor diastereoisomer (contaminated with $Cy_3P(O)$)

Flash chromatography (EtOAc/10% MeOH) yielded 19.5% **5g**; ^{1}H NMR δ 6.73 (dd, *J* = 42.7, 8.5 Hz, 1H), 5.95 (dddd, *J* = 28.7, 8.4, 1.8, 1.7 Hz, 1H), 5.73 (ddd, *J* = 16.7, 10.5,

6.0 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 5.00 (d, *J* = 10.3 Hz, 1H), 4.09-4.06 (m, 1H), 3.45-3.38 (m, 1H), 3.03 (br. d, *J* = 8.7 Hz, 1H), 2.49 (br. t, *J* = 10.1 Hz, 1H), 1.77-1.68 (m, 4H), 1.39-1.24 (m, 2H), 0.96 (d, *J* = 6.6 Hz), 0.95 (d, *J* = 6.5 Hz), 0.90 (d, *J* = 6.6 Hz), 0.89 (d, *J* = 6.6 Hz)(12H); ^{13}C NMR δ 148.9 (dd, J_p = 15.6), 141.5 (d), 121.6 (dd, J_p = 142.7), 113.3 (t), 55.4 (dd, J_p = 19.8), 52.0 (d), 46.7 (t), 45.3 (t), 25.5 (d), 24.4 (d), 23.3 (q), 22.8 (q), 22.3 (q), 21.6 (q); ^{31}P NMR δ 40.66.

Allylbisphosphonamide 6a (R^1=*E*-Ph, R^2=Me) major diastereoisomer

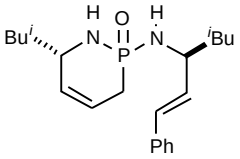


RCM reaction conditions: 24 h reflux, 6 mol% **4**[3]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 1.3:1. Flash chromatography (EtOAc/4% MeOH) yielded 50.2% **6a**; $[\alpha]_D$ +26.3 (c 2.36, CH_2Cl_2); ^{1}H NMR δ 7.36-7.20 (m, 5H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 5.7 Hz, 1H), 5.68-5.57 (m, 2H), 4.02-3.99 (m, 2H), 2.62 (br. s, 1H), 2.49-2.37 (m, 3H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.30 (dd, *J* = 6.8, 1.2 Hz, 3H); ^{13}C NMR δ 136.7 (s), 133.9 (dd, J_p = 3.6), 131.6 (dd, J_p = 15.0), 128.6 (d), 128.5 (d), 127.5 (d), 126.3 (d), 119.7 (dd, J_p = 8.6), 50.8 (dd, J_p = 3.2), 48.3 (d), 25.1 (dt, J_p = 111.9), 24.2 (dq, J_p = 4.9), 24.1 (dq, J_p = 5.5); ^{31}P NMR δ 19.66; IR (CH_2Cl_2) 3392, 3053, 2979, 1494, 1418, 1374, 1267, 1197, 1140, 1077, 976, 895 cm^{-1}; Exact mass: calculated for $C_{15}H_{22}N_2OP$ (M+1) 277.1470; found 277.1469 (FAB).

Allylbisphosphonamide 6a (R^1=*E*-Ph, R^2=Me) minor diastereoisomer

Flash chromatography (EtOAc/10% MeOH) yielded 33.4% **6a** ; ^{1}H NMR δ 7.36-7.21 (m, 5H), 6.50 (dd, *J* = 15.9, 0.8 Hz, 1H), 6.17 (dd, *J* = 15.9, 5.8 Hz, 1H), 5.69-5.54 (m, 2H), 4.19 (br. s, 1H), 4.02-3.94 (m, 1H), 2.61 (br. s, 1H), 2.52-2.29 (m, 3H), 1.32 (d, *J* = 6.7 Hz, 3H), 1.24 (dd, *J* = 6.7, 1.3 Hz, 3H); ^{13}C NMR δ 136.6 (s), 133.5 (dd, J_p = 3.8), 131.2 (dd, J_p = 13.8), 128.6 (d), 128.5 (d), 127.6 (d), 126.3 (d), 119.5 (dd, J_p = 8.5), 49.4 (dd, J_p = 2.7), 49.1 (d), 25.8 (dt, J_p = 111.6), 24.4 (dq, J_p = 4.9), 24.3 (q); ^{31}P NMR δ 21.42.

Allylbisphosphonamide 6b (R^1=*E*-Ph, R^2= ^{i}Bu) major diastereoisomer

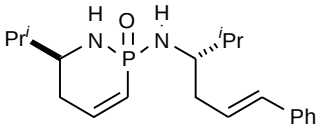


RCM reaction conditions: 24 h reflux, 6 mol% **4**[3]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 1.8:1. Flash chromatography (EtOAc/2% MeOH) yielded 50.5% **6b** as white solid; m.p. 116-18 ˚C; $[\alpha]_D$ +28.6 (c 2.62, CH_2Cl_2); ^{1}H NMR δ 7.36-7.20 (m, 5H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.70-5.60 (m, 2H), 3.89-3.87 (m, 2H), 2.59 (br. s, 1H), 2.49-2.38 (m, 3H), 1.78-1.67 (m, 2H), 1.53-1.37 (m, 4H), 0.94 (d, *J* = 6.6 Hz), 0.93 (d, *J* = 6.6 Hz), 0.91 (d, *J* = 6.6 Hz), 0.85 (d, *J* = 6.6 Hz)(12H); ^{13}C NMR δ 136.7 (s), 133.3 (d), 130.8 (dd, J_p = 15.4), 129.2 (d), 128.6 (d), 127.5 (d), 126.3 (d), 120.1 (dd, J_p = 8.7), 52.9 (dd, J_p = 3.2), 51.6 (d), 47.3 (dt, J_p = 6.6), 47.0 (dt, J_p = 4.0), 26.0 (dt, J_p = 111.4), 24.6 (d), 24.4 (d), 22.9 (q), 22.7 (q), 22.5 (q), 21.8 (q); ^{31}P NMR δ 19.71; IR (CH_2Cl_2) 3394, 3052, 2957, 2925, 2870, 1494, 1420, 1265, 1197, 1076, 968, 895 cm^{-1}; Exact mass: calculated for $C_{21}H_{34}N_2OP$ (M+1) 361.2409; found 361.2407 (FAB)**.**

Allylbisphosphonamide 6b (R^1=*E*-Ph, R^2= ^{i}Bu) minor diastereoisomer (contaminated with $Cy_3P(O)$)

Flash chromatography (EtOAc/4% MeOH) yielded 27.8% **6b**; ^{1}H NMR δ 7.38-7.23 (m, 5H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.71-5.57 (m, 2H), 4.13 (br. s, 1H), 3.85-3.79 (m, 2H), 2.55-2.78 (m, 4H), 2.01-1.69 (m, signals overlapping with $Cy_3P(O)$), 0.96 (d, *J* = 6.6 Hz), 0.95 (d, *J* = 6.6 Hz), 0.93 (d, *J* = 6.7 Hz), (12H); ^{31}P NMR δ 22.03.

Vinylbisphosphonamide 6c (R^1=*E*-Ph, R^2=^{i}Pr) major diastereoisomer (the two diastereoisomers couldn't be separated completely)



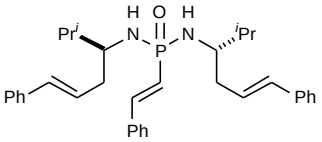
RCM reaction conditions: 24 h reflux, 6 mol% **4**[3]. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 1.1:1. Flash chromatography

(EtOAc/4% MeOH) yielded 42.4% **6c**; $[\alpha]_D$ –78.5 (*c* 2.32, CH_2Cl_2); ^{1}H NMR δ 7.35-7.18 (m, 5H), 6.64 (dddd, *J* = 41.1, 12.8, 4.8, 3.4 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.6 Hz, 1H), 5.91 (br. t, *J* = 13.8 Hz, 1H), 3.17-3.07 (m, 2H), 2.45-2.27 (m, 4H), 2.12-2.07 (m, 2H), 1.87-1.62 (m, 2H), 0.95 (d, *J* = 6.8 Hz), 0.92 (d, *J* = 6.7 Hz), 0.91 (d, *J* = 6.8 Hz), 0.87 (d, *J* = 6.7 Hz) (12H); ^{13}C NMR δ 146.1, 137.4, 132.4, 128.5, 127.3, 127.1, 126.0, 121.8 (d, J_p = 140.7), 57.6 (d, J_p = 2.7), 56.0 (d), 38.1 (d, J_p = 3.0), 33.1 (d, J_p = 7.8), 32.0 (d, J_p = 4.5), 30.6 (d, J_p = 10.7), 19.4, 18.8, 18.5, 17.5; ^{31}P NMR δ 14.39; IR (CH_2Cl_2) 3391, 3053, 2963, 1732, 1608, 1494, 1467, 1420, 1264, 1195, 1050, 967, 896 cm^{-1}; Exact mass: calculated for $C_{20}H_{32}N_2OP$ (M+1) 347.2252; found 347.2268 (FAB).

Vinylbisphosphonamide 6c (R^1=*E*-Ph, R^2=^{i}Pr) minor diastereoisomer (contaminated with $Cy_3P(O)$)

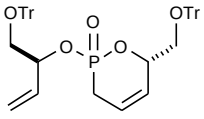
Flash chromatography (EtOAc/4% MeOH) yielded 36.6% **6c**; ^{1}H NMR δ 7.34-7.18 (m, 5H), 6.58 (dddd, *J* = 42.6, 12.6, 6.0, 2.1 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.7, 7.7 Hz, 1H), 5.82-5.74 (m, 1H), 3.42-3.37 (m, 1H), 3.06-2.99 (m, 1H), 2.40-1.94 (m, 6H), 1.76-1.61 (m, 2H), 0.96 (d, *J* = 6.8 Hz), 0.91 (d, *J* = 6.8 Hz), 0.88 (d, *J* = 6.8 Hz), 0.87 (d, *J* = 6.8 Hz) (12H).

Vinylbisphosphonamide 9 (R^1=*E*-Ph, R^2=^{i}Pr)



Flash chromatography (EtOAc/2% MeOH) yielded 13.9% **9**; ^{1}H NMR δ 7.53-7.12 (m, 16H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.30-6.09 (m, 4H), 3.19-3.11 (m, 2H), 2.39-2.09 (m, 6H), 1.80-1.72 (m, 2H), 0.93 (d, *J* = 6.7 Hz), 0.89 (d, *J* = 6.6 Hz), 0.88 (d, *J* = 6.6 Hz) (12H); ^{13}C NMR δ 146.5 (d, J_p = 5.5), 137.2, 132.3, 132.2, 129.3, 128.7, 128.6, 128.5, 127.6, 127.5, 127.1, 127.0, 126.5, 125.9, 120.4 (d, J_p = 157.4), 56.2, 38.1 (d, J_p = 3.3), 34.6 (d, J_p = 4.2), 32.9 (d, J_p = 3.6), 32.4 (d, J_p = 4.9), 19.2, 18.8, 17.9, 17.6; ^{31}P NMR δ 18.27.

Allylbisphosphonate 7 major diastereoisomer



RCM reaction conditions: 6 h RT, 3 mol% **4**. Ratio of the two diastereomeric products in ^{31}P NMR of the crude reaction mixture: 3.4:1. Flash chromatography (60% Hexanes/EtOAc yielded 74.7% **7**; $[\alpha]_D$ –42.1 (c 4.48, CH_2Cl_2); ^1H NMR δ 7.48-7.44 (m, 12H), 7.33-7.22 (m, 18H), 5.80-5.71 (m, 3H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.23-5.17 (m, 3H), 3.42-3.20 (m, 4H), 2.62-2.52 (m, 2H); ^{13}C NMR δ 143.7 (s), 143.6 (s), 133.8 (d), 128.7 (d), 128.6 (d), 127.8 (d), 127.1 (d), 126.9 (dd, J_p = 16.9), 121.4 (dd, J_p = 9.5), 118.3 (t), 86.7 (s), 86.6 (s), 78.6 (dd, J_p = 7.0), 77.1 (dd, J_p = 6.2), 66.2 (dt, J_p = 6.3), 66.7 (dt, J_p = 6.0), 23.0 (dt, J_p = 132.7) ; ^{31}P NMR δ 21.66; IR (CH_2Cl_2) 3054, 2985, 2926, 2874, 1596, 1491, 1448, 1421, 1261, 1081, 994, 896 cm^{-1}; Exact mass: calculated for $C_{47}H_{44}O_5P$ (M+1) 719.2926; found 719.2928 (FAB).

Allylbisphosphonate 7 minor diastereoisomer

Flash chromatography (60% Hexanes/EtOAc yielded 20.3% **7**; ^1H NMR δ 7.49-7.15 (m, 30H), 5.90-5.66 (m, 3H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.11-5.03 (m, 2H), 3.28-3.17 (m, 4H), 2.68-2.57 (m, 1H), 2.48-2.38 (m, 1H).