Supporting Information for:

Thermal and Catalyzed [3,3]-Phosphorimidate Rearrangements

Bin Chen and Anna K. Mapp*

General. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Benzene, Et_2O, and toluene were dried by passage through activated alumina columns and degassed by stirring under a dry argon atmosphere.[1] Purification by flash chromatography was carried out with E. Merck Silica Gel 60 (230-400 mesh) according to the procedure of Still, Kahn, and Mitra.[2] All reactions involving air- or moisture-sensitive compounds were performed under an argon atmosphere. Benzyl azide,[3] allyl azide,[4] 4-methoxybenzyl azide,[5] tosyl azide and Cbz azide[6] were prepared according to literature procedures. 1-(*Tert*-butyl-dimethyl-silanyloxy)-but-3-en-2-ol,[7] 1-benzyloxy-but-3-en-2-ol,[7] 2–(1-hydroxy-propyl)-acrylic acid methyl ester[8] and *(E)*-3-octen-2-ol[9] were prepared following literature procedures. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz and 125 MHz, respectively. IR spectra were measured as thin films on NaCl plates. Melting points are uncorrected. Compounds found in the article text but not described in the Supporting Information (**3c, 3d, 3e, 7, 11, 12, 16-19, 21, 24**) were prepared using previously reported methods, and spectral data for these compounds were consistent with the literature reported values.[7] Computations were performed with Spartan 4.0[10] with the B3LYP/631G* level of theory.

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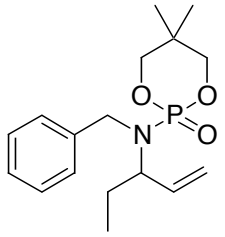
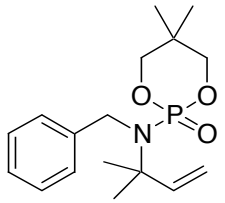
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518-1520.
[2] Still, W. C.; Kahn, M.; Mitra. A. *J. Org. Chem.* **1978**, *43*, 2923.
[3] Theocharis, A. B.; Alexandrou, N. E.; Terzis, A. *J. Heterocyclic Chem.* **1990**, *27*, 1741-1744.
[4] Koziara, A.; Zwierzak, A. *Synthesis* **1992**, 1063-1065.
[5] Buckle, D. R.; Rockell, C. J. M. *J. Chem. Soc. Perkin Trans. 1* **1982**, 627-630.
[6] Ghosh, A. K.; Bischoff, A.; Cappiello, J. *Eur. J. Org.* Chem. **2003**, 821-832.
[7] Chen, B.; Mapp, A. K. *J. Am. Chem. Soc.* **2004**, *126*, 5364-5365.
Davoille, R. J.; Rutherford, D. T.; Christie, S. D. R. *Tetrahedron Lett.* **2000**, *41*, 1255-1259.
[8] Brezinski, L. J.; Rafel, S.; Leahy, J. W. *Tetrahedron* **1997**, *53*, 16423-16434.
[9] Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738-8739.
[10] *Spartan '04*, version 1.0.0; Wavefunction, Inc.; Irvine, CA, **2003**.

General procedure for the thermal rearrangement: To a solution of Et_2O (50 mL) cooled in an ice/H_2O bath was added the allylic alcohol (10 mmol, 1.25 eq) and Et_3N (10 mmol, 1.25 eq), followed by a solution of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, diphenylchlorophosphite or diethylchlorophosphite (10 mmol, 1.25 eq) in 10 ml Et_2O. The solution was then allowed to stir for 20 min and the precipitated Et_3N•HCl was removed by filtration. The Et_2O was removed under vacuum and the residue was dissolved in 10 mL xylenes. The resulting solution was added dropwise to a solution of benzyl azide or Cbz azide (8 mmol, 1.0 eq) in 5 mL xylenes cooled in an ice/H_2O bath. The reaction mixture was slowly warmed to rt over 1 h, heated at 80 °C for 2 h, then diluted with an additional 10 mL xylenes, heated at reflux for 1-4 h and monitored by ^{31}P NMR. Upon cooling, the crude reaction mixture was subjected to flash chromatography (1:9 hexanes/EtOAc) for isolation of the phosphoramidate product (1:2 hexanes/EtOAc for compound **27-28**).



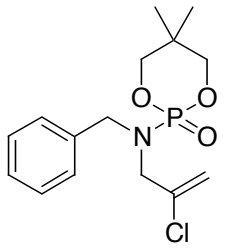
3f

Benzyl -(5,5-dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl) – (1-ethyl-allyl)-amine (3f): Prepared following the general procedure in 85% yield (2.20 g) from *trans*-2-penten-1-ol and 81% yield (2.10 g) from *cis*-2-penten-1-ol as a colorless oil. ^1H NMR: δ 0.72 (t, *J* = 7.5 Hz, 3H), 0.81 (s, 3H), 1.18 (s, 3H), 1.43-1.58 (m, 2H), 3.69-3.80 (m, 3H), 4.19-4.22 (m, 2H), 4.36 (d, *J* = 11.0 Hz, 2H), 4.99-5.05 (m, 2H), 5.67-5.76 (m, 1H), 7.19-7.27 (m, 3H), 7.34-7.35 (m, 2H); ^{13}C NMR: δ 11.27, 21.00, 22.76, 25.85, 32.03, 47.95, 61.74, 76.40, 116.56, 127.20, 128.33, 138.22, 139.76; IR (film): 3065, 3029, 2967, 2934, 2884, 1456, 1244 cm^{-1}; Anal calcd for $C_{17}H_{26}NO_3P$: C, 63.14; H, 8.10; N, 4.33. Found: C, 63.45; H, 8.19; N, 4.24.



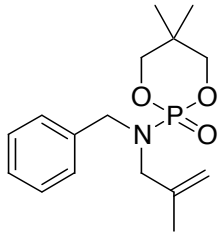
15

Benzyl-(1,1-dimethyl-allyl)-(5,5-dimethyl-2-oxo-2λ⁵- [1,3,2] dioxaphosphinan-2-yl)-amine (15): Prepared following the general procedure from 3-methyl-2-buten-1-ol in 70% yield (1.81 g)) as a white solid. mp 84-85 °C; ^{1}H NMR: 0.80 (s, 3H), 1.08 (s, 3H), 1.41 (s, 6H), 3.69 (dd, *J* = 10.6, 20.7 Hz, 2H), 4.32 (d, *J* = 11.7 Hz, 4H), 4.93-5.04 (m, 2H), 5.92 (dd, *J* = 10.7, 17.5 Hz, 1H), 7.14-7.17 (m, 1H), 7.22-7.27 (m, 2H), 7.32 (m, 2H); ^{13}C NMR: δ 21.33, 23.15, 27.87, 32.22, 49.43, 60.72, 76.31, 112.34, 126.54, 126.93, 128.27, 141.48, 145.31; IR (film): 2971, 2884, 1470, 1454, 1366, 1256 cm^{-1}; Anal calcd for $C_{17}H_{26}NO_3P$: C, 63.14; H, 8.10; N, 4.33. Found: C, 62.77; H, 8.07; N, 4.38.



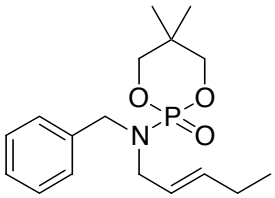
13

Benzyl-(2-chloro-allyl)-(5,5-dimethyl-2-oxo-2λ⁵- [1,3,2] dioxaphosphinan-2-yl)-amine (13): Prepared following the general procedure from 2-chloro-2-propen-1-ol in 75% yield (1.98 g) as a colorless oil. ^{1}H NMR: δ 0.84 (s, 3H), 1.22 (s, 3H), 3.68 (d, *J* = 11.8 Hz, 2H), 3.82 (dd, *J* = 9.9, 22.0 Hz, 2H), 4.22 (d, *J* = 10.3 Hz, 2H), 4.38 (d, *J* = 9.9 Hz, 2H), 5.31 (s, 1H), 5.34 (s, 1H), 7.22-7.30 (m, 5H); ^{13}C NMR: δ 20.89, 22.65, 32.03, 48.78, 50.59, 76.65, 114.58, 127.89, 128.52, 128.75, 136.58, 137.75; IR (film): 2968, 2887, 1634, 1496, 1456, 1368, 1247 cm^{-1}; Anal calcd for $C_{15}H_{21}ClNO_3P$: C, 54.63; H, 6.42; N, 4.25. Found: C, 54.36; H, 6.41; N, 4.27.



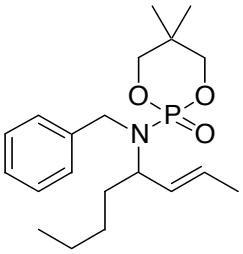
14

Benzyl -(5,5-dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl) – (2-methyl-allyl)-amine (14): Prepared following the general procedure from 2-methyl-2-propen-1-ol in 60% yield (1.48 g) as a white solid. mp 76-78 °C; ^{1}H NMR: δ 0.82 (s, 3H), 1.21 (s, 3H), 1.68 (s, 3H), 3.44 (d, *J* =11.0 Hz, 2H), 3.78 (dd, *J* = 9.9, 22.0 Hz, 2H), 4.14 (d, *J* = 10.7 Hz, 2H), 4.37 (d, *J* = 10.3 Hz, 2H), 4.74 (s, 1H), 4.88 (s, 1H), 7.22-7.28 (m, 5H); ^{13}C NMR: δ 19.94, 20.92, 22.72, 32.03, 48.11, 50.49, 76.53, 114.01, 127.53, 128.57, 137.38, 140.78; IR (film): 3067, 3031, 2968, 2887, 1456, 1368, 1244 cm^{-1}; Anal calcd for $C_{16}H_{24}NO_3P$: C, 62.12; H, 7.82; N, 4.53. Found: C, 62.45; H, 7.83; N, 4.53.



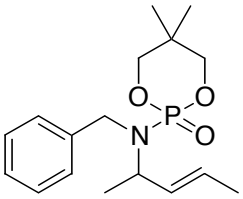
20

Benzyl -(5,5-dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl)-pent-2-enyl-amine (20): Prepared following the general procedure from 1-penten-3-ol in 50% yield (1.29 g) as a colorless oil. ^{1}H NMR: δ 0.81 (s, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 1.19 (s, 3H), 1.97 -1.98 (m, 2H), 3.42 (dd, *J* = 6.4, 11.6 Hz, 2H), 3.76 (dd, *J* = 9.9, 21.6 Hz, 2H), 4.19 (d, *J* = 10.3 Hz, 2H), 4.34 (d, *J* = 10.6 Hz, 2H), 5.27-5.33 (m, 1H), 5.41-5.47 (m, 1H), 7.18-7.26 (m, 5H); ^{13}C NMR: δ 13.67, 20.92, 22.63, 25.36, 31.99, 46.80, 48.23, 76.44, 124.57, 127.37, 128.41, 128.52, 136.82, 137.85; IR (film): 3030, 2964, 2933, 2886, 1456, 1368, 1243 cm^{-1}; Anal calcd for $C_{17}H_{26}NO_3P$: C, 63.14; H, 8.10; N, 4.33. Found: C, 62.79; H, 8.12; N, 4.37.



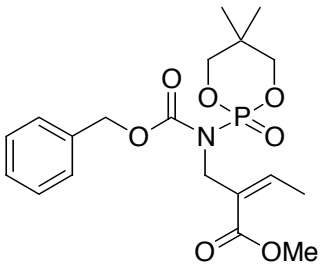
22

Benzyl-(1-butyl-but-2-enyl)-(5,5-dimethyl-2-oxo-2λ⁵-[1,3,2] dioxaphosphinan-2-yl)-amine (22): Prepared following the general procedure from *(E)*-3-octen-2-ol in 75% yield (2.19 g) as a colorless oil. ^{1}H NMR: δ 0.71 (t, *J* = 6.9 Hz, 3H), 0.79 (s, 3H), 1.06-1.07 (m, 4H), 1.17 (s, 3H), 1.33-1.51 (m, 2H), 1.54 (d, *J* = 6.2 Hz, 3H), 3.69-3.78 (m, 3H), 4.18 (d, *J* = 11.4 Hz, 2H), 4.34 (d, *J* = 11.0 Hz, 2H), 5.32-5.45 (m, 2H), 7.14-7.17 (m, 1H), 7.21-7.24 (m, 2H), 7.32-7.33 (m, 2H); ^{13}C NMR: δ 14.08, 17.92, 21.00, 22.48, 22.78, 28.76, 32.05, 32.93, 47.58, 59.24, 76.35, 127.10, 127.61, 128.25, 128.35, 131.58, 140.02; IR (film): 2960, 1454, 1367, 1245 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{32}NO_3P + H]^+$: 366.2198, Found: 366.2208.



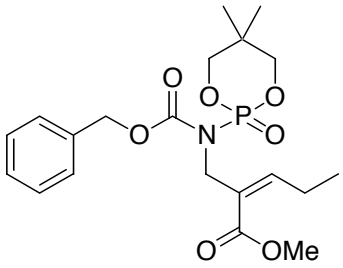
23

Benzyl -(5,5-dimethyl-2-oxo-2λ⁵- [1,3,2] dioxaphosphinan-2-yl) – (1-methyl-but-2-enyl)-amine (23): Prepared following the general procedure) from 3-penten-2-ol in 80% yield (2.07 g) as a colorless oil. ^{1}H NMR: δ 0.80 (s, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.16 (s, 3H), 1.55 (d, *J* = 4.5 Hz, 3H), 3.70-3.79 (m, 2H), 4.09-4.16 (m, 2H), 4.21-4.28 (m, 1H), 4.34 (d, *J* = 11.0 Hz, 2H), 5.33-5.48 (m, 2H), 7.15-7.16 (m, 1H), 7.21-7.25 (m, 2H), 7.30-7.32 (m, 2H); ^{13}C NMR: δ 17.74, 19.31, 20.98, 22.71, 32.02, 46.96, 53.79, 76.34, 126.71, 126.91, 127.95, 128.30, 132.66, 140.51; IR (film): 2968, 1455, 1368, 1241 cm^{-1}; Anal calcd for $C_{17}H_{26}NO_3P$: C, 63.14; H, 8.10; N, 4.33. Found: C, 62.91; H, 8.26; N, 4.32.



27

2-{[Benzyloxycarbonyl -(5,5-dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl) –amino]–methyl}-but-2-enoic acid methyl ester (27): Prepared following the general procedure except the rearrangement reaction was carried out at 40 °C for 4 h from 2–(1-hydroxy-ethyl)-acrylic acid methyl ester in 65% yield (2.14 g) as a colorless oil. ^{1}H NMR: δ 0.73 (s, 3H), 1.26 (s, 3H), 1.72 (d, *J* = 7.3 Hz, 3H), 3.60 (s, 3H), 3.89 (dd, *J* = 9.7, 17.2 Hz, 2H), 4.28 (d, *J* = 9.9 Hz, 2H), 4.48 (d, *J* = 9.8 Hz, 2H), 5.10 (s, 2H), 6.90 (q, *J* = 7.3 Hz, 1H), 7.22-7.33 (m, 5H); ^{13}C NMR: δ 14.40, 20.74, 22.77, 32.36, 42.78, 51.73, 69.01, 79.62, 128.87, 128.95, 129.16, 129.21, 135.03, 142.31, 155.78, 167.47; IR (film): 2966, 1714, 1459, 1438, 1396, 1278 cm^{-1}; Anal calcd for $C_{19}H_{26}NO_7P$: C, 55.47; H, 6.37; N, 3.40. Found: C, 55.49; H, 6.46; N, 3.34.



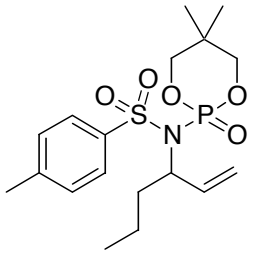
28

2-{[Benzyloxycarbonyl -(5,5-dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl) –amino]–methyl}-pent-2-enoic acid methyl ester (28): Prepared following the general procedure except the rearrangement reaction was carried out at 40 °C for 4 h from 2–(1-hydroxy-propyl)-acrylic acid methyl ester in 60% yield (2.04 g) as a colorless oil. ^{1}H NMR: δ 0.72 (s, 3H), 0.92 (t, *J* = 7.7 Hz, 3H), 1.25 (s, 3H), 2.16-2.20 (m, 2H), 3.60 (s, 3H), 3.93 (dd, *J* = 10.3, 17.2 Hz, 2H), 4.30 (d, *J* = 9.9 Hz, 2H), 4.48 (d, *J* = 9.8 Hz, 2H), 5.10 (s, 2H), 6.80 (t, *J* = 7.5 Hz, 1H), 7.22-7.33 (m, 5H); ^{13}C NMR: δ 13.35,

20.74, 21.86, 22.78, 32.36, 43.02, 51.77, 68.95, 79.60, 127.81, 128.88, 128.92, 129.09, 135.08, 148.81, 155.79, 167.63; IR (film): 2967, 2361, 1714, 1459, 1395, 1283 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{28}NO_7P + Na]^+$: 448.1501, Found: 448.1501.

General procedure for the Pd (II) catalyzed rearrangement:

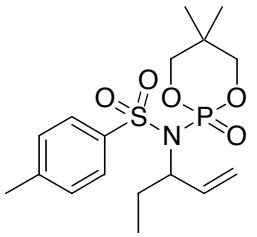
To a solution of Et_2O (25 mL) cooled in an ice/H_2O bath was added the allylic alcohol (2.5 mmol, 1.0 eq) and Et_3N (2.5 mmol, 1.0 eq), followed by a solution of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (2.5 mmol, 1.0 eq) in 5 mL Et_2O. The solution was then allowed to stir for 20 min and the precipitated Et_3N•HCl was removed by filtration. The Et_2O was removed under vacuum and the residue was dissolved in 5 mL CH_2Cl_2. The resulting solution was added dropwise to a solution of tosyl azide or cbz azide (3.7 mmol, 1.5 eq) in 2 mL CH_2Cl_2 cooled in an ice-H_2O bath. The reaction mixture was slowly warmed to rt over 1 h and then 10 mol% $PdCl_2(CH_3CN)_2$ was added to the reaction mixture. After stirring at rt for 30 min –1 h, the reaction mixture was then concentrated *in vacuo*, and the crude product was subjected to flash chromatography (2:3 hexanes/EtOAc) for isolation of the phosphoramidate product.



25

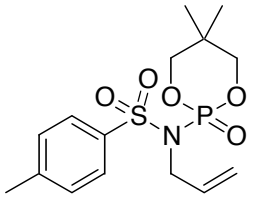
***N*- (5,5-dimethyl-2-oxo-2λ^5-[1,3,2] dioxaphosphinan-2-yl)–4-methyl-*N*-(1-propyl-allyl) -benzenesulfonamide (25)**: Prepared following the general procedure in 95% yield (953 mg) from *trans*-2-hexen-1-ol and 90% yield (903 mg) from *cis*-2-hexen-1-ol as a colorless oil. ^{1}H NMR: δ 0.75 (t, *J* = 7.3 Hz, 3H), 0.93 (s, 3H), 1.08-1.18 (m, 2H), 1.33 (s, 3H), 1.64-1.76 (m, 1H), 1.83-1.93 (m, 1H), 2.39 (s, 3H), 3.89-4.08 (m, 3H), 4.53-4.61 (m, 3H), 4.84 (d, *J* = 10.6 Hz, 1H), 5.95-6.04 (m, 1H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR: δ 13.75,19.94, 21.05, 21.79, 22.87, 32.67 (d, *J* = 10.6 Hz), 36.13, 64.49, 79.41 (2d, *J* = 6.8, 6.9 Hz), 117.91, 128.22, 129.76, 136.94, 144.62; IR

(film): 2964, 2875, 1599, 1466, 1345, 1274, 1165 cm^{-1}; Anal calcd for $C_{18}H_{28}NO_5PS$: C, 53.85; H, 7.03; N, 3.49. Found: C, 53.90; H, 7.19; N, 3.49.



29

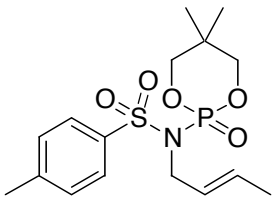
***N*- (5,5-dimethyl-2-oxo-2λ^5-[1,3,2] dioxaphosphinan-2-yl)–*N*-(1-ethyl-allyl)-4-methyl-benzenesulfonamide (29)**: Prepared following the general procedure in 90% yield (871 mg) from *trans*-2-penten-1-ol as a white solid. mp 122-124 °C; ^{1}H NMR: δ 0.75 (t, *J* = 7.5 Hz, 3H), 0.93 (s, 3H), 1.32 (s, 3H), 1.82-1.86 (m, 2H), 2.38 (s, 3H), 3.81-3.92 (m, 1H), 3.99-4.08 (m, 2H), 4.52-4.63 (m, 3H), 4.84 (d, *J* = 10.6 Hz, 1H), 5.93-6.02 (m, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ 11.30, 21.03, 21.77, 22.82, 27.07, 32.65 (d, *J* = 10.7 Hz), 66.16, 79.39 (2d, *J* = 7.7, 7.7 Hz), 117.94, 128.19, 129.76, 136.82, 144.62; IR (film): 2971, 2878, 1598, 1464, 1345, 1273, 1162 cm^{-1}; Anal calcd for $C_{17}H_{26}NO_5PS$: C, 52.70; H, 6.76; N, 3.62. Found: C, 52.37; H, 6.70; N, 3.57.



30

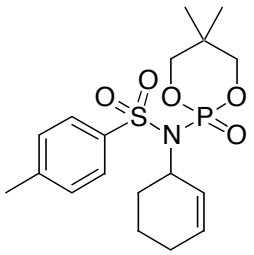
***N*- Allyl-*N*- (5,5-dimethyl-2-oxo-2λ^5-[1,3,2] dioxaphosphinan-2-yl)-4-methyl-benzenesulfonamide (30)**: Prepared following the general procedure in 95% yield (854 mg) from allyl alcohol as a white solid. mp 85-86 °C; ^{1}H NMR: δ 0.99 (s, 3H), 1.34 (s, 3H), 2.43 (s, 3H), 4.00 (dd, *J* = 6.0, 12.5 Hz, 2H), 4.08 (dd, *J* = 9.9, 16.6 Hz, 2H), 4.55 (dd, *J* = 5.1, 9.9 Hz, 2H), 5.11 (d, *J* = 9.5 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.78-5.86 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ 20.92, 21.73,

22.52, 32.55 (d, J = 9.9 Hz), 51.23, 79.25 (d, J = 6.9 Hz), 118.60, 127.87, 129.90, 133.46, 136.42, 144.73; IR (film): 2971, 1598, 1474, 1352, 1279, 1167 cm^{-1}; Anal calcd for $C_{15}H_{22}NO_5PS$: C, 50.13; H, 6.17; N, 3.90. Found: C, 50.02; H, 6.12; N, 3.91.



31

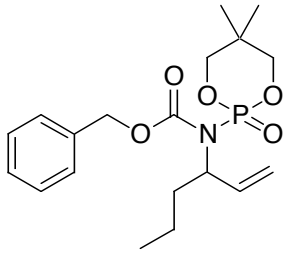
***N*- But-2-enyl-*N*- (5,5-dimethyl-2-oxo-2λ^5-[1,3,2] dioxaphosphinan-2-yl)-4-methyl-benzenesulfonamide (31)**: Prepared following the general procedure in 82% yield (765 mg) from 3-buten-2-ol as a colorless oil. ^{1}H NMR: δ 0.92 (s, 3H), 1.26 (s, 3H), 1.50 (d, J = 6.3 Hz, 3H), 2.36 (s, 3H), 3.88 (dd, J = 6.4, 12.3 Hz, 2H), 4.01 (dd, J = 10.5, 16.7 Hz, 2H), 4.47 (dd, J = 5.5, 10.3 Hz, 2H), 5.36-5.54 (m, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR: δ 17.81, 21.01, 21.74, 22.64, 32.57 (d, J = 10.0 Hz), 50.94, 79.19 (d, J = 6.9 Hz), 126.21, 127.97, 129.79, 130.50, 136.74, 144.56; IR (film): 2969, 1598, 1473, 1347, 1280, 1167 cm^{-1}; Anal calcd for $C_{16}H_{24}NO_5PS$: C, 51.46; H, 6.48; N, 3.75. Found: C, 51.46; H, 6.52; N, 3.77.



32

***N*- Cyclohex-2-enyl-*N*- (5,5-dimethyl-2-oxo-2λ^5-[1,3,2] dioxaphosphinan-2-yl)-4-methyl-benzenesulfonamide (32):** Prepared following the general procedure from 2-cyclohexen-1-ol in 55% yield (549 mg) as a white solid. mp 130-132 °C; ^{1}H NMR: δ 0.92 (s, 3H), 1.29 (s, 3H), 1.34-1.45 (m, 1H), 1.62-1.72 (m, 2H), 1.75-1.80 (m, 1H), 1.93-2.00 (m, 1H), 2.15-2.25 (m, 1H), 2.37 (s, 3H), 3.99-4.06 (m, 2H), 4.20-4.26 (m, 1H), 4.48-4.53 (m, 2H), 5.26-5.29 (m, 1H), 5.60-5.63 (m, 1H), 7.26 (d, J = 8.4 Hz, 2H) 7.77

(d, J = 8.1 Hz, 2H); ^{13}C NMR: δ 21.07, 21.77, 22.69, 22.73, 24.06, 28.45, 32.66 (d, J = 10.7 Hz), 58.73, 79.30, 127.84, 129.58, 129.95, 136.93, 144.64; IR (film): 2967, 2940, 1598, 1463, 1344, 1284, 1167 cm^{-1}; Anal calcd for $C_{18}H_{26}NO_5PS$: C, 54.12; H, 6.56; N, 3.51. Found: C, 53.89; H, 6.78; N, 3.42.



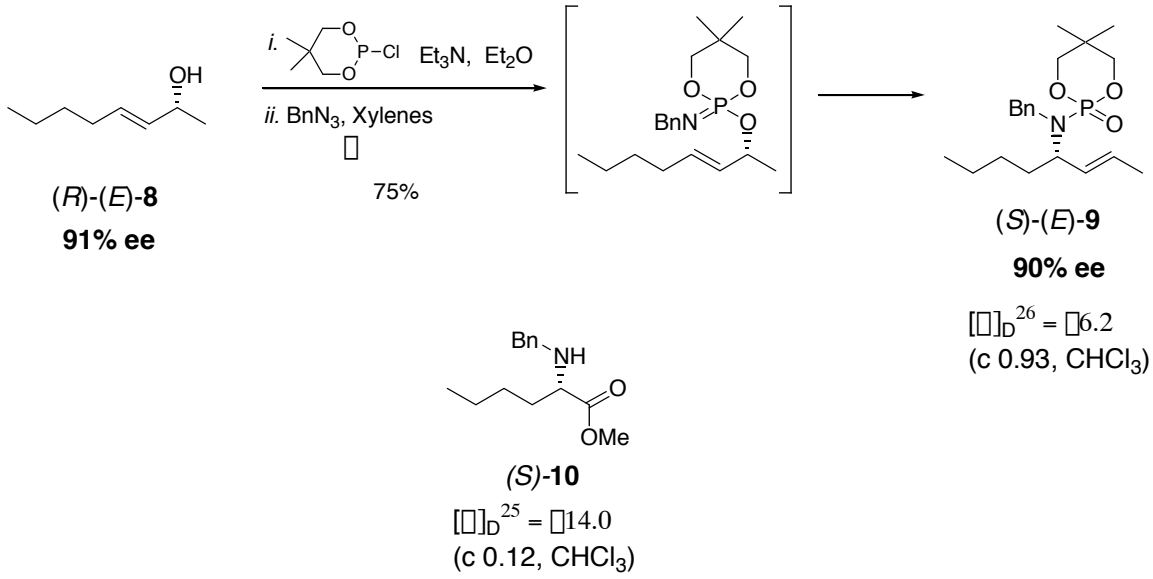
26

(5,5-Dimethyl-2-oxo-2λ^5- [1,3,2] dioxaphosphinan-2-yl) – (1-propyl-allyl)-carbamic acid benzyl ester (26): Prepared following the general procedure in 90% yield (858 mg) from *trans*-2-hexen-1-ol as a white solid. mp 99-101 °C; ^{1}H NMR: δ 0.66 (s, 3H), 0.82 (t, J = 7.4 Hz, 3H), 1.22-1.26 (m, 2H), 1.22 (s, 3H), 1.57-1.66 (m, 1H), 1.84-1.94 (m, 1H), 3.85 (dd, J = 10.3, 16.9 Hz, 2H), 4.17-4.20 (m, 2H), 4.62-4.71 (m, 1H), 5.02 (d, J = 10.3 Hz, 1H), 5.08-5.16 (m, 1H), 5.12 (d, J = 7.4 Hz, 2H), 5.99-6.06 (m, 1H), 7.29-7.31 (m, 5H); ^{13}C NMR: δ 13.87, 19.85, 20.82, 22.72, 32.37 (d, J = 9.9 Hz), 35.36, 61.16, 68.63, 79.49, 116.58, 128.76, 128.79, 128.84, 135.30, 138.56, 155.45; IR (film): 2963, 2874, 1708, 1466, 1374, 1229 cm^{-1}; Anal calcd for $C_{19}H_{28}NO_5P$: C, 59.83; H, 7.40; N, 3.67. Found: C, 59.51; H, 7.52; N, 3.67.

Enantiopurity and absolute stereochemistry determination for chirality transfer:

(R)-(E)-3-octen-2-ol **8** was prepared according to the published procedure.[9] To determine the ee, a sample of **8** was converted to the benzyl ester and a 91% ee was obtained by chiral HPLC (Chiral Whelk column, 3% EtOH in hexanes at 1ml/min, *S* isomer, t_R = 5.60 min, *R* isomer, t_R = 6.34 min). *(R)-(E)*-3-octen-2-ol **8** undergoes clean conversion to phosphoramidate *(S)-(E)*-**9** with no erosion of stereochemical purity. A 90% ee of phosphoramidate *(S)-(E)*-**9** was obtained by chiral HPLC (Chiral Whelk column, 3% EtOH in hexanes at 1ml/min, *R* isomer, t_R = 42.22 min, *S* isomer, t_R = 43.93 min).

A sample of phosphoramidate *(S)-(E)*-**9** was converted to β-amino ester **10** following the known procedure.[7, 11] By comparing the measured optical rotation of **10** and that of the previously reported enantiomer of **10**,[12] the absolute configuration of **9** was determined to be *S*.



Scheme S1. Determination of absolute configuration of **9**

[11] Marshall, J. A.; Garofalo, A. W. *J. Org. Chem.* **1993**, *58*, 3675-3680.

[12] Caddick, S.; Afonso, C. A. M.; Candeias, S. X.; Hitchcock, P. B.; Jenkins, K.; Murtagh, L.; Pardoe, D.; Gil Santos, A.; Treweeke, N. R.; Weaving, R. *Tetrahedron* **2001**, *57*, 6589-6605.

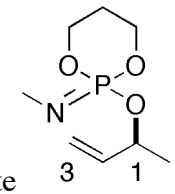
Crossover experiment:

Phosphorimidates **2e** and **2f** were formed in separate reaction flasks following the general procedure outlined for thermal rearrangement. After heating at 80 °C for 2 h, ^{31}P NMR confirmed the absence of the rearranged products. The crude mixtures of **2e** and **2f** were then combined in 1:1 ratio and refluxed for 4h. Upon cooling, the reaction mixture was subjected to flash chromatography (1:9 hexanes/EtOAc) for isolation of the phosphoramidate products. The four possible products were obtained in 75% combined yield and the product ratio was determined by GC analysis of the crude reaction mixture. All four possible products were individually synthesized and used as standards to confirm the identity of the products formed in the crossover experiment.

Coordinates and energies from DFT B3LYP/631G* calculations

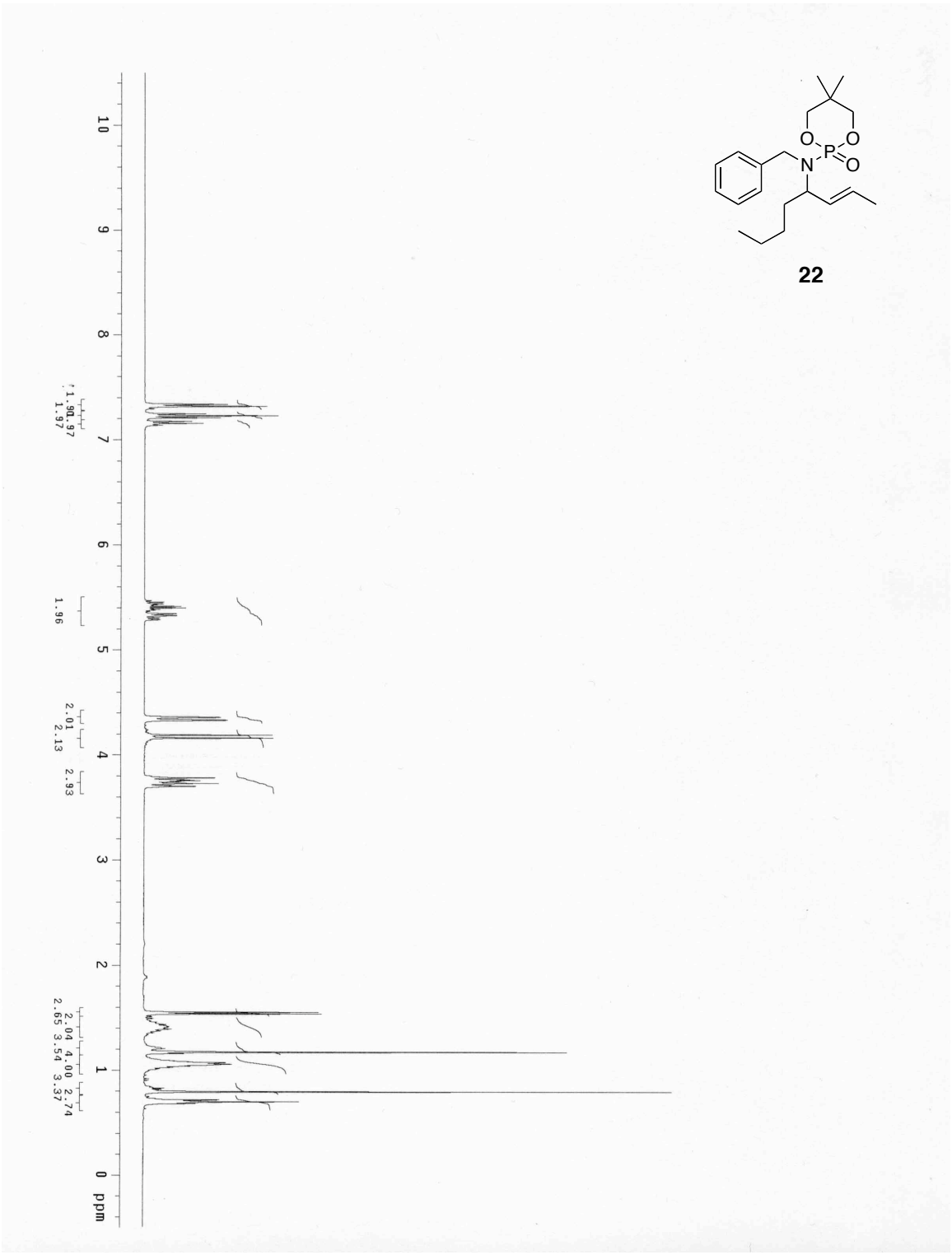
Transition state of the phosphorimidate rearrangement
Energy: -936.2245446

P	0.36133833129	-0.33190580765	-0.25916203073
N	-0.4442277875	-1.6792785948	-0.37434230562
O	1.2278042026	-0.27704234474	1.1338080904
O	-0.49872357621	0.95251500294	-0.35955422234
O	1.5318664453	-0.22014034008	-1.3864884665
C	-2.1859618299	0.94324176713	0.33012943893
H	-1.8897586672	0.93525129667	1.376764538
C	-2.855577609	-0.18743504031	-0.18208220808
H	-3.299386564	-0.11980740293	-1.1723256873
C	-2.4480616441	-1.4196943876	0.29193488171
H	-2.7918293241	-2.3378592421	-0.17505086113
H	-2.1170590378	-1.5255239561	1.3209640557
C	2.5529786289	0.79062716746	-1.2309508085
H	3.251929388	0.63496905844	-2.0566751574
C	2.2357166026	0.74764889699	1.2650719736
H	2.7110951366	0.57871105657	2.2351474812
H	2.0941132926	1.7805009095	-1.3479387078
H	1.7483912911	1.7313125117	1.2833782946
C	3.2475290894	0.6640967987	0.12346440139
H	3.9898162862	1.4653520524	0.23068498307
H	3.7780980553	-0.29401767315	0.17544686827
C	0.12930571818	-2.9945191445	-0.13884246687
H	0.90016113547	-3.2439987168	-0.88195641006
H	-0.66335412262	-3.7479440003	-0.23715920042
H	0.57491633365	-3.1118531166	0.86095622417
C	-2.6970065918	2.3012657569	-0.11767382538
H	-3.6998906738	2.4977263511	0.27321693675
H	-2.7204872697	2.3756130343	-1.2106583966
H	-2.0237352395	3.0921881069	0.22989258679



Starting phosphorimidate
Energy: -936.2625867

P	0.6240881	-0.6751180	-0.2335680
N	0.0897729	-2.1025170	-0.2565512
O	1.5171593	-0.2525479	1.0703909
O	-0.5584195	0.4207545	-0.2902012
O	1.5625944	-0.1837190	-1.4666323
C	-1.8977306	0.1222428	0.2184936
H	-2.1029052	-0.9291585	-0.0001400
C	-2.8429345	1.0124847	-0.5369319
H	-2.6326504	2.0807945	-0.4772550
C	-3.8984248	0.5688963	-1.2176194
H	-4.5800994	1.2474034	-1.7234986
H	-4.1218846	-0.4930006	-1.2948635
C	2.2039706	1.1098759	-1.4118291
H	2.8359472	1.1636211	-2.3019772
C	2.1473866	1.0460924	1.1005664
H	2.7364940	1.0699215	2.0210520
H	1.4354740	1.8899857	-1.4834282
H	1.3704159	1.8190590	1.1639966
C	3.0231452	1.2577773	-0.1322920
H	3.4716481	2.2588061	-0.0969662
H	3.8379747	0.5242277	-0.1315263
C	0.7649560	-3.3790811	-0.1578970
H	1.4043485	-3.5850862	-1.0288624
H	0.0162947	-4.1790387	-0.1117664
H	1.3913694	-3.4679620	0.7422327
C	-1.9379941	0.3679690	1.7263801
H	-1.2193129	-0.2755278	2.2430260
H	-2.9397700	0.1496453	2.1117051
H	-1.7009136	1.4131999	1.9559628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3.37

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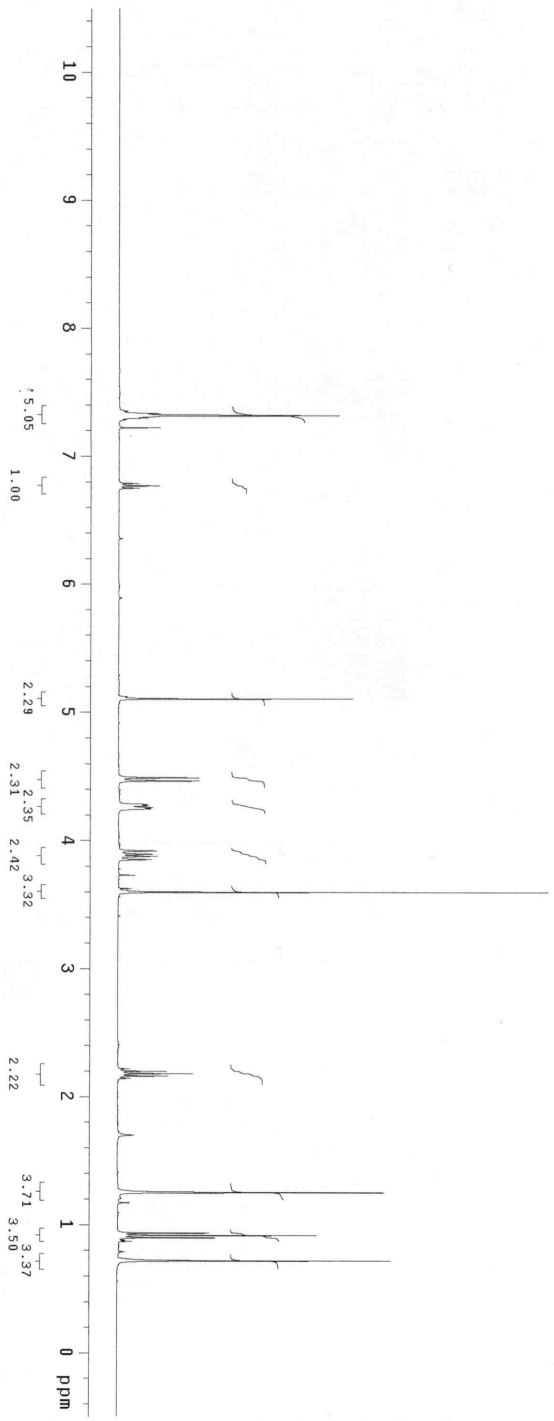
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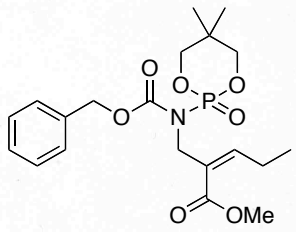
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