Supporting Information for:

A phosphorimidate rearrangement for the facile and selective preparation of allylic amines

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General. Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Benzene, Et₂O, and toluene were dried by passage through activated alumina columns and degassed by stirring under a dry argon atmosphere. 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.¹ All reactions involving air- or moisture-sensitive compounds were performed under an argon atmosphere. Benzyl azide,² allyl azide,³ and 4-methoxybenzyl azide⁴ were prepared according to literature procedures. 1-(*Tert*-butyl-dimethylsilyloxy)-but-3-en-2-ol and 1-benzyloxy-but-3-en-2-ol were prepared following literature procedures.⁵ ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 500 MHz and 125 MHz, respectively, unless otherwise specified. IR spectra were measured as thin films on NaCl plates. Melting points are uncorrected.

General procedure for the thermal rearrangement: To a solution of Et₂O (50 mL) cooled in an ice/H₂O bath was added the allylic alcohol (5 mmol, 1.25 equiv) and Et₃N (5 mmol, 1.25 equiv), followed by a solution of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane or diethylchlorophosphite (5 mmol, 1.25 equiv) in 5 mL Et₂O. The solution was then allowed to stir for 20 min and the precipitated Et₃N•HCl was removed by filtration using standard Schlenk techniques.⁶ The Et₂O was removed under vacuum and the residue was dissolved in 5 mL xylene. The solution was added dropwise to a solution of benzyl azide or 4-methoxybenzyl azide (4 mmol, 1 equiv) in 2 mL xylene cooled in an ice-H₂O bath. When allyl azide was used as a reactant, an excess (3 equiv) was used due to the volatility this material. The reaction mixture was slowly warmed to rt over 1 h, heated to 80 °C for 1 h, then diluted with an additional 10 mL xylene and heated at reflux for 4 h. Upon cooling, the reaction mixture was subjected to flash chromatography (1:9 hexanes/EtOAc) for isolation of the phosphoramidate product.

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³ Koziara, A.; Zwierzak, A. *Synthesis* **1992**, 1063-1065.

⁴ Buckle, D. R.; Rockell, C. J. M. *J. Chem. Soc. Perkin Trans. 1* **1982**, 627-630.

⁵ Davoille, R. J.; Rutherford, D. T.; Christie, S. D. R. *Tetrahedron Lett.* **2000**, *41*, 1255-1259.

⁶ Clark, P. W.; Curtis, J. L. S.; Garrou, P. E.; Hartwell, G. E. *Can. J. Chem.* **1974**, *52*, 1714-1720.

6c

Benzyl -(5,5-dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl) – (1-propyl-allyl)-amine (6c): Prepared following the general procedure in 88% yield (1.19 g) from *trans*-2-hexen-1-ol and 75% yield (1.01 g) from *cis*-2-hexen-1-ol as a colorless oil. ^1H NMR: δ 0.66 (t, J = 7.3 Hz, 3H), 0.80 (s, 3H), 1.18 (s, 3H), 1.09-1.21 (m, 2H), 1.36-1.51 (m, 2H), 3.71-3.84 (m, 3H), 4.12-4.26 (m, 2H), 4.36 (d, J = 11.0 Hz, 2H), 4.98-5.03 (m, 2H), 5.68-5.76 (m, 1H), 7.17-7.20 (m, 1H), 7.22-7.26 (m, 2H), 7.33-7.35 (m, 2H); ^{13}C NMR: δ 13.81, 19.69, 20.98, 22.77, 32.04, 34.70, 47.79, 59.61, 76.37, 116.45, 127.22, 128.33, 138.50, 139.76; IR (film): 3066, 3029, 2961, 2933, 2874, 1456, 1257 cm^{-1} ; Anal calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_3\text{P}$: C, 64.08; H, 8.36; N, 4.15. Found: C, 63.99; H, 8.19; N, 4.13.

8

Allyl-benzyl -(5,5-dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl)-amine (8): Prepared following the general procedure from allyl alcohol in 80% yield (945 mg) as a colorless oil. ^1H NMR: δ 0.82 (s, 3H), 1.20 (s, 3H), 3.49 (dd, J = 6.1, 11.9 Hz, 2H), 3.77 (dd, J = 9.9, 22.0 Hz, 2H), 4.21 (d, J = 10.3 Hz, 2H), 4.35 (d, J = 9.9 Hz, 2H), 5.09 (m, 2H), 5.66-5.73 (m, 1H), 7.22-7.28 (m, 5H); ^{13}C NMR: δ 20.92, 22.65, 32.04, 47.33, 48.42, 76.50, 118.28, 127.55, 128.43, 128.63, 134.05, 137.55; IR (film): 3065, 3029, 2965, 2931, 2885, 1472, 1456, 1368, 1260 cm^{-1} ; Anal calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_3\text{P}$: C, 61.01; H, 7.51; N, 4.74. Found: C, 61.23; H, 7.43; N, 4.79.

9

Benzyl -(5,5-dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl) – (1-phenyl-allyl)-amine (9): Prepared following the general procedure from *trans*-3-phenyl-prop-2-en-1-ol in 70% yield (1.04 g) as a colorless oil. ^1H NMR: 0.83 (s, 3H), 1.18 (s, 3H), 3.79 (dd, J = 11.2, 21.8 Hz, 2H), 4.01 (dd, J = 12.7, 16.3 Hz, 1H), 4.33 (dd, J = 11.2, 16.3 Hz, 1H), 4.40 (d, J = 10.3 Hz, 2H),

5.11-5.16 (m, 2H), 5.22 (dd, $J = 7.9, 12.7$ Hz, 1H), 5.86-5.95 (m, 1H), 7.18-7.29 (m, 10H); ^{13}C NMR: δ 21.03, 22.78, 32.10, 48.18, 63.00, 76.60, 117.94, 127.09, 127.65, 128.20, 128.30, 128.47, 128.51, 136.49, 139.40; IR (film): 3062, 3030, 2966, 2931, 2885, 1453, 1258 cm^{-1} ; Anal calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{P}$: C, 67.91; H, 7.06; N, 3.77. Found: C, 67.61; H, 7.14; N, 3.76.

10

Benzyl-(5,5-dimethyl-2-oxo-2 λ^5 -[1,3,2] dioxaphosphinan-2-yl) - (1,5-dimethyl-1-vinyl-hex-4-enyl)-amine (10): Prepared following the general procedure from geraniol in 60% yield (940 mg) as a colorless oil. ^1H NMR: 0.78 (s, 3H), 1.07 (s, 3H), 1.36 (s, 3H), 1.51 (s, 3H), 1.59 (s, 3H), 1.77-1.92 (m, 3H), 2.00-2.07 (m, 1H), 3.69 (dd, $J = 11.2, 21.5$ Hz, 2H), 4.23-4.40 (m, 4H), 4.95-5.04 (m, 3H), 5.84 (dd, $J = 10.8, 17.4$ Hz, 1H), 7.14-7.17 (m, 1H), 7.22-7.27 (m, 2H), 7.32 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR: δ 17.79, 21.28, 23.15, 23.56, 23.88, 25.84, 32.23, 40.03, 49.55, 64.09, 76.27, 113.86, 124.52, 126.56, 127.13, 128.28, 131.43, 141.39, 143.70; IR (film): 2966, 2930, 2884, 1453, 1260 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{34}\text{NO}_3\text{P}$: C, 67.50; H, 8.75; N, 3.58. Found: C, 67.25; H, 8.67; N, 3.55.

11

Benzyl-but-2-enyl- (5,5-dimethyl-2-oxo-2 λ^5 -[1,3,2] dioxaphosphinan-2-yl)-amine (11): Prepared following the general procedure from 3-buten-2-ol in 70% yield (0.866 g) as a colorless oil. ^1H NMR: δ 0.82 (s, 3H), 1.20 (s, 3H), 1.64 (d, $J = 6.2$ Hz, 3H), 3.42 (dd, $J = 6.2, 11.7$ Hz, 2H), 3.77 (dd, $J = 9.9, 21.6$ Hz, 2H), 4.20 (d, $J = 10.3$ Hz, 2H), 4.35 (d, $J = 9.9$ Hz, 2H), 5.36-5.43 (m, 2H), 7.18-7.28 (m, 5H); ^{13}C NMR: δ 17.85, 20.94, 22.65, 32.04, 46.63, 48.13, 76.46, 126.82, 127.46, 128.40, 128.58, 129.82, 137.79; IR (film): 3063, 3029, 3003, 2964, 2934, 2885, 1455, 1367, 1258 cm^{-1} ; Anal calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_3\text{P}$: C, 62.12; H, 7.82; N, 4.53. Found: C, 61.98; H, 7.73; N, 4.46.

12

Benzyl- [4-(*tert*-butyl-dimethyl-silanyloxy)-but-2-enyl]-(5,5-dimethyl-2-oxo-2 λ^5 -[1,3,2] dioxaphosphinan-2-yl)-amine (12): Prepared following the general procedure from 1-(*tert*-butyl-dimethyl-silanyloxy)-but-3-en-2-ol in 55% yield (0.965 g) as a colorless oil. ^1H NMR (C_6D_6): δ -0.04 (s, 6H), 0.04 (s, 3H), 0.79 (s, 3H), 0.90 (s, 9H), 3.27 (dd, $J = 9.9, 21.8$ Hz, 2H), 3.60 (dd, $J = 6.2, 11.7$ Hz, 2H), 3.91 (dd $J = 1.5, 4.8$ Hz, 2H), 4.15 (d, $J = 10.3$ Hz, 2H), 4.35 (d, $J = 10.3$ Hz, 2H), 5.44-5.50 (m, 1H), 5.63-5.70 (m, 1H), 6.97-7.01 (m, 1H), 7.07-7.10 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR: δ -5.01, 18.56, 20.92, 22.65, 26.11, 32.03, 46.15, 48.37, 63.30, 76.45, 125.71, 127.50, 128.42, 128.61, 133.57, 137.62; IR (film): 3064, 3030, 2958, 2930, 2885, 2857, 1472, 1367, 1259 cm^{-1} ; Anal calcd for $\text{C}_{22}\text{H}_{38}\text{NO}_4\text{PSi}$: C, 60.11; H, 8.71; N, 3.19. Found: C, 60.26; H, 8.81; N, 3.22.

13

Benzyl- [4-benzyloxy-but-2-enyl]-(5,5-dimethyl-2-oxo-2 λ^5 -[1,3,2] dioxaphosphinan-2-yl)-amine (13): Prepared following the general procedure from 1-benzyloxy-but-3-en-2-ol in 65% yield (1.08 g) as a colorless oil. ^1H NMR (C_6D_6): δ 0.03 (s, 3H), 0.78 (s, 3H), 3.25 (dd, $J = 10.3, 21.6$ Hz, 2H), 3.58 (dd, $J = 6.1, 11.7$ Hz, 2H), 3.70 (dd $J = 1.3, 5.3$ Hz, 2H), 4.15 (d, $J = 10.3$ Hz, 2H), 4.23 (s, 2H), 4.31 (d, $J = 10.2$ Hz, 2H), 5.46-5.53 (m, 1H), 5.60-5.67 (m, 1H), 6.96-7.12 (m, 6H), 7.22 (d, $J = 6.7$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR: δ 20.93, 22.68, 32.06, 46.30, 48.60, 70.22, 72.28, 76.51, 127.59, 127.83, 127.94, 128.42, 128.60, 128.67, 129.08, 130.56, 137.54, 138.43; IR (film): 3063, 3030, 2964, 2931, 2884, 1367, 1258 cm^{-1} ; HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{30}\text{NO}_4\text{P} + \text{Na}]^+$: 438.1810, Found: 438.1806.

14

Benzyl-cyclohex-2-enyl- (5,5-dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl)-amine (14): Prepared following the general procedure from 2-cyclohexen-1-ol in 65% yield (0.87 g) as a white solid. mp 105-106 $^{\circ}\text{C}$ ^1H NMR: δ 0.81 (s, 3H), 1.16 (s, 3H), 1.34-1.51 (m, 2H), 1.61-1.65 (m, 1H), 1.70-1.74 (m, 1H), 1.82-1.86 (m, 2H), 3.69-3.79 (m, 2H), 4.10 (dd $J =$

13.5, 16.5 Hz, 1H), 4.19-4.26 (m, 1H), 4.33-4.42 (m, 3H), 5.45-5.48 (m, 1H), 5.73-5.76 (m, 1H), 7.16-7.18 (m, 1H) 7.22-7.26 (m, 2H), 7.33 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR: δ 20.98, 22.21, 22.68, 24.65, 29.12, 32.05, 46.88, 54.49, 76.35, 126.83, 127.51, 128.30, 129.88, 131.36, 140.85; IR (film): 3062, 3028, 2962, 2934, 2884, 1454, 1368, 1259 cm^{-1} ; Anal calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_3\text{P}$: C, 64.46; H, 7.81; N, 4.18. Found: C, 64.24; H, 7.55; N, 4.19.

15

Allyl -(5,5-dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl) - (1-propyl-allyl)-amine (15): Prepared following the general procedure from *trans*-2-hexen-1-ol in 60% yield (0.431 g) as a colorless oil. ^1H NMR: δ 0.80 (s, 3H), 0.87 (t, $J = 7.3$ Hz, 3H), 1.20 (s, 3H), 1.25-1.41 (m, 2H), 1.48-1.65 (m, 2H), 3.54-3.64 (m, 2H), 3.73 (dd, $J = 11.2, 21.8$ Hz, 2H), 3.95-4.00 (m, 1H), 4.31 (d, $J = 10.3$ Hz, 2H), 5.01 (d, $J = 14.3$ Hz, 1H), 5.07-5.14 (m, 3H), 5.78-5.90 (m, 2H); ^{13}C NMR: δ 13.97, 19.68, 20.96, 22.68, 31.99, 34.50, 46.28, 58.99, 76.29, 116.08, 116.28, 137.62, 138.88; IR (film): 3369, 2969, 2360, 1664, 1612, 1360, 1205 cm^{-1} ; Anal calcd for $\text{C}_{14}\text{H}_{26}\text{NO}_3\text{P}$: C, 58.52; H, 9.12; N, 4.87. Found: C, 58.30; H, 9.43; N, 5.00.

16

(5,5-Dimethyl-2-oxo-2 λ^5 - [1,3,2] dioxaphosphinan-2-yl)-(4-methoxy-benzyl)-(1-propyl-allyl)-amine (16): Prepared following the general procedure from *trans*-2-hexen-1-ol in 80% yield (1.18 g) as a colorless oil. ^1H NMR: δ 0.67 (t, $J = 7.3$ Hz, 3H), 0.79 (s, 3H), 1.17 (s, 3H), 1.08-1.19 (m, 2H), 1.35-1.51 (m, 2H), 3.73 (s, 3H), 3.70-3.78 (m, 3H), 4.10-4.14 (m, 2H), 4.34 (d, $J = 11.0$ Hz, 2H), 4.96-5.01 (m, 2H), 5.66-5.74 (m, 1H), 6.76-6.78 (m, 2H), 7.22-7.25 (m, 2H); ^{13}C NMR: δ 13.86, 19.69, 20.98, 22.78, 32.05, 34.76, 47.23, 55.40, 59.48, 76.37, 113.71, 116.31, 129.62, 131.81, 138.66, 158.91; IR (film): 3074, 2961, 2934, 2884, 1613, 1514, 1248 cm^{-1} ; Anal calcd for $\text{C}_{19}\text{H}_{30}\text{NO}_4\text{P}$: C, 62.11; H, 8.23; N, 3.81. Found: C, 61.85; H, 8.41; N, 3.83.

6b

Benzyl -(1-propyl-allyl)-phosphoramidic acid diethyl ester (6b): Prepared following the general procedure from *trans*-2-hexen-1-ol and diethylchlorophosphite in 55% yield (715

mg) as a colorless oil. ^1H NMR: δ 0.71 (t, $J = 7.3$ Hz, 3H), 1.13-1.15 (m, 2H), 1.21-1.26 (m, 6H), 1.45-1.49 (m, 2H), 3.61-3.67 (m, 1H), 3.90-4.07 (m, 4H), 4.10 (d, $J = 10.6$ Hz, 2H), 4.96-5.05 (m, 2H), 5.72-5.81 (m, 1H), 7.17-7.19 (m, 1H), 7.22-7.26 (m, 2H), 7.32 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR: δ 13.91, 16.33, 19.88, 35.19, 48.28, 59.94, 62.30, 116.43, 127.15, 128.31, 128.55, 138.81, 140.19; IR (film): 3066, 3029, 2979, 2960, 2932, 2906, 2872, 1455, 1391, 1253 cm^{-1} ; Anal calcd for $\text{C}_{17}\text{H}_{28}\text{NO}_3\text{P}$: C, 62.75; H, 8.67; N, 4.30. Found: C, 62.77; H, 8.95; N, 4.32.

7c

Benzyl -(5,5-dimethyl-2-oxo-2-[(1,3,2) dioxaphosphinan-2-yl]-hex-2-enyl-amine: (7c): Prepared following the general procedure from *trans*-2-hexen-1-ol in acetonitrile in 14% yield (190 mg) as white solid. mp 74-75 $^{\circ}\text{C}$; ^1H NMR: δ 0.88 (s, 3H), 0.91 (t, $J = 7.4$ Hz, 3H), 1.26 (s, 3H), 1.38-1.42 (m, 2H), 1.99-2.04 (m, 2H), 3.49 (dd, $J = 6.3, 11.5$ Hz, 2H), 3.83 (dd, $J = 9.8, 21.7$ Hz, 2H), 4.20 (d, $J = 10.3$ Hz, 2H), 4.35 (d, $J = 9.9$ Hz, 2H), 5.34-5.40 (m, 1H), 5.44-5.50 (m, 1H), 7.26-7.28 (m, 1H), 7.31-7.33 (m, 4H); ^{13}C NMR: δ 13.84, 20.95, 22.56, 22.68, 32.05, 34.46, 46.71, 48.08, 76.46, 125.62, 127.43, 128.41, 128.59, 135.32, 137.79; IR (film): 3029, 2960, 2930, 2884, 1367, 1259 cm^{-1} ; Anal calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_3\text{P}$: C, 64.08; H, 8.36; N, 4.15. Found: C, 64.02; H, 8.40; N, 4.18.

Procedure for the cleavage of phosphoramidate 11: Ethanethiol (3 mmol, 0.22 mL, 3 equiv) dissolved in 2 mL DMF was added dropwise to an ice-cooled suspension of NaH (3 mmol, 72 mg, 3 equiv) in 2 mL DMF.⁷ The mixture was then stirred for 20 min before a solution of phosphoramidate **11** (1 mmol, 309 mg, 1 equiv) in 2 mL DMF was added. After refluxing for 2 h, the reaction mixture was cooled to rt, quenched with saturated NH_4Cl and then extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residual oil was then dissolved in 5 mL of methanol and added to 5 mL of 1 N solution of HCl in MeOH.⁸ After continuous stirring at rt for 4 h, 10 mL of 2N NaOH was added to the reaction mixture, which was then extracted with EtOAc (3 x 50 mL). The combined organic extracts were concentrated to about 25 mL and extracted with 1 N HCl (3 x 10 mL). The aqueous solution was washed with 10 mL EtOAc and then cooled in ice- H_2O bath. The pH was adjusted to 10 with 3 N NaOH. The basified opaque mixture was extracted with EtOAc (3 x 50 mL) and the combined organic extracts were dried over Na_2SO_4 , filtered and N-crotylbenzylamine was obtained after distillation in 90% yield. The spectral data for the obtained N-crotylbenzylamine was consistent with that reported in the literature.⁹

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⁹ Davies, S. G.; Fox, J. F.; Jones, S.; Price, A. J.; Sanz, M. A.; Sellers, T. G. R.; Smith, A. D.; Teixeira, F. C. J. *Chem. Soc. Perkin Trans. 1* **2002**, 1757-1765.