Supporting Information

for

Tandem Polar/Radical Crossover Sequences for the Formation of Fused and Bridged Bicyclic Nitrogen Heterocycles Involving Radical Ionic Chain Reactions, and Alkene Radical Cation Intermediates, Performed Under Reducing Conditions: Scope and Limitations

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General. All solvents were dried and distilled by standard methods. All spectra were recorded in CDCl₃ solution. Microanalyses were carried out by Midwest Microlabs, Indianapolis, In.

1-(Diphenylphosphatoxy)-1-phenyl-2-methyl-2-nitropropane (3). 1-Phenyl-2-methyl-2-nitropropanol¹ (3.0 g, 15 mmol) was allowed to react with ClP(O)(OPh)₂ (6.0 g, 22.5 mmol) and DMAP (2.8 g, 22.5 mmol) in dichloromethane (100 mL) overnight at room temperature before it was diluted with EtOAc, washed with saturated aqueous NH₄Cl, water and brine, then dried (Na₂SO₄) and concentrated under vacuum. Chromatography on silica gel then gave **3** (4.80 g, 75%). ¹H NMR δ: 7.35-6.94 (m, 15 H), 6.15 (d, *J* = 8.0 Hz, 1 H), 1.64 (s, 3 H), 1.43 (s, 3 H); ¹³C NMR δ: 150.3 (d), 134.0, 129.8, 129.7, 129.5, 128.4, 128.0, 125.5, 125.4, 120.1, 120.0, 119.9 (d), 90.8 (d), 84.3 (d), 23.9, 19.6; ³¹P NMR δ: -12.6. Anal. Calcd for C₂₂H₂₂NO₆P: C, 61.83; H, 5.19. Found: C, 62.16; H, 5.28.

cis- and trans-2,2,4-Trimethyl-3-phenyltetrahydrofuran (4). Nitrophosphate **3** (107 mg, 0.25 mmol), triphenyltin hydride (131 mg, 0.38 mmol), allyl alcohol (0.34 mL, 5.0 mmol), and AIBN (18 mg, 0.1 mmol) were dissolved in benzene (1 mL) and purged with Argon before being rapidly brought to reflux. After heating to reflux overnight, the reaction mixture was cooled to room temperature and the volatiles removed under vacuum. Chromatography of the residue on silica gel (eluent: EtOAc/hexanes 1/5) gave the title tetrahydrofuran as an approximately 1/10 *cis/trans* mixture (28 mg, 59%) whose spectra were identical to those of an authentic sample.²

1-Phenyl-1-(tetrahydropyranoxy)-2-nitropropane (5). 1-Phenyl-2-nitro-propanol³ (5.64 g, 31 mmol), pyridinium *p*-toluenesulfonate (3.1 g, 12 mmol) and dihydropyran (5.2 g, 62 mmol) were stirred at room temperature in dichloromethane (100 mL) over night, then washed with saturated aqueous sodium bicarbonate, water and brine. Drying (Na₂SO₄), concentration and filtration on silica gel gave **5** in the form of an undefined mixture of stereoisomers (8.13 g, 99%). ¹H NMR δ: 7.38 (m, 5 H), 5.34 (d, *J* = 5.5 Hz), 5.30 (d, *J* = 4.5 Hz), 5.04 (d, *J* = 9.8 Hz), 4.79 (d, *J* = 6.4 Hz) (1 H), 4.84 (m), 4.67 (m) (1H), 4.76 (m), 4.51 (br. t), 4.43 (br. t) (1 H), 3.80-3.07 (m, 2 H), 1.90-1.29 (m, 6 H), 1.60 (d, *J* = 6.7 Hz), 1.49 (d, *J* = 6.7 Hz), 1.28 (d, *J* = 6.8 Hz), 1.26 (d, *J* = 6.4 Hz) (3 H). Anal. Calcd for C₁₄H₁₉NO₄: C, 63.38; H, 7.22. Found: C, 62.92; H, 7.13.

Methyl 4-Methyl-4-nitro-5-phenyl-5-(tetrahydropyranoxy)pentanoate (6). DBU (0.597 mL, 3.98 mmol) was added at room temperature to a solution of **5** (1.054 g, 3.98 mmol) and methyl acrylate (0.511 mL, 4.77 mmol) in CH₃CN (3.0 mL). The resulting reaction mixture was stirred overnight, then quenched with saturated NH₄Cl solution (20 mL) and EtOAc (50 mL). The EtOAc layer was washed with HCl (1N) until the water phase was acidic to pH paper. The combined water layers were extracted with EtOAc (3 x 15 mL) and the combined organic phases washed with water (15 mL) and brine (15 mL), then dried (Na₂SO₄). The solvent was removed under vacuum and the residue was subjected to flash chromatography

on silica gel (hexane/EtOAc 5/1) to afford **6** as an undefined mixture of stereoisomers (1.17 g, 84%). ^1H NMR δ : 7.36-7.20 (m, 5 H), 5.21 (s), 5.18 (s), 5.03 (s) (1 H), 4.64 (br. s), 4.57 (br. s), 4.37 (br. s) (1 H), 3.58 (s), 3.57 (s), 3.52 (s) (3 H), 3.18-3.03 (m, 2 H), 2.70 (m), 2.47-2.01 (m, 4 H), 1.73-1.31 (m, 6 H), 1.45 (d, $J = 6.7$ Hz), 1.32 (d, $J = 8.0$ Hz) (3 H); ^{13}C NMR δ : 172.9, 172.8, 172.2, 172.1, 137.5, 137.1, 135.2, 135.1, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 100.6, 100.4, 94.6, 93.9, 93.7, 93.6, 93.1, 84.5, 84.3, 82.2, 81.0, 80.9, 61.8, 61.7, 61.3, 51.6, 31.9, 30.1, 30.0, 29.7, 29.0, 28.5, 28.4, 28.0, 25.2, 25.0, 19.4, 19.0, 18.6 (d), 18.2, 15.1, 15.0. Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_6$: C, 61.52; H, 7.17; Found: C, 61.49; H, 7.30.

Methyl 4-Methyl-4-nitro-5-phenyl-5-(diphenylphosphatoxy)pentanoate (8). *p*-Toluenesulfonic acid monohydrate (0.496 g, 2.60 mmol) was added to a solution of **6** (0.6087 g, 1.73 mmol) in MeOH (25 mL) at room temperature. After 3 h, the reaction was quenched with saturated NaHCO_3 solution (15 mL) and EtOAc (75 mL), then the water layer was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with water (15 mL) and brine (15 mL), and dried (Na_2SO_4). The solvent was removed under vacuum to afford the free alcohol **7** (0.443 g, 96%). This alcohol was then phosphorylated with $\text{CIP(O)(OPh)}_2/\text{DMAP}$ as, described for **3** above, to give **8** in 66% yield as an undefined mixture of stereoisomers. ^1H NMR δ : 7.36-6.91 (m, 15 H), 6.11 (d, $J = 7.7$ Hz), 6.02 (d, $J = 8.8$ Hz) (1 H), 3.65 (s), 3.61 (s) (3 H), 2.68 (m), 2.39 (m), 2.23 (m), 2.15 (m), 1.70 (m) (4 H), 1.58 (s), 1.45 (s) (3 H); ^{31}P NMR δ : -12.40, -12.85. Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_8\text{P}$: C, 60.12; H, 5.25; Found: C, 60.08; H, 5.31.

4-Methyl-4-nitro-5-phenyl-5-(diphenylphosphatoxy)pentanoic Acid (9). LiOH (1N, 0.889 mL, 0.889 mmol) was added at room temperature to a solution of **8** (88.7 mg, 0.178 mmol) in THF/ $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (3.0 mL, 3/2/1). After 6 min, the reaction was quenched with saturated NH_4Cl solution (10 mL) and EtOAc (50 mL) and the water layer was extracted with EtOAc (3 x 10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL), and dried (Na_2SO_4). The solvent was removed under vacuum to afford **9** (86.4 g, 100%), which was not subjected to further purification but used as such in the next step. ^1H NMR δ : 7.41-6.76 (m, 15 H), 6.17 (d, $J = 7.7$ Hz), 6.06 (d, $J = 8.7$ Hz) (1 H), 2.66 (m), 2.50-2.08 (m), 1.70 (m) (4 H), 1.60 (s), 1.47 (s) (3 H); ^{13}C NMR δ : 176.9, 176.1, 156.4, 156.2, 150.3, 133.6, 129.9, 129.8, 129.5, 128.7, 128.6, 128.1, 125.8, 125.7, 125.6, 125.5, 120.2, 120.1, 119.9 (d), 115.5, 93.6, 93.5, 93.0 (d), 84.7, 84.6, 84.4 (d), 31.5, 28.2, 18.5, 15.5; ^{31}P NMR δ : -12.38, -12.86.

5-Benzyl-5-methyl-2-tetrahydrofuranone (10)⁴ A solution of **9** (78 mg, 0.16 mmol), triphenyltin hydride (84 mg, 0.24 mmol) and AIBN (11 mg, 0.064 mmol) in benzene (0.75 mL) was immersed under Ar in an oil bath preheated to 100 $^\circ\text{C}$. The reaction was maintained at reflux for 36 h with periodic additions of AIBN before it was cooled to room temperature and the solvent removed under vacuum. The residue was taken up in MeOH (1.0 mL) and treated with NaBH_4 (20 mg) for 10 min.⁵ Water was then added and the reaction mixture extracted with EtOAc. The extracts were washed with water and brine, dried (Na_2SO_4)

and concentrated. Purification by chromatography over silica gel afforded **10** (27.5 mg, 90%). ^1H NMR δ : 7.29 (m, 5 H), 3.03 (d, $J = 13.0$ Hz, 1 H), 2.88 (d, $J = 13.0$ Hz, 1 H), 2.47 (m, 1 H), 2.26-1.91 (s, 3 H), 1.46 (s, 3 H).

4-Methyl-4-nitro-5-phenyl-5-(tetrahydropyranoxy)-1-pentanol (11). LiAlH_4 (38.0 mg, 1.0 mmol) in ether (3.0 mL) was added dropwise to a solution of **6** (0.701 g, 2.0 mmol) in ether (6.0 mL) at -42°C . The resulting reaction mixture was stirred at that temperature for 2 h, then quenched by dropwise addition of EtOAc (0.3 mL) and stirring for 5 min. The cold bath was then removed and water (0.13 mL), aqueous NaOH (15%, 0.3 mL), water (0.3 mL) and Na_2SO_4 (1.2 g) were added successively. The resulting mixture was stirred at room temperature for 15 min before filtration and removal of the solvent under vacuum to afford the crude product, which was subjected to flash chromatography on silica gel (hexane/EtOAc 3/1 to 1:1) to give **11** as an undefined mixture of stereoisomers (0.623 g, 97%). ^1H NMR δ : 7.42-7.23 (m, 5 H), 5.29 (s), 5.23 (s), 5.14 (s), 5.06 (s) (1 H), 4.73 (t, $J = 3.1$ Hz), 4.64 (t, $J = 2.9$ Hz), 4.44 (t, $J = 2.8$ Hz), 4.39 (t, $J = 3.5$ Hz) (1 H), 3.81 (m), 3.62 (m), 3.50 (m), 3.35 (m), 3.14 (m) (4 H), 2.46 (m), 2.17 (m), 1.94 (m) (2 H), 1.82-1.18 (m, 8 H), 1.56 (s), 1.52 (s), 1.44 (s), 1.41 (s) (3 H); ^{13}C NMR δ : 138.0, 137.5, 135.8, 135.6, 129.0 (d), 128.8, 128.6, 128.5, 128.3, 128.2, 100.9, 100.7, 95.8, 95.5, 95.1, 94.7, 94.3, 94.0, 84.9, 84.7, 81.4, 62.7, 62.6, 62.3, 62.2, 62.0, 61.6, 34.0, 31.4, 30.6, 30.4, 30.3, 27.1, 26.6, 25.4, 25.3, 19.3, 18.9, 18.8, 18.7, 18.4, 15.4. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_5$: C, 63.14; H, 7.79. Found: C, 62.86; H, 7.83.

5-Iodo-2-methyl-2-nitro-1-phenyl-1-(tetrahydropyranoxy)pentane (12). Alcohol **11** (613 mg, 1.90 mmol), triphenylphosphine (700 mg, 2.66 mmol) and imidazole (200 mg, 2.85 mmol) in acetonitrile (10 mL) and ether (10 mL) were treated at 0°C with iodine (772 mg, 3.04 mmol). After stirring overnight at room temperature the reaction mixture was diluted with ether (200 mL) and washed with 5% aqueous Na_2SO_3 , then saturated aqueous CuSO_4 , water and brine. Drying (Na_2SO_4), concentration and silica gel chromatography (eluent: EtOAc/hexane 1/5) of the extracts then gave **12** (582 mg, 71%) as an undefined mixture of stereoisomers. ^1H NMR δ : 7.43-7.24 (m, 5 H), 5.28 (s), 5.23 (s), 5.14 (s), 5.07 (s) (1 H), 4.73 (br. t), 4.65 (br. t), 4.44 (m) (1 H), 3.82-2.98 (m, 4 H), 2.45 (m), 2.21 (m), 2.00-1.38 (m) (10 H), 1.55 (s), 1.52 (s), 1.42 (s), 1.41 (s) (3 H); ^{13}C NMR δ : 137.8, 137.3, 135.6, 135.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 100.9, 100.7, 95.1, 95.0, 94.4, 94.0, 93.8, 84.6, 84.5, 81.4, 81.2, 62.3, 62.0, 61.6, 38.5, 36.1, 35.2, 30.5, 30.4, 30.3, 27.9, 27.4, 25.4, 25.3, 19.4, 19.0, 18.8, 18.4, 15.6, 15.5, 6.0, 4.8, 4.7. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{INO}_4\cdot\text{H}_2\text{O}$: C, 45.24; H, 5.81. Found: C, 45.65; H, 5.33.

***N*-Allyl-*N*-(*tert*-butoxycarbonyl) 4-Methyl-4-nitro-5-phenyl-5-(tetrahydropyranoxy)pentylamine (13).** Iodide **12** (572 mg, 1.33 mmol) and allylamine (0.99 mL, 13.25 mmol) were heated to reflux in ether (6 mL) overnight after which it was cooled to room temperature and diluted with saturated aqueous K_2CO_3 . The aqueous layer was extracted with ether and the combined organic phases washed with water and brine, then dried (Na_2SO_4). Filtration on silica gel (eluent: hexane/ethyl acetate/triethylamine: 1/1/0.05) and

concentration unprotected amine which was taken up in THF (15.0 mL) and treated with triethylamine (0.61 mL, 4.41 mmol) and Boc₂O (481 mg, 2.21 mmol), then stirred at room temperature overnight, before addition of saturated aqueous NH₄Cl (20 mL) and EtOAc (75 mL). The aqueous phase was further extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with water (15 mL) and brine (15 mL), dried (Na₂SO₄) and concentrated under vacuum. Chromatography on silica gel (eluent: hexane/EtOAc: 3/1) gave the title product (559 mg, 83%) as a mixture of diastereomers. ¹H NMR δ: 7.37-7.22 (m, 5 H), 5.67 (m, 1 H), 5.26 (s), 5.20-5.00 (m) (3 H), 4.71 (br. t), 4.62 (br. t), 4.43 (br. t), 4.39 (br. t) (1 H), 3.82-3.00 (m, 6 H), 2.36 (m), 2.04 (m) (1 H), 1.84-1.20 (m, 12 H), 1.50 (s), 1.40 (s) (9 H); ¹³C NMR δ: 155.6, 155.5, 146.9, 138.0, 137.5, 135.8, 135.6, 134.3, 134.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.2 (d), 128.1, 116.7, 116.3, 100.9, 100.7, 95.7, 95.0, 94.6, 94.3, 93.9, 85.3, 84.8, 84.7, 81.5, 81.4, 79.7, 62.2, 62.0, 61.6, 49.6, 46.6, 46.1, 34.7, 32.0 (d), 31.3, 30.4 (d), 28.5, 27.6, 25.4, 25.3, 22.4, 18.9, 18.8, 18.6, 18.4, 15.4. Anal. Calcd for C₂₅H₃₈N₂O₆: C, 64.91; H, 8.28. Found: C, 65.09; H, 8.36.

***N*-Allyl-*N*-(*tert*-butoxycarbonyl) 4-Methyl-4-nitro-5-phenyl-5-(diphenylphosphatoxy)pentylamine (14).** *p*-Toluenesulfonic acid monohydrate (0.34 g, 1.79 mmol) was added to a solution of THP ether **13** (549 mg, 1.19 mmol) in methanol (20 mL). After stirring at room temperature for 1.5 h the reaction mixture was diluted with ether (100 mL) and washed with saturated aqueous NaHCO₃, water and brine, then dried (Na₂SO₄) and concentrated under vacuum. Filtration on silica gel (eluent: hexane/EtOAc: 5/1) gave the deprotected alcohol (0.382 g) which was taken up in dichloromethane (14 mL) and treated at room temperature with DMAP (0.16 g, 1.31 mmol) and a solution of ClP(O)(OPh)₂ (0.35 g, 1.31 mmol) in dichloromethane (1 mL). After stirring overnight at room temperature, the reaction mixture was diluted with EtOAc, washed with saturated aqueous NH₄Cl, water and brine, then dried (Na₂SO₄) and concentrated under vacuum. Chromatography on silica gel (eluent: hexane/EtOAc: 5/1) gave the title phosphate (0.484 g, 78%) as a mixture of stereoisomers. ¹H NMR δ: 7.30-6.90 (m, 15 H), 6.09 (d, *J* = 7.6 Hz), 5.96 (d, *J* = 9.0 Hz) (1 H), 5.68 (m, 1 H), 5.04 (m, 2 H), 3.66 (m, 2 H), 3.10 (m, 2 H), 2.22 (m), 1.97 (m), 1.74 (m) (2 H), 1.58 (s), 1.45 (s) (3 H), 1.61-1.25 (m, 8 H), 1.43 (s), 1.40 (s) (9 H); ¹³C NMR δ: 155.4, 150.4 (t), 134.2, 134.1 (d), 133.7, 129.9, 129.8, 129.7, 129.6, 128.6, 128.5, 128.1, 128.0, 125.7, 125.5, 125.3, 120.2, 120.1, 120.0, 119.9, 116.7, 116.4, 94.3 (d), 93.8 (d), 84.8 (d), 84.4 (d), 79.8, 49.7, 46.4, 45.9, 34.3, 28.5, 22.3, 17.6, 15.4; ³¹P NMR δ: -12.3, -12.8. Anal. Calcd for C₃₂H₃₉N₂O₈P: C, 62.94; H, 6.44. Found: C, 63.02; H, 6.48.

***N*-Allyl 4-Methyl-4-nitro-5-phenyl-5-(diphenylphosphatoxy)pentylamine (15).** TMSOTf (0.21 mL, 1.164 mmol) was added at room temperature to a stirred solution of **14** (0.474 g, 0.78 mmol) and 2,6-lutidine (0.180 mL, 1.55 mmol) in CH₂Cl₂ (15 mL). After 30 min the reaction mixture was diluted with saturated aqueous NH₄Cl (10 mL) and EtOAc (50 mL). The water layer was extracted with EtOAc (3 x 10 mL) and the combined organic phases were washed with NaHCO₃ solution (10 mL), water (15 mL) and brine (15 mL), then dried (Na₂SO₄). The solvent was removed under vacuum and the residue was

subjected to flash chromatography on silica gel (hexane/EtOAc/NEt₃ 1/1/0.05) to afford **15** as a mixture of stereoisomers (0.317 g, 80%). ¹H NMR δ: 7.32-6.91 (m, 15 H), 6.09 (d, *J* = 7.6 Hz), 5.98 (d, *J* = 9.0 Hz) (1 H), 5.82 (m, 1 H), 5.08 (m, 2 H), 3.20 (d, *J* = 6.0 Hz), 3.15 (d, *J* = 6.0 Hz) (2 H), 2.49 (m, 2 H), 2.30 (m), 2.10 (m), 1.82 (m) (2 H), 1.58 (s), 1.46 (s) (3 H), 1.56-1.18 (m, 8 H); ¹³C NMR δ: 150.5 (d), 136.7, 134.3, 133.7, 130.0, 129.8, 129.7, 129.6, 128.6, 128.5, 128.2, 128.0, 125.8, 125.6, 125.4, 120.2 (d), 120.0 (d), 116.2, 94.4 (d), 94.1 (d), 84.9 (d), 84.4 (d), 52.4 (d), 48.8, 48.6, 34.8, 34.2, 24.3, 24.0, 17.1, 15.6; ³¹P NMR δ: -12.3, -12.8. Anal. Calcd for C₂₇H₃₁N₂O₆P: C, 63.52; H, 6.12. Found: C, 63.30; H, 6.39.

2,7-Dimethyl-1-phenylpyrrolizidine (16). A solution of **15** (0.304 g, 0.60 mmol), Ph₃SnH (0.311 g, 0.89 mmol) and AIBN (42.68 mg, 0.24 mmol) in benzene (12.0 mL) was heated under Argon at reflux overnight with periodic addition of two further portions of AIBN (5 mol % each). After cooling the solvent was removed under vacuum and the crude reaction mixture was dissolved in MeOH (3.0 mL) and treated with NaBH₄ (34 mg) at room temperature for 10 min.⁵ Water was then added slowly, followed by EtOAc (50 mL). The water layer was extracted with EtOAc (3 x 10 mL) and the combined organic phases were washed with water (15 mL) and brine (15 mL), then dried (Na₂SO₄) and concentrated under vacuum. Extensive chromatography on silica gel (hexane/EtOAc/NEt₃ 100/0/5 to 1/9/0.5) afforded the four diastereomers of **16** in 85% total yield and in the ratio **16a**:**16b**:**16c**:**16d** = 2.7:1.6:1:1. **1,2-trans-1,7-cis (16a):** ¹H NMR δ: 7.33-7.17 (m, 5 H), 3.42 (dd, *J* = 9.1, 6.1 Hz, 1 H), 3.07 (m, 1 H), 2.69 (m, 2 H), 2.46 (d, *J* = 11.9 Hz, 1 H), 2.25 (dd, *J* = 10.6, 9.1 Hz, 1 H), 1.89 (m, 3 H), 1.48 (m, 1 H), 0.93 (d, *J* = 6.4 Hz, 3 H), 0.78 (s, 3 H); ¹³C NMR δ: 139.7, 128.8, 128.4, 126.6, 73.8, 63.0, 62.6, 56.1, 40.1, 37.7, 27.0, 25.9, 15.9; HRMS Calcd. for C₁₅H₂₁N: 215.1673; Found: 265.1672. **1,2-cis-1,7-cis (16b):** ¹H NMR δ: 7.33-7.18 (m, 5 H), 3.22 (m, 1 H), 3.18 (dd, *J* = 10.4, 7.4 Hz, 1 H), 3.06 (d, *J* = 7.1 Hz, 1 H), 2.90 (m, 1 H), 2.78 (t, *J* = 8.3 Hz, 1 H), 2.70 (m, 1 H), 1.87 (m, 2 H), 1.76 (m, 2 H), 0.98 (s, 3 H), 0.64 (d, *J* = 6.6 Hz, 3 H); ¹³C NMR δ: 139.6, 130.6, 129.8, 128.2, 126.5, 75.8, 62.6, 61.0, 57.1, 41.8, 35.7, 26.0, 25.2, 14.4; MS (EI, *m/z*): 216 (M⁺+1). **1,2-cis-1,7-trans (16c):** ¹H NMR δ: 7.33-7.18 (m, 5 H), 3.42 (dd, *J* = 7.2, 5.0 Hz, 1 H), 3.21 (m, 1 H), 3.04 (d, *J* = 3.0 Hz, 1 H), 3.02 (m, 1 H), 2.70 (m, 1 H), 2.60 (t, *J* = 8.2 Hz, 1 H), 1.94 (m, 2 H), 1.59 (m, 1 H), 1.37 (s, 3 H), 1.22 (m, 1 H), 0.78 (d, *J* = 5.0 Hz, 3 H); MS (EI, *m/z*): 216 (M⁺+1). **1,2-trans-1,7-trans (16d):** ¹H NMR δ: 7.32-7.20 (m, 5 H), 3.28 (m, 1 H), 2.82 (m, 2 H), 2.61 (d, *J* = 11.4 Hz, 1 H), 2.52 (m, 1 H), 1.71 (m, 2 H), 1.49 (m, 1 H), 1.27 (s, 3 H), 0.92 (m, 1 H), 0.89 (d, *J* = 6.0 Hz, 3 H); ¹³C NMR δ: 139.4, 128.6, 128.2, 126.4, 73.7, 63.2, 61.0, 57.6, 34.6, 34.3, 29.3, 25.2, 15.0; MS (EI, *m/z*): 216 [M+1]⁺.

N-Allyl 4-Hydroxybutyramide (18). γ-Butyrolactone (3.85 mL, 50 mmol) and allylamine (5.63 mL, 75 mmol) were heated together with stirring under Argon at 120-130° C for 3 h, then cooled to room temperature. The excess allylamine was removed under reduced pressure and the residue was purified by bulb to bulb distillation to give **18** (7.1 g, 99%) as a viscous oil which crystallized after prolonged cooling. M.p. 27 °C (lit.⁶ m.p. 27-27.5 °C); ¹H NMR δ: 6.65 (br. s, 1 H), 5.83-5.70 (m, 1 H), 5.16-5.04 (m, 2 H),

3.97 (br. s, 1 H), 3.81-3.77 (m, 2 H), 3.59 (t, $J = 5.8$ Hz, 2 H), 2.31 (t, $J = 6$ Hz, 2 H), 1.81 (m, $J = 6$ Hz, 2 H); ^{13}C NMR δ : 173.7, 134.2, 116.4, 62.1, 42.1, 33.8, 28.4.

4-Allylamino-1-butanol (20). To a solution of LiAlH_4 (0.47 g, 12.5 mmol) in THF (35 mL) at 0 °C was added dropwise a solution of **18** (1.0 g, 6.98 mmol). After stirring for 15 min at room temperature the reaction mixture was heated to reflux for 18 h then cooled and poured into THF (75 mL). $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (8.0 g, 25 mmol) was added and the mixture was heated to reflux until a white crystalline precipitate was observed, after which the contents were cooled to room temperature and filtered. The filtrate was then concentrated under reduced pressure and the residue was purified by silica gel chromatography (eluent: $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$, 1:1) to give **20** (0.67 g, 75%) as a pale yellow oil. ^1H NMR δ : 5.91-5.82 (m, 1 H), 5.19-5.05 (m, 2 H), 3.55 (t, $J = 5$ Hz, 4 H), 3.22 (d, $J = 6.6$ Hz, 2 H), 2.63 (t, $J = 6$ Hz, 2 H), 1.64 (m, 4 H); ^{13}C NMR δ : 135.9, 116.7, 62.6, 52.0, 49.1, 32.3, 28.5. Anal. Calcd for $\text{C}_7\text{H}_{15}\text{NO}$: C, 65.07; H, 11.7. Found: C, 64.85; H, 11.8.

4-[*N*-Allyl *N*-(*tert*-butoxycarbonyl)]amino-1-butanol (22). Triethylamine (1.03 mL, 7.27 mmol) then di-*tert*-butyl dicarbonate (0.826 g, 3.78 mmol) were added to a solution of **20** (0.376 g, 2.91 mmol) in THF (11 mL) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was diluted with ethyl acetate (150 mL). The organic layer was washed with water (2×50 mL) and brine (2×50 mL), dried (Na_2SO_4) and concentrated under reduced pressure to give a crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 3:1) then afforded **22** (0.441 g, 70 %) as a pale yellow oil. ^1H NMR δ 5.80-5.71 (m, 1H), 5.09 (br, d, $J = 13.5$ Hz, 2 H), 3.78 (br. s, 2 H), 3.67-3.62 (br. m, 2 H), 3.20 (br. s, 2 H), 1.60-1.48 (m, 4 H), 1.44 (s, 9 H); ^{13}C δ 155.7, 134.4, 116.2, 79.6, 62.7, 49.6, 46.4, 29.8, 28.5, 28.4, 24.8. Anal. Calcd for: $\text{C}_{12}\text{H}_{23}\text{NO}_3$ C, 62.85; H, 10.11. Found: C, 62.53; H, 9.97.

4-[*N*-Allyl *N*-(*tert*-butoxycarbonyl)]aminobutanal (24). $4\text{\AA}$ Molecular sieves (0.765 g) were added to a stirred solution of **22** (0.408 g, 1.78 mmol) in CH_2Cl_2 (25 mL) followed, after cooling to 0 °C, by PCC (0.765 g, 3.56 mmol). After stirring for 2 h the reaction mixture was concentrated under reduced pressure to 75% of the initial volume then loaded onto the silica gel column directly and **24** eluted: hexanes/ethylacetate (5:1) as a colorless oil (0.35 g, 87%). ^1H NMR δ 9.68 (t, $J = 1.3$ Hz, 1 H), 5.78-5.61 (m, 1 H), 5.03 (br, d, $J = 12$ Hz, 2 H), 3.74 (br, s, 2 H), 3.13 (t, $J = 6.3$ Hz, 2 H), 2.37 (t, $J = 7.2$ Hz, 2 H), 1.75 (quintet, $J = 7.2$ Hz, 2 H), 1.36 (s, 9 H); ^{13}C NMR δ 201.8, 155.2, 134.1, 116.6, 116.4, 116.3, 79.7, 49.8, 49.3, 45.7, 45.6, 41.1, 28.5, 23.6, 20.8. Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{NO}_3$: C, 63.41; H, 9.31. Found: C, 63.16; H, 9.19.

3-(Diphenylphosphatoxy)-6-[*N*-allyl *N*-(*tert*-butoxycarbonyl)]amino-2-methyl-2-nitrohexane (26). 2-Nitropropane (0.41 mL, 4.78 mmol) and **24** (0.435 g, 1.91 mmol) were dissolved in a 1:1 mixture of

acetonitrile and *tert*-butanol (7.5 mL). After cooling to 0 °C, potassium *tert*-butoxide (0.043 g, 0.383 mmol) was added and the reaction mixture stirred for 24 h with gradual warming to room temperature. Saturated aqueous ammonium chloride (15 mL) and ethyl acetate (50 mL) were then added, the organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with water (2 x 30 mL) and brine (2 x 30 mL), dried (Na₂SO₄) and the solvent removed under reduced pressure to yield crude nitroaldol (0.636 g, 2.01 g). This was redissolved in dry CH₂Cl₂ (15 mL) and cooled to 0 °C before DMAP (0.365 g, 3.02 mmol) was added followed by a solution of ClP(O)(OPh)₂ (0.6 mL, 3.02 mmol) in CH₂Cl₂ (2 mL). The reaction mixture was stirred over night with gradual warming to room temperature then was poured into ethyl acetate (50 mL) and washed with saturated aqueous ammonium chloride (2 x 25 mL), water (2 x 25 mL), and brine (2 x 25 mL), dried (Na₂SO₄), and concentrated under reduced pressure. Purification by silica gel column chromatography (eluent: hexanes/ ethyl acetate 1:1) yielded the title compound (0.61g, 55 %) as a pale yellow oil. ¹H NMR δ: 7.34- 7.13 (m, 10 H), 5.69-5.61 (m, 1 H), 5.14 (br, s, 1 H), 5.03 (br. t, 2 H), 3.65 (br. s, 2 H), 3.16 (br. s, 2 H), 1.75-1.54 (m, 10 H), 1.41 (s, 9 H); ¹³C NMR δ: 155.2, 150.6, 150.5, 150.4, 134.1, 129.9, 129.8, 125.7, 125.6, 120.2, 120.1, 116.7, 116.6, 90.6, 83.7, 83.6, 49.8, 49.7, 45.7, 28.5, 21.2, 21.1, 23.2, 21.2; ³¹P NMR δ: -11.94, -12.26. Anal. Calcd. for C₂₇H₃₇N₂O₈P: C, 59.12; H, 6.80. Found: C, 59.02; H, 6.79.

3-(Diphenylphosphatoxy)-6-allylamino-2-methyl-2-nitrohexane (28). TMSOTf (0.28 mL, 1.59 mmol) was added to a solution of **26** (0.584 g, 1.06 mmol) and 2,6-lutidine (0.25 mL, 2.126 mmol) in dry CH₂Cl₂ (20 mL) and the reaction mixture stirred at room temperature for 0.5 h. Saturated aqueous ammonium chloride (30 mL) was then added and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic layer was washed with saturated sodium bicarbonate solution (2 x 25 mL), water (2 x 25 mL) and brine (2 x 25 mL), dried (Na₂SO₄), and concentrated under reduced pressure. Chromatography on silica gel column (eluent: hexanes/ ethyl acetate 1:1 with 5 % methanol and 1 % triethylamine.) then afforded the title compound (0.38 g, 80 %). ¹H NMR (CDCl₃) δ: 7.35-7.15 (m, 10 H), 5.92-5.79 (m, 1 H), 5.19-5.04 (m, 3 H), 3.15 (d, *J* = 6.3 Hz, 2 H), 2.54 (t, *J* = 6.3 Hz, 2 H), 1.65- 1.56 (m, 10 H); ¹³C NMR (CDCl₃) δ: 150.5, 136.8, 129.9, 129.8, 125.6, 125.5, 120.4, 120.3, 120.2, 116.1, 90.4, 83.8, 52.4, 48.6, 29.3, 26.3, 21.8; ³¹P NMR (CDCl₃) δ: -11.87; ESIHRMS Calcd. for: C₂₂H₃₀N₂O₆P [M+H]⁺, Found: 449.1845 [M+H]⁺.

1,1,2-*exo*-Trimethylpyrrolizidine and 1,1,2-*endo*-Trimethylpyrrolizidine (30). Tributyltin hydride (0.219 mL, 0.804 mmol) and AIBN (0.036 g, 0.214 mmol) were added to a solution of **28** (0.240 g, 0.536 mmol) in degassed benzene (25 mL), and heated to reflux for 40 h with addition of further AIBN (5 mol %) every 12 h. The reaction mixture was then cooled to room temperature, HCl (2M, 20 mL) was added, and stirred for 20 min. The aqueous layer was then washed with petroleum ether (3 x 30 mL), basified to pH 14 with NaOH (5M, 30mL) and extracted with ethyl ether (4 x 30 mL). HCl gas was then passed into the ethereal solution for 1 h, followed by concentration to dryness, basification with NaOH (5 M, 10 mL),

extraction into CDCl_3 (3 x 5 mL) and drying (Na_2SO_4). Spectroscopic investigation of the CDCl_3 solution revealed **30** as a 1/1 mixture. Careful concentration then gave the mixture of volatile pyrrolizidines (63 mg, 75%). **2-exo-30** ^1H NMR δ 3.29 (t, J = 7.0 Hz, 1 H), 3.20-3.17 (m, 1 H), 3.08-3.06 (m, 1 H), 2.43-2.40 (m, 1 H), 2.24-2.19 (m, 1 H), 2.16-2.11 (m, 1 H), 1.73-1.69 (m, 1 H), 1.64-1.59 (m, 1 H), 0.93 (s, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.66 (s, 3 H); ^{13}C NMR δ 75.8, 60.8, 55.6, 41.9, 30.1, 26.7, 23.3, 17.8, 11.5. **2-endo-30** ^1H NMR δ 3.24-3.20 (m, 1 H), 3.09-3.06 (m, 1 H), 2.81 (br. t, J = 10.7 Hz, 1 H), 2.63 (dd, J = 7.4, 11.3 Hz, 1 H), 2.48-2.46 (m, 1 H), 1.84-1.81 (m, 1 H), 1.67-1.65 (m, 1 H), 1.40-1.35 (m, 1 H), 1.2-1.17 (m, 1 H), 0.98-0.96 (m, 1 H), 0.94 (s, 3 H), 0.91 (s, 3 H), 0.84 (d, J = 6.8 Hz, 3 H); ^{13}C NMR δ 76.7, 62.4, 57.8, 40.1, 28.9, 27.1, 23.4, 23.3, 11.5. ESIHRMS Calcd for $\text{C}_{10}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 154.1596, found 154.1593

5-[N-Allyl-N-(tert-butyloxycarbonyl)]amino-1-pentanol (23). To a solution of the known 5-allylamino-1-pentanol⁷ **21** (1.23 g, 8.6 mmol) in CH_2Cl_2 (20 mL) was added drop wise a solution of di-*tert*-butyl dicarbonate (2.51 g, 11.1 mmol) in CH_2Cl_2 (10 mL) with cooling, followed by stirring at room temperature for 12 h. The organic layer was then washed with saturated NH_4Cl (50 mL), brine (30 mL), water (50 mL), dried and concentrated to give the crude product. Purification by silica gel column chromatography (eluent : hexanes / EtOAc 2:1) then afforded **23** (1.92 g, 92%) as a colorless oil. ^1H NMR : δ 5.76-5.70 (m, 1 H), 5.08 (br. d, J = 11.7 Hz, 2 H), 3.76 (br. s, 2 H), 3.61 (br. dd, J = 12.0, 6.3 Hz, 2 H), 3.15 (br. s, 2 H), 1.6-1.46 (m, 4 H), 1.43 (s, 9 H), 1.35-1.30 (m, 2 H); ^{13}C NMR : δ 155.7, 134.6, 116.0, 79.4, 62.8, 49.7, 46.6, 32.5, 28.5, 28.1, 23.0. Anal. Calcd. for $\text{C}_{13}\text{H}_{25}\text{NO}_3$: C, 64.16; H, 10.36. Found: C, 63.95; H, 10.33.

5-[N-Allyl-N-(tert-butyloxycarbonyl)]aminopentanal (25). To a stirred and cooled solution of **23** (1.5 g, 6.17 mmol) in CH_2Cl_2 (40 mL) were added 4Å molecular sieves (2.5 g) followed by PCC (2.66 g, 12.34 mmol). After stirring for 3 h, the reaction mixture was concentrated and loaded directly onto a silica gel column and eluted with hexane/ EtOAc (3:1) to give the aldehyde **25** (1.20 g, 81%) as a colorless oil. ^1H NMR : δ 9.75 (s, 1 H), 5.76-5.70 (m, 1 H), 5.10 (br. d, J = 11.1 Hz, 2 H), 3.77 (br. s, 2 H), 2.46 (t, J = 6.0 Hz, 2 H), 1.64-1.51 (m, 4 H), 1.44 (s, 9 H); ^{13}C NMR : δ 202.2, 155.8, 134.7, 116.5, 79.9, 50.0, 46.6, 43.8, 28.8, 28.2, 19.7; ESIHRMS Calcd. for: $\text{C}_{13}\text{H}_{23}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 264.1576. Found: 264.1593.

3-(Diphenylphosphatoxy)-7-[N-Allyl-N-(tert-butyloxycarbonyl)]amino-2-methyl-2-nitroheptane (27). 2-Nitropropane (0.89 mL, 10.38 mmol) and **25** (1.0 g, 4.15 mmol) were dissolved in a 1:1 mixture of acetonitrile and *tert*-butanol (14 mL). After cooling to 0 °C, potassium *tert*-butoxide (0.233 g, 2.08 mmol) was added and the reaction mixture stirred for 24 h with gradual warming to room temperature. Saturated aqueous NH_4Cl (25 mL) and ethyl acetate (50 mL) were then added, the organic layer was separated and the aqueous layer was again extracted with ethyl acetate (2 x 30 mL). The combined organics were washed with water and brine, dried (Na_2SO_4) and the solvent removed under reduced pressure to yield crude nitroaldol (1.14 g, 3.45 mmol). This was redissolved in dry CH_2Cl_2 (25 mL) and cooled to 0 °C before DMAP (0.63 g, 5.18 mmol) was added followed by a solution of $(\text{PhO})_2\text{P}(\text{O})\text{Cl}$ (1.07 mL, 5.18 mmol). The

reaction mixture was allowed to warm to room temperature and stirred overnight. Dilution with ethyl acetate (50 mL) followed by washing with saturated NH_4Cl (20 mL), brine (20 mL), water (20 mL), drying (Na_2SO_4) and concentration gave the crude product which was purified by silica gel chromatography (eluent : hexane/EtOAc 1:1) yielding **27** (1.21 g, 52%). ^1H NMR : δ 7.34-7.16 (m, 10 H), 5.86-5.81 (m, 1 H), 5.17-5.03 (m, 3 H), 3.72 (br. s, 2 H), 3.0 (br. s, 2 H), 1.60 (s, 3 H), 1.55 (s, 3 H), 1.41 (s, 9 H), 1.64-1.34 (m, 6 H); ^{13}C NMR : δ 155.8, 150.9, 134.7, 130.3, 125.8, 125.7, 120.5, 120.48, 120.43, 120.40, 116.4, 90.6, 84.0, 79.8, 50.0, 46.5, 31.7, 28.8, 28.2, 23.5, 22.8, 21.3; ^{31}P NMR : δ -11.90. Anal. Calcd. for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{O}_8\text{P}$: C, 59.78; H, 6.99. Found: C, 59.82; H, 7.09.

3-(Diphenylphosphatoxy)-7-N-allylamino-2-methyl-2-nitroheptane (29). TMSOTf (0.49 mL, 2.70 mmol) was added to a solution of **27** (1.0 g, 1.8 mmol) and 2,6-lutidine (0.41 mL, 3.6 mmol) in dry CH_2Cl_2 (20 mL). The reaction mixture stirred at room temperature for 0.5 h before saturated aqueous NH_4Cl (10 mL) was added and the organics were extracted with ethyl acetate (2 x 25 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Chromatography on silica gel column (eluent : hexanes/EtOAc 1:1 with 10% methanol) then afforded the title compound (0.63 g, 76%). ^1H NMR : δ 7.35-7.16 (m, 10 H), 5.84 (m, 1 H), 5.11 (m, 3 H), 3.17 (dd, J = 5.7, 1.2 Hz, 2 H), 2.47 (t, J = 5.7 Hz, 2 H), 1.64-1.36 (m, 6 H), 1.61 (s, 3 H), 1.55 (s, 3 H); ^{13}C NMR : δ 150.4, 150.2, 130.1, 127.0, 126.1, 125.9, 124.9, 120.4, 120.0, 118.2, 90.5, 83.6, 50.3, 46.5, 30.3, 24.9, 23.7, 22.3, 20.4; ^{31}P NMR : δ -11.86. Anal. Calcd. for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_6\text{P}$: C, 59.73; H, 6.76. Found: C, 59.44; H, 6.83.

1,1,2-exo-Trimethylindolizidine and 1,1,2-endo-Trimethylindolizidine (31). Tri-n-butyltin hydride (0.22 mL, 0.80 mmol) and AIBN (0.036 g, 0.21 mmol) were added to a solution of **29** (0.25 g, 0.54 mmol) in degassed benzene (25 mL), and heated to reflux for 40 h with addition of further AIBN (5 mol%) every 12 h. After cooling to room temperature, HCl (2 M, 20 mL) was added, and the reaction mixture stirred for 20 min. The aqueous layer was then washed with diethyl ether (2 x 30 mL), basified with NaOH (5 M, 20 mL) and then extracted with diethyl ether. HCl gas was then bubbled through the ethereal solution followed by concentration, basification with NaOH (5 M, 10 mL) and extraction with CDCl_3 (2 x 5 mL) and drying (Na_2SO_4). Spectroscopic investigation of the CDCl_3 solution revealed a 1:1 mixture of indolizidines **31** (0.07 g, 78%). ^1H NMR (**31**, 1:1 mixture) : δ 3.14-3.02 (m, 4 H), 2.64 (dd, J = 9.3, 6.3 Hz, 1 H), 2.44 (t, J = 10.2 Hz, 1 H), 2.00-1.10 (m, 18 H), 0.86 (d, J = 7.8 Hz, 3 H), 0.85 (s, 6 H), 0.84 (d, J = 6.9 Hz, 3 H), 0.80 (s, 3 H), 0.74 (s, 3 H); ^{13}C NMR (*exo*-**31**) : δ 75.1, 63.7, 54.7, 41.8, 27.5, 26.8, 26.2, 25.1, 23.0, 17.7, 14.8; ^{13}C NMR (*endo*-**31**) : δ 66.1, 60.7, 53.8, 41.6, 26.3, 26.0, 25.6, 24.8, 20.5, 15.9, 14.6. ESIHRMS Calcd. for: $\text{C}_{11}\text{H}_{22}\text{N}$ [$\text{M}+\text{H}$] $^+$: 168.1752. Found: 168.1751.

N-Allyl levulinamide (33). To a solution of α -angelicalactone (5 g, 50 mmol) in chloroform (35 mL) cooled in an ice-bath, an equivalent amount of allylamine (3.83 mL, 50 mmol) was added followed by stirring at room temperature for 6 h. Concentration gave a yellow oil (6.97 g, 90%) which crystallized when

cooled. ^1H NMR : δ 5.86-5.80 (m, 1 H), 5.21-5.08 (m, 1 H), 3.84 (t, J = 6.0 Hz, 2 H), 2.80 (t, J = 6.9 Hz, 2 H), 2.43 (t, J = 6.6 Hz, 2 H), 2.17 (s, 3 H); ^{13}C NMR : δ 208.0, 171.9, 134.3, 116.2, 42.0, 38.7, 30.0, 29.9. ESIHRMS Calcd. for: $\text{C}_8\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 156.1025. Found: 156.1020.

5-(*N*-Benzylamino)-2-pentanol. To a suspension of LiAlH_4 (1.46 g, 38.5 mmol) in ether (150 mL) was added dropwise a solution of **32**⁸ (3.0 g, 14.63 mmol) in THF (50 mL) at gentle reflux, followed by refluxing at 60 $^\circ\text{C}$ for 12 h. The reaction mixture was then poured into ice and extracted with ethyl acetate (2 x 100 mL). The organic layer was washed with brine (2 x 50 mL) and water (2 x 50 mL) and concentrated to give the crude amine (2.26 g, 80%) which was taken to the next step without further purification. ^1H NMR : δ 7.33-7.25 (m, 5 H), 3.77-3.74 (m, 1 H), 3.75 (s, 2 H), 2.78 (m, 1 H), 2.61 (m, 1 H), 1.74-1.69 (m, 2 H), 1.52-1.43 (m, 1 H), 1.18 (d, J = 6.3 Hz, 3 H); ^{13}C NMR : δ 137.8, 128.8, 127.7, 126.9, 67.4, 53.4, 49.1, 38.3, 26.5, 23.7. ESIHRMS Calcd. for: $\text{C}_{12}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 194.1545. Found : 194.1551.

5-[*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-pentanol (35**).** To the above amine (2.1 g, 11.0 mmol) and di-*tert*-butyl dicarbonate (2.9 g, 13.2mmol) dissolved in CH_2Cl_2 (50 mL) was added triethylamine (3.1 mL, 21.9 mmol) dropwise with cooling. After stirring at room temperature overnight, the reaction mixture was worked up by washing with saturated NH_4Cl (50 mL), followed by washing with water (30 mL), brine (20 mL), concentrated and purified on silica gel column (eluent: hexanes/EtOAc 3:1) to give pure **11** (2.64 g, 82%) as a colorless oil. ^1H NMR : δ 7.36-7.21 (m, 5 H), 4.42 (br. s, 2 H), 3.76 (br. s, 1 H), 3.16 (br. s, 2 H), 1.6-1.34 (m, 4 H), 1.46 (s, 9 H), 1.15 (d, J = 6.0 Hz, 3 H); ^{13}C NMR : δ 156.0, 138.8, 128.2, 127.5, 127.4, 127.1, 79.7, 67.7, 50.5, 46.7, 36.4, 28.5, 24.4, 23.6. ESIHRMS Calcd. for: $\text{C}_{17}\text{H}_{27}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 316.1889. Found: 316.1874.

5-(*N*-Allylamino)-2-pentanol. In a similar procedure as outlined for the formation of 5-(*N*-benzylamino)-2-pentanol, **33** (3.0 g, 19.3 mmol) was reduced with LiAlH_4 (1.93 g, 50.9 mmol) to give the title amine (2.15 g, 78%) which was taken through to the next step without further purification. ^1H NMR : δ 5.93-5.84 (m, 1 H), 5.21-5.08 (m, 2 H), 3.72 (m, 1 H), 3.22 (dt, J = 2.7, 1.2 Hz, 2 H), 2.76 (m, 1 H), 2.56 (m, 1 H), 1.73-1.69 (m, 2 H), 1.52-1.38 (m, 2 H), 1.16 (d, J = 3.0 Hz, 3 H); ^{13}C NMR : δ 136.0, 116.5, 67.3, 52.0, 49.3, 38.8, 27.3, 23.7. ESIHRMS Calcd. for: $\text{C}_8\text{H}_{18}\text{NO}$ $[\text{M}+\text{H}]^+$ 144.1388. Found: 144.1387.

5-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-pentanol (36**).** In a similar procedure as outlined for **35**, protection of 5-(*N*-allylamino)-2-pentanol (2.0 g, 13.9 mmol) gave **36** (2.53 g, 75%) as a colorless oil. ^1H NMR : δ 5.73 (m, 1 H), 5.08 (m, 2 H), 3.76 (m, 3 H), 3.16 (q, J = 7.2 Hz, 2 H), 1.62-1.33 (m, 4 H), 1.41 (s, 9 H), 1.14 (d, J = 5.7 Hz); ^{13}C NMR : δ 155.6, 134.5, 116.1, 79.5, 67.6, 49.7, 46.7, 36.3, 28.5, 27.5, 24.6, 23.6. ESIHRMS Calcd. for: $\text{C}_{13}\text{H}_{25}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 266.1732. Found: 266.1740.

5-[*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromopentane. To a stirred ice-cold solution of **35** (1.0 g, 3.41 mmol) in CH₂Cl₂ (6 mL) was added CBr₄ (1.48 g, 4.46 mmol), followed in portions over 30 min by freshly powdered PPh₃ (1.34 g, 5.11 mmol). The reaction mixture was stirred whilst being allowed to attain room temperature overnight and then evaporated to dryness. The reaction mixture was concentrated and loaded directly onto a silica gel column (eluent : hexanes/EtOAc 3:1) to give the title compound (0.97 g, 80%). ¹H NMR : δ 7.34-7.22 (m, 5 H), 4.43 (d, *J* = 3.9 Hz, 2 H), 4.08 (br. m, 1 H), 3.21 (br. s, 2 H), 1.79-1.61 (m, 4 H), 1.66 (d, *J* = 6.9 Hz, 3 H), 1.48 (s, 9 H). ¹³C NMR : δ 155.9, 138.6, 128.5, 127.6, 127.1, 79.8, 50.9, 50.4, 45.9, 38.4, 28.6, 26.5, 26.4. ESIHRMS Calcd. for: C₁₇H₂₆NO₂BrNa [M+Na]⁺ 378.1045. Found : 378.1056.

5-[*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-nitropentane (38**).** To the above bromide (0.38 g, 1.07 mmol) dissolved in DMF (3 mL) was added NaNO₂ (0.15 g, 1.74 mmol), phloroglucinol (0.18 g, 1.10 mmol), urea (0.14 g, 2.37 mmol) followed by stirring for 48 h in the dark. The reaction mixture was then poured into ice and extracted with diethyl ether (20 mL) and concentrated. Purification on a silica gel column (eluent : hexanes/EtOAc 3:1) gave **38** (0.19 g, 55%) as a very pale yellow oil. ¹H NMR : δ 7.34-7.20 (m, 5 H), 4.53-4.47 (m, 1 H), 4.40 (d, *J* = 6.0 Hz, 2 H), 3.21 (t, *J* = 6.6 Hz, 2 H), 1.97-1.90 (m, 1 H), 1.69-1.64 (m, 1 H), 1.56-1.40 (m, 2 H), 1.49 (s, 3 H), 1.47 (s, 9 H); ¹³C NMR : δ 155.9, 138.5, 128.6, 127.6, 127.3, 83.1, 80.0, 50.5, 45.8, 32.4, 28.5, 24.4, 19.2. ESIHRMS Calcd. for: C₁₇H₂₆N₂O₄Na [M+Na]⁺ 345.1790. Found: 345.1788.

5-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromopentane. In an identical procedure to the one outlined above for 5-[*N*-benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromopentane, bromination of **36** (0.52 g, 2.14 mmol) gave the title compound (0.55 g, 84%) as a colorless oil. ¹H NMR : δ 5.77-5.71 (m, 1 H), 5.10 (d, *J* = 12.9 Hz, 1 H), 4.14-4.10 (m, 1 H), 3.79 (br. s, 2 H), 3.18 (br. s, 2 H), 1.80-1.60 (m, 4 H), 1.67 (d, *J* = 6.9 Hz, 1 H), 1.44 (s, 9 H); ¹³C NMR : δ 155.9, 134.4, 116.3, 79.5, 50.9, 49.6, 45.9, 38.4, 28.5, 26.6, 26.5. ESIHRMS Calcd. for: C₁₃H₂₄NO₂BrNa [M+Na]⁺ 328.0888. Found: 328.0889.

5-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-nitropentane (39**).** In an identical procedure to the one outlined above for the formation of **38**, nitration of 5-[*N*-allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromopentane (0.50 g, 1.64 mmol) gave the title compound (0.24 g, 55%) as a pale yellow oil. ¹H NMR : δ 5.79-5.68 (m, 1 H), 5.13-5.06 (m, 2 H), 4.57 (m, 1 H), 3.76 (d, *J* = 4.5 Hz, 2 H), 3.20 (m, 2 H), 2.00-1.90 (m, 1 H), 1.75-1.64 (m, 1 H), 1.58-1.44 (m, 2 H), 1.50 (d, *J* = 5.6 Hz, 3 H), 1.43 (s, 9 H); ¹³C NMR : δ 155.5, 134.4, 116.3, 83.1, 79.8, 49.7, 45.7, 32.4, 28.5, 24.6, 19.2. ESIHRMS Calcd. for: C₁₃H₂₄N₂O₄Na [M+Na]⁺ 295.1634. Found: 295.1622.

5-[*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-pentanol. To a well stirred solution of **38** (0.5 g, 1.55 mmol) in THF (5 mL) under Ar was added paraformaldehyde (0.08 g, 2.6 mmol) and

NaOMe (0.13 mL of 4 M, 0.52 mmol), followed by refluxing for 4 h. The reaction mixture was then diluted with CH₂Cl₂ (20 mL), washed with water (15 mL), and concentrated to give the crude product. Purification on silica gel column (eluent : hexanes/EtOAc 1:1) gave the pure title compound (0.52 g, 96%) as a colorless oil. ¹H NMR : δ 7.34-7.19 (m, 5 H), 4.40 (s, 2 H), 3.90 (d, *J* = 12.5 Hz, 1 H), 3.71 (d, *J* = 12.5 Hz, 1 H), 3.19 (t, *J* = 7.2 Hz, 2 H), 2.33 (br. s, 1 H), 1.93-1.67 (m, 2 H), 1.49 (s, 3 H), 1.44 (s, 9 H), 1.56-1.34 (m, 2 H); ¹³C NMR : δ 156.2, 138.7, 128.9, 127.7, 92.0, 80.4, 67.4, 51.0, 46.8, 38.7, 30.5, 28.8, 20.5. ESIHRMS Calcd. for: C₁₈H₂₈N₂O₅Na [M+Na]⁺ 375.1896. Found: 375.1904.

5-[*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-(diphenylphosphatoxy)-pentane

(41). To a solution of the above nitroalcohol (0.35 g, 0.99 mmol) in CH₂Cl₂ (10 mL), was added DMAP (0.18 g, 1.49 mmol) and (PhO)₂P(O)Cl (0.31 mL, 1.49 mmol) under Argon atmosphere and stirred at room temperature overnight. The reaction mixture was quenched with saturated NH₄Cl (10 mL) and extracted with CH₂Cl₂ (20 mL) followed by concentration to give the crude phosphate. Purification by silica gel column (eluent : hexanes/EtOAc 2:1) gave **41** (0.53 g, 92%) as a colorless oil. ¹H NMR : δ 7.36-7.17 (m, 15 H), 4.56 (dd, *J* = 10.8, 5.1 Hz, 1 H), 4.37 (s, 2 H), 4.32 (dd, *J* = 10.8, 5.1 Hz, 1 H), 3.14 (br. t, 2 H), 1.85-1.81 (m, 1 H), 1.71-1.67 (m, 1 H), 1.49 (s, 3 H), 1.46 (br. s, 9 H), 1.49-1.37 (m, 2 H); ¹³C NMR : δ 156.1, 152.2, 150.7, 138.7, 130.6, 130.2, 129.7, 128.9, 127.8, 126.0, 124.6, 120.6, 120.2, 89.7, 80.4, 71.6, 50.9, 46.5, 34.2, 30.5, 28.8, 20.1; ³¹P NMR : δ -11.97. ESIHRMS Calcd. for: C₃₀H₃₇N₂O₈PNa [M+Na]⁺ 607.2185. Found: 607.2191.

5-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-pentanol. In an identical procedure to the one outlined above for 5-[*N*-benzyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-pentanol, **39** (0.20 g, 0.73 mmol) gave the title compound (0.22 g, 98%) as a colorless oil. ¹H NMR : δ 5.78-5.67 (m, 1 H), 5.12-5.06 (m, 2 H), 3.96 (d, *J* = 12.6 Hz, 1 H), 3.75 (br. d, *J* = 12 Hz, 3 H), 3.16 (br. s, 2 H), 1.97-1.73 (m, 2 H), 1.55 (s, 3 H), 1.52-1.38 (m, 2 H), 1.43 (s, 9H); ¹³C NMR : δ 155.6, 134.2, 116.5, 91.8, 79.9, 49.9, 46.5, 33.5, 28.5, 22.7, 20.2. ESIHRMS Calcd. for: C₁₄H₂₆N₂O₅Na [M+Na]⁺ 325.1739. Found: 325.1730.

5-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-(diphenylphosphatoxy)-pentane (42).

In an identical procedure to the one outlined above for **41**, the above *N*-allyl nitroalcohol (0.20 g, 0.66 mmol) was phosphorylated to give **42** (0.32 g, 92%) as a colorless oil. ¹H NMR : δ 7.36-7.17 (m, 10 H), 5.78-5.68 (m, 1 H), 5.11-5.05 (m, 2 H), 4.61 (dd, *J* = 10.6, 5.7 Hz, 1 H), 4.37 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.74 (d, *J* = 5.4 Hz, 2 H), 3.14 (t, *J* = 7.2 Hz, 2 H), 1.97-1.87 (m, 1 H), 1.81-1.58 (m, 1 H), 1.55 (s, 3 H), 1.42 (s, 9 H), 1.58-1.40 (m, 2 H); ¹³C NMR : δ 155.5, 150.5, 150.4, 134.2, 129.9, 125.7, 120.2, 120.1, 116.5, 89.6, 79.9, 71.4, 49.8, 46.2, 33.4, 28.5, 22.6, 19.9; ³¹P NMR : δ -11.99. ESIHRMS Calcd. for: C₂₆H₃₅N₂O₈PNa [M+Na]⁺ 557.2029. Found 557.2034.

5-(*N*-Benzylamino)-2-methyl-2-nitro-1-(diphenylphosphatoxy)-pentane (44). The phosphate **41** (0.50 g, 0.86 mmol) gave the amine **44** (0.37 g, 90%) as a colorless oil by a protocol similar to that used to form compound **29**. ^1H NMR : δ 7.36-7.14 (m, 15 H), 5.37 (br. s, 1 H), 4.60 (dd, J = 10.8, 5.4 Hz, 1 H), 4.38 (dd, J = 11.2, 5.9 Hz, 1 H), 3.85 (s, 2 H), 2.65 (t, J = 6.3 Hz, 2 H), 1.99-1.77 (m, 2 H), 1.61-1.41 (m, 2 H), 1.50 (s, 3 H); ^{13}C NMR : δ 152.8, 150.2, 129.5, 129.1, 129.0, 125.8, 123.7, 120.4, 120.2, 89.5, 71.5, 51.6, 46.2, 32.9, 21.4, 19.4; ^{31}P NMR : δ -12.11. ESIHRMS Calcd. for: $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 485.1842. Found : 485.1855.

5-(*N*-Allylamino)-2-methyl-2-nitro-1-(diphenylphosphatoxy)-pentane (45). The phosphate **42** (0.30 g, 0.56 mmol) gave the amine **45** (0.23 g, 93%) as a colorless oil by a protocol similar to that used to form compound **29**. ^1H NMR : δ 7.36-7.16 (m, 10 H), 5.89-5.80 (m, 1 H), 5.19-5.07 (m, 2 H), 4.62 (dd, J = 10.9, 5.7 Hz, 1 H), 4.38 (dd, J = 10.9, 5.7 Hz, 1 H), 3.19 (d, J = 6.0 Hz, 2 H), 2.63 (br. s, 1 H), 2.56 (t, J = 7.2 Hz, 2 H), 1.99-1.82 (m, 2 H), 1.55 (s, 3 H), 1.45-1.38 (m, 2 H); ^{13}C NMR : δ 150.4, 150.3, 136.1, 130.0, 125.8, 120.2, 120.1, 116.7, 89.8, 71.3, 52.1, 48.4, 33.8, 23.8, 19.9; ^{31}P NMR : δ -11.99. ESIHRMS Calcd. for: $\text{C}_{21}\text{H}_{28}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 435.1685. Found: 435.1692.

1-Benzyl-3-methylpiperidine (47). Tributyltin hydride (0.032 mL, 0.12 mmol) and AIBN (0.005 g, 0.032 mmol) were added to a solution of **44** (0.039 g, 0.08 mmol) in degassed benzene (6 mL), and heated to reflux for 20 h. After concentration of the solvent, the residue was taken up in ether and washed with HCl (2 M, 10 mL). The aqueous layer was washed with diethyl ether (2 x 10 mL), basified with NaOH (2 M, 15 mL), extracted with diethyl ether (2 x 15 mL) and concentrated. Purification on silica gel column (eluent : Methanol/ CHCl_3 1/1) gave the known **47**⁹ (0.014 g, 90%) as a colorless oil. ^1H NMR : δ 7.31 (m, 5 H), 3.49 (s, 2 H), 2.87-2.63 (m, 4 H), 1.87-1.53 (m, 5 H), 0.84 (d, J = 5.7 Hz, 3 H); ^{13}C NMR (CDCl_3) : δ 129.2, 128.1, 126.8, 63.5, 61.8, 53.9, 32.9, 31.0, 25.4, 19.6.

5,6-Dimethyl-1-aza-bicyclo[3.2.1]octane (48) and 1-Allyl-3-methylpiperidine (49) In a similar procedure as outlined above for **47**, the reaction of tributyltin hydride (0.072 mL, 0.27 mmol) and AIBN (0.012 g, 0.08 mmol) with **45** (0.078 g, 0.18 mmol) gave the title compounds **49** (0.004 g, 17%) and **48** (0.018 g, 78%) as colorless oils. ^1H NMR (**49**) : δ 6.24-6.15 (m, 1 H), 5.54-5.43 (m, 2 H), 3.56-3.34 (m, 3 H), 2.49-1.65 (m, 7 H), 1.14-0.99 (m, 1 H), 0.94 (d, J = 6.6 Hz, 3 H); ^{13}C NMR : δ 126.6, 125.7, 60.2, 58.6, 52.4, 30.9, 28.9, 22.7, 19.0. **48**, 2:1 mixture of two isomers) ^1H NMR ($\text{C}_6\text{D}_6 + \text{CF}_3\text{CO}_2\text{H}$) : δ 3.34-3.24 (m, 1 H), 2.89-2.70 (m, 1 H), 2.68-2.57 (m, 4 H), 2.48-2.41 (m, 2 H), 2.12 (d, J = 6.46 Hz, 1H), 1.50-0.89 (m, 3 H), 1.01, s, 1.5 H), 0.67-0.65 (m, 2 H), 0.60 (d, J = 6.5 Hz, 1.5 H), (0.55-0.54, m, 1 H), 0.44 (d, J = 7.76 Hz, 3 H), 0.38 (s, 3 H); ^{13}C (major) : δ 60.7 (CH_2), 59.1 (CH_2), 52.3 (CH_2), 40.6, 36.9, 36.1, 18.3, 16.6, 16.5; (minor) : δ 64.3 (CH_2), 60.2 (CH_2), 57.0 (CH_2), 39.0, 38.1, 30.3, 24.2, 20.8, 14.7. ESIHRMS Calcd. for: $\text{C}_9\text{H}_{17}\text{NNa}$ $[\text{M}+\text{Na}]^+$ 140.1439. Found: 140.1438.

***N*-Allyl 2-hydroxy-hexanamide (34).** 5-Methyl- δ -pentanolactone (2.5g, 21.9 mmol) and allylamine (3.3 mL, 44.0 mmol) in benzene (10 mL) were refluxed for 3h. After completion, the solvent was evaporated to give the amide **34** (3.55g, 95%). ^1H NMR (CDCl_3): δ 6.0 (br, s, 1 H), 5.84-5.75 (m, 1 H), 5.18-5.07 (m, 2 H), 3.86-3.73 (m, 3 H), 2.63 (br, s, 1 H), 2.22 (t, J = 7.2 Hz, 2 H), 1.77-1.67 (m, 2 H), 1.48-1.41 (m, 2 H), 1.15 (d, J = 6.3 Hz, 3 H); ^{13}C NMR: δ 173.3, 134.3, 116.4, 67.4, 42.0, 38.6, 36.3, 23.6, 21.8. ESIHRMS Calcd. for: $\text{C}_9\text{H}_{17}\text{NO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 194.1151. Found: 194.1148.

6-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-hexanol (37). The amide **34** (3.0 g, 17.5 mmol) was reduced with LiAlH_4 (1.48 g, 38.5 mmol) by an identical procedure to the one described above for **32**, affording 6-(*N*-allylamino)-2-hexanol (1.86 g, 68%) which was taken through to the next step without further purification. ^1H NMR (CDCl_3): δ 5.92-5.82 (m, 1 H), 5.17-5.03 (m, 2 H), 3.76-3.72 (m, 1 H), 3.20 (td, J = 6.6, 1.2 Hz, 2 H), 2.58 (t, J = 7.8 Hz, 2 H), 1.91 (br, s, 1 H), 1.53-1.32 (m, 6 H), 1.14 (d, J = 7.8 Hz, 2 H), 1.91 (br, s, 1H), 1.53-1.32 (m, 6 H), 1.14 (d, J = 6.0 Hz, 3 H). Protection of 6-(*N*-allylamino)-2-hexanol (1.2 g, 7.6 mmol) with $(\text{Boc})_2\text{O}$ by an identical procedure to the one described for **35** afforded **37** (1.48 g, 76%) as a colorless oil. ^1H NMR (CDCl_3): δ 5.80-5.73 (m, 1 H), 5.10-5.04 (m, 2 H), 3.77-3.72 (m, 3 H), 3.15 (t, J = 7.2 Hz, 2 H), 1.74 (br, s, 1 H), 1.52-1.20 (m, 6 H), 1.42 (s, 9 H), 1.14 (d, J = 6.0 Hz, 3 H); ^{13}C NMR: δ 155.6, 134.6, 116.0, 79.4, 67.7, 49.7, 46.6, 39.0, 28.5, 28.3, 23.5, 22.9. ESIHRMS Calcd. for: $\text{C}_{14}\text{H}_{28}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 258.2069. Found: 258.2071.

6-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-nitrohexane (40). Bromination of **37** (0.92 g, 3.58 mmol), carried out by a similar procedure to the one described for 5-[*N*-benzyl-(*N*-*tert*-butyloxycarbonyl)]amino-2-bromopentane, afforded 6-[*N*-allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromohexane (0.98 g, 86%) as a colorless oil. ^1H NMR (CDCl_3): δ 5.81-5.72 (m, 1 H), 5.13-5.06 (m, 2 H), 4.13-4.06 (m, 1 H), 3.79 (d, J = 5.7 Hz, 2 H), 3.17 (t, J = 6.9 Hz, 2 H), 1.85-1.74 (m, 2 H), 1.68 (d, J = 6.6 Hz, 3 H), 1.56-1.41 (m, 4 H), 1.44 (s, 9 H); ^{13}C NMR: δ 155.6, 134.6, 116.1, 79.4, 51.2, 49.7, 46.5, 40.9, 28.5, 27.8, 26.4, 25.1. ESIHRMS Calcd. for $\text{C}_{14}\text{H}_{26}\text{NO}_2\text{NaBr}$ $[\text{M}+\text{Na}]^+$: 344.1024. Found: 344.1012. Nitration of 6-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-bromohexane (0.80 g, 2.50 mmol) by an identical procedure to the one described for **38** afforded the title compound **40** (0.37 g, 52%) as a pale yellow oil. ^1H NMR (CDCl_3): δ 5.78-5.72 (m, 1 H), 5.13-5.07 (m, 2 H), 4.56-4.47 (m, 1 H), 3.78 (d, J = 4.8 Hz, 2 H), 3.17 (t, J = 7.2 Hz, 2 H), 2.05-1.97 (m, 1 H), 1.73-1.70 (m, 1 H), 1.58-1.49 (m, 2 H), 1.51 (d, J = 6.9 Hz, 3 H), 1.45 (s, 9 H), 1.38-1.26 (m, 2H); ^{13}C NMR: δ 155.6, 134.5, 116.2, 83.4, 79.6, 49.8, 46.3, 34.9, 28.5, 27.8, 23.1, 19.1. ESIHRMS Calcd. for: $\text{C}_{14}\text{H}_{27}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 287.1971. Found: 287.1984.

6-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-(diphenylphosphatoxy)-hexane (43). The nitro compound **40** (0.30 g, 1.04 mmol) was condensed with paraformaldehyde by an identical procedure to the one described for 5-[*N*-benzyl-(*N*-*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitropentanol to afford the title compound 6-[*N*-Allyl-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-nitro-1-hexanol (0.32

g, 97%) as a colorless oil. ^1H NMR (CDCl_3): δ 5.81-5.69 (m, 1 H), 5.10-5.05 (m, 2 H), 3.91 (d, J = 12.6 Hz, 1 H), 3.79-3.75 (m, 3 H), 3.18 (t, J = 6.9 Hz, 2 H), 1.98-1.80 (m, 2 H), 1.56-1.45 (m, 2 H), 1.54 (s, 3 H), 1.43 (s, 9 H), 1.31-1.20 (m, 2 H); ^{13}C NMR : δ 155.6, 116.3, 91.9, 79.8, 66.6, 49.7, 45.8, 33.0, 28.5, 28.1, 20.7, 20.5. The above *N*-allyl nitroalcohol (0.25 g, 0.79 mmol) was phosphorylated by an identical procedure to the one described for **41** to give **43** (0.40 g, 93%) as a colorless oil. ^1H NMR (CDCl_3): δ 7.35-7.17 (m, 10 H), 5.81-5.73 (m, 1 H), 5.11-5.05 (m, 2 H), 4.62 (dd, J = 10.8, 5.1 Hz, 1 H), 4.36 (dd, J = 11.4, 5.7 Hz, 1 H), 3.75 (d, J = 5.1 Hz, 2 H), 3.13 (t, J = 6.9 Hz, 2 H), 1.94-1.78 (m, 2 H), 1.54 (s, 3 H), 1.52-1.38 (m, 2 H), 1.43 (s, 9 H), 1.37-1.15 (m, 2 H); ^{13}C NMR: δ 155.5, 150.5, 150.4, 134.4, 129.9, 125.7, 120.2, 120.1, 116.2, 89.8, 79.6, 71.4, 49.8, 46.1, 35.9, 28.5, 28.2, 20.8, 19.8; ^{31}P NMR: δ -12.0. ESIHRMS Calcd. for: $\text{C}_{27}\text{H}_{38}\text{N}_2\text{O}_8\text{P}$ $[\text{M}+\text{H}]^+$ 549.2366. Found: 549.2341.

6-(*N*-Allylamino)-2-methyl-2-nitro-1-(diphenylphosphatoxy)-hexane (46). Following the procedure described to obtain **29** phosphate **43** (0.35 g, 0.63 mmol) on treatment with TMSOTf gave the amine **46** (0.26 g, 91%) as a colorless oil. ^1H NMR (CDCl_3): δ 7.36-7.17 (m, 10 H), 5.81-5.73 (m, 1 H), 5.11-5.05 (m, 2 H), 4.62 (dd, J = 10.8, 5.1 Hz, 1 H), 4.36 (dd, J = 11.4, 5.7 Hz, 1 H), 3.40 (d, J = 5.1 Hz, 2 H), 2.71 (t, J = 7.5 Hz, 2 H), 1.86-1.55 (m, 4 H); ^{13}C NMR: δ 150.2, 150.1, 136.0, 129.8, 125.6, 120.1, 120.0, 116.5, 89.6, 71.3, 50.1, 46.2, 35.1, 25.6, 20.6, 19.7; ^{31}P NMR: δ -12.2. ESIHRMS Calcd. for: $\text{C}_{22}\text{H}_{30}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 449.1842. Found: 449.1826.

5,6-Dimethyl-1-aza-bicyclo[4.2.1]nonane (50). Tributyltin hydride (0.146 mL, 0.53 mmol) and AIBN (0.025 g, 0.16 mmol) were added to a solution of **46** (0.156 g, 0.35 mmol) in degassed benzene (20 mL), and heated to reflux for 20h. After concentration, the residue was taken up in ether and washed with HCl (2 M, 10 mL). The aqueous layer was washed with diethyl ether (2 x 10 mL), basified with NaOH (2M, 15 mL), extracted with diethyl ether (2 x 15 mL) and concentrated. Purification on silica gel column (Methanol/ CHCl_3 1:1) gave title compound **50** (0.031 g, 58%) as 2:1 mixture of isomers. ^1H NMR (CDCl_3): δ 4.23 (t, J = 7.2 Hz, 0.3 H), 3.68-3.60 (m, 3 H), 3.52 (dd, J = 7.8, 3.6 Hz, 1 H), 3.22-3.16 (m, 2 H), 3.08-3.05 (m, 1 H), 2.96 (d, J = 7.5 Hz, 1 H), 2.40 (t, J = 7.2 Hz, 0.3 H), 1.76-1.70 (m, 1 H), 1.55-1.50 (m, 4 H), 1.42-0.96 (m, 7 H), 0.75 (d, J = 4.5 Hz, 3 H), 0.68 (s, 1 H), 0.65 (s, 3 H), 0.57 (d, J = 4.2 Hz, 1 H); ^{13}C NMR (**major**): δ 64.2 (CH_2), 57.9 (CH_2), 54.7 (CH_2), 44.4, 42.6, 39.7, 23.9, 22.7, 21.9, 17.0; ^{13}C NMR (**minor**): δ 62.9 (CH_2), 59.9 (CH_2), 54.5 (CH_2), 44.1, 41.7, 34.9, 24.6, 23.8, 22.7, 10.3. ESIHRMS Calcd. for: $\text{C}_{20}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 154.1596. Found: 154.1589.

4-[*N*-(Phenylpropargyl)]aminobutyraldehyde diethylacetal (51). To a stirred, ice-cooled solution of 4-aminobutyraldehyde diethylacetal (6.77 g, 42.03 mmol) in DMF (11 mL) was added a solution of phenylpropargyl bromide¹⁰ (2.05 g, 10.51 mmol) in DMF (25 mL) dropwise. After 20 min. potassium carbonate (1.45 g, 10.51 mmol) was added and the contents stirred overnight with the gradual warming to room temperature. The reaction mixture was then poured in water (75 mL) and the aqueous layer extracted

with ethyl acetate (3 x 75 mL). The combined organic layers were washed with water (2 x 50 mL), brine (50 mL), dried (Na₂SO₄) and concentrated under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 1:1) afforded **51** (2.11 g, 73%) as a pale yellow oil. ¹H NMR δ: 7.40- 7.25 (m, 5 H), 4.50 (t, *J* = 5.2 Hz, 1 H), 3.68- 3.57 (m, 4 H), 3.52-3.44 (m, 2 H), 2.76 (t, *J* = 7.0 Hz, 2 H), 1.81 (br. s, 1 H), 1.69- 1.57 (m, 4 H), 1.17 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR δ: 131.7, 128.4, 128.1, 123.4, 106.2, 87.8, 83.5, 61.1, 48.7, 39.1, 31.6, 25.3, 15.5. ESIHRMS Calcd. for: C₁₇H₂₅NO₂Na [M+Na]⁺ 298.1783. Found: 298.1779.

3-[N-(Phenylpropargyl)]aminopropionaldehyde diethylacetal (52). To a stirred, ice-cooled solution of 3-aminopropionaldehyde diethylacetal (4.54 g, 42.03 mmol) in DMF (8 mL) was added a solution of phenylpropargyl bromide¹⁰ (1.50 g, 7.71 mmol) in DMF (20 mL) drop wise. After 20 min. potassium carbonate (1.06 g, 7.71 mmol) was added and the contents were stirred overnight with the gradual warming to room temperature. The reaction mixture was then poured in water (75 mL) and the aqueous layer extracted with ethyl acetate (3 x 50 mL). The combined organic layers washed well with water (2 x 50 mL), brine (50 mL), dried (Na₂SO₄) and concentrated under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 1:1) afforded **53** (1.50 g, 75%) as a pale yellow oil. ¹H NMR δ: 7.36- 7.20 (m, 5 H), 4.56 (t, *J* = 5.8 Hz, 1 H), 3.65- 3.55 (m, 4 H), 3.49- 3.39 (m, 2 H), 2.77 (t, *J* = 6.7 Hz, 2 H), 1.79 (q, *J* = 6.3 Hz, 2 H), 1.42 (br. s, 1 H), 1.14 (t, *J* = 7.0 Hz, 6 H); ¹³C NMR δ: 131.7, 128.3, 128.0, 123.4, 101.9, 87.9, 83.4, 61.4, 44.7, 39.2, 33.8, 15.4. ESIHRMS Calcd. for: C₁₆H₂₃NO₂Na [M+Na]⁺ 284.1626. Found: 284.1635.

4-[N-(Phenylpropargyl)-N-(tert-butyloxycarbonyl)]aminobutyraldehyde diethylacetal (53). To a stirred solution of **51** (1.89 g, 6.87 mmol) in CH₂Cl₂ (40 mL) at 0 °C was added di-*tert*-butyl dicarbonate (1.95 g, 8.94 mmol) in CH₂Cl₂ (10 mL) followed by triethylamine (1.85 mL, 13.06 mmol). After stirring overnight with the gradual warming to room temperature, the reaction mixture was diluted with ethyl acetate (150 mL) and the organic layer washed with saturated NaHCO₃ solution (2 x 30 mL), water (50 mL) brine (50 mL), dried (Na₂SO₄) and concentrated under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 10:1) afforded **53** (2.46 g, 96%) as colorless oil. ¹H NMR δ: 7.41- 7.25 (m, 5 H), 4.48 (t, *J* = 5.2 Hz, 1 H), 4.24 (br. s, 2 H), 3.66- 3.43 (m, 4 H), 3.38 (t, *J* = 6.9 Hz, 2 H), 1.72-1.61 (m, 4 H), 1.47 (br. s, 9 H), 1.16 (t, *J* = 7.05 Hz, 6 H); ¹³C NMR δ: 155.2, 131.7, 128.3, 128.1, 123.2, 102.8, 85.4, 83.7, 80.0, 61.2, 46.5, 37.1, 31.2, 28.5, 23.5, 15.4. ESIHRMS calcd. for: C₂₂H₃₃NO₄Na [M+Na]⁺ 398.2307. Found: 398.2326.

3-[N-(Phenylpropargyl)-N-(tert-butyloxycarbonyl)]aminopropionaldehyde diethylacetal (54). To a stirred solution of **52** (1.47 g, 5.61 mmol) in CH₂Cl₂ (30 mL) at 0 °C was added di-*tert*-butyl dicarbonate (1.58 g, 7.28 mmol) in CH₂Cl₂ (10 mL) followed by triethylamine (1.52 mL, 10.65 mmol). After stirring overnight with the gradual warming to room temperature, the reaction mixture was then diluted with ethyl

acetate (120 mL) and the organic layer washed well with saturated NaHCO₃ solution (2 × 30 mL), water (50 mL) brine (50 mL), dried (Na₂SO₄) and concentrated under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 10:1) afforded **54** (1.89 g, 94%) as colorless oil. ¹H NMR δ: 7.40- 7.23 (m, 5 H), 4.52 (t, *J* = 5.7 Hz, 1 H), 4.23 (br. s, 2 H), 3.67-3.40 (m, 6 H), 1.97-1.90 (m, 2 H), 1.46 (br. s, 9 H), 1.16 (t, *J* = 7.3 Hz, 6 H); ¹³C NMR δ: 155.0, 131.7, 128.3, 128.1, 123.2, 101.3, 85.4, 83.5, 80.0, 61.2, 43.0, 37.4, 32.6, 28.5, 15.3. ESIHRMS calcd. for: C₂₁H₃₁NO₄Na [M+Na]⁺ 384.2151. Found: 384.2152.

4-[N-(Phenyl propargyl)-N-(tert-butyloxycarbonyl)]aminobutanal (55). To a solution of **53** (2.46 g, 6.56 mmol) in a CH₃CN:H₂O (9:1) solvent mixture (45 mL) was added DDQ (0.29 g, 1.31 mmol) at room temperature. The solution was stirred for 8 h and then the solvent removed under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate, 5:1) afforded **55** (1.64 g, 83%) as a colorless oil. ¹H NMR δ: 9.75 (br. s, 1 H), 7.40- 7.20 (m, 5 H), 4.22 (br. s, 2 H), 3.40 (t, *J* = 6.75 Hz, 2 H), 2.46 (t, *J* = 7.1 Hz, 2 H), 1.99- 1.91 (m, 2 H), 1.47 (br. s, 9 H). ¹³C NMR δ: 201.4, 155.2, 131.7, 128.4, 128.2, 122.9, 85.2, 83.4, 80.4, 46.0, 41.1, 37.5, 28.5, 20.9. ESIHRMS calcd. for: C₁₈H₂₃NO₃Na [M+Na]⁺ 324.1576. Found: 324.1583.

3-[N-(Phenylpropargyl)-N-(tert-butyloxycarbonyl)]aminopropanal (56). To a solution of **54** (1.74 g, 4.82 mmol) in a CH₃CN:H₂O (9:1) solvent mixture (30 mL) was added DDQ (0.21 g, 0.96 mmol) at room temperature. The solution was stirred for 8 h and then the solvent removed under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate, 5:1) afforded **56** (1.17 g, 85%) as a colorless oil. ¹H NMR δ: 9.79 (br. s, 1 H), 7.40- 7.25 (m, 5 H), 4.20 (br. s, 2 H), 3.69 (t, *J* = 6.6 Hz, 2 H), 2.77 (t, *J* = 6.6 Hz, 2 H), 1.48 (br. s, 9 H); ¹³C NMR δ: 200.5, 154.9, 131.7, 128.4, 128.3, 122.9, 84.9, 83.7, 80.7, 43.3, 40.9, 37.8, 28.4. ESIHRMS calcd. for: C₁₇H₂₁NO₃Na [M+Na]⁺ 310.1419. Found: 310.1408.

6-[N-(Phenylpropargyl)-N-(tert-butyloxycarbonyl)]amino-3-hydroxy-2-methyl-2-nitrohexane (57). 2-Nitropropane (11.20 mL, 129 mmol) and **55** (1.95 g, 6.45 mmol) were dissolved in a 1:1 mixture of acetonitrile and *tert*-butanol (35 mL). After cooling to 0 °C, potassium *tert*-butoxide (0.72 g, 6.45 mmol) was added and the reaction mixture stirred for 24 h with gradual warming to room temperature. Saturated ammonium chloride solution (30 mL) and ethyl acetate (75 mL) were then added, the organic layer was separated, and the aqueous layer extracted with ethyl acetate (2× 35 mL). The combined organic layers were washed with water (2× 50 mL) and brine, dried (Na₂SO₄) and the solvent removed under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 5:1) afforded **57** (1.76 g, 70%) as a pale yellow oil. ¹H NMR δ: 7.40- 7.25 (m, 5 H), 4.22 (br. s, 2 H), 4.05- 4.0 (br. d, 1 H), 3.61- 3.31 (m, 2 H), 1.91- 1.68 (m, 3 H), 1.53- 1.27 (m, 16 H); ¹³C

NMR δ : 155.5, 131.7, 128.5, 128.3, 122.9, 92.2, 85.3, 83.4, 80.5, 76.0, 46.3, 37.3, 28.5, 25.4, 23.4, 23.2, 20.8. ESIHRMS calcd. for: $C_{21}H_{30}N_2O_5Na$ $[M+Na]^+$ 413.2052. Found : 413.2035.

5-[*N*-(Phenylpropargyl)-*N*-(*tert*-butyloxycarbonyl)]amino-3-hydroxy-2-methyl-2-nitropentane (58).

2-Nitropropane (6.7 mL, 76.6 mmol) and **56** (1.10 g, 3.83 mmol) were dissolved in a 1:1 mixture of acetonitrile and *tert*-butanol (25 mL). After cooling to 0 °C, potassium *tert*-butoxide (0.43 g, 3.83mmol) was added and the reaction mixture was stirred for 24 h with gradual warming to room temperature. Saturated ammonium chloride solution (30 mL) and ethyl acetate (75 mL) were then added, the organic layer was separated, and the aqueous layer extracted with ethyl acetate (2× 35 mL). The combined organic layers washed with water (2× 50 mL) and brine, dried (Na_2SO_4) and the solvent was removed under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 5:1) afforded **58** (0.96 g, 66%) as a pale yellow oil. 1H NMR δ : 7.43- 7.25 (m, 5 H), 4.30- 4.10 (m, 2 H), 4.12- 4.08 (br. d, 1 H), 3.85- 3.82 (m, 1 H), 3.36- 3.30 (m, 1 H), 1.92- 1.82 (m, 1 H), 1.56-1.47 (m, 16 H); ^{13}C NMR δ : 155.6, 131.8, 128.5, 128.3, 122.7, 91.6, 84.9, 83.7, 81.3, 72.5, 44.0, 38.0, 30.1, 28.5, 23.1, 20.8. ESIHRMS calcd. for: $C_{20}H_{28}N_2O_5Na$ $[M+Na]^+$ 399.1896. Found: 399.1886.

3-(Diphenylphosphatoxy)-6-[*N*-(phenylpropargyl)-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-

nitro-hexane (59). Chloro diphenylphosphate (1.47 mL, 7.50 mmol) was added to a solution of **57** (1.73 g, 4.41 mmol) and DMAP (0.89 g, 7.70 mmol) in CH_2Cl_2 (40 mL) at room temperature. The reaction mixture was stirred overnight and quenched by diluting with ethyl acetate (80 mL). The organic layer was washed with saturated aqueous ammonium chloride (2 x 25 mL), water (2 x 25 mL), and brine (2 x 25 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 3:1) afforded **59** (2.19 g, 80%) as a pale yellow oil. 1H NMR δ : 7.41- 7.13 (m, 15 H), 5.17- 5.13 (m, 1 H), 4.14 (br. s, 2 H), 3.40- 3.34 (m, 2 H), 1.90- 1.67 (m, 4 H), 1.58 (s, 3 H), 1.52 (s, 3 H), 1.47 (s, 9 H); ^{13}C NMR δ : 155.2, 150.7, 131.8, 129.8, 128.4, 128.3, 125.5, 123.0, 120.2, 90.3, 85.3, 83.7, 83.3, 80.3, 45.9, 37.0, 28.8, 28.5, 24.7, 22.8, 21.8; ^{31}P NMR δ : -12.0. ESIHRMS calcd. for: $C_{33}H_{39}N_2O_8NaP$ $[M+Na]^+$ 645.2342. Found: 645.2344.

3-(Diphenylphosphatoxy)-5-[*N*-(phenylpropargyl)-*N*-(*tert*-butyloxycarbonyl)]amino-2-methyl-2-

nitropentane (60). Chloro diphenylphosphate (0.7 mL, 3.46 mmol) was added to a solution of **58** (0.73 g, 1.92 mmol) and DMAP (0.41 g, 3.46 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred overnight and quenched by diluting with ethyl acetate (60 mL). The organic layer was washed with saturated aqueous ammonium chloride (2 x 25 mL), water (2 x 25 mL), and brine (2 x 25 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 3:1) afforded **60** (0.79 g, 72%) as a pale yellow oil. 1H NMR δ : 7.39- 7.13 (m, 15 H), 5.23- 5.16 (m, 1 H), 4.27 (d, J = 17.4 Hz, 1H), 4.17 (d, J = 17.4 Hz, 1H), 3.58- 3.46 (m, 2 H), 2.08- 2.00 (m, 2 H), 1.61 (s, 3 H), 1.57 (s, 3 H), 1.47 (br. s, 9 H); ^{13}C NMR δ : 155.0,

150.6, 131.8, 129.9, 128.5, 128.2, 125.6, 123.0, 120.2, 90.3, 85.3, 83.5, 81.9, 80.6, 45.1, 38.2, 30.9, 28.5, 22.8, 21.6; ^{31}P NMR δ : -12.1. ESIHRMS calcd. for: $\text{C}_{32}\text{H}_{37}\text{N}_2\text{O}_8\text{NaP}$ $[\text{M}+\text{Na}]^+$ 631.2185. Found: 631.2172.

3-(Diphenylphosphatoxy)-6-*N*-phenylpropargylamino-2-methyl-2-nitrohexane (61). To a solution of **59** (1.168 g, 1.87 mmol) in CH_2Cl_2 (25 mL) at room temperature was added TFA (0.70 mL, 9.37 mmol) and the contents stirred for 16 h. The reaction mixture was then taken-up in ethyl acetate (80 mL) and washed well with saturated aqueous NaHCO_3 (3 x 25 mL), water (2 x 25 mL), and brine (25 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 1:1 with 5% MeOH) afforded **61** (0.86 g, 88%) as yellow oil. ^1H NMR δ : 7.39- 7.14 (m, 15 H), 5.23- 5.17 (m, 1 H), 3.56 (s, 2 H), 2.71-2.69 (m, 2 H), 1.68-1.65 (m, 4 H), 1.61 (s, 3 H), 1.56 (s, 3 H), 1.2 (br, s, 1 H); ^{13}C NMR δ : 150.5, 131.8, 129.9, 128.5, 128.2, 125.6, 123.3, 120.2, 90.4, 87.7, 83.9, 83.6, 48.1, 39.0, 29.3, 26.1, 22.9, 21.7; ^{31}P NMR δ : -11.8. ESIHRMS calcd. for: $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 523.1998. Found: 523.1996.

3-(Diphenylphosphatoxy)-5-*N*-phenylpropargylamino-2-methyl-2-nitropentane (62). To a solution of **60** (0.77 g, 1.26 mmol) in CH_2Cl_2 (18 mL) at room temperature was added TFA (0.60 mL, 7.56 mmol) and the contents stirred for 16 h. The reaction mixture was then taken-up in ethyl acetate (80 mL) and washed well with saturated NaHCO_3 solution (3 x 25 mL), water (2 x 25 mL), and brine (25 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford the crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 1:1 with 5% MeOH) afforded **62** (0.57 g, 90%) as yellow oil. ^1H NMR δ : 7.38- 7.13 (m, 15 H), 5.38- 5.32 (m, 1 H), 3.54 (s, 2 H), 2.88- 2.82 (m, 2 H), 1.78 (q, J = 6.6 Hz, 2 H), 1.62 (s, 3 H), 1.58 (s, 3 H), 1.48 (br. s, 1 H); ^{13}C NMR δ : 150.5, 131.8, 129.9, 128.4, 128.1, 125.7, 123.3, 120.6, 90.4, 87.6, 83.6, 81.6, 44.3, 39.0, 31.8, 23.2, 21.4; ^{31}P NMR δ : -11.6. ESIHRMS calcd. for: $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_6\text{NaP}$ $[\text{M}+\text{Na}]^+$ 531.1661. Found: 531.1677.

2-(*E,Z*)-Benzylidene-1,1-dimethylpyrrolizidine (63). Tributyltin hydride (0.38 mL, 1.39 mmol) and AIBN (0.04 g, 0.28 mmol) were added to a solution of **61** (0.49 g, 0.93 mmol) in degassed benzene (46 mL) and the mixture heated to reflux for 40 h with addition of further AIBN (5 mol%) every 12 h. The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure. To the residue, 1M HCl in ether (20 mL) was added and the contents stirred for 30 min. The organic layer was then extracted with dilute HCl (3 x 25 mL) and the combined aqueous layers washed well with petroleum ether (4 x 25 mL), followed by basification with NaOH (5M, 40 mL). The aqueous layer was extracted with diethyl ether (4 x 25 mL) and the combined organic layers washed with water (3 x 25 mL), brine (25 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford crude product. Purification by silica gel column chromatography (eluent: hexanes/ethyl acetate 1:1, 10% MeOH) afforded **63** (0.12 g, 60%) as a mixture of geometrical isomers (*E/Z*, 5.7/1). ^1H NMR δ : 7.32- 7.17 (m, 10 H), 6.44 (s, 1 H), 6.18 (s, 1 H), 4.24 (d, J = 15.8 Hz, 1 H), 4.02 (d, J = 14.6 Hz, 1 H), 3.42 (d, J = 15.8 Hz, 1 H), 3.31 (d, J = 14.6 Hz, 1 H),

3.16- 3.09 (m, 4 H), 2.77-2.72 (m, 2 H), 1.97-1.95 (m, 2 H), 1.77- 1.67 (m, 4 H), 1.48- 1.42 (m, 2 H), 1.30 (s, 3 H), 1.27 (s, 3 H), 1.19 (s, 3 H), 0.87 (s, 3 H); ^{13}C NMR δ : 150.9, 149.6, 138.3, 138.1, 129.5, 128.7, 128.6, 128.1, 126.7, 126.6, 122.1, 119.7, 79.4, 76.1, 61.9, 58.4, 55.4, 55.3, 45.7, 44.3, 30.9, 29.9, 27.0, 26.9, 25.5, 25.4, 23.6, 23.5. ESIHRMS calcd. for: $\text{C}_{16}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 228.1752. Found: 228.1743.

4-(2-Tetrahydropyranyloxy)-1-nitro-1-phenylbutane (66). To an ice cooled mixture of the known alcohol¹¹ **65** (0.58 g, 2.97 mmol) and DHP (0.27 mL, 3 mmol) in CH_2Cl_2 (5 mL) was added catalytic PTSA. After stirring for 0.5 h, the reaction mixture was poured into cold water (5 mL) and extracted with CH_2Cl_2 (10 mL). Purification on a silica gel column (eluent: hexanes/ EtOAc 10:1) gave **66** (0.79 g, 96%) as a colorless oil. ^1H NMR : δ 7.38-7.13 (m, 5 H), 5.54 (t, J = 6.9 Hz, 1 H), 4.55 (d, J = 2.4 Hz, 1 H), 3.84-3.75 (m, 2 H), 3.50-3.39 (m, 2 H), 2.61-2.56 (m, 1 H), 2.27-2.22 (m, 1 H), 1.82-1.50 (m, 8 H); ^{13}C NMR : δ 134.7, 129.9, 129.1, 127.9, 99.0, 91.3, 66.5, 62.5, 31.2, 30.8, 26.3, 25.5, 19.7. Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{NO}_4$: C, 64.50; H, 7.58. Found: C, 64.58; H, 7.54.

5-(2-Tetrahydropyranyloxy)-2-nitro-2-phenyl-1-(diphenylphosphatoxy)-pentane (67). Treatment of **66** (0.5 g, 1.79 mmol) with paraformaldehyde under similar conditions as those described for 5-[*N*-benzyl-*N*-(*tert*-butoxycarbonyl)]amino-2-methyl-2-nitro-1-pentanol, followed by phosphorylation by a protocol similar to that used for compound **41** gave the phosphate **67** (0.52 g, 94%) as a colorless oil. ^1H NMR : δ 7.38-7.13 (m, 15 H), 5.19 (dd, J = 10.8, 3.3 Hz, 1 H), 4.85-4.80 (m, 1 H), 4.54-4.48 (m, 1 H), 3.80-3.65 (m, 2 H), 3.44 (m, 1 H), 3.29 (m, 1 H), 2.61-2.45 (m, 2 H), 1.79-1.41 (m, 8 H); ^{13}C NMR : δ 150.4, 134.8, 130.0, 129.8, 129.3, 125.9, 125.7, 120.2, 120.1, 98.8, 94.4, 68.9, 66.5, 62.4, 30.7, 30.5, 25.5, 24.4, 19.6; ^{31}P : δ -11.98. ESIHRMS Calcd. For: $\text{C}_{28}\text{H}_{32}\text{NO}_8\text{PK}$ $[\text{M}+\text{K}]^+$ 580.1503. Found: 580.1472.

1-(Diphenylphosphatoxy)-2-nitro-2-phenyl-5-pentanol (68). To a solution of **67** (0.12 g, 0.22 mmol) in CH_2Cl_2 (3 mL) was added TMSOTf (0.047 mL, 0.26 mmol) and stirred for 2 h at room temperature. The reaction was quenched with cold water (5 mL) and extracted with EtOAc (10 mL). Purification by column chromatography gave the title compound **68** (0.096 g, 96%) as a colorless oil. ^1H NMR : δ 7.39-7.14 (m, 15 H), 5.18 (dd, J = 10.8, 4.8 Hz, 1 H), 4.85 (dd, J = 11.1, 5.1 Hz, 1 H), 3.52 (dt, J = 6.0, 1.8 Hz, 2 H), 2.58-2.44 (m, 2 H), 1.70 (br. s, 1 H), 1.38 (m, 1 H); ^{13}C NMR : δ 150.2, 135.0, 130.1, 129.8, 125.9, 125.7, 120.2, 120.1, 94.4, 68.7, 61.9, 30.2, 27.1; ^{31}P NMR : δ -11.80. Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_7\text{P}$: C, 60.39; H, 5.29. Found: C, 60.46; H, 5.34.

3-Phenyltetrahydropyran (69) and 5-(diphenylphosphatoxy)-4-phenyl-1-pentanol (70). Tributyltin hydride (0.059 mL, 0.22 mmol) and AIBN (0.009 g, 0.059 mmol) in degassed acetonitrile/benzene (3:1, 3 mL) were added to a solution of **68** (0.067 g, 0.15 mmol) in degassed acetonitrile/benzene (3:1, 9 mL), and the mixture was heated to reflux for 20 h. After removal of the solvent, the residue was loaded on a silica gel column. Elution with hexanes/EtOAc 3:1, gave the known¹² **69** (0.007 g, 30%) as a colorless oil. ^1H

NMR (**69**) : δ 7.15-6.96 (m, 5 H), 4.04-4.0 (m, 2 H), 3.48 (dt, J = 11.2, 2.0 Hz, 1 H), 3.41 (t, J = 11.0 Hz, 1 H), 2.88 (tt, J = 11.0, 3.9 Hz, 1 H), 1.92-1.82 (m, 1 H), 1.71-1.35 (m, 3 H). Further elution with hexanes/EtOAc 1:10 gave **70** (0.037 g, 60%) as a colorless oil. ^1H NMR (**70**) : δ 7.30-7.07 (m, 15 H), 4.32 (dt, J = 6.7, 3.0 Hz, 2 H), 3.53 (t, J = 6.3 Hz, 2 H), 2.96 (m, 1 H), 1.86 (m, 2 H), 1.62 (m, 1 H), 1.39 (m, 2 H); ^{13}C NMR : δ 150.6, 150.5, 140.6, 129.9, 128.8, 128.1, 127.2, 125.5, 120.1, 72.8, 62.6, 46.2, 30.3, 27.9. ESIHRMS Calcd. For: $\text{C}_{23}\text{H}_{25}\text{O}_5\text{PK}$ $[\text{M}+\text{K}]^+$ 451.1077. Found: 451.1082.

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