Supporting Information

For

Enantioselective Cyclization of Alkene Radical Cations

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General. All solvents were dried and distilled by standard methods. Mp's were determined on a hotstage microscope and are uncorrected. IR Spectra (cm^{-1}) were recorded on a FT-IR spectrometer, ^1H , & ^{13}C NMR spectra were measured as solutions in CDCl_3 , C_6D_6 or CD_3OD and chemical shifts are expressed in ppm relative to the internal standard (Me_4Si or H_3PO_4) and were recorded on Bruker 300 MHz or 500 MHz spectrometers. For compounds containing the Boc group spectra were recorded at 50 °C. High resolution mass spectra were measured by the Research Resources Center at the University of Illinois at Chicago. Microanalyses were carried out by Midwest Microlabs, Indianapolis, In.

General procedures:

Typical Protocol for the Henry reaction. 2-Nitropropane (1.97 g, 22.1 mmol.) and aldehyde **1** (3.01 g, 10.9 mmol) were dissolved in a 1/1 mixture of acetonitrile and *tert*-BuOH (20 mL). To this solution was added potassium *tert*-butoxide (597 mg, 5.32 mmol) and the reaction mixture was stirred overnight. Sat. aq. NH_4Cl and ether were then added. The organic layer was separated and the aq. layer was extracted with ether. The combined organic layer was washed with water, brine then dried over Na_2SO_4 , and the solvent was removed under reduced pressure. Purification by silica gel column chromatography afforded the respective nitroaldol product **3** (3.74 g, 94%).

Typical Protocol for the Swern oxidation of nitroaldol adducts. A solution of oxalyl chloride (1.3 mL, 14.9 mmol) in CH_2Cl_2 (50 mL) was cooled to -78°C under N_2 followed by the dropwise addition of a solution of DMSO (1.5 mL, 21.1 mmol) in CH_2Cl_2 (7 mL) then the reaction mixture was stirred for 15 min. To this mixture was added dropwise a solution of nitroaldol adduct **3** (2.58 g, 7.04 mmol) in CH_2Cl_2 (17 mL) and stirred at -78°C for 1 h. Triethylamine (7.4 mL, 53.1 mmol) was added dropwise. After stirring for 20 min., the reaction mixture was allowed to warm up to rt. Sat. aq. NH_4Cl was then added and the separated organic layer was washed with H_2O and brine then dried over Na_2SO_4 . The solvent was removed under reduced pressure. Purification by silica gel column chromatography afforded the respective nitro ketone **5** (2.26 g, 88%).

Typical Protocol for the CBS reduction of nitroketones. To a solution of (*S*)-(-)- α,α -diphenyl-2-pyrrolidinemethanol (135 mg, 0.533 mmol, 9 mol %) in THF (4 mL) was added borane-dimethyl sulfide (2 M in THF, 7.20 mL, 14.4 mmol) under Ar. The mixture was stirred at 45-50 °C overnight. Ketone **5** (2.23 g, 6.12 mmol) in THF (35 mL) was added dropwise to the solution of the catalyst for 30 min at 45-50 °C then the reaction mixture was stirred for 20 min. Then the reaction solution was cooled to rt and quenched by dropwise addition of sat. aq. NH_4Cl until the vigor of the reaction subsided. The aq. layer was extracted with ethyl acetate and the combined organic layer was washed with water and brine then dried over Na_2SO_4 . Concentration under reduced pressure and purification by silica gel chromatography gave the corresponding enantiomerically enriched nitro alcohol **7** (1.57 g, 70%).

Typical Protocol for the Phosphorylation of nitroaldols. Diphenyl chlorophosphate (179 mg, 0.67 mmol) was added to nitro alcohol **7** (207 mg, 0.565 mmol) in CH_2Cl_2 (5 mL) followed by the addition of DMAP (91 mg, 0.74 mmol) in one portion at rt. The reaction mixture was stirred overnight then quenched by sat. aq. NH_4Cl . The aq. layer was extracted with CH_2Cl_2 , the combined organic layer was washed with water and brine then dried over Na_2SO_4 . Concentration

under reduced pressure, purification by silica gel column chromatography afforded the corresponding phosphate **9** (331 mg, 98 %).

Typical Protocol for the removal of Boc group. Phosphate **9** (257 mg, 0.429 mmol) was stirred in 10% TFA/CH₂Cl₂ (10 mL) under N₂ at rt overnight. 15% NaOH was then added to pH 11 and the aq. layer was extracted with ethyl acetate. The combined organic layer was washed with water and brine then dried over Na₂SO₄, followed by concentration under reduced pressure. Chromatography on a silica gel column afforded the respective radical precursor **11** (207 mg, 99%).

Typical Protocol for the Radical cyclization. To the solution of the radical precursor **11** (200 mg, 0.401 mmol) and AIBN (14 mg, 0.085 mmol) in deoxygenated benzene (30 mL) was added tributyltin hydride (0.173 mL, 0.643 mmol) and heated to reflux for 30 h with addition of further AIBN (8 mg, 0.05 mmol) twice in 12 h intervals. The reaction mixture was then cooled to rt, 2M HCl (12 mL) was added, and the biphasic mixture was stirred for 20 min. The organic layer was washed with aq. 2M HCl and the combined aq. layer was washed with hexane, then basified to pH 11 with 15% NaOH and extracted with ethyl ether. The combined organic layer was washed with water and brine then dried over Na₂SO₄. Concentration under reduced pressure followed by chromatography on a silica gel column afforded the corresponding cyclized amine **13** (35 mg, 43%).

Determination of Enantiomeric Excess.

HPLC conditions

Chiral HPLC Column: Chiralcel OD [250 x 4.6 mm (1 x id)]

Solvent: 0.5%, 1.7% or 2.0% 2-propanol/hexane

Flow rate: 0.5 mL/min or 1.0 mL/min

Detector: UV 254 nm

GC conditions

Chiral GC Column:

SupelcoTM ALPHA DEXTM 120 Capillary Column (α -cyclodextrin) (30 m x 0.25 μ m film thickness) or

SupelcoTM GAMMA DEXTM 120 Capillary Column (γ -cyclodextrin) (30 m x 0.25 μ m film thickness)

Detector: FID

Carrier gas: He

Flow rate: 20 or 30 cm/sec

(4R)-N-Benzyl-N-(tert-butyloxycarbonyl)-4-hydroxy-5-methyl-5-nitro-hexylamine (**7**)¹.

Following the general procedure for CBS reduction, **5** (136 mg, 0.373 mmol) was converted to **7** (98 mg, 72%, 85% ee: chiral HPLC: 1.7% 2-propanol/hexane, flow rate: 1.0 mL/min, t_R [min.]: 24.5 [minor], 31.0 [major]) as colorless oil, $[\alpha]_D^{23} +12.2$ (c 1.02, CHCl₃).

(4R)-N-Benzyl-N-(tert-butyloxycarbonyl)-4-diphenylphosphatoxy-5-methyl-5-nitro-

hexylamine (9). Following the general procedure for phosphorylation, **7** (207 mg, 0.565 mmol) was converted to **9** (331 mg, 98%) as colorless oil. $[\alpha]_D^{23} +0.16$ (*c* 2.47, CHCl₃), ¹H NMR (CDCl₃): δ 7.34-7.14 (m, 15H), 5.10 (t, *J* = 6.9 Hz, 1H), 4.37 (d, *J* = 15.6 Hz, 1H), 4.29 (d, *J* = 15.6 Hz, 1H), 3.18 (m, 2H), 1.83-1.75 (m, 1H), 2.21 (s, 1H), 1.66-1.64 (m, 4H), 1.70-1.47 (m, 4H), 1.60 (s, 3H), 1.53 (s, 3H), 1.44 (s, 9H); ¹³C NMR (CDCl₃): δ 155.9, 138.5, 129.8, 128.5, 127.5, 127.2, 125.5, 120.2, 90.3, 83.6, 79.9, 50.2, 45.9, 28.8, 28.5, 24.7, 22.7; ³¹P NMR (CDCl₃): δ -12.2; ESIHRMS: Calcd for C₃₁H₃₉N₂O₈PNa [M+Na]⁺ 621.2342, Found 621.2344.

(4R)-N-Benzyl-4-diphenylphosphatoxy-5-methyl-5-nitro-hexylamine (11).

Following the general procedure for removal of Boc group, **9** (257 mg, 0.429 mmol) was converted to **11** (207 mg, 99%) as colorless oil. $[\alpha]_D^{23} +3.2$ (*c* 2.0, CHCl₃), ¹H NMR (CDCl₃): δ 7.37-7.14 (m, 15H), 5.19 (m, 1H), 3.69 (s, 2H), 2.58 (m, 2H), 1.74-1.64 (m, 4H), 1.61 (s, 3H), 1.56 (s, 3H); ¹³C NMR (CDCl₃): δ 150.5, 140.5, 131.0, 129.9, 128.5, 128.2, 127.0, 125.6, 120.4, 120.3, 120.2, 90.5, 83.9, 54.0, 48.6, 29.2, 26.3, 22.9, 21.8; ³¹P NMR (CDCl₃): δ -11.9; ESIHRMS: Calcd for C₂₆H₃₂N₂O₆P [M+H]⁺ 499.1998, Found 499.1991

(S)-1-Benzyl-2-isopropyl-pyrrolidine (13).

Following the general procedure for radical cyclization, **11** (203 mg, 0.407 mmol) afforded **13** (36 mg, 43%, 61% ee: chiral GC: γ -cyclodextrin column, flow rate: 20 cm/sec, detector temperature: 350 °C, injection port temperature: 350 °C, initial oven temperature: 120 °C for 30 min, final oven temperature: 140 °C, gradient temperature: 0.5 °C/min, *t_R* [min.]: 59.9 min [minor], 60.4 min [major]) as colorless oil, $[\alpha]_D^{23} -32.4$ (*c* 1.0, CHCl₃). ¹H NMR (CDCl₃): δ 7.38-7.22 (m, 5H), 4.04 (d, *J* = 13.2 Hz, 1H), 3.10 (d, *J* = 13.2 Hz, 1H), 2.88 (m, 1H), 2.34 (m, 1H), 2.03 (m, 1H), 1.95 (m, 1H), 1.61 (m, 4H), 0.94 (s, 3H), 0.92 (s, 3H); ¹³C NMR (CDCl₃): δ 131.4, 129.9, 129.2, 127.9, 71.6, 29.7, 28.7, 26.1, 22.1, 21.1; ESIHRMS: Calcd for C₁₄H₂₂N [M+H]⁺ 204.1752, Found 204.1747.

(S)-1-Tosyl-2-isopropyl-pyrrolidine (22).

Pyrrolidine **13** (15 mg, 0.074 mmol) was treated in EtOAc (10 mL) with 20% Pd(OH)₂-C (18 mg) under H₂ atmosphere for 4 h. The reaction mixture was carefully filtered through Celite and residue was washed with EtOAc (10 mL). To the filtrate was added diisopropyl ethylamine (0.1 mL, 0.57 mmol) and TsCl (45 mg, 0.24 mmol) then stirred for overnight at rt. The reaction was quenched with sat. aq. NaHCO₃ and aq. layer was extracted with EtOAc. The combined organic layer was washed with H₂O and brine then dried over Na₂SO₄. After the evaporation, the residue was purified by silica gel chromatography. The reported tosylated amine **22** (9 mg, 45%) was obtained as the colorless solid, $[\alpha]_D^{23} -78.1$ (*c* 0.9, CHCl₃) [lit.² $[\alpha]_D^{23} -91.3$ (*c* 1.0, CHCl₃)].

***N*-Benzyl-*N*-(*tert*-butoxycarbonyl)-5-hydroxy-6-methyl-6-nitroheptylamine (4).** Following

the general procedure for Henry reaction, **2** (1.98 g, 6.79 mmol) was converted to **4** (2.37 g, 92%) as colorless oil. ^1H NMR (CDCl_3): δ 7.32-7.19 (m, 5H), 4.41 (s, 2H), 3.91 (m, 1H), 3.18 (m, 2H), 1.61-1.47 (m, 6H), 1.54 (s, 3H), 1.51 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (CDCl_3): δ 156.1, 138.7, 128.5, 127.5, 1127.2, 92.2, 79.9, 77.3, 75.9, 50.6, 46.3, 31.3, 31.1, 28.5, 23.2, 20.8; ESIHRMS: Calcd for $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 403.2209, Found 403.2227.

***N*-Benzyl-*N*-(*tert*-butoxycarbonyl)-6-methyl-6-nitro-5-oxoheptylamine (6).** Following the

general procedure for Swern oxidation, **4** (1.26 g, 3.32 mmol) was converted to **6** (1.17 g, 93%) as colorless oil. ^1H NMR (CDCl_3): δ 7.30-7.19 (m, 3H), 4.41 (s, 2H), 3.17 (t, J = 6.6 Hz, 2H), 1.70 (s, 6H), 1.57 (m, 4H), 1.46 (s, 9H); ^{13}C NMR (CDCl_3): δ 206.7, 188.5, 138.7, 128.5, 127.5, 127.20, 127.17, 94.1, 79.8, 77.3, 50.5, 46.2, 35.8, 28.5, 27.4, 23.3, 21.0; ESIHRMS: Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_5$ Na $[\text{M}+\text{Na}]^+$ 401.2052, Found 401.2037.

(5*R*)-*N*-Benzyl-*N*-(*tert*-butoxycarbonyl)-5-hydroxy-6-methyl-6-nitroheptylamine (8).

Following the general procedure for CBS reduction, **6** (313 mg, 0.827 mmol) was converted to **8** (245 mg, 78%) as colorless oil. $[\alpha]_{\text{D}}^{23} +1.6$ (c 1.0, CHCl_3). Enantiomeric excess was determined by chiral HPLC after the derivatization to the phosphate **10**.

(5*R*)-*N*-Benzyl-*N*-(*tert*-butoxycarbonyl)-5-diphenylphosphatoxy-6-methyl-6-nitroheptylamine (10). Following the general procedure for

phosphorylation, **8** (192 mg, 0.51 mmol) was converted to **10** (306 mg, 99%, 86% ee: chiral HPLC: 2.0% 2-propanol/hexane, flow rate: 1.0 mL/min, t_{R} [min.]: 26.6 [minor], 38.2 [major]) as colorless oil. $[\alpha]_{\text{D}}^{23} +4.0$ (c 1.0, CHCl_3), ^1H NMR (CDCl_3): δ 7.33-7.10 (m, 15H), 5.10 (m, 1H), 4.36 (s, 2H), 3.05 (m, 2H), 1.65-1.46 (m, 6H), 1.61 (s, 3H), 1.54 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (CDCl_3): δ 172.2, 138.7, 129.8, 129.4, 128.5, 127.4, 127.2, 125.4, 120.2, 100.2, 90.3, 83.7, 79.7, 77.3, 50.5, 46.3, 31.2, 28.5, 23.2, 22.6; ^{31}P NMR (CDCl_3): δ -12.2; ESIHRMS: Calcd for $\text{C}_{32}\text{H}_{41}\text{N}_2\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$ 635.2498, Found 635.2489.

(5*R*)-*N*-Benzyl-5-diphenylphosphatoxy-6-methyl-6-nitroheptylamine (12). Following the

general procedure for removal of Boc group, **10** (231 mg, 0.377 mmol) was converted to **12** (183 mg, 95%) as colorless oil. $[\alpha]_{\text{D}}^{23} +3.1$ (c 0.9, CHCl_3), ^1H NMR (CDCl_3): δ 7.35-7.12 (m, 15H), 5.14 (t, J = 9.0 Hz, 1H), 3.72 (s, 2H), 2.50 (m, 2H), 1.78-1.40 (m, 4H), 1.60 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (CDCl_3): δ 150.6, 129.9, 128.6, 128.3, 128.2, 127.1, 125.6, 120.32, 120.26, 120.2, 120.1, 90.3, 83.8, 54.0, 48.8, 31.3, 29.8, 29.6, 23.7, 22.8; ^{31}P NMR (CDCl_3): δ -11.9; ESIHRM: Calcd for $\text{C}_{27}\text{H}_{34}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 513.2155, Found 513.2167.

(S)-1-Benzyl-2-isopropyl-piperidine (14). Following the general procedure for radical cyclization, **12** (180 mg, 0.351 mmol) afforded **14** (31 mg, 41%, 60% ee: chiral GC: γ -cyclodextrin column, flow rate: 30 cm/sec, detector temperature: 350 °C, injection port temperature: 350 °C, initial oven temperature: 50 °C for 2 min, final oven temperature: 150 °C, gradient temperature: 5.0 °C /min, t_R [min.]: 46.4 [minor], 46.7 [major]) as colorless oil. $[\alpha]_D^{23}$ -23.7 (c 0.27, CHCl_3); ^1H NMR (CDCl_3): δ 7.39-7.19 (m, 5H), 4.10 (d, J = 13.5 Hz, 1H), 3.09 (d, J = 13.5 Hz, 1H), 2.81 (m, 1H), 2.26 (m, 1H), 2.00 (m, 1H), 1.92 (m, 1H), 1.73 (m, 1H), 1.60 (m, 2H), 1.42 (m, 1H), 1.23 (m, 2H), 0.94 (d, J = 3.0 Hz, 3H), 0.91 (d, J = 3.0 Hz, 3H); ^{13}C NMR (CDCl_3): δ 129.0, 128.2, 126.6, 77.4, 66.6, 56.6, 27.7, 24.9, 24.7, 23.6, 20.3, 16.1; 23.2, 22.6; ^{31}P NMR: δ -11.9; ESIHRMS: Calcd for $\text{C}_{15}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 218.1909, Found 218.1911.

Ethyl 2,2-dibenzyl-pent-4-enoate (23). $n\text{-BuLi}$ (2.4 M in $n\text{-hexane}$, 1.0 mL, 2.4 mmol) was added dropwise to diisopropylamine (30 mg, 2.3 mmol) in THF (3 mL) over 5 min at -78 °C under N_2 followed by stirring for 30 min. To this LDA solution was added 2-benzyl-3-phenyl-propionate³ (51 mg, 1.86 mmol) in THF (3 mL) dropwise for 5 min. The reaction mixture was stirred for 45 min. at -78 °C followed by dropwise addition of allyl bromide in THF (3 mL) at -78 °C. The reaction was slowly warmed up to 0 °C over a period of 2.5 h and quenched with sat. aq. NH_4Cl . The aqueous mixture was extracted with EtOAc, combined organic layer was washed with brine and dried over Na_2SO_4 . The organic layer was concentrated and the residue was purified by silica gel column chromatography (Hex / EtOAc, 9/1) to provide the **23** (510 mg, 89 %). ^1H NMR (CDCl_3): δ 7.31-7.17 (m, 10H), 6.08-5.94 (m, 1H), 5.28-5.16 (m, 2H), 4.09 (q, J = 7.2, 2H), 3.13 (d, J = 14.1 Hz, 2H), 2.92 (d, J = 13.2 Hz, 2H), 2.35 (dd, J = 7.2, 7.2 Hz), 1.190 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CDCl_3): δ 175.4, 137.6, 134.4, 130.3, 128.2, 126.7, 119.1, 60.6, 51.8, 42.2, 36.0, 14.2; ESIHRMS: Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 331.1674, Found 331.1669.

2,2-Dibenzyl-pent-4-en-1-ol (24). Ester **23** (51 mg, 1.7 mmol) in dry ether (2 mL) was added to a solution of LiAlH_4 (75 mg, 2.0 mmol) in dry ether (20 mL) at 0 °C under Ar. The resulting mixture was refluxed for 12 h and quenched by dropwise addition of 10 % NaOH (1 mL) at rt. The organic layer was decanted off and the residue was washed with EtOAc. The combined organic layer was washed with water, brine and dried over Na_2SO_4 . Concentration and purification of the crude mixture by silica gel column chromatography (Hex / EtOAc, 4 / 1) afforded the alcohol **24** (41 mg, 95%). ^1H NMR (CDCl_3): δ 1H 7.32-7.20 (m, 10H), 6.09-6.03 (m, 1H), 5.20-5.10 (m, 2H), 3.35 (d, J = 5.7 Hz, 2H), 2.73 (qt, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl_3): δ 138.4, 135.0, 130.8, 128.2, 126.3, 118.3, 66.5, 43.0, 41.3, 38.2; EIHRMS: Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 266.1671, Found 266.1688.

2,2-Dibenzylpen-4-en-1-al (25). Following the general procedure for Swern oxidation, alcohol **24** (4.767 g, 17.89 mmol) was converted to aldehyde **25** (crude yield 5.23 g) as colorless oil which was directly taken to the next reaction after the extraction. ^1H NMR (CDCl_3): δ 9.71 (s, 1H), 7.33-7.12 (m, 10H), 8.87 (m, 1H), 5.22 (m, 2H), 3.02 (d, J = 13.8 Hz, 2H), 2.85 (d, J = 13.8 Hz, 2H), 2.29 (d, J = 7.5 Hz, 2H); ^{13}C NMR (CDCl_3): δ 206.6, 136.6, 133.4, 130.6, 128.5, 126.9, 119.5, 53.7, 40.3, 35.6; ESIHRMS: Calcd for $\text{C}_{19}\text{H}_{20}\text{ONa}$ $[\text{M}+\text{Na}]^+$ 287.1412, Found 287.1424.

5-Benzylamino-4,4-dibenzyl-pent-1-ene (26). To the CH₃OH (50 mL) solution of crude aldehyde **25** (5.23 g), benzylamine (3.86 g, 36.0 mmol) and CH₃CO₂H (1.10 mL, 18.5 mmol) was added sodium cyanoborohydride (1.48 g, 22.4 mmol) in portions at 0 °C under N₂. The reaction was stirred at rt for 2 h. Sat. aq. NaHCO₃ was added then CH₃OH was removed by the evaporation.

The aq. layer was extracted with ether, the combined organic layer was washed with sat. aq. NH₄Cl, sat. aq. NaHCO₃, H₂O and brine then dried over Na₂SO₄. The evaporation gave yellow oil which was purified by silica gel chromatography. Colorless oil of amine **26** (4.835 g, 76% from alcohol) was obtained. ¹H NMR (CDCl₃): δ 7.42-7.12 (m, 15H), 6.03 (m, 1H), 5.13 (m, 1H), 3.70 (s, 2H), 2.77 (d, *J* = 6.0 Hz, 2H), 2.70 (d, *J* = 7.5 Hz, 2H), 2.34 (s, 2H), 2.03 (d, *J* = 6.9 Hz, 2H); ¹³C NMR (CDCl₃): δ 138.7, 135.2, 130.9, 129.4, 128.8, 128.2, 128.0, 127.1, 126.2, 118.1, 68.1, 54.7, 54.3, 51.5, 42.1, 39.4; ESIHRM: Calcd for C₂₆H₃₀N [M+H]⁺ 356.2378, Found 356.2376.

5-[N-Benzyl-N-(tert-butyloxycarbonyl)]amino-4,4-dibenzyl-pent-1-ene (27). To the CH₂Cl₂ (50 mL) solution of **26** (4.552 g, 12.80 mmol) and TEA (2.8 mL, 20.1 mmol) was added Boc₂O (3.781 g, 17.32 mmol) in CH₂Cl₂ (7 mL) at 0 °C under N₂ then it was stirred for 19 h at rt. The reaction was quenched with sat. aq. NH₄Cl then aq. layer was extracted with CH₂Cl₂. The combined organic layer was washed with sat. aq. NH₄Cl, H₂O and brine then dried over Na₂SO₄.

Concentration gave the crude product. Purification by silica gel column chromatography then afforded Boc-protected amine **27** (5.617 g, 96%) as a colorless oil. ¹H NMR (CDCl₃): δ 7.31-7.04 (m, 15H), 5.99 (m, 1H), 5.09 (m, 2H), 4.49 (s, 2H), 3.42 (s, 2H), 2.82 (d, *J* = 13.8 Hz, 2H), 2.74 (d, *J* = 13.8 Hz, 2H), 2.19 (d, *J* = 6.9 Hz, 2H), 1.39 (s, 9H); ¹³C NMR (CDCl₃): δ 138.5, 135.5, 131.2, 130.8, 129.1, 128.5, 128.0, 127.1, 126.9, 126.2, 117.8, 80.1, 57.5, 43.0, 42.6, 40.1, 28.6, 28.4; ESIHRMS: Calcd for C₃₁H₃₇NO₂Na [M+Na]⁺ 478.2722, Found 478.2716.

4-[N-Benzyl-N-(tert-butyloxycarbonyl)]amino-3,3-dibenzyl-butan-1-al (28). A solution of **27** (5.05 g, 11.1 mmol) in CH₂Cl₂ (50 mL) was bubbled with O₃ at -78 °C until the solution turned blue. On complete disappearance of the starting material, N₂ gas was bubbled through the reaction mixture for 15 min at -78 °C. To the resulting mixture was added Ph₃P (3.33g, 12.7 mmol) at -78 °C and the reaction was allowed to warm up to rt. After stirring the reaction mixture overnight, it was concentrated under evaporation followed by purification by silica gel column chromatography to afford aldehyde **28** (1.74 g, 34%).

¹H NMR (CDCl₃): δ 9.69 (t, *J* = 1.5 Hz, 1H), 7.34-7.09 (m, 15H), 4.43 (s, 1H), 3.51 (s, 1H), 3.00 (d, *J* = 13.8 Hz, 2H), 2.84 (d, *J* = 13.8 Hz, 2H), 2.37 (d, *J* = 1.5 Hz, 2H), 1.36 (s, 9H); ¹³C NMR (CDCl₃): δ 202.2, 157.0, 138.4, 137.3, 131.20, 131.15, 128.7, 128.6, 128.4, 128.3, 127.2, 126.7, 106.2, 80.6, 54.3, 53.5, 48.0, 43.9, 43.8, 28.3; ESIHRMS: Calcd for C₃₀H₃₅NO₃Na [M+Na]⁺ 480.2515, Found 480.2500.

N-Benzyl-N-(tert-butyloxycarbonyl)-2,2-dibenzyl-4-hydroxy-5-methyl-5-nitro-

hexylamine (29). To the mixture of aldehyde **28** (1.299 g, 2.838 mmol) and 2-nitropropane (20 mL, 222 mmol) was added *tert*-BuOK (177 mg, 1.58 mmol) at rt. After stirring for 12 h, the tlc detection exposed 50% of production of nitroaldol adduct, then the reaction was quenched with sat. aq. NH₄Cl, diluted with water and the aq. layer was extracted with Et₂O.

The combined organic layer was washed with H₂O and brine then dried over Na₂SO₄. Concentration and purification of the residue by silica gel column chromatography (Et₂O/CH₂Cl₂, 0.5/99.5) afforded nitroalcohol **29** (838 mg, 54%). ¹H NMR (CDCl₃): δ 7.33-7.13 (m, 13H), 7.01 (m, 2H), 4.67 (d, *J* = 15.9 Hz, 1H), 4.30 (br. t, *J* = 8.7 Hz, 1H), 4.10 (d, *J* = 15.0 Hz, 1H), 4.03 (d, *J* = 15.0 Hz, 1H), 3.03-2.07 (m, 5H), 1.64 (dd, *J* = 12.0, 11.4 Hz, 1H), 1.55 (s, 3H), 1.49-1.41 (m, 1H), 1.38 (s, 12H); ¹³C NMR (CDCl₃): δ 138.3, 138.1, 137.8, 131.2, 131.1, 128.6, 128.3, 128.24, 128.17, 127.3, 126.9, 126.6, 126.5, 92.8, 81.4, 77.2, 73.6, 43.0, 42.1, 28.3, 22.2, 21.8; ESIHRMS: Calcd for C₃₃H₄₂N₂O₅Na [M+Na]⁺ 569.2991, Found 569.2997.

***N*-Benzyl-2,2-dibenzyl-5-methyl-5-nitro-4-oxo-hexylamine (30).** Following the general

procedure for removal of Boc group, **29** (140 mg, 0.256 mmol) afforded the crude secondary amine, which was directly taken to the next step after the extraction. Following the general procedure for Swern oxidation, ketone **30** (97 mg, 86%) was obtained as colorless oil. ¹H NMR (CDCl₃): δ 8.32 (br. s, 1H), 7.47-7.06 (m, 15H), 4.05 (s, 2H), 3.35 (s, 2H), 3.11 (d, *J* = 13.5 Hz, 2H), 3.00 (d, *J* = 13.5 Hz, 2H), 2.37 (s, 2H), 1.67 (s, 6H); ¹³C NMR (CDCl₃): δ 202.1, 162.2, 138.2, 130.92, 130.90, 130.7, 130.6, 130.1, 129.0, 128.4, 128.3, 126.5, 94.9, 63.6, 57.5, 42.0, 40.5, 39.2, 23.8; ESIHRMS: Calcd for C₃₃H₄₂N₂O₅ [M+H]⁺, Found coming.

(4*R*)-*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)-2,2-dibenzyl-4-hydroxy-5-methyl-5-nitro-

hexylamine (31). Following the general procedure for CBS reduction, ketone **30** (95 mg, 0.21 mmol) was converted to alcohol. The colorless oil was obtained by the extraction then Boc protection was directly accomplished. To the CH₂Cl₂ solution (15 mL) of obtained alcohol, Boc₂O (160 mg, 0.733 mmol) and TEA (0.5 mL, 3.6 mmol) were added. The reaction was stirred overnight and the solvent was removed by evaporation. Purification by silica gel column chromatography gave enantiomerically enriched alcohol **31** (80 mg, 70%) as colorless oil, which showed similar spectrum to racemate **29**. Enantiomeric excess was determined after the derivatization to **15**.

(4*R*)-*N*-Benzyl-*N*-(*tert*-butyloxycarbonyl)-2,2-dibenzyl-4-diphenylphosphatoxy-5-methyl-5-

nitro-hexylamine (32). I₂ (306 mg, 1.21 mmol) was added to a stirred solution of ethyldiphenylphosphite (250 mg, 0.953 mmol) in CH₂Cl₂ (2 mL) at 0 °C under N₂. After 15 min, so formed phosphorylating agent was added to a mixture of nitroalcohol **31** (345 mg, 0.631 mmol), pyridine (0.120 mL, 1.48 mmol) in CH₂Cl₂ (3 mL) under N₂ at 0 °C. The reaction mixture was stirred at 0 °C for 1 h then NH₄Cl was added. The aq layer was extracted with CH₂Cl₂, the combined organic layer was washed with 10% Na₂S₂O₃, H₂O and brine then dried over Na₂SO₄. Concentration and purification by silica gel column chromatography afforded phosphorylated product **32** (371 mg, 75%). ¹H NMR (CDCl₃): δ 7.36-7.03 (m, 25H), 5.78 (t, *J* = 9.0 Hz, 1H), 4.45 (d, *J* = 16.2 Hz, 1H), 4.29 (d, *J* = 16.2 Hz, 1H), 3.71 (d, *J* = 14.7 Hz, 1H), 3.45 (d, *J* = 14.7 Hz, 1H), 3.11 (d, *J* = 14.7 Hz, 1H), 3.02 (d, *J* = 14.4 Hz, 1H), 2.99 (d, *J* = 14.7 Hz, 1H), 2.83 (d, *J* = 14.4 Hz, 1H), 1.91 (dd, *J* = 15.3, 10.8 Hz, 1H), 1.75 (dd, *J* = 15.3, 4.5 Hz, 1H), 1.61 (s, 3H), 1.42 (s, 3H), 1.33 (s, 9H); ¹³C NMR (CDCl₃): δ 157.3, 138.8, 138.1, 131.5, 130.08, 129.7, 128.7, 128.5, 128.3, 128.2, 126.8, 126.4, 125.3,

120.2, 91.7, 82.1, 80.2, 53.2, 53.0, 42.3, 41.7, 41.3, 35.8, 28.4, 27.7, 24.4, 21.3; ^{31}P NMR (CDCl_3): δ -12.9; ESIHRMS: Calcd for $\text{C}_{45}\text{H}_{51}\text{N}_2\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$ 801.3281, Found 801.3263.

(4R)-N-Benzyl-2,2-dibenzyl-4-diphenylphosphatoxy-5-methyl-5-nitro-hexylamine (15).

Following the general procedure for removal of Boc group, phosphate **32** (294 mg, 0.377 mmol) gave the secondary amine **15** (245 mg, 96%, 79% ee: chiral HPLC: 0.5% 2-propanol/hexane, 0.5 mL/min, t_R [min.]: 36.6 [major], 41.2 [minor]). ^1H NMR (CDCl_3): δ 7.33-7.09 (m, 25H), 5.96 (t, J = 8.4 Hz, 1H), 3.67 (d, J = 13.5 Hz, 1H), 3.61 (d, J = 13.5 Hz, 1H), 3.01 (s, 2H), 2.77 (s, 2H), 2.73 (d, J = 12.3 Hz, 1H), 2.63 (d, J = 12.3 Hz, 1H), 1.76 (m, 2H), 1.65 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (CDCl_3): δ 150.7, 138.4, 138.0, 131.1, 131.0, 129.9, 128.8, 128.7, 128.2, 128.1, 127.7, 126.6, 126.4, 125.5, 120.2, 91.7, 82.2, 54.9, 54.6, 43.3, 42.4, 41.0, 35.7, 24.7, 20.8; ^{31}P NMR (CDCl_3): δ -12.8; ESIHRMS: Calcd for $\text{C}_{40}\text{H}_{44}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 679.2937, Found 679.2943.

(S)-1,4,4-Tribenzyl-2-isopropyl-pyrrolidine (16). Following the general procedure for radical

cyclization, **15** afforded **16** (51 mg, 44%, 60% ee: 0.5% 2-propanol/hexane, 0.5 mL/min, t_R [min.]: 14.6 [major], 15.6 [minor]) as colorless oil. $[\alpha]_D^{23}$ -24.4 (c 1.0, CHCl_3), ^1H NMR (CDCl_3): δ 7.35-7.00 (m, 15H), 3.96 (d, J = 13.5 Hz, 1H), 2.90-2.75 (m, 3H), 2.62 (s, 2H), 2.20 (d, J = 9.6 Hz, 2H), 1.64 (dd, J = 12.6, 8.4 Hz, 1H), 1.56 (dd, J = 12.6, 8.4 Hz, 1H), 0.91 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3): δ 140.1, 139.3, 131.0, 131.0, 128.8, 128.2, 128.0, 127.8, 126.7, 126.0, 125.9, 69.1, 62.8, 58.0, 46.1, 44.0, 35.0, 30.4, 27.8, 20.3, 15.3; ESIHRMS: Calcd for $\text{C}_{28}\text{H}_{34}\text{N}$ $[\text{M}+\text{H}]^+$ 384.2691, Found 384.2691.

(4R)-N-(tert-Butyloxycarbonyl)-4-diphenylphosphatoxy-5-methyl-5-nitrohexylamine (33).

Phosphate **9** (103 mg, 0.172 mmol) was treated with PdCl_2 (64 mg, 0.36 mmol) in methanol (10 mL) under hydrogen atmosphere for 4 h. Sat. aq. NaHCO_3 was added then it was extracted with EtOAc. The organic layer was washed with H_2O and brine then dried over Na_2SO_4 . It was purified by silica gel column chromatography which gave the secondary amine **33** (84 mg, 97%) as colorless oil. $[\alpha]_D^{23}$ +0.3 (c 0.94, CHCl_3); ^1H NMR (CDCl_3): δ 7.36-7.14 (m, 10H), 5.15 (m, 1H), 4.43 (br. s, 1H), 3.06 (m, 2H), 1.75-1.48 (m, 4H), 1.61 (s, 3H), 1.56 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (CDCl_3): δ 155.6, 129.9, 129.3, 125.6, 120.4, 120.1, 90.3, 83.5, 39.8, 28.5, 26.5, 23.0, 21.5; ^{31}P NMR (CDCl_3): δ -12.0; ESIHRMS: Calcd for $\text{C}_{24}\text{H}_{33}\text{N}_2\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$ 531.1872, Found 531.1859.

(4R)-N-(tert-butyloxycarbonyl)-N-ethynyl-4-diphenylphosphatoxy-5-methyl-5-nitrohexyl-

amine (34). Secondary amine **33** (161 mg, 0.317 mmol) was treated with NaH (60% in oil, 37 mg, 0.93 mmol) in DMF (15 mL) at 0 °C under N_2 for 20 min then propargyl bromide (75 mg, 0.63 mmol) was added dropwise. The reaction was stirred for 1 h then quenched with H_2O . It was extracted with EtOAc then washed with H_2O and brine. It was dried over Na_2SO_4 followed by the evaporation which gave brown oil. It was purified by silica gel column

chromatography. **34** (160 mg, 92%) was obtained as colorless oil. ^1H NMR (CDCl_3): δ 7.34-7.18 (m, 10H), 5.15 (m, 1H), 3.92 (m, 2H), 3.31 (t, $J = 7.2$ Hz, 2H), 2.13 (t, $J = 2.1$ Hz, 1H), 1.90-1.78 (m, 2H), 1.75-1.65 (m, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (CDCl_3): δ 155.1, 129.8, 125.5, 120.2, 83.6, 80.4, 71.7, 46.1, 36.3, 28.8, 28.4, 24.7, 23.8, 22.7, 22.2; ^{31}P NMR (CDCl_3): δ -12.1; ESIHRMS: Calcd for $\text{C}_{27}\text{H}_{35}\text{N}_2\text{O}_8\text{PNa}$ $[\text{M}+\text{Na}]^+$ 569.2029, Found 569.2036.

(4R)-4-Diphenylphosphatoxy-N-ethynyl-5-methyl-5-nitrohexylamine (17). Following the

general procedure for removal of Boc group, **34** (211 mg, 0.386 mmol) gave the precursor of radical cyclization **17** (170 mg, 99%). ^1H NMR (CDCl_3): δ 7.33-7.17 (m, 10H), 5.17 (m, 1H), 3.36 (s, 2H), 2.66 (m, 2H), 2.52 (br. s, 1H), 2.21 (s, 1H), 1.66-1.64 (m, 4H), 1.61 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (CDCl_3): δ 129.8, 125.5, 120.2, 106.2, 90.4, 83.7, 71.8, 47.7, 37.9, 29.2, 25.7, 22.7, 22.0; ^{31}P NMR (CDCl_3): δ -11.9; ESIHRMS: Calcd for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_6\text{P}$ $[\text{M}+\text{H}]^+$ 447.1685, Found 447.1677.

(7S)-1,1-Dimethyl-2-methylene-pyrrolizidine (18). The general procedure for radical

cyclization was followed but extraction method was changed. On complete consumption of **17** (144 mg, 0.323 mmol) disappeared, the reaction mixture was cooled to rt, then 2M HCl (12 mL) was added, and stirred for 20 min. The aq. layer was washed with hexane then basified to pH 11 with 15% aq. NaOH and extracted with ethyl ether. The combined organic layer washed with water and 2M HCl (12 mL) was added again.

After stirring for 30 min, aq. layer was separated and concentrated under reduced pressure which gave the pure HCl salt of pyrrolizidine **18** (39 mg, 64%, 60% ee: free amine which was extracted with CH_2Cl_2 from 15% aq. NaOH was analyzed: α -cyclodextrin, Detector temperature: 250 $^\circ\text{C}$, Injection port temperature: 250 $^\circ\text{C}$, initial oven temperature: 50 $^\circ\text{C}$, final oven temperature: 220 $^\circ\text{C}$, gradient temperature: 8.0 $^\circ\text{C}/\text{min}$, flow rate: 30 cm/sec, t_R [min]: 11.3 [major], 11.4 [minor]) without further purification. $[\alpha]_D^{23}$ -9.2 (c 1.0, CHCl_3); ^1H NMR (CDCl_3): δ 12.8 (br.s, 1H), 5.09 (d, $J = 3.6$ Hz, 2H), 4.57 (dd, $J = 14.1, 6.3$ Hz, 1H), 3.96 (m, 2H), 3.41 (d, $J = 15.6$ Hz, 2H), 2.83 (m, 1H), 2.06 (m, 3H), 1.63 (m, 1H), 1.35 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (CDCl_3): δ 108.9, 100.2, 76.9, 57.9, 56.2, 33.0, 28.8, 27.4, 25.2, 21.5; ESIHRMS: Calcd for $\text{C}_{10}\text{H}_{18}\text{N}$ $[\text{M}+\text{H}]^+$ 152.1439, Found 152.1439.

4,4-Diphenyl-cyclohexanone oxime (35). 4,4-Diphenyl-cyclohexanone⁴ (4.70 g, 18.8 mmol) in

EtOH (94 mL) was added to a stirred solution of hydroxylamine hydrochloride (6.27 g, 90.0 mmol) and sodium acetate (12.6 g, 154.0 mmol) in water (25 mL) at rt. The resulting milky white solution was stirred for 2 h and concentrated under rotary evaporation. The residue was extracted with EtOAc, dried by Na_2SO_4 and concentrated. Purification of the crude mixture by silica gel column chromatography (EtOAc/Hex, 1/5) afforded oxime **35** (4.85 g, 97%). IR (film): 3243, 1446 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.31-7.26 (m, 10H), 2.66 (t, $J = 6.9$ Hz, 2H), 2.50-2.34 (m, 6H); ^{13}C NMR (CDCl_3): δ 159.8, 146.6, 128.6, 127.0, 126.1, 46.3, 36.5, 35.5, 28.5, 21.4; ESIHRMS: Calcd for $\text{C}_{18}\text{H}_{19}\text{NONa}$ $[\text{M}+\text{Na}]^+$ 288.1364, Found 288.1360.

1-Chloro-1-nitro-4,4-diphenyl-cyclohexane (36). Trichloroisocyanuric acid (20.1 g, 87.5 mmol)

was added in 5 portions at 5 min intervals to a well stirred two phase mixture of

EtOAc-H₂O (1:1, 1534 mL), oxime **35** (4.60 g, 17.5 mmol) and NaHCO₃ (36.4 g, 433.9 mmol). The reaction mixture developed a distinct blue color after 20 min and stirring was continued at rt until the organic layer became colorless for 24 h. The reaction mixture was transferred into a separatory funnel and 0.2 M aq. NaOH solution (230 mL) was added. The aq. layer was extracted with EtOAc. The combined organic layer was washed with water, brine and dried over Na₂SO₄. Concentration and purification by silica gel column chromatography (EtOAc/Hex, 1/5) afforded **36** (1.54 g, 28%). IR (film): 1555, 698 cm⁻¹; ¹H NMR (CDCl₃): δ 7.38-7.18 (m, 10 H), 2.67-2.43 (m, 8H); ¹³C NMR (CDCl₃): δ 129.0, 128.8, 128.7, 126.9, 126.6, 126.5, 126.4, 43.3, 35.7, 35.2, 34.0, 33.1; EIHRMS: Calcd for C₁₈H₁₈NO₂Cl [M]⁺ 315.1.26, Found 315.1025.

1-Nitro-4,4-diphenyl-cyclohexane (37). 10%-Pd/C (106 mg, 5%) and NaBH₄ (337 mg, 8.87 mmol) was added to a solution of **36** (2.00 g, 6.33 mmol) in EtOH (33 mL) at rt. The reaction was stirred for 1 h after which it was filtered and concentrated. The residue was diluted with water and the aq. layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated. Purification of the crude mixture by silica gel column chromatography (EtOAc/Hex, 1/4) afforded **37** (85 mg, 48%). IR (film): 1543 cm⁻¹; ¹H NMR (CDCl₃): δ 7.38-7.14 (m, 10H), 4.52-4.48 (m, 1H), 2.78-2.71 (m, 2H), 2.26-2.14 (m, 6H); ¹³C NMR (CDCl₃): δ 149.6, 144.0, 128.9, 128.6, 127.3, 126.4, 126.3, 126.2, 83.8, 34.0, 27.2; EIHRMS: Calcd for C₁₈H₁₉NO₂ [M]⁺ 281.1415, Found 281.1414.

4-(tert-Butyl-dimethyl-silyloxy)-1-(1'-nitro-4',4'-diphenyl-cyclohexyl)-butan-1-ol (38). To a stirred solution of **37** (166 mg, 0.59 mmol) in THF (1 mL) was added 0.025 M NaOH (0.87 mL) solution at rt and further stirred for 2 min. 4-(tert-Butyl-dimethyl-silyloxy)-butan-1-al (107 mg, 0.53 mmol) was added followed by cetyl ammonium bromide (21 mg, 0.059 mmol) at rt. After stirring the reaction for 12 h at ambient temperature, the reaction was quenched with sat. aq. NH₄Cl solution (5 mL) and the aq. layer was extracted with EtOAc. The organic layer was washed with water, brine and dried over Na₂SO₄. Concentration and purification of the residue by silica gel column chromatography (EtOAc/Hex, 1/9) afforded nitro alcohol **38** (0.142 g, 50%) as a colorless oil. ¹H NMR (CDCl₃): δ 7.38-7.10 (m, 10H), 3.68-3.57 (m, 3H), 3.39 (d, *J* = 4.8 Hz, 1H), 2.67-2.53 (m, 4H), 2.09-1.60 (m, 8H), 0.87 (s, 9H), 0.03 (s, 6H); ¹³C NMR (CDCl₃): δ 149.6, 144.0, 128.8, 128.4, 127.5, 126.2, 126.1, 126.0, 94.9, 76.4, 63.2, 45.3, 32.4, 29.1, 28.8, 27.5, 27.1, 26.0, 18.4, -5.3; Anal: Calcd for C₂₈H₄₁NO₄Si C 69.52, H 8.54, Found C 69.78, H 8.45.

4-(tert-Butyl-dimethyl-silyloxy)-1-(1'-nitro-4',4'-diphenyl-cyclohexyl)-butan-1-one (39).

Following the general procedure for Swern oxidation, nitroalcohol **38** (62.0 mg, 1.29 mmol), provided ketone **39** (388 mg, 62%). IR (film) 1725, 1542 cm⁻¹; ¹H NMR (CDCl₃): δ 7.34-7.12 (m, 10H), 3.54 (t, *J* = 6.3 Hz, 2H), 2.62 (d, *J* = 11.4 Hz, 4H), 2.53 (t, *J* = 6.9 Hz, 2H), 2.16 (d, *J* = 10.5 Hz, 4H), 1.73 (q, *J* = 6.0 Hz, 2H), 0.87 (s, 9H), 0.01 (s, 6H); ¹³C NMR (CDCl₃): δ 201.7, 148.3, 144.1, 129.0, 128.5, 127.1, 126.5, 126.2, 98.4, 61.4, 44.9, 32.4, 32.1, 28.3, 26.4, 26.0, 18.4, -5.2; Anal: Calcd for C₂₈H₃₉NO₄Si C 69.82, H 8.16, Found C 69.74, H 8.25.

(1*R*)-4-(*tert*-Butyl-dimethyl-silyloxy)-1-(1'-nitro-4',4'-diphenyl-cyclohexyl)-butan-1-ol (40).

Following the general procedure for CBS reduction, ketone **39** (563 mg, 1.00 mmol) afforded alcohol **40** (420 mg, 87%, 96% ee: chiral HPLC: 0 to 80 % of 2-propanol / hexane, flow rate: 1.0 mL/min, t_R [min.]: 17.475 [minor], 21.138 [major]). $[\alpha]_D^{23} +9.0$ (c 1.0, CHCl_3); IR (film) 3422, 1536 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.41-7.33 (m, 4H), 7.25-7.11 (m, 6H), 3.66-3.59 (m, 3H), 3.44 (s, 1H), 2.69-2.55 (m, 4H), 2.11-1.84 (m, 4H), 1.66-1.60 (bs, 3H), 1.27-1.25 (m, 1H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (CDCl_3): δ 149.7, 144.0, 128.9, 128.4, 127.5, 126.2, 126.0, 94.9, 76.4, 63.2, 45.3, 32.4, 29.2, 28.7, 27.5, 27.1, 26.0, 18.4, -5.2; ESIHRMS: Calcd for $\text{C}_{28}\text{H}_{41}\text{NO}_4\text{SiK}$ $[\text{M}+\text{K}]^+$ 522.2442, Found 522.2437.

(1*R*)-4-(*tert*-Butyl-dimethyl-silyloxy)-1-(1'-nitro-4',4'-diphenyl-cyclohexyl)-1-

diphenylphosphatoxy butane (41). Following general procedure for phosphorylation, alcohol **40** (104 mg, 0.215 mmol) afforded phosphate **41** (109 mg, 74%). ^1H NMR (CDCl_3): δ 7.37-7.08 (m, 20H), 4.73 (t, $J = 1.5$ Hz, 1H), 3.64-3.48 (m, 2H), 2.69-2.60 (m, 4H), 2.05-1.82 (m, 5H), 1.63-1.51 (m, 3H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (CDCl_3): δ 150.5, 149.3, 143.5, 129.9, 129.8, 129.0, 128.8, 128.4, 127.5, 127.3, 126.4, 126.2, 126.1, 126.0, 125.5, 120.3, 120.2, 120.1, 93.5, 93.4, 84.4, 84.3, 76.4, 63.2, 61.9, 45.0, 32.2, 32.1, 29.2, 28.7, 27.8, 27.7, 27.5, 27.2, 27.1, 26.0, 18.4, -5.2; ^{31}P NMR (CDCl_3): δ -11.80; ESIHRMS: Calcd for $\text{C}_{40}\text{H}_{50}\text{NO}_7\text{PSiNa}$ $[\text{M}+\text{Na}]^+$ 738.2992, Found 738.2984.

(4*R*)-4-Diphenylphosphatoxy-4-(1'-nitro-4',4'-diphenyl-cyclohexyl)-butan-1-ol (42).

To a solution of **41** (100 mg, 0.146 mmol) in acetonitrile (6 mL) at rt was added aq. solution of HF (49%, 0.146 mmol, 4 mL). The reaction was further stirred for 5 min and diluted with EtOAc. The organic layer was washed with water, brine and dried over Na_2SO_4 . Concentration and purification of the residue by silica gel column chromatography (EtOAc/Hex, 1/1) afforded alcohol **42** (55 mg, 63%, 94% ee: chiral HPLC: 0-80 % of 2-propanol / hexane, flow rate: 1.0 mL/min, t_R [min.]: 25.667 [minor], 30.108 [major]). ^1H NMR (CDCl_3): δ 7.35-7.06 (m, 20H), 4.76 (t, $J = 7.6$ Hz, 1H), 3.54-3.47 (m, 2H), 2.69-2.61 (m, 4H), 2.03-1.55 (m, 8H); ^{13}C NMR (CDCl_3): δ 149.2, 143.4, 129.9, 129.0, 128.4, 127.4, 126.4, 126.1, 125.6, 120.2, 120.1, 93.5, 93.4, 84.2, 84.1, 62.0, 45.0, 32.1, 28.4, 27.8, 27.7, 27.5, 27.4; ^{31}P NMR (CDCl_3): δ -11.72; ESIHRMS: Calcd for $\text{C}_{34}\text{H}_{38}\text{NO}_7\text{P}$ $[\text{M}+\text{H}]^+$ 602.2308, Found 602.2335.

2-(4',4'-Diphenyl-cyclohexyl)-tetrahydrofuran (20).

To the mixture of **42** (158 mg, 0.26 mmol), AIBN (22 mg, 0.14 mmol) and tributyltin hydride (169 mg, 0.58 mmol) was added deoxygenated benzene (6.5 mL) and refluxed for 12 h. The reaction mixture was cooled, concentrated and purified by silica gel chromatography to provide tetrahydrofuran **20** (20 mg, 25%) and the cyclic phosphate **21** (68 mg, 52%). ^1H NMR (CDCl_3): δ 7.38-7.16 (m, 10H), 3.81-3.79 (m, 1H), 3.67-3.65 (m, 1H), 3.40-3.35 (m, 2H), 2.72 (d, $J = 12.4$ Hz, 1H), 1.97-1.80 (m, 5H), 1.59-0.98 (m, 6H); ^{13}C NMR (CDCl_3): δ 151.3, 146.1, 128.5, 128.2, 128.1, 126.3, 125.6, 125.5,

83.8, 67.8, 46.1, 43.1, 36.3, 29.4, 26.6, 25.9, 25.4; ESIHRMS: Calcd for C₂₂H₂₆ONa [M+Na]⁺ 329.1881, Found 329.1886.

(7R)-7-(4', 4'-Diphenyl-cyclohexyl)-2-phenoxy-[1, 3, 2]dioxaphosphepane-2-oxide (21).

¹H NMR (CDCl₃): δ 7.37-7.06 (m, 15H), 4.23-4.05 (m, 3H), 2.79-2.74 (m, 2H), 1.95-1.91 (m, 5H), 1.73-1.67 (m, 4H), 1.41-1.36 (m, 2H); ¹³C NMR (CDCl₃): δ 151.0, 144.7, 129.8, 128.6, 128.4, 128.2, 127.9, 126.2, 125.8, 125.6, 125.0, 120.2, 120.1, 82.9, 68.9, 68.8, 45.9, 43.1, 43.0, 36.2, 36.1, 31.8, 29.1, 25.4, 24.5; ³¹P NMR (CDCl₃): δ -2.92;

ESIHRMS: Calcd for C₂₈H₃₁O₄PNa [M+Na]⁺ 485.1858, Found 485.1838.

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