Supporting Information

for

Catalytic Asymmetric Vinylation of Ketone Enolates

André Chieffi, Ken Kamikawa, Jens Åhman, Joseph M. Fox

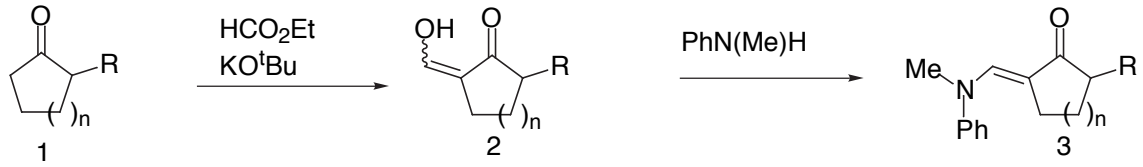
and Stephen L. Buchwald*

Preparation and characterization of all new substrates and products (22 pages).

General Considerations. THF and Et_2O were distilled under argon from sodium/benzophenone ketyl. Toluene was distilled under nitrogen from molten sodium. Vinyl bromides, 2-methyl-1-tetralone and 2-methyl-1-indanone were purchased from Aldrich Chemical Co. Tris(dibenzylideneacetone) dipalladium(0), (S)-BINAP, (R)-(+)-2,2'-diiodo-1,1'-binaphthyl and (rac)-2,2'-dibromo-1,1'-binaphthyl were acquired from Strem Chemicals, Inc. NaO^tBu was purchased from Aldrich; the bulk of this material was stored in a nitrogen-filled glove box. Small portions (1-2 g) were removed from the glove box in glass vials, stored in the air in desiccators filled with anhydrous calcium sulfate, and weighed in the air. All other reagents were available from commercial sources and were used without further purification, unless otherwise noted. Unless stated otherwise, all reactions were conducted in flasks sealed with a rubber septum under a positive pressure of argon. Flash chromatography was performed on E. M. Science Kieselgel 60 (230-400 mesh) unless otherwise noted. Yields refer to isolated yields of compounds of greater than 95% purity as estimated by capillary GC, ^1H NMR, and in most cases elemental analysis. Yields reported in this section refer to a single experiment, while those reported in the tables are an average of two or more runs. All compounds were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy, and in most cases elemental analysis (Atlantic Microlab, Inc. and E & R Microanalytical Laboratory Inc.). Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 300 or a Varian Unity 300. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; q, quartet; qd, quartet of doublets; m, multiplet. All ^1H NMR spectra are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^1H decoupling. Infrared (IR) spectra were recorded on an

ASi Applied Systems ReactIR 1000 (liquids were measured neat on a DiComp probe.) Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5890 or 6890 gas chromatograph with an FID detector using a 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. GC-mass spectrometry (GS-MS) analyses were performed on a Hewlett-Packard G1800B gas chromatograph with an electron ionization detector using the same GC column described above. Chiral HPLC analyses were performed on a Hewlett-Packard 1100 system with an HP 1100 Diode Array Detector (monitoring at 254 nm) using a Chiracel OD column (25 cm x 0.46 cm).[1] Racemic compounds analogous to the enantiomerically enriched compounds described below were prepared by reaction with (rac)-**2a**. The HPLC retention times of the racemic products were the same as those of the enantiomerically enriched products.

General Procedure for 2-alkyl-5-(N-methyl-anilinomethylene) cycloalkanones



Ethyl formate (10 mL) was added dropwise to a stirred solution of KO^{t}Bu (3.70 g, 33 mmol) in THF (25 mL) at 0 °C; CAUTION: evolution of gas occurs. The mixture was cooled to –10 °C and the desired ketone (30 mmol) in ethyl formate (20 mL) was added via cannula. The resulting mixture was stirred at –10°C for 30 min and then warmed to r.t. and stirred for an additional 12 h. The mixture was transferred to a separatory funnel, acidified to pH = 1 with HCl (1 M) and

extracted with Et_2O (3 X 100 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo to give the crude hydroxymethylene ketone **2**.

The crude ketone **2** was dissolved in benzene (60 mL) and N-methylaniline (4.2 mL, 39 mmol) was added. The flask was fitted with a Dean-Stark trap and the mixture was refluxed for 3 h with azeotropic removal of water. The mixture was allowed to cool to r.t. and concentrated in vacuo. Excess of N-methyl aniline was removed by distillation, and the resulting solid purified by recrystallization from hexane.

2-Methyl-5-(N-methyl-anilinomethylene)-cyclopentanone (4a)

This procedure gave 5.31 g (82% yield) of a yellow solid. mp 88-90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (t, J = 1.8 Hz, 1 H), 7.37-7.31 (m, 2H), 7.15-7.10 (m, 3H), 3.49 (s, 3H),2.52-2.07 (m, 4H), 1.43-1.30 (m, 1H), 1.12 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz) δ 208.3, 146.2, 141.3, 129.1, 124.4, 121.1, 108.9, 42.8, 40.0, 29.8, 26.2, 15.5 ppm; IR (neat, cm^{-1}) 2954, 2867, 1679, 1559, 1497, 1364, 1185. Anal Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96. Found: C, 78.36; H, 8.08.

2-Propyl-5-(N-methyl-anilinomethylene)-cyclopentanone (4b)

This procedure gave 5.18 g (71% yield) of a yellow solid. mp 78–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (t, J = 1.8 Hz, 1 H), 7.36-7.31 (m, 2H), 7.15-7.10 (m, 3H), 3.48 (s, 3H), 2.58-2.37 (m, 2H), 2.27-2.05 (m, 2H), 1.87-1.76 (m, 1H), 1.48-1.16 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz) δ 208.1, 146.2, 141.3, 129.0, 124.4, 121.1, 109.3, 48.0, 40.0, 33.0, 27.5, 26.3, 20.9, 14.3 ppm; IR (neat, cm^{-1}) 2952, 2925, 2856, 1677, 1559, 1492, 1362, 1216, 1187. Anal Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70. Found: C, 78.99; H, 8.72.

2-Pentyl-5-(N-methyl-anilinomethylene)-cyclopentanone (4c)

This procedure gave 6.18 g (76% yield) of a yellow solid. mp 72-73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (t, J = 1.8 Hz, 1 H), 7.37-7.31 (m, 2H), 7.15-7.10 (m, 3H), 3.49 (s, 3H),2.52-2.43 (m, 2H), 2.20-2.04 (m, 2H), 1.87-1.81 (m, 1H), 1.48-1.19 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz) δ 208.1, 146.2, 141.2, 129.1, 124.4, 121.1, 109.4, 48.2, 40.0, 32.1, 30.8, 27.5, 27.4, 26.5, 22.7, 14.2 ppm; IR (neat, cm^{-1}) 2927, 2858, 1679, 1559, 1493, 1268, 1212, 1181. Anal Calcd for $C_{18}H_{25}NO$: C, 79.66; H, 9.28. Found: C, 79.84; H, 9.30.

2-Methyl-5-(N-methyl-anilinomethylene)-cyclohexanone (4d)

The crude material was purified by flash chromatography on silica gel, followed by recrystallization from hexane. This procedure gave 3.50 g (51% yield) of a yellow solid. mp 50-51 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, J = 1.8 Hz, 1 H), 7.31-7.24 (m, 2H), 7.07-6.97 (m, 3H), 3.38 (s, 3H),2.38-2.28 (m, 1H), 2.08-2.04 (m, 2H), 1.93-1.86 (m, 1H), 1,71- 1.66 (m, 1H), 1.51-1.41 (m, 2H), 1.15 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (75 MHz) δ 202.6, 146.2, 141.9, 129.0, 123.8, 121.1, 112.7, 42.7, 42.3, 31.6, 28.1, 22.4, 17.9 ppm; IR (neat, cm^{-1}) 2929, 2854, 1656, 1542, 1407, 1231, 1189, 1152, 922; Anal Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35. Found: C, 78.81; H, 8.42.

Experimental procedures for the preparation of 2-N,N-dimethylamino-2'-phosphino-1,1'-binaphthyl ligands

The 2-N,N-dimethylamino-2'-phosphino-1,1'-binaphthyl ligands were prepared using the procedure recently reported for the racemic ligand.[2] Optically active 2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl was prepared using the resolution procedure described below. The preparation of ligand **2c** in racemic form has been previously reported.[2] That procedure, starting with (S)-(–)-2-

N,N-dimethylamino-2'-bromo-1,1'-binaphthyl, gives (S)-(+)-**2c:** α_D^{23} = +304 (c 0.5, toluene).

Optical resolution of 2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl

A round-bottom flask was charged with 2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl (4.50 g, 12.2 mmol) and (1S)-(+)-10-camphorsulfonic acid (3.10 g, 13.5 mmol). Ethanol (40 mL) was added to the residue and the resulting mixture was heated gently until it became a clear solution. Hexane (80 mL) was added to the solution. The flask was fitted with a reflux condenser and the resulting cloudy mixture was heated gently until it became a clear solution, heating was discontinued and the solution was then allowed to stand at room temperature overnight. The crystals which had formed were collected on a sintered-glass funnel and washed with hexane (15 mL) to afford 2.4 g of complex (66% based on one enantiomer). The filtrate was stored for recovery of the antipode. The crystalline material (2.4 g, 4.0 mmol) was treated with 1N aqueous sodium hydroxide (20 mL) and the mixture was extracted with ethyl acetate (2x 20 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give 1.42 g of colorless crystals (98 % based on the complex used). HPLC analysis indicated a 98% ee (Daicel chiralcel OJ, 5% isopropanol in hexane, 0.3 mL/min). Recrystallization from methanol and dichloromethane gave 1.26 g (87% based on the complex used) of optically pure (S)- (–)-2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl. $[\alpha]_D^{22}$ –55 (c 1.0, toluene)

The mother liquor and the filtrate from the first resolution were combined and concentrated in vacuo. The residue was treated with 1 N aqueous sodium hydroxide (50 mL) and the mixture was extracted with ethyl acetate (2x 30 mL). The combined organic layers were washed with brine, and dried over

anhydrous magnesium sulfate, filtered, and concentrated in vacuo. A round-bottom flask was charged with this recovered 2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl (3.5 g, 8.3 mmol) and (1R)–(–)-10-camphorsulfonic acid (2.1 g, 9.1 mmol). Ethanol (27 mL) was added to the residue and the resulting mixture was heated gently until it became clear solution. Hexane (54 mL) was added to the solution. The flask was fitted with a reflux condenser and the resulting cloudy mixture was heated gently until it became a clear solution. Heating was then discontinued and the solution was allowed to stand at room temperature overnight. The crystals which had formed were collected on a sintered-glass funnel and washed with hexane (10 mL) to afford 2.5 g of complex (67% based on one enantiomer). This crystalline material (2.5 g, 4.2 mmol) was treated with 1 N aqueous sodium hydroxide (30 mL) and the mixture was extracted with ethyl acetate (2x 20 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo to give 1.50 g of (R)-(+)-2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl (97% based on the complex used). HPLC analysis indicates >99% ee (Daicel chiralcel OJ, 5 % isopropanol in hexane, 0.3 mL/min) $[\alpha]_D^{22}$ +55 (c 1.0, toluene).

(S)-(+)-2-N,N-Dimethylamino-2'-dicyclohexylphosphino-1,1'-binaphthyl (2a)

An oven dried 20 ml round bottomed flask was charged with (S)-(–)-2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl (400 mg, 1.1 mmol) and THF (12 ml). The mixture was purged with argon and cooled to –78 °C, and then n-BuLi (0.73 mL of a 1.6 M solution in hexane, 1.2 mmol) was added dropwise. The solution was stirred at –78 °C for 45 min, and then chlorodicyclohexylphosphine (304 mg, 1.4 mmol) was added dropwise. The reaction was stirred for 1 h at –78 °C, and then allowed to warm to rt ansd

stirred for 18 h. The crude material was recrystallized from dichloromethane and methanol to give 441 mg (84%) of **6** as colorless crystals. mp 202-203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.91 (m, 3H), 7.82 (d, J = 5.3 Hz, 2H), 7.47 (d, J = 5.3 Hz, 2H), 7.46 (d, J = 5.3 Hz, 1 H), 7.38 (d, J = 4.9 Hz, 1H), 7.26 (t, J = 4.6 Hz, 1H), 7.24 (t, J = 4.6 Hz, 1H), 7.05 (dd, J = 4.5, J = 0.9 Hz, 1H), 6.83 (d, J = 5.1 Hz, 1H), 2.53 (s, 6H), 2.55-0.69 (m, 22H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 134.5, 134.2 134.1, 133.6, 129.9, 129.2, 129.0, 127.9, 127.8, 126.6, 126.5, 126.2, 125.2, 123.0, 119.0, 43.7, 36.7, 36.5, 34.6, 34.4, 31.3, 31.0, 30.9, 30.7, 30.4, 30.3, 29.9, 29.8, 27.9, 27.8, 27.7, 27.5, 26.9, 26.5 ppm (observed complexity due to P-C splitting); IR (neat, cm^{-1}) 3056, 2919, 2848, 2790, 1596, 1505, 1443, 1349, 1329, 1219, 1140, 984, 814, 749, 687; ^{31}P NMR ($CDCl_3$, 121 Hz) –8.03 ppm; Anal. calcd for $C_{34}H_{40}NP$: C, 82.72; H, 8.17. Found; C, 82.73; H, 8.41; $[\alpha]_D^{21}$ +224 (c 1.0, toluene)

(S)-(+)-2-N,N-Dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl (2b)

An oven dried 20 mL round bottomed flask was charged with (S)-(–)-2-N,N-dimethylamino-2'-bromo-1,1'-binaphthyl (300 mg, 0.8 mmol) and THF (8 mL). the mixture as purged with argon and cooled to –78 °C, then n-BuLi (0.6 mL of a 1.6 M solution in hexane, 0.9 mmol) was added dropwise. The solution was stirred at –78 °C for 45 min, then chlorodiphenylphosphine (229 mg, 1.0 mmol) was added dropwise. The reaction was stirred for 1 h at –78 °C, then warmed to rt and stirred for 18 h. Saturated ammonium chloride (2 mL) was added, and the reaction mixture was extracted twice with ether (10 mL). The combined organics were dried ($MgSO_4$), filtered, concentrated and chromatographed to give 340 mg of the title compound as colorless crystals. α_D^{21} = +21(c 1.0, THF)

The spectral properties were in close agreement with those reported in the literature.[3]

General procedures for the preparation of 2-alkyl-2'-phosphino-1,1'-binaphthyl ligands.

An oven-dried 20 mL round-bottom flask was charged with (R)-(+)-2,2'-diiodo-1,1'-binaphthyl (2.53 g, 5 mmol), THF (10 mL), and Et_2O (10 mL). The mixture was purged with argon and cooled to –78 °C, then t-butyllithium in hexanes (1.7 M, 5.9 mL, 10 mmol) was added dropwise to the reaction mixture. The solution was stirred at –78 °C for 45 min, then the corresponding electrophile (10 mmol) was added dropwise. The reaction was stirred for 1 h at –78 °C, then was allowed to warm to room temperature and stirred overnight. Saturated aqueous ammonium chloride (20 mL) was added and the reaction mixture was extracted with ether (2 x 10 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude material was separated form the starting diiodide by flash chromatography on silica gel. Some of the dialkylated compound formed as by-product was still present in the chromatographed material. An oven-dried 20 mL round-bottom flask was charged with the material obtained above and THF (10 mL). The mixture was purged with argon and cooled to –78 °C, then t-butyllithium in hexanes (1.7 M, 2 equiv.) was added dropwise. The solution was stirred at –78 °C for 45 min, then chlorodicyclohexylphosphine (1.5 equiv.) was added dropwise. The reaction was stirred for 1 hour at –78 °C, then was allowed to warm to room temperature and stirred overnight. Saturated aqueous ammonium chloride (20 mL) was added and the reaction mixture was extracted with ether (2 x 10 mL). The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo.

The crude material was purified by flash chromatography on silica gel followed by recrystallization from dichloromethane and methanol.

(R)-(–)-2-Butyl-2'-dicyclohexylphosphino-1,1'-binaphthyl (2e)

The general procedure gave 460 mg (29 %) of the title compound as colorless crystals. mp 75-77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.74 (m, 5H), 7.54 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7,2 Hz, 1H), 7.33 (t, J = 7,2 Hz, 1H), 7,21-7.10 (m, 3H), 6.90 (d, J = 8.4 Hz, 1H), 2.49-2.39 (m, 1H), 2.29-2.19 (m, 1H), 1.98 (bb, 1H), 1.74-0.82 (m, 25H), 0.61 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 145.1, 138.6, 135.2, 135.1, 133.4, 133.1, 133.1, 131.5, 128.8, 127.6, 127.3, 127.2, 126.8, 126.6, 126.2, 125.7, 125.0, 124.5, 35.6, 35.3, 34.0, 33.9, 32.1, 30.7, 30.5, 30.3, 30.0, 29.8, 27.6, 27.3, 27.2, 26.5, 26.3, 22.8, 13.8 ppm (observed complexity due to P-C splitting); ^{31}P NMR (121 MHz, $CDCl_3$), δ –8.76; IR (neat, cm^{-1}) 3053, 2921, 2848, 1501, 1445, 1266, 814, 744; Anal. calcd for $C_{37}H_{47}P$: C, 85.01; H, 9.06. Found; C, 85.40; H, 9.17, $[\alpha]_D^{22}$ –37 (c 1.0, toluene).

(R)-(+)-2-Methyl-2'-dicyclohexylphosphino-1,1'-binaphthyl (2d)

The general procedure gave 215 mg (9 %) of the title compound as colorless crystals. mp 196-198 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 7.93-7.74 (m, 5H), 7.48-7.42 (m, 2H), 7.33 (t, J = 72. Hz, 1H), 7.23-7.07 (m, 3H), 6.94 (d, J = 8,7 Hz, 1H), 2.06 (s, 3H), 2.05-1.95 (m, 1H), 1.78-0.85 (m, 21H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9, 145.5, 135.9, 135.0, 134.4, 133.7, 133.5, 133.1, 133.0, 131.8, 129.1, 128.6, 128.0, 127.9, 127.2, 126.9, 126.5, 126.3, 125.3, 124.7, 35.7, 35.5, 30.8, 30.5, 30.3, 30.1, 27.7, 27.6, 26.7, 26.5, 21.4 ppm (observed complexity due to P-C splitting); ^{31}P NMR (121 MHz, $CDCl_3$) δ –8.30 ppm; IR

(neat, cm^{-1}) 3054, 2931, 2846, 1509, 1447, 1264, 810, 749; Anal. calcd for $C_{34}H_{41}P$: C, 85.31; H, 8.03. Found: C, 84.82; H, 8.03 , $[\alpha]_D^{22}$ +30 (c 1.0, toluene)

(R)-(+)-2-Trimethylsilyl-2'-dicyclohexylphosphino-1,1'-binaphthyl (2f)

The general procedure gave 320 mg (12%)of the title compound as colorless crystals. mp 92-94 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93-7.73 (m, 6H), 7.50-7.34 (m, 2H), 7.22-7.15 (m, 3H), 7.01 (d, J = 8.4 Hz, 1H),1.90-0.80 (m, 22H), –0.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 146.6, 143.5, 138.3, 135.5, 134.6, 134.5, 130.8, 128.7, 128.0, 127.9, 127.8, 127.7, 127.4, 127.2, 127.0, 126.8, 126.4, 126.3, 126.2, 126.0, 125.6, 34.7, 34.5, 34.0, 33.8, 31.7, 31.5, 31.3, 30.0, 29.8, 29.1, 28.9, 27.8, 27.7, 27.5, 27.4, 26.7, 26.5, 0.3 ppm (observed complexity due to P-C splitting); ^{31}P NMR (121 MHz, $CDCl_3$) δ –8.71 ppm; IR (neat, cm^{-1}) 3051, 3039, 1499, 1445, 1246, 829, 812, 758, 748; Anal. calcd for $C_{36}H_{47}PSi$: C, 80.25; H, 8.79. Found; C, 80.42; H, 8.87, $[\alpha]_D^{22}$ +55 (c 1.0, toluene).

General procedure for asymmetric vinylation

An oven-dried Schlenk tube equipped with a rubber septum was allowed to cool under an argon purge. The septum was removed and the tube was charged with tris(dibenzylideneacetone)dipalladium(0) (9.2 mg, 0.01 mmol, 1 mol%), **2a** (12.4 mg, 0.025 mmol, 2.5 mol %) and the ketone **4** (1.0 mmol). Toluene (2 mL) was added and the mixture was stirred for 15 min at room temperature. 1-Bromopropene (0.17 mL, 2.0 mmol) and sodium t-butoxide (192 mg, 2.0 mmol) were added to the tube. The tube was capped with a septum, purged with argon, and additional toluene (4 mL) was added through the septum. The mixture was stirred at room temperature until the starting ketone had been completely consumed as judged by GC analysis. The reaction

mixture was quenched with saturated aqueous ammonium chloride (10 mL) and diluted with ether (20 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with ether (20 mL) and the combined organic layers were washed with brine (20 mL), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The crude materials were purified by silica gel chromatography.

(S)-(+)-2-Methyl-2-(trans-1-propene)-5-(N-methyl-anilinomethylene)cyclopentanone (Table 2, Entry 1)

The reaction was run with 1.0 mmol of the ketone **4a** (216 mg), 2.0 mmol of trans-1-bromopropene (0.17 mL), 2 mmol of NaO^{t}Bu (192 mg), 1 mol% of $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and 2.5 mol % of (R)-(–)-**2a** (12.4 mg, 0.025 mmol). This procedure gave 242 mg (95%) of a yellow oil. This material was judged to be 90% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min.) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (t, J = 1.5 Hz, 1 H), 7.36-7.30 (m, 2H), 7.15-7.10 (m, 3H), 5.50-5,46 (m, 2H), 3.48 (s, 3H), 2.48 (dt, J = 7.8, J = 1.5 Hz, 3H), 1.99-1.90 (m, 1H), 1.68-1.59 (m, 6H), 1.15 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8, 146.2, 142.1, 134.6, 129.1, 124.6, 123.5, 121.1, 108.0, 50.7, 40.0, 35.0, 24.7, 23.0, 18.4 ppm; IR (neat, cm^{-1}) 2956, 2871, 1688, 1569, 1493, 1364, 1206, 1129; Anal Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.28. Found: C, 79.87; H,8.31; $[\alpha]_D^{22}$ +69 (c 0.8, ethanol).

(–)-2-Methyl-2-(2-methylpropene)-5-(N-methyl-anilinomethylene)cyclopentanone (Table 2, Entries 4 and 5)

The reaction was run with 0.5 mmol of the ketone **4a** (108 mg), 1.0 mmol of 1-bromo-2-methylpropene (0.09 mL), 1 mmol of NaO^{t}Bu (96 mg) 2.5 mol% of $Pd_2(dba)_3$ (11.5 mg, 0.0125 mmol), and 6.5 mol% of (R)-(–)-**2a** (16.0 mg,

0.0325 mmol). This procedure gave 127 mg (95%) of a yellow oil. This material was judged to be 71% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (t, J = 1.5 Hz, 1 H), 7.37-7.31 (m, 2H), 7.16-7.11 (m, 3H), 5.37-5.34 (m, 1H), 3.50 (s, 3H), 2.48 (dt, J = 6.9, J = 1.2 Hz, 2H), 1.98-1.83 (m, 2H), 1.71 (d, J = 1.2 Hz, 3H), 1.63 (d, J = 0.9 Hz, 3H) 1.19 (s, 3H) ppm; ^{13}C NMR (75 MHz) δ 208.9, 146.2, 142.3, 134.1, 129.4, 129.1, 124.6, 121.2, 107.7, 49.5, 40.3, 36.8, 27.1, 24.8, 24.3, 19.8 ppm; IR (neat, cm^{-1}) 2958, 2863, 1688, 1569, 1493, 1360, 1210, 1129, 917. Anal Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61. Found: C, 80.30; H,8.68; $[\alpha]_D^{22}$ –62 (c 0.8, ethanol).

An analogous procedure with 1-chloro-2-methylpropene gave (–)-2-Methyl-2-(2-methylpropene)-5-(N-methyl-anilinomethylene)cyclopentanone in 76% yield and 71% ee.

(+)-2-Propyl-2-vinyl-5-(N-methyl-anilinomethylene)cyclopentanone

(Table 2, Entry 7)

The reaction was run with 1.0 mmol of the ketone **4b** (244 mg), 2.0 mmol of vinylbromide (1 M in THF, 2 mL), 2 mmol of NaO^tBu (192 mg) 2.5 mol% of $Pd_2(dba)_3$ (23.0 mg, 0.025 mmol), and 6.5 mol% of (R)-(–)-**2a** (32.2 mg, 0.065 mmol). This procedure gave 312 mg (86 %) of a yellow oil. This material was judged to be 90% ee by chiral HPLC analysis (Chiracel OD column, 10 \% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (t, J = 1.5 Hz, 1 H), 7.36-7.31 (m, 2H), 7.16-7.10 (m, 3H), 5.84 (dd, J = 17.4, J = 10.8 Hz, 1H), 5,08 (dd, J = 10.8 Hz, J = 1.2 Hz, 1H), 5.05 (dd, J = 17.4, J = 1.3 Hz, 1H), 3.49 (s, 3H), 2.48-2.43 (m, 2H), 2.03-1.95 (m, 1H), 1.78-1.59 (m, 2H), 1.46-1.17 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz) δ 207.0, 146.2, 142.4, 140.9, 129.2, 124.7, 121.4, 113.6, 108.2, 55.8, 40.4, 38.9, 30.5, 24.9, 17.9, 14.9 ppm;

IR (neat, cm^{-1}) 2956, 2871, 1688, 1569, 1493, 1364, 1206, 1129; Anal Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.61. Found: C, 80.00; H,8.57; $[\alpha]_D^{22}$ +19 (c 0.5, ethanol).

(S)-(+)-2-Methyl-2-vinyl-5-(N-methyl-anilinomethylene)cyclopentanone (Table 2, Entry 2)

The reaction was run with 1.0 mmol of the ketone **4a** (216 mg), 2.0 mmol of vinylbromide (2 M in THF, 2 mL), 2 mmol of NaO^tBu (192 mg) 1 mol% of $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and 2.5 mol% of (R)-(–)-**2a** (12.4 mg, 0.025 mmol). This procedure gave 226 mg (94%) of a yellow oil. This material was judged to be 92% ee by chiral HPLC analysis (chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55 (s, 1H), 7.32 (m, 2H), 7.17-7.10 (m, 3H), 5.87 (dd, J = 17.7, 10.8 Hz, 1H), 5.06 (dd, J = 17.7, 1.2 Hz, 1H), 5.04 (dd, J = 10.8, 1.2 Hz, 1H), 3.47 (s, 3H), 2.47 (m, 2H), 1.99-1.95 (m, 1H), 1.70-1.60 (m, 1H), 1.16 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.1, 207.2, 146.2, 142.5, 141.9, 129.2, 124.8, 121.4, 113.0, 107.7, 51.6, 40.2, 34.3, 24.6, 22.5 ppm; IR (neat, cm^{-1}) 2958, 2863, 1688, 1565, 1493, 1362, 1208, 947, 756, 695 ; Anal. calcd for $C_{16}H_{19}ON$: C, 79.63 ; H, 7.94 Found; C, 79.54; H, 7.79 , $[\alpha]_D^{22}$ +55 (c 1.0, ethanol).

(–)-2-Pentyl-2-vinyl-5-(N-methyl-anilinomethylene)cyclopentanone (Table 2, Entry 8)

The reaction was run with 0.5 mmol of the ketone **4c** (135 mg), 1.0 mmol of vinylbromide (2 M in THF, 1 mL), 1 mmol of NaO^tBu (96 mg) 2.5 mol% of $Pd_2(dba)_3$ (11.5 mg, 0.0125 mmol), and 6.5 mol% of (S)-(+)-**2a** (16.0 mg, 0.0325 mmol). This procedure gave 125 mg (84%) of a yellow oil. This material was judged to be 92% ee by chiral HPLC analysis (Chiracel OD column, 10% i-

propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (t, J = 1.9 Hz, 1H), 7.36-7.32 (m, 2H), 7.18-7.13 (m, 3H), 5.84 (dd, J = 17.4, 10.5 Hz, 1H), 5.08 (dd, J = 10.5, 1.2 Hz, 1H), 5.06 (dd, J = 17.4, 1.2 Hz, 1H), 3.48 (s, 3H), 2.47 (t, J = 6.9 Hz, 2H), 2.04-1.95 (m, 1H), 2.50-2.45 (m, 2H), 1.78-1.60 (m, 2H), 1.48-1.11 (m, 7H), 0.86 (3H, t, J = 6.8 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 146.2, 142.2, 140,9, 129.2, 124.7, 121.3, 113.6, 108.3, 99.2, 55.7, 40.2, 36.6, 32.5, 30.5, 24.9, 22.8, 14.1 ppm; IR (neat, cm^{-1}) 2956, 2931, 2858, 1688, 1607, 1571, 1493, 1294, 1117, 905; Anal. calcd for $C_{20}H_{27}ON$: C, 80.76 ; H, 9.15; Found; C, 80.66; H, 9.24, , $[\alpha]_D^{22}$ –23 (c 1.0, ethanol).

(+)-2-Methyl-2-styryl-5-(N-methyl-anilinomethylene)cyclopentanone (Table 2, Entry 3)

The reaction was run with 1.0 mmol of the ketone **4a** (216 mg), 2.0 mmol of β-bromostyrene (0.26 mL), 2 mmol of NaO^tBu (192 mg) 1 mol% of $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and 2.5 mol% of (R)-(–)-**2a** (12.4 mg, 0.025 mmol). This procedure gave 291 mg (92%) of a yellow oil. This material was judged to be 89% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (t, J = 1.8 Hz, 1H), 7.38-7.10 (m, 10H), 6.34 (d, J = 16.2 Hz, 1H), 6.20 (d, J = 16.2 Hz, 1H), 3.48 (s, 3H), 2.55-2.50 (m, 2H), 2.15-2.06 (m, 1H), 1.77 (dt, J = 12.6, 7.8 Hz, 1H), 1.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 146.1, 142.7, 137.5, 133.9, 129.2, 128.9, 127.7, 127.1, 126.3, 124.8, 121.4, 121.3, 107.7, 51.2, 40.3, 34.9, 24.8, 23.3 ppm; IR (neat, cm^{-1}) 3025, 2958, 2925, 2863, 1686, 1605, 1565, 1493, 1443, 1362, 1204, 1129, 917; Anal. calcd for $C_{22}H_{23}ON$: C, 83.24 ; H, 7.30, Found; C, 83.34, H, 7.62, $[\alpha]_D^{22}$ +90 (c 1.0, ethanol).

(+)-2-Methyl-2-(trans-1-propene)-1-indanone (Table 2, Entry 11)

The reaction was run with 1.0 mmol of the ketone **4f** (0.14 mL), 2.0 mmol of trans-1-bromopropene (0.17 mL), 2 mmol of NaO^{t}Bu (192 mg) 1 mol% of $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and 2.5 mol% of (R)-(–)-**2a** (12.4 mg, 0.025 mmol). This procedure gave 177 mg (95%) of a yellow oil. This material was judged to be 74% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, $J_{aprox.}$ = 7.5 Hz, 1H), 7.59 (t, $J_{aprox.}$ = 7.5 Hz, 1H), 7,43 (d, $J_{aprox.}$ = 7.5 Hz), 7.36 (t, $J_{aprox.}$ = 7.5 Hz, 1 H), 5.65-5.50 (m, 2H), 3.27 (d, J = 17.1, 1H), 3.00 (d, J = 17.1, 1H), 1.67 (d, $J_{aprox.}$ = 5.1 Hz, 3H), 1.34 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.8, 152.3, 135.5, 134.9, 133.7, 127.6, 126.6, 124.8, 124.7, 51.7, 41.8, 23.8, 18.3 ppm; IR (neat, cm^{-1}) 3029, 2962, 2919, 2856, 1713, 1609, 1465, 1436, 1275, 966, 737; Anal. calcd for $C_{13}H_{14}O$: C, 83.83 ; H, 7.58, Found; C, 83.61, H, 7.47, $[\alpha]_D^{22}$ +56 (c 1.0, ethanol).

(–)-2-Methyl-2-vinyl-1-tetralone (Table 2, Entry 10)

The reaction was run with 1.0 mmol of the ketone **4e** (0.15 mL), 2.0 mmol of vinylbromide (1 M in THF, 2 mL), 2 mmol of NaO^{t}Bu (192 mg) 1 mol% of $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol), and 2.5 mol% of (R)-(–)-**2a** (12.4 mg, 0.025 mmol). This procedure gave 178 mg (96%) of a yellow oil. This material was judged to be 80% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, $J_{aprox.}$= 7.8 Hz, 1H), 7.44 (t, $J_{aprox.}$ = 7.8 Hz, 1H), 7.29 (t, $J_{aprox.}$ = 7.8 Hz, 1H), 7.20 (d, $J_{aprox.}$ = 7.8 Hz, 1H), 5.99 (dd, J = 17.7, 10.8 Hz, 1H), 5.09 (d, J = 10.8 Hz, 1H), 4.97 (d, J = 17.7 Hz, 1H), 3.10-2.85 (m, 2H), 2.17-2.00 (m, 2H), 1.32 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 143.6, 140.7, 133.2, 132.0, 128.8, 127.9, 162.7, 114.9, 48.8, 35.5, 26.1, 23.7 ppm; IR (neat, cm^{-1}) 3068, 2966, 2929,

2858, 1683, 1602, 1455, 1295, 1223, 913, 741 ; Anal. calcd for $C_{13}H_{14}O$: C, 83.80 ; H, 7.58, Found; C, 83.71 H, 7.81, $[\alpha]_D^{22}$ –76 (c 1.0, ethanol).

(–)-2-Methyl-2-vinyl-5-(N-methyl-anilinomethylene)cyclohexanone (Table 1, Entry 9)

The reaction was run with 0.5 mmol of the ketone **4d** (115 mg), 1.0 mmol of vinylbromide (2 M in THF, 1 mL), 1 mmol of NaO^{t}Bu (96 mg) 2.5 mol% of $Pd_2(dba)_3$ (11.5 mg, 0.0125 mmol), and 6.5 mol% of (R)-(–)-**2a** (16.0 mg, 0.0325 mmol). This procedure gave 105 mg (78%) of a yellow oil. This material was judged to be 50% ee by chiral HPLC analysis (Chiracel OD column, 10% i-propanol in hexane, 1mL/min). ^{1}H NMR (300 MHz, $CDCl_3$,) δ 7.51-7.00, (6H, m), 5.96 (dd, J = 17.4, 10.8 Hz, 1H), 5.06 (d, J = 10.8 Hz, 1H), 5.01 (d, J = 17.4 Hz, 1H), 3.41 (s, 3H), 2.07-2.03 (m, 2H), 1.90-1.82 (m, 1H), 1.70-1.56 (m, 3H), 1.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 142.1, 129.9, 129.7, 129.2, 126.6, 122.5, 117.5, 114.,9 114.7, 46.3, 35.5, 32.9, 32.4, 28.6, 20.8, 16.8 ppm; IR (neat, cm^{-1}) 2971, 2935, 2881, 2159, 1725, 1675, 1596, 1497, 1353, 1115, 920, 762 ; Anal. calcd for $C_{17}H_{21}ON$: C, 79.96 ; H, 8.29, Found; C, 80.03, H, 8.27; $[\alpha]_D^{22}$ –120 (c 1.0, ethanol).

(–)-2-Methyl-2-(cis-2-methyl-1-ethenyl)cyclopentanone (Table 1 Entry 6)

The reaction was run with 0.5 mmol of the ketone **4d** (115 mg), 1.0 mmol of cis-2-bromopropene, 1 mmol of NaO^{t}Bu (96 mg) 2.5 mol% of $Pd_2(dba)_3$ (11.5 mg, 0.0125 mmol), and 6.5 mol% of (R)-(–)-**2a** (16.0 mg, 0.0325 mmol). This procedure gave 214 mg (84%) of a yellow oil that was judged to be 76% ee by HPLC analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (m, 1H), 7.38-7.33 (m, 2H), 7.17-7.13 (m, 3H), 5.61-5.44 (m, 2H), 3.52 (s, 3H), 2.52-2.48 (m, 2H), 2.02-

1.85 (m, 2H), 1.67 (dd, J= 6.9, 1.2 Hz. 3H), 1.23 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 146.2, 142.4, 134.9, 129.2, 126.1, 124.7, 121.4, 107.4, 49.9, 40.4, 36.7, 24.9, 24.0, 15.2 ppm; IR (neat, cm^{-1}) 3014, 2958, 2865, 1686, 1605, 1561, 1493, 1358, 1206, 1129, 1104, 922; Anal. calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.28, Found: C, 79.32; H, 8.29.

General procedure for removing the blocking group

The ketone corresponding N-methyl-anilinomethyleneketone (1 mmol) was dissolved in THF (5 mL) in a round-bottomed flask. An aqueous HCl solution (2 M, 3 mL) was added and the mixture stirred at room temperature until the ketone **4** had been completely consumed, as judged by GC analysis (ca. 3 h). The mixture was diluted with water (10 mL) and ether (10 mL), poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with ether (10 mL), the organic layers were combined and concentrated in vacuo. The resulting oil was dissolved in aqueous NaOH solution (1 M) (10 mL) in a round bottomed flask equipped with a reflux condenser and the resulting solution was stirred at 90 °C until the 5-(hydroxymethylene)ketone, formed in the previous step, had been completely consumed, as judged by GC analysis (ca. 4 h).

Workup method 1: The mixture was cooled to room temperature, neutralized with aqueous HCl (1 M) and diluted with ether (20 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with ether (10 mL), the combined organic layers were washed with brine (10 mL), dried over anhydrous magnesium sulfate, filtered and the solvent evaporated (atmospheric pressure). The crude material was purified by distillation.

Workup method 2: The mixture was cooled to room temperature, neutralized with aqueous HCl (1 M) and diluted with ether (20 mL). The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with ether (10 mL), the combined organic layers were washed with brine (10 mL), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The crude material was purified flash chromatography on silica gel.

2-Methyl-2-styrylcyclopentanone

Workup method 2 was used to afford 188 mg (94%) of the title compound as a mixture of trans/cis isomers (5:1 by NMR). ^{1}H NMR (300 MHz, $CDCl_3$,) δ 7.36-7.16 (m, 5H),6.59 (minor isomer d, J = 12.0 Hz, 1H), 6.40 (major isomer, d, J = 16.2 Hz, 1 H), 6.17 (major isomer, d, J = 16.2, 1H), 5.81 (minor isomer, J = 12.0, 1 H), 2.34-1.87 (m, 4H), 1.23 (major isomer, s, 3H), 1.16 (minor isomer, s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.3, 138.2, 136.9, 134.9, 132.2, 130.6, 129.4, 128.8, 128.6, 127.9, 127.5, 126.9, 126.3, 51.7, 51.2, 37.3, 36.9, 36.8, 24.1, 23.1, 19.0, 18.8 ppm; IR (neat, cm^{-1}) 3025, 2964, 2869, 1735, 1449, 1152, 1063, 967; Anal. calcd for $C_{14}H_{16}O$: C, 83.96 ; H, 8.05, Found; C, 84.09, H, 8.00.

2-Methyl-2-(trans-1-propene)cyclopentanone

Workup method 1 was used to afford 121 mg (88%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$,) δ 5.53-5.34 (m, 2H), 2.29-1.72 (m, 6H), 1.67 (dd, J = 4.8 Hz, J = 0.9 Hz, 3H), 1.11 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 221.2, 133.3, 125.1, 51.4, 37.3, 37.1, 22.8, 18.9, 18.4 ppm; IR (neat, cm^{-1}) 3015, 2962, 2869, 1737, 1451, 1154, 1063, 1048, 965; HRMS (EI) found, m/z 138.1042; calcd for $C_9H_{14}O$, 138.1044.

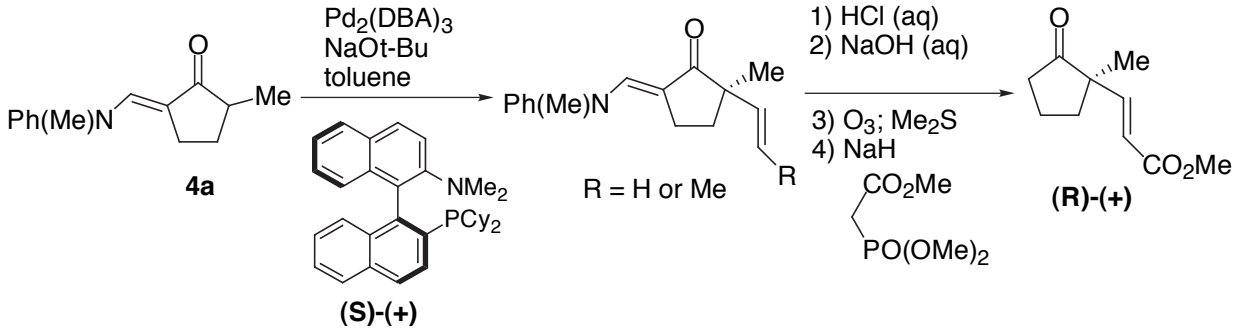
2-Methyl-2-vinylcyclopentanone

Workup method 1 was used to afford 93 mg (75%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$,) δ 5.77 (dd, J = 17.4, J = 10.8 Hz, 1H), 5.09 (dd, J = 10.8 , J = 0.9 Hz, 1H), 5.05 (dd, J = 17.4, J = 0.9 Hz, 1H), 2.30-1.75 (m, 6H), 1.13 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.5, 140.4, 114.2, 52.2, 37.3, 36.3, 22.3, 18.8 ppm; IR (neat, cm^{-1}) 3087, 2966, 2871, 1737, 1638, 1453, 1407, 1156, 1046, 916; HRMS (EI) found, m/z 124.0887; calcd for $C_8H_{12}O$, 124.0888.

2-Propyl-2-vinylcyclopentanone

Workup method 1 was used to afford 118 mg (78%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$,) δ 5.73 (dd, J = 17.4, J = 10,5 Hz, 1H), 5.13 (dd, J = 10.5, J = 0.9 Hz, 1H), 5.05 (dd, J = 17.4, J = 0.9 Hz, 1H), 2.35- 1.15 (m, 10 H), 0.88 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.6, 139,0, 114.6, 38.2, 37.4, 32.4, 28.6, 17.4, 14.3 ppm; IR (neat, cm^{-1}) 3085, 2960, 2875, 1737, 1632, 1466, 1457, 1154, 1001, 915; HRMS (EI) found, m/z 152.1202; calcd for $C_{10}H_{16}O$, 152.1201.

The absolute configurations of (R)-(–)-2-Dimethylamino-2'-dicyclohexylphosphino-1,1'-binaphthyl and of two vinylation products:



(R)-(–)-2-Dimethylamino-2'-dicyclohexylphosphino-1,1'-binaphthyl (**2a**) was prepared from (R)-(+)-2-bromo-2'-dimethylamino-1,1'-binaphthyl. The absolute configurations could be assigned, because the latter compound, when treated sequentially with n-BuLi and Ph_2PCl, gave (R)-(–)-dimethylamino-2'-diphenylphosphino-1,1'-binaphthyl (**2b**), the absolute stereochemistry of which is known.[3]

(R)-(+)-2-Formyl-2-methylcyclopentanone: (+)-2-Methyl-2-(2-trans-methyl-1-ethenyl)cyclopentanone **6a** [93 mg, 0.67 mmol; α_D^{23} = +45 (c 0.95, hexane); prepared from (R)-(–)-2-methyl-2-(2-trans-methyl-ethenyl)-5-(N-methyl-anilinomethylene)cyclopentanone (**5a**) of 64% ee] was dissolved in 4 mL of CH_2Cl_2/MeOH (1:1), and cooled in a dry ice/acetone bath. Ozone was then bubbled through the solution at a rate of ca. 1 mmol/min for 5 min, at which time the solution had turned pale blue, and analysis by TLC indicated that the starting material had been consumed. After argon was bubbled through the solution for 5 min, Me_2S (210 mg, 0.25 mL, 3.4 mmol) was added and the cooling bath was removed. After the solution stirred at rt for 30 min, the crude mixture was directly loaded onto a column of silica gel, which was washed with pentane to remove the solvents. Chromatography with a gradient of ether/pentane gave 42 mg (49%) of the title compound, a clear oil. α_D^{23} = +177

(c 4.2, CD_2Cl_2). ^1H NMR (300 MHz, CD_2Cl_2) 9.40 (s, 1H), 2.55–2.47 (m, 1H), 2.31–2.26 (m, 2H), 2.00–1.88 (m, 2H), 1.79–1.70 (m, 1H), 1.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2) 215.9, 199.4, 63.0, 38.6, 31.9, 19.7, 18.3 ppm. IR (neat, cm^{-1}) 2967, 1744, 1712, 1454, 1404. The spectra were in agreement with those reported in the literature for the racemic aldehyde.[4]

(R)-(+)-2-Formyl-2-methylcyclopentanone was also obtained in 16% yield from the ozonolysis of (R)-(+)-2-Methyl-2-vinylcyclopentanone **6d** [α_D^{23} = +66 (c 0.35, Et_2O); prepared from (R)-(–)-2-methyl-2-vinyl-5-(N-methyl-anilinomethylene)cyclopentanone of 85% ee]. The conditions of the ozonolysis were identical to those above, as were the GC/MS and the ^1H NMR spectrum of the product: α_D^{23} = +205 (c 1.4, CD_2Cl_2).

(R)-(+)-2-Methyl-2-(2-trans-methoxycarbonyl-1-ethenyl)cyclopentanone A 10 mL round bottomed flask was charged with a stirbar and NaH (7 mg of a 60% dispersion in mineral oil, 0.18 mmol), and the flask was evacuated and backfilled with argon. DME (0.5 mL) and trimethyl-phosphonoacetate (32 mg, 0.028 μL, 0.18 mmol) were sequentially added via syringe. Additional DME (0.5 mL) was then added to facilitate stirring, and subsequently, (R)-(+)-2-Formyl-2-methylcyclopentanone [from (+)-**6a**] was added via syringe as a solution in DME (1 mL). After the mixture was stirred for 22 h at rt, it was partitioned between ether and water. The aqueous layer was extracted twice with ether, and the organics were combined, dried (Na_2SO_4), filtered and concentrated. Chromatography (eluting with a gradient of ethyl acetate/hexane) gave 18 mg (57%) of the title compound, an oil, α_D^{23} = +33 (c 1.8, $CDCl_3$). The purity was estimated by ^1H NMR and GC to be >97%, and the ^1H NMR, ^{13}C NMR, IR, and MS(EI) spectra are in close agreement with those previously reported for (R)-(+)-2-methyl-2-(2-trans-methoxycarbonyl-1-

ethenyl)cyclopentanone [71% ee, α_D^{20} = +24.7 (c 1.5, $CDCl_3$)].[5,6] ^1H NMR (300 MHz, $CDCl_3$) 6.92 (d, 1H, J = 16.2 Hz), 5.85 (d, 1H, J = 16.2 Hz), 2.38-2.30 (m, 2H), 2.20-2.10 (m, 1H), 2.02-1.86 (m, 3H), 1.21 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) 218.3, 166.8, 149.9, 120.6, 52.0, 51.9, 37.5, 36.5, 22.2, 19.1 ppm; IR (neat, cm^{-1}) 2966, 1739, 1723, 1649, 1436.

References and Footnotes

1. Slightly different ee's were obtained monitoring at other wavelengths

2. Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. J. Am. Chem. Soc. **1999**, 121, 4369.

3. Vyskočil, Š.; Smrčina, M.; Hanuš, V.; Polášek, M.; Kočovskỳ, P. J. Org. Chem. **1998**, 63, 7738.

4. Sathyamoorthi, G.; Thangaraj, K.; Srinivasan, P. C.; Swaminathan, S. Tetrahedron, **1990**, 46, 3559.

5. Tori, M.; Miyake, T.; Hamaguchi, T.; Sono, M. Tetrahedron Asymmetry **1997**, 8, 2731.

6. For the assignment of the absolute configuration of (R)-(+)-2-Methyl-2-(2-trans-methoxycarbonyl-1-ethenyl)cyclopentanone, see ref and: Pfau, M.; Revial, G.; Guingant, A.; d'Angelo, J. J. Am. Chem. Soc. **1985**, 107, 273.