General Procedures. High field NMR spectra were recorded on Varian XL-200E (^{1}H at 200 MHz and ^{13}C at 50 MHz respectively) and Unity Plus 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz and ^{31}P at 121 MHz) spectrometers. Chemical shifts of ^{1}H and ^{13}C spectra are referenced to the NMR solvents; ^{31}P spectra are referenced to H_3PO_4 external standard (0 ppm). Melting points are uncorrected. Optical rotations were measured on Jasco DIP-360 digital polarimeter. Flash chromatography was performed using silica gel (230–600 mesh). Thin layer chromatography was performed on glass plates coated with silica gel 60 F254 (E. Merck, Darmstadt, Germany). CH_2Cl_2 was distilled over CaH_2 and THF over Na/benzophenone. Other solvents were purchased from commercial supplier and were used without further purification. L-Aspartic acid, 1,1-dimethoxypropane, acetyl chloride, triethylamine, di-*tert*-butyl dicarbonate and *p*-toluenesulfonic acid monohydrate were purchased from Aldrich. 1,3-Dimethylpropenyl pivalate was synthesized following a literature procedure.[5] (*S*)-N-*tert*-Butoxycarbonyl-aspartic acid diethyl ester, (*S*)-2-(*tert*-Butoxycarbonylamino)-1,4-butanediol**,** (*S*)-N-*tert*-butoxycarbonyl-4-(2-hydroxy)ethyl-2,2-dimethyloxazolidine **5** were prepared via literature procedures.[1-3]

(*S*)-N-*tert*-Butoxycarbonyl-2,2-dimethyl-4-hydroxymethyl-1,3-oxazine 6. A sample of pure **6** was isolated in the preparation of **5** via flash chromatography using ethyl acetate/hexanes (3:1 v/v) as eluant. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.37-3.77 (m, 5H), 1.62 (m, 2H), 1.35 (s, 9H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (50 MHz, , $CDCl_3$) δ 155.0, 101.2, 79.1, 63.8, 57.9, 48.5, 35.7, 28.3, 24.7, 24.6.

(*S*)-2-(*tert*-Butoxycarbonyl-4-(4-toluenesulfonyloxyethyl)-2,2-dimethyloxazolidine 7. Dry, freshly crystallized *p*-toluenesulfonyl chloride (1.86 g, 9.8 mmol) and 4-dimethylaminopyridine (10 mg, 0.082 mmol) were added to a solution of alcohol **5** (2.00 g, 8.15 mmol) and triethylamine (2.6 mL, 18.75 mmol) in dichloromethane (20 mL) at 5 °C with stirring. The resulting solution was protected from moisture and kept at 5 °C until all the starting material **5** had reacted (33 h, TLC). A colorless solid, presumably triethylamine hydrochloride, crystallized out of the reaction, and was filtered away. The filtrate was diluted with dichloromethane to a volume of 90 mL, and washed with water (2 × 20 mL), brine (20 mL), dried over Na_2SO_4, and concentrated to give the crude tosylate **7** as white solid. This material was purified by dissolving in ether (*ca*. 330 mL), filtering through celite 545 on a wad of cotton to give 2.95 g (90 %) of **7**. $[\alpha]^{24}_{D}$ +3.1 (c = 1.5, $CHCl_3$) ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.35 (d, 2H), 4.09 (m, 2H), 4.09 (m, 2H), 3.90 (m, 2H), 3.73 (m, 1H), 2.95 (m, 2H), 1.51 (s, 6H), 1.44 (s, 9H).

(*S*)-*N*-*tert*-Butoxycarbonyl-4-ethylenediphenylphosphinoborane-2,2-dimethyloxazolidine 8. *n*-Butyl lithium in hexanes (1.6 M, 17.1 mL, 27.4 mmol) was added to a solution of diphenylphosphine (4.52g, 24.3 mmol) and THF (100 mL) at 0 °C. The orange-red solution was stirred at 0 °C for 30 min. A solution of tosylate **7** (8.44 g, 21.1 mmol) in THF (60 mL) was then added dropwise to the solution of the diphenylphosphide anion at 0 °C. The reaction mixture was stirred for another 30 min. Borane-THF complex (1 M, 26 mL, 26 mmol) was added to the solution at 0 °C and this was then stirred for an additional 20 min. The solvent was removed, and the remaining

material was dissolved in ethyl acetate (600 mL) and washed with 1 M $HCl_{(aq)}$ (100 mL), sat. $NaHCO_3$ (100 mL), brine (100 mL), dried over Na2SO4, and filtered. The solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel using ethyl acetate/hexane eluant (3:7 v/v) to give 8.1 g (18.9 mmol, 90%) of a colorless oil, which crystallized upon standing at 25°C. M.p. 95.0-96.5°C; R_f 0.81 (ethyl acetate/hexane, 1:1 v/v). $[\alpha]^{24}_D$ +34.0 (c = 10.0, $CHCl_3$) ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.63 (m, 4H), 7.43 (m, 6H), 3.92 (m, 2H), 3.67 (m, 1H), 2.17 (m, 2H), 1.83 (m, 2H), 1.60 (s, 3H), 1.54 (s, 9H), 1.34 (s, 3H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 151.9, 131.9-132.1, 131.2, 128.9, 128.8, 94.0, 19.9, 67.0, 57.4, 28.3, 26.7, 22.9, 22.3, 21.8; ^{31}P-NMR ($CDCl_3$, 121 MHz): δ 16.76 (br). HRMS (M + Na^+) *m/z* Calcd. for $C_{24}H_{35}NO_3PBNa$: 450.23453. Found 450.23672

(*S*)-2-Phenyl-4-[(diphenylphosphino)ethyl]oxazoline 2a. The protected phosphine **8** (500 mg, 1.17 mmol) was dissolved in 8 mL of methanol and cooled to 0 °C. Gaseous HCl was bubbled through the solution for 10 min. The methanol was removed under vacuum and the residue was dissolved in 8 mL of 1,2-dichloroethane. Triethylamine (1.5 mL, 9.3 mmol) and benzimidic acid ethyl ester hydrochloride[4] (230 mg, 1.24 mmol) were added, and the reaction was refluxed for 6 h. The solvent was removed giving a colorless oil, and the crude product was purified by column chromatography on silica gel using ethyl acetate/hexane eluant (2:8 v/v) to afford oxazoline **2a** (210 mg, 0.58 mmol, 50% yield) as a colorless solid. M.p. 52.5-54°; R_f 0.76 (ethyl acetate/hexane, 3:7 v/v). $[\alpha]^{24}_D$ -72.7 (c = 1.0, $CHCl_3$) ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.93 (d, *J* = 7 Hz), 7.29-7.49 (m, 13H), 4.34-4.49 (m, 4H), 4.00 (dd, *J* = 7.5

Hz, J = 7.5 Hz), 2.24-2.34 (m, 2H), 2.07-2.15 (m, 2H), 1.67-1.85 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 163.7, 138.6, 138.3, 132.8, 132.6, 128.6, 128.5-128.2, 127.7, 72.2, 67.5 (d, J = 13.5 Hz), 32.1(d, J = 16.5 Hz), 24.1(d, J = 11.5 Hz); ^{31}P-NMR ($CDCl_3$, 121 MHz): δ –15.81; HRMS (M^+ + 1) m/z Calcd. for $C_{23}H_{23}NOP$: 360.15170. Found 360.15147.

General Procedure for Preparation of Oxazolines 2b-d, As In The Case Of (*S*)-2-(1-Admantyl)-4-[(diphenylphosphino)ethyl]oxazoline 2b. The protected phosphine **8** (500 mg, 1.17 mmol) was dissolved in 8 mL of methanol and cooled to 0 °C. Gaseous HCl was bubbled through the reaction for 10 min, and the methanol was removed under vacuum. The residue was dissolved in 8 mL of 1,2-dichloroethane and triethylamine (0.44 mL, 4.1mmol), catalytic 4-dimethylaminopyridine (2 mg), then 1-admantanecarbonyl chloride (256 mg, 1.28 mmol) were added and reaction was stirred for 12 h. Subsequently, borane•THF (1 M, 2 mL, 2 mmol) was added to the reaction mixture at 0 °C, and this was stirred for 10 min. The reaction mixture was diluted with 15 mL of dichloromethane and washed with $HCl_{(aq)}$ (0.5 M, 10 mL × 2) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated. 1,4-Diazobicyclo[2.2.2]octane (656 mg, 5.85 mmol) and THF (8 mL) were added to this material. The reaction mixture was cooled to 0 °C and methanesulfonyl chloride (86 μL, 1.28 mmol) was added. The reaction was stirred at 25 °C for 4 h then heated to 50 °C for another 4 h. The resulting slurry was filtered and concentrated at reduced pressure, and the residue was flash chromatographed using ethyl acetate/hexane eluant (2:8 v/v) to give 370 mg (0.89 mmol, 75%) of the product **2b** as an oil. R_f 0.76 (ethyl acetate/hexane, 3:7 v/v) $[\alpha]^{24}_D$ -47.7 (c

= 1.0, $CHCl_3$) ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.43-7.48 (m, 4H), 7.34-7.41 (m, 6H), 4.14-4.23 (m, 2H), 3.81 (m, 1H), 2.18-2.24 (m, 1H), 2.03-2.08 (m, 3H), 1.90 (m, 3H), 1.64-1.83 (m, 12H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 173.5, 138.6, 138.2, 132.9, 132.7, 132.4, 128.6-128.3, 71.5, 66.4 (d, *J* = 13.5 Hz), 39.6, 36.5, 35.1, 32.1(d, *J* = 16.5 Hz), 28.1, 23.6 (d, *J* = 11.5 Hz); ^{31}P-NMR ($CDCl_3$, 121 MHz): δ –15.81. HRMS (M^+ + 1) *m/z* Calcd. for $C_{27}H_{33}NOP$: 418.22998. Found 418.22583.

(*S*)-2-(3,5-Di-*tert*-butylphenyl)-4-[(diphenylphosphino)ethyl]oxazoline 2c. This compound was prepared via the same method used to prepare **2b**. Beginning with 500 mg (1.17 mmol) of **8**, 227 mg (0.48 mmol, 41%) of the oxazoline **2c** was produced as colorless oil. R_f 0.77 (ethyl acetate/hexane, 3:7 v/v). $[\alpha]^{24}_D$ -39.5 (c = 0.6, $CHCl_3$) ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38-7.44 (m, 4H), 7.27-7.37 (m, 6H), 4.21 (m, 1H), 4.12 (m, 1H), 3.80 (dd, *J* = 6.3 Hz, *J* = 7.8 Hz), 2.14 (m, 1H), 2.01 (m, 1H), 1.60 (m, 2H), 1.57 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 164.4, 150.9, 138.5, 138.3, 132.9, 132.8, 132.6, 128.7-128.4, 127.0, 125.6, 122.5, 72.0, 67.5 (d, *J* = 13.5 Hz), 34.9, 32.1(d, *J* = 16.5 Hz), 31.4, 24.0 (d, *J* = 12.0 Hz); ^{31}P-NMR ($CDCl_3$, 121 MHz): δ –15.20. HRMS (M^+ + 1) *m/z* Calcd. for $C_{31}H_{39}NOP$ 472.27693. Found 472.27524

(*S*)-2-*tert*-Butyl-4-[(diphenylphosphino)ethyl]oxazoline 2d. This compound was prepared via the same method used for compound **2b**, but beginning with 500 mg (1.17 mmol) of **8**, 117 mg (0.34 mmol, 30%) of the oxazoline **2d** was produced as colorless oil. R_f 0.68 (ethyl acetate/hexane, 3:7 v/v). $[\alpha]^{24}_D$ -46.9 (c = 1.1, $CHCl_3$) ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.78 (s, 2H), 7.38-7.56 (m, 5H), 7.26-7.34 (m, 6H), 4.33-4.47 (m, 2H), 3.97 (t, *J* = 7 Hz, 1H), 2.14-2.27 (m, 1H), 2.04-2.12 (m, 1H), 1.70-1.84 (m,

1H), 1.65-1.70 (m, 1H), 1.33 (s, 18H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 174.0, 138.6, 138.2, 132.7, 132.4, 132.1, 128.6-128.3, 72.0, 66.6 (d, J = 13.5 Hz), 33.2, 32.1(d, J = 16.5 Hz), 27.8, 23.6 (d, J = 11.5 Hz); ^{31}P-NMR ($CDCl_3$, 121 MHz): δ –15.37. HRMS ($M^+ + 1$) m/z Calcd. for $C_{21}H_{27}NOP$ 340.18303. Found 340.18281.

Typical Procedure for the Enantioselective Allylation. Methyl (*R*)-*E*-2-Methoxycarbonyl-3,5-diphenylpent-4-enoate (Reaction 1). In a nitrogen atmosphere, allylpalladium chloride dimer (1.8 mg, 0.0049 mmol), the ligand **11a** (3.2 mg, 0.009 mmol), and solid potassium acetate (2 mg, 0.02 mmol) was weighed into a half-dram vial equipped with a small glass bead to enhance agitation. Dichloromethane (800 μL) was added to the vial, and the solution was cooled to 0 ˚C and allowed to equilibrate for 0.5 h. Neat dimethyl malonate (46 μL, 0.4 mmol) was added, followed by *N,O*-bis(trimethylsilyl)acetamide (100 μL, 0.4 mmol), and a 0.2 M stock solution of 1,3-diphenylpropenyl acetate (1 mL, 0.2 mmol). The reaction was agitated for 12 h at 0 ˚C. The solvent was removed, and the residue was passed through a short silica plug (20% EtOAc/hexanes). The reaction mixture was analyzed via HPLC (Chiralcel OD analytical column; eluting with 99:1 hexanes/2-propanol, flow rate 0.5 mL/min, 254 nm, t_1=20.5 min, t_2=21.4 min). The HPLC separation was calibrated using racemic material. The optical rotation of the product was compared with the literature rotation to assign absolute configuration.[6]

Methyl (*R*)-*E*-2-Methoxycarbonyl-3,5-dimethylpent-4-enoate (Reaction 2). In a nitrogen atmosphere, allylpalladium chloride dimer (1.8 mg, 0.0049 mmol), the ligand **11a** (3.2 mg, 0.009 mmol), and solid potassium acetate (2 mg, 0.02 mmol) was

weighed into a half-dram vial equipped with a small glass bead to enhance agitation. Dichloromethane (800 μL) was added to the vial and allowed to equilibrate for 0.5 h at 25 ˚C. Neat dimethyl malonate (46 μL, 0.4 mmol) was added, followed by *N,O*-bis(trimethylsilyl)acetamide (100 μL, 0.4 mmol), and a 0.2 M stock solution of 1,3-dimethylpropenyl pivalate (1 mL, 0.2 mmol). The reaction was agitated for 48 h at 25 ˚C. The solvent was removed, and the residue was passed through a short silica plug (20% EtOAc/hexanes). Then the reaction mixture was analyzed via GC (70 ˚C; retention time, t_1=71.7 min, t_2=72.9 min; the chiral column was prepared by Vigh *et al.*,[7] Texas A & M; 30.7 mx0.25 mm, 30% β-*tert*-butyldimethylsilyl cyclodextrin derivative in OV-1701-vi of 0.25 μm film thickness). The GC separation was calibrated using racemic material.

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