Experimental Section

General Procedures. All reactions were performed in oven-dried glassware under nitrogen unless otherwise noted. All reagents were purchased from Aldrich and used as received. Hydrogenations were assembled in a Braun Labmaster 100 Glovebox. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl under nitrogen. Methanol was distilled from $Mg(OCH_3)_2$. Chiral DuPHOS and BPE ligands as well as the corresponding rhodium catalysts were prepared as described in the literature.[4] The Diisopropylferroucenyl (DiPFc)-Rh^+ catalyst was prepared as in the literature. Hydrogen gas (99.99%) was purchased from National Welders Inc. (Raleigh, NC) and used as received. All other chemicals were purchased from Aldrich and used as received. Column chromatography was performed using EM Science silica gel 60 (230-400 mesh). GC analyses were performed on a Hewlett Packard Model HP 5890 Series II GC. HPLC analyses were performed on a Hewlett Packard Model HP 1090 Series II LC interfaced with a HP Vectra 486/66U computer workstation. Optical rotations were obtained using a Perkin Elmer Model 241 Polarimeter. HRMS were obtained using a Jeol JMS-SX 102A Mass Spectrometer. NMR data were obtained using a Varian XL-400 (400 MHz ^1H, 100.6 MHz ^{13}C, 161.9 MHz ^{31}P).

α-HYDROXY PHOSPHONATES

1-Benzoyloxy-1-dimethylphosphonylethene (3a). Acetyl chloride (9.0 mL, 127.0 mmol) was chilled to 0 °C in an oven dried flask fitted with an addition funnel. Trimethylphosphite (15.0 mL, 127.0 mmol) was added dropwise. A balloon was used to compensate for the released methylchloride. When the addition was complete the reaction was warmed to 70 °C and stirred for 15 minutes. Vacuum distillation was used to isolate 15.7 g (81%) of dimethyl acetyl phosphonate as a colorless oil. Benzoic anhydride (11.2 g, 49.3 mmol) was combined with the α-keto phosphonate (5.00 g, 32.9 mmol) and chilled to 0 °C. DBU (4.90 mL, 32.9 mmol) was added slowly and the reaction was stirred for 15 minutes, warming to room temperature. The reaction mixture was diluted with EtOAc (150 mL), washed with sat. $NaHCO_3$ (75 mL x 3) and brine (75 mL) then dried with $MgSO_4$. Solvent was removed *in vacuo* to give a colorless oil. Purification using silica gel chromatography (4:1 EtOAc/Hex) gave 3.79 g (45%) of **3a** as a waxy white solid. ^1H NMR ($CDCl_3$) δ 8.10 (d, 2H, J=7.8 Hz), 7.63 (t, 1H, J=7.6 Hz), 7.49 (t, 2H, J=7.9 Hz), 6.20 (dd, 1H, J_{PH}=11.1 Hz, J=2.0 Hz), 5.94 (dd, 1H, J_{PH}=35.2 Hz, J=2.0 Hz), 3.84 (d, 6H, J_{PH}=11.3 Hz). ^{13}C NMR ($CDCl_3$) δ 163.8 (d, J_{PC}=2.3 Hz), 144.8 (d, J_{PC}=223.8 Hz), 133.7, 130.0, 128.4, 121.8 (d, J_{PC}=24.5Hz), 53.1 (d, J_{PC}=5.0 Hz). ^{31}P NMR ($CDCl_3$) δ 12.36. HRMS (FAB) *m/z* 257.0587 (MH^+ exact mass calculated for $C_{11}H_{14}O_5P$, 257.0579).

The following compounds (**3b-e**) were prepared by the model procedure.
***E*-1-Benzoyloxy-1-dimethylphosphonyl-1-propene (3b)**. Obtained **3b** as a colorless oil (55%). ^1H NMR ($CDCl_3$) δ 8.13 (d, 2H, J=7.1 Hz), 7.63 (t, 1H, J=7.5 Hz), 7.50 (t, 2H, J=7.4 Hz), 6.69 (dq, 1H, J_{PH}=10.5 Hz, J=7.0 Hz), 3.80 (d, 6H, J_{PH}=11.2 Hz), 1.75 (dd, 3H, J_{PH}=3.0 Hz, J=7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 163.2, 138.1 (d, J_{PC}=230.5 Hz), 134.8 (d, J_{PC}=26.7 Hz), 133.6, 130.0, 128.4, 52.9 (d, J_{PC}=4.9 Hz), 11.9 (d, J_{PC}=13.0 Hz). ^{31}P NMR ($CDCl_3$) δ 13.70. HRMS (FAB) *m/z* 271.0743 (MH^+ exact mass calculated for $C_{12}H_{16}O_5P$, 271.0735).

***E*-1-Benzoyloxy-1-dimethylphosphonyl-1-butene (3c)**. After chromatography, **3c** was obtained as a colorless oil (69%). ^1H NMR ($CDCl_3$) δ 8.11 (d, 2H, J=8.0 Hz), 7.63 (t, 1H, J=7.6 Hz), 7.50 (t, 2H, J=7.6 Hz), 6.59 (dt, 1H, J_{PH}=10.8 Hz, J=7.6 Hz), 3.79 (d, 6H, J=11.2 Hz), 2.15 (ddq, 2H, J_{PH}=3.2 Hz, J=7.2, 7.2 Hz), 1.07 (t, 3H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 163.3, 141.1 (d, J_{PC}=25.2 Hz), 136.3 (d, J_{PC}=229.4 Hz),

133.5, 129.9, 128.9, 52.8 (d, J_{PC}=4.9 Hz), 19.8 (d, J_{PC}=12.2 Hz), 12.2. ^{31}P ($CDCl_3$) NMR δ 13.90. HRMS (FAB) *m/z* 285.0889 (MH^+ exact mass calculated for $C_{13}H_{18}O_5P$, 285.0892).

***E*-1-Benzoyloxy-1-dimethylphosphonyl-3-methyl-1-butene (3d)**. After chromatography, **3d** was obtained as a colorless oil (43%). ^{1}H NMR ($CDCl_3$) δ 8.05 (d, 2H, J=8.0 Hz), 7.57 (t, 1H, J=7.2 Hz), 7.43 (t, 2H, J=7.2 Hz), 6.38 (dd, 2H, J_{PH}=10.0 Hz, J=10.0 Hz), 3.74 (d, 6H, J=11.2 Hz), 2.63-2.57 (m, 1H), 1.00 (d, 6H, J=6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 163.8, 146.2 (d, J_{PC}=24.4 Hz), 133.7, 134.9 (d, J_{PC}=229.3 Hz), 130.1, 128.5, 53.0 (d, J_{PC}=5.0 Hz), 26.5(d, J_{PC}=11.9 Hz), 21.5. ^{31}P NMR ($CDCl_3$) δ 14.26. HRMS (FAB) *m/z* 299.1063 (MH^+ exact mass calculated for $C_{14}H_{20}O_5P$, 299.1048).

***E*-1-Benzoyloxy-1-dimethylphosphonyl-1-hexene (3e)**. After chromatography, **3e** was obtained as a colorless oil (86%). ^{1}H NMR ($CDCl_3$) δ 8.12 (d, 2H, J=7.2 Hz), 7.63 (t, 1H, J=7.6 Hz), 7.50 (t, 2H, J=8.0 Hz), 6.60 (dt, 1H, J_{PH}=10.8 Hz, J=7.2 Hz), 3.79 (d, 6H, J_{PH}=10.8 Hz), 2.15 (dt, 2H, J=7.2 Hz), 1.45 (tt, 2H, J=7.6 Hz, 7.6 Hz, 7.6 Hz), 1.34 (tt, 2H, J=7.6 Hz, 7.6 Hz, 7.6 Hz), 0.88 (t, 3H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 163.4, 140.0 (d, J_{PC}=25.3 Hz), 136.9 (d, J_{PC}=229.0 Hz), 133.6, 130.0, 128.5, 128.4, 52.9 (d, J_{PC}=3.4 Hz), 29.8, 26.0 (d, J_{PC}=12.3 Hz). ^{31}P NMR ($CDCl_3$) δ 13.90. HRMS (FAB) *m/z* 313.1192 (MH^+ exact mass calculated for $C_{15}H_{22}O_5P$, 313.1205).

***E*-1-Benzoyloxy-1-dimethylphosphonyl-1-decene (3f).** Decanoyl chloride (10.9 mL, 52.4 mmol) was chilled to 0 ºC in an oven dried flask fitted with an addition funnel. Trimethylphosphite (6.2 mL, 52.4 mmol) was added dropwise. A balloon was used to compensate for the released methylchloride. When the addition was complete the reaction was warmed to 70 ºC and stirred for 15 minutes. Mixture was pumped on to remove volatile impurities then the crude material was taken directly to next step. Benzoic anhydride (7.0 g, 26.5 mmol) and THF (10 mL) were combined with the dimethyldecanoylphosphonate and chilled to 0 ºC. DBU (4.8 mL, 31.8 mmol) was added slowly and the reaction was stirred for 15 minutes, warming to room temperature. The reaction mixture was diluted with EtOAc (150 mL) and washed with sat. $NaHCO_3$ (75 mL x 3) and brine (75 mL). Organic phase was dried with $MgSO_4$ and the solvent was removed *in vacuo*. Material was purified by silica gel chromatography (1:3 EtOAc/Hex). Obtained 7.93 g (81%, 2 steps) of **3f** as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 8.11 (d, 2H, J=7.6 Hz), 7.63 (t, 1H, J=7.2 Hz), 7.50 (t, 2H, J=8.0 Hz), 6.60 (dt, 1H, J_{PH}=3.2 Hz, J=7.6 Hz), 3.79 (d, 6H, J_{PH}=10.4 Hz), 2.13 (ddt, 2H, J_{PH}=3.2 Hz, J=7.6 Hz, 7.6 Hz), 1.46 (dt, 2H, J=7.6 Hz), 1.31-1.19 (m, 10H), 0.86 (t, 3H, J=6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 163.5, 140.2 (d, J_{PC}=25.7 Hz), 136.9 (d, J_{PC}=229.0 Hz), 133.7, 130.1, 128.7, 128.5, 53.0 (d, J_{PC}=4.9 Hz), 31.7, 29.1, 29.0, 27.8, 26.4, 26.3, 22.5, 14.0. ^{31}P NMR ($CDCl_3$) δ 14.00. HRMS (FAB) *m/z* 369.1830 (MH^+ exact mass calculated for $C_{19}H_{30}O_5P$, 369.1831).

The following compounds (**3g-h**) were prepared by the model procedure.

***E*-1-Benzoyloxy-3-cyclopentyl-1-dimethylphosphonyl-1-propene (3g).** After chromatography, **3g** was obtained as a colorless oil (59%, 2 steps). ^{1}H NMR ($CDCl_3$) δ 8.11 (d, 2H, J=7.6 Hz), 7.63 (t, 1H, J=7.6 Hz), 7.50 (t, 2H, J=7.6 Hz), 6.62 (dt, 1H, J_{PH}=10.8 Hz, J=7.2 Hz), 3.79 (d, 6H, J_{PH}=10.8 Hz), 2.15 (ddd, 2H, J_{PH}=2.8 Hz, J=7.2 Hz, 7.2 Hz), 1.95 (ttt, 1H, J=7.6 Hz, 7.6 Hz, 7.6 Hz), 1.81-1.74 (m, 2H), 1.64-1.46 (m, 4H), 1.19-1.09 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 163.5, 139.5 (d, J_{PC}=25.6 Hz), 137.0 (d, J_{PC}=229.0 Hz), 133.7, 130.1, 128.7, 128.5, 53.0 (d, J_{PC}=4.9 Hz), 38.7, 32.4, 32.3, 24.9. ^{31}P NMR ($CDCl_3$) δ 14.10. HRMS (FAB) *m/z* 339.1352 (MH^+ exact mass calculated for $C_{17}H_{24}O_5P$, 339.1361).

***E*-1-Benzoyloxy-1-dimethylphosphonyl-2-(4-methoxyphenyl)ethene (3h)**. After chromatography, **3h** was obtained a viscous, colorless oil (58%, 2 steps). ^{1}H NMR ($CDCl_3$) δ 8.17 (d, 2H, J=7.6 Hz), 7.66 (t, 1H, J=7.6 Hz), 7.53 (d, 2H, J=8.0 Hz), 7.49 (d, 2H, J=9.2 Hz), 7.26 (d, 2H, J_{PH}=11.6 Hz), 6.81 (d, 2H, J=9.2 Hz), 3.84 (d, 6H, J_{PH}=11.2 Hz), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 163.6, 160.7, 134.4 (d, J_{PC}=230.1 Hz), 134.5 (d, J_{PC}=29.7 Hz), 131.4, 130.6, 130.2, 128.7, 124.7 (d, J_{PC}=16.4 Hz), 55.2, 53.1 (d, J_{PC}=4.9 Hz). ^{31}P NMR ($CDCl_3$) δ 15.33. HRMS (FAB) *m/z* 363.1009 (MH^+ exact mass calculated for $C_{13}H_{20}O_6P$, 363.0998).

Asymmetric Hydrogenations: General Procedure: Under an N_2 atmosphere, a Fisher-Porter tube was charged with the enolbenzoate phosphonate substrate (~0.050 g), anhydrous, degassed solvent and catalyst (0.001 g). After five vacuum/H_2 cycles, the tube was pressurized to an initial pressure of 4 or 6 atms H_2. Reactions stirred at room temperature for the times indicated. Conversion determined by ^{1}H or ^{31}P NMR analyses. Reaction mixtures were concentrated then passed through a silica gel plug using ethyl acetate as an elutant to remove catalyst. Without further purification, the enantiomeric excesses were determined with an aliquot of the crude product. Racemate for **4a** was prepared through hydrogenation of **3a** with the DiPFc-Rh^+ catalyst. Other racemates were prepared by the hydrogenation of the corresponding enolbenzoates with 10% Pd/C. Enantiomeric excesses determined by comparison of the enantiomerically enriched sample to the racemate on chiral HPLC. Enantiomeric excesses of benzoyl protected α-hydroxy phosphonates determined by HPLC analysis using Daicel chiral columns and UV detection at 230 nm. Column and conditions are given for each compound.

(*S*)-1-Benzoyloxy-1-dimethylphosphonylethane (4a). ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, J=7.6 Hz), 7.59 (t, 1H, J=7.6 Hz), 7.46 (t, 2H, J=8.0 Hz), 5.57 (dq, 1H, J_{PH}=8.4 Hz, J=7.2 Hz), 3.84 (d, 3H, J_{PH}=10.4 Hz), 3.83 (d, 3H, J_{PH}=10.4 Hz), 1.61 (dd, 3H, J_{PH}=16.4 Hz, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 165.2, 133.4, 129.8, 129.3, 128.4, 64.5 (d, J_{PC}=170.9 Hz), 53.5 (d, J_{PC}=6.8 Hz), 53.2 (d, J_{PC}=6.8 Hz), 15.2. ^{31}P NMR ($CDCl_3$) δ 25.84. HRMS (FAB) *m/z* 259.0741 (MH^+ exact mass calculated for $C_{11}H_{16}O_5P$, 259.0735). $[\alpha]^{25}_D$=-17.87° (c=0.0043, $CHCl_3$). Enantiomeric excess determination; Chiralcel OJ, 2-propanol, flow rate 0.5 mL/min., t_R=15.93 (*S*, 98%), 18.31 (*R*, 2%) min.

(*R*)-1-Benzoyloxy-1-dimethylphosphonylpropane (4b). ^{1}H NMR ($CDCl_3$) δ 8.09 (d, 2H, J=6.8 Hz), 7.60 (t, 1H, J=7.2 Hz), 7.47 (t, 2H, J=7.2 Hz), 5.49 (ddd, 1H, J_{PH}=9.6 Hz, J=8.4 Hz, 4.4 Hz), 3.81 (d, 3H, J_{PH}=10.8 Hz), 3.80 (d, 3H, J_{PH}=10.8 Hz), 2.14 (m, 2H), 1.05 (dt, 3H, J_{PH}=0.8 Hz, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 165.6, 133.4, 129.8, 129.2, 128.5, 69.2 (d, J_{PC}=167.2 Hz), 53.4 (d, J_{PC}=7.6 Hz), 53.1 (d, J_{PC}=6.1 Hz), 10.3, 10.1. ^{31}P NMR ($CDCl_3$) δ 25.19. HRMS (FAB) *m/z* 273.0888 (MH^+ exact mass calculated for $C_{12}H_{18}O_5P$, 273.0892). $[\alpha]^{25}_D$=-12.10° (c=0.0050, $CHCl_3$). Enantiomeric excess determination; Chiralpak OT, hexanes/2-propanol 9:1, flow rate 0.5 mL/min., t_R=31.09 (*S*, 7%), 34.89 (*R*, 93%) min.

(*R*)-1-Benzoyloxy-1-dimethylphosphonylbutane (4c). ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, J=7.2 Hz), 7.60 (t, 1H, J=7.2 Hz), 7.46 (t, 2H, J=7.2 Hz), 5.58 (dt, 1H, J_{PH}=5.6 Hz, J=8.4 Hz), 3.81 (d, 3H, J_{PH}=10.8 Hz), 3.80 (d, 3H, J_{PH}=10.8 Hz), 2.03-1.94 (m, 2H), 1.55-1.46 (m, 2H), 0.95 (t, 3H, J=7.6 Hz). ^{13}C NMR ($CDCl_3$) δ 165.5 (d, J_{PC}=5.0 Hz), 133.4, 129.8, 129.2, 128.5, 67.6 (d, J_{PC}=167.1 Hz), 53.4 (d, J_{PC}=6.9 Hz), 53.1 (d, J_{PC}=6.0 Hz), 31.4, 18.9, 18.8. ^{31}P NMR ($CDCl_3$) δ 25.40. HRMS (FAB) *m/z* 287.1047 (MH^+ exact mass calculated for $C_{13}H_{20}O_5P$, 287.1048). $[\alpha]^{25}_D$=-14.29° (c=0.0035, $CHCl_3$). Enantiomeric excess determination; Chiralpak OT, hexanes/2-propanol 9:1, flow rate 0.5 mL/min., t_R=23.85 (*S*, 4%), 27.70 (*R*, 96%) min.

(*R*)-1-Benzoyloxy-1-dimethylphosphonyl-3-methylbutane (4d). ^{1}H NMR ($CDCl_3$) δ 8.04 (d, 2H, J=7.2 Hz), 7.55 (t, 1H, J=7.2 Hz), 7.42 (t, 2H, J=7.6 Hz), 5.62 (ddd, 1H, J_{PH}=11.6 Hz, J=8.8 Hz, 2.8 Hz), 3.75 (d, 6H, J_{PH}=10.8 Hz), 2.02-1.91 (m, 1H), 1.76-1.62 (m, 1H), 0.91 (dd, 6H, J=4.4 Hz, 6.4 Hz). ^{13}C NMR ($CDCl_3$) δ 165.4 (d, J_{PC}=4.6 Hz), 133.4, 129.8, 129.3, 128.5, 66.3 (d, J_{PC}=166.7 Hz), 53.4 (d, J_{PC}=7.2 Hz), 53.2 (d, J_{PC}=6.1 Hz), 38.0, 24.6, 24.5, 23.19, 23.15, 21.3, 21.2. ^{31}P NMR ($CDCl_3$) δ 25.70. $[\alpha]^{25}_{D}$=-20.29° (c=0.0066, $CHCl_3$). HRMS (FAB) *m/z* 301.1197 (MH^+ exact mass calculated for $C_{14}H_{22}O_5P$, 301.1205). Enantiomeric excess determination; Chiralpak OT, hexanes/2-propanol 95:5, flow rate 0.5 mL/min., t_R=33.47 (*S*, 4%), 38.18 (*R*, 96%) min.

(*R*)-1-Benzoyloxy-1-dimethylphosphonylhexane (4e). ^{1}H NMR ($CDCl_3$) δ 8.09 (d, 2H, J=7.2 Hz), 7.60 (t, 1H, J=7.6 Hz), 7.47 (t, 2H, J=7.6 Hz), 5.56 (dt, 1H, J_{PH}=6.0 Hz, J=8.0 Hz), 3.83-3.76 (m, 6H), 2.03-1.94 (m, 2H), 1.49-1.35 (m, 2H), 1.34-1.24 (m, 4H), 0.86 (t, 3H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 165.5 (d, J_{PC}=4.9 Hz), 133.4, 129.8, 129.3, 128.5, 67.9 (d, J_{PC}=167.1 Hz), 53.4 (d, J_{PC}=7.2 Hz), 53.1 (d, J_{PC}=6.4 Hz), 31.2, 29.4, 25.3, 25.2, 22.3, 13.9. ^{31}P NMR ($CDCl_3$) δ 25.37. HRMS (FAB) *m/z* 315.1370 (MH^+ exact mass calculated for $C_{15}H_{24}O_5P$, 315.1361). $[\alpha]^{25}_{D}$=-16.80° (c=0.0035, $CHCl_3$). Enantiomeric excess determination; Chiralpak OT, hexanes/2-propanol 9:1, flow rate 0.5 mL/min., t_R=14.70 (*S*, 5%), 23.22 (*R*, 95%) min.

(*R*)-1-Benzoyloxy-1-dimethylphosphonyldecane (4f). ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, J=8.4 Hz), 7.60 (t, 1H, J=7.6 Hz), 7.47 (t, 2H, 7.6 Hz), 5.56 (dt, 1H, J_{PH}=5.6 Hz, J=8.4 Hz), 3.804 (d, 3H, J_{PH}=10.8 Hz), 3.801 (d, 3H, J_{PH}=10.8), 2.03-1.94 (m, 2H), 1.48-1.18 (m, 14H), 0.86 (t, 3H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 165.5 (d, J_{PC}=4.9 Hz), 133.4, 129.9, 129.3, 128.5, 67.9 (d, J_{PC}=166.8 Hz), 53.4 (d, J_{PC}=6.9 Hz), 53.2 (d, J_{PC}=6.1 Hz), 31.8, 29.43, 29.40, 29.3, 29.2, 29.1, 25.7, 25.5, 22.6, 14.1. ^{31}P NMR ($CDCl_3$) δ 25.39. HRMS (FAB) *m/z* 371.1978 (MH^+ exact mass calculated for $C_{19}H_{32}O_5P$, 371.1987). $[\alpha]^{25}_{D}$=-14.51° (c=0.0057, $CHCl_3$). Enantiomeric excess determination; Chiralpak OT, 2-propanol, flow rate 0.5 mL/min., t_R=16.10 (*S*, 6%), 19.86 (*R*, 94%) min.

(*R*)-1-Benzoyloxy-3-cyclopentyl-1-dimethylphosphonylpropane (4g). ^{1}H NMR ($CDCl_3$) δ 8.09 (d, 2H, J=7.2 Hz), 7.60 (t, 1H, J=7.2 Hz), 7.47 (t, 2H, J=7.6 Hz), 5.55 (dt, 1H, J_{PH}=5.6 Hz, J=8.4 Hz), 3.81 (d, 3H, J_{PH}=10.4 Hz), 3.80 (d, 3H, J_{PH}=10.8), 2.08-1.91 (m, 2H), 1.79-1.70 (m, 2H), 1.60-1.35 (m, 7H), 1.12-1.00 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 165.4 (d, J_{PC}=4.6 Hz), 133.3, 129.8, 129.2, 128.4, 68.1 (d, J_{PC}=166.7 Hz), 53.3 (d, J_{PC}=6.8 Hz), 53.1 (d, J_{PC}=6.1 Hz), 39.6, 32.5, 32.4, 32.0, 31.9, 28.7, 25.0. ^{31}P NMR ($CDCl_3$) δ 25.32. HRMS (FAB) *m/z* 341.1522 (MH^+ exact mass calculated for $C_{11}H_{16}O_5P$, 341.1518). $[\alpha]^{25}_{D}$=-17.06° (c=0.0036, $CHCl_3$). Enantiomeric excess determination; Chiralpak OT, hexanes/2-propanol 3:2, flow rate 0.5 mL/min., t_R=14.87 (*S*, 5%), 23.05 (*R*, 95%) min.

(*S*)-1-Benzoyloxy-1-dimethylphosphonyl-1-(4-methoxyphenyl)ethane (4h). ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 2H, J=7.2 Hz), 7.57 (t, 1H, J=7.2 Hz), 7.43 (t, 2H, J=7.2 Hz), 7.17 (d, 2H, J=8.8 Hz), 6.76 (d, 2H, J=8.8 Hz), 5.72 (ddd, 1H, J_{PH}=10.0 Hz, J=8.0 Hz, 4.0 Hz), 3.78 (d, 3H, J=10.8 Hz), 3.77 (d, 3H, J=10.8 Hz), 3.73 (s, 3H), 3.33-3.25 (m, 1H), 3.23-3.12 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 165.0, 158.5, 133.3, 131.4, 130.2, 129.8, 129.1, 128.4, 128.1, 113.9, 68.7 (d, J_{PC}=164.8 Hz), 55.1, 53.4 (d, J_{PC}=6.9 Hz), 53.2 (d, J_{PC}=6.1 Hz), 34.9. ^{31}P NMR ($CDCl_3$) δ 24.56. HRMS (FAB) *m/z* 365.1165 (MH^+ exact mass calculated for $C_{18}H_{22}O_6P$, 365.1154). $[\alpha]^{25}_{D}$=+55.29° (c=0.0168, $CHCl_3$). Enantiomeric excess determination; Chiralcel OB, hexanes/2-propanol 9:1, flow rate 0.5 mL/min., t_R= 55.28 (*S*, 84%), 84.63 (*R*, 16%) min.

(*R*)-1-dimethylphosphonyl-1-hydroxy-3-methylbutane (5d). A purified sample of **4d** (20.4 mg, 0.1 mmol) was combined with anhydrous K_2CO_3 (30 mg, 3 eq.) in MeOH. Reaction was stirred 2 hours at room temperature. Methanol was removed by evaporation. Residue was diluted in EtOAc (10 mL) and washed with sat. $NaHCO_3$ (10 mL) and brine (10mL). Organic phase was dried with $MgSO_4$ and solvent was removed *in vacuo*. Recovered 10 mg (75%) of **5** as a colorless oil. Spectral data matched that appearing in the literature.[6a]

α-AMINO PHOSPHONATES

Asymmetric Hydrogenations: General Procedure: Under an N_2 atmosphere, a Fisher-Porter tube was charged with the enamido phosphonate substrate (0.050 to 0.100 g), anhydrous, degassed solvent (3 mL) and catalyst (0.001 g). After five vacuum/H_2 cycles, the tube was pressurized to an initial pressure of 4 atms H_2. Reactions were stirred at room temperature for the times indicated. Conversions were determined by ^1H or ^{31}P NMR analyses. Upon completion, reaction mixtures were concentrated and passed through a silica gel plug using ethyl acetate as an elutant to remove catalyst. Without further purification, the enantiomeric excesses were determined on an aliquot of the crude product. Racemates for each sample were prepared by hydrogenation of the corresponding enamide with the DiPFc-Rh^+ catalyst. Enantiomeric Excesses determined by comparison of the enantiomerically enriched sample to the racemate on chiral GC. GC conditions and column used are given for each compound separation.

(*R*)-1-(Acetylamino)-1-dimethylphosphonylethane (8). ^1H NMR ($CDCl_3$) δ 6.88 (d, 1H, J=8.8 Hz), 4.62-4.50 (m, 1H), 3.78 (d, 3H, J_{PH}=10.8 Hz), 3.77 (d, 3H, J_{PH}=10.8 Hz), 2.034 (s, 1.5H), 2.032 (s, 1.5H), 1.38 (dd, 3H, J_{PH}=16.8 Hz, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 169.64, 169.59, 53.4 (d, J_{PC}=6.8 Hz), 52.8 (d, J_{PC}=6.8 Hz), 40.1 (d, J_{PC}=157.5 Hz), 22.9, 15.5. ^{31}P NMR ($CDCl_3$) δ 30.20. HRMS (FAB) *m/z* 196.0743 (MH^+ exact mass calculated for $C_6H_{15}NO_4P$, 196.0739). $[\alpha]_D^{25}$=-55.31° ($CHCl_3$, c=0.0113). Enantiomeric excess determination; Chirasil-*L*-Val column, inj. press. 10 psi, T=155 °C, t_R=9.74 (*R*), 10.82 (*S*) min. Under optimized reaction conditions observed 95% ee.

(*S*)-1-(Benzyloxycarbonylamino)-1-dimethylphosphonylethane (9a). ^1H NMR ($CDCl_3$) δ 7.30-7.38 (m, 5H), 5.25 (d, 1H, J=9.2 Hz), 5.12 (s, 2H), 4.26-4.16 (m, 1H), 3.77 (d, 2H, J_{PH}=10.4 Hz), 3.73 (d, 2H, J_{PH}=10.4 Hz), 1.39 (dd, 3H, J_{PH}=16.8 Hz, J=7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 155.6, 136.1, 128.5, 128.1, 128.0, 67.1, 53.3 (d, J_{PC}=7.2 Hz), 53.0 (d, J_{PC}=7.2 Hz), 42.8 (d, J_{PC}=158.3 Hz), 15.8. ^{31}P NMR ($CDCl_3$) δ 29.92. HRMS (FAB) *m/z* 288.1002 (MH^+ exact mass calculated for $C_{12}H_{19}NO_5P$, 288.1001). $[\alpha]_D^{25}$=+15.62° ($CHCl_3$, c=0.0065). Enantiomeric excess determination; Chirasil-*L*-Val column, inj. press. 20 psi, T=180 °C, t_R=10.59 (*R*), 11.73 (*S*) min. Under optimized reaction conditions observed 95% ee.