Supporting information:

Phosphonate-Directed Catalytic Asymmetric Hydroboration: Delivery of Boron to the More Substituted Carbon Leading to Chiral Tertiary Benzylic Boronic Esters

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(1) General information

All preparative reactions were carried out under a dry nitrogen atmosphere unless otherwise indicated. Tetrahydrofuran (THF) was freshly distilled over sodium and benzophenone before using in CAHB reactions. Pinacolborane (pinBH) was obtained from Acros Organics MS (97% purity, stabilized with triethylamine) and was distilled under nitrogen (760 mm Hg, 150 ^{o}C) prior to use. For long term storage, the distilled pinacolborane was stored in freezer in 8 mL vials with airtight screw cap under nitrogen. All substrates were subjected to high vacuum (*ca.* 1 mm Hg) at 100 ^{o}C for an hour to remove any residual diethyl phosphite, triethyl phosphite or triethyl phosphate. The latter are trace contaminants in commercial diethyl phosphite, and if present in even trace quantitates in the substrate, can greatly diminish the activity of the chiral rhodium catalyst. For convenience, CAHB reactions were set up in glovebox under a dry nitrogen atmosphere, although we have no evidence that use of the glove box is essential. Yields reported for the boronic esters/derivatives are an average of at least 2 runs.

Synthesized compounds were purified by flash chromatography using EMD Silica Gel 60 Geduran®. Thin Layer Chromatography analyses were performed on Analtech Silica Gel HLF (0.25 mm) precoated analytical plates and visualized with use of handheld short wavelength UV light, iodine stain (molecular iodine adsorbed on silica gel) or $KMnO_4$ stain ($KMnO_4$, K_2CO_3, NaOH and H_2O). HPLC analyses were performed with use of an ISCO model 2360 HPLC and Chiral Technologies, Inc Daicel Chiral HPLC 250 x 4.6 mm columns (column used is indicated below). HPLC grade solvents were used and samples were prepared in the indicated eluent solvent. HPLC analysis is monitored with UV-VIS detector (Shimadzu SPD-10AVP/10AVP, typical λ = 210 nm unless otherwise indicated).

NMR spectra were recorded on 300, 400 or 700 MHz Bruker Advance NMR spectrometers in the deuterated solvent specified. The solvent residual peaks were used for reference and spectra calibration unless otherwise indicated. Rather complex splitting patterns are found in the NMR spectra due to phosphorus-hydrogen coupling ($J_{P\text{-}H}$) and phosphorus-carbon coupling ($J_{C\text{-}P}$). Phosphorus-carbon coupling is seen up to 5 bonds ($^{5}J_{C\text{-}P}$); these splitting patterns were resolved and the corresponding coupling constants assigned. The quaternary carbon atoms connected directly to boron in tertiary boronic esters or trifluoroborate salts were not seen in the ^{13}C NMR spectra due to quadrupolar relaxation of boron. Peaks in the NMR spectra are described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), quin (quintet), dd (doublet of doublets), m (unresolved multiplet), etc. In several cases, C_6D_6 proved to be a superior NMR solvent for resolving the signals for diastereomers in ^{31}P NMR spectra for diastereoenriched chiral boronic esters. However, ^{1}H and ^{13}C NMR data are reported only for the major diastereomer.

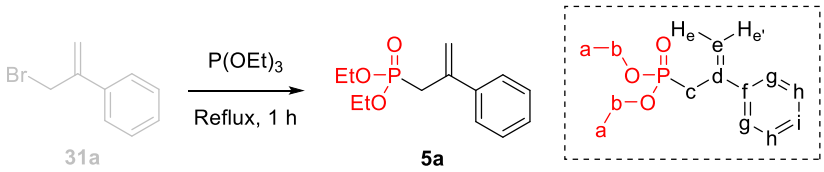
IR spectra were recorded using an Avatar 360 FT-IR instrument. Optical rotations were typically measured as 1.0 g/100 mL (i.e., c = 1.0) solutions in the indicated solvent using an Autopol III automatic polarimeter. Specific rotation values are reported in units of deg dm^{-1} cm^3 g^{-1}. EI/ESI-HRMS analyses were carried out by the Nebraska Center for Mass Spectrometry.

The Routine Preparation of Synthetic Precursors. The Supporting Information given below for the preparation and CAHB of allylic phosphonates starts with the allyl bromide. These precursors were obtained either from (1) direct allylic bromination of α-methyl styrene using NBS (for substrate **5a**),[1] or (2) bromination of allylic alcohols using PBr_3[2] or NBS/PPh_3.[3] The allyl alcohols were obtained either via the CuI-catalyzed addition of the corresponding aryl Grignard reagent to propargyl alcohol[4] (e.g., for substrates **5b-k** and **5n**) or via Suzuki cross-coupling of the arylboronic acids with 2-iodoprop-2-en-1-ol (e.g., for thiophene derivatives **5l** and **5m**; typical conditions: 5 mol% $Pd(PPh_3)_4$, 2 eq. Cs_2CO_3, EtOH at 70ºC for 12 hours), or via the Horner-Wadsworth-Emmons olefination of triethyl-2-phosphono-2-(*o*-tolyl)acetate with formaldehyde (37% w/w in H_2O) in the case of substrate **5o**. The allyl alcohol precursors for the β-aryl trisubstituted substrates were derived from the Suzuki cross-coupling reaction of the corresponding (*Z*)-β-iodo-γ-(alkyl/aryl)-2-en-1-ol with the arylboronic acid derivatives for substrates in which the phosphonate and the γ-alkyl chain are trans to each other or via Stille cross coupling (with corresponding aryl bromides; typical conditions: 5 mol% $Pd(PPh_3)_4$, 2 eq. Cs_2CO_3, EtOH at 70ºC for 12 hours) for substrates in which the phosphonate and the γ-alkyl chain are cis to each other. The vinyl tin precursors were obtained via Pd-catalyzed hydrostannation of the corresponding alkynyl ester.[5] The α-vinyl tin allyl esters were reduced to the corresponding alcohols using DIBAL-H prior to their use in Stille cross coupling. Ligand **T2** was prepared according to our previously reported procedure.[6] Davis' Oxaziridine was prepared according to reported protocols.[7]

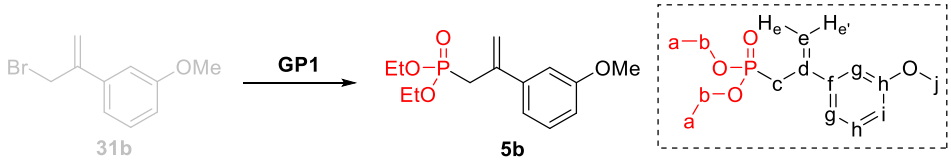
Comment on the Oxidation. We found that attempted oxidation of the crude CAHB reaction mixture led to unexpected side products and lower yields of the alcohol. In some cases, the boronic esters could not be cleanly separated by flash chromatography; nonetheless, the partially purified mixture of boronic esters and reduced products (if any) could be efficiently oxidized using standard conditions.

Comment on Absolute Configuration. The presence of the 2-thiophene subunit in the beta position of the substrates requires that the typical *E*-substrate substitution pattern is correctly described as Z since the 2-thienyl unit is assigned the highest priority. This also results in a switch from the expected *R*-configuration of boronic esters obtained using (*R,R*)-**T2** to S for the 2-thienyl products.

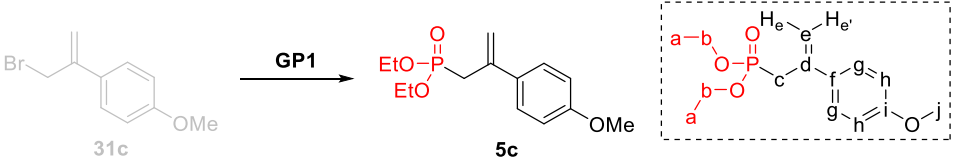
(2) Synthesis of methylidene substrates



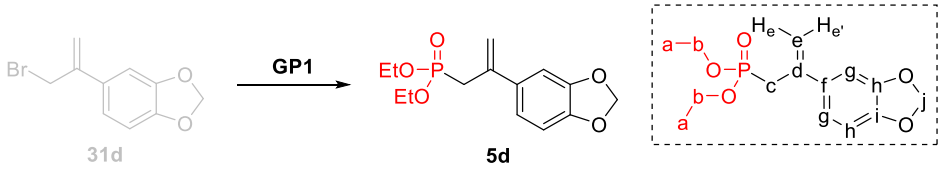
General procedure for the synthesis of conjugated allyl methylidene phosphonates via Michaelis-Arbuzov Rearrangement (GP1). Synthesis of **5a**: A mixture of allyl bromide **31a** (1.00 g, 5.07 mmol, 1.00 eq) and triethyl phosphite (0.38 mL, 2.20 mmol, 1.10 eq) is heated to reflux for 1 hour. Afterwards, the reaction mixture is cooled down to room temperature and flash chromatography on silica gel (ethyl acetate/hexanes 2:1) affords the desired phosphonate substrate **5a** (1.13 g, 88%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.26 (5H, m, aryl), 5.53 (1H, dd, J = 5.5 ($^4J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 5.37 (1H, dd, J = 5.5 ($^4J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 4.09-3.94 (4H, m, b), 3.08 (2H, dd, J = 22.4 ($^2J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, c), 1.21 (6H, t, J = 7.2 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.87 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 138.89 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 128.44 (aryl), 127.88 (aryl), 126.45 (aryl), 117.33 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 62.14 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 33.18 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 16.44 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.53 ppm; IR (neat) 2981 (aromatic C-H), 2906 (aliphatic C-H), 1624 (C=C), 1250 (P=O), 1052 (C-O), 1020 (C-O), 934 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{13}H_{19}O_3P$ = 254.1072, found 254.1071 *m/z*.



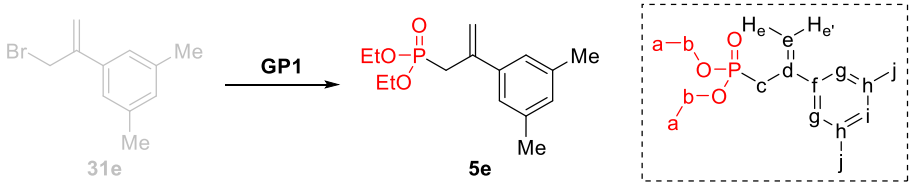
Synthesis of phosphonate functionalized alkene 5b: Following **GP1**, allyl bromide **31b** (568 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5b** (604 mg, 85%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, t, J = 8.0 Hz, aryl), 7.07-7.03 (2H, m, aryl), 6.83 (1H, dd, J = 2.0, 0.6 Hz, aryl), 5.52 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 5.36 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.09-3.94 (4H, m, b), 3.82 (3H, s, j), 3.05 (2H, d, $^2J_{P\text{-}H}$ = 22.0 Hz, c), 1.24 (6H, t, J = 7.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.69 (h), 142.43 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 138.77 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 129.39 (aryl), 118.96 (aryl), 117.47 (d, $^3J_{C\text{-}P}$ = 10 Hz, e), 113.30 (aryl), 112.29 (aryl), 62.14 (d, $^2J_{C\text{-}P}$ = 6 Hz, b), 55.39 (j), 33.19 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 16.44 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.50 ppm; IR (neat) 3056 (aromatic C-H), 2980 (aliphatic C-H), 1687 (C=C), 1665 (C=C), 1249 (P=O), 1022 (C-O), 952 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_4P$ = 284.1177, found 284.1175 *m/z*.



Synthesis of phosphonate functionalized alkene 5c: Following **GP1**, allyl bromide **31c** (568 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5c** (533 mg, 75%) as a colorless viscous oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, d, *J* = 8.8 Hz, g), 6.87 (2H, d, *J* = 8.8 Hz, g), 5.45 (1H, dd, *J* = 6.4 ($^4J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 5.26 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.09-3.94 (4H, m, b), 3.81 (3H, s, j), 3.04 (2H, d, $^2J_{P\text{-}H}$ = 22.0 Hz, c), 1.22 (6H, t, *J* = 7.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.46 (h), 138.11 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 133.23 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 127.59 (g), 115.64 (d, $^3J_{C\text{-}P}$ = 10 Hz, e), 113.75 (h), 62.14 (d, $^2J_{C\text{-}P}$ = 6 Hz, b), 55.43 (j), 33.25 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 16.47 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.72 ppm; IR (neat) 3056 (aromatic C-H), 2980 (aliphatic C-H), 1606 (C=C), 1512 (aromatic C=C), 1246 (P=O), 1051 (C-O), 1021 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_4P$ = 284.1177, found 284.1171 *m/z*.

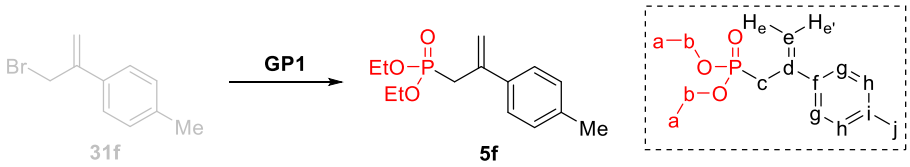


Synthesis of phosphonate functionalized alkene 5d: Following **GP1**, allyl bromide **31d** (602 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5d** (537 mg, 72%) as a colorless oil (Note: This substrate is air sensitive and slowly decomposes on exposure to air and turns into a dark brown mass. This compound was stored in vial with airtight screw cap under nitrogen in the freezer): TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (1H, d, *J* = 2.4 Hz, aryl), 6.97 (1H, d, *J* = 1.6 Hz, aryl), 6.78 (1H, d, *J* = 8.0 Hz, aryl), 5.96 (2H, s, j), 5.43 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 5.27 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.11-3.97 (4H, m, b), 3.01 (2H, d, $^2J_{P\text{-}H}$ = 22.4 Hz, c), 1.25 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.85 (h or i), 147.42 (h or i), 138.34 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 135.18 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 120.20 (aryl), 116.28 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 108.11 (aryl), 107.04 (aryl), 101.28 (j), 62.19 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 33.43 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 16.51 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.52 ppm; IR (neat) 2980 (aromatic C-H), 2903 (aliphatic C-H), 1604 (C=C), 1489 (aromatic C=C), 1441 (aromatic C=C), 1231 (P=O), 1020 (C-O), 933 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{19}O_5P$ = 298.0970, found 298.0974 *m/z*.

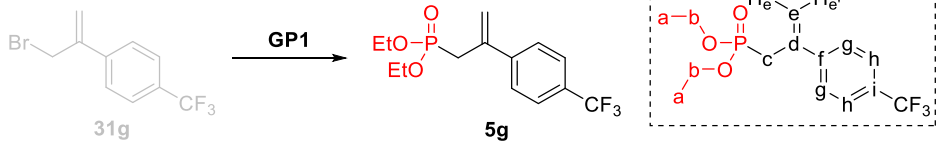


Synthesis of phosphonate functionalized alkene 5e: Following **GP1**, allyl bromide **31e** (563 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5e** (600 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (2H, s, g), 6.93 (1H, s, i), 5.50 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 5.33 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 4.09-3.95 (4H, m, b), 3.05 (2H, d, $^2J_{P\text{-}H}$ = 22 Hz, c), 2.32 (6H, s, j), 1.23 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.92 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 139.00 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 137.82 (h), 129.49 (i),

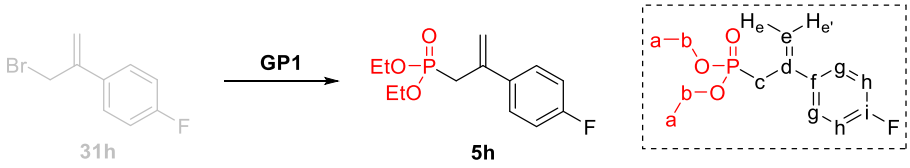
124.33 (g), 116.89 (d, $^{3}J_{C\text{-}P}$ = 10.8 Hz, e), 62.09 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b), 33.15 (d, $^{1}J_{C\text{-}P}$ = 138.65, c), 21.49 (j), 16.43 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.74 ppm; IR (neat) 2979 (aromatic C-H), 2910 (aliphatic C-H), 1599 (C=C), 1252 (P=O), 1053 (C-O), 1022 (C-O), 953 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{15}H_{23}O_3P$ = 282.1385, found 282.1380 *m/z*.



Synthesis of phosphonate functionalized alkene 5f: Following **GP1**, allyl bromide **31f** (528 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5f** (610 mg, 91%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (2H, d, *J* = 8.0 Hz, g or h), 7.16 (2H, d, *J* = 8.0 Hz, g or h), 5.52 (1H, d, $^{4}J_{P\text{-}H}$ = 5.2 Hz, H_e or $H_{e'}$), 5.33 (1H, d, $^{4}J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.10-3.95 (4H, m, b), 3.07 (2H, d, $^{2}J_{P\text{-}H}$ = 22.4 Hz, c), 2.36 (3H, s, j), 1.23 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.65 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, f), 137.97 (d, $^{2}J_{C\text{-}P}$ = 5 Hz, d), 137.74 (i), 129.16 (g or h), 126.34 (g or h), 116.53 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, e), 62.20 (d, $^{2}J_{C\text{-}P}$ = 7 Hz, b), 33.18 (d, $^{1}J_{C\text{-}P}$ = 138 Hz, c), 21.29 (j), 16.50 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.72 ppm; IR (neat) 2980 (aromatic C-H), 2905 (aliphatic C-H), 1621 (C=C), 1514 (aromatic C=C), 1391 (aromatic C=C), 1249 (P=O), 1052 (C-O), 1021 (C-O), 939 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_3P$ = 268.1228, found 268.1230 *m/z*.

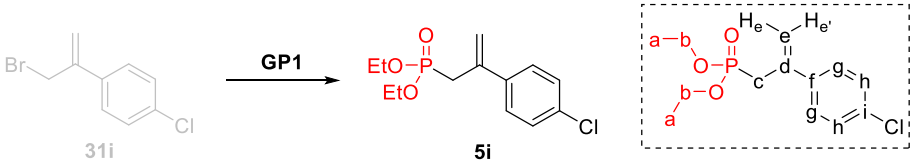


Synthesis of phosphonate functionalized alkene 5g: Following **GP1**, allyl bromide **31g** (663 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5g** (580 mg, 72%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (4H, s, aryl), 5.59 (1H, d, $^{4}J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 5.45 (1H, d, $^{4}J_{P\text{-}H}$ = 5.2 Hz, H_e or $H_{e'}$), 4.10-3.96 (4H, m, b), 3.07 (2H, d, $^{2}J_{P\text{-}H}$ = 22 Hz, c), 1.22 (6H, t, *J* = 7.2 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.41 (d), 138.09 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, f), 129.89 (q, $^{2}J_{C\text{-}F}$ = 32 Hz, i), 126.86 (j), 125.42 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, h), 124.31 (q, $^{1}J_{C\text{-}F}$ = 271 Hz, CF_3), 119.27 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, e), 62.26 (d, $^{2}J_{C\text{-}P}$ = 6 Hz, b), 33.21 (d, $^{1}J_{C\text{-}P}$ = 138 Hz, c), 16.45 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.83 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.61 ppm; IR (neat) 2984 (aromatic C-H), 2907 (aliphatic C-H), 1616 (C=C), 1324 (C-F), 1250 (P=O), 1052 (C-O), 1023 (C-O), 959 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{18}F_3O_3P$ = 322.0946, found 322.0950 *m/z*.

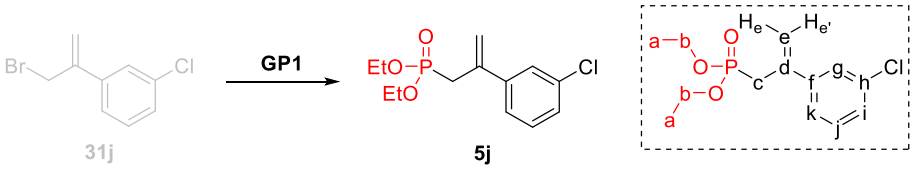


Synthesis of phosphonate functionalized alkene 5h: Following **GP1**, allyl bromide **31h** (538 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5h** (517 mg, 76%) as a colorless oil: TLC

analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (2H, m, g), 7.06-7.00 (2H, m, h), 5.47 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 5.33 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.10-3.96 (4H, m, b), 3.04 (2H, d, $^2J_{P\text{-}H}$ = 22 Hz, c), 1.23 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.63 (d, $^1J_{C\text{-}F}$ = 245 Hz, i), 138.00 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 136.97 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 128.21 (d, $^3J_{C\text{-}F}$ = 8 Hz, g), 117.31 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 115.27 (d, $^2J_{C\text{-}F}$ = 21 Hz, h), 62.20 (d, $^2J_{C\text{-}P}$ = 6 Hz, b), 33.45 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 16.49 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.28 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.75 ppm; IR (neat) 2982 (aromatic C-H), 2907 (aliphatic C-H), 1624 (C=C), 1601 (C=C), 1509 (C-F), 1249 (P=O), 1052 (C-O), 1022 (C-O), 902 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{13}H_{18}FO_3P$ = 272.0978, found 272.0982 *m/z*.

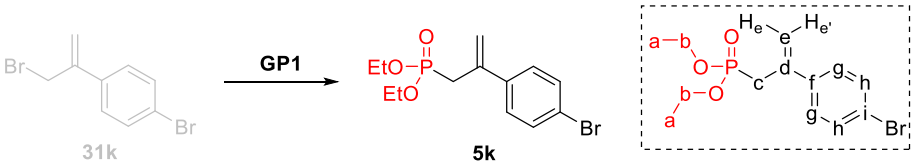


Synthesis of phosphonate functionalized alkene 5i: Following **GP1**, allyl bromide **31i** (579 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5i** (577 mg, 80%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 8.8 Hz, g or h), 7.29 (2H, d, J = 8.8 Hz, g or h), 5.50 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 5.35 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.06-3.96 (4H, m, b), 3.01 (2H, d, $^2J_{P\text{-}H}$ = 22.4 Hz, c), 1.21 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.23 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 137.87 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 133.72 (i), 128.52 (g or h), 127.78 (g or h), 117.79 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 62.17 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 33.17 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 16.44 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.13 ppm; IR (neat) 2981 (aromatic C-H), 2905 (aliphatic C-H), 1623 (C=C), 1248 (P=O), 1022 (C-O), 940 (P-O), 835 (C-Cl) cm^{-1}; HRMS (EI) calculated for $C_{13}H_{18}ClO_3P$ = 288.0682, found 288.0690 *m/z*.

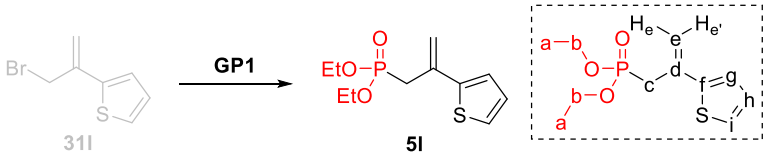


Synthesis of phosphonate functionalized alkene 5j: Following **GP1**, allyl bromide **31j** (579 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5j** (584 mg, 81%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (1H, dd, J = 2.0, 0.8 Hz, aryl), 7.39-7.34 (1H, m, aryl), 7.29-7.25 (2H, m, aryl), 5.53 (1H, dd, J = 5.5 ($^4J_{P\text{-}H}$), 0.4 ($^4J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 5.39 (1H, dd, J = 5.6 ($^4J_{P\text{-}H}$), 0.5 ($^4J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 4.10-3.96 (4H, m, b), 3.03 (2H, dd, J = 22 ($^2J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, c), 1.23 (6H, t, J = 7.2 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.74 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 137.90 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 134.38 (h), 129.69 (aryl), 127.89 (aryl), 126.72 (aryl), 124.71 (aryl), 118.47 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 62.21 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 33.15 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 16.45 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.96 ppm; IR (neat) 2981 (aromatic C-H), 2906 (aliphatic C-H), 1625 (C=C), 1248 (P=O), 1051 (C-O), 1021 (C-O),

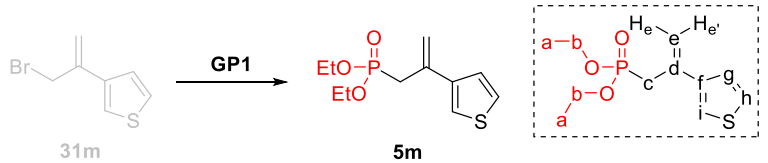
960 (P-O), 788 (C-Cl) cm^{-1}; HRMS (EI) calculated for $C_{13}H_{18}ClO_3P$ = 288.0682, found 288.0691 *m/z*.



Synthesis of phosphonate functionalized alkene 5k: Following **GP1**, allyl bromide **31k** (690 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5k** (616 mg, 74%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J* = 8.8 Hz, g or h), 7.36 (2H, d, *J* = 8.8 Hz, g or h), 5.52 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 5.37 (1H, d, $^4J_{P\text{-}H}$ = 5.6 Hz, H_e or $H_{e'}$), 4.10-3.96 (4H, m, b), 3.03 (2H, dd, *J* = 22.4 ($^2J_{P\text{-}H}$), 0.8 ($^4J_{H\text{-}H}$) Hz, c), 1.23 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.75 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 137.98 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 131.54 (g or h), 128.15 (g or h), 121.94 (i), 117.91 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 62.24 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 33.16 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 16.49 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.15 ppm; IR (neat) 2980 (aromatic C-H), 2902 (aliphatic C-H), 1620 (C=C), 1248 (P=O), 1052 (C-O), 1021 (C-O), 955 (P-O), 759 (C-Br) cm^{-1}; HRMS (EI) calculated for $C_{13}H_{18}BrO_3P$ = 332.0177, found 332.0168 *m/z*.

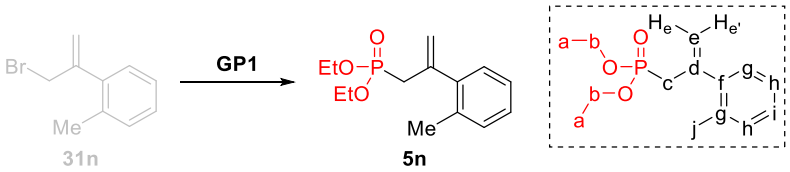


Synthesis of phosphonate functionalized alkene 5l: Following **GP1**, allyl bromide **31l** (508 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5l** (540 mg, 83%) as a light buff colored oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (1H, d, *J* = 5.2 Hz, i), 7.15 (1H, d, *J* = 3.2 Hz, g), 7.00-6.98 (1H, m, h), 5.61 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 5.23 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 4.14-4.00 (4H, m, b), 3.05 (2H, d, $^2J_{P\text{-}H}$ = 22 Hz, c), 1.26 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.60 (d, $^2J_{C\text{-}P}$ = 5 Hz, d), 132.33 (d, $^3J_{C\text{-}P}$ = 10 Hz, f), 127.63 (h), 125.05 (g), 124.98 (i), 115.56 (d, $^3J_{C\text{-}P}$ = 10 Hz, e), 62.38 (d, $^2J_{C\text{-}P}$ = 6 Hz, b), 33.46 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 16.53 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.85 ppm; IR (neat) 3091 (aromatic C-H), 2980 (aliphatic C-H), 1622 (C=C), 1247 (P=O), 1051 (C-O), 1020 (C-O/C=S), 954 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{11}H_{17}O_3PS$ = 260.0636, found 260.0630 *m/z*.

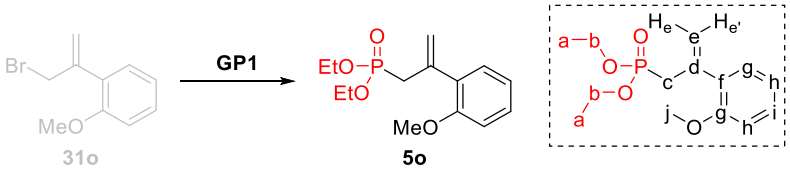


Synthesis of phosphonate functionalized alkene 5m: Following **GP1**, allyl bromide **31m** (508 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5m** (555 mg, 85%) as a light buff oil: TLC analysis (ethyl acetate) R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, s, i), 7.28-7.25 (2H, m, g+h), 5.57 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 5.28 (1H, d, $^4J_{P\text{-}H}$ = 5.5 Hz, H_e or $H_{e'}$), 4.12-4.98 (4H,

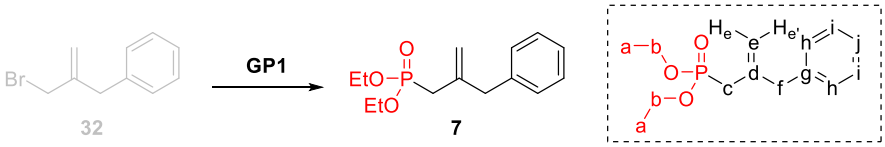
m, b), 3.02 (2H, d, $^{2}J_{P\text{-}H}$ = 22 Hz, c), 1.25 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.96 (d, $^{2}J_{C\text{-}P}$ = 4 Hz, d), 133.37 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, f), 125.94 (g or h), 125.77 (g or h), 121.97 (i), 115.87 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, e), 62.27 (d, $^{2}J_{C\text{-}P}$ = 7 Hz, b), 33.59 (d, $^{1}J_{C\text{-}P}$ = 138 Hz, c), 16.49 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.63 ppm; IR (neat) 3090 (aromatic C-H), 2978 (aliphatic C-H), 1621 (C=C), 1250 (P=O), 1052 (C-O), 1020 (C-O/C=S), 955 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{11}H_{17}O_3PS$ = 260.0636, found 260.0630 *m/z*.



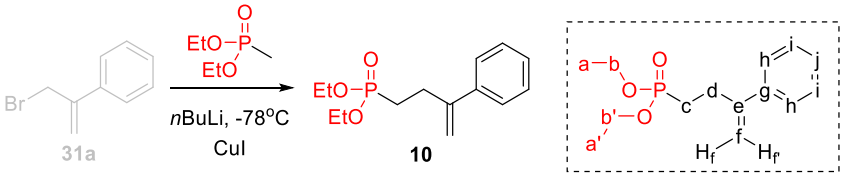
Synthesis of phosphonate functionalized alkene 5n: Following **GP1**, allyl bromide **31n** (528 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5n** (590 mg, 88%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.13 (4H, m, aryl), 5.50 (1H, d, J = 5.2 ($^{4}J_{P\text{-}H}$), 1.0 ($^{4}J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 5.13 (1H, d, J = 5.0 ($^{4}J_{P\text{-}H}$), 1.2 ($^{4}J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 4.05-3.88 (4H, m, b), 2.95 (2H, dd, J = 22 ($^{2}J_{P\text{-}H}$), 1.0 ($^{4}J_{H\text{-}H}$) Hz, c), 1.20 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.15 (d, $^{2}J_{C\text{-}P}$ = 5 Hz, d), 139.73 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, f), 134.98 (g), 130.34 (aryl), 128.76 (aryl), 127.41 (aryl), 125.64 (aryl), 119.59 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, e), 61.87 (d, $^{2}J_{C\text{-}P}$ = 7 Hz, b), 35.01 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 20.09 (j), 16.40 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.25 ppm; IR (neat) 2980 (aromatic C-H), 2906 (aliphatic C-H), 1633 (C=C), 1251 (P=O), 1052 (C-O), 1022 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_3P$ = 268.1228, found 268.1226 *m/z*.



Synthesis of phosphonate functionalized alkene 5o: Following **GP1**, allyl bromide **31o** (568 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **5o** (570 mg, 80%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.30 (2H, m, aryl), 6.95-6.87 (1H, m, aryl), 6.86 (1H, d, J = 8.0 Hz, h), 5.38-5.36 (1H, m, H_e or $H_{e'}$), 5.25 (1H, dd, J = 5.0 ($^{4}J_{P\text{-}H}$), 1.6 ($^{4}J_{H\text{-}H}$) Hz, H_e or $H_{e'}$), 3.18 (2H, dd, J = 21.6 ($^{2}J_{P\text{-}H}$), 1.0 ($^{4}J_{H\text{-}H}$) Hz, c), 1.70 (6H, t, J = 7.2 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.53 (g), 139.39 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, f), 131.15 (d, $^{2}J_{C\text{-}P}$ = 4 Hz, d), 130.75 (aryl), 129.11 (aryl), 120.79 (aryl), 119.45 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, e), 110.57 (h), 61.73 (d, $^{2}J_{C\text{-}P}$ = 6 Hz, b), 55.53 (j), 33.48 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 16.40 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.34 ppm; IR (neat) 2980 (aromatic C-H), 2905 (aliphatic C-H), 1629 (C=C), 1598 (C=C), 1241 (P=O), 1047 (C-O), 1021 (C-O), 957 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_4P$ = 284.1177, found 284.1167 *m/z*.

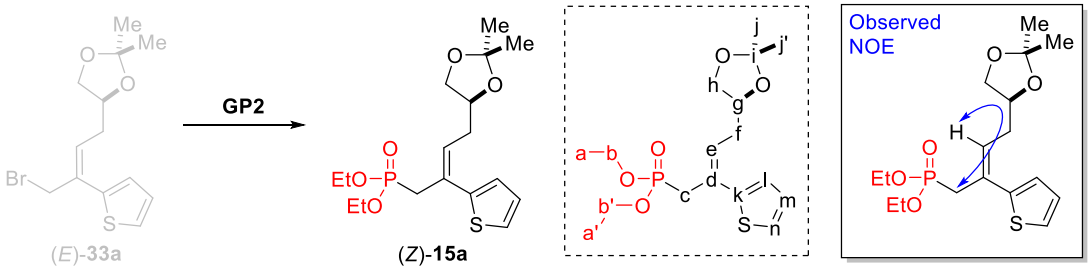


Synthesis of phosphonate functionalized alkene 7: Following **GP1**, allyl bromide **32** (527 mg, 2.50 mmol, 1.00 eq) yields the alkene substrate **7** (543 mg, 81%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (5H, m, aryl), 5.06 (1H, d, $^4J_{P\text{-}H}$ = 5.2 Hz, H_e or $H_{e'}$), 4.98 (1H, d, $^4J_{P\text{-}H}$ = 5.2 Hz, H_e or $H_{e'}$), 4.17-4.08 (4H, m, b), 3.53 (2H, s, f), 2.52 (2H, d, $^2J_{P\text{-}H}$ = 22 Hz, c), 1.33 (6H, t, J = 7.2 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.60 (d, $^2J_{C\text{-}P}$ = 11 Hz, d), 138.94 (g), 129.29 (aryl), 128.51 (aryl), 126.46 (aryl), 116.50 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 62.00 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 43.40 (d, $^3J_{C\text{-}P}$ = 4 Hz, f), 32.91 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 16.56 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.02 ppm; IR (neat) 2981 (aromatic C-H), 2904 (aliphatic C-H), 1645 (C=C), 1247 (P=O), 1052 (C-O), 1023 (C-O), 956 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_3P$ = 268.1228, found 268.1231 *m/z*.

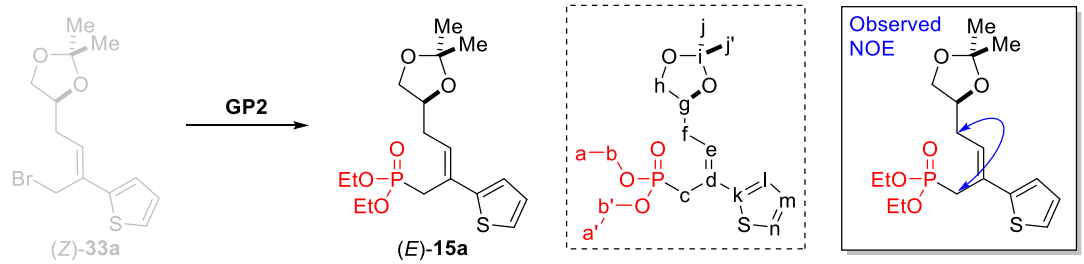


Synthesis of homoallylic phosphonate substrate 10: This synthesis was carried out according to our previously reported procedure.[6] Allyl bromide **31a** (492 mg, 2.50 mmol, 1.10 eq) yields the homoallylic phosphonate **10** (470 mg, 70%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.28 (5H, m, aryl), 5.32 (1H, s, H_f or $H_{f'}$), 5.12 (1H, d, $^4J_{H\text{-}H}$ = 1.0 Hz, H_f or $H_{f'}$), 4.14-4.07 (4H, m, b), 2.84-2.78 (2H, m, d), 1.94-1.85 (2H, m, c), 1.34 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.45 (d, $^3J_{C\text{-}P}$ = 19 Hz, e), 140.27 (g), 128.60 (aryl), 127.84 (aryl), 126.23 (aryl), 112.76 (f), 61.70 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 28.29 (d, $^2J_{C\text{-}P}$ = 4 Hz, d), 24.96 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.64 (d, $^3J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.46 ppm; IR (neat) 3082 (aromatic C-H), 2980 (aliphatic C-H), 1629 (C=C), 1243 (P=O), 1054 (C-O), 1024 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{14}H_{21}O_3P$ = 268.1228, found 268.1232 *m/z*.

(3) Synthesis of conjugated (β-aryl) trisubstituted substrates

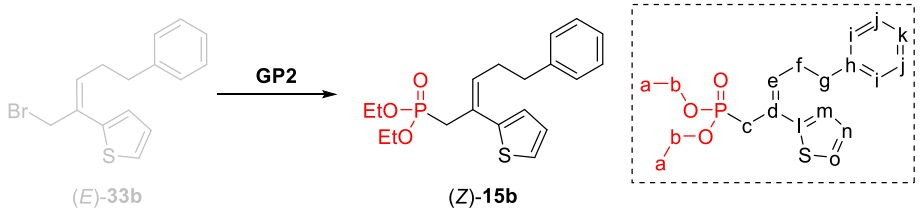


Synthesis of phosphonate functionalized alkene (*Z*)-15a: The substrates in this class of trisubstituted alkenes were prepared according to our previously reported synthesis of trialkyl substituted allyl alkenes (**GP2**).[6] Following **GP2**, allyl bromide (*E*)-**33a** (317 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15a** (326 mg, 87%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +25.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, dd, *J* = 5.2, 1.2 Hz, n), 7.07 (1H, dd, *J* = 3.6, 0.8 Hz, l), 7.02 (1H, dd, *J* = 5.2, 3.6 Hz, m), 5.79 (1H, dd, *J* = 12.8, 7.0 Hz, e), 4.21-3.96 (6H, m, b+b'+g+h(1H)), 3.57 (1H, dd, *J* = 8.0, 7.0 Hz, h(1H)), 2.99 (2H, d, $^2J_{P\text{-}H}$ = 21.6 Hz, c), 2.64-2.58 (2H, m, f), 1.42 (3H, s, j or j'), 1.36 (3H, s, j or j'), 1.24 (3H, t, *J* = 7.0 Hz, a or a'), 1.23 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.46 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 128.87 (d, $^3J_{C\text{-}P}$ = 11 Hz, e), 127.06 (l or m), 126.98 (l or m), 126.12 (d, $^3J_{C\text{-}P}$ = 11 Hz, k), 125.35 (n), 109.25 (i), 75.62 (d, $^5J_{C\text{-}P}$ = 3 Hz, g), 69.17 (h), 62.10 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b+b'), 37.15 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 34.02 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, f), 27.05 (j or j'), 25.84 (j or j'), 16.53 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.20 ppm; Proof of stereochemistry: Strong NOE is observed between vinyl hydrogen (H_e) and the methylene hydrogens adjacent to phosphonate functionality (H_c). IR (neat) 2983 (aromatic C-H), 2905 (aliphatic C-H), 1368 (aromatic C=C), 1248 (P=O), 1022 (C-O), 958 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{27}O_5PS + Na^+$ = 397.1215, found 397.1218 *m/z*.

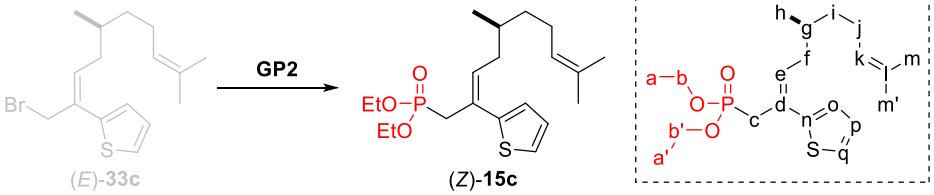


Synthesis of phosphonate functionalized alkene (*E*)-15a: Following **GP2**, allyl bromide (*Z*)-**33a** (158 mg, 0.50 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15a** (150 mg, 80%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +7.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (1H, d, *J* = 5.0 Hz, n), 7.09 (1H, d, *J* = 3.5 Hz, l), 6.96 (1H, dd, *J* = 5.0, 3.5 Hz, m), 6.12 (1H, dd, *J* = 13.5, 7.0 Hz, e), 4.29-4.23 (1H, m, g), 4.10-3.95 (5H, m, b+b'+h(1H)), 3.65 (1H, dd, *J* = 8.0, 7.0 Hz, h(1H)), 3.08 (2H, d, $^2J_{P\text{-}H}$ = 22.0 Hz, c), 2.66-2.53 (2H, m, f), 1.45 (3H, s, j or j'), 1.37 (3H, s, j or j'), 1.22 (3H, t, *J* = 7.0 Hz, a or a'), 1.21 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.93 (d, $^3J_{C\text{-}P}$ = 3.0 Hz, d), 127.46 (m), 126.29 (d, $^3J_{C\text{-}P}$ =

11.0 Hz, e & k), 124.00 (l), 123.97 (n), 109.24 (i), 75.34 (d, $^{5}J_{C\text{-}P}$ = 3.0 Hz, g), 69.05 (h), 62.27 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 62.23 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 33.17 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, f), 29.58 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 27.04 (j or j'), 25.80 (j or j'), 16.48 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.78 ppm; Proof of stereochemistry: Strong NOE is observed between methylene hydrogens H_f and the methylene hydrogens adjacent to phosphonate functionality H_c. IR (neat) 2985 (aromatic C-H), 2903 (aliphatic C-H), 1370 (aromatic C=C), 1248 (P=O), 1023 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{27}O_5PS+Na^+$ = 397.1215, found 397.1214 *m/z*.

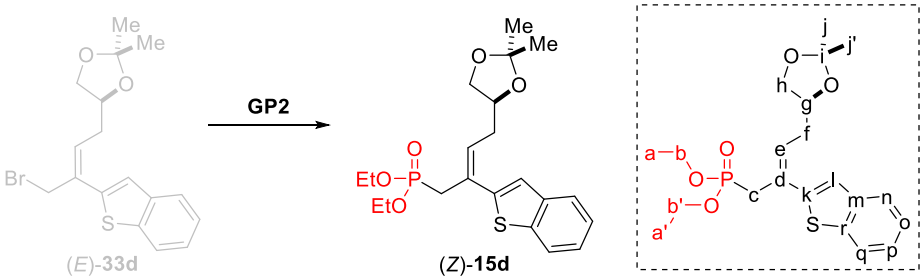


Synthesis of phosphonate functionalized alkene (*Z*)-15b: Following **GP2**, allyl bromide (*E*)-**33b** (307 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15b** (295 mg, 81%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (3H, m, aryl), 7.22-7.18 (3H, m, aryl), 7.02-7.00 (2H, m, m+n), 5.82 (1H, dd, *J* = 12.5, 7.0 Hz, e), 4.08-3.92 (4H, m, b), 2.98 (2H, d, $^{2}J_{P\text{-}H}$ = 21.5 Hz, c), 2.78 (2H, t, *J* = 7.5 Hz, g), 2.68-2.61 (2H, m, f), 1.23 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.75 (d, $^{2}J_{C\text{-}P}$ = 4.0 Hz, d), 141.65 (h), 133.49 (d, $^{3}J_{C\text{-}P}$ = 11.0 Hz, e), 128.63 (aryl), 128.52 (aryl), 126.85 (aryl), 126.70 (aryl), 126.10 (aryl), 125.07 (aryl), 124.02 (d, $^{3}J_{C\text{-}P}$ = 11.0 Hz, l), 62.04 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b), 36.90 (d, $^{1}J_{C\text{-}P}$ = 139 Hz, c), 36.00 (d, $^{5}J_{C\text{-}P}$ = 3.5 Hz, g), 31.66 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, f), 16.51 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.55 ppm; IR (neat) 2983 (aromatic C-H), 2904 (aliphatic C-H), 1605 (C=C), 1494 (aromatic C=C), 1368 (aromatic C=C), 1249 (P=O), 1023 (C-O), 957 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{19}H_{25}O_3PS$ = 364.1262, found 364.1253 *m/z*.

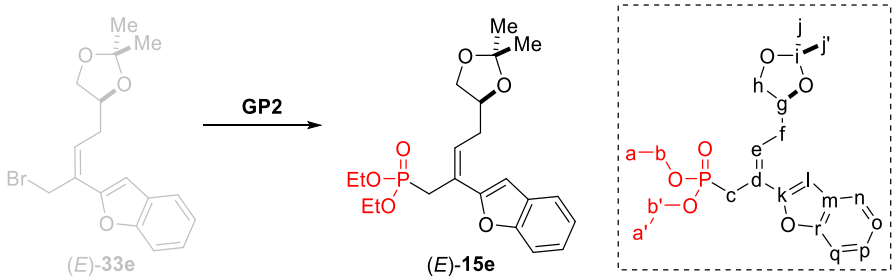


Synthesis of phosphonate functionalized alkene (*Z*)-15c: Following **GP2**, allyl bromide (*E*)-**33c** (327 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15c** (308 mg, 80%) as a light buff oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +24.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (1H, m, q), 7.04-7.00 (2H, m, o+p), 5.78 (1H, dd, *J* = 13.0, 7.0 Hz, e), 5.09 (1H, t, *J* = 7.0 Hz, k), 4.08-3.93 (4H, m, b+b'), 2.98 (2H, d, $^{2}J_{P\text{-}H}$ = 21.2 Hz, c), 2.35-2.11 (2H, m, f), 2.05-1.89 (2H, m, j), 1.68 (3H, s, m or m'), 1.63-1.55 (1H, m, g), 1.60 (3H, s, m or m'), 1.42-1.32 (1H, m, i), 1.23 (6H, t, *J* = 7.0 Hz, a+a'), 1.26-1.13 (1H, m, i), 0.92 (3H, d, *J* = 7.0 Hz, h) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.12 (d, $^{2}J_{C\text{-}P}$ = 4.0 Hz, d), 133.82 (d, $^{3}J_{C\text{-}P}$ = 11.0 Hz, e), 131.35 (l), 126.75 (*o* or p), 126.64 (*o* or p), 124.91 (k), 126.64 (d, $^{4}J_{C\text{-}P}$ = 1.0 Hz, o), 123.74 (d, $^{3}J_{C\text{-}P}$ = 11.0 Hz, n), 61.98 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b+b'), 36.98 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 36.99 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz, f), 36.97 (i), 33.49 (d, $^{5}J_{C\text{-}P}$ = 3.0 Hz, g), 25.89 (m or m'), 25.74 (j), 19.74 (h), 17.81 (m or

m'), 16.51 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, d) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.77 ppm; IR (neat) 2963 (aromatic C-H), 2907 (aliphatic C-H), 1440 (aromatic C=C), 1377 (aromatic C=C), 1252 (P=O), 1051 (C-O), 1025 (C-O), 957 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{20}H_{33}O_3PS$ = 384.1888, found 384.1897 *m/z*.

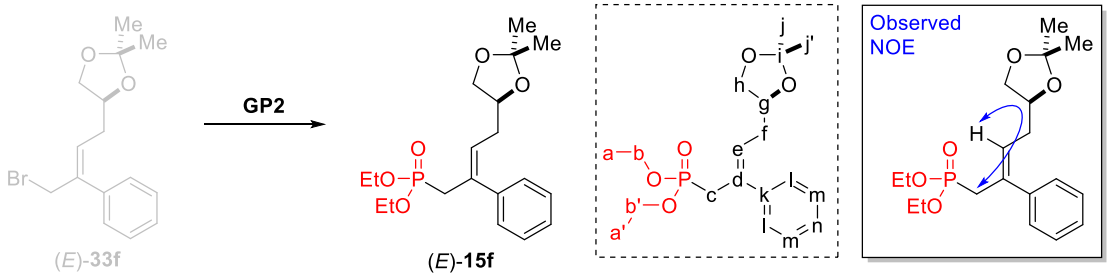


Synthesis of phosphonate functionalized alkene (*E*)-15d: Following **GP2**, allyl bromide (*E*)-**33d** (367 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15d** (378 mg, 89%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +13.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.81 (1H, d, *J* =8.8 Hz, q), 7.76 (1H, d, *J* = 7.7 Hz, l), 7.37-7.29 (3H, m, n+o+p), 5.93 (1H, dd, *J* = 12.6, 7.0 Hz, e), 7.23-7.20 (1H, m, g), 4.08-4.00 (5H, m, b+b'+h(1H)), 3.59 (1H, dd, *J* = 7.7, 7.0 Hz, h(1H)), 3.05 (2H, d, $^{2}J_{P\text{-}H}$ = 21 Hz, c), 2.71-2.61 (2H, m, f), 1.43 (3H, s, j or j'), 1.37 (3H, s, j or j'), 1.24-1.21 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 141.67 (d, $^{2}J_{C\text{-}P}$ = 3.5 Hz, d), 139.90 (m or *r*), 139.70 (m or *r*), 130.70 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, e), 126.51 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, k), 124.58 (aryl), 123.83 (aryl), 123.79 (aryl), 122.20 (q), 109.32 (i), 75.55 (d, $^{5}J_{C\text{-}P}$ = 1.72 Hz, g), 69.18 (h), 62.21 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 62.19 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 36.78 (d, $^{1}J_{C\text{-}P}$ = 136.5 Hz, c), 34.06 (d, $^{4}J_{C\text{-}P}$ = 1.75 Hz, f), 27.06 (j or j'), 25.84 (j or j'), 16.55 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, a or a'), 16.53 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.96 ppm; IR (neat) 2982 (aromatic C-H), 2904 (aliphatic C-H), 1661 (C=C), 1456 (aromatic C=C), 1437 (aromatic C=C), 1248 (P=O), 1052 (C-O), 1022 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{21}H_{29}O_5PS$ = 424.1473, found 424.1453 *m/z*.

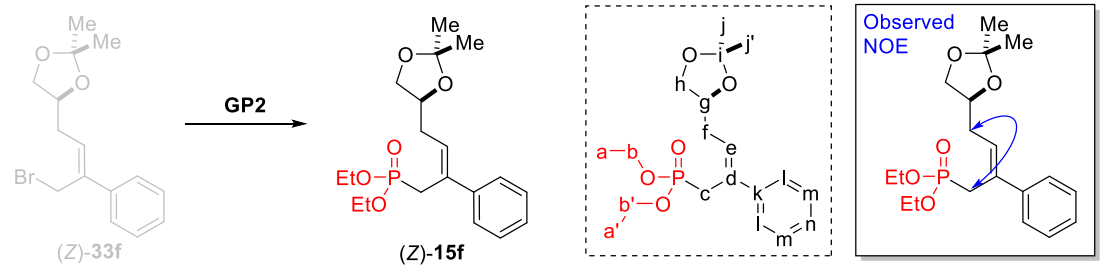


Synthesis of phosphonate functionalized alkene (*E*)-15e: Following **GP2**, allyl bromide (*E*)-**33e** (351 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15e** (319 mg, 78%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.6; $[\alpha]_D^{20}$ = +5.45° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57 (1H, d, *J* = 7.7 Hz, n), 7.46 (1H, d, *J* = 8.4 Hz, q), 7.31-7.28 (1H, m, *o* or q), 7.24 (1H, dd, *J* = 7.7, 7.0 Hz, *o* or q), 6.82 (1H, s, l), 5.90 (1H, dd, *J* = 12.6, 7.0 Hz, e), 4.32-4.28 (1H, m, g), 4.11 (1H, dd, *J* = 7.7, 6.3 Hz, h(1H)), 4.09-4.00 (4H, m, b+b'), 3.67 (1H, t, *J* = 7.7 Hz, h(1H)), 3.08 (2H, d, $^{2}J_{P\text{-}H}$ = 21.7 Hz, c), 2.94-2.87 (2H, m, f), 1.46 (3H, s, j or j'), 1.39 (3H, s, j or j'), 1.23-1.20 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.63 (d, $^{2}J_{C\text{-}P}$ = 4.50 Hz, d),

154.45 (r), 130.90 (d, $^{3}J_{C\text{-}P}$ = 11.0 Hz, e), 128.56 (m), 124.79 (*o* or p), 123.11 (*o* or p), 122.27 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, k), 121.28 (n), 111.22 (q), 109.34 (i), 106.50 (l), 75.65 (d, $^{5}J_{C\text{-}P}$ = 3.5 Hz, g), 69.23 (h), 62.22 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b+b'), 34.11 (d, $^{4}J_{C\text{-}P}$ = 1.75 Hz, f), 33.24 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 27.11 (j or j'), 25.89 (j or j'), 16.54 (d, $^{3}J_{C\text{-}P}$ = 6.50 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.35 ppm; IR (neat) 2981 (aromatic C-H), 2904 (aliphatic C-H), 1474 (aromatic C=C), 1369 (aromatic C=C), 1252 (P=O), 1048 (C-O), 1022 (C-O), 960 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{21}H_{29}O_6P$ = 408.1702, found 408.1710 *m/z*.

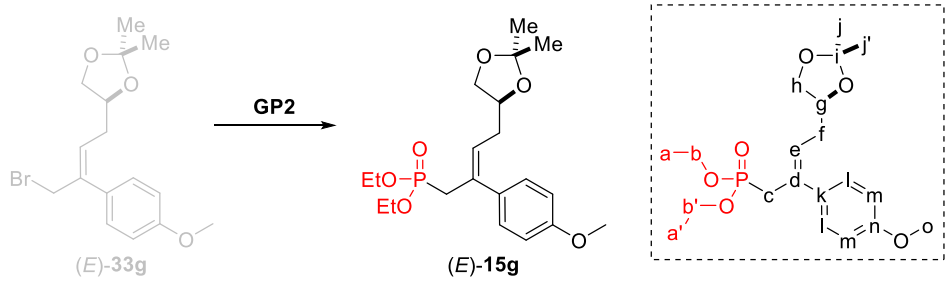


Synthesis of phosphonate functionalized alkene (*E*)-15f: Following **GP2**, allyl bromide (*E*)-**33f** (311 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15f** (313 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +17.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35-7.24 (5H, m, aryl), 5.75 (1H, dd, *J* = 13.3, 7 Hz, e), 4.12-4.09 (1H, m, g), 4.00-3.89 (5H, m, b+b'+h(1H)), 3.49 (1H, t, *J* = 7.7 Hz, h(1H)), 2.95 (2H, d, $^{2}J_{P\text{-}H}$ = 21.7 Hz, c), 2.20-2.46 (2H, m, f), 1.37 (3H, s, j or j'), 1.34 (3H, s, j or j'), 1.21-1.17 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.05 (d, $^{2}J_{C\text{-}P}$ = 3.5 Hz, d), 133.65 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, k), 128.77 (aryl), 128.34 (aryl), 127.28 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, e), 109.11 (i), 75.67 (d, $^{5}J_{C\text{-}P}$ = 5.25 Hz, g), 69.15 (h), 61.89 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.85 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 36.51 (d, $^{1}J_{C\text{-}P}$ = 138.5 Hz, c), 33.60 (d, $^{4}J_{C\text{-}P}$ = 1.75 Hz, f), 26.99 (j or j'), 25.83 (j or j'), 16.47 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, a or a'), 16.45 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, a or a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 26.59 ppm; Proof of stereochemistry: Strong NOE is observed between vinyl hydrogen (H_e) and the methylene hydrogens adjacent to phosphonate functionality (H_c). IR (neat) 2982 (aromatic C-H), 2904 (aliphatic C-H), 1600 (C=C), 1442 (aromatic C=C), 1368 (aromatic C=C), 1249 (P=O), 1048 (C-O), 1023 (C-O), 957 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{19}H_{29}O_5P$ = 368.1753, found 368.1767 *m/z*.

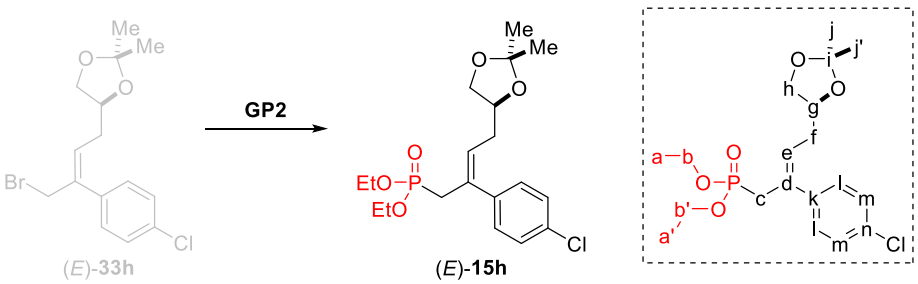


Synthesis of phosphonate functionalized alkene (*Z*)-15f: Following **GP2**, allyl bromide (*Z*)-**33f** (311 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15f** (321 mg, 87%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +7.3° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.44-7.25 (5H, m, aryl), 5.94 (1H, dd, *J* = 13.3, 6.3 Hz, e), 4.28 (1H, m, g), 4.30-4.09 (1H, m, h(1H)), 4.01-3.95 (2H, m, b or b'), 3.94-3.87 (2H, m, b or b'), 3.69-3.67 (1H, m,

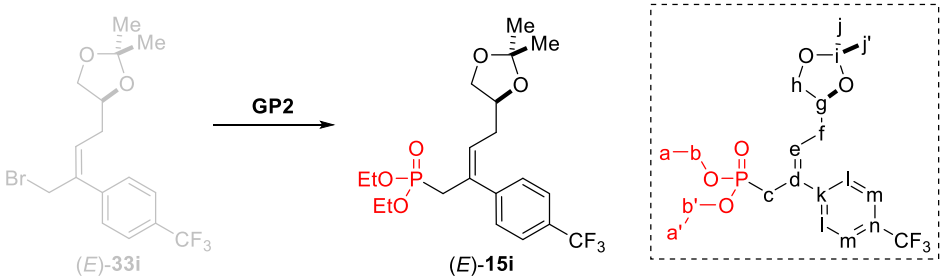
h(1H)), 3.13 (2H, d, $^{2}J_{P\text{-}H}$ = 22.4 Hz, c), 2.67-2.60 (2H, m, f), 1.46 (3H, s, j or j'), 1.38 (3H, s, j or j'), 1.18-1.16 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 142.47 (d, $^{2}J_{C\text{-}P}$ = 1.75 Hz, d), 132.74 (d, $^{3}J_{C\text{-}P}$ = 12.25 Hz, k), 128.45 (aryl), 127.84 (d, $^{3}J_{C\text{-}P}$ = 12.25 Hz, k), 127.42 (aryl), 126.80 (aryl), 109.23 (i), 75.57 (d, $^{5}J_{C\text{-}P}$ = 1.75 Hz, g), 69.16 (h), 62.06 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 62.02 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 33.52 (d, $^{4}J_{C\text{-}P}$ = 3.50 Hz, f), 29.28 (d, $^{1}J_{C\text{-}P}$ = 138.25 Hz, c), 27.13 (j or j'), 25.84 (j or j'), 16.44 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, a+a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 26.42 ppm; Proof of stereochemistry: Strong NOE is observed between methylene hydrogens H_f and the methylene hydrogens adjacent to phosphonate functionality H_c. IR (neat) 2983 (aromatic C-H), 2903 (aliphatic C-H), 1599 (C=C), 1444 (aromatic C=C), 1368 (aromatic C=C), 1248 (P=O), 1052 (C-O), 1023 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{29}O_5P$+Na^+ = 391.1650, found 391.1649 *m/z*.



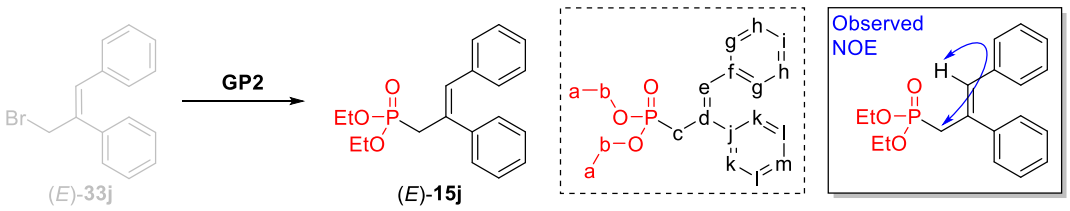
Synthesis of phosphonate functionalized alkene (*E*)-15g: Following **GP2**, allyl bromide (*E*)-**33g** (341 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15g** (311 mg, 78%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +13.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.18 (2H, d, *J* = 8.4 Hz, l), 6.88 (2H, d, *J* = 8.4 Hz, m), 5.71 (1H, dd, *J* = 13.3, 7.0 Hz, e), 4.12-4.09 (1H, m, g), 4.03-3.91 (5H, m, b+b'+h(1H)), 3.83 (3H, s, o), 3.49 (1H, dd, *J* = 7.7, 7.0 Hz, h(1H)), 2.97-2.89 (2H, m, c), 2.43-2.27 (2H, m, f), 1.38 (3H, s, j or j'), 1.35 (3H, s, j or j'), 1.22 (3H, t, *J* = 7.0 Hz, a or a'), 1.21 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.82 (n), 133.16 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, k), 132.36 (d, $^{2}J_{C\text{-}P}$ = 3.5 Hz, d), 129.93 (l), 126.90 (d, $^{3}J_{C\text{-}P}$ = 12.25 Hz, e), 113.73 (m), 109.11 (i), 75.74 (d, $^{3}J_{C\text{-}P}$ = 3.5 Hz, g), 69.18 (h), 61.90 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.87 (d, $^{2}J_{C\text{-}P}$ = 5.25 Hz, b or b'), 55.45 (o), 36.61 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 33.66 (d, $^{4}J_{C\text{-}P}$ = 3.50 Hz, f), 27.02 (j or j'), 25.85 (j or j'), 16.53 (d, $^{3}J_{C\text{-}P}$ = 7.0 Hz, a or a'), 16.52 (d, $^{3}J_{C\text{-}P}$ = 5.25 Hz, a or a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 26.82 ppm; IR (neat) 2983 (aromatic C-H), 2905 (aliphatic C-H), 1608 (C=C), 1512, 1456 (aromatic C=C), 1368 (aromatic C=C), 1244 (P=O), 1024 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{20}H_{31}O_6P$ = 398.1858, found 398.1874 *m/z*.



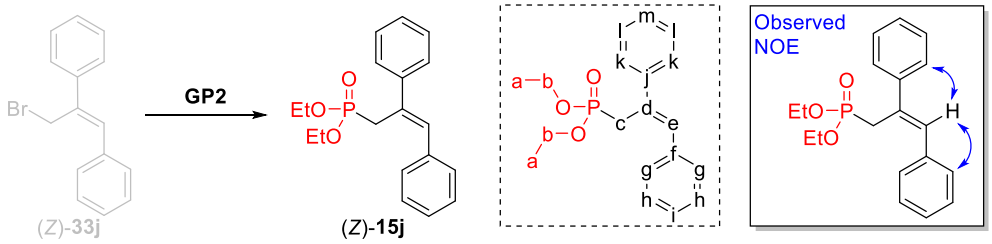
Synthesis of phosphonate functionalized alkene (*E*)-15h: Following **GP2**, allyl bromide (*E*)-**33h** (346 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15h** (326 mg, 81%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +21.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, d, *J* = 8.4 Hz, m), 7.20 (2H, d, *J* = 8.4 Hz, l), 5.76 (1H, dd, *J* = 13.0, 7.0 Hz, e), 4.11-3.92 (6H, m, b+b'+g+h(1H)), 3.49-3.45 (1H, m, h(1H)), 2.90 (2H, d, $^2J_{P\text{-}H}$ = 21.6 Hz, c), 2.34-2.23 (2H, m, f), 1.37 (3H, s, j or j'), 1.33 (3H, s, j or j'), 1.23-1.19 (6H, m, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.49 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 133.20 (n), 132.61 (d, $^3J_{C\text{-}P}$ = 11 Hz, k), 130.22 (d, $^4J_{C\text{-}P}$ = 1.75 Hz, l), 128.54 (m), 128.08 (d, $^3J_{C\text{-}P}$ = 12 Hz, e), 109.19 (i), 75.51 (d, $^5J_{C\text{-}P}$ = 3.0 Hz, g), 69.10 (h), 61.97 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.94 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 36.44 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 33.65 (d, $^4J_{C\text{-}P}$ = 4.0 Hz, f), 26.99 (j or j'), 25.79 (j or j'), 16.49 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.23 ppm; IR (neat) 2983 (aromatic C-H), 2904 (aliphatic C-H), 1595 (C=C), 1491 (aromatic C=C), 1369 (aromatic C=C), 1248 (P=O), 1024 (C-O), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{19}H_{28}ClO_5P$ = 402.1363, found 402.1349 *m/z*.



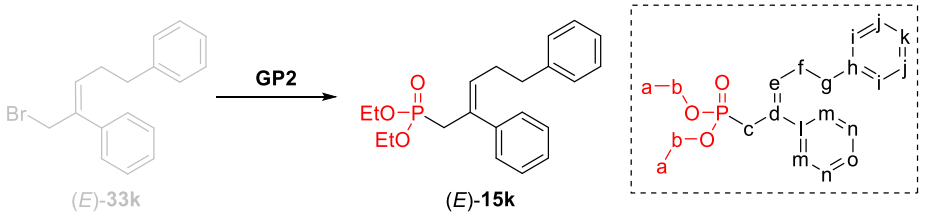
Synthesis of phosphonate functionalized alkene (*E*)-15i: Following **GP2**, allyl bromide (*E*)-**33i** (379 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15i** (319 mg, 73%) as a light buff colored oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; $[\alpha]_D^{20}$ = +19° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (2H, d, *J* = 8.0 Hz, m), 7.39 (2H, d, *J* = 8.0 Hz, m), 5.82 (1H, dd, *J* = 13.0, 7.0 Hz, e), 4.16-3.90 (6H, m, b+b'+g+h(1H)), 3.49 (1H, dd, *J* = 7.6, 7.2 Hz, h(1H)), 2.93 (2H, d, $^2J_{P\text{-}H}$ = 21.6 Hz, c), 2.27-2.20 (2H, m, f), 1.37 (3H, s, j or j'), 1.34 (3H, s, j or j'), 1.22-1.17 (6H, m, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.86 (d), 132.62 (d, $^3J_{C\text{-}P}$ = 11 Hz, k), 129.53 (q, $^2J_{C\text{-}F}$ = 32 Hz, n), 129.26 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, l), 128.73 (d, $^3J_{C\text{-}P}$ = 12 Hz, e), 125.34 (q, $^3J_{C\text{-}F}$ = 4 Hz, m), 124.32 (q, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 109.26 (i), 75.43 (d, $^5J_{C\text{-}P}$ = 4.0 Hz, g), 69.08 (h), 62.01 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.98 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 36.39 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 33.68 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, f), 26.98 (j or j'), 25.77 (j or j'), 16.46 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.44 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.93 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59 ppm; IR (neat) 2984 (aromatic C-H), 2905 (aliphatic C-H), 1616 (C=C), 1369 (aromatic C=C), 1323 (C-F), 1249 (P=O), 1024 (C-O), 959 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{20}H_{28}F_3O_5P$ = 436.1626, found 436.1636 *m/z*.



Synthesis of phosphonate functionalized alkene (*E*)-15j: Following **GP2**, allyl bromide (*E*)-**33j** (273 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15j** (281 mg, 85%) as a light buff oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (5H, m, aryl), 7.13-7.11 (3H, m, aryl), 6.99-6.97 (2H, m, aryl), 6.70 (2H, d, $^4J_{P\text{-}H}$ = 6.0 Hz, e), 4.10-3.94 (4H, m, b), 3.09 (2H, d, $^2J_{C\text{-}P}$ = 22 Hz, c), 1.23 (6H, t, *J* = 7.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.70 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 136.96 (d, $^4J_{C\text{-}P}$ = 4.0 Hz, f), 132.66 (d, $^3J_{C\text{-}P}$ = 12 Hz, j), 131.16 (d, $^3J_{C\text{-}P}$ = 12 Hz, e), 129.29 (aryl), 129.26 (aryl), 129.11 (aryl), 129.09 (aryl), 128.64 (aryl), 128.06 (aryl), 127.50 (aryl), 126.86 (aryl), 62.05 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 37.56 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 16.52 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.31 ppm; Proof of stereochemistry: Strong NOE is observed between vinyl hydrogen (H_e) and the methylene hydrogens adjacent to phosphonate functionality (H_c). IR (neat) 2979 (aromatic C-H), 2905 (aliphatic C-H), 1598 (C=C), 1493 (aromatic C=C), 1443 (aromatic C=C), 1390 (aromatic C=C), 1248 (P=O), 1055 (C-O), 1019 (C-O), 957 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{19}H_{23}O_3P$ = 330.1385, found 330.1384 *m/z*.



Synthesis of phosphonate functionalized alkene (*Z*)-15j: Following **GP2**, allyl bromide (*Z*)-**33j** (273 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*Z*)-**15j** (274 mg, 83%) as a light buff oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.0 Hz, g or k), 7.51 (2H, d, *J* = 8.0 Hz, g or k), 7.41-7.35 (4H, m, aryl), 7.32-7.26 (2H, m, aryl), 6.90 (1H, d, $^4J_{P\text{-}H}$ = 5.25 Hz, e), 3.97-3.75 (4H, m, b), 3.34 (2H, d, *J* = 22.4 Hz, c), 1.09 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.41 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, f), 137.16 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, d), 132.77 (d, $^3J_{C\text{-}P}$ = 11 Hz, j), 132.33 (d, $^3J_{C\text{-}P}$ = 13 Hz, e), 128.88 (aryl), 128.86 (aryl), 128.37 (aryl), 128.24 (aryl), 127.49 (aryl), 127.16 (aryl), 126.81 (aryl), 61.63 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 29.15 (d, $^1J_{C\text{-}P}$ = 140.11 Hz, c), 16.09 (d, $^3J_{C\text{-}P}$ = 6.4 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.33 ppm; Proof of stereochemistry: Strong NOE is observed between vinyl hydrogen (H_e) and the ortho hydrogens of the aromatic ring (H_g and H_k). IR (neat) 2979 (aromatic C-H), 2904 (aliphatic C-H), 1599 (C=C), 1494 (aromatic C=C), 1444 (aromatic C=C), 1391 (aromatic C=C), 1245 (P=O), 1053 (C-O), 1023 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{19}H_{23}O_3P$+Na^+ = 353.1283, found 353.1285 *m/z*.

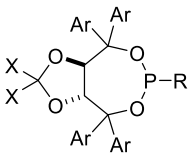


Synthesis of phosphonate functionalized alkene (*E*)-15k: Following **GP2**, allyl bromide (*E*)-**33k** (301 mg, 1.00 mmol, 1.00 eq) yields the alkene substrate (*E*)-**15k** (319 mg, 89%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.11 (10H, m, aryl), 5.77 (1H, dd, *J* = 12.5, 7.0 Hz, e), 4.02-3.58 (4H, m, b), 2.92 (2H, d, $^{2}J_{P\text{-}H}$ = 21.5 Hz, c), 2.68 (2H, t, *J* = 7.5 Hz, g), 2.39-2.32 (2H, m, f), 1.18 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.76 (h), 140.34 (d, $^{2}J_{C\text{-}P}$ = 4.0 Hz, d), 131.84 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, e), 131.47 (d, $^{3}J_{C\text{-}P}$ = 10.5 Hz, l), 128.70 (aryl), 128.63 (aryl), 128.42 (aryl), 128.18 (aryl), 127.07 (aryl), 125.98 (aryl), 61.79 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b), 36.26 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 36.12 (d, $^{5}J_{C\text{-}P}$ = 4.00 Hz, g), 31.24 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, f), 16.44 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.98 ppm; IR (neat) 2989 (aromatic C-H), 2904 (aliphatic C-H), 1601 (C=C), 1494 (aromatic C=C), 1453 (aromatic C=C), 1442 (aromatic C=C), 1391 (aromatic C=C), 1249 (P=O), 1048 (C-O), 1023 (C-O), 956 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{21}H_{27}O_3P$ = 358.1698, found 358.1685 *m/z*.

(4) Ligand screening data

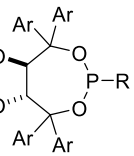
The data presented here is for the series of ligands that were tested on methylidene phosphonate substrate **5a**. Borane screening demonstrated pinacolborane is optimal for this reaction as it yielded significant amounts of hydroboration products. Usage of tmdBH resulted in very high (*ca.* 40-50%) amounts of reduction side products and usage of catecholborane (catBH) resulted in uncatalyzed background reactions. The yields for ligand screenings were determined post CAHB via crude ^{31}P NMR analysis. The enantiomer ratios were determined after oxidation to the corresponding alcohols via chiral HPLC analysis. The ligand **T2** was chosen empirically from the screening data as the ligand of choice for subsequent development of the chemistry because of its superior performance as compared to the others tested.

Ligands screened:

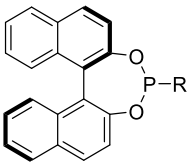


T1: X = Me; Ar = 3,5-Me_2-C_6H_3; R = OPh
T2: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(2-Me-C_6H_4)
T3: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(1-naphthyl)
T4: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(2-naphthyl)
T5: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(3,4,5-$(OMe)_3$-C_6H_2)
T6: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(C_6F_5)
T7: X = Me; Ar = Ph; R = OPh
T8: X = Me; Ar = 4-Me-C_6H_4; R = OPh
T9: X = Me; Ar = 4-*t*Bu-C_6H_4; R = OPh
T10: X = Me; Ar = 3,5-*i*Pr_2-C_6H_3; R = OPh
T11: X = Ph; Ar = 3,5-Me_2-C_6H_3; R = OPh

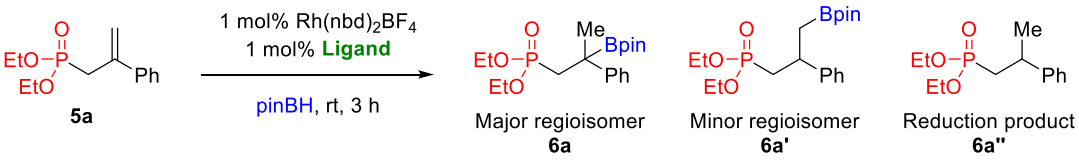
T12: X = Me; Ar = Ph; R = N(Me)Ph
T13: X = Me; Ar = 3,5-Me_2-C_6H_3; R = N(Me)Ph
T14: X = Me; Ar = 4-Me-C_6H_4; R = N(Bn)Ph
T15: X = Me; Ar = 4-*t*Bu-C_6H_4; R = N(Bn)Ph
T16: X = Ph; Ar = 3,5-Me_2-C_6H_3; R = N(Me)Ph



T17: X = Me; Ar = Ph; R = OPh
T18: X = Me; Ar = Ph; R = N(Me)Ph



B1: R = OPh
B2: R = N(Me)Ph

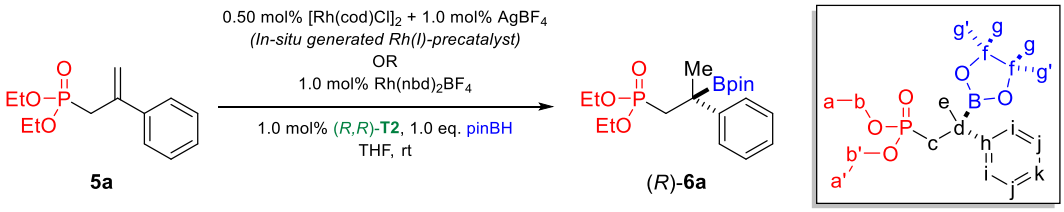


Summary of the small-scale screening results. (**Note: Yields are estimated by ^{31}P NMR analysis of the crude reaction mixtures**.)

Entry	Ligand used	**5a** unreacted (%)	**6a** yield (%)	**6a** er	**6a'** yield (%)	**6a'** er	**6a:6a'** ratio	**6a''** yield (%)
1	**T1**	0	81	95:5	13	92:8	6.2:1	5

2	**T2**	0	84	97:3	11	88:12	7.6:1	3
3	**T3**	0	75	96:4	12	92:8	6.2:1	13
4	**T4**	0	65	68:32	25	88:12	2.5:1	9
5	**T5**	0	9	51:49	50	59:41	1:5.5	40
6	**T6**	0	48	63:37	49	82:18	1:1	3
7	**T7**	0	75	92:8	13	64:36	5.6:1	12
8	**T8**	0	77	91:9	10	70:30	7.7:1	13
9	**T9**	0	69	94:6	12	63:37	5.3:1	19
10	**T10**	0	70	91:9	20	89:11	3.5:1	10
11	**T11**	0	75	92:8	11	88:12	6.8:1	12
12	**T12**	0	3	70:30	36	62:38	1:12	27
13	**T13**	0	4	56:44	32	76:24	1:8	18
14	**T14**	0	3	66:34	41	57:43	1:14	27
15	**T15**	0	14	52:48	45	53:47	1:3.1	28
16	**T16**	49	0	--	12	66:34	--	35
17	**T17**	0	73	90:10	14	65:35	5.3:1	13
18	**T18**	0	4	65:35	35	63:37	1:8.8	36
19	**B1**	10	0	--	45	48:52	--	42
20	**B2**	39	17	68:32	25	56:44	--	19
21	**BINAP**	100	--	--	--	--	--	--

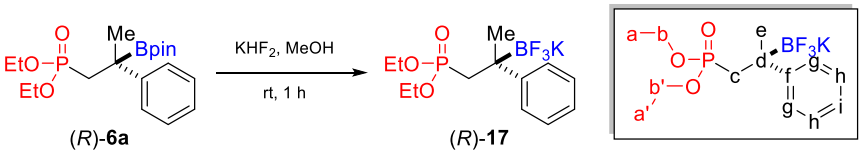
(5) General procedure for catalytic asymmetric hydroboration (CAHB) and stereospecific functionalizations of chiral tertiary benzylic boronic esters.



Representative procedure for Catalytic Asymmetric HydroBoration (CAHB) of conjugated methylidenes and trisubstituted alkenes (GP3): *Catalyst Preparation:* The active hydroboration catalyst is prepared in the dry nitrogen glovebox as follows: $[Rh(cod)Cl]_2$ (2.5 mg, 5.1 μmol) is dissolved in dry dichloromethane (0.5 mL) in an 8 mL glass vial equipped with a small teflon stirbar. To the resultant yellow/orange solution, a 0.05 *M* solution of $AgBF_4$ in THF (0.21 mL, 10.5 μmol) is added and the mixture is allowed to stir vigorously for 10 minutes at room temperature. The formed AgCl precipitate is filtered through a Pasteur pipette packed with cotton into a dry 8 mL vial and the cotton pack was further washed with additional 0.5 mL THF. The combined washings were dried in the vacuum chamber over 30 minutes. Following this, 1.02 mL of a stock solution of the ligand (*R,R*)-**T2** (Prepared by dissolving 8.65 mg of the ligand in 1.21 mL THF) is added to the dry Rh(I)-precursor and the resultant mixture is stirred vigorously for 15 minutes at room temperature to afford the active hydroboration catalyst. *Alternative Catalyst Preparation:* Alternatively, the catalyst can be prepared from $Rh(nbd)_2BF_4$ as follows: $Rh(nbd)_2BF_4$ (3.8 mg, 10 μmol) is weighed out in a dry 8 mL glass vial equipped with a small teflon stirbar and to the weighed crystals is added a 1.02 mL of a stock solution of the ligand (*R,R*)-**T2** (Prepared by dissolving 8.65 mg of the ligand in 1.21 mL THF). The resultant mixture is stirred vigorously for 1 hour to afford the active hydroboration catalyst. *Note:* In both the procedures above, the total volume of the active hydroboration catalyst is 1.02 mL which is about 1 mol% catalyst load for five 0.2 mmol CAHB reactions. Catalysts prepared using either methods described above are comparable in their efficiencies for CAHB reactions.

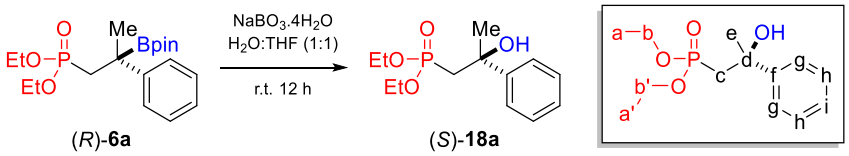
CAHB procedure: Substrate **5a** (51 mg, 0.2 mmol) is weighed out in a dry 8 mL vial charged with a small teflon stirbar. Dry THF (0.2 mL) is added, followed by neat pinacolborane (29 μL, 0.2 mmol, 1.0 eq) and the resultant mixture is stirred for 10 minutes. Afterwards, 0.2 mL of the chiral rhodium catalyst is added drop wise (over 10 minutes) and the reaction mixture is capped, taken outside of the glovebox and is stirred at room temperature (18 ºC) for *ca.* 3 hours. The completion of the reaction is indicated by the disappearance of the starting material peak (~26 ppm) and the appearance of the product peak (~30 ppm) in the crude ^{31}P NMR spectrum of the reaction mixture. Afterwards, the reaction mixture is concentrated under reduced pressure and the crude mixture is purified by flash chromatography on silica gel (ethyl acetate/hexanes 1:1) to afford the chiral tertiary benzylic boronic ester (*R*)-**6a** as a colorless oil (62 mg, 81%). [*Note:* Typical CAHB reactions were carried out with an overall substrate concentration of 0.5 M in THF and the typical reaction times were 3 hours at r.t. Gram scale reactions, however, were carried out with an overall

substrate concentration of 1.0M in THF and with a reduced catalyst loading (0.5 mol%) and the reactions were run for 12 hours at r.t. Absolute configuration assignment: See section **9**. (*R*,*R*)-**T2** affords (*R*)-**6a**.] Characterization data for (*R*)-**6a**: TLC analysis (ethyl acetate/hexanes 2:3) R_f = 0.5; $[\alpha]_D^{20}$ = -3.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, d, *J* = 7.5 Hz, i), 7.28 (2H, dd, *J* = 7.5, 7.0 Hz, j), 7.15 (1H, d, *J* = 7.0 Hz, k), 4.06-3.91 (4H, m, b+b'), 2.51-2.12 (2H, m, c), 1.58 (3H, s, e), 1.28-1.20 (18H, a+a'+g) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.28 (d, $^3J_{C-P}$ = 16.0 Hz, h), 128.30 (j), 126.67 (i), 125.68 (k), 83.93 (f), 61.32 (d, $^2J_{C-P}$ = 6.0 Hz, b or b'), 60.95 (d, $^2J_{C-P}$ = 6 Hz, b or b'), 35.49 (d, $^1J_{C-P}$ = 138 Hz, c), 24.85 (g or g'), 24.71 (g or g'), 22.27 (d, $^3J_{C-P}$ = 4.0 Hz, e), 16.58 (d, $^3J_{C-P}$ = 5.0 Hz, a or a'), 16.53 (d, $^3J_{C-P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.0 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.58 ppm; IR (neat) 2977 (aromatic C-H), 2931 (aliphatic C-H), 1495 (aromatic C=C), 1469 (aromatic C=C), 1444 (aromatic C=C), 1240 (P=O), 1053 (C-O), 1023 (C-O), 953 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{19}H_{32}BO_5P$ = 382.2080, found 382.2087 *m/z*. The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18a**.



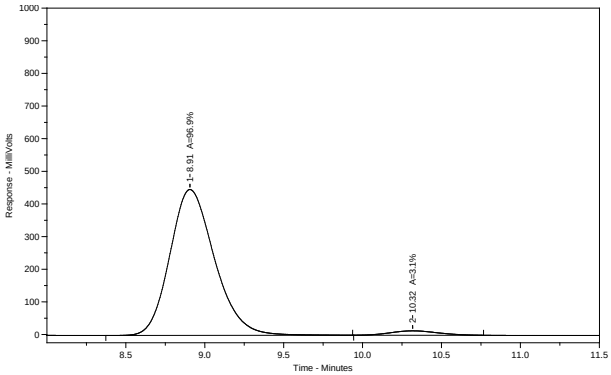
(*R*)-**6a** (*R*)-**17**

Representative procedure for transformation of chiral tertiary benzylic boronic esters to the corresponding potassium trifluoroborate salts (GP4): This transformation was carried out with a slight modification of the original procedure reported procedure[8] by Aggarwal as follows: To a solution of the chiral tertiary benzylic boronic ester (*R*)-**6a** (57 mg, 0.15 mmol, 1.0 eq) in methanol (0.75 mL) was added 4.5M solution of KHF_2 in H_2O (0.15 mL, 0.67 mmol, 4.5 eq) dropwise at room temperature and the resultant mixture was stirred vigorously for 1 hour. Afterwards, the volatiles were removed under reduced pressure and the residue was redissolved in 1:1 Ethanol: Benzene (3 mL) and the mixture was evaporated in rotary evaporator to get rid of the solvents. This process was repeated 4 times to get rid of pinacol diol. To the resultant residue was added dry acetone (3 mL) and the resultant mixture was evaporated. This process was repeated 3 times. Finally, the resultant residue was triturated with dry acetone (3 mL x 4) and the combined organics were dried under reduced pressure to afford the potassium trifluoroborate salt (*R*)-**17** as white powder (47 mg, 87%): $[\alpha]_D^{20}$ = -21° (*c* = 1.0, CH_3CN); ^{1}H NMR (400 MHz, CD_3OD) δ 7.42 (2H, d, *J* = 8.0 Hz, g), 7.23 (2H, dd, *J* = 8.0, 7.0 Hz, h), 7.05 (2H, dd, *J* = 7.0 Hz, h), 3.88-3.56 (4H, m, b+b'), 2.62 (1H, t, *J* = 16.0 Hz, c(1H)), 2.18 (1H, t, *J* = 17.0 Hz, c(1H)), 1.45 (3H, s, e), 1.13 (3H, t, *J* = 7.0 Hz, a or a'), 1.06 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, CD_3OD) δ 151.29 (d, $^3J_{C-P}$ = 4.0 Hz, f), 128.07 (g+h), 124.39 (i), 61.89 (d, $^2J_{C-P}$ = 7.0 Hz, b or b'), 61.87 (d, $^2J_{C-P}$ = 7.0 Hz, b or b'), 34.46 (d, $^1J_{C-P}$ = 133 Hz, c), 21.09 (d, $^3J_{C-P}$ = 4.0 Hz, e), 16.55 (d, $^3J_{C-P}$ = 6.0 Hz, a or a'), 16.49 (d, $^3J_{C-P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, CD_3OD) δ 36.04 ppm; ^{19}F NMR (376 MHz, CD_3OD) δ -153.57 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ 4.87 (br, s) ppm; IR (neat) 2983 (aromatic C-H), 2909 (aliphatic C-H), 1599, 1442 (aromatic C=C), 1409 (aromatic C=C), 1280 (P=O), 1187, 1056 (C-O), 1005 (C-O), 967, 856, 823, 791, 700 cm^{-1}. HRMS (ESI) calculated for $C_{13}H_{20}BF_3KO_3P+K^+$ = 401.0469, found 401.0459 *m/z*.

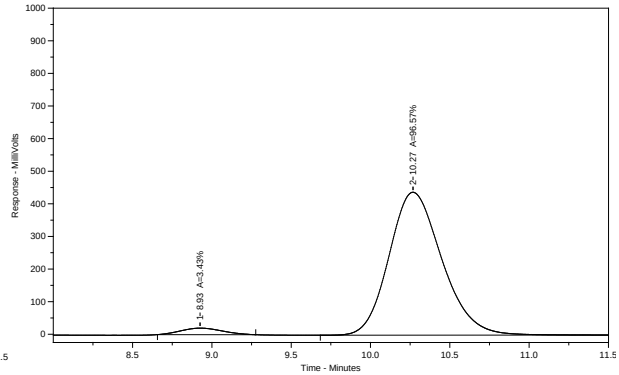


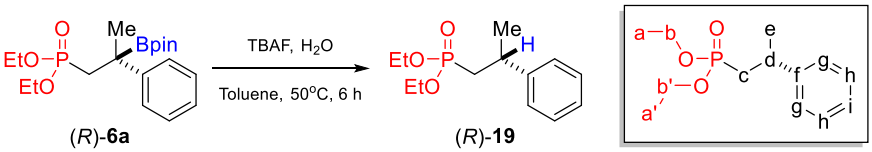
Representative procedure for oxidation of chiral tertiary benzylic boronic esters to the corresponding chiral tertiary benzylic alcohols (GP5): A mixture of the chiral tertiary benzylic boronic ester (*R*)-**6a** (57 mg, 0.15 mmol, 1.0 eq) and $NaBO_3.4H_2O$ (115 mg, 0.75 mmol, 5.0 eq) in a 1:1 solvent mixture of THF: H_2O (2 mL) was stirred vigorously at room temperature for 12 hours. Afterwards, 1 mL of brine is added to the reaction mixture and the mixture was extracted with ethyl-acetate (3 mL x 5). The combined organics were filtered through a small plug of silica gel and is concentrated in vacuum. The resultant residue is redissolved in 1:1 ethanol:benzene (6 mL) and is evaporated under reduced pressure. The dissolution/evaporation cycle is repeated 4 times to get rid of the pinacol diol to afford the clean chiral tertiary benzylic boronic ester (*S*)-**18a** (37 mg, 90%): TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +2.5 º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, *J* = 8.0 Hz, g), 7.36 (2H, dd, *J* = 8.0, 7.5 Hz, h), 7.25 (1H, t, *J* = 7.5 Hz, i), 5.00 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.78-3.67 (1H, m, b or b'), 3.45-3.35 (1H, m, b or b'), 2.53-2.32 (2H, m, c), 1.64 (3H, d, *J* = 2.5 Hz, e), 1.33 (3H, t, *J* = 7.0 Hz, a or a'), 1.02 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.40 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, f), 128.31 (h), 126.94 (i), 124.98 (g), 72.18 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.95 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.63 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 39.93 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 32.68 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.53 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.28 (d, $^3J_{C\text{-}P}$ = 6.3 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.90 ppm; IR (neat) 3400 (O-H), 2979 (aromatic C-H), 2932 (aliphatic C-H), 1491 (aromatic C=C), 1446 (aromatic C=C), 1215 (P=O), 1048 (C-O), 1021 (C-O), 960 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{21}O_4P$+Na^+ = 295.1075, found 295.1081 *m/z*. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile Phase = 95:5 Hexanes:Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 3:97, CAHB of **5a** with (*R*,*R*)-**T2**, then oxidation



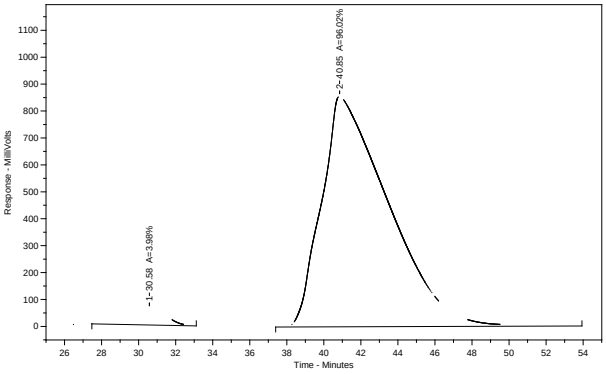
(b) R:S = 97:3, CAHB of **5a** with (*S*,*S*)-**T2**, then oxidation



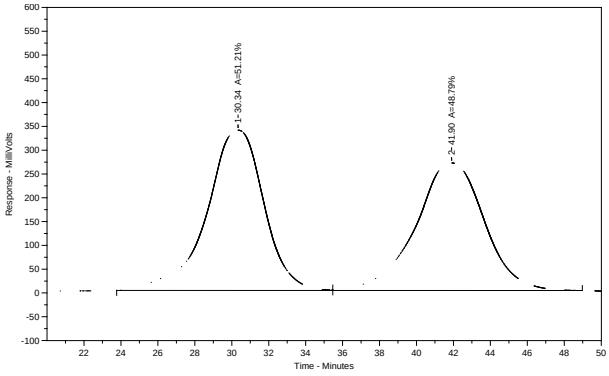


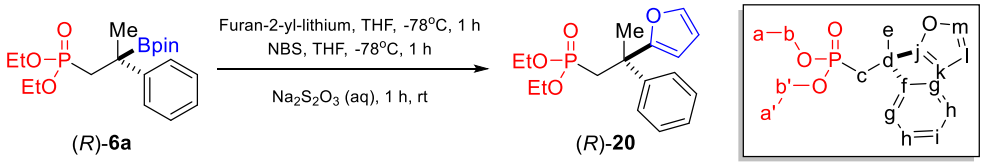
Representative procedure for protodeboronation of chiral tertiary benzylic boronic esters to the corresponding chiral reduced products (GP6): This transformation was carried out according to the procedure reported[9] by Aggarwal as follows. To a solution of the chiral tertiary benzylic boronic ester (*R*)-**6a** (57 mg, 0.15 mmol, 1.0 eq) in toluene (0.75 mL) was added tetrabutylammonium fluoride (TBAF, 0.3 mL; 1M solution in THF) and the resultant mixture was vigorously stirred at 50°C for 6 hours. (Note: Commercial TBAF is contaminated with up to 5% H_2O and hence addition of water separately was not necessary). Afterwards, the reaction mixture was concentrated and purified by flash chromatography on silica gel (ethyl acetate) to afford the chiral reduced product (*R*)-**19** as a colorless oil (33 mg, 85%): TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +15.9 ° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (5H, m, aryl), 4.08-3.87 (4H, m, b+b'), 3.29-3.17 (1H, m, d), 2.21-1.96 (2H, m, c), 1.41 (3H, d, *J* = 7.0 Hz, e), 1.26 (3H, t, *J* = 7.0 Hz, a or a'), 1.22 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.90 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, f), 128.68 (g or h), 126.85 (g or h), 126.56 (i), 61.56 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.39 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 34.87 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, d), 34.48 (d, $^1J_{C\text{-}P}$ = 138.5 Hz, c), 23.71 (d, $^3J_{C\text{-}P}$ = 9.0 Hz, e), 16.52 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a or a'), 16.51 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.16 ppm; IR (neat) 2978 (aromatic C-H), 2905 (aliphatic C-H), 1453 (aromatic C=C), 1391 (aromatic C=C), 1246 (P=O), 1053 (C-O), 1022 (C-O), 953 (P-O), 699 cm^{-1}; Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALCEL OJ-H; Mobile Phase = 97:3 Hexanes:Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 96:4, CAHB of **5a** with (*R*,*R*)-**T2**, then protodeboronation.



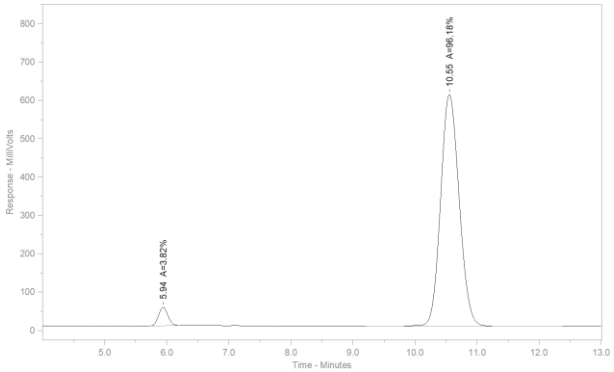
(b) Racemate



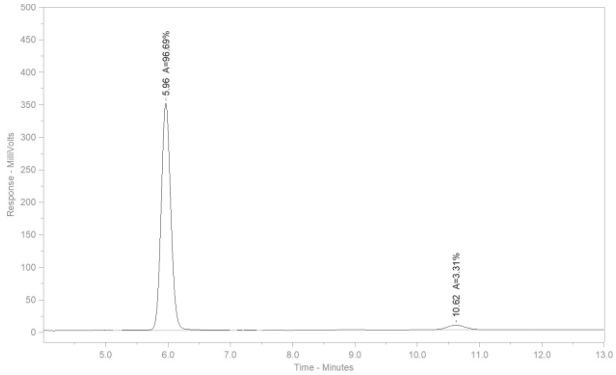


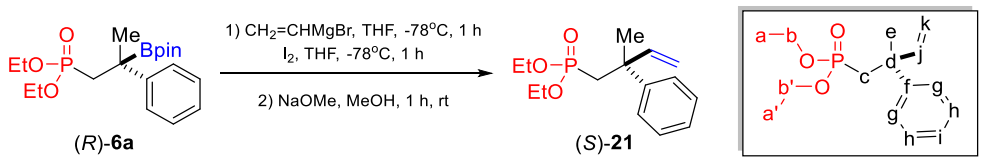
Representative procedure for the cross coupling of chiral tertiary benzylic boronic esters with furan (GP7): This transformation was carried out according to our previously reported modified procedure[5] of the original procedure[10] reported by Aggarwal: The chiral tertiary benzylic boronic ester (*R*)-**6a** (57 mg, 0.15 mmol, 1.0 eq) affords the coupling product (*R*)-**20** (44 mg, 91%) as a light-yellow oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +4.1 ^{o} (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.19 (6H, m, g+h+i+m), 6.33 (1H, dd, *J* = 3.0, 2.0 Hz, l), 6.20 (1H, d, *J* = 3.0 Hz, k), 3.97-3.72 (4H, m, b+b'), 2.79-2.59 (2H, m, c), 1.93 (3H, s, e), 1.18 (3H, t, *J* = 7.0 Hz, a or a'), 1.16 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.14 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, j), 146.59 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, f), 141.56 (m), 128.36 (g or h), 126.64 (i), 126.26 (g or h), 110.15 (l), 105.83 (k), 61.35 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 41.49 (d, $^2J_{C\text{-}P}$ = 2.0 Hz, d), 36.97 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 26.16 (d, $^3J_{C\text{-}P}$ = 2.0 Hz, e), 16.42 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.52 ppm; IR (neat) 2920 (aromatic C-H), 2853 (aliphatic C-H), 1715, 1496 (aromatic C=C), 1445 (aromatic C=C), 1240 (P=O), 1054 (C-O), 1024 (C-O), 956 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{23}O_4P$+Na^+ = 345.1232, found = 345.1235 *m/z*. Enantiomer ratio = 97.5:3.5, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC (3 micron); Mobile Phase = 80:20 Hexanes:Isopropanol; Flow rate = 1.0 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 96:4, CAHB of **5a** with (*R*,*R*)-**T2**, then coupling



(b) R:S = 3:97, CAHB of **5a** with (*S*,*S*)-**T2**, then coupling

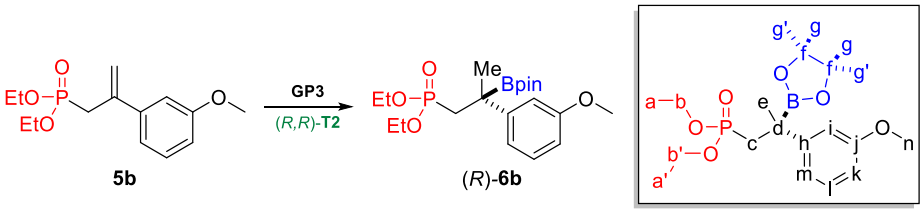




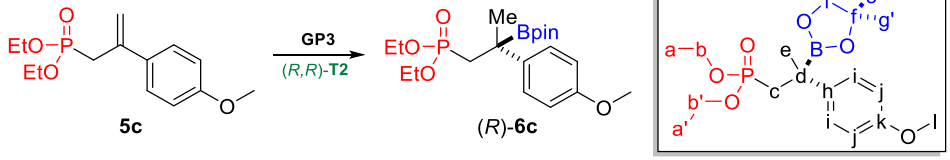
Representative procedure for vinylation of chiral tertiary benzylic boronic esters to the corresponding vinylated derivative (GP8): This transformation was carried out according to our

previously reported modified procedure[5] of the original procedure[11] reported by Aggarwal: The chiral tertiary benzylic boronic ester (*R*)-**6a** (57 mg, 0.15 mmol, 1.0 eq) affords the vinylated product (*S*)-**21** (30 mg, 71%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -7.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (2H, d, *J* = 8.0 Hz, g), 7.31 (2H, dd, *J* = 8.0, 7.0 Hz, h), 7.20 (1H, t, *J* = 7.0 Hz, i), 6.16 (1H, dd, *J* = 17.0, 11.0 Hz, j), 5.13 (1H, d, *J* = 11.0 Hz, k(1H)), 5.08 (1H, d, *J* = 17.0 Hz, k(1H)), 3.98-3.67 (4H, m, b+b'), 2.43-2.26 (2H, m, c), 1.67 (3H, s, e), 1.19 (3H, t, *J* = 7.0 Hz, a or a'), 1.13 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.70 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, j), 146.25 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, f), 128.24 (h), 126.77 (g), 126.41 (i), 111.85 (k), 61.25 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.20 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 42.37 (d, $^2J_{C\text{-}P}$ = 2.0 Hz, d), 37.94 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 25.97 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.45 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.39 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.47 ppm; IR (neat) 2978 (sp^2 C-H), 2905 (sp^3 C-H), 1635 (C=C), 1600 (C=C), 1494 (aromatic C=C), 1445 (aromatic C=C), 1391 (aromatic C=C), 1238 (P=O), 1054 (C-O), 1024 (C-O), 954 (P-O), 698 cm^{-1}; Enantiomer ratio = 97:3, determined from derivatives obtained via oxophosphonate intermediate **25**.

(6) Synthesis of phosphonate-functionalized chiral tertiary benzylic boronic esters.

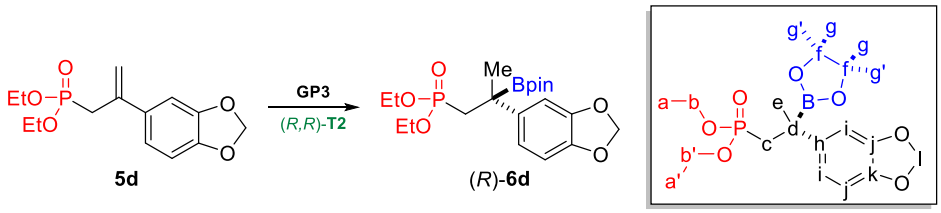


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6b: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5b** (57 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6b** (63 mg, 76%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -18° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (2H, t, *J* = 8.0 Hz, l), 7.00 (1H, s, i), 6.97-6.86 (1H, m, m), 6.72 (1H, dd, *J* = 6.5, 2.0 Hz, k), 4.09-3.95 (4H, m, b+b'), 3.80 (3H, d, *J* = 2.0 Hz, n), 2.47 (1H, dd, *J* = 18.0., 15.0 Hz, c(1H)), 2.15 (1H, dd, *J* = 17.5, 15.0 Hz, c(1H)), 1.56 (3H, s, e), 1.31-1.23 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.60 (j), 148.20 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, h), 129.13 (l), 119.08 (i), 112.74 (m), 110.93 (k), 83.90 (f), 41.42 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.04 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.33 (n), 35.56 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.94 (g or g'), 24.80 (g or g'), 22.38 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, e), 16.62 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, a or a'), 16.57 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.8 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.55 ppm; IR (neat) 2977 (aromatic C-H), 2933 (aliphatic C-H), 1599, 1580, 1486 (aromatic C=C), 1464 (aromatic C=C), 1240 (P=O), 1143, 1024 (C-O), 955 (P-O) cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18b**.

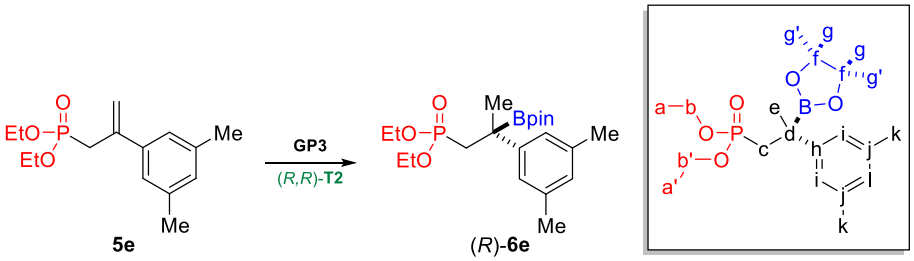


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6c: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5c** (57 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6c** (58 mg, 70%) as a dense waxy liquid: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; $[\alpha]_D^{20}$ = +4.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, *J* = 9.0 Hz, i), 6.83 (2H, d, *J* = 9.0 Hz, j), 4.08-3.90 (4H, m, b+b'), 3.78 (3H, s, l), 2.43 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.12 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.55 (3H, s, e), 1.29-1.21 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.55 (k), 138.32 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, h), 127.71 (i), 113.71 (j), 83.92 (f), 61.35 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.02 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 55.40 (l), 35.73 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.89 (g or g'), 24.76 (g or g'), 22.50 (e), 16.53 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, a or a'), 16.58 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.0 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.65 ppm; IR (neat) 2976 (aromatic C-H), 2906 (aliphatic C-H), 1607, 1510, 1463 (aromatic C=C), 1242 (P=O), 1142, 1024 (C-O), 954 (P-O) cm^{-}

[1]; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18c**.

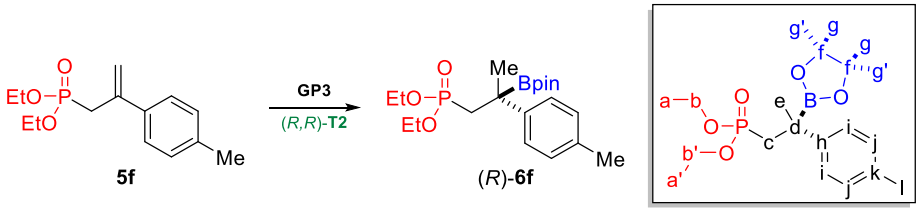


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6d: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5d** (60 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6d** (66 mg, 77%) as a colorless liquid (*Note: This boronic ester was air sensitive. After purification, this product was stored under nitrogen in the freezer)*: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -7.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (1H, d, *J* = 2.0 Hz, i), 6.83 (1H, dd, *J* = 8.0, 2.0 Hz, i), 6.73 (1H, d, *J* = 8.0 Hz, j), 5.90 (2H, s, l), 4.06-3.93 (4H, m, b+b'), 2.38 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.09 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.52 (3H, s, e), 1.29-1.21 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.65 (j or k), 145.45 (j or k), 140.33 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, h), 119.57 (i), 108.00 (j), 107.62 (i), 100.89 (l), 83.95 (f), 61.33 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.98 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 35.38 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.85 (g or g'), 24.70 (g or g'), 22.57 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, e), 16.56 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a'), 16.49 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.1 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.34 ppm; IR (neat) 2977 (aromatic C-H), 2906 (aliphatic C-H), 1487 (aromatic C=C), 1321, 1234 (P=O), 1142, 1024 (C-O), 956 (P-O), 936, 729 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18d**.

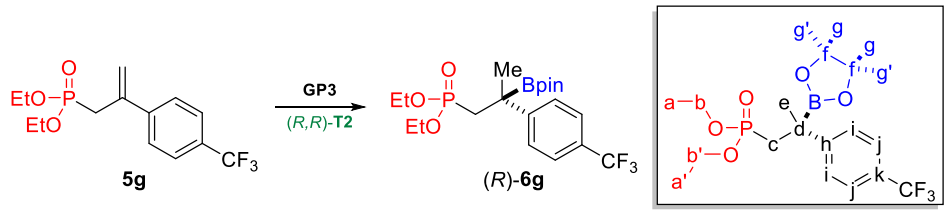


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6e: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5e** (56 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6e** (62 mg, 76%) as a colorless liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = -4.3° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (2H, s, i), 6.80 (1H, s, l), 4.11-3.92 (4H, m, b+b'), 2.46 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.29 (6H, s, k), 2.12 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.56 (3H, s, e), 1.30 (3H, t, *J* = 7.0, a or a'), 1.25 (3H, t, *J* = 7.0, a or a'), 1.22 (12H, s, g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.32 (d, $^3J_{C\text{-}P}$ = 17 Hz, h), 137.53 (j), 127.33 (l), 124.41 (i), 83.86 (f), 61.32 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.91 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 35.39 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 24.86 (g or g'), 24.67 (g or g'), 22.45 (d, $^3J_{C\text{-}P}$ = 3.5 Hz, e), 21.63 (k), 16.58 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.52 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.30 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.90 ppm;

IR (neat) 2976 (aromatic C-H), 2915 (aliphatic C-H), 1598, 1461 (aromatic C=C), 1321 (aromatic C=C), 1240 (P=O), 1164, 1053 (C-O), 1025 (C-O), 954 (P-O), 839, 697 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18e**.

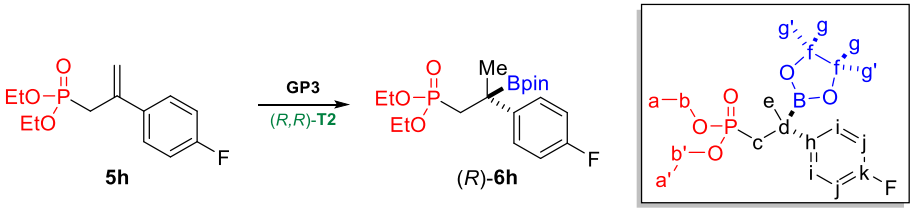


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6f: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*R*,*R*)-**T2**, the substrate **5f** (54 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6f** (64 mg, 81%) as a colorless liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = -3.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (2H, d, *J* = 8.0 Hz, i), 7.09 (2H, d, *J* = 8.0 Hz, j), 4.09-3.90 (4H, m, b+b'), 2.46 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.30 (3H, s, l), 2.12 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.56 (3H, s, e), 1.28 (3H, t, *J* = 7.0 Hz, a or a'), 1.24 (3H, t, *J* = 3.0 Hz, a or a'), 1.20 (12H, s, g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.22 (d, $^3J_{C\text{-}P}$ = 16.0 Hz, h), 135.01 (k), 128.99 (j), 126.45 (i), 83.86 (f), 61.32 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.96 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 35.50 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 24.83 (g or g'), 24.70 (g or g'), 22.34 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, e), 20.98 (l), 16.54 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, a or a'), 16.49 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.25 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.75 ppm; IR (neat) 2977 (aromatic C-H), 2906 (aliphatic C-H), 1511, 1463 (aromatic C=C), 1345, 1240 (P=O), 1153, 1054, 1025 (C-O), 955 (P-O), 836, 729 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18f**.

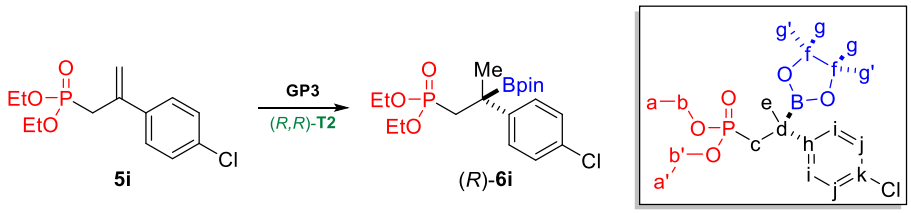


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6g: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5g** (64 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6g** (69 mg, 77%) as a colorless liquid: TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.5; $[\alpha]_D^{20}$ = -5.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (4H, dd, *J* = 12.5, 9.0 Hz, i+j), 4.06-3.86 (4H, m, b+b'), 2.41 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.20 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.60 (3H, s, e), 1.25-1.18 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.46 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, h), 127.96 (q, $^2J_{C\text{-}F}$ = 32.0 Hz, k), 127.25 (i), 125.11 (q, $^3J_{C\text{-}F}$ = 4.0 Hz, j), 124.55 (q, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 84.22 (f), 61.41 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.07 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 35.49 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 22.24 (g or g'), 22.19 (g or g'), 22.21 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.49 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.43 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.28 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.66 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.37 ppm; IR (neat) 2979 (aromatic C-H), 2932 (aliphatic

C-H), 1616, 1469 (aromatic C=C), 1381 (aromatic C=C), 1324 (C-F), 1240 (P=O), 1120, 1053 (C-O), 1025 (C-O), 955 (P-O), 844, 831, 679 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18g**.

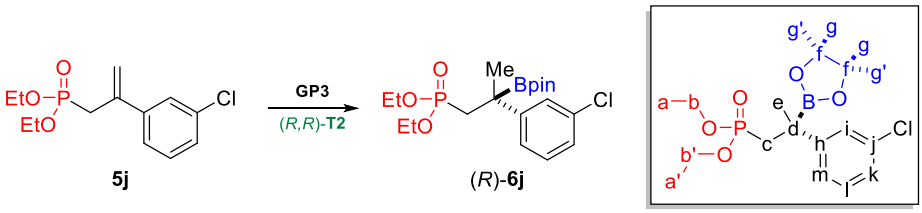


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6h: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5h** (54 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6h** (51 mg, 6%) as a colorless liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -5.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (2H, dd, *J* = 8.5, 5.5 Hz, i), 6.96 (2H, t, *J* = 8.5 Hz, j), 4.06-3.88 (4H, m, b+b'), 2.39 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.14 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.56 (3H, s, e), 1.27-1.20 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.15 (d, $^1J_{C\text{-}F}$ = 244 Hz, k), 141.78 (dd, $^4J_{C\text{-}F}$ = 3.0 Hz, $^3J_{C\text{-}P}$ = 15.0 Hz, h), 128.28 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, i), 114.89 (d, $^2J_{C\text{-}F}$ = 21 Hz, j), 84.01 (f), 61.32 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.99 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 35.76 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.80 (g or g'), 24.68 (g or g'), 22.46 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.55 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, a or a'), 16.49 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.00 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.12 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.33 ppm; IR (neat) 2977 (aromatic C-H), 2932 (aliphatic C-H), 1603, 1508 (C-F), 1469 (aromatic C=C), 1343 (aromatic C=C), 1323 (aromatic C=C), 1237 (P=O), 1143, 1053 (C-O), 1024 (C-O), 955 (P-O), 838 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18h**.

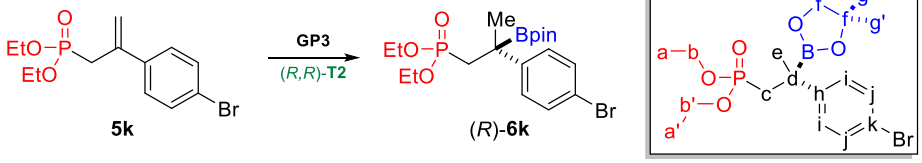


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6i: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5i** (58 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6i** (68 mg, 82%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -8.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (2H, d, *J* = 8.5 Hz, i or j), 7.24 (2H, d, *J* = 8.5 Hz, i or j), 4.06-3.88 (4H, m, b+b'), 2.38 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.13 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.55 (3H, s, e), 1.27-1.19 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.75 (d, $^3J_{C\text{-}P}$ = 15 Hz, h), 131.44 (k), 128.28 (i or j), 128.24 (i or j), 84.06 (f), 61.36 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.02 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 35.52 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 24.80 (g or g'), 24.68 (g or g'), 22.24 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.54 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a'), 16.48 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.13 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.99 ppm; IR (neat) 2977 (aromatic C-H), 2931 (aliphatic C-H), 1740, 1492 (aromatic C=C), 1323 (aromatic C=C), 1240 (P=O), 1143,

1053 (C-O), 1024 (C-O), 954 (P-O), 830 (C-Cl) cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18i**.

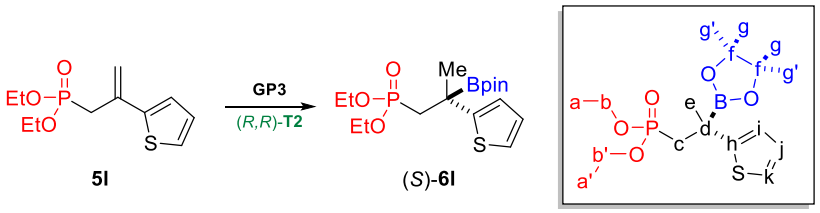


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6j: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5j** (58 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6j** (53 mg, 64%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 2:5) R_f = 0.5; $[\alpha]_D^{20}$ = -12.4° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (1H, s, i), 7.27 (1H, d, *J* = 8.0 Hz, m or k), 7.20 (1H, t, *J* = 8.0 Hz, l), 7.12 (1H, d, *J* = 8.0 Hz, m or k), 4.07-3.89 (4H, m, b+b'), 2.39 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.13 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.55 (3H, s, e), 1.27-1.20 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.49 (d, $^3J_{C\text{-}P}$ = 15 Hz, h), 134.17 (j), 129.43 (l), 127.06 (i), 125.82 (m or k), 125.06 (m or k), 84.11 (f), 61.39 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.00 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 35.40 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 24.79 (g or g'), 24.65 (g or g'), 22.16 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, e), 16.53 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a'), 16.47 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.19 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.99 ppm; IR (neat) 2977 (aromatic C-H), 2931 (aliphatic C-H), 1593, 1567, 1472 (aromatic C=C), 1323 (aromatic C=C), 1240 (P=O), 1143, 1053 (C-O), 1024 (C-O), 955 (P-O), 833 (C-Cl) cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18j**.

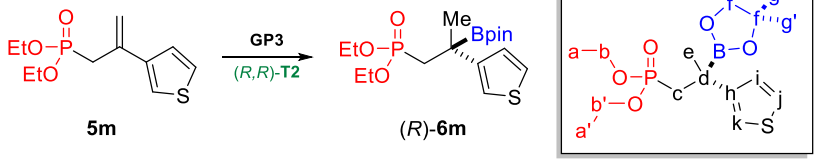


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6k: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5k** (67 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6k** (63 mg, 68%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = -5.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J* = 8.6 Hz, i or j), 7.27 (2H, d, *J* = 8.6 Hz, i or j), 4.07-3.89 (4H, m, b+b'), 2.39 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.14 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.55 (3H, s, e), 1.28-1.20 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.32 (d, $^3J_{C\text{-}P}$ = 15 Hz, h), 131.25 (i or j), 128.68 (i or j), 119.59 (k), 84.10 (f), 61.40 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.06 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 35.74 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.83 (g or g'), 24.71 (g or g'), 22.19 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.56 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a'), 16.51 (d, $^3J_{C\text{-}P}$ = 5.5 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.05 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.96 ppm; IR (neat) 2977 (aromatic C-H), 2930 (aliphatic C-H), 1488 (aromatic C=C), 1371 (aromatic C=C), 1240 (P=O), 1142, 1053

(C-O), 1023 (C-O), 955 (P-O), 830, 686 (C-Br) cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18k**.

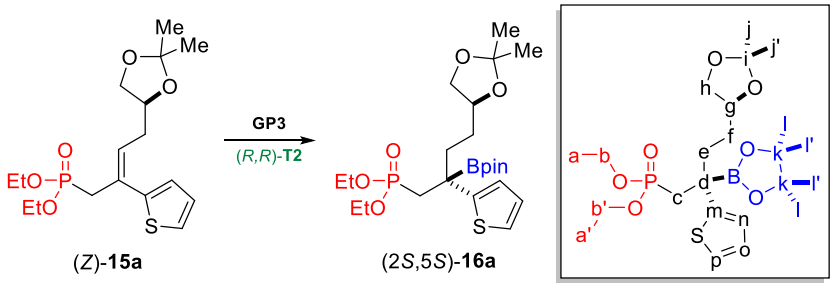


Synthesis of chiral tertiary benzylic boronic ester (*S*)-6l: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5l** (52 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*S*)-**6l** (66 mg, 85%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +6.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.11 (1H, m, k), 6.92-6.90 (2H, m, i+j), 4.09-3.98 (4H, m, b+b'), 2.51 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.15 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.62 (3H, s, e), 1.31-1.23 (18H, m, a+a'+g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.35 (d, $^3J_{C\text{-}P}$ = 20 Hz, h), 126.78 (i or j), 123.24 (i or j), 122.97 (k), 84.19 (f), 61.53 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.10 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 37.03 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.83 (g or g'), 24.76 (g or g'), 24.17 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.57 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a+a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.78 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.16 ppm; IR (neat) 2978 (aromatic C-H), 2931 (aliphatic C-H), 1739, 1463 (aromatic C=C), 1325 (aromatic C=C), 1236 (P=O), 1142, 1052 (C-O), 1023 (C-O/C=S), 955 (P-O), 731, 692 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18l**.

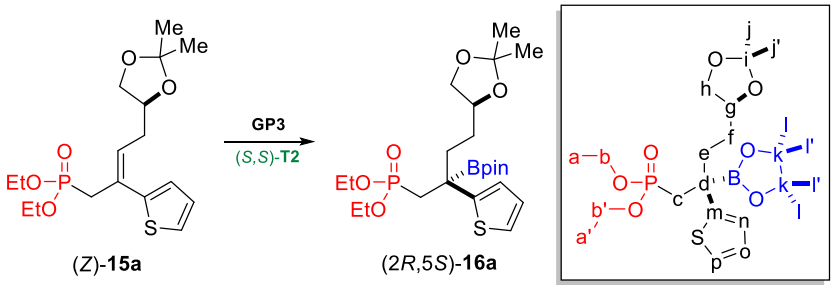


Synthesis of chiral tertiary benzylic boronic ester (*R*)-6m: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate **5m** (52 mg, 0.2 mmol) yields the tertiary benzylic boronic ester product (*R*)-**6m** (62 mg, 80%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = -6.4° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, dd, *J* = 5.0, 3.0 Hz, j), 7.10 (1H, dd, *J* = 5.0, 1.3 Hz, i), 7.03 (1H, dd, *J* = 3.0, 1.3 Hz, k), 4.11-3.94 (4H, m, b+b'), 2.45 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.10 (1H, dd, *J* = 18.0, 15.0 Hz, c), 1.55 (3H, s, e), 1.30-1.24 (6H, m, a+a'), 1.20 (12H, s, g+g') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.64 (d, $^3J_{C\text{-}P}$ = 17.5 Hz, h), 127.28 (i), 125.00 (j), 119.11 (k), 83.97 (f), 61.39 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.06 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 35.64 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 24.82 (g or g'), 24.74 (g or g'), 22.84 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 16.58 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.56 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.29 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.08 ppm; IR (neat) 2977 (aromatic C-H), 2931 (aliphatic C-H), 1739, 1462 (aromatic C=C), 1339 (aromatic C=C), 1320 (C=C), 1239 (P=O), 1143, 1053 (C-O), 1024 (C-

O/C=S), 954 (P-O), 776 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **18m**.

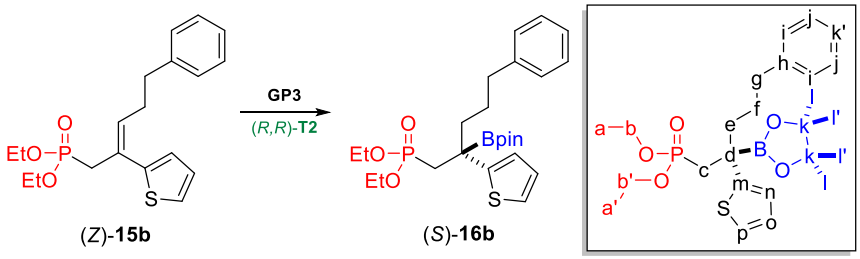


Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16a: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*R*,*R*)-**T2**, the substrate (*Z*)-**15a** (56 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16a** (62 mg, 82%) as a colorless viscous liquid. Alternatively, following **GP3** using (*R*,*R*)-**T2**, the diastereomeric substrate (*E*)-**15a** (56 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16a** (61 mg, 81%) as a colorless viscous liquid. TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +2.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (1H, dd, *J* = 5.0, 1.3 Hz, p), 6.93-6.90 (2H, m, n+o), 4.06-3.87 (6H, m, b+b'+g+h(1H)), 3.48-3.43 (1H, m, h(1H)), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.34 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.15 (1H, ddd, *J* = 18.0, 13.5, 4.5 Hz, e(1H)), 1.96 (1H, ddd, *J* = 18.0, 13.5, 4.5 Hz, e(1H)), 1.69-1.61 (1H, m, f(1H)), 1.39-1.30 (1H, m, f(1H)), 1.35 (3H, s, j or j'), 1.32 (3H, s, j or j'), 1.29-1.22 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.73 (d, $^3J_{C\text{-}P}$ = 18 Hz, m), 126.76 (n or *o*), 124.41 (n or *o*), 123.30 (p), 108.66 (i), 84.24 (k), 76.55 (g), 69.67 (h), 61.55 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.14 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 33.74 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, e), 33.20 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.72 (f), 27.04 (j or j'), 25.84 (j or j'), 24.93 (l or l'), 24.91 (l or l'), 16.56 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a+a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.01 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.31 ppm; IR (neat) 2979 (aromatic C-H), 2933 (aliphatic C-H), 1369 (aromatic C=C), 1326 (aromatic C=C), 1239 (P=O), 1142, 1052 (C-O), 1024 (C-O/C=S), 956 (P-O), 833, 692 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol (2*R*,5*S*)-**34a**.

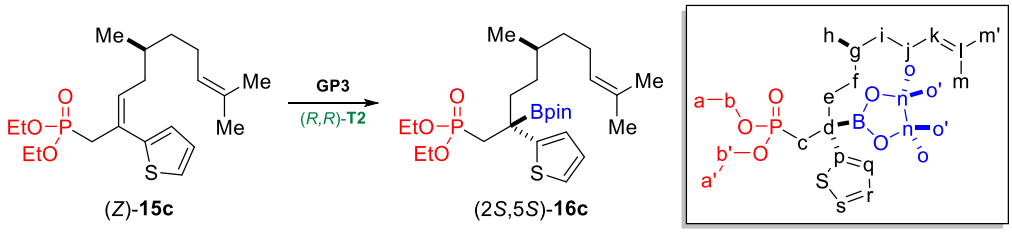


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16a: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*S*,*S*)-**T2**, the substrate (*Z*)-**15a** (56 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16a** (61 mg, 81%) as a colorless viscous liquid. Alternatively, following **GP3** with (*S*,*S*)-**T2**, the diastereomeric substrate (*E*)-**15a** (56 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16a** (60 mg, 79%) as a colorless viscous liquid.: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ =

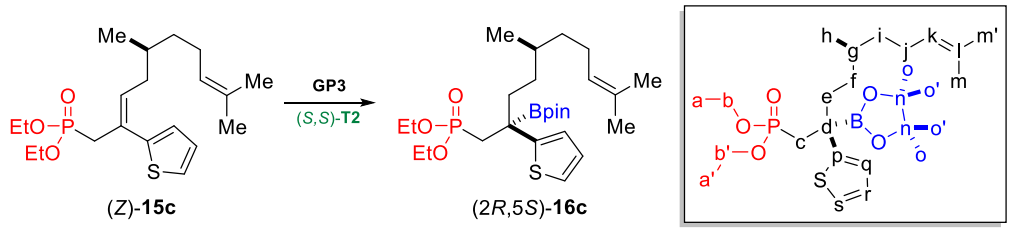
+6.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (1H, dd, *J* = 5.0, 1.0 Hz, p), 6.95 (1H, dd, *J* = 3.5, 1.0 Hz, o), 6.91 (1H, dd, *J* = 5.0, 3.5 Hz, n), 4.07-3.86 (6H, m, b+b'+g+h(1H)), 3.52-3.43 (1H, m, h(1H)), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.34 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.16 (1H, ddd, *J* = 17.0, 13.0, 4.0 Hz, e(1H)), 1.93 (1H, ddd, *J* = 18.0, 13.5, 4.5 Hz, e(1H)), 1.58-1.41 (2H, m, f), 1.35 (3H, s, j or j'), 1.32 (3H, s, j or j'), 1.30-1.22 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.56 (d, $^3J_{C\text{-}P}$ = 18 Hz, m), 126.78 (n), 124.66 (o), 123.26 (p), 108.67 (i), 84.23 (k), 76.60 (g), 69.59 (h), 61.60 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.11 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 33.89 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, e), 33.44 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.86 (f), 27.08 (j or j'), 25.87 (j or j'), 24.95 (l or l'), 24.88 (l or l'), 16.55 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a+a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.59 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.32 ppm; IR (neat) 2978 (aromatic C-H), 2933 (aliphatic C-H), 1369 (aromatic C=C), 1326 (aromatic C=C), 1240 (P=O), 1142, 1051 (C-O), 1024 (C-O/C=S), 959 (P-O), 833, 693 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol (2*S*,5*S*)-**34a**.



Synthesis of chiral tertiary benzylic boronic ester (*S*)-16b: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*Z*)-**15b** (56 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (*S*)-**16b** (63 mg, 85%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -8.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (2H, m, aryl), 7.18-7.13 (4H, m, aryl), 6.95 (1H, dd, *J* = 3.5, 1.0 Hz, o), 6.92 (1H, dd, *J* = 5.0, 3.5 Hz, n), 4.08-3.84 (4H, m, b+b'), 2.66-2.54 (2H, m, g), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.37 (1H, dd, *J* = 18.0, 15.0 Hz, c), 2.18-2.07 (2H, m, e), 1.67-1.44 (2H, m, f), 1.30-1.23 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.12 (d, $^3J_{C\text{-}P}$ = 17 Hz, m), 142.83 (h), 128.53 (aryl), 128.35 (aryl), 126.70 (n), 125.73 (aryl), 124.43 (o), 123.09 (aryl), 84.15 (k), 61.48 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.02 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 37.87 (d, $^3J_{C\text{-}P}$ = 8.0 Hz, e), 36.60 (g), 33.61 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 26.70 (f), 24.94 (l or l'), 24.90 (l or l'), 16.63 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a or a'), 16.56 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.83 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.58 ppm; IR (neat) 2976 (aromatic C-H), 2933 (aliphatic C-H), 1371 (aromatic C=C), 1324 (aromatic C=C), 1241 (P=O), 1142, 1051 (C-O), 1024 (C-O/C=S), 958 (P-O), 696 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol (*R*)-**34b**.

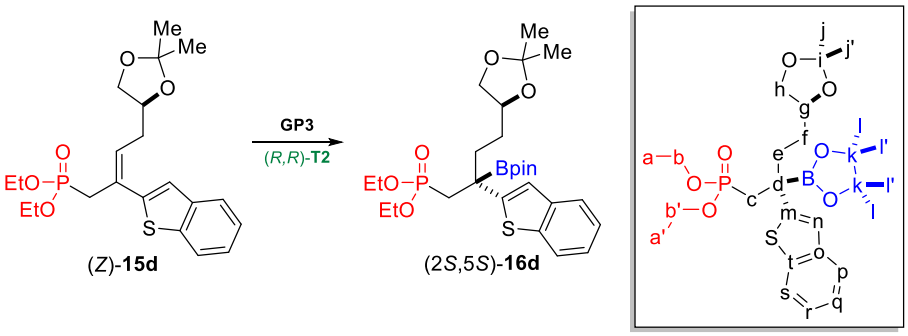


Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16c: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2** (Note: 2 mol% catalyst loading was used), the substrate (*Z*)-**15c** (58 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16c** (42 mg, 55%) as a colorless viscous liquid (Note: 2 mol% catalyst loading used. Even when higher catalyst loading is used, the reactions with this substrate did not proceed to complete consumption of substrate, perhaps due to the presence of three chelating sites leading to catalyst inactivation): TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +9.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (1H, dd, *J* = 5.0, 1.0 Hz, s), 7.00 (1H, dd, *J* = 3.5, 1.0 Hz, r), 6.92 (1H, dd, *J* = 5.0, 3.5 Hz, q), 5.09-5.06 (1H, m, k), 4.07-3.78 (4H, m, b+b'), 2.45-2.32 (2H, m, c), 2.11-1.87 (4H, m, e+j), 1.68 (3H, s, m or m'), 1.58 (3H, s, m or m'), 1.44-1.20 (21H, a+a'+f+g+o+o'), 1.14-0.94 (2H, m, i), 0.87 (3H, d, *J* = 6.5 Hz, h) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.34 (d, $^3J_{C\text{-}P}$ = 15 Hz, p), 131.07 (l), 126.63 (q), 125.24 (k), 124.70 (r), 123.02 (s), 84.12 (n), 61.38 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.03 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 37.33, 35.91 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, e) , 34.11 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 33.15, 31.86, 25.90 (m or m'), 25.81, 25.01 (o *or* o'), 24.94 (o *or* o'), 19.71 (h), 17.83 (m or m'), 16.58 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.55 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.81 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.71 (92%; major diastereomer), 30.67 (8%; minor diastereomer) ppm; IR (neat) 2977 (aromatic C-H), 2933 (aliphatic C-H), 1373 (aromatic C=C), 1325 (aromatic C=C), 1239 (P=O), 1143, 1053 (C-O), 1025 (C-O/C=S), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{26}H_{46}BO_5PS$ = 512.2897, found 512.2907 *m/z*.

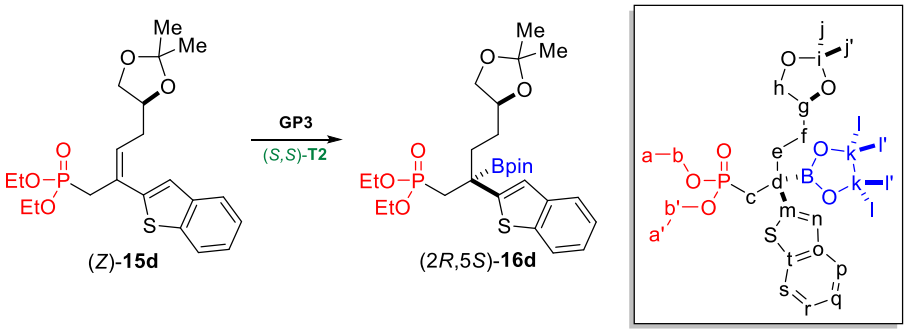


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16c: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*S*,*S*)-**T2** (Note: 2 mol% catalyst loading was used), the substrate (*Z*)-**15c** (58 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16c** (44 mg, 58%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +6.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (1H, dd, *J* = 5.0, 1.0 Hz, s), 7.00 (1H, dd, *J* = 3.5, 1.0 Hz, r), 6.92 (1H, dd, *J* = 5.0, 3.5 Hz, q), 5.07 (1H, t, *J* = 7.0 Hz, k), 4.09-3.75 (4H, m, b+b'), 2.45-2.31 (2H, m, c), 2.08-1.82 (4H, m, e+j), 1.68 (3H, s, m or m'), 1.58 (3H, s, m or m'), 1.42-1.04 (23H, a+a'+f+g+i+o+o'), 0.87 (3H, d, *J* = 6.5 Hz, h) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.34 (d, $^3J_{C\text{-}P}$ = 15 Hz, p), 131.07 (l), 126.63 (q), 125.25

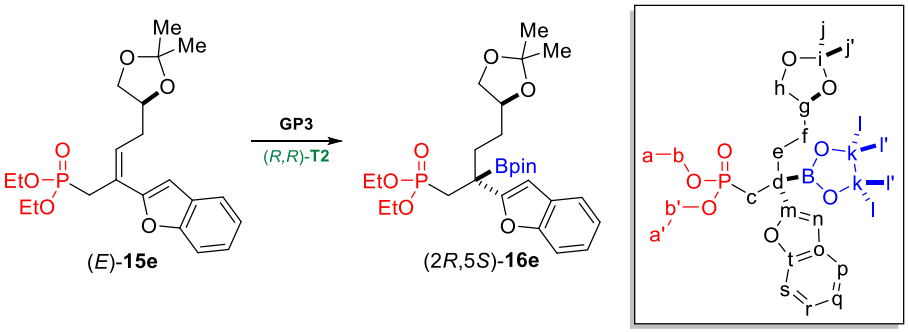
(k), 124.77 (r), 84.12 (n), 61.39 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.02 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 37.13, 36.10 (d, $^{3}J_{C\text{-}P}$ = 9.0 Hz, e), 34.26 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 33.23, 31.79, 25.91, 25.74 (m or m'), 25.03 (o *or* o'), 24.95 (o *or* o'), 19.85 (h), 17.83 (m or m'), 16.58 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.55 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.41 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.71 (9%; minor diastereomer), 30.67 (91%; major diastereomer) ppm; IR (neat) 2978 (aromatic C-H), 2933 (aliphatic C-H), 1373 (aromatic C=C), 1325 (aromatic C=C), 1239 (P=O), 1143, 1053 (C-O), 1025 (C-O/C=S), 958 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{26}H_{46}BO_5PS$ = 512.2897, found 512.2900 *m/z*.



Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16d: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*Z*)-**15d** (64 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16d** (56 mg, 68%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +11.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.62-7.60 (2H, m, p+s), 7.26 (1H, s, n), 7.21-7.19 (1H, m, q or r), 7.10-7.07 (1H, m, q or r), 4.10-3.91 (5H, m, b+b'+g), 3.84-3.79 (1H, m, h(1H)), 3.51-3.43 (1H, m, h(1H)), 2.79-2.68 (2H, m, c(1H)+e(1H)), 2.58-2.54 (1H, m, c(1H)), 2.49-2.44 (1H, m, e(1H)), 1.96-1.91 (1H, m, f(1H)), 1.64-1.59 (1H, m, f(1H)), 1.43 (3H, s, j or j'), 1.37 (3H, s, j or j'), 1.30 (6H, s, l or l'), 1.25 (6H, s, l or l'), 1.15 (3H, t, *J* = 7.0 Hz, a or a'), 1.09 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 152.07 (d, $^{3}J_{C\text{-}P}$ = 20 Hz, m), 141.01 (*o* or t), 140.07 (*o* or t), 124.71 (q or r), 124.25 (q or r), 123.62 (p or s), 122.70 (p or s), 121.79 (n), 109.98 (i), 84.73 (k), 77.20 (g), 70.05 (h), 61.70 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.34 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 34.71 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, e), 33.40 (d, $^{1}J_{C\text{-}P}$ = 141 Hz, c), 28.95 (f), 27.55 (j or j'), 26.25 (j or j'), 25.49 (l or l'), 25.38 (l or l'), 16.82 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.79 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 34.00 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 30.55 (92%; major diastereomer), 30.51 (8%; minor diastereomer) ppm; IR (neat) 2980 (aromatic C-H), 2933 (aliphatic C-H), 1370 (aromatic C=C), 1329 (aromatic C=C), 1239 (P=O), 1141, 1052 (C-O), 1024 (C-O/C=S), 960 (P-O), 734 cm^{-1}; HRMS (EI) calculated for $C_{27}H_{42}BO_7PS$ = 552.2482, found 552.2499 *m/z*.

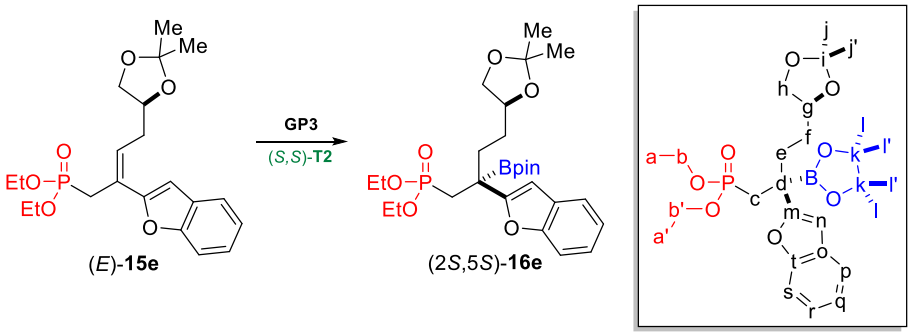


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16d: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*S*,*S*)-**T2**, the substrate (*Z*)-**15d** (64 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16d** (57 mg, 69%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +5.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.63-7.60 (2H, m, p+s), 7.43 (1H, s, n), 7.20-7.18 (1H, m, q or r), 7.11-7.08 (1H, m, q or r), 4.08-3.94 (4H, m, b+b'), 3.89-3.80 (2H, m, g+h(1H)), 3.51-3.47 (1H, m, h(1H)), 2.74-2.67 (2H, m, c(1H)+e(1H)), 2.58-2.52 (1H, m, c(1H)), 2.39-2.35 (1H, m, e(1H)), 1.81-1.72 (2H, m, f), 1.46 (3H, s, j or j'), 1.38 (3H, s, j or j'), 1.32 (6H, s, l or l'), 1.26 (6H, s, l or l'), 1.11 (3H, t, *J* = 7.0 Hz, a or a'), 1.02 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 151.79 (d, $^3J_{C\text{-}P}$ = 18 Hz, m), 141.05 (*o* or t), 140.07 (*o* or t), 124.65 (q or r), 124.22 (q or r), 123.67 (p or s), 122.69 (p or s), 122.42 (n), 109.05 (i), 84.71 (k), 77.08 (g), 69.90 (h), 61.74 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.20 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 35.23 (d, $^3J_{C\text{-}P}$ = 9.0 Hz, e), 34.36 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 29.52 (f), 27.65 (j or j'), 26.32 (j or j'), 25.49 (l or l'), 25.46 (l or l'), 16.78 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.72 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 33.96 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 30.55 (8%; minor diastereomer), 30.51 (92%; major diastereomer) ppm; IR (neat) 2980 (aromatic C-H), 2933 (aliphatic C-H), 1372 (aromatic C=C), 1333 (aromatic C=C), 1239 (P=O), 1141, 1050 (C-O), 1023 (C-O/C=S), 958 (P-O), 735 cm^{-1}; HRMS (EI) calculated for $C_{27}H_{42}BO_7PS$ = 552.2482, found 552.2496 *m/z*.

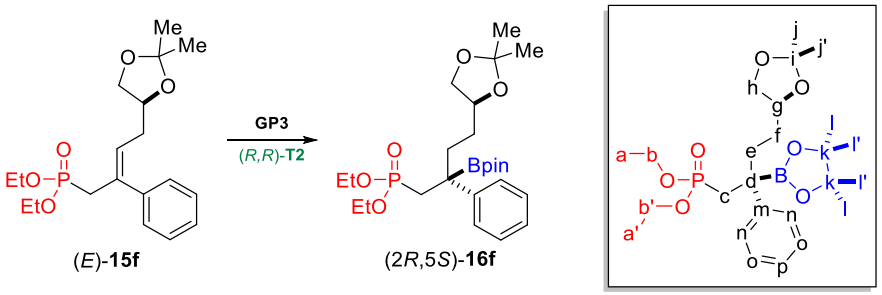


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16e: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*E*)-**15e** (61 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16e** (61 mg, 76%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +5.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.40-7.36 (2H, m, p+s), 7.07-7.01 (2H, m, q+r), 6.85 (1H, s, n), 3.93-3.60 (6H, m, b+b'+g+h(1H)), 3.41-3.38 (1H, m, h(1H)), 2.63 (1H, dd, *J* = 15.0, 17.5

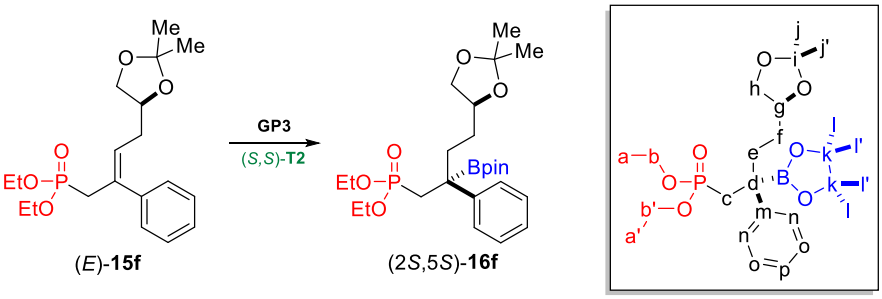
Hz, c(1H)), 2.51 (1H, dd, *J* = 15.0, 17.5 Hz, c(1H)), 2.48-2.43 (1H, m, e(1H)), 2.30-2.19 (1H, m, e(1H)), 1.75-1.68 (1H, m, f(1H)), 1.61-1.56 (1H, m, f(1H)), 1.35 (3H, s, j or j'), 1.26 (3H, s, j or j'), 1.23 (6H, s, l or l'), 1.20 (6H, s, l or l'), 0.99 (3H, t, *J* = 7.0 Hz, a or a'), 0.80 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 161.81 (d, $^{3}J_{C\text{-}P}$ = 14 Hz, m), 155.58 (t), 129.87 (o), 123.95 (q or *r*), 123.14 (q or *r*), 121.19 (p or s), 111.28 (p or s), 109.00 (i), 104.90 (n), 84.70 (k), 76.81 (g), 69.83 (h), 61.42 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.32 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 32.68 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, e), 32.40 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 30.28 (f), 27.58 (j or j'), 26.23 (j or j'), 25.53 (l or l'), 25.46 (l or l'), 16.75 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.52 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 34.01 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 30.00 (7%; minor diastereomer), 29.95 (93%; major diastereomer) ppm; IR (neat) 2980 (aromatic C-H), 2932 (aliphatic C-H), 1455 (aromatic C=C), 1370 (aromatic C=C), 1242 (P=O), 1141, 1051 (C-O), 1024 (C-O), 960 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{27}H_{42}BO_8P$ = 536.2710, found 536.2733 *m/z*.



Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16e: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*S*,*S*)-**T2**, the substrate (*E*)-**15e** (61 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*R*)-**16e** (59 mg, 73%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +1.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.41-7.36 (2H, m, p+s), 7.07-7.01 (3H, m, n+q+r), 3.92-3.56 (6H, m, b+b'+g+h(1H)), 3.31-3.29 (1H, m, h(1H)), 2.64 (1H, dd, *J* = 15.0, 17.5 Hz, c(1H)), 2.53-2.43 (2H, m, c(1H)+e(1H)), 2.23-2.19 (1H, m, e(1H)), 1.74-1.66 (1H, m, f(1H)), 1.51-1.66 (1H, m, f(1H)), 1.36 (3H, s, j or j'), 1.27 (9H, s, j or j' and l or l'), 1.23 (6H, s, l or l'), 1.00 (3H, t, *J* = 7.0 Hz, a or a'), 0.72 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 161.32 (d, $^{3}J_{C\text{-}P}$ = 12 Hz, m), 155.58 (t), 129.92 (o), 123.95 (q or *r*), 123.13 (q or *r*), 121.23 (p or s), 111.28 (p or s), 109.03 (i), 105.61 (n), 84.70 (k), 76.78 (g), 69.93 (h), 61.40 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.30 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 33.78 (d, $^{3}J_{C\text{-}P}$ = 14 Hz, e), 33.29 (d, $^{1}J_{C\text{-}P}$ = 141 Hz, c), 30.80 (f), 27.61 (j or j'), 26.28 (j or j'), 25.68 (l or l'), 25.46 (l or l'), 16.76 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.41 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 33.90 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 30.00 (80%; major diastereomer), 29.95 (20%; minor diastereomer) ppm; IR (neat) 2979 (aromatic C-H), 2933 (aliphatic C-H), 1454 (aromatic C=C), 1370 (aromatic C=C), 1242 (P=O), 1141, 1052 (C-O), 1024 (C-O), 961 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{27}H_{42}BO_8P$ = 536.2710, found 536.2696 *m/z*.

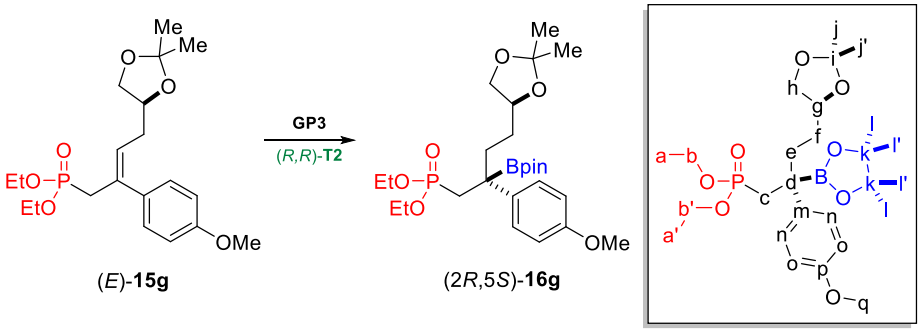


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16f: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*E*)-**15f** (55 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16f** (60 mg, 80%; 91:9 dr, determined via ^{31}P NMR analysis) as a colorless viscous liquid. Alternatively, following **GP3** with (*R*,*R*)-**T2**, the diastereomeric substrate (*Z*)-**15f** (55 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16f** (62 mg, 83%; 96:4 dr, determined via ^{31}P NMR analysis) as a colorless viscous liquid. Characterization data for (2*R*,5*S*)-**16f** obtained from (*Z*)-**15f** is as follows: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +10.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.42 (2H, d, *J* = 7.5 Hz, n), 7.17 (2H, t, *J* = 7.5 Hz, o), 7.02 (1H, t, *J* = 7.5 Hz, p), 3.97-3.83 (5H, m, b+b'+g), 3.68 (1H, dd, *J* = 7.5, 6.0 Hz, h(1H)), 3.30 (1H, t, *J* = 7.5 Hz, h(1H)), 2.62-2.26 (4H, m, c+e), 1.75-1.70 (1H, m, f), 1.33 (j or j'), 1.33-1.28 (1H, m, f(1H)), 1.27 (3H, s, j or j'), 1.16 (6H, s, l or l'), 1.13 (6H, s, l or l'), 1.08-1.06 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 145.37 (d, $^3J_{C\text{-}P}$ = 18 Hz, m), 128.87 (o), 127.79 (n), 126.19 (p), 108.86 (i), 84.23 (k), 77.34 (g), 70.13 (h), 61.47 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.10 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 32.80 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 31.45 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.79 (f), 27.55 (j or j'), 26.31 (j or j'), 25.46 (l or l'), 25.27 (l or l'), 16.91 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.85 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 33.02 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 32.30 (4%; minor diastereomer), 32.18 (96%; major diastereomer) ppm; IR (neat) 2979 (aromatic C-H), 2934 (aliphatic C-H), 1369 (aromatic C=C), 1320 (aromatic C=C), 1241 (P=O), 1143, 1052 (C-O), 1025 (C-O), 954 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{25}H_{42}BO_7P$ = 496.2761, found 496.2780 *m/z*.

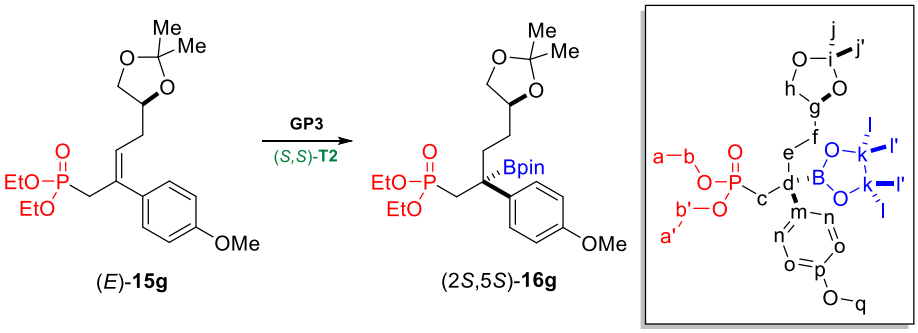


Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16f: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*S*,*S*)-**T2**, the substrate (*E*)-**15f** (55 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16f** (58 mg, 78%; 85:15 dr, determined via ^{31}P NMR analysis) as a colorless viscous liquid. Alternatively, following **GP3** with (*S*,*S*)-**T2**, the diastereomeric substrate (*Z*)-**15f** (55 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16f** (63 mg, 84%; 97:3 dr, determined via ^{31}P NMR analysis) as a

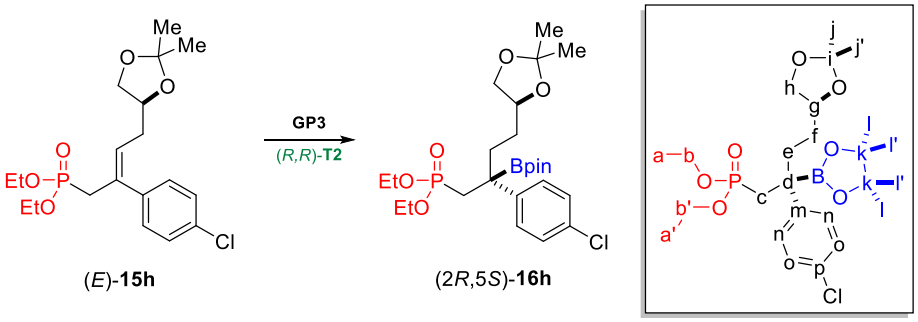
colorless viscous liquid. Characterization data for (2*S*,5*S*)-**16f** obtained from (*Z*)-**15f** is as follows: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +6.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.45 (2H, d, *J* = 8.0 Hz, n), 7.17 (2H, dd, *J* = 8.0, 7.5 Hz, o), 7.02 (1H, t, *J* = 7.5 Hz, p), 3.96-3.82 (5H, m, b+b'+g), 3.75 (1H, dd, *J* = 7.5, 6.0 Hz, h(1H)), 3.40 (1H, t, *J* = 7.5 Hz, h(1H)), 2.62-2.25 (4H, m, c+e), 1.55-1.44 (2H, m, f), 1.35 (j or j'), 1.28 (3H, s, j or j'), 1.16 (6H, s, l or l'), 1.12 (6H, s, l or l'), 1.07-1.02 (6H, m, a+a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 145.09 (d, $^3J_{C\text{-}P}$ = 17 Hz, m), 128.83 (o), 127.91 (n), 126.18 (p), 108.86 (i), 84.22 (k), 77.22 (g), 69.94 (h), 61.61 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.00 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 32.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, e), 31.70 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 29.03 (f), 27.66 (j or j'), 26.36 (j or j'), 25.39 (l or l'), 25.30 (l or l'), 16.90 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.80 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 32.71 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 32.30 (97%; major diastereomer), 32.18 (3%; major diastereomer) ppm; IR (neat) 2979 (aromatic C-H), 2933 (aliphatic C-H), 1369 (aromatic C=C), 1320 (aromatic C=C), 1240 (P=O), 1143, 1051 (C-O), 1024 (C-O), 954 (P-O) cm^{-1}; HRMS (EI) calculated for $C_{25}H_{42}BO_7P$ = 496.2761, found 496.2781 *m/z*.



Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16g: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*R*,*R*)-**T2**, the substrate (*E*)-**15g** (60 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16g** (59 mg, 75%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +22° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.35 (2H, d, *J* = 8.5 Hz, n), 6.81 (2H, d, *J* = 8.5 Hz, o), 4.00-3.87 (5H, m, b+b'+g), 3.73 (1H, dd, *J* = 7.5, 6.5 Hz, h(1H)), 3.36 (1H, t, *J* = 7.5 Hz, h(1H)), 3.31 (3H, s, q), 2.58-2.29 (4H, m, c+e), 1.79-1.73 (1H, m, f(1H)), 1.38-1.32 (1H, m, f(1H)), 1.35 (3H, s, j or j'), 1.29 (3H, s, j or j'), 1.19 (6H, s, l or l'), 1.15 (6H, s, l or l'), 1.08 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 158.52 (p), 137.02 (d, $^3J_{C\text{-}P}$ = 18 Hz, m), 128.74 (n), 114.38 (o), 108.89 (i), 84.19 (k), 77.40 (g), 70.17 (h), 61.49 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.13 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.04 (q), 32.90 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, e), 31.75 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.81 (f), 27.58 (j or j'), 28.30 (j or j'), 25.49 (l or l'), 25.31 (l or l'), 16.92 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.86 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 34.66 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 32.40 (10%; minor diastereomer), 32.29 (90%; major diastereomer) ppm; IR (neat) 2980 (aromatic C-H), 2934 (aliphatic C-H), 1608, 1510, 1378 (aromatic C=C), 1245 (P=O), 1142, 1052 (C-O), 1026 (C-O), 955 (P-O), 835, 733 cm^{-1}; HRMS (EI) calculated for $C_{26}H_{44}BO_8P$ = 526.2867, found 526.2868 *m/z*.

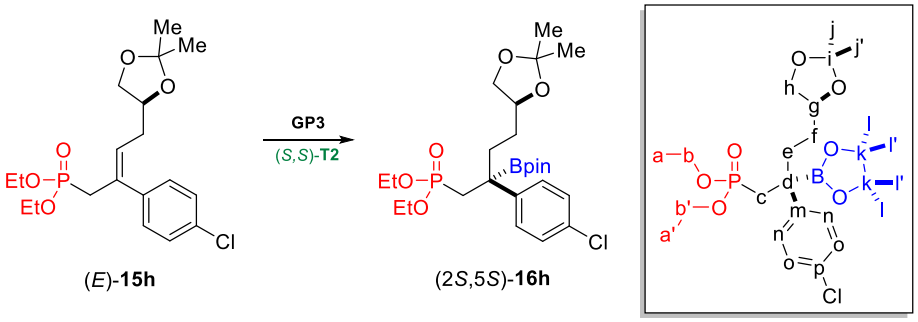


Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16g: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*S*,*S*)-**T2**, the substrate (*E*)-**15g** (60 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16g** (59 mg, 75%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +13.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, C_6D_6) δ 7.38 (2H, d, *J* = 8.5 Hz, n), 6.82 (2H, d, *J* = 8.5 Hz, o), 4.00-3.85 (5H, m, b+b'+g), 3.78 (1H, t, *J* = 7.5 Hz, h(1H)), 3.43 (1H, t, *J* = 7.5 Hz, h(1H)), 3.31 (3H, s, q), 2.61-2.25 (4H, m, c+e), 1.59-1.51 (1H, m, f(1H)), 1.38 (3H, s, j or j'), 1.30 (3H, s, j or j'), 1.18 (6H, s, l or l'), 1.14 (6H, s, l or l'), 1.07 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, C_6D_6) δ 158.51 (p), 136.78 (d, $^3J_{C\text{-}P}$ = 17.5 Hz, m), 128.88 (n), 114.35 (o), 108.94 (i), 84.17 (k), 77.31 (g), 70.00 (h), 61.61 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.00 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.04 (q), 32.82 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, e), 31.94 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.97 (f), 27.69 (j or j'), 26.37 (j or j'), 25.43 (l or l'), 25.35 (l or l'), 16.92 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, a or a'), 16.86 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, C_6D_6) δ 34.52 (br s) ppm; ^{31}P NMR (283 MHz, C_6D_6) δ 32.40 (90%; major diastereomer), 32.29 (10%; minor diastereomer) ppm; IR (neat) 2982 (aromatic C-H), 2937 (aliphatic C-H), 1608, 1510 , 1379 (aromatic C=C), 1246 (P=O), 1142, 1051 (C-O), 1027 (C-O), 958 (P-O), 835, 732 cm^{-1}; HRMS (EI) calculated for $C_{26}H_{44}BO_8P$ = 526.2867, found 526.2881 *m/z*.

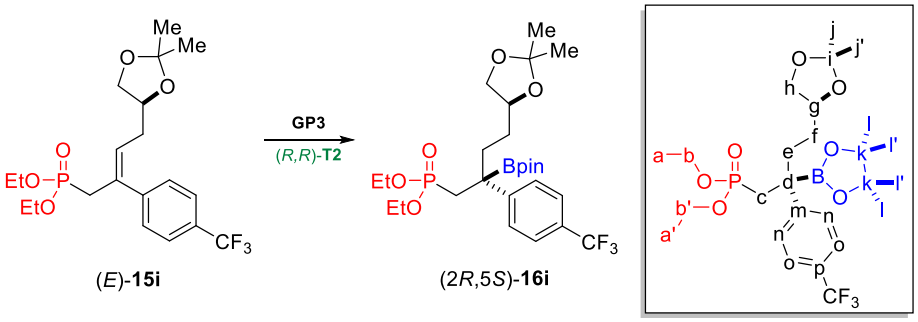


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16h: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*R*,*R*)-**T2**, the substrate (*E*)-**15h** (60 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16h** (50 mg, 63%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +3.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30 (2H, d, *J* = 8.5 Hz, n or o), 7.27 (2H, d, *J* = 8.5 Hz, n or o), 4.03-3.88 (6H, m, b+b'+g+h(1H)), 3.42-3.40 (1H, m, h(1H)), 2.37-2.28 (2H, m, c), 2.22-2.15 (1H, m, e(1H)), 2.01-1.94 (1H, m, e(1H)), 1.58-1.53 (1H, m, f(1H)), 1.38-1.32 (7H, m, f(1H)+j+j'), 1.28-1.20 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 142.70 (d, $^3J_{C\text{-}P}$ =

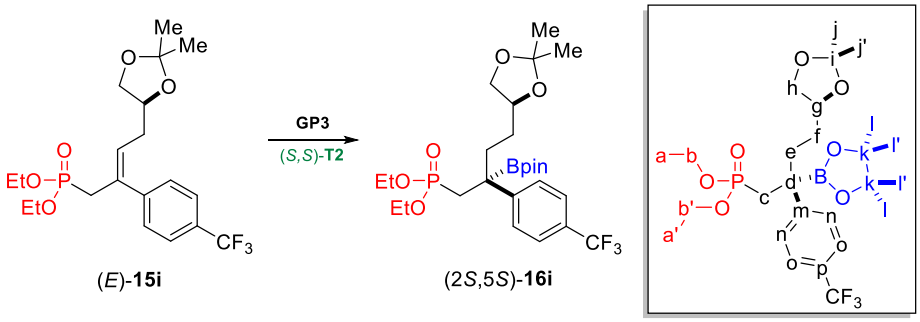
14.0 Hz, m), 131.62 (p), 128.77 (n or o), 128.46 (n or o), 108.74 (i), 84.19 (k), 76.56 (g), 69.71 (h), 61.48 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.12 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 31.55 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, e), 31.36 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 28.91 (f), 27.07 (j or j'), 25.86 (j or j'), 24.94 (l+l'), 16.55 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.54 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.02 (br s) ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 31.35 (17%; minor diastereomer), 31.16 (83%; major diastereomer) ppm; IR (neat) 2979 (aromatic C-H), 2935 (aliphatic C-H), 1492, 1510, 1369 (aromatic C=C), 1325 (aromatic C=C), 1240 (P=O), 1142, 1052 (C-O), 1026 (C-O), 958 (P-O), 836, 729 (C-Cl) cm^{-1}; HRMS (EI) calculated for $C_{25}H_{41}BClO_7P$ = 530.2372, found 530.2391 *m/z*.



Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16h: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*S*,*S*)-**T2**, the substrate (*E*)-**15h** (60 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16h** (48 mg, 60%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +2.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31 (2H, d, *J* = 8.5 Hz, n or o), 7.27 (2H, d, *J* = 8.5 Hz, n or o), 4.08-3.89 (6H, m, b+b'+g+h(1H)), 3.50-3.48 (1H, m, h(1H)), 2.44-2.28 (2H, m, c), 2.22-2.15 (1H, m, e(1H)), 2.02-1.95 (1H, m, e(1H)), 1.39-1.31 (8H, m, f+j+j'), 1.28-1.20 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 142.55 (d, $^{3}J_{C\text{-}P}$ = 15.0 Hz, m), 131.63 (p), 128.77 (n or o), 128.46 (n or o), 108.73 (i), 84.18 (k), 76.59 (g), 69.61 (h), 61.61 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.10 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 31.47 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, e), 31.17 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 28.78 (f), 27.11 (j or j'), 25.88 (j or j'), 24.94 (l or l'), 24.92 (l or l'), 16.59 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.56 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.56 (br s) ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 31.35 (83%; major diastereomer), 31.16 (17%; minor diastereomer) ppm; IR (neat) 2979 (aromatic C-H), 2934 (aliphatic C-H), 1491, 1511, 1369 (aromatic C=C), 1324 (aromatic C=C), 1242 (P=O), 1141, 1052 (C-O), 1028 (C-O), 959 (P-O), 836, 732 (C-Cl) cm^{-1}; HRMS (EI) calculated for $C_{25}H_{41}BClO_7P$ = 530.2372, found 530.2393 *m/z*.

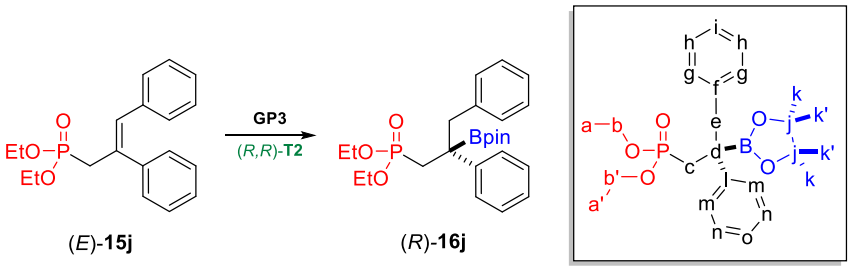


Synthesis of chiral tertiary benzylic boronic ester (2*R*,5*S*)-16i: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*E*)-**15i** (65 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*R*,5*S*)-**16i** (57 mg, 56%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +4.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.5 Hz, o), 7.50 (2H, d, *J* = 8.5 Hz, n), 4.06-3.83 (6H, m, b+b'+g+h(1H)), 3.46-3.41 (1H, m, h(1H)), 2.43-2.30 (2H, m, c), 2.26-2.18 (1H, m, e(1H)), 2.09-1.98 (1H, m, e(1H)), 1.59-1.49 (1H, m, f(1H)), 1.40-1.30 (7H, m, h(1H)+j+j'), 1.29-1.19 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.52 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, m), 129.13 (q, $^2J_{C\text{-}F}$ = 32.0 Hz, p), 127.82 (n), 125.23 (q, $^3J_{C\text{-}F}$ = 3.75 Hz, o), 124.54 (q, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 108.79 (i), 84.33 (k), 76.49 (g), 69.68 (h), 61.46 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.15 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 31.68 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 31.68 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, e), 29.11 (f), 27.06 (j or j'), 25.85 (j or j'), 24.96 (l or l'), 24.95 (l or l'), 16.48 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.71 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.00 (13%; minor diastereomer), 30.75 (87%; major diastereomer) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.37 (85%; major diastereomer), -62.39 (15%; minor diastereomer) ppm; IR (neat) 2982 (aromatic C-H), 2932 (aliphatic C-H), 1617, 1370 (aromatic C=C), 1326 (aromatic C=C/C-F), 1240 (P=O), 1120, 1051 (C-O), 1025 (C-O), 959 (P-O), 844, 735, 678 cm^{-1}; HRMS (EI) calculated for $C_{26}H_{41}BF_3O_7P$ = 564.2635, found 564.2654 *m/z*.

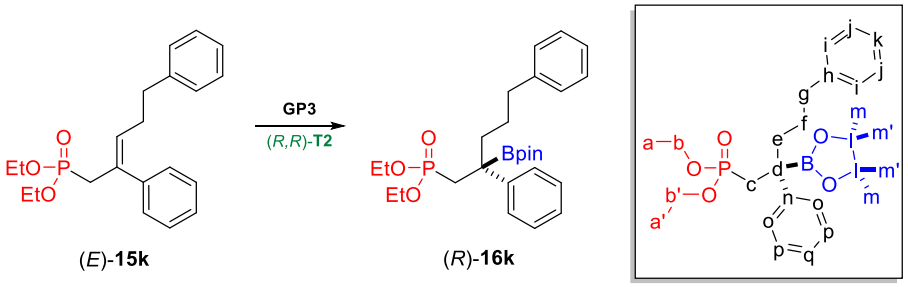


Synthesis of chiral tertiary benzylic boronic ester (2*S*,5*S*)-16i: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*S*,*S*)-**T2**, the substrate (*E*)-**15i** (65 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (2*S*,5*S*)-**16i** (58 mg, 57%) as a colorless viscous liquid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +2.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, *J* = 8.5 Hz, o), 7.50 (2H, d, *J* = 8.5 Hz, n), 4.06-3.85 (6H, m, b+b'+g+h(1H)), 3.52-3.45 (1H, m, h(1H)), 2.43-2.35 (2H, m, c), 2.31-2.19 (1H, m, e(1H)), 2.09-1.98 (1H, m, e(1H)), 1.43-1.32 (8H, m, h+j+j'), 1.26-1.15 (18H, m, a+a'+l+l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.38 (d, $^3J_{C\text{-}P}$ = 15.0 Hz, m), 129.12 (q, $^2J_{C\text{-}F}$ = 32.0 Hz, p), 127.77 (n), 125.24 (q, $^3J_{C\text{-}F}$ = 3.75 Hz, o), 124.88 (q, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 108.78 (i), 84.31 (k), 76.49 (g), 69.55 (h), 61.60 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.14 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 31.61 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 31.38 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, e), 28.92 (f), 27.08 (j or j'), 25.84 (j or j'), 24.95 (l or l'), 24.91 (l or l'), 16.41 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.73 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.00 (85%; major diastereomer), 30.75 (15%; minor diastereomer) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.37 (17%; minor diastereomer), -62.39 (83%; major diastereomer) ppm; IR (neat) 2983 (aromatic C-H), 2932 (aliphatic C-H), 1618, 1369 (aromatic

C=C), 1325 (aromatic C=C/C-F), 1241 (P=O), 1122, 1053 (C-O), 1025 (C-O), 958 (P-O), 845, 736, 681 cm^{-1}; HRMS (EI) calculated for $C_{26}H_{41}BF_3O_7P$ = 564.2635, found 564.2648 *m/z*.



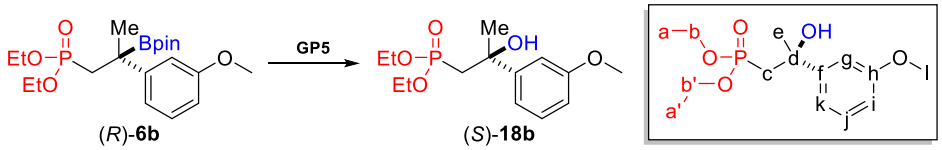
Synthesis of chiral tertiary benzylic boronic ester (*R*)-16j: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) using (*R*,*R*)-**T2**, the substrate (*E*)-**15j** (50 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (*R*)-**16j** (41 mg, 60%) as a colorless liquid. Alternatively, following **GP3** with (*R*,*R*)-**T2**, the diastereomeric substrate (*Z*)-**15j** (50 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (*R*)-**16j** (49 mg, 71%). Characterization data of (*R*)-**16j** derived using (*R*,*R*)-**T2** is as follows: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +55° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (4H, m, aryl), 7.19-7.10 (6H, m, aryl), 7.08-3.71 (4H, m, b+b'), 3.48 (1H, dd, *J* = 71, 14 Hz, e), 2.43-2.20 (2H, m, c), 1.29-1.16 (18H, m, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.00 (d, $^3J_{C\text{-}P}$ = 13.0 Hz, l), 139.06 (f), 130.95 (aryl), 128.20 (aryl), 127.64 (aryl), 127.59 (aryl), 126.02 (aryl), 125.84 (aryl), 84.12 (j), 61.23 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.95 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 40.52 (d, $^3J_{C\text{-}P}$ = 3.75 Hz, e), 30.12 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 25.05 (k or k'), 24.99 (k or k'), 16.57 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.42 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.54 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.81; IR (neat) 2978 (aromatic C-H), 2930 (aliphatic C-H), 1497 (aromatic C=C), 1379 (aromatic C=C), 1371 (aromatic C=C), 1321 (aromatic C=C), 1241 (P=O), 1051 (C-O), 1027 (C-O), 956 (P-O), 701 cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **34j**.



Synthesis of chiral tertiary benzylic boronic ester (*R*)-16k: Following the general procedure for catalytic asymmetric hydroboration (**GP3**) with (*R*,*R*)-**T2**, the substrate (*E*)-**15k** (54 mg, 0.15 mmol) yields the tertiary benzylic boronic ester product (*R*)-**16k** (60 mg, 82%) as a colorless liquid: TLC analysis (ethyl acetate/hexanes 1:2) R_f = 0.5; $[\alpha]_D^{20}$ = +6.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.11 (10H, m, aryl), 4.05-3.84 (4H, m, b+b'), 2.65-2.53 (2H, m, g), 2.40 (2H, d, *J* = 18.0 Hz, c), 2.27-2.12 (2H, m, e), 1.56-1.49 (1H, m, f(1H)), 1.45-1.34 (1H, m, f(1H)), 1.27-1.21 (18H, m, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.33 (d, $^3J_{C\text{-}P}$ = 15 Hz, n), 142.91 (h), 128.48 (aryl), 128.29 (aryl), 128.25 (aryl), 127.16 (aryl), 125.65 (aryl), 125.57 (aryl), 83.86 (l),

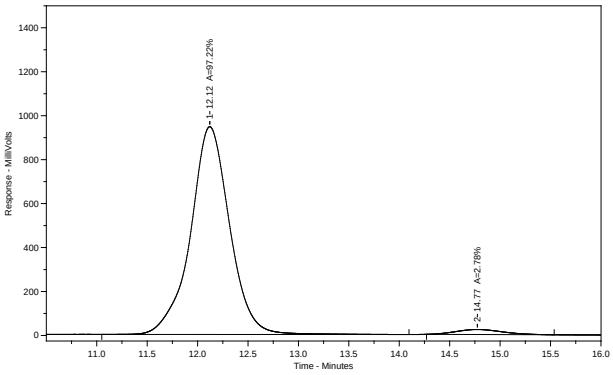
61.32 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 60.81 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b or b'), 36.70 (g), 35.14 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, e), 31.11 (d, $^{1}J_{C\text{-}P}$ = 139 Hz, c), 26.58 (f), 24.87 (m or m'), 24.84 (m or m'), 16.58 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.54 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.54 (br s) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.13; IR (neat) 2983 (aromatic C-H), 2932 (aliphatic C-H), 1618, 1373 (aromatic C=C), 1327 (aromatic C=C), 1239 (P=O), 1055 (C-O), 1024 (C-O), 957 (P-O) cm^{-1}; The enantiomer ratio of this boronic ester is determined after oxidation to the chiral tertiary alcohol **34k**.

(7) Synthesis of phosphonate-functionalized chiral tertiary benzylic alcohols

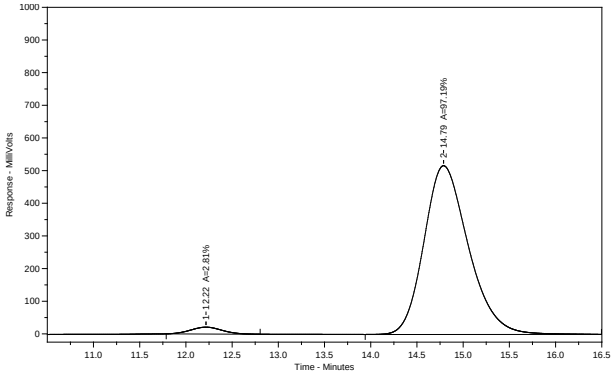


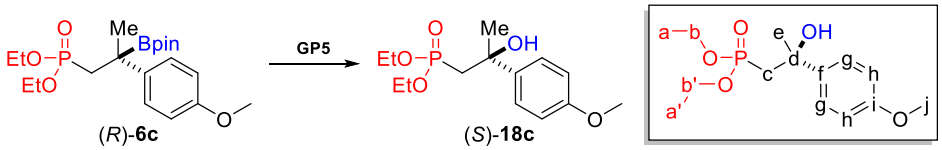
Synthesis of chiral tertiary benzyl alcohol (*S*)-18b: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6b** (41 mg, 0.10 mmol) yields the chiral tertiary benzylic alcohol (*S*)-**18b** (26 mg, 85%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +3.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, t, *J* = 8.0 Hz, j), 7.09 (1H, t, *J* = 2.0 Hz, g), 7.02 (1H, d, *J* = 8.0 Hz, k), 6.78 (1H, dd, *J* = 8.0, 2.0 Hz, i), 5.00 (1H, br s, OH), 4.11-4.05 (2H, m, b or b'), 3.84 (3H, s, l), 3.79-3.70 (1H, m, b or b'), 3.52-3.42 (1H, m, b or b'), 2.50-2.29 (2H, m, c), 1.61 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.04 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.71 (h), 149.23 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 129.26 (j), 117.36 (k), 112.36 (g), 110.73 (i), 72.09 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.97 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.59 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.39 (l), 39.76 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 32.54 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.48 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.24 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.84 ppm; IR (neat) 3403 (O-H), 2979 (aromatic C-H), 2933 (aliphatic C-H), 1600, 1583, 1455 (aromatic C=C), 1390 (aromatic C=C), 1215 (P=O), 1020 (C-O), 961 (P-O), 781 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_5P$+Na^+ = 325.1181, found 325.1186 *m/z*. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile phase = 95:5 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 3:97, CAHB of **5b** with (*R*,*R*)-**T2**, then oxidation to yield **18b**.



(b) R:S = 97:3, CAHB of **5b** with (*S*,*S*)-**T2**, then oxidation to yield **18b**.

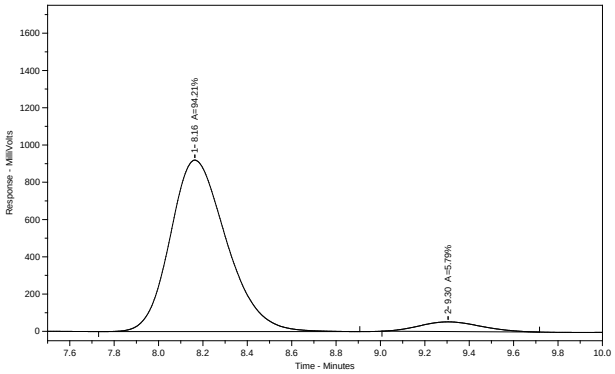




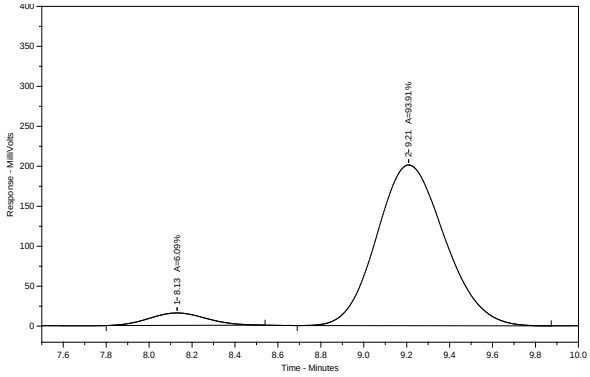
Synthesis of chiral tertiary benzyl alcohol (*S*)-18c: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6c** (41 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18c** (24 mg, 78%) as a colorless viscous

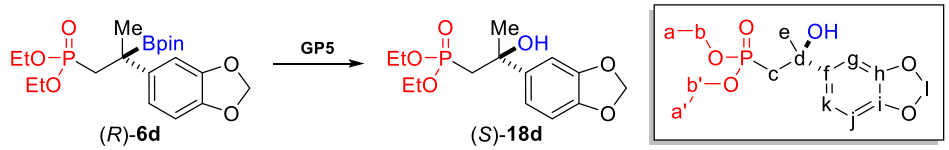
oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +2.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, d, *J* = 8.75 Hz, g), 6.89 (2H, d, *J* = 8.75 Hz, h), 4.95 (1H, br s, OH), 4.14-3.99 (2H, m, b or b'), 3.81 (3H, s, j), 3.81-3.71 (1H, m, b or b'), 3.53-3.43 (1H, m, b or b'), 2.49-2.29 (2H, m, c), 1.61 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.06 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.59 (i), 139.69 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 126.12 (g), 113.59 (h), 71.92 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.96 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.60 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.49 (j), 39.98 (d, $^1J_{C\text{-}P}$ = 135 Hz, c), 32.71 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.52 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.32 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.00 ppm; IR (neat) 3400 (O-H), 2980 (aromatic C-H), 2931 (aliphatic C-H), 1610, 1510, 1443 (aromatic C=C), 1391 (aromatic C=C), 1245 (P=O), 1021 (C-O), 961 (P-O), 832 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_5P+Na^+$ = 325.1181, found 325.1184 *m/z*. Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile phase = 90:10 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 6:94, CAHB of **5c** with (*R*,*R*)-**T2**, then oxidation to yield **18c**.



(b) R:S = 94:6, CAHB of **5c** with (*S*,*S*)-**T2**, then oxidation to yield **18c**.

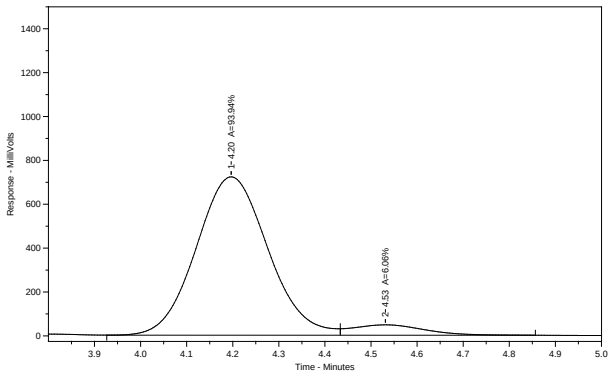




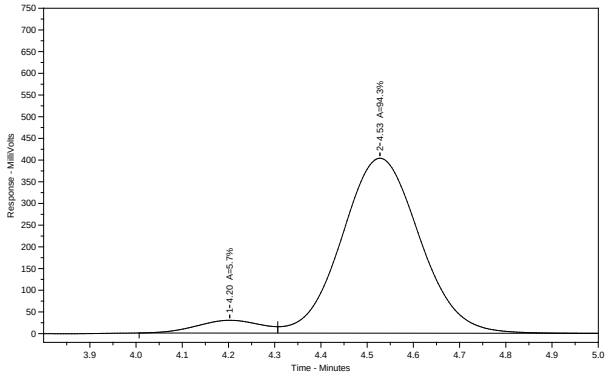
Synthesis of chiral tertiary benzyl alcohol (*S*)-18d: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6d** (43 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18d** (24 mg, 75%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = +6.4° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (1H, d, *J* = 2.0 Hz, g), 6.95 (1H, dd, *J* = 8.0, 2.0 Hz, k), 6.77 (1H, d, *J* = 8.0 Hz, j), 5.93 (2H, s, l), 4.95 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.86-3.76 (1H, m, b or b'), 3.65-3.55 (1H, m, b or b'), 2.45-2.25 (2H, m, c), 1.59 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.10 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.147.64 (h or i), 146.38 (h or i), 141.78 (d, $^3J_{C\text{-}P}$ = 8.0 Hz, f), 118.02 (k), 107.89 (j), 106.09 (g), 101.10 (l), 72.05 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.98 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.66 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.89 (d, $^1J_{C\text{-}P}$ = 135 Hz, c), 32.65 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.49 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.29 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.79 ppm; IR (neat) 3397 (O-H),

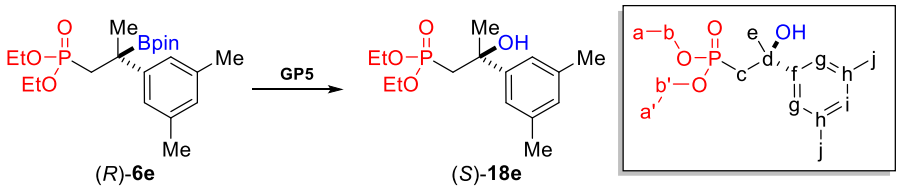
2980 (aromatic C-H), 2908 (aliphatic C-H), 1488 (aromatic C=C), 1434 (aromatic C=C), 1231 (P=O), 1021 (C-O), 938 (P-O), 813, 730 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_6P+Na^+$ = 339.0973, found 339.0979 *m/z*. Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile phase = 60:40 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 6:94, CAHB of **5d** with (*R*,*R*)-**T2**, then oxidation to yield **18d**.



(b) R:S = 94:6, CAHB of **5d** with (*S*,*S*)-**T2**, then oxidation to yield **18d**.



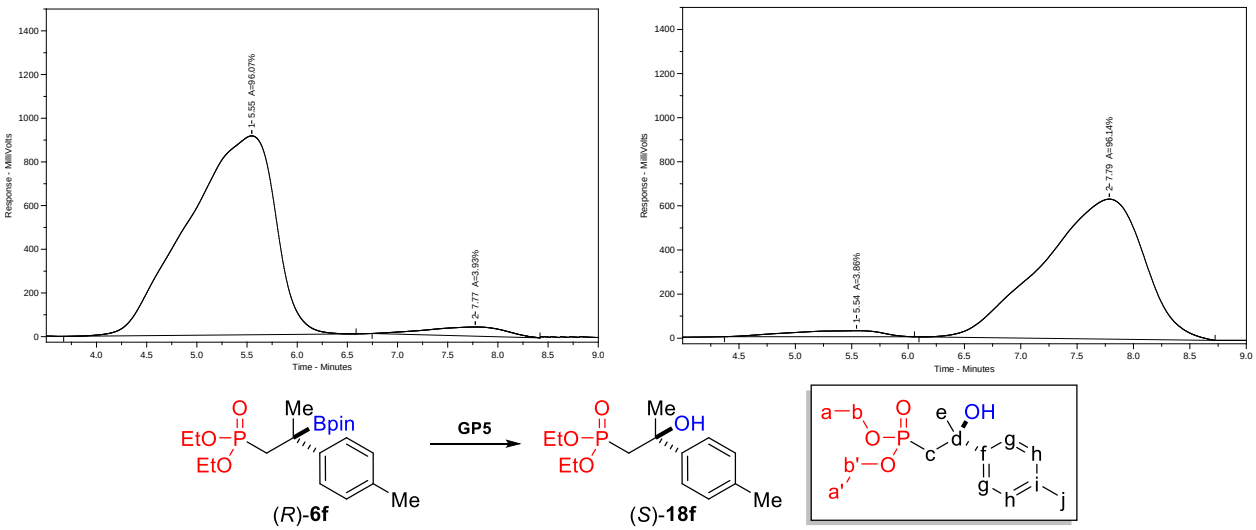


(*R*)-**6e** (*S*)-**18e**

Synthesis of chiral tertiary benzyl alcohol (*S*)-18e: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6e** (41 mg, 0.1 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18e** (25 mg, 83%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +7° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (2H, s, g), 6.88 (1H, s, i), 4.91 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.80-3.70 (1H, m, b or b'), 3.51-3.41 (1H, m, b or b'), 2.49-2.29 (8H, m, c+j), 1.61 (3H, d, $^4J_{P-H}$ = 2.0 Hz, e), 1.33 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.37 (d, $^3J_{C-P}$ = 8.0 Hz, f), 137.70 (h), 128.45 (i), 122.67 (g), 72.06 (d, $^2J_{C-P}$ = 5.0 Hz, d), 61.93 (d, $^2J_{C-P}$ = 6.5 Hz, b or b'), 61.51 (d, $^2J_{C-P}$ = 6.5 Hz, b or b'), 39.89 (d, $^1J_{C-P}$ = 135 Hz, c), 32.52 (d, $^3J_{C-P}$ = 13.5 Hz, e), 21.61 (j), 16.48 (d, $^3J_{C-P}$ = 6.5 Hz, a or a'), 16.22 (d, $^3J_{C-P}$ = 6.5 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.05 ppm; IR (neat) 3407 (O-H), 2980 (sp^2 C-H), 2915 (sp^3 C-H), 1443 (aromatic C=C), 1392 (aromatic C=C), 1217 (P=O), 1051 (C-O), 1021 (C-O), 960 (P-O), 849 cm^{-1}. HRMS (ESI) calculated for $C_{15}H_{25}O_4P+Na^+$ = 323.1388 found 323.1392 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile phase = 90:10 Hexanes: Isopropanol; Flow rate = 1.5 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

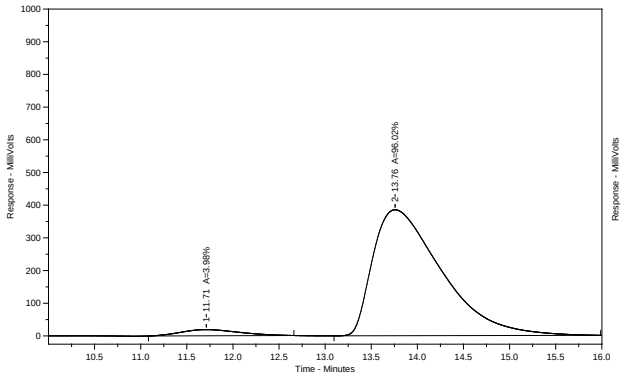
(a) R:S = 4:96, CAHB of **5e** with (*R*,*R*)-**T2**, then oxidation to yield **18e**.

(b) R:S = 96:4, CAHB of **5e** with (*S*,*S*)-**T2**, then oxidation to yield **18e**.

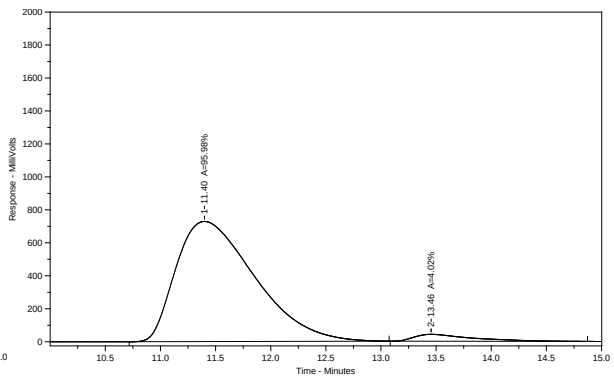


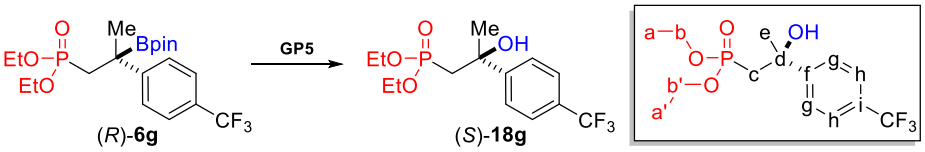
Synthesis of chiral tertiary benzyl alcohol (*S*)-18f: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6f** (40 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18f** (28 mg, 91%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -8.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (2H, d, *J* = 8.0 Hz, g), 7.16 (2H, d, *J* = 8.0 Hz, h), 4.94 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.79-3.69 (1H, m, b or b'), 3.49-3.40 (1H, m, b or b'), 2.49-2.29 (5H, m, c+j), 1.62 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.03 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.49 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 136.43 (i), 128.91 (h), 124.82 (g), 72.04 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.93 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.56 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.95 (d, $^1J_{C\text{-}P}$ = 135 Hz, c), 32.58 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 21.07 (j), 16.49 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.22 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.98 ppm; IR (neat) 3397 (O-H), 2979 (aromatic C-H), 2923 (aliphatic C-H), 1513 (aromatic C=C), 1392 (aromatic C=C), 1214 (P=O), 1019 (C-O), 960 (P-O), 819 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1238 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 95:5 Hexanes:Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 4:96, CAHB of **5f** with (*R*,*R*)-**T2**, then oxidation to yield **18f**.



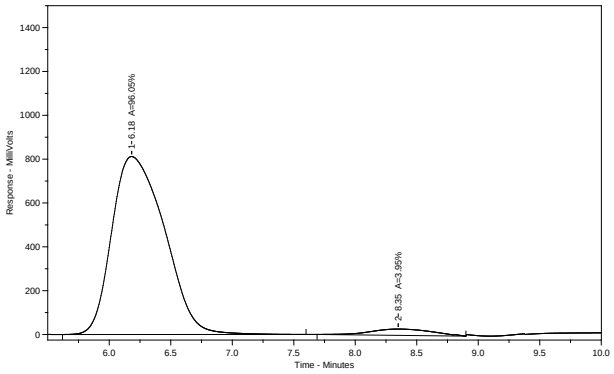
(b) R:S = 96:4, CAHB of **5f** with (*S*,*S*)-**T2**, then oxidation to yield **18f**.



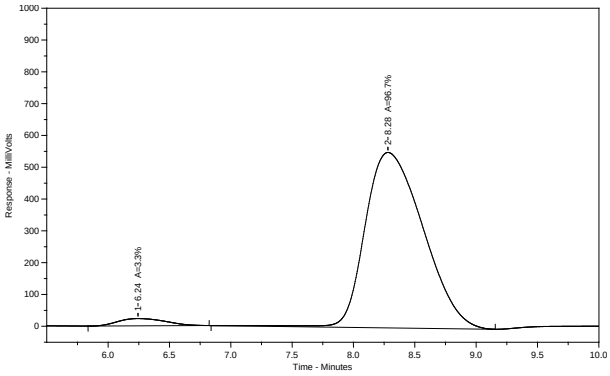


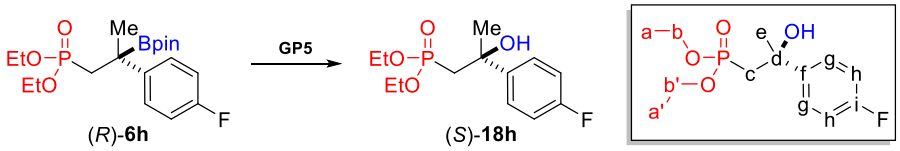
Synthesis of chiral tertiary benzyl alcohol (*S*)-18g: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6g** (45 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18g** (28 mg, 83%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +10.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (4H, br s, g+h), 5.17 (1H, br s, OH), 4.16-4.02 (2H, m, b or b'), 3.79-3.69 (1H, m, b or b'), 3.55-3.45 (1H, m, b or b'), 2.47 (1H, dd, *J* = 17.0, 15.0 Hz, c (1H)), 2.36 (1H, dd, *J* = 17.0, 15.0 Hz, c(1H)), 1.64 (3H, s, e), 1.34 (3H, t, *J* = 7.0 Hz, a or a'), 0.99 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.45 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 129.31 (q, $^2J_{C\text{-}F}$ = 32.0 Hz, i), 125.55 (g), 125.40 (d, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 125.25 (q, $^3J_{C\text{-}F}$ = 4.0 Hz, h), 72.12 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.99 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.96 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.58 (d, $^1J_{C\text{-}P}$ = 136.0 Hz, c), 32.52 (d, $^3J_{C\text{-}P}$ = 14.5 Hz, e), 16.53 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.09 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.30 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48 ppm; IR (neat) 3385 (O-H), 2982 (sp^2 C-H), 2933 (sp^3 C-H), 1618, 1444 (aromatic C=C), 1409 (aromatic C=C), 1325 (C-F), 1218 (P=O), 1049 (C-O), 1015 (C-O), 961 (P-O), 840 cm^{-1}. HRMS (ESI) calculated for $C_{14}H_{20}F_3O_4P+Na^+$ = 363.0949, found 363.0955 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile phase = 95:5 Hexanes: Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 4:96, CAHB of **5g** with (*R*,*R*)-**T2**, then oxidation to yield **18g**.



(b) R:S = 96:4, CAHB of **5g** with (*S*,*S*)-**T2**, then oxidation to yield **18g**.

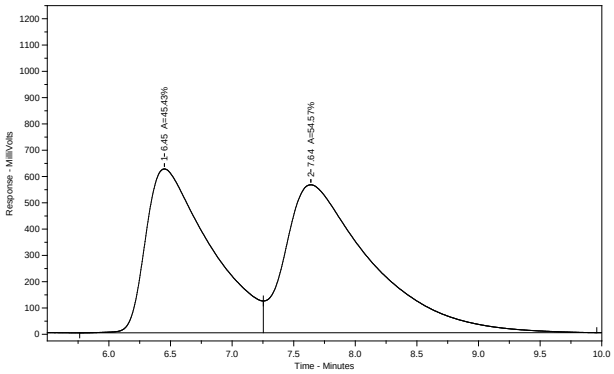




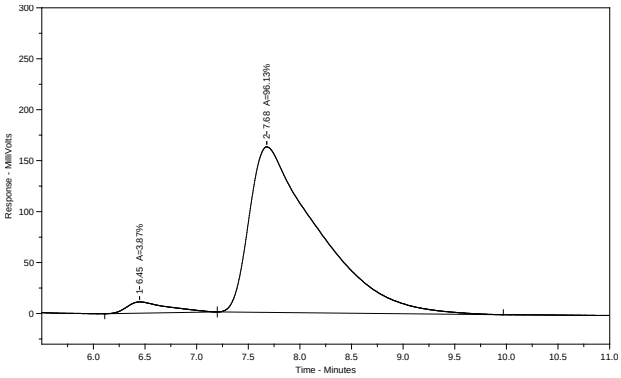
Synthesis of chiral tertiary benzyl alcohol (*S*)-18h: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6h** (40 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18h** (23 mg, 80%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +4.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR

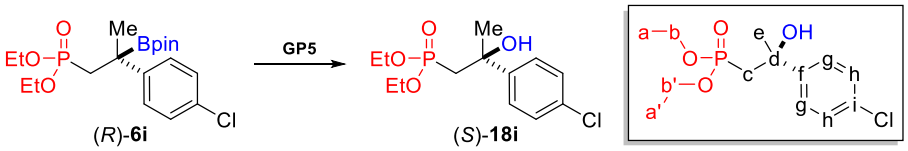
(400 MHz, $CDCl_3$) δ 7.48-7.43 (2H, m, g), 7.05-6.99 (2H, m, h), 5.05 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.80-3.81 (1H, m b or b'), 3.56-3.46 (1H, m, b or b'), 2.44 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.32 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.61 (3H, d, $^4J_{P\text{-}H}$ = 2.5 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.90 (d, $^1J_{C\text{-}F}$ = 245 Hz, i), 143.24 (dd, $^3J_{C\text{-}P}$ = 7.5 Hz, $^4J_{C\text{-}F}$ = 3.0 Hz, f), 126.74 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, g), 114.93 (d, $^2J_{C\text{-}F}$ = 21 Hz, h), 71.91 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.94 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.77 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.83 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 32.73 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.50 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.26 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.65 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.79 ppm; IR (neat) 3395 (O-H), 2981 (sp^2 C-H), 2932 (sp^3 C-H), 1602, 1508 (C-F), 1444 (aromatic C=C), 1392 (aromatic C=C), 1219 (P=O), 1021 (C-O), 960 (P-O), 836 cm^{-1}. HRMS (ESI) calculated for $C_{13}H_{20}FO_4P+Na^+$ = 313.0981, found 313.0992 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile phase = Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) **18h** Racemate



(b) R:S = 96:4, CAHB of **5h** with (*S*,*S*)-**T2**, then oxidation to yield **18h**.

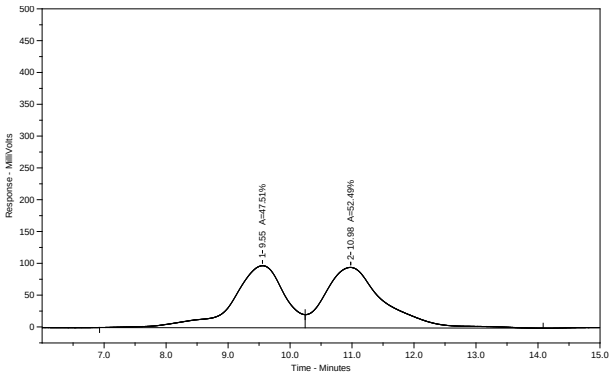




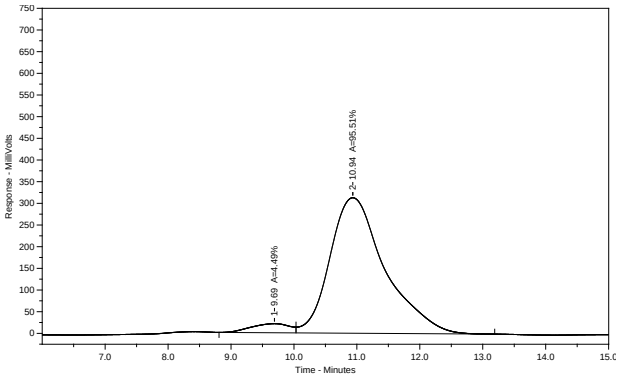
Synthesis of chiral tertiary benzyl alcohol (*S*)-18i: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6i** (42 mg, 0.10 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18i** (29 mg, 95%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -5.7° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, d, *J* = 8.5 Hz, h), 7.31 (2H, d, *J* = 8.5 Hz, g), 5.06 (1H, s, OH), 4.14-4.00 (2H, m, b or b'), 3.81-3.72 (1H, m, b or b'), 3.58-3.48 (1H, m, b or b'), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.32 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.60 (3H, d, $^4J_{C\text{-}P}$ = 2.5 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.01 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 131.74 (i), 127.32 (g), 125.56 (h), 70.91 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 60.99 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 60.82 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 38.66 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 31.55 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 15.51 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 15.23 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P

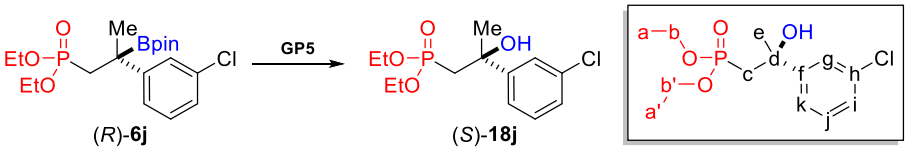
NMR (162 MHz, $CDCl_3$) δ 28.52 ppm; IR (neat) 3382 (O-H), 2979 (sp^2 C-H), 2929 (sp^3 C-H), 1489 (aromatic C=C), 1391 (aromatic C=C), 1215 (P=O), 1022 (C-O), 961 (P-O), 831 (C-Cl) cm^{-1}. HRMS (ESI) calculated for $C_{13}H_{20}ClO_4P+Na^+$ = 329.0685, found 329.0693 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IA; Mobile phase = 95:5 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) **18i** Racemate



(b) R:S = 96:4, CAHB of **5i** with (*S*,*S*)-**T2**, then oxidation to yield **18i**.

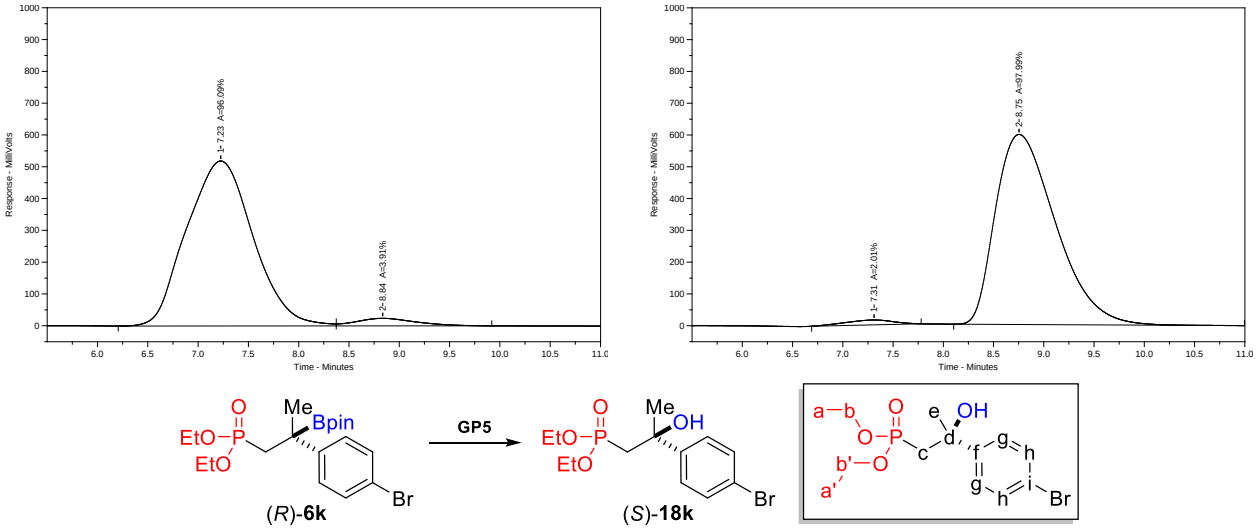




Synthesis of chiral tertiary benzyl alcohol (*S*)-18j: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6j** (42 mg, 0.10 mmol) yields the chiral tertiary alcohol (*S*)-**18j** (27 mg, 88%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -5.7° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (1H, t, *J* = 2.0 Hz, aryl), 7.37 (1H, dt, *J* = 7.5, 1.5 Hz, aryl), 7.27 (1H, t, *J* = 7.5 Hz, aryl), 7.22 (1H, dt, *J* = 7.5, 1.5 Hz, aryl), 5.07 (1H, br s, OH), 4.14-3.99 (2H, m, b or b'), 3.82-3.71 (1H, m, b or b'), 3.59-3.49 (1H, m, b or b'), 2.43 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.31 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.60 (3H, d, $^4J_{P-H}$ = 2.5 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.63 (d, $^3J_{C-P}$ = 7.5 Hz, f), 134.25 (h), 129.59 (aryl), 127.03 (aryl), 125.47 (aryl), 123.23 (aryl), 71.90 (d, $^2J_{C-P}$ = 5.0 Hz, d), 61.99 (d, $^2J_{C-P}$ = 6.5 Hz, b or b'), 61.82 (d, $^2J_{C-P}$ = 6.5 Hz, b or b'), 39.51 (d, $^1J_{C-P}$ = 136 Hz, c), 32.51 (d, $^3J_{C-P}$ = 14.0 Hz, e), 16.49 (d, $^3J_{C-P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.36 ppm; IR (neat) 3370 (O-H), 2980 (sp^2 C-H), 2931 (sp^3 C-H), 1596, 1571, 1475 (aromatic C=C), 1392 (aromatic C=C), 1215 (P=O), 1020 (C-O), 960 (P-O), 738 (C-Cl) cm^{-1}. HRMS (ESI) calculated for $C_{13}H_{20}ClO_4P+Na^+$ = 329.0685, found 329.0688 *m/z*. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 90:10 Hexanes:Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

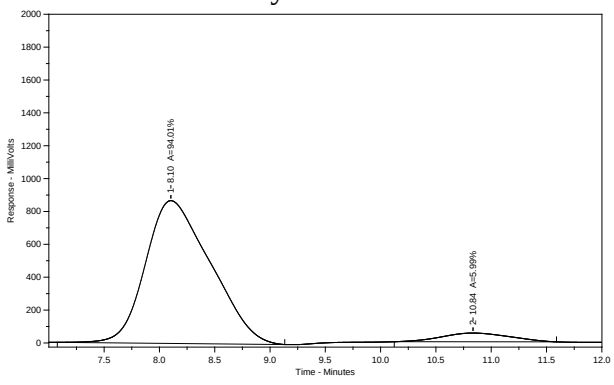
(a) R:S = 4:96, CAHB of **5j** with (*R*,*R*)-**T2**, then oxidation to yield **18j**.

(b) R:S = 98:2, CAHB of **5j** with (*S*,*S*)-**T2**, then oxidation to yield **18j**.

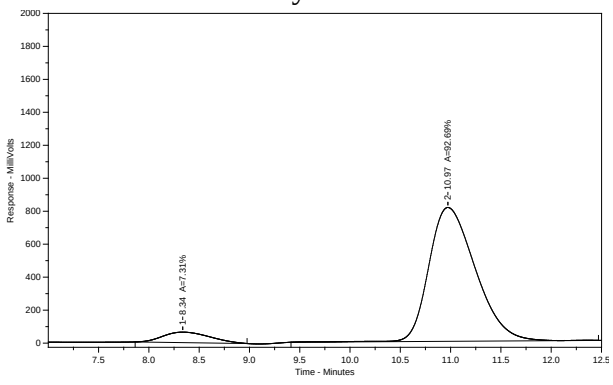


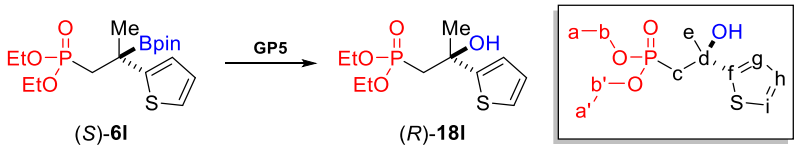
Synthesis of chiral tertiary benzyl alcohol (*S*)-18k: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6k** (46 mg, 0.1 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18k** (28 mg, 81%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -1.3° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J* = 8.5 Hz, h), 7.37 (2H, d, *J* = 8.5 Hz, g), 5.05 (1H, br s, OH), 4.14-4.00 (2H, m, b or b'), 3.82-3.72 (1H, m, b or b'), 3.59-3.49 (1H, m, b or b'), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.31 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.60 (3H, d, $^4J_{C\text{-}P}$ = 2.0 Hz, e), 1.33 (3H, t, *J* = 7.0 Hz, a or a'), 1.05 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.55 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, f), 131.29 (h), 126.95 (g), 120.86 (i), 71.96 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 62.01 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.84 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.62 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 32.51 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.52 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.23 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.49 ppm; IR (neat) 3391 (O-H), 2980 (sp^2 C-H), 2931 (sp^3 C-H), 1590, 1486 (aromatic C=C), 1393 (aromatic C=C), 1214 (P=O), 1021 (C-O), 960 (P-O), 828, 731 (C-Br) cm^{-1}. HRMS (ESI) calculated for $C_{13}H_{20}BrO_4P$+Na^+ = 375.0160, found 375.0173 *m/z*. Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 90:10 Hexanes:Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

(a) R:S = 6:94, CAHB of **5k** with (*R*,*R*)-**T2**, then oxidation to yield **18k**.



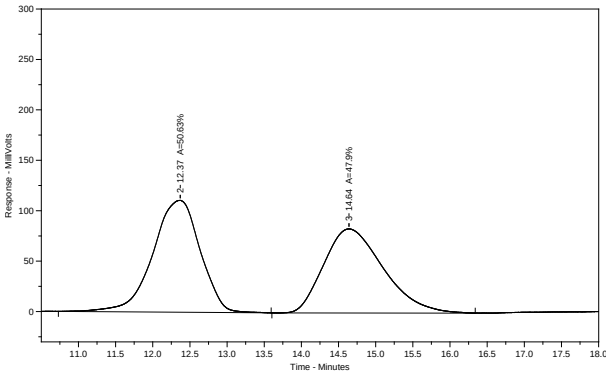
(b) R:S = 93:7, CAHB of **5k** with (*S*,*S*)-**T2**, then oxidation to yield **18k**.



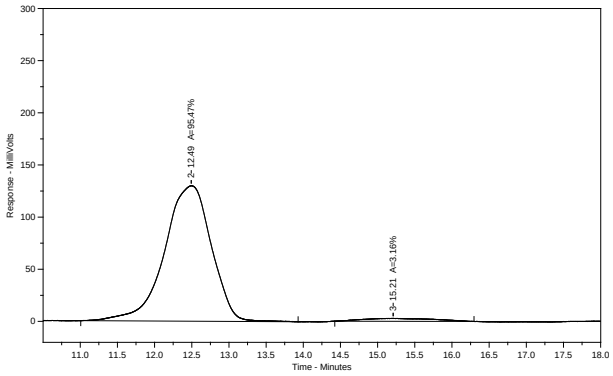


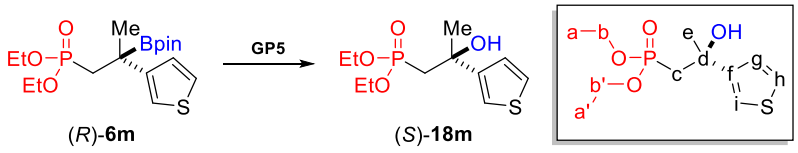
Synthesis of chiral tertiary benzyl alcohol (*R*)-18l: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*S*)-**6l** (39 mg, 0.1 mmol) yields the chiral tertiary benzyl alcohol (*R*)-**18l** (23 mg, 83%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; $[\alpha]_D^{20}$ = +16° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, dd, *J* = 4.0, 2.0 Hz, i), 6.96-6.94 (2H, m, g+h), 5.29 (1H, br s, OH), 4.15-4.05 (2H, m b or b'), 3.94-3.84 (1H, m, b or b'), 3.73-3.63 (1H, m, b or b'), 2.50 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.39 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.73 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.34 (3H, t, *J* = 7.0 Hz, a or a'), 1.16 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.07 (d, $^3J_{C\text{-}P}$ = 10.0 Hz, f), 126.84 (g or h), 124.12 (i), 122.54 (g or h), 71.45 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 62.22 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.77 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 40.73 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 33.36 (d, $^3J_{C\text{-}P}$ = 12.5 Hz, e), 16.52 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.40 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.09 ppm; IR (neat) 3367 (O-H), 2980 (sp^2 C-H), 2930 (sp^3 C-H), 1442 (aromatic C=C), 1391 (aromatic C=C), 1214 (P=O), 1018 (C-O), 959 (P-O), 836, 695 cm^{-1}. HRMS (ESI) calculated for $C_{11}H_{19}O_4PS+Na^+$ = 301.0639, found 301.0644 *m/z*. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 90:10 Hexanes:Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

(a) **18l** Racemate



(b) R:S = 7:93, CAHB of **5l** with (*S*,*S*)-**T2**, then oxidation to yield **18l**.

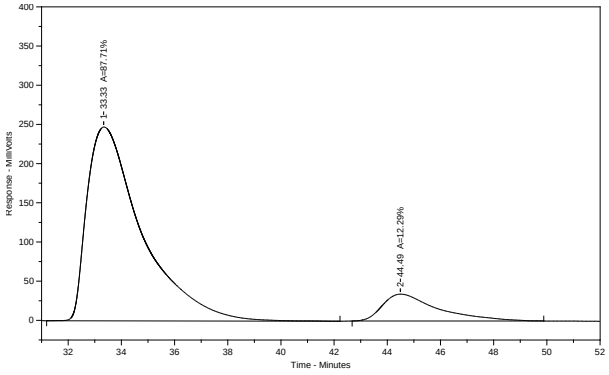




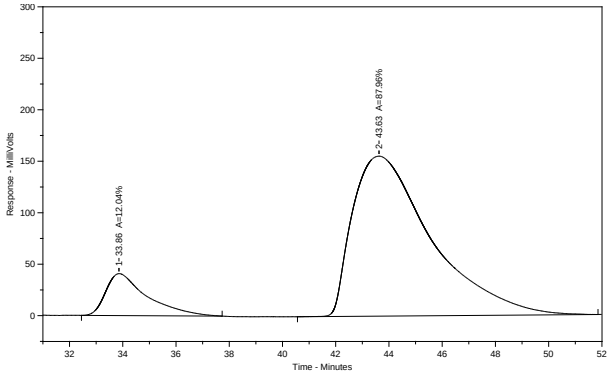
Synthesis of chiral tertiary benzyl alcohol (*S*)-18m: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**6m** (39 mg, 0.1 mmol) yields the chiral tertiary benzyl alcohol (*S*)-**18m** (24 mg, 87%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; $[\alpha]_D^{20}$ = -11.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.03 (1H, dd, *J* = 4.0, 2.0 Hz, h), 7.28-7.26 (2H, m, g+i), 5.04 (1H, br s, OH), 4.14-4.00 (2H, m b or b'), 3.87-3.77 (1H, m, b or b'), 3.62-3.52 (1H, m, b or b'), 2.42 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 2.32 (1H, dd, *J* = 18.0, 15.0 Hz, c(1H)), 1.62 (3H, d, $^4J_{P\text{-}H}$ = 2.0 Hz, e), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.11 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.48 (d, $^3J_{C\text{-}P}$ = 8.0 Hz, f), 125.91 (g or i), 125.68 (g or i), 120.04 (h), 71.17 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.98 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.66 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 39.89 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 32.27 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 16.51 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.38 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.66 ppm; IR (neat) 3391 (O-H), 2978 (sp^2 C-H), 2922 (sp^3 C-H), 1443 (aromatic C=C), 1392 (aromatic C=C), 1221 (P=O), 1020 (C-O), 960 (P-O), 790 cm^{-1}. HRMS (ESI) calculated for $C_{11}H_{19}O_4PS+Na^+$ = 301.0639, found 301.0646 *m/z*. Enantiomer ratio = 88:12, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile phase = 90:10 Hexanes: Isopropanol; Flow rate = 1.5 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

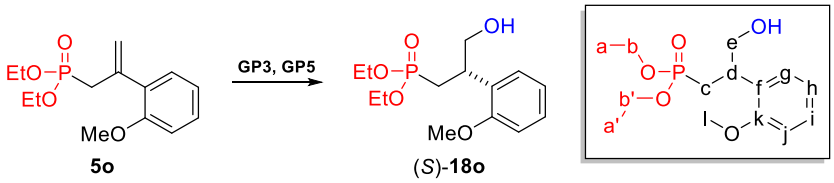
(a) R:S = 12:88, CAHB of **5m** with (*R*,*R*)-**T2**, then oxidation to yield **18m**.



(b) R:S = 88:12, CAHB of **5m** with (*S*,*S*)-**T2**, then oxidation to yield **18m**.



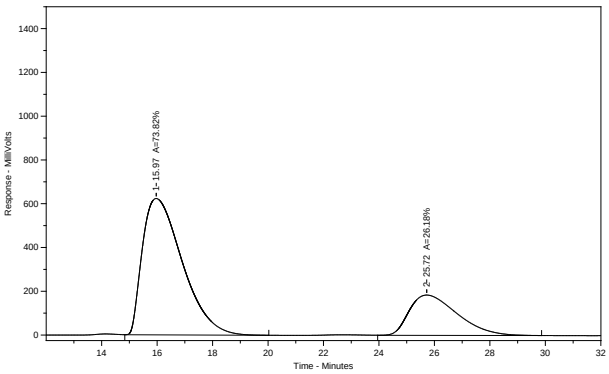
Synthesis of chiral primary alcohol (*S*)-18n: See sec. 9.2 (Absolute configuration assignments).



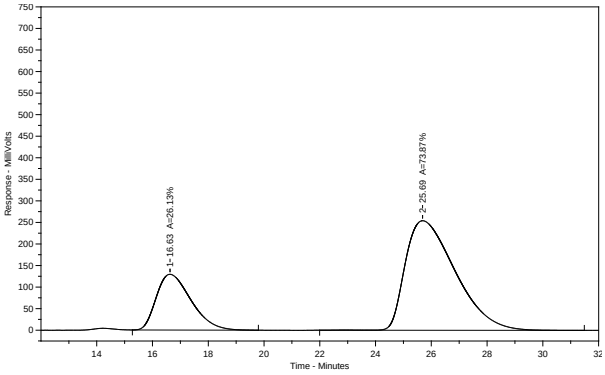
Synthesis of chiral primary alcohol (*S*)-18o: Following the general procedure for CAHB (**GP3**), the substrate **5o** (57 mg, 0.2 mmol) yields a mixture of boronic esters and reduced products that were not separable via silica gel chromatography. The crude CAHB mixture was chromatographed (ethyl acetate/hexanes 3:1) over silica gel to get rid of the non-polar colored complex and the polar metal residues. The crude mixture obtained after this partial purification was subjected to oxidation following **GP5** to obtain the chiral primary alcohol (*S*)-**18o** (48 mg, 80%) as a colorless oil: TLC analysis (ethyl acetate/methanol 19:1) R_f = 0.5; $[\alpha]_D^{20}$ = +4.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (2H, m, aryl), 7.94 (1H, t, *J* = 7.5 Hz, aryl), 6.88 (1H, d, *J* = 8.0 Hz, j), 4.10-4.01 (4H, m, b+b'), 3.87-3.84 (5H, m, e+l), 3.67-3.58 (1H, m, d), 3.27 (1H, br s, OH), 2.32 (1H, ddd, *J* = 18.0, 15.0, 8.5 Hz, c(1H)), 2.19 (1H, ddd, *J* = 19.0, 18.0, 5.5 Hz, c(1H)), 1.30 (3H,

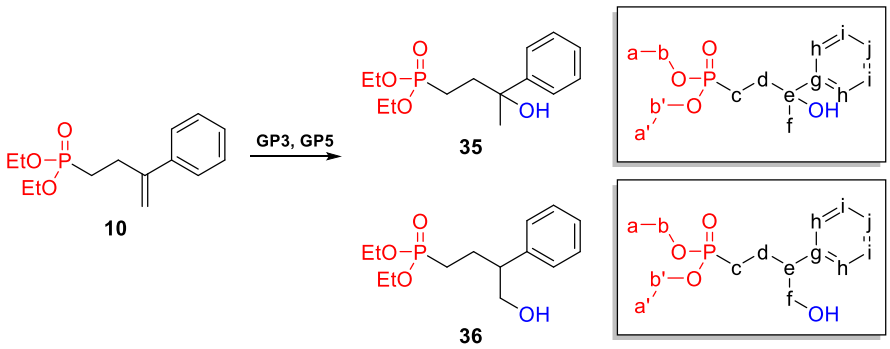
t, J = 7.0 Hz, a or a'), 1.28 (3H, t, J = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.07 (k), 130.48 (d, $^3J_{C\text{-}P}$ = 12.5 Hz, f), 128.61 (aryl), 128.08 (aryl), 120.82 (aryl), 110.85 (j), 66.40 (d, $^3J_{C\text{-}P}$ = 8.0 Hz, e), 61.97 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.75 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.45 (l), 37.47 (d, $^2J_{C\text{-}P}$ = 2.0 Hz, d), 28.24 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 16.48 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.46 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.39 ppm; IR (neat) 3369 (O-H), 2980 (sp^2 C-H), 2907 (sp^3 C-H), 1493 (aromatic C=C), 1391 (aromatic C=C), 1239 (P=O), 1020 (C-O), 958 (P-O), 752 cm^{-1}. HRMS (ESI) calculated for $C_{14}H_{23}O_5P+Na^+$ = 325.1181, found 325.1184 *m/z*. Enantiomer ratio = 74:26, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile phase = 90:10 Hexanes: Isopropanol; Flow rate = 1.5 mL/min. HPLC UV detector λ = 220 nm, rt. HPLC traces:

(a) R:S = 26:74, CAHB of **5o** with (*R*,*R*)-**T2**, then oxidation to yield **18o**.



(b) R:S = 74:26, CAHB of **5o** with (*S*,*S*)-**T2**, then oxidation to yield **18o**.

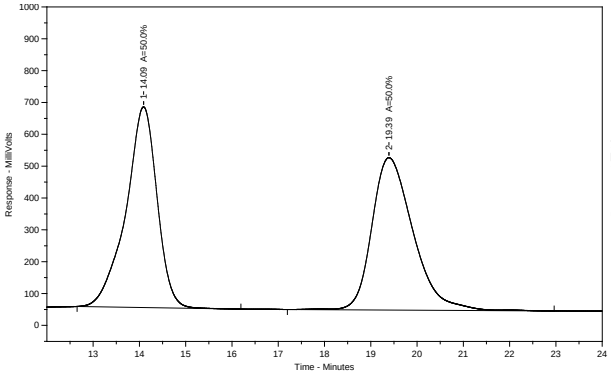




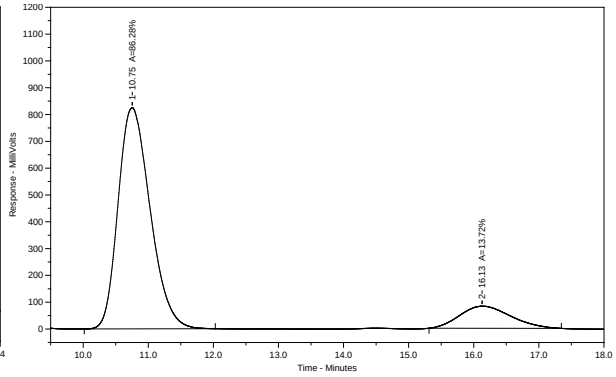
Synthesis of chiral alcohols 35 & 36: Following the general procedure for CAHB (**GP3**; 12 h total reaction time), the substrate **10** (54 mg, 0.2 mmol) yields about a 1:1 mixture of regioisomers that were not separable at the boronate stage. The crude CAHB mixture was chromatographed (ethyl acetate/hexanes 1:1) over silica gel to get rid of the non-polar colored complex and the polar metal residues. The crude mixture obtained after this partial purification is subjected to oxidation following **GP5** to obtain the corresponding alcohols that were separated and purified by silica gel chromatography.

The tertiary alcohol **35** is obtained as a colorless oil (23 mg, 40%): TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +1.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.44 (2H, d, *J* = 8.0 Hz, h), 7.36 (2H, dd, *J* = 8.0, 7.5 Hz, i), 7.26 (1H, t, *J* = 7.5 Hz, j), 4.12-4.02 (4H, m, b+b'), 2.80 (1H, br s, OH), 2.18-2.08 (2H, m, d), 1.79-1.72 (1H, m, c(1H)), 1.62-1.55 (4H, m, c(1H)+f), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.92 (g), 128.52 (i), 126.94 (j), 125.04 (h), 74.21 (d, $^3J_{C\text{-}P}$ = 13.5 Hz, e), 61.87 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 36.65 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 30.97 (f), 20.76 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.64 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.60 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 33.68 ppm; IR (neat) 3361 (O-H), 3025 (aromatic C-H), 2931 (aliphatic C-H), 1446 (aromatic C=C), 1392 (aromatic C=C), 1219 (P=O), 1052 (C-O), 1021 (C-O), 960 (P-O) 700 cm^{-1}; Enantiomer ratio = 86:14, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile Phase = 40:60 Hexanes:Isopropanol. Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) Racemate



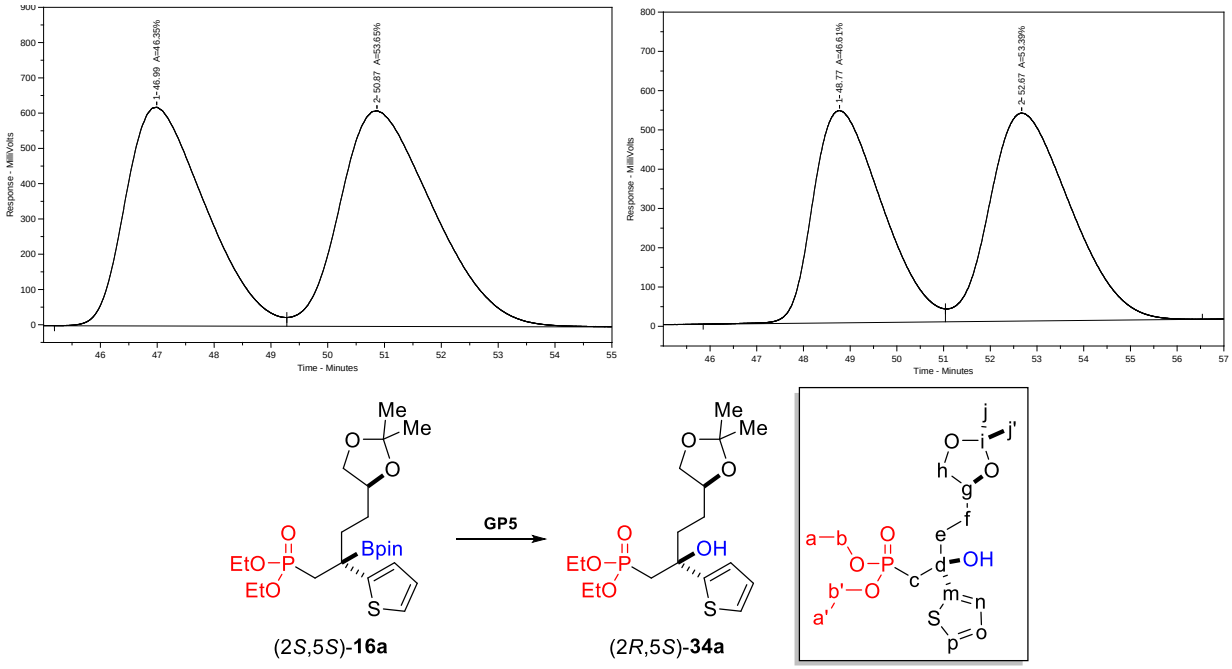
(b) Er = 86:14, CAHB of **10** with (*S*,*S*)-**T2**, then oxidation to yield **35**.



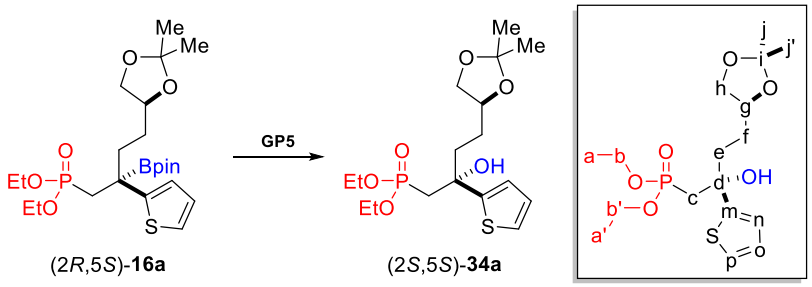
The primary alcohol **36** is obtained as a colorless oil (24 mg, 41%): TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -1.6° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (5H, m, aryl), 4.13-4.00 (4H, m, b+b'), 3.78 (2H, br t, *J* = 5.0 Hz, f), 2.88-2.81 (1H, m, e), 2.16-2.05 (1H, m, d(1H)), 1.95-1.84 (1H, m, d(1H)), 1.76 (1H, br s, OH), 1.70-1.56 (2H, m, c), 1.31 (3H, t, *J* = 7.0 Hz, a or a'), 1.30 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.18 (g), 129.04 (h or i), 128.25 (h or i), 127.31 (j), 67.27 (f), 61.71 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b+b'), 49.34 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 24.98 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 23.75 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.65 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.17 ppm; IR (neat) 3363 (O-H), 2989 (aromatic C-H), 2930 (aliphatic C-H), 1447 (aromatic C=C), 1389 (aromatic C=C), 1220 (P=O), 1052 (C-O), 1021 (C-O), 963 (P-O) 702 cm^{-1}; Enantiomer ratio = 46:54, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 30:70 Hexanes:Isopropanol. Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) Er = 54:46, CAHB of **10** with (*R*,*R*)-**T2** then oxidation to yield **36**.

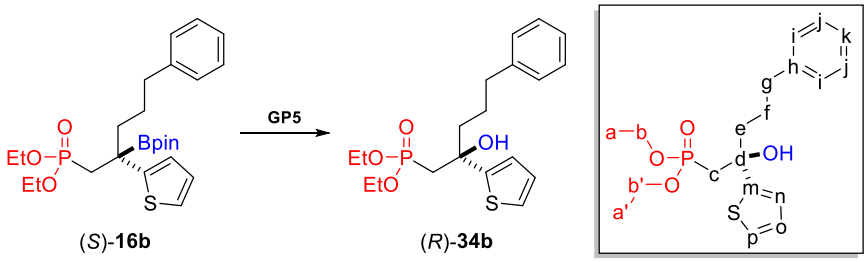
(b) Er = 53:47, CAHB of **10** with (*S*,*S*)-**T2**, then oxidation to yield **36**.



Synthesis of chiral tertiary benzyl alcohol (2*R*,5*S*)-34a: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (2*S*,5*S*)-**16a** (38 mg, 75 µmol; obtained via CAHB of (*Z*)-**15a** using (*R*,*R*)-**T2**) yields the chiral tertiary benzyl alcohol product (2*R*,5*S*)-**34a** (24 mg, 82%; 95:5 dr, determined via ^{31}P NMR analysis) as a light buff colored viscous oil. Alternatively, the chiral boronic ester (2*S*,5*S*)-**16a** (38 mg, 75 µmol; obtained via CAHB of (*E*)-**15a** using (*R*,*R*)-**T2**) yields the chiral tertiary benzyl alcohol product (2*R*,5*S*)-**34a** (23 mg, 80%; 95:5 dr, determined via ^{31}P NMR analysis) as a buff colored viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +10.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 6.83 (1H, dd, *J* = 5.0, 1.0 Hz, aryl), 6.81 (1H, dd, *J* = 3.5, 1.0 Hz, aryl), 6.71 (1H, dd, *J* = 5.0, 3.5 Hz, aryl), 6.21 (1H, br s, OH), 3.88-3.56 (5H, m, b+b'(total 3H)+g+h(1H)), 3.37-3.23 (2H, m, b or b'(1H)+h(1H)), 2.28 (1H, dd, *J* = 19.0, 15.0 Hz, c(1H)), 2.24 (1H, dd, *J* = 19.0, 15.0 Hz, c(1H)), 2.09 (1H, ddd, *J* = 18.0, 13.0, 5.0 Hz, e(1H)), 1.97 (1H, dd, *J* = 18.0, 13.0, 4.5 Hz, e(1H)), 1.82-1.73 (1H, m, f(1H)), 1.53-1.43 (1H, m, f(1H)), 1.34 (3H, s, j or j'), 1.29 (3H, s, j or j'), 0.98 (3H, t, *J* = 7.0 Hz, a or a'), 0.80 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 152.45 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, m), 127.19 (aryl), 124.63 (aryl), 123.77 (aryl), 109.05 (i), 76.70 (g), 73.94 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 69.94 (h), 62.15 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.59 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 43.09 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 40.50 (d, $^1J_{C\text{-}P}$ = 135 Hz, c), 28.66 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, f), 27.64 (j or j'), 26.36 (j or j'), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.56 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, C_6D_6) δ 28.85 (5%, minor diastereomer), 28.77 (95%, major diastereomer) ppm; IR (neat) 3377 (O-H), 2983 (aromatic C-H), 2933 (aliphatic C-H), 1443 (aromatic C=C), 1368 (aromatic C=C), 1214 (P=O), 1158, 1021 (C-O/C=S), 962 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{29}O_6PS+Na^+$ = 415.1320, found 415.1327 *m/z*.



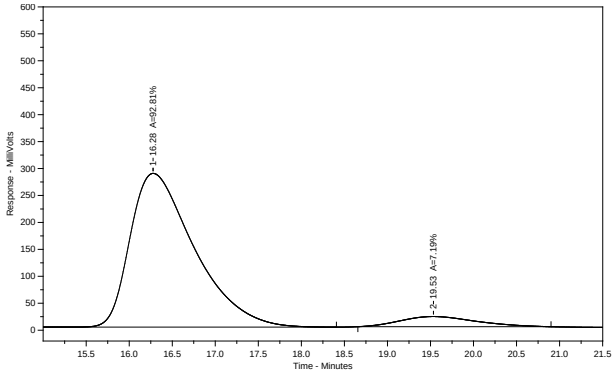
Synthesis of chiral tertiary benzyl alcohol (2*S*,5*S*)-34a: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (2*R*,5*S*)-**16a** (38 mg, 75 µmol; obtained via CAHB of (*Z*)-**15a** using (*S*,*S*)-**T2**) yields the chiral tertiary benzyl alcohol product (2*S*,5*S*)-**34a** (25 mg, 85%; 94:6 dr, determined via ^{31}P NMR analysis) as a light buff colored viscous oil. Alternatively, the chiral boronic ester (2*R*,5*S*)-**16a** (38 mg, 75 µmol; obtained via CAHB of (*E*)-**15a** using (*S*,*S*)-**T2**) yields the chiral tertiary benzyl alcohol product (2*S*,5*S*)-**34a** (24 mg, 82%; 95:5 dr, determined via ^{31}P NMR analysis) as a buff colored viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +3.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 6.84 (1H, dd, *J* = 5.0, 1.0 Hz, aryl), 6.80 (1H, dd, *J* = 3.5, 1.0 Hz, aryl), 6.72 (1H, dd, *J* = 5.0, 3.5 Hz, aryl), 6.21 (1H, br s, OH), 3.85-3.57 (5H, m, b+b'(total 3H)+g+h(1H)), 3.37-3.23 (2H, m, b or b'(1H)+h(1H)), 2.31-2.16 (3H, m, c+e(1H)), 1.93-1.76 (2H, m, e(1H)+f(1H)), 1.51-1.43 (1H, m, f(1H)), 1.38 (3H, s, j or j'), 1.29 (3H, s, j or j'), 0.99 (3H, t, *J* = 7.0 Hz, a or a'), 0.80 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 152.85 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, m), 127.22 (aryl), 124.58 (aryl), 123.77 (aryl), 109.09 (i), 76.54 (g), 73.77 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 69.88 (h), 62.14 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.60 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 43.08 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 40.06 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 28.49 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, f), 27.60 (j or j'), 26.32 (j or j'), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.56 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, C_6D_6) δ 28.85 (94%, minor diastereomer), 28.77 (6%, major diastereomer) ppm; IR (neat) 3378 (O-H), 2981 (aromatic C-H), 2933 (aliphatic C-H), 1445 (aromatic C=C), 1363 (aromatic C=C), 1213 (P=O), 1158, 1021 (C-O/C=S), 963 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{29}O_6PS$+Na^+ = 415.1320, found 415.1329 *m/z*.



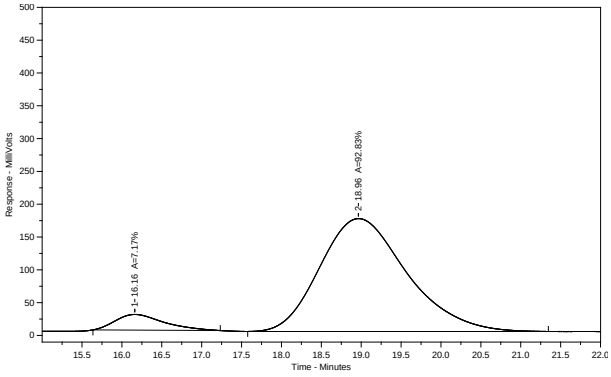
Synthesis of chiral tertiary benzyl alcohol (*R*)-34b: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*S*)-**16b** (37 mg, 75 µmol) yields the chiral tertiary benzyl alcohol (*R*)-**34b** (25 mg, 87%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -3.0° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.12 (6H, m, aryl), 3.96 (1H, dd, *J* = 4.5, 4.0 Hz, aryl), 6.90 (1H, d, *J* = 3.5 Hz, aryl), 5.42 (1H, br s, OH), 4.09-3.99 (2H, m, b or b'), 3.86-3.76 (1H, m, b or b'), 3.59-3.49

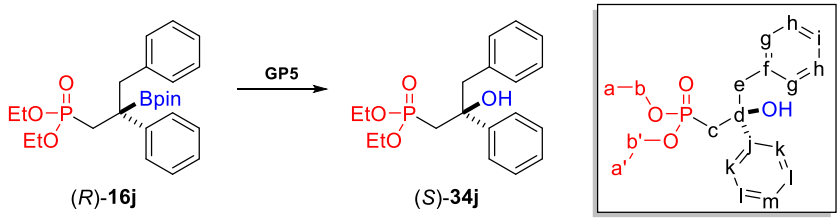
(1H, m, b or b'), 2.64-2.52 (2H, m, g), 2.43 (1H, dd, J = 22.0, 15.0 Hz, c(1H)), 2.38 (1H, dd, J = 22.0, 15.0 Hz, c(1H)), 2.00-1.73 (3H, m, e+f(1H)), 1.57-1.47 (1H, m, e(1H)), 1.32 (3H, t, J = 7.0 Hz, a or a'), 1.10 (3H, t, J = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.39 (d, $^3J_{C\text{-}P}$ = 7.5 Hz, m), 142.33 (h), 128.57 (aryl), 128.40 (aryl), 126.85 (aryl), 125.86 (aryl), 124.23 (aryl), 123.22 (aryl), 73.68 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 62.14 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.67 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 45.65 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 39.49 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 35.94 (g), 25.39 (d, $^4J_{C\text{-}P}$ = 2.0 Hz, f), 16.50 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.35 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{13}C NMR (162 MHz, $CDCl_3$) δ 28.57 ppm; IR (neat) 3380 (O-H), 2982 (sp^2 C-H), 2908 (sp^3 C-H), 1453 (aromatic C=C), 1391 (aromatic C=C), 1217 (P=O), 1049 (C-O), 1020 (C-O/C=S), 962 (P-O), 728, 697 cm^{-1}. HRMS (ESI) calculated for $C_{19}H_{27}O_4PS+Na^+$ = 405.1265, found 405.1265 *m/z*. Enantiomer ratio = 93:7, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 95:5 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) R:S = 93:7, CAHB of **15b** with (*R*,*R*)-**T2**, then oxidation to yield **34b**.



(b) R:S = 7:93, CAHB of **15b** with (*S*,*S*)-**T2**, then oxidation to yield **34b**.

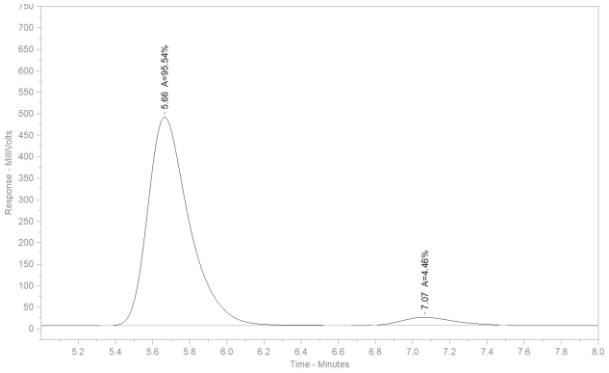




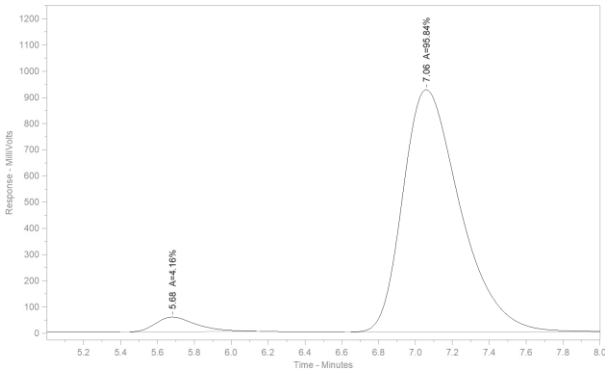
Synthesis of chiral tertiary alcohol (*S*)-34j: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**16j** (34 mg, 75 μmol; obtained via CAHB of (*E*)-**15j** using (*R*,*R*)-**T2**) yields the chiral tertiary benzyl alcohol product (*S*)-**34j** (21 mg, 80%; 97:3 er, determined via chiral HPLC analysis) as a light buff colored viscous oil. Alternatively, the chiral boronic ester (*R*)-**16j** (34 mg, 75 μmol; obtained via CAHB of (*Z*)-**15j** using (*R*,*R*)-**T2**) yielded the chiral tertiary benzyl alcohol product (*S*)-**34j** (20 mg, 76%; 70:30 er, determined via chiral HPLC analysis) as a buff colored viscous oil. Characterization data for enantioenriched (*S*)-**34j**: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = -19.3° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.42-7.20 (8H, m, aryl), 7.06-7.05 (2H, m, aryl), 5.05 (1H, br s, OH), 4.04-3.96 (2H, m, b or b'), 3.66-3.57 (1H, m, b or b'), 3.25-3.04 (3H, m, b or b'

(1H)+e), 2.55 (1H, dd, J = 19.0, 15.0 Hz, c(1H)), 2.34 (1H, dd appearing as t, J = 16.0 Hz, c(1H)), 1.28 (3H, t, J = 7.0 Hz, a or a'), 0.95 (3H, t, J = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.54 (d, $^{3}J_{C\text{-}P}$ = 4.5 Hz, j), 136.64 (f), 131.10 (aryl), 128.00 (aryl), 127.85 (aryl), 127.00 (aryl), 126.61 (aryl), 125.99 (aryl), 74.63 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 61.93 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.50 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 51.62 (d, $^{3}J_{C\text{-}P}$ = 17.0 Hz, e), 37.26 (d, $^{1}J_{C\text{-}P}$ = 137 Hz, c), 16.43 (d, $^{3}J_{C\text{-}P}$ = 6.5 Hz, a or a'), 16.22 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.49 ppm; IR (neat) 3398 (O-H), 2981 (sp^2 C-H), 2917 (sp^3 C-H), 1495 (aromatic C=C), 1392 (aromatic C=C), 1222 (P=O), 1022 (C-O), 967 (P-O), 728, 698 cm^{-1}. HRMS (ESI) calculated for $C_{19}H_{25}O_4P$+Na^+ = 371.1388, found 371.1393 *m/z*. Enantiomer ratio determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 90:10 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

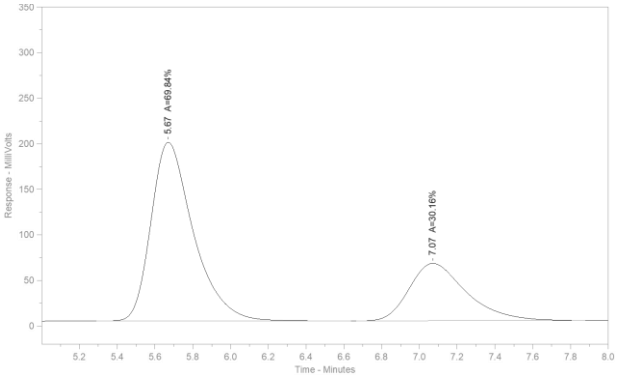
(a) R:S = 4:96, CAHB of (*E*)-**15j** with (*R*,*R*)-**T2**, then oxidation to yield **34j**.



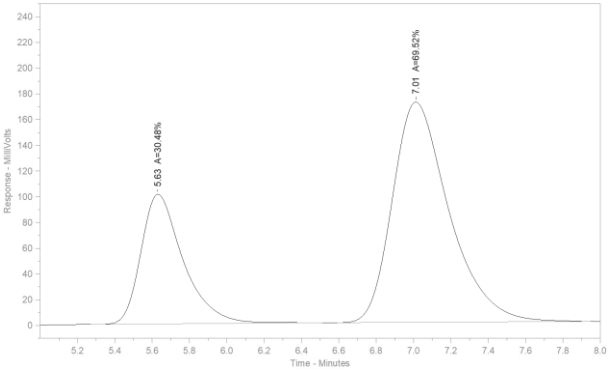
(b) R:S = 96:4, CAHB of (*E*)-**15j** with (*S*,*S*)-**T2**, then oxidation to yield **34j**.

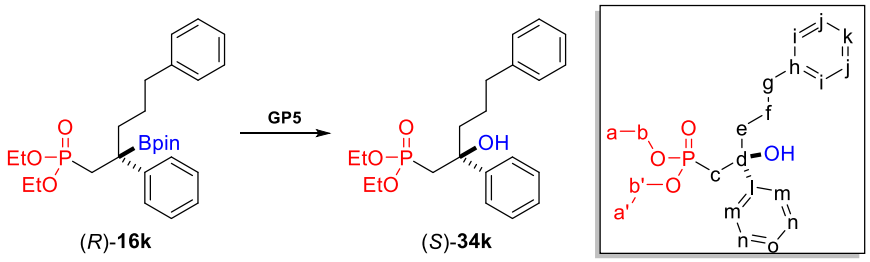


(c) R:S = 30:70, CAHB of (*Z*)-**15j** with (*R*,*R*)-**T2**, then oxidation to yield **34j**.



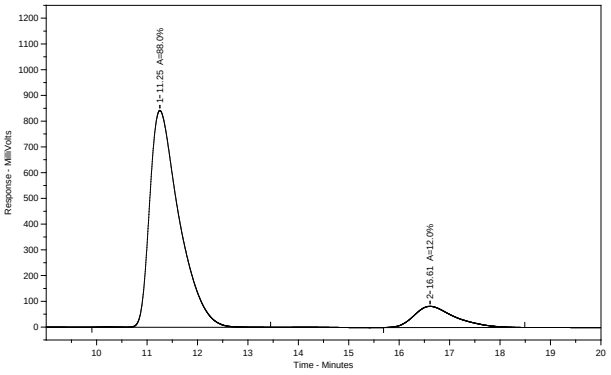
(d) R:S = 70:30, CAHB of (*Z*)-**15j** with (*S*,*S*)-**T2**, then oxidation to yield **34j**.



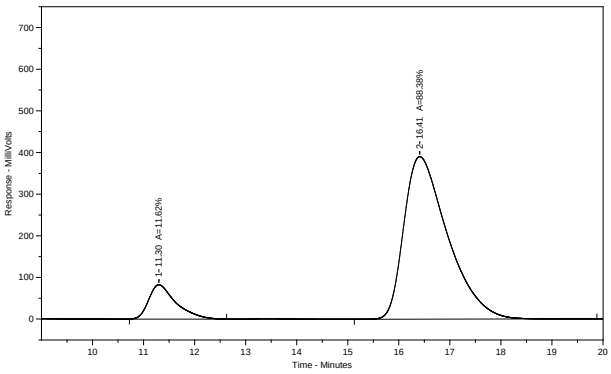


Synthesis of chiral tertiary benzyl alcohol (*S*)-34k: Following the general procedure for oxidation of chiral tertiary benzylic boronic esters (**GP5**), the chiral boronic ester (*R*)-**16k** (36 mg, 75 μmol) yields the chiral tertiary alcohol (*S*)-**34k** (25 mg, 88%) as a colorless viscous oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +0.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.09 (10H, m, aryl), 5.04 (1H, br s, OH), 4.10-3.97 (2H, m, b or b'), 3.68-3.59 (1H, m, b or b'), 3.31-3.21 (1H, m, b or b'), 2.61-2.32 (4H, m, c+g), 1.97-1.69 (3H, m, e+f(1H)), 1.41-1.29 (4H, m, a or a' + f(1H)), 0.97 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.57 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, l), 142.40 (h), 128.52 (aryl), 128.34 (aryl), 128.17 (aryl), 128.79 (aryl), 125.77 (aryl), 125.60 (aryl), 74.16 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 61.81 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.49 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 44.61 (d, $^3J_{C\text{-}P}$ = 15.5 Hz, e), 38.87 (d, $^1J_{C\text{-}P}$ = 136 Hz, c), 36.00 (g), 25.13 (d, $^4J_{C\text{-}P}$ = 2.5 Hz, f), 16.45 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.20 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.28 ppm; IR (neat) 3376 (O-H), 2985 (sp^2 C-H), 2908 (sp^3 C-H), 1451 (aromatic C=C), 1396 (aromatic C=C), 1220 (P=O), 1049 (C-O), 1021 (C-O/C=S), 965 (P-O), 729, 699 cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{29}O_4P+Na^+$ = 399.1701, found 399.1706 *m/z*. Enantiomer ratio = 93:7, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile phase = 95:5 Hexanes:Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

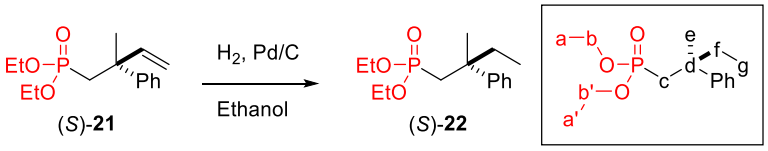
(a) R:S = 12:88, CAHB of **15k** with (*R*,*R*)-**T2**, then oxidation to yield **34k**.



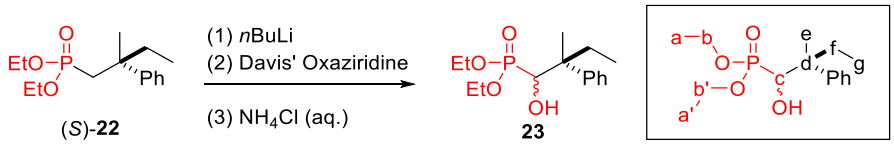
(b) R:S = 88:12, CAHB of **15k** with (*S*,*S*)-**T2**, then oxidation to yield **34k**.



(8) Oxidations leading to α-hydroxy and oxophosphonates and their synthetic utility

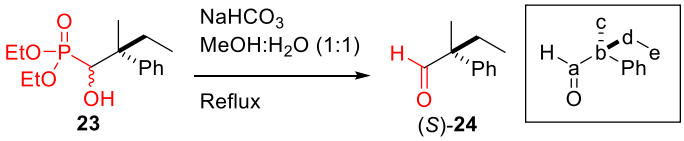


Synthesis of phosphonate (*S*)-22 via hydrogenation of vinylated derivative (*S*)-21: A mixture of vinylated derivative (*S*)-**21** (282 mg, 1.00 mmol) and 10% Pd on activated carbon (20 mg, 2.0 mol% Pd loading) in ethanol (10 mL) is stirred under a hydrogen atmosphere (balloon pressure) for 6 hours. Afterwards, the mixture is concentrated under reduced pressure and the concentrate is dissolved in ethyl acetate (20 mL) and is filtered over a bed of celite to get rid of insoluble materials. The celite bed is washed with ethyl acetate (2 x 20 mL) and the combined filtrates were concentrated under reduced pressure to yield the reduced product (*S*)-**22** (270 mg, 95%): TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; $[\alpha]_D^{20}$ = -5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.19 (5H, m, aryl), 3.92-3.66 (4H, m, b+b'), 2.29-2.10 (2H, m, c), 1.92-1.76 (2H, m, f), 1.56 (3H, s, e), 1.18 (3H, t, *J* = 7.0 Hz, a or a'), 1.12 (3H, t, *J* = 7.0 Hz, a or a'), 0.66 (3H, t, *J* = 7.4 Hz, g) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.67 (d, $^3J_{C\text{-}P}$ = 8 Hz, ipso C of phenyl group), 128.19 (aryl), 126.51 (aryl), 125.98 (aryl), 61.18-61.02 (m, b+b'), 39.68 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 39.66 (d, $^2J_{C\text{-}P}$ = 3 Hz, d), 36.88 (d, $^3J_{C\text{-}P}$ = 14 Hz, f), 24.09 (d, $^3J_{C\text{-}P}$ = 4 Hz, f), 16.50-16.40 (m, a+a'), 8.81 (g) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.12 ppm; IR (neat) 3021 (aromatic C-H), 2915 (aliphatic C-H), 1251 (P=O), 1015 (C-O), 940 (P-O) cm^{-1}.

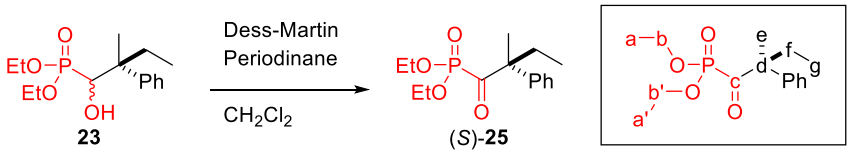


Synthesis of α-hydroxyphosphonate 23: This transformation is carried out with few modifications of the original procedure[12] reported by Weimer as follows: A solution of the chiral phosphonate (*S*)-**22** (213 mg, 0.75 mmol, 1.00 eq) in dry THF (15 mL) is cooled down to -78°C using a dry ice-acetone bath and a solution of *n*BuLi in hexanes (2.5M; 0.6 mL, 1.5 mmol, 2.0 eq) is added drop-wise. The resultant mixture is stirred at -78°C for 5 minutes and then the cooling bath is removed and the mixture is stirred at room temperature for an hour. The mixture is re-cooled to -78°C and a solution of Davis' Oxaziridine (392 mg, 1.50 mmol, 2.00 eq) in dry THF (5 mL) is added drop-wise. The resultant mixture is maintained at -78°C for a total of *ca.* 3 hours and then quenched with the addition of saturated aqueous NH_4Cl solution (25 mL) at -78°C. The resultant frozen mixture is allowed to slowly warm up to room temperature over 1 hour and is then extracted with ethyl acetate (25 mL x 3). The combined organics are washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum. Flash chromatography over silica gel (ethyl acetate/hexanes 6:4) affords the product as an opaque semi-solid material (186 mg, 83%; formed as a ~2:1 mixture of diastereomers): TLC analysis (ethyl acetate/hexanes 6:4) R_f = 0.5; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45-7.23 (5H, m, aryl), 4.10-3.75 (5H, m, b+b'+c), 2.11-2.07 (1H, m, f), 2.00-1.97 (1H, m, f), 1.57 (0.9H, s, e (minor diastereomer)), 1.53 (2.1H, s, e (major

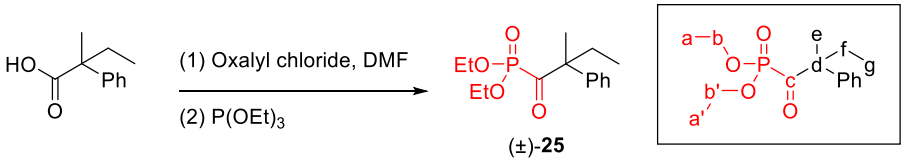
diastereomer)), 1.30 (0.98H, t, J = 7.0 Hz, a or a' (minor diastereomer)), 1.21 (0.89H, t, J = 7.0 Hz, a or a' (minor diastereomer)), 1.17 (2.01H, t, J = 7.0 Hz, a or a' (major diastereomer)), 1.11 (1.99H, t, J = 7.0 Hz, a or a' (major diastereomer)), 0.70-0.66 (3H, m, g) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 143.57 (d, $^3J_{C\text{-}P}$ = 10 Hz, ipso C of aromatic ring (minor diastereomer)), 143.28 (d, $^3J_{C\text{-}P}$ = 10 Hz, ipso C of aromatic ring (major diastereomer)), 128.43 (meta C's of aromatic ring (minor diastereomer)), 128.20 (meta C's of aromatic ring (major diastereomer)), 127.74 (ortho C's of aromatic ring (major diastereomer)), 127.66 (ortho C's of aromatic ring (minor diastereomer)), 126.61 (para C of aromatic ring (minor diastereomer)), 126.46 (para C of aromatic ring (major diastereomer)), 76.93 (d, $^1J_{C\text{-}P}$ = 155 Hz, c (major diastereomer)), 76.66 (d, $^1J_{C\text{-}P}$ = 155 Hz, c (minor diastereomer)), 62.43 (d, $^2J_{C\text{-}P}$ = 7 Hz, b or b' (minor diastereomer)), 62.43 (d, $^2J_{C\text{-}P}$ = 7 Hz, b or b' (major diastereomer)), 62.27 (d, $^2J_{C\text{-}P}$ = 8 Hz, b or b' (minor diastereomer)), 62.19 (d, $^2J_{C\text{-}P}$ = 6 Hz, b or b' (major diastereomer)), 31.26-31.18 (m, f), 19.27 (d, $^3J_{C\text{-}P}$ = 3 Hz, e (minor diastereomer)), 18.76 (d, $^3J_{C\text{-}P}$ = 3 Hz, e (major diastereomer)), 16.62 (d, $^3J_{C\text{-}P}$ = 6 Hz, a or a' (minor diastereomer)), 16.56 (d, $^3J_{C\text{-}P}$ = 6 Hz, a or a' (minor diastereomer)), 16.48 (d, $^3J_{C\text{-}P}$ = 6 Hz, a or a' (major diastereomer)), 16.41 (d, $^3J_{C\text{-}P}$ = 6 Hz, a or a' (major diastereomer)), 8.41 (g, minor diastereomer), 8.29 (g, major diastereomer) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.43 (67%, major diastereomer), 23.32 (33%, minor diastereomer) ppm; IR (neat) 3256 (O-H), 2971 (aromatic C-H), 2906 (aliphatic C-H), 1212 (P=O), 1026 (C-O), 975 (P-O), 699 cm^{-1}.



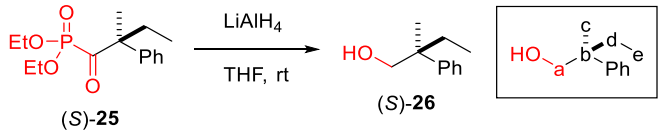
Synthesis of aldehyde (*S*)-24 from α-hydroxyphosphonate 23:[11] This transformation is carried out with some modifications of the original procedure[13] reported by Spilling and coworkers as follows: A stirred suspension of hydroxyphosphonate **23** (60 mg, 0.2 mmol, 1 eq) and sodium bicarbonate (84 mg, 1.0 mmol, 5 eq) in 1:1 MeOH:H_2O (5 mL) is refluxed for 1 hour. Following this, the mixture is diluted with ethyl acetate (25 mL) and the aqueous layer separated. The organic layer is washed with brine (10 mL), dried over Na_2SO_4 and concentrated in vacuum to afford pure aldehyde (*S*)-**24** (29 mg, 89%): TLC analysis (ethyl acetate/hexanes 1:40) R_f = 0.5; $[\alpha]_D^{20}$ = +9.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (1H, s, aldehyde H), 7.42-7.27 (5H, m, aryl), 2.07-1.88 (2H, m, d), 1.46 (3H, s, c), 0.82 (3H, t, J = 7.4 Hz, e) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.91 (a), 140.14 (aryl), 128.98 (aryl), 127.39 (aryl), 127.33 (aryl), 54.47 (b), 28.73 (d), 18.45 (c), 8.56 (e) ppm; IR (neat) 3057 (aldehyde C-H), 2968 (aromatic C-H), 2936 (aliphatic C-H), 1722 (C=O), 1494 (aromatic C=C), 1446 (aromatic C=C) cm^{-1}. Upon reduction with $NaBH_4$ in MeOH, aldehyde (*S*)-**24** is transformed to the alcohol (*S*)-(+)-**26** (*vide infra*), which unambiguously confirmed its absolute configuration to be *"S"* based on the positive value of the optical rotation of (*S*)-(+)-**26**. The formed alcohol (*S*)-**26** was derivatized using (*S*)-(−)-α-methoxy-α-(trifluoromethyl) phenylacetyl chloride to obtain the corresponding ester, the ^{19}F-NMR of which yielded a dr of 97:3. Enantiomer ratio of aldehyde (*S*)-**24** also determined via chiral HPLC analysis of the formed alcohol (upon reduction using $NaBH_4$): 95:5 er (*vide infra*).



Synthesis of α-oxophosphonate (*S*)-25: A suspension of hydroxyphosphonate **23** (60 mg, 0.2 mmol, 1 eq) and Dess-Martin Periodinane (170 mg, 0.4 mmol, 2 eq) in dichloromethane (5 mL) is stirred at room temperature for 3 hours. The completion of the reaction is indicated by the disappearance of the diastereomeric hydroxyphosphonate peaks at ~25 ppm and appearance of a new peak at -3 ppm indicative of the presence of oxophosphonate in the reaction mixture. The mixture is diluted with ethyl acetate (25 mL), washed with saturated $NaHCO_3$ (10 mL), saturated $Na_2S_2O_3$ (10 mL) and brine (5 mL). The resultant organic extract is dried over Na_2SO_4 and concentrated in vacuum. Flash chromatography on silica gel (ethyl acetate/hexanes 1:1) affords the desired product (*S*)-**25** as a colorless viscous oil (55 mg, 92%) : TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +54.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (5H, m, aryl), 3.94-3.72 (4H, m, b+b'), 2.17-1.96 (2H, m, f), 1.60 (3H, s, e), 1.13 (6H, m, a+a'), 0.75 (3H, t, *J* = 7.4 Hz, g) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.14 (d, $^1J_{C\text{-}P}$ = 155 Hz, c), 139.44 (aryl), 128.73 (aryl), 127.50 (aryl), 127.37 (aryl), 63.48-63.23 (m, b+b'), 57.41 (d, $^2J_{C\text{-}P}$ = 51 Hz, d), 29.49 (f), 19.31 (e), 16.29 (dd, $^3J_{C\text{-}P}$ = 5 Hz, a+a'), 8.49 (g) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ -3.21 ppm; IR (neat) 2878 (aromatic C-H), 2936 (aliphatic C-H), 1678 (C=O), 1496 (aromatic C=C), 1446 (aromatic C=C), 1255 (P=O), 1014 (C-O), 967 (P-O) cm^{-1}. HRMS (EI) calculated for $C_{15}H_{23}O_4P$ = 298.1334, found 298.1329 *m/z*.

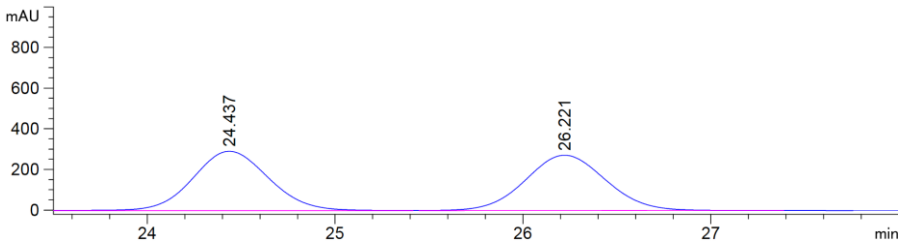


Synthesis of oxophosphonate (±)-25: To a solution of (±)-2-methyl-2-phenylbutanoic acid (1.00 g, 5.61 mmol, 1.00 eq.) in dry dichloromethane (10 mL) is added oxalyl chloride (0.72 mL, 8.42 mmol, 1.5 eq.) dropwise at 0°C. After complete addition of oxalyl chloride, a drop of DMF is added and the reaction mixture is stirred at room temperature for a total of 2 hours. Following this, the reaction mixture is concentrated in vacuum to get rid of the volatiles and the concentrate is dissolved in dry dichloromethane (10 mL). Triethylphosphite (0.96 mL, 5.61 mmol, 1.50 eq) is added drop-wise to the solution of the intermediate acyl chloride in dichloromethane at room temperature.[14] The completion of the reaction (*ca.* 1 hour) is determined by the ^{31}P NMR analysis of the crude reaction mixture following disappearance of the triethylphosphite peak at ~130 ppm and appearance of a new peak at -3 ppm corresponding to the oxophosphonate product. Afterwards the reaction mixture is concentrated under reduced pressure. Flash chromatography on silica gel (ethyl acetate/hexanes 1:1) affords the desired product (±)-**25** as a colorless viscous oil (1.49 g, 89%).



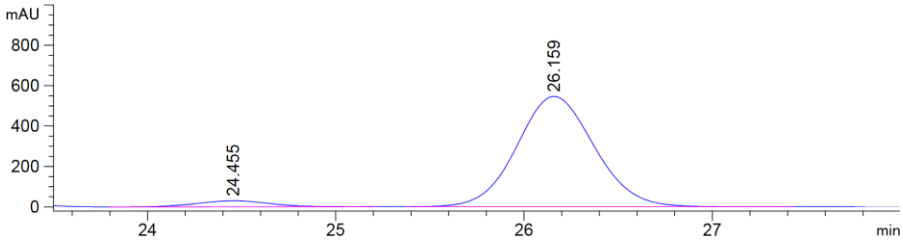
Synthesis of alcohol (*S*)-26:[11] This transformation is carried out with some modifications of the original reported procedure[15] by Yamamoto and coworkers as follows: To a solution of acylphosphonate (*S*)-**25** (60 mg, 0.2 mmol, 1 eq) in THF (2 mL) is added lithium aluminum hydride (30 mg, 0.8 mmol, 4 eq) at 0°C. The resultant mixture is stirred for 2 hours at room temperature. The disappearance of the peak corresponding to oxo-phosphonate in crude ^{31}P NMR (~ -3 ppm) is indicative of reaction completion. The reaction mixture is cooled down to 0°C and is quenched with the addition of 2M HCl till pH 2. The resultant mixture is extracted with diethyl ether (3 mL x 4), the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum to yield the desired product (*S*)-**26** (29 mg, 89%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:8) R_f = 0.5; $[\alpha]_D^{20}$ = +8.8° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (4H, m, aryl), 7.28-7.22 (1H, m, aryl), 3.75 (1H, d, *J* = 10.8 Hz, a), 3.57 (1H, d, *J* = 10.8 Hz, a), 1.89-1.80 (1H, m, d), 1.64-1.55 (1H, m, d), 1.37 (3H, s, c), 1.29 (1H, br s, OH), 0.75 (3H, t, *J* = 7.4 Hz, e) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.78 (aryl), 128.62 (aryl), 127.04 (aryl), 126.30 (aryl), 72.59 (a), 43.89 (b), 31.07 (d), 21.14 (c), 8.42 (e) ppm; IR (neat) 3300 (O-H), 2920 (aromatic C-H), 2851 (aliphatic C-H), 1495 (aromatic C=C), 1463 (aromatic C=C), 1034, 756 cm^{-1}. The above alcohol (*S*)-**26** was derivatized using (*S*)-(−)-α-methoxy-α-(trifluoromethyl) phenylacetyl chloride to obtain the corresponding ester, the ^{19}F-NMR of which yielded a dr of 97:3 (See spectra in SI-2). Enantiomer ratio also determined by chiral HPLC analysis: 95:5. HPLC conditions:[11] Stationary phase = CHIRALPAK IB; Mobile Phase = 99.5:0.5 Hexanes:Isopropanol; Flow rate = 0.5 mL/min; HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) Racemate:

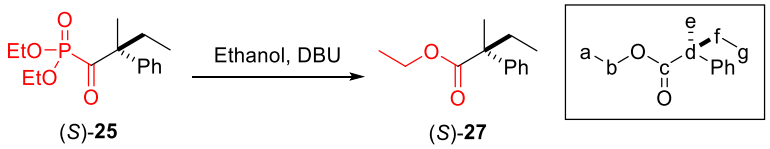


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	24.437	VB	0.4381	8230.35547	50.3273
2	26.221	BB	0.4642	8123.31299	49.6727

(b) R:S = 5:95. CAHB of **5a** with (*R*,*R*)-**T2**, followed by transformations to yield (*S*)-**26**.

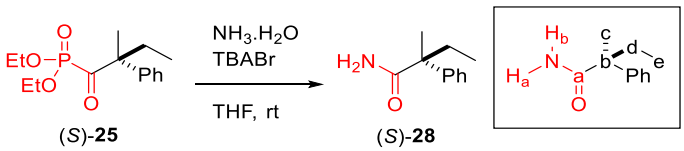


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	24.455	VB	0.4110	781.75848	4.7521
2	26.159	BB	0.4440	1.56692e4	95.2479



(*S*)-**25** (*S*)-**27**

Synthesis of ethyl ester (*S*)-27: This transformation is carried out with some modifications of the original procedure[14] reported by Yamamoto and coworkers as follows: To a solution of acylphosphonate (*S*)-**25** (60 mg, 0.2 mmol, 1 eq) in anhydrous ethanol (1 mL), DBU (30 µL, 0.2 mmol, 1 eq) is added at room temperature. The completion of the reaction (*ca.* 30 min) is indicated by the disappearance of the oxophosphonate peak at -3 ppm and appearance of the diethylphosphite peak at ~8 ppm. The reaction mixture is concentrated under reduced pressure and is dissolved in 10% ethyl acetate in hexanes (2 mL) and is filtered over a small plug of silica gel. The plug is subsequently washed with 2 more portions of the eluent (2 mL each time) and the combined filtrates are concentrated under reduced pressure to afford the ethyl ester (*S*)-**27** as a colorless oil (39 mg, 95%): TLC analysis (ethyl acetate/hexanes 1:20) R_f = 0.6; $[\alpha]_D^{20}$ = +6.1° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (5H, m, aryl), 4.16 (2H, q, *J* = 7.2 Hz, b), 2.18-2.09 (1H, m, f), 2.02-1.93 (1H, m, f), 1.55 (3H, s, e), 1.21 (3H, t, *J* = 7.2 Hz, a), 0.86 (3H, t, *J* = 7.2 Hz, g) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.43 (c), 144.24 (aryl), 128.45 (aryl), 126.70 (aryl), 126.23 (aryl), 60.83 (b), 50.75 (d), 31.98 (f), 22.42 (e), 14.28 (a), 9.33 (g) ppm; IR (neat) 2975 (aromatic C-H), 2938 (aliphatic C-H), 1724 (C=O), 1496 (aromatic C=C), 1446 (aromatic C=C), 1031 (C-O) cm^{-1}. Ester (*S*)-**27** is transformed to the carboxylic acid (*S*)-**29** (*vide infra*) via hydrolysis using LiOH in H_2O. The formed carboxylic acid was derivatized to the L-phenyl-alanine ethyl ester derivative and the dr of the same was found to be 96:4 via ^{1}H NMR analysis. Therefore, er of ethyl ester (*S*)-**27** = 96:4.

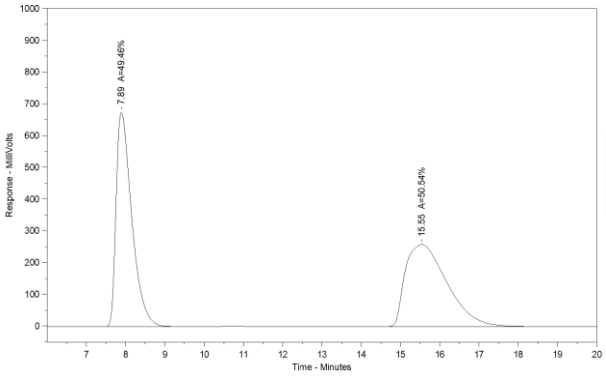


(*S*)-**25** (*S*)-**28**

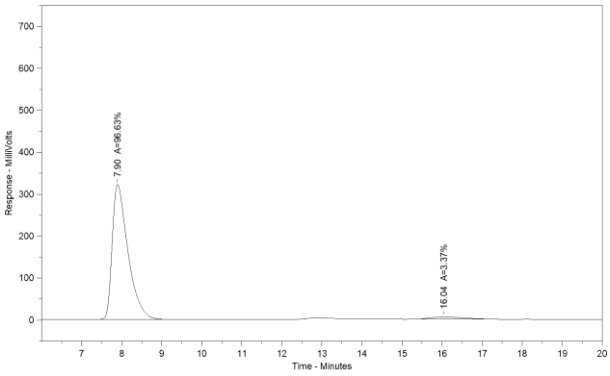
Synthesis of acetamide (*S*)-28:[16] This transformation is carried out with some modifications of the original reported procedure[17] by Liu and Feng as follows: To a solution of acylphosphonate (*S*)-**25** (45 mg, 0.15 mmol, 1 eq) in THF (1 mL) is added NH_3 solution in H_2O (32%, 3 mL) under

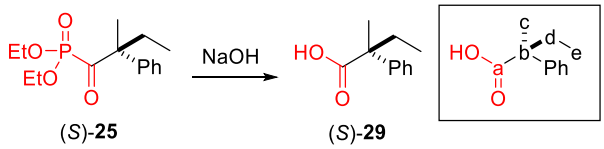
stirring. To the resultant mixture is added tetrabutylammonium bromide (TBABr; 4.8 mg, 15 μmol, 0.1 eq) and the reaction mixture is stirred at room temperature for 9 hours. Afterwards, the mixture is subjected to high vacuum to get rid of ammonia and the resultant mixture is extracted with ethyl acetate (5 mL x 3). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. Flash chromatography over silica gel (ethyl acetate/hexanes 1:1) affords the desired product (*S*)-**28** (23 mg, 85%) as colorless waxy solid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; $[\alpha]_D^{20}$ = +14° (*c* = 1.0, C_6H_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (5H, m, aryl), 6.14 (1H, br s, NH_a or NH_b), 5.25 (1H, br s, NH_a or NH_b), 2.11-1.97 (2H, m, d), 1.53 (3H, s, c), 0.82 (3H, t, *J* = 7.4 Hz, e) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 180.06 (a), 144.07 (aryl), 128.73 (aryl), 127.03 (aryl), 126.90 (aryl), 50.83 (b), 31.57 (d), 23.19 (c), 8.94 (e) ppm; IR (neat) 3400 (N-H), 3203 (N-H), 2982 (aromatic C-H), 2969 (aliphatic C-H), 1648 (C=O), 1494 (aromatic C=C), 1459 (aromatic C=C), 1363, 694 cm^{-1}. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile Phase = 60:40 Hexanes:Isopropanol; Flow rate = 1.25 mL/min; HPLC UV detector λ = 210 nm, rt. HPLC traces:

(a) Racemate



(b) R:S = 3:97. CAHB of **5a** with (*R*,*R*)-**T2**, followed by transformations to yield **28**.

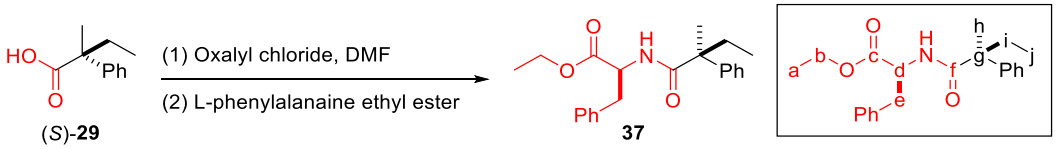




(*S*)-**25** (*S*)-**29**

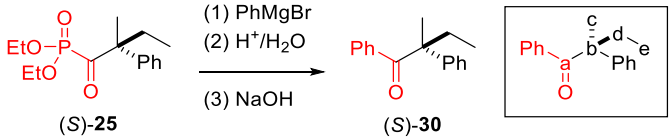
Synthesis of carboxylic acid (*S*)-(+)-29:[18] This transformation is carried out with some modifications of the original procedure[14] reported by Yamamoto and coworkers as follows: To a solution of acylphosphonate (*S*)-**25** (60 mg, 0.2 mmol, 1 eq) in tetrahydrofuran (0.5 mL), 2M aqueous NaOH solution (0.5 mL, 1 mmol, 5 eq.) is added and the resultant biphasic mixture is stirred for 3 hours at room temperature. The completion of the reaction is indicated by the disappearance of the oxophosphonate peak at -3 ppm and appearance of the diethylphosphite peak at ~8 ppm. Afterwards, the reaction mixture is acidified to pH 1 using 2N HCl and the resultant mixture is extracted with dichloromethane (10 mL x 3). The combined organic extracts are washed with brine (5 mL), dried over Na_2SO_4 and concentrated in vacuum to afford pure carboxylic acid (*S*)-**29** (32.5 mg, 91%): TLC analysis (ethyl acetate/hexanes 2:8) R_f = 0.5; $[\alpha]_D^{20}$ = +10.2° (*c* = 1.0,

$CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 12.37 (1H, br s, COOH), 7.34-7.20 (5H, m, aryl), 2.03-1.84 (2H, m, d), 1.43 (3H, s, c), 0.78 (3H, t, *J* = 7.4 Hz, e) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.15 (COOH), 144.29 (aryl), 126.41 (aryl), 126.02 (aryl), 49.90 (b), 31.37 (d), 22.16 (c), 9.23 (e) ppm; IR (neat) 3200 (br, O-H), 2976 (aromatic C-H), 2941 (aliphatic C-H), 1690 (C=O), 1495 (aromatic C=C), 1445 (aromatic C=C), 1155 (C-O) cm^{-1}. The above carboxylic acid, (*S*)-**29** is transformed into the amino acid derivative **37** and the dr (96:4) is determined via ^1H NMR analysis. Therefore, er of the carboxylic acid (*S*)-**29** = 96:4.



(*S*)-**29** **37**

Synthesis of the amino acid derivative 37: To a stirred solution of the carboxylic acid (*S*)-**29** (36 mg, 0.2 mmol, 1 eq) in dry dichloromethane (2 mL), oxalyl chloride (34 µL, 0.4 mmol, 2 eq) is added followed by a drop of dry DMF at 0°C. The mixture is allowed to warm up to room temperature and stirred for a total of 2 hours. Afterwards, the mixture is concentrated under high vacuum and the resultant residue is dissolved in dry dichloromethane (1 mL). A solution of L-phenylalanine ethyl ester (77 mg, 0.4 mmol, 2 eq) in dry dichloromethane (1 mL) is added drop-wise to the mixture mixture. Following that, triethylamine (70 µL, 0.5 mmol, 2.5 eq) is added and the resultant mixture is stirred for 2 hours at room temperature. The reaction mixture is concentrated in high vacuum and flash chromatography on silica gel (ethyl acetate/hexanes 1:9) results in the pure product **37** as a sticky waxy liquid (64 mg, 90%): TLC analysis (ethyl acetate/hexanes 1:9) R_f = 0.5; $[\alpha]_D^{20}$ = +32° (*c* = 1.0, $CHCl_3$); ^1H NMR (700 MHz, $CDCl_3$) δ 7.36-7.18 (8H, m, aryl), 6.89-6.86 (2H, m, aryl), 5.58 (1H, t, *J* = 9.0 Hz, NH), 4.86-4.82 (1H, m, d), 4.13 (2H, q, *J* = 7.2 Hz, b), 3.03-2.96 (2H, m, e), 2.05-1.99 (2H, m, i), 1.50 (0.12H, s, h (minor diastereomer, 4%)), 1.46 (2.88H, s, h (major diastereomer, 96%)), 1.23 (3H, t, *J* = 7.2 Hz, a), 0.81 (2.89H, t, *J* = 7.2 Hz, j (major diastereomer, 96%)), 0.70 (0.11H, t, *J* = 7.2 Hz, j (minor diastereomer, 4%)) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 176.56 (f), 171.65 (c), 143.73 (aryl), 136.04 (aryl), 129.34 (aryl), 128.83 (aryl), 128.66 (aryl), 127.11 (aryl), 61.55 (b), 53.06 (d), 50.92 (g), 37.96 (e), 31.42 (i), 23.20 (h), 14.29 (a), 8.93 (j) ppm; IR (neat) 3359 (amide N-H), 2973 (aromatic C-H), 2879 (aliphatic C-H), 1735 (ester C=O), 1660 (amide C=O), 1495 (aromatic C=C), 1445 (aromatic C=C) cm^{-1}. The ^1H NMR analysis provided the dr to be 96:4.



(*S*)-**25** (*S*)-**30**

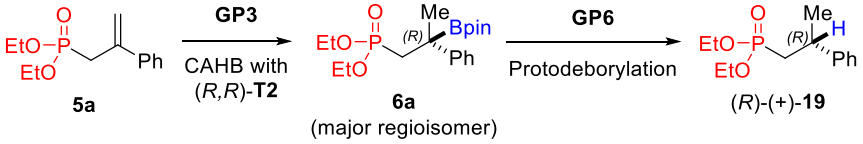
Synthesis of the aryl ketone (*S*)-30:[19] This transformation is carried out with some modifications of the original reported procedure[20] by Maeda et. al. as follows: To a suspension of magnesium turnings (11 mg, 0.46 mmol) in dry THF (1.5 mL) under a nitrogen atmosphere was added bromobenzene (47 µL, 0.45 mmol, 3 eq) and the resultant mixture was refluxed for a total of 2 hours until the solution turned brown and all of the magnesium dissolved. The resultant Grignard reagent is cooled down to room temperature and then to -78°C using a dry ice-acetone bath. A

solution of acylphosphonate (*S*)-**25** (45 mg, 0.15 mmol, 1 eq) in dry THF (0.75 mL) is added to the reaction mixture and the resultant mixture is stirred at -78^{o}C for 15 minutes. Following this, the reaction mixture is acidified to pH 1 using 1N HCl and the resultant mixture is extracted with dichloromethane (25 mL x 3). The combined organic extracts are dried over Na_2SO_4 and concentrated in vacuum. The resultant residue is dissolved in THF (1 mL) and a 2N solution of NaOH (0.5 mL) is added drop-wise. The resultant mixture is stirred for 1 hour. Afterwards, the mixture is extracted with diethyl ether (10 mL x 3) and the combined organics were washed with brine, dried over Na_2SO_4 and concentrated in vacuum to afford pure phenyl ketone (*S*)-**30** (28 mg, 78%): TLC analysis (ethyl acetate/hexanes 1:49) R_f = 0.5; $[\alpha]_D^{20}$ = +37^{o} (*c* = 1.0, C_6H_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (10H, m, aryl), 2.24-2.05 (2H, m, d), 1.58 (3H, s, c), 0.77 (3H, t, *J* = 7.4 Hz, e) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 204.00 (a), 144.56 (aryl), 137.15 (aryl), 131.72 (aryl), 129.63 (aryl), 129.08 (aryl), 128.10 (aryl), 126.95 (aryl), 126.48 (aryl), 55.16 (b), 32.27 (d), 23.92 (c), 8.83 (e) ppm; IR (neat) 3059 (aromatic C-H), 2971 (aliphatic C-H), 1674 (C=O), 1495 (aromatic C=C), 1445 (aromatic C=C), 1232, 907 cm^{-1}.

(9) Absolute configuration assignments

9.1 CAHB of conjugated methylidene substrate 5a

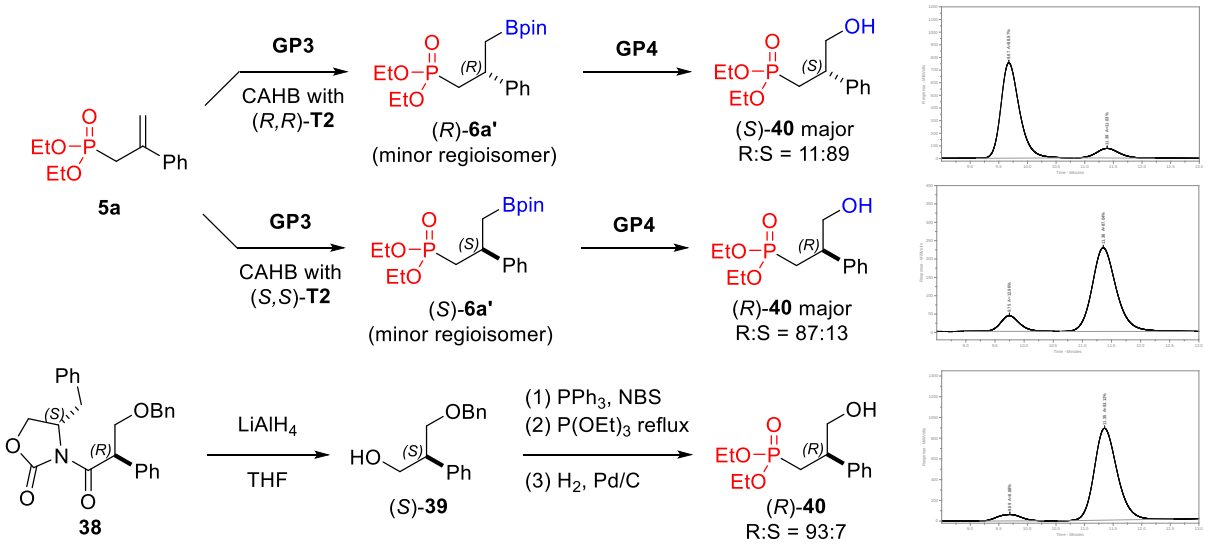
9.1.1 Absolute configuration assignment of the major regioisomer: tertiary boronic ester 6a:



The configurations of all other chiral tertiary benzylic boronic esters derived from conjugated methylidene substrates are assigned based on the following. CAHB of phenyl-substituted methylidene substrate **5a** with (*R,R*)-**T2** results in the formation of chiral tertiary benzylic boronic ester **6a** as the major product. The latter is protodeboronated to **19** (see **GP6**) using conditions reported by Aggarwal[8] giving the corresponding chiral reduced product whose configuration is assigned *"R"* based on the positive value of its optical rotation for this previously reported compound.[21] Since protodeboronation of chiral tertiary benzylic boronic esters proceeds with retention of stereochemistry, the chiral boronic ester **6a** derived from CAHB with (*R,R*)-**T2** is assigned as *"R"*, the result of B-H addition to the *top-face* of the alkene in the perspective drawn.

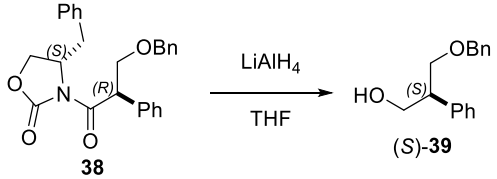
The assigned absolute configuration is further supported by conversion of (*R*)-**6a** to (*S*)-**21** setting the all-carbon quaternary carbon stereocenter with retention of stereochemistry; the details are described above. [Note: Aggarwal[11] has shown that chiral tertiary boronic esters undergo vinylation reaction with stereoretention]. Hydrogenation to (*S*)-**22** sets the stage for conversions to the known alcohol (*S*)-(+)-**26**, carboxylic acid (*S*)-(+)-**29** and ketone (*S*)-(+)-**30**, each of which gives the expected (+) sign of optical rotation. However, the literature indicates that aldehyde (*S*)-**24** and amide (*S*)-**28** should have the (-) sign of rotation which we believe is incorrect. We find (+)-rotations for each, and furthermore, $NaBH_4$ reduction of our (+)-**24** affords (*S*)-(+)-**26**.

9.1.2 Absolute configuration assignment of minor regioisomer: primary boronic ester 6a':



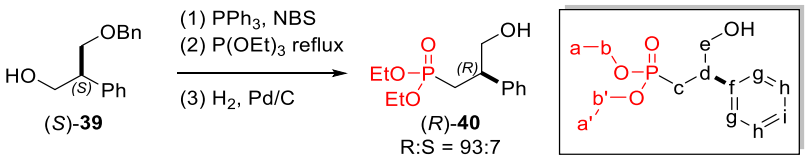
CAHB of the conjugated methylidene substrate **5a** also gives a small amount of the chiral primary boronic ester **6a'** as a minor product. For mechanistic interest and to compare to other directed-CAHBs, we proved the stereochemistry of the major enantiomer of **6a'** that is formed. Oxidation of **6a'** resulted in the formation of chiral γ-hydroxy phosphonate **40**; (*R*,*R*)-**T2** gives the S-isomer and (*S*,*S*)-**T2** gives the R-isomer. To establish those assignments, (*R*)-**40** was synthesized using the Evans' chiral auxillary for asymmetric alkylation to establish the stereochemistry. The oxazolidinone derivative **38** was prepared according to literature procedure.[22] Reduction of the oxazolidinone derivative **38** using $LiAlH_4$ in THF afforded the chiral alcohol (*S*)-**39**; the negative value of its optical rotation confirms the absolute configuration.[18] Sequential bromination (PPh_3/NBS), Michaelis-Arbuzov rearrangement (**GP1**) and benzyl-ether cleavage (H_2/Pd-C) afforded the enantiopure chiral γ-hydroxy phosphonate (*R*)-**40**. As illustrated above, analysis of the chiral HPLC traces and optical rotations revealed that the chiral γ-hydroxy phosphonate (*R*)-**40** obtained via asymmetric alkylation is the enantiomer of the minor product obtained from CAHB of **5a** using (*R*,*R*)-**T2** followed by oxidation. (*S*)-**40** arises from the B-H addition to the *"top-face"* of the alkene **5a** in the perspective drawn.

Characterization Data:



To a solution of oxazolidinone derivative **38** (623 mg, 1.50 mmol, 1.00 eq) in dry THF (15 mL) at 0°C was added $LiAlH_4$ (230 mg, 6.00 mmol, 4.00 eq) slowly and the resultant mixture was stirred vigorously for 1 hour. Afterwards, the reaction mixture was carefully quenched with the addition

of ethyl acetate (20 mL) and water (2 mL) and the resultant mixture was filtered over a small pad of silica gel and the silica pad was washed with ethyl acetate (20 mL). The combined filtrates were concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexanes 1:3) afforded the alcohol (*S*)-**39** (309 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.5; $[\alpha]_D^{20}$ = -35° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (10H, m), 4.59 (2H, s), 4.07-4.02 (1H, m), 3.93-3.79 (3H, m), 3.28-3.22 (1H, m), 2.47 (1H, br d, *J* = 9.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.77, 138.05, 128.86, 128.69, 128.20, 127.99, 127.87, 127.28, 73.88, 73.66, 66.75, 48.01 ppm; IR (neat) 3396 (O-H), 3028 (sp^2 C-H), 2863 (sp^3 C-H), 1495 (aromatic C=C), 1452 (aromatic C=C), 1363, 1075 (C-O), 1027 (C-O), 735, 696 cm^{-1}.

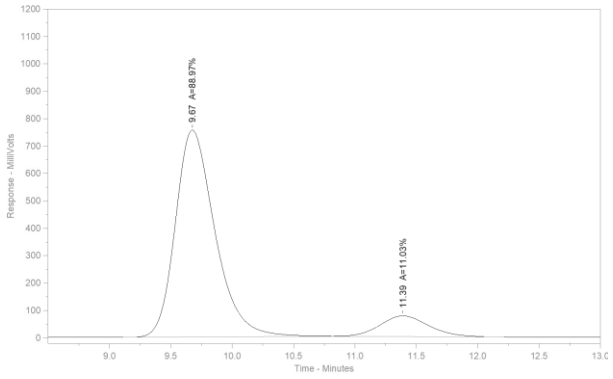


To a solution of the alcohol (*S*)-**39** (242 mg, 1.00 mmol, 1.00 eq) in dry dichloromethane (10 mL) at 0°C was added PPh_3 (393 mg, 1.50 mmol, 1.5 eq) and NBS (267 mg, 1.50 mmol, 1.5 eq). The resultant mixture was stirred for 1 hour when TLC (ethyl acetate/hexanes 1:3) indicated complete consumption of starting material. The solvent was evaporated under reduced pressure and to the residue was added 20% ethyl acetate in hexanes. The resultant mixture was filtered over a small bed of silica gel and the bed was further washed with more 20% ethyl acetate in hexanes (40 mL total). The combined filtrates were concentrated under reduced pressure. The resultant residue was refluxed with triethylphosphite (0.51 mL) under a nitrogen atmosphere for 6 hours. Following the Arbuzov rearrangement (crude NMR analysis: appearance of a phosphonate peak at ~31 ppm), excess triethylphosphite was distilled off in the Kugelrohr. A mixture of the resultant residue and 10% Pd on activated carbon (40 mg, 4.0 mol% Pd-loading) in ethanol (10 mL) is stirred under a hydrogen atmosphere (balloon pressure) for 6 hours. Afterwards, the mixture was filtered and concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/methanol 24:1) afforded the phosphonate (*R*)-**40** as a colorless viscous oil (169 mg, 62% overall): TLC analysis (ethyl acetate/methanol 24:1) R_f = 0.5; $[\alpha]_D^{20}$ = -22° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (5H, m, aryl), 4.06-3.88 (4H, m, b+b'), 3.82-3.73 (2H, m, e), 3.48 (1H, br s, OH), 3.27-3.18 (1H, m, d), 2.38-2.28 (1H, m, c(1H)), 2.14-2.00 (1H, m, c(1H)), 1.23 (3H, t, *J* = 7.0 Hz, a or a'), 1.21 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.34 (d, $^3J_{C\text{-}P}$ = 11 Hz, f), 128.75 (g or h), 127.73 (g or h), 127.10 (i), 67.65 (d, $^3J_{C\text{-}P}$ = 10.25 Hz, e), 61.91 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.79 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 43.12 (d, $^2J_{C\text{-}P}$ = 3.0 Hz, d), 29.36 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.42 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.38 ppm; IR (neat) 3372 (O-H), 2981 (sp^2 C-H), 2906 (sp^3 C-H), 1453 (aromatic C=C), 1391 (aromatic C=C), 1222 (P=O), 1051 (C-O), 1019 (C-O), 957 (P-O), 699 cm^{-1}.

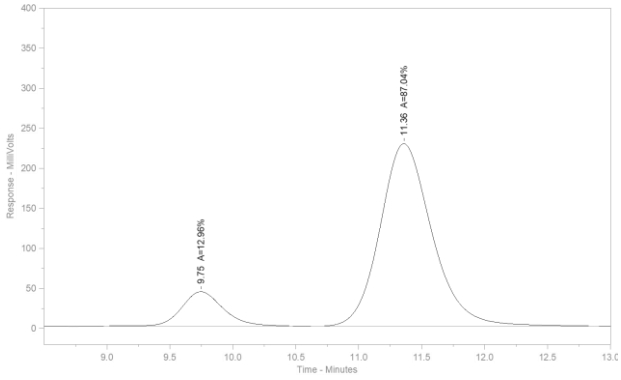
Obtaining γ-hydroxyphosphonate 40 from alkene substrate 5a: Substrate **5a** (1.02 g, 4.00 mmol) was subjected to CAHB according to **GP3**. After purification of the major product (tertiary boronic ester **6a**), the minor regioisomer **6a'** and the reduced product **6a''** were flushed out of the silica packed column with methanol, the mixture is concentrated under reduced pressure and is subjected to oxidation following **GP5**. Afterwards, the mixture was extracted with ethyl acetate (20 mL x 5) and the combined extracts were concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/methanol 24:1) afforded the hydroxy phosphonate **40** as a colorless viscous oil (109 mg, 10% overall from the hydroboration/oxidation sequence).

Enantiomer ratio is determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AD; Mobile Phase = 90:10 Hexanes:Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

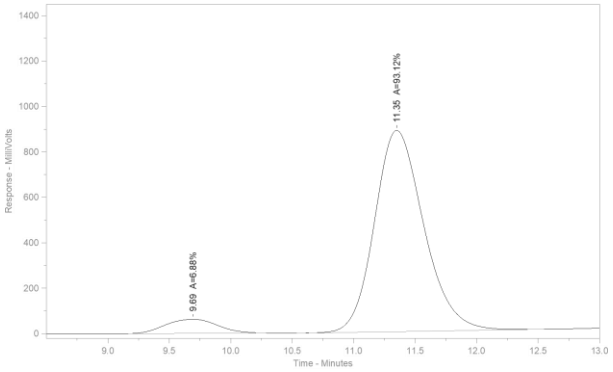
(a) R:S = 11:89, CAHB of **5a** with (*R*,*R*)-**T2** to form (*R*)-**6a'**, then oxidation to yield **40**.



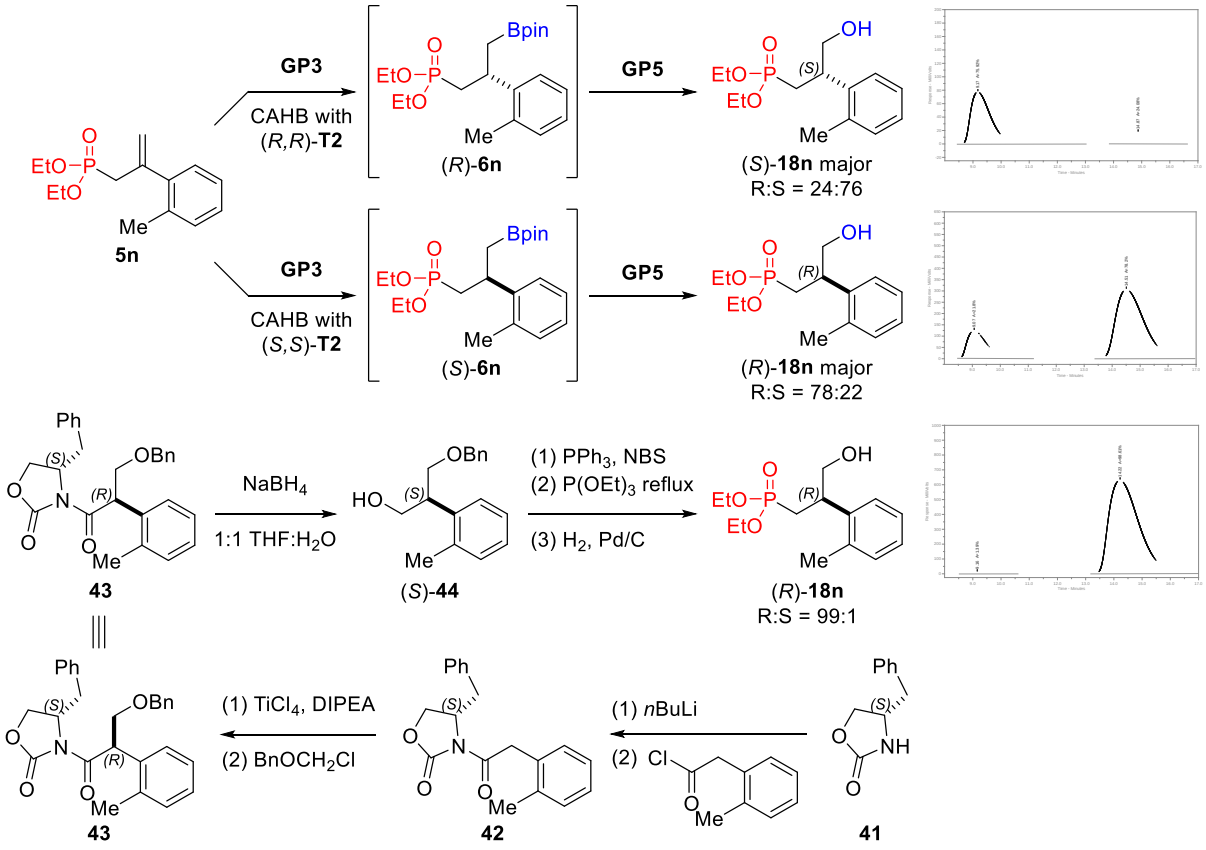
(b) R:S = 87:13, CAHB of **5a** with (*S*,*S*)-**T2** to form (*S*)-**6a'**, then oxidation to yield **40**.



(c) R:S = 93:7, **40** (enriched with *"R"* enantiomer) obtained via chiral auxillary sequence.

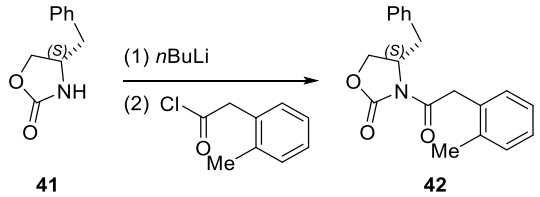


9.2 CAHB of conjugated methylidene substrate 5n bearing an *ortho*-methylphenyl group:



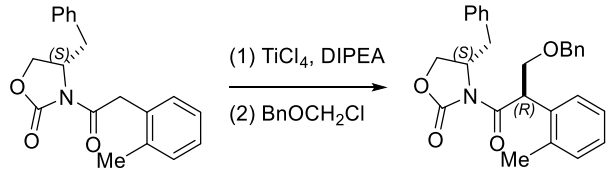
CAHB of conjugated methylidene substrate **5n** bearing an *ortho*-methyl phenyl group at the beta position resulted in an inseparable mixture of primary boronic ester **6n** (major product) along with the reduction side product. Oxidation of this CAHB mixture after partial purification (ref. **GP5**) allowed for the separation of the chiral γ-hydroxy phosphonate **18n** from other products. (*R*)-**18n** was independently synthesized via asymmetric alkylation using the Evans' chiral auxiliary to set the required stereochemistry. The chiral oxazolidinone auxillary (*S*)-**41** (derived from L-phenylalanine) was treated with *n*BuLi, followed by 2-(o-tolyl)acetyl chloride to obtain intermediate **42**. Alkylation of **42** with benzyl-chloromethyl ether under standard conditions afforded the oxazolidinone derivative **43**. Reduction of the oxazolidinone derivative **43** using $NaBH_4$ resulted in the chiral alcohol (*S*)-**44**. Sequential bromination (PPh_3/NBS), Michaelis-Arbuzov Rearrangement ($P(OEt)_3$ reflux) and benzyl-ether cleavage (H_2/Pd-C) afforded the enantiopure chiral primary alcohol (*R*)-**18n**. Chiral HPLC analysis and optical rotation measurements show that (*R*)-**18n** obtained via asymmetric synthesis opposite the major enantiomer obtained via CAHB of **5n** using (*R,R*)-**T2** followed by oxidation. The latter (i.e., (*S*)-**18n**) arise B-H addition to the *"top-face"* of the alkene **5n** in the perspective drawn. The absolute configuration of chiral primary boronic ester derived from *ortho*-methoxy substituted substrate **5o** is assigned based on analogy.

Characterization Data:



41 **42**

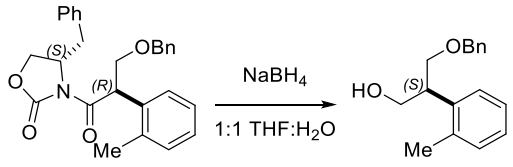
To a solution of the oxazolidinone auxillary (*S*)-**41** (1.77 g, 10.0 mmol, 1 eq) in THF (20 mL) at -78ºC was added *n*BuLi (2.5M solution in hexanes; 4.0 mL, 10 mmol, 1.0 eq) dropwise. The resultant mixture was stirred for 30 minutes, following which, a solution of 2-(o-tolyl)acetyl chloride (1.68 g, 10.0 mmol, 1.00 mmol) in THF (10 mL) was added dropwise. The resultant mixture was stirred for 1 hour at -78ºC, warmed up to room temperature and stirred for an additional 1 hour and then quenched with the addition of saturated aqueous NH_4Cl. The resultant mixture was extracted with ethyl acetate (20 mL x 3) and the combined organics were washed with brine, dried over anhydrous sodium sulfate and concentrated in vacuum. Flash chromatography on silica gel (dichloromethane/ethyl-acetate/hexanes 1:2:17) afforded the desired oxazolidinone derivative **42** as a light yellow solid (2.56 g, 83%): TLC analysis (ethyl acetate/hexanes 1:4) R_f = 0.5; $[\alpha]_D^{20}$ = +68º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (9H, m), 4.76-4.70 (1H, m), 4.42-4.22 (4H, m), 3.36 (1H, dd, *J* = 13.0, 3.0 Hz), 2.82 (1H, dd, *J* = 13.0, 10.0 Hz), 2.35 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.14, 153.75, 137.28, 135.38, 132.55, 130.54, 130.37, 129.57, 129.13, 127.71, 127.53, 126.29, 66.47, 55.62, 40.11, 38.04, 19.81 ppm; IR (neat) 3060 (sp^2 C-H), 2921 (sp^3 C-H), 1771 (C=O), 1697 (C=O), 1387, 1357, 1249, 1210, 1104, 741, 695 cm^{-1}.



42 **43**

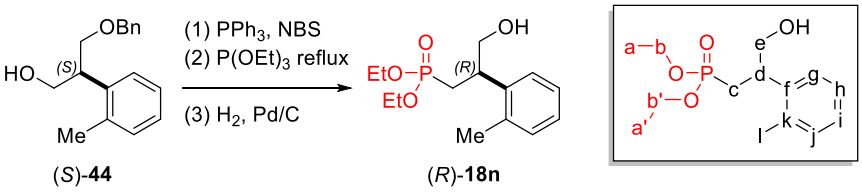
To a solution of the oxazolidinone derivative **42** (1.24 g, 4.00 mmol, 1.00 mmol) in dry dichloromethane (8 mL) was added $TiCl_4$ (1M solution in dichloromethane; 6 mL, 1.5 eq) dropwise at 0ºC. To the resultant solution was added diisopropylethylamine (1.4 mL, 8.0 mmol, 2.0 eq) and the dark blue solution was stirred for 1 hour at 0ºC. Following this, benzyl chloromethyl ether (1.14 mL, 8.00 mmol, 2.00 eq) was added dropwise and the resultant mixture was stirred at room temperature for 12 hours. (Note: Commercial benzylchloromethyl ether is contaminated with ~25% benzyl chloride, which can be removed via Kugelrohr distillation at 2 mmHg vacuum at 60ºC. After distillation of benzyl chloride, about 90% clean benzyl chloromethyl ether is obtained which is contaminated with ~10% of formaldehyde dibenzyl acetal: this was used for synthesis). Afterwards, saturated aqueous NH_4Cl was added to quench the reaction and the resultant mixture was extracted with ethyl acetate (25 mL x 3). The combined organics were washed with brine, dried over sodium sulfate and concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexanes 15:85) afforded **43** as a viscous light-yellow liquid (1.39 g, 81%):

TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.6; $[\alpha]_D^{20}$ = +220° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.14 (14 H, m), 5.61-5.57 (1H, m), 4.74-4.59 (3H, m), 4.19-4.09 (3H, m), 3.59-3.55 (1H, m), 3.37-3.33 (1H, m), 2.96-2.90 (1H, m), 2.49 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.72, 152.97, 138.39, 137.95, 135.41, 133.43, 131.14, 129.78, 129.12, 128.57, 127.86, 127.82, 127.51, 126.70, 126.29, 73.46, 71.65, 65.92, 55.82, 46.76, 37.91, 19.64 ppm; IR (neat) 3063 (sp^2 C-H), 2941 (sp^3 C-H), 1769 (C=O), 1691 (C=O), 1391, 1357, 1212, 1099, 743, 6951 cm^{-1}.



43 (*S*)-**44**

The oxazolidinone derivative **43** was cleaved to afford the chiral alcohol (*S*)-**44** according to literature procedure as follows: To a solution of oxazolidinone **43** (859 mg, 2.00 mmol, 1.00 eq) in 1:1 THF: H_2O mixture (40 mL) at 0°C was added $NaBH_4$ (302 mg, 8.00 mmol, 4.00 eq) and the resultant mixture was stirred vigorously for 9 hours. Afterwards, the reaction mixture was cooled down to 0°C and was quenched with saturated aqueous NH_4Cl (Caution: careful addition is required, quenching is exothermic). The resultant mixture was extracted with ethyl acetate (3 x 30 mL). The combined organics were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/hexanes 1:3) afforded the alcohol (*S*)-**44** as a colorless liquid (456 mg, 89%): TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.5; $[\alpha]_D^{20}$ = -25° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (5H, m), 7.22-7.12 (4H, m), 4.60 (2H, s), 4.08-4.00 (1H, m), 3.92-3.82 (2H, m), 3.76 (1H, dd, *J* = 9.0, 4.5 Hz), 3.57-3.50 (1H, m), 2.62 (1H, br s), 2.40 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.01, 137.76, 136.65, 130.89, 128.71, 128.02, 127.87, 126.99, 126.42, 74.05, 73.69, 66.66, 43.08, 19.87 ppm; IR (neat) 3425 (O-H), 3027 (sp^2 C-H), 2861 (sp^3 C-H), 1493, 1453, 1362, 1093, 1067, 1027, 727, 696 cm^{-1}.



(*S*)-**44** (*R*)-**18n**

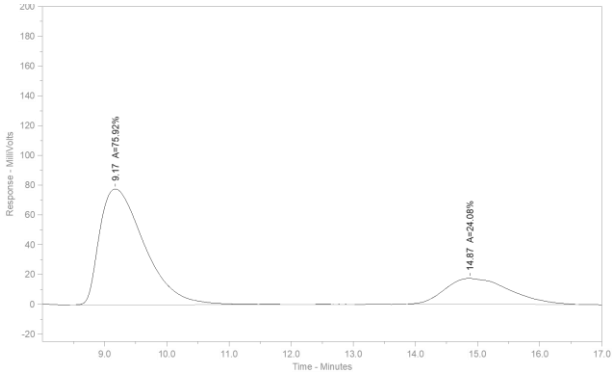
To a solution of the alcohol (*S*)-**44** (256 mg, 1.00 mmol, 1.00 eq) in dry dichloromethane (10 mL) at 0°C was added PPh_3 (393 mg, 1.50 mmol, 1.5 eq) and NBS (267 mg, 1.50 mmol, 1.5 eq). The resultant mixture was stirred for 1 hour when TLC (ethyl acetate/hexanes 1:3) indicated complete consumption of starting material. The solvent was evaporated under reduced pressure and to the residue was added 20% ethyl acetate in hexanes. The resultant mixture was filtered over a small bed of silica gel and the bed was further washed with more 20% ethyl acetate in hexanes (40 mL total). The combined filtrates were concentrated under reduced pressure. The resultant residue was refluxed with triethylphosphite (0.51 mL) under a nitrogen atmosphere for 6 hours. Following the

Arbuzov rearrangement (crude NMR analysis: appearance of a phosphonate peak at ~31 ppm), excess triethylphosphite was distilled off in the Kugelrohr. A mixture of the resultant residue and 10% Pd on activated carbon (80 mg, 8.0 mol% Pd-loading) in ethanol (10 mL) is stirred under a hydrogen atmosphere (balloon pressure) for 12 hours. Afterwards, the mixture was filtered and concentrated under reduced pressure. Flash chromatography over silica gel (ethyl acetate/methanol 49:1) afforded the phosphonate (*R*)-**18n** as a colorless viscous oil (146 mg, 51% overall): TLC analysis (ethyl acetate/methanol 49:1) R_f = 0.5; $[\alpha]_D^{20}$ = -16.9° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.13 (4H, m, aryl), 4.11-3.97 (4H, m, b+b'), 3.85-3.77 (2H, m, e), 3.60-3.50 (1H, m, d), 2.41 (3H, s, l), 2.29 (1H, ddd, *J* = 18.0, 15.0, 8.5 Hz, c(1H)), 2.09 (1H, ddd, *J* = 19.0, 18.0, 5.5 Hz, c(1H)), 1.28 (3H, t, *J* = 7.0 Hz, a or a'), 1.28 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.79 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, f), 136.13 (k), 130.86 (aryl), 126.92 (aryl), 126.61 (aryl), 126.05 (aryl), 67.63 (d, $^3J_{C\text{-}P}$ = 8.0 Hz, e), 62.11 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 62.01 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 38.00 (d, $^2J_{C\text{-}P}$ = 3.0 Hz, d), 29.94 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 19.85 (l), 16.57 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a'), 16.54 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.90 ppm; IR (neat) 3364 (O-H), 2980 (sp^2 C-H), 2914 (sp^3 C-H), 1456 (aromatic C=C), 1391 (aromatic C=C), 1218 (P=O), 1019 (C-O), 961 (P-O), 757 cm^{-1}. HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1228 *m/z*.

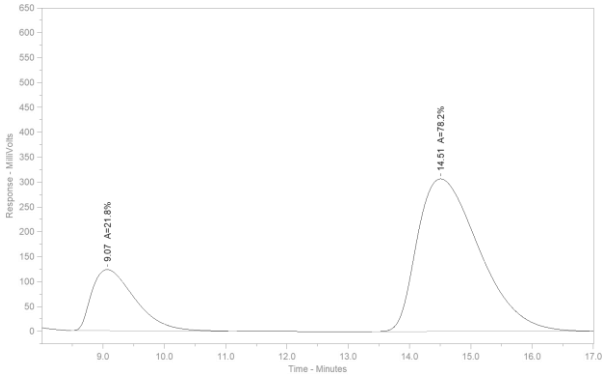
Obtaining γ-hydroxyphosphonate 18n from alkene substrate 5n: Following the general procedure for CAHB (**GP3**), the substrate **5n** (54 mg, 0.2 mmol) yielded a mixture of boronic esters and reduced products that were not separable via silica gel chromatography. The crude CAHB mixture was chromatographed (ethyl acetate/hexanes 3:1) over silica gel to get rid of the non-polar colored complex and the polar metal residues. The crude mixture obtained after this partial purification was subjected to oxidation following **GP5** to obtain the γ-hydroxyphosphonate **18n** (47 mg, 82% overall from the hydroboration/oxidation sequence) as a colorless oil.

Enantiomer ratio is determined by chiral HPLC analysis: Stationary phase = CHIRALPAK AS-H; Mobile Phase = 90:10 Hexanes:Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

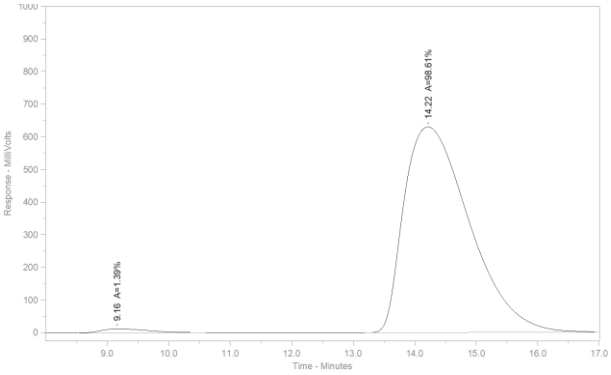
(a) R:S = 24:76, CAHB of **5n** with (*R*,*R*)-**T2**, followed by oxidation to yield (*S*)-**18n**



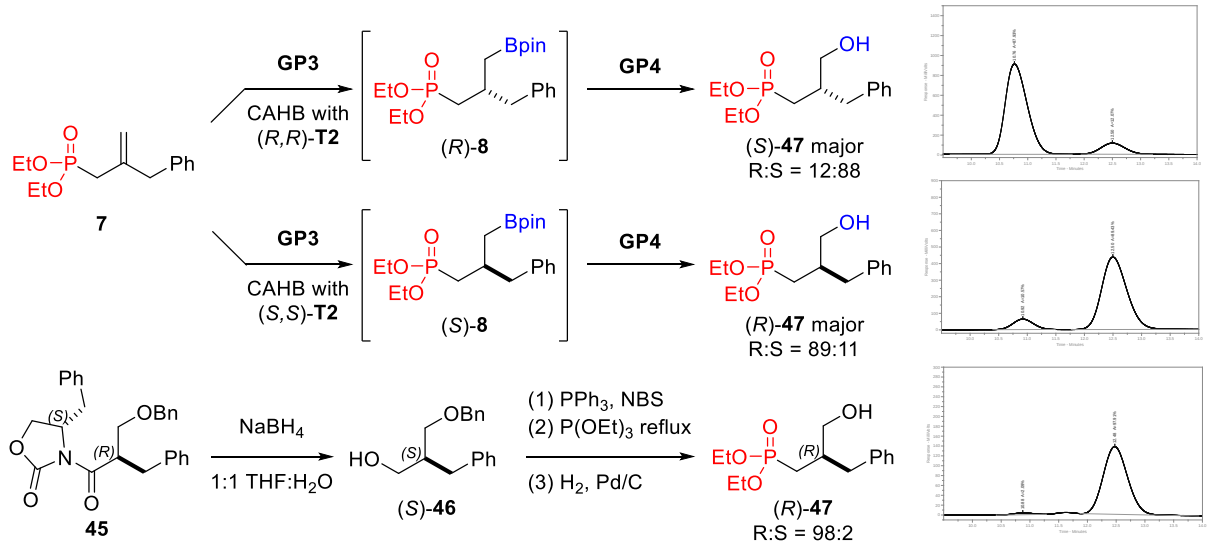
(b) R:S = 78:22, CAHB of **5n** with (*S*,*S*)-**T2**, followed by oxidation to yield (*R*)-**18n**



(c) R:S = 99:1, **18n** (enantioenriched *"R"*) obtained via chiral auxillary sequence.

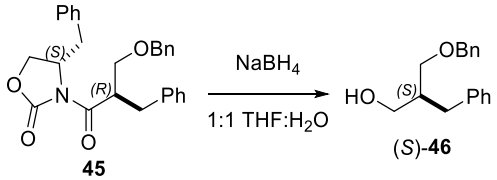


9.3 CAHB of non-conjugated methylidene substrate 7:



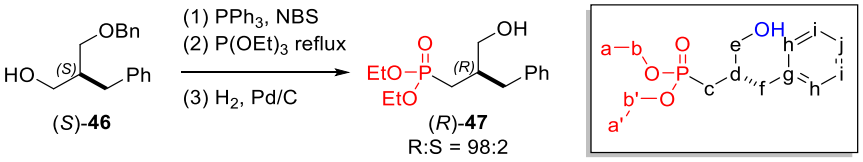
CAHB of the non-conjugated methylidene substrate **7** resulted in an inseparable mixture of primary boronic ester **8** (major product) along with the tertiary boronic ester **9** (minor product) along with some of the reduction product. Oxidation of the mixture after partial purification (ref. **GP5**) allowed for the separation of the chiral γ-hydroxy phosphonate **47** from the other products. (*R*)-**47** was independently synthesized via asymmetric alkylation using the Evans' chiral auxiliary. Oxazolidinone derivative **45** was prepared according to its literature report.[23] Reduction of the oxazolidinone derivative using $NaBH_4$ resulted in the chiral alcohol (*S*)-**46** whose absolute configuration was verified by the observed strong negative optical rotation.[24] Sequential bromination (PPh_3/NBS), Michaelis-Arbuzov rearrangement ($P(OEt)_3$ reflux) and benzyl-ether cleavage (H_2/Pd-C) afforded primary alcohol (*R*)-**47**. Chiral HPLC analysis revealed that the product obtained via asymmetric synthesis is and that of CAHB (using (*S,S*)-**T2**) and oxidation sequence from substrate **7** are enriched with the same configuration (*i.e., "R"*). The alcohol obtained from substrate **7** after CAHB (using (*R,R*)-**T2**) followed by oxidation is enriched with *"S"* configuration, which comes from the precursor boronic ester **8** enriched with the *"R"* configuration: which resulted from the B-H addition to the *"top-face"* of the alkene **7** in the perspective drawn.

Characterization Data:



The oxazolidinone derivative was cleaved to afford the chiral alcohol (*S*)-**46** according to the procedure outlined for the reduction of oxazolidinone derivative **43** in Sec. 9.2: The oxazolidinone

derivative **45** (859 mg, 2.00 mmol, 1.00 eq) afforded the chiral alcohol (*S*)-**46** (471 mg, 92%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.5; $[\alpha]_D^{20}$ = -34.5° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.21 (10H, m), 4.54 (2H, dd, *J* = 18.0, 12.0 Hz), 3.80-3.62 (3H, m), 3.53 (1H, dd, *J* = 9.0, 6.5 Hz), 2.76-2.67 (2H, m), 2.61 (1H, t, *J* = 5.0 Hz), 2.23-2.16 (1H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.15, 138.16, 129.22, 128.62, 128.53, 127.91, 127.81, 126.21, 73.59, 72.86, 65.35, 42.76, 34.64 ppm; IR (neat) 3378 (O-H), 3027 (aromatic C-H), 2857 (aliphatic C-H), 1494 (aromatic C=C), 1453 (aromatic C=C), 1362 (aromatic C=C), 1027 (C-O), 735, 696 cm^{-1}.



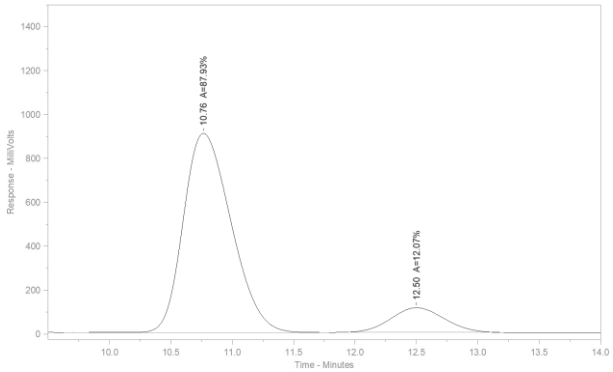
(*S*)-**46** → (*R*)-**47**, R:S = 98:2

The chiral alcohol (*S*)-**46** was transformed to the chiral γ-hydroxyphosphonate (*R*)-**47** according to the procedure detailed out in Sec. 9.1. The chiral alcohol (*S*)-**46** (256 mg, 1.00 mmol) underwent bromination, Arbuzov rearrangement and benzyl ether cleavage to afford (*R*)-**47** (175 mg, 61%) as a colorless viscous liquid: TLC analysis (ethyl acetate/methanol 49:1) R_f = 0.5; $[\alpha]_D^{20}$ = +15° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (5H, m, aryl), 4.16-3.98 (4H, m, b+b'), 3.77 (1H, dd, *J* = 12.0, 4.0 Hz, e(1H)), 3.59 (1H, dd, *J* = 12.0, 6.0 Hz, e(1H)), 2.79 (1H, ddd, *J* = 13.5, 7.0, 2.5 Hz, f(1H)), 2.64 (1H, dd, *J* = 13.0, 8.0 Hz, f(1H)), 2.33-2.20 (1H, m, d), 1.89-1.73 (2H, m, c), 1.33 (3H, t, *J* = 7.0 Hz, a or a'), 1.32 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.86 ppm; IR (neat) 3378 (O-H), 2981 (aromatic C-H), 2909 (aliphatic C-H), 1453 (aromatic C=C), 1391 (aromatic C=C), 1216 (P=O), 1049 (C-O), 1021 (C-O), 959 (P-O), 700 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1230 *m/z*.

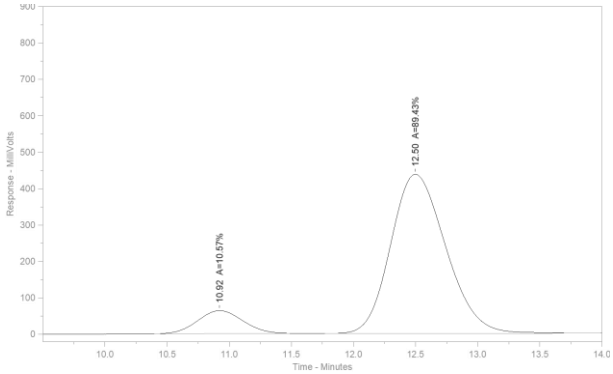
Obtaining γ-hydroxyphosphonate 47 from alkene substrate 7: Following the general procedure for CAHB (**GP3**; 6 h total reaction time), the substrate **7** (54 mg, 0.2 mmol) yielded a mixture of boronic ester regioisomers and reduced products that were not separable via silica gel chromatography. The crude CAHB mixture was chromatographed (ethyl acetate/hexanes 1:1) over silica gel to get rid of the non-polar colored complex and the polar metal residues. The crude mixture obtained after this partial purification was subjected to oxidation following **GP5** to obtain the γ-hydroxyphosphonate **47** (47 mg, 71% overall from the hydroboration/oxidation sequence) as a colorless oil.

Enantiomer ratio is determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC 3 micron; Mobile Phase = 80:20 Hexanes: Isopropanol; Flow rate = 1.25 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

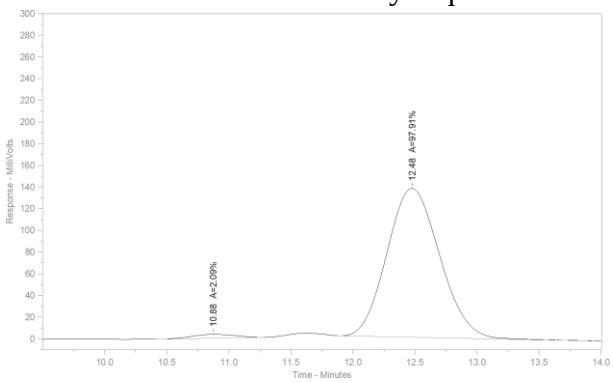
(a) R:S = 12:88, CAHB of **7** with (*R*,*R*)-**T2**, followed by oxidation to yield (*S*)-**47**.



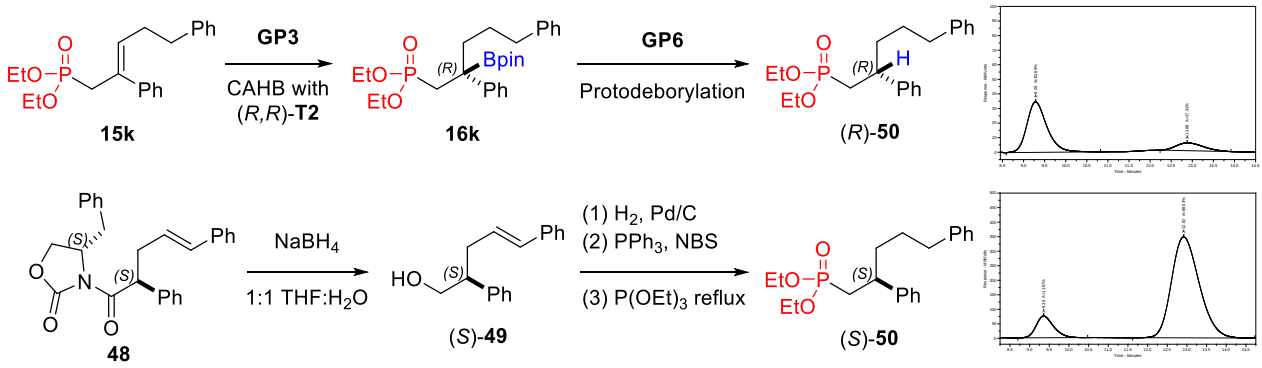
(b) R:S = 89:11, CAHB of **7** with (*S*,*S*)-**T2**, followed by oxidation to yield (*R*)-**47**.



(c) R:S = 98:2, (*R*)-**47** (enantioenriched *"R"*) obtained via chiral auxillary sequence.

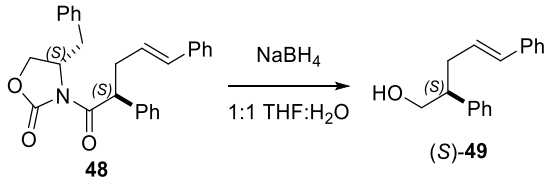


9.4 CAHB of β-aryl trisubstituted alkene substrate 15k:

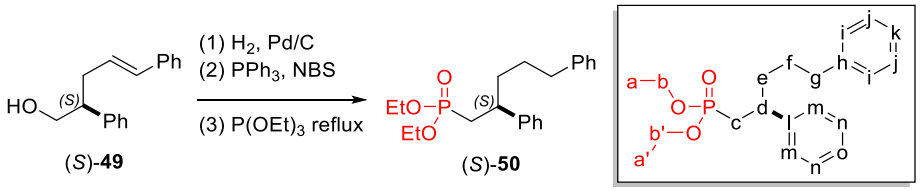


CAHB of the conjugated (β-aryl) trisubstituted substrate **15k** with (*R*,*R*)-**T2** resulted in the formation of chiral tertiary benzylic boronic ester product **16k**. The latter is protodeboronated (**GP6**) using conditions reported by Aggarwal to the corresponding chiral reduced product **50**. The (*S*)-**50** enantiomer of the chiral reduced product was obtained via asymmetric alkylation using the Evans chiral auxiliary. Chiral HPLC analysis establishes that the protodeborylated product from the chiral boronic ester is (*R*)-**50**. Since protodeborylation of chiral boronic esters proceed with retention of configuration, the configuration of the chiral boronic ester **16k** obtained from (*E*)-**15k** using (*R*,*R*)-**T2** is also assigned as *"R"*. The configurations of all other chiral tertiary benzylic boronic esters derived from conjugated (β-aryl) trisubstituted substrates using (*R*,*R*)-**T2** are assigned as *"R"* by analogy.

Characterization data:



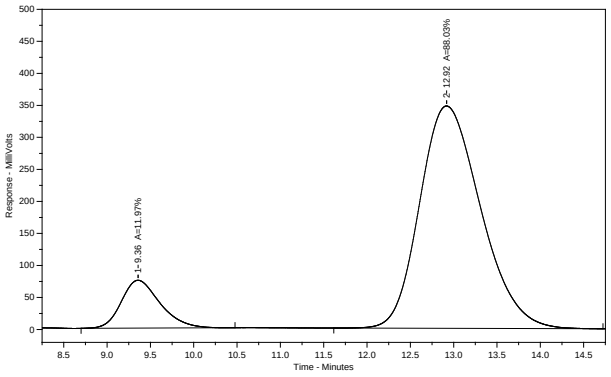
Compound **48** was prepared according to literature procedure.[25] The oxazolidinone derivative was cleaved to afford the chiral alcohol (*S*)-**49** according to the procedure outlined for the reduction of oxazolidinone derivative **43** in Sec. 9.2. The oxazolidinone derivative **48** (410 mg, 1.00 mmol, 1.00 eq) afforded the chiral alcohol (*S*)-**49** (203 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:3) R_f = 0.5; $[\alpha]_D^{20}$ = +41° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.20 (10H, m), 6.44 (1H, d, *J* = 16.0 Hz), 6.20-6.12 (2H, m), 3.90-3.81 (2H, m), 3.03 (1H, quin, *J* = 7.0 Hz), 2.72-2.55 (2H, m), 1.46 (br s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.99, 137.62, 131.79, 128.85, 128.60, 128.21, 128.17, 127.18, 127.02, 126.16, 66.99, 48.70, 35.99 ppm; IR (neat) 3397 (O-H), 3025 (sp^2 C-H), 2926 (sp^3 C-H), 1599 (C=C), 1493 (aromatic C=C), 1451 (aromatic C=C), 1026 (C-O), 964, 746, 692 cm^{-1}.



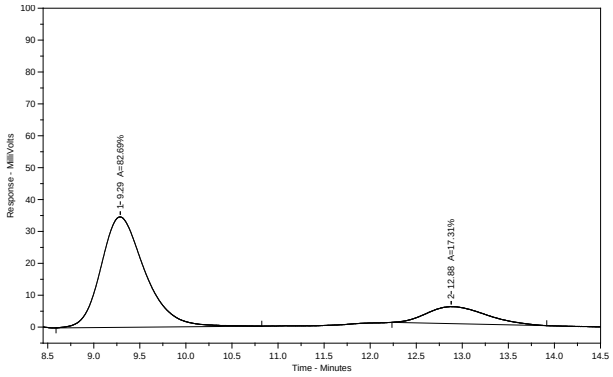
A mixture of (*S*)-**49** (191 mg, 0.80 mmol, 1.00 eq) and 10% Pd over activated carbon (10 mg) in ethanol (10 mL) was stirred under hydrogen atmosphere (balloon pressure) for 6 hours. Following this, the reaction mixture was filtered over a bed of celite to get rid of the insoluble catalyst particles. The celite bed was washed with ethanol (10 mL) and the combined organics were concentrated under reduced pressure. To the resultant residue was added PPh_3 (315 mg, 1.20 mmol, 1.5 eq) and dry dichloromethane (16 mL) and the resultant solution was cooled down to 0^{o}C. NBS (214 mg, 0.12 mmol, 1.5 eq) was added portion wise and the resultant mixture was allowed to warm up to room temperature and stirred for a total of 2 hours. Afterwards, the reaction mixture was concentrated under reduced pressure and 15 mL of 10% ethyl acetate in hexanes was added. The resultant mixture was filtered over a small pad of silica gel to get rid of the insoluble components. The silica pad was washed with 2 more portions of 15 mL of 10% ethyl acetate in hexanes and the combined organics were concentrated under reduced pressure. To the resultant residue in a 10 mL round bottomed flask charged with a stirbar was added triethylphosphite (0.27 mL, 1.6 mmol, 2.0 eq) and the resultant mixture was refluxed vigorously under nitrogen for 1 hour. Afterwards, the volatiles were removed under reduced pressure and the residue was purified by flash chromatography over silica gel (ethyl acetate) to afford the desired chiral phosphonate product (*S*)-**50** (187 mg, 65%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +9.3^o (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.09 (10H, m, aryl), 4.02-3.74 (4H, m, b+b'), 3.11-3.01 (1H, m, d), 2.65-2.50 (2H, m, h), 2.13-2.07 (2H, m, c), 1.93-1.84 (1H, m, e(1H)), 1.73-1.64 (1H, m, e(1H)), 1.57-1.38 (2H, m, f), 1.21 (3H, t, *J* = 7.0 Hz, a or a'), 1.15 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.57 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, l), 142.38 (h), 128.55 (aryl), 128.48 (aryl), 128.36 (aryl), 127.66 (aryl), 126.61 (aryl), 125.79 (aryl), 61.43 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.26 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 40.29 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, d), 37.45 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, e), 35.79 (g), 33.39 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 29.15 (f), 16.43 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a or a'), 16.41 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.18 ppm; IR (neat) 3026 (sp^2 C-H), 2933 (sp^3 C-H), 1495 (aromatic C=C), 1453 (aromatic C=C), 1241 (P=O), 1053 (C-O), 1024 (C-O), 955 (P-O), 697 cm^{-1}. HRMS (EI) calculated for $C_{21}H_{29}O_3P$ = 360.1854, found 360.1843 *m/z*.

Enantiomer ratio is determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 20:80 Hexanes:Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

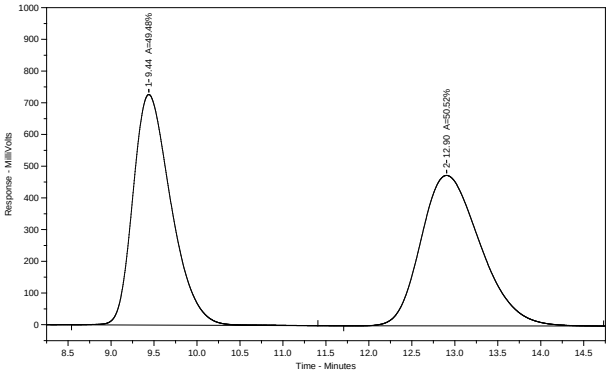
(a) R:S = 12:88, **50** synthesized via chiral auxillary synthesis.



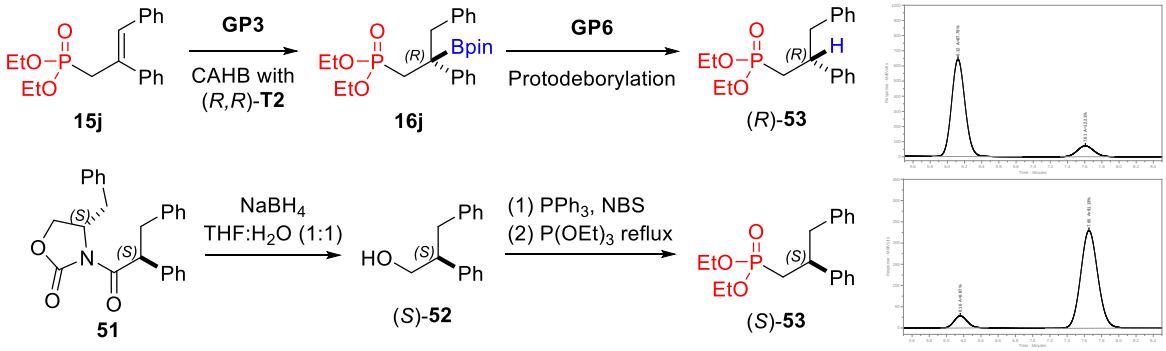
(b) R:S = 83:17, CAHB of **15k** with (*R,R*)-**T2** to form **16k** and then protodeboronation to form **50**.



(c) Racemic mixture of **50** obtained by hydrogenation of (*E*)-**15k** with H_2 over Pd/C.

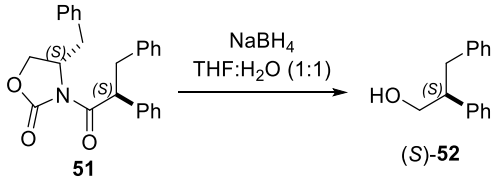


9.5 CAHB of β,γ-diaryl trisubstituted alkene substrate 15j:

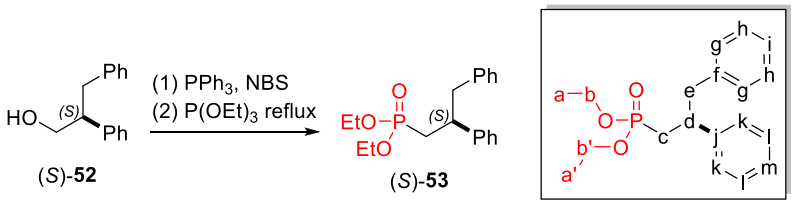


CAHB of the β,γ-diphenyl trisubstituted substrate **15j** with (*R,R*)-**T2** resulted in β-borylation with the formation of chiral tertiary benzylic boronic ester product **16j**. The latter is protodeboronated using **GP6** to afford the corresponding chiral reduced product with the retention of configuration at the chiral carbon.[8] Enantioenriched (*S*)-**53** was obtained via asymmetric alkylation using the Evans chiral auxiliary to give the known chiral alcohol (*S*)-**52.**[26] Chiral HPLC analysis shows that the protodeborylated product obtained from the chiral tertiary boronic ester **16j** is (*R*)-**53**.

Characterization Data:



Compound **51** was prepared as previously reported.[27] The oxazolidinone derivative **51** was cleaved to afford the chiral alcohol (*S*)-**52** according to the procedure outlined for the reduction of oxazolidinone derivative **43** in Sec. 9.2. The oxazolidinone derivative **51** (385 mg, 1.00 mmol, 1.00 eq) afforded the chiral alcohol (*S*)-**52** (174 mg, 82%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:3) $R_f = 0.5$; $[\alpha]_D^{20} = +49^o$ (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.11 (10H, m), 3.86-3.77 (2H, m), 3.16-2.92 (3H, m), 1.34 (1H, t, *J* = 6.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.11, 140.12, 129.26, 128.84, 128.45, 128.30, 127.06, 126.23, 66.57, 50.39, 38.91 ppm; IR (neat) 3320 (O-H), 3025 (sp^2 C-H), 2920 (sp^3 C-H), 1601, 1494 (aromatic C=C), 1451 (aromatic C=C), 1060 (C-O), 1028 (C-O), 757, 695 cm^{-1}.

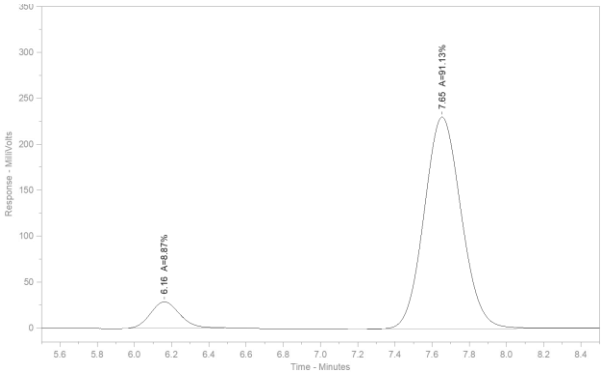


To a solution of the chiral alcohol (*S*)-**52** (106 mg, 0.5 mmol, 1.0 eq) in dry dichloromethane (10 mL) was added PPh_3 (197 mg, 0.75 mmol, 1.50 eq) and the resultant solution was cooled down to

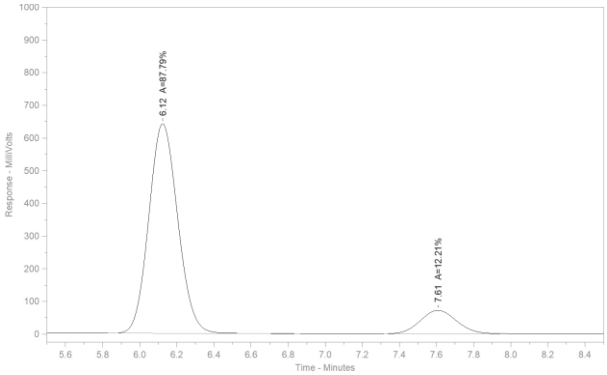
0ºC. To the resultant solution was added NBS (134 mg, 0.75 mmol, 1.50 eq) portion wise and the resultant mixture was allowed to warm up to room temperature and stirred for a total of 2 hours. Afterwards, the reaction mixture was concentrated under reduced pressure and 10 mL of 15% ethyl acetate in hexanes was added. The resultant mixture was filtered over a small pad of silica gel to get rid of the insoluble components. The silica pad was washed with 2 more portions of 10 mL of 10% ethyl acetate in hexanes and the combined organics were concentrated under reduced pressure. To the resultant residue was added triethylphosphite (0.17 mL, 1.0 mmol, 2.0 eq) and the resultant mixture was refluxed vigorously under nitrogen atmosphere for 2 hours. Afterwards, the volatiles were removed under reduced pressure and the residue was purified by flash chromatography over silica gel (ethyl acetate) to afford the desired chiral phosphonate product (*S*)-**53** (116 mg, 70%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +34º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28-7.26 (2H, m, aryl), 7.23-7.15 (6H, m, aryl), 7.03 (2H, d, *J* = 7.0 Hz, aryl), 3.97-3.91 (1H, m, b or b'), 3.90-3.84 (2H, m, b or b'), 3.74-3.68 (1H, m, b or b'), 3.35-3.29 (1H, m, d), 3.05 (1H, dd, *J* = 13.5, 7.5 Hz, e (1H)), 2.94 (1H, ddd, *J* = 13.5, 7.5, 1.5 Hz, e (1H)), 2.22-2.11 (2H, m, c), 1.18 (3H, t, *J* = 7.0 Hz, a or a'), 1.13 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 143.99 (d, $^3J_{C\text{-}P}$ = 7.0 Hz, j), 139.56 (f), 129.51 (aryl), 128.46 (aryl), 128.36 (aryl), 127.91 (aryl), 126.75 (aryl), 126.35 (aryl), 61.56 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.34 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 44.70 (d, $^3J_{C\text{-}P}$ = 14.0 Hz, e), 42.46 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, d), 31.75 (d, $^1J_{C\text{-}P}$ = 139 Hz, c), 16.44 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a+a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 30.09 ppm; IR (neat) 3018 (sp^2 C-H), 2943 (sp^3 C-H), 1496 (aromatic C=C), 1451 (aromatic C=C), 1239 (P=O), 1051 (C-O), 1025 (C-O), 955 (P-O), 698 cm^{-1}. HRMS (EI) calculated for $C_{19}H_{25}O_3P$ = 332.1541, found = 332.1538 *m/z*.

Enantiomer ratio is determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 20:80 Hexanes: Isopropanol; Flow rate = 1 mL/min. HPLC UV detector λ = 210 nm, rt. HPLC traces:

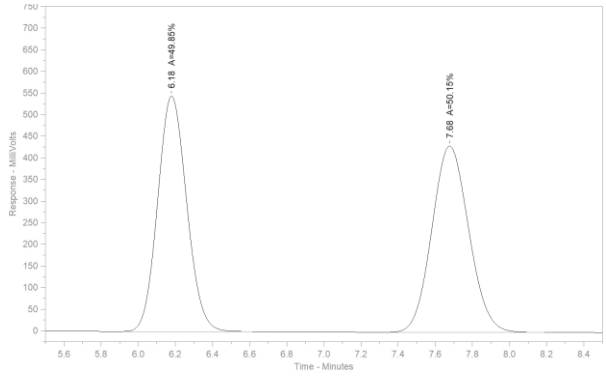
(a) R:S = 9:91, **53** synthesized via chiral auxillary synthesis.



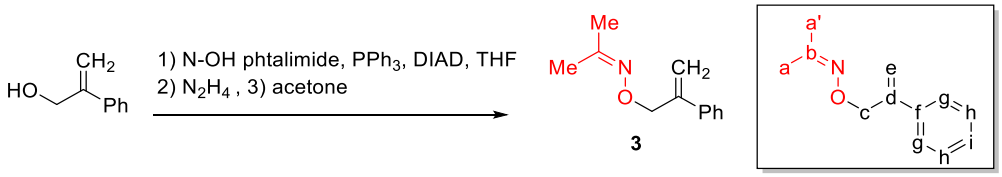
(b) R:S = 88:12, CAHB of **15j** with (*R*,*R*)-**T2** to form **16j** which protodeboronates to form **53**.



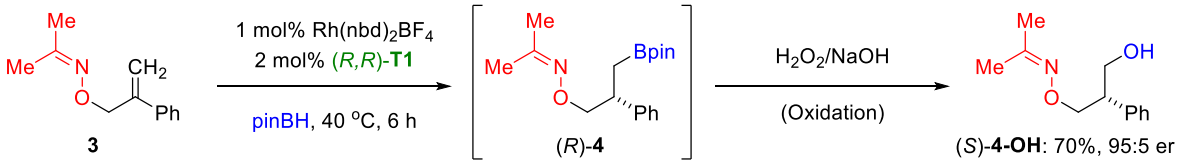
(c) Racemic mixture of **53** obtained by hydrogenation of (*E*)-**15j** with H_2 over Pd/C.



(10) Experimental procedures and characterization data for oximes



Preparation of acetone oxime substrate 3: Unsaturated acetone-derived oxime ether substrate **3** was prepared according to the recently reported procedure by Zhao[28] with minor modification. To a solution (room temperature) of 2-phenylprop-2-en-1-ol (1.0 equiv, 3.00 g, 22.4 mmol), *N*-hydroxyphthalimide (1.1 equiv, 4.01 g, 24.6 mmol) and PPh_3 (1.1 equiv, 6.45 g, 24.6 mmol) in anhydrous THF (45.0 ml) was added diisopropyl azodicarboxylate (1.1 equiv, 4.85 mL, 24.6 mmol) dropwise. After 3 hours neat hydrazine (1.2 equiv, 0.85 mL, 26.9 mmol) was added dropwise. At this point, the formation of milky precipitation was observed. After 30 min acetone was added (10 mL, excess). After 1 hour the resulting mixture was filtered through Celite to remove precipitate, washed with acetone and the filtrate was concentrated under reduced pressure. Flash chromatography on silica gel (ethyl acetate/hexanes 1:9) affords the desired unsaturated acetone-derived oxime ether **3** (3.50 g, 83 %) as a clear, colorless oil: TLC analysis (ethyl acetate/hexanes 1:9) R_f = 0.7; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.48 (2H, m, aryl), 7.41-7.27 (3H, m, aryl), 5.56 (1H, s, e), 5.37 (1H, d, *J* = 1.1 *Hz*, e'), 1.91 (3H, s, a or a'), 1.87 ppm (3H, s, a or a'); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.53 (b), 144.38 (d), 138.96 (f), 128.39 (h), 127.79 (i), 126.21 (g), 114.32 (e), 75.15 (c), 21.98 (a'), 15.86 ppm (a); IR (neat) 3084, 3056, 3031, 2916 (C–H), 1631 (C=C), 1438 (C=N), 1367, 1070, 1027, 905 (C–O, N–O); HRMS (EI) calculated for $C_{12}H_{15}NO$ = 189.1154, found 189.1157 *m/z*.

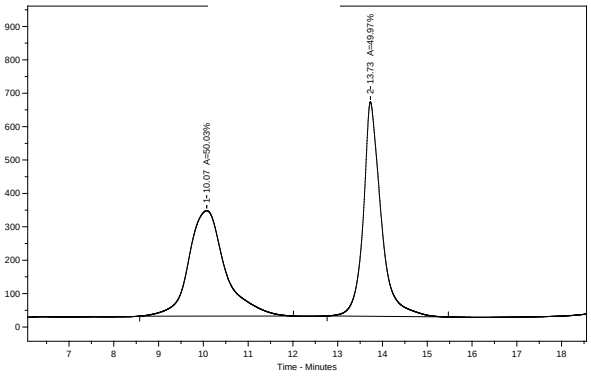


Procedure for the CAHB-Oxidation sequence for oxime-substrate 3: A stock solution of Rhodium-ligand complex was prepared by dissolving $Rh(nbd)_2BF_4$ (2.0 mg, 5.35 μmol) and (*R,R*)-**T1** (7.5 mg, 10.7 μmol) in THF (1.0 mL) (room temperature, 1 h). A 0.5 mL aliquot of the resulting yellow solution was added to an unsaturated oxime ether **3** (50.3 mg, 266 μmol). Solution of pinacolborane (pinBH, 51.1 mg, 399 μmol) in THF (0.75 mL) was added and reaction mixture was stirred (40 ˚C) for 12 h. *Oxidation step:* The reaction mixture was cooled (0 ˚C), diluted with MeOH (3.0 mL) and 3 M aq NaOH (4.0 mL) followed by dropwise addition of 30% aq H_2O_2 (0.5 mL). The resulting mixture was warmed to room temperature by removing the ice bath and stirred for additional 2 h. Afterwards the mixture was diluted with brine (5.0 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried (anhydrous Na_2SO_4), filtered, and concentrated under reduced pressure. Flash chromatography on silica (progressing from 10:90 to 30:70 ethyl acetate/hexanes) affords the ϒ-hydroxylated product (*S*)-**4-OH** (38.6 mg, 70%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:7) R_f = 0.4; Chiral HPLC analysis of alcohol (Chiralpak-IC, 70:30 hexanes/isopropanol@ 1.0 mL/min) showed peaks at 10.09 (*R*-enantiomer, 5%) 13.77 min (*S*-enantiomer, 95%); $[\alpha]_D^{210}$ = -8.0˚ (c=1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)

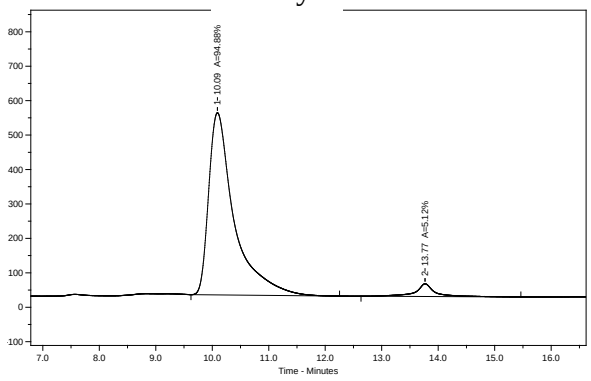
δ 7.38-7.25 (5H, m, aryl), 4.39-4.31 (2H, m, c), 3.99-3,85 (2H, m, e), 3.23 (1H, quin, J = 6.4 Hz, d), 2.47 (1H, t, J = 6.4 Hz, OH), 1.92 (3H, s, a'), 1.88 ppm (3H, s, a); 155.56 (b), 140.27 (f), 128.67 (g), 128.30 (h), 127.00 (i), 74.77 (c), 64.82 (e), 48.14 (d), 21.94 (a'), 15.75 ppm (a); IR (neat) 3378 (O–H), 3028, 2919, 2872 (C–H), 1495, 1453, 1437, 1367 (C=N), 1069, 1029, 1005, 910 cm^{-1} (C–O, N–O); HRMS (ESI) calculated for $C_{12}H_{17}NO_2+Na^+$ = 230.1157, found 230.1154 *m/z.*

HPLC traces: Chiralpak-IC, 70:30 hexanes/isopropanol@ 1.0 mL/min

Racemic mixture:



(*S*)-4-OH: CAHB of **3** with (*R*,*R*)-**T1**, followed by oxidation:



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