Supporting information for:

Facile Access to Functionalized Chiral Secondary Benzylic Boronic Esters via Catalytic Asymmetric Hydroboration

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Part 1: Experimental Procedures and Characterization Data

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(1) General Information

All preparative reactions are carried out under a dry nitrogen atmosphere unless otherwise indicated. Tetrahydrofuran (THF) is freshly distilled over sodium and benzophenone before using in catalytic asymmetric hydroboration (CAHB) reactions. Pinacolborane (pinBH) is obtained from Acros Organics MS (97% purity, stabilized with triethylamine) and is distilled under nitrogen (760 mm Hg, 150^{o}C) before use. For long term storage, the distilled pinacolborane is stored in freezer in sealed 8 mL vial with airtight screw cap sealed with parafilm under dry nitrogen. All phosphonate-functionalized substrates are subjected to high vacuum (*ca.* 0.5-1.0 mm Hg) at 100 ^{o}C for 1 hour to remove any residual diethyl phosphite, triethyl phosphite or triethyl phosphate. The latter are trace contaminants in commercial diethyl phosphite used for substrate synthesis, and if present in even trace quantities in the substrate, can greatly diminish the activity of the chiral rhodium catalyst. For convenience, CAHB reactions are set up in a glovebox under a dry nitrogen atmosphere.

Synthesized compounds are purified by flash chromatography using EMD Silica Gel 60 Geduran®. Thin Layer Chromatography analyses are performed on Analtech Silica Gel HLF (0.25 mm) precoated analytical plates and visualized with the 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). Chiral HPLC analyses were performed with the use of either (1) An ISCO model 2360 HPLC and Chiral Technologies Inc: monitored with US-VIS detector (Shimadzu SPD-10AVP/10AVP; or (2) A 1220 Infinity II LC (Agilent Technologies) Model Number G4290C. Typical λ used for HPLC UV detectors = 210 nm unless otherwise indicated. Daicel HPLC 250 x 4.6 mm columns are used for chiral separations (specific column used is indicated in the appropriate experimental section). OpenLAB CDS ChemStation Edition (Rev. C.01.08(210)) software is used for integration/analysis of HPLC results.

NMR spectra are recorded on 300, 400 or 700 MHz Bruker Advance NMR spectrometers in the deuterated solvent specified. The solvent residual peaks are 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 ($J_{C\text{-}P}$). These splitting patterns are resolved, and the corresponding coupling constants assigned. 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), dt (doublet of triplets) or m (unresolved multiplet), etc.

IR spectra are recorded using an Avatar 360 FT-IR instrument. Optical rotations are 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 cm^{-1} cm^3 g^{-1}. High resolution mass spectrometry (HRMS) analyses using electron impact ionization (EI) or electrospray ionization (ESI) are carried out by the Nebraska Center for Mass Spectrometry (NCMS).

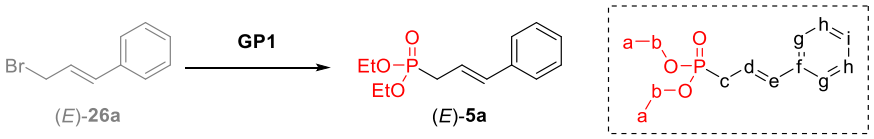
Routine Preparation of Synthetic Precursors. The Supporting Information given for the preparation and CAHB of allylic phosphonates starts with the allyl bromide or allyl carbonate. These precursors were obtained either from (1) bromination of allyl alcohols using PBr_3[1] or NBS/PPh_3;[2] or (2) allyl carbonate formation from allyl alcohols using ethyl chloroformate and triethylamine. The allyl alcohols are obtained via the reduction of the corresponding α,β-unsaturated esters with DIBAL-H;[3] α,β-unsaturated esters are prepared through Wittig[4] or Horner-Wadsworth-Emmons olefination. The (*Z*)-substrates are prepared by our colleagues via

photoisomerization of the corresponding (*E*)-substrates.[5] Deuterated pinacolborane (pinBD) used for mechanistic studies is prepared according to literature procedure.[6]

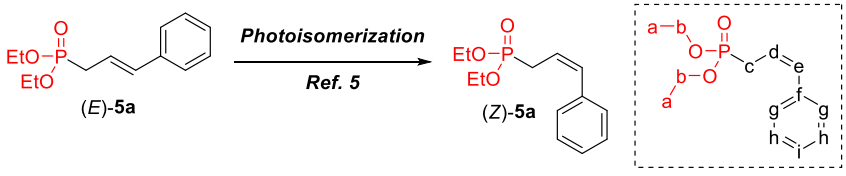
(2) Synthesis of Substrates

Synthesis of allyl phosphonates via substitution of the corresponding allyl bromides (GP1): Our previously reported procedure[7] for the synthesis of allyl phosphonates from the corresponding allyl bromides is followed.

Synthesis of allyl phosphonates via palladium-catalyzed substitution of the corresponding allyl carbonates (GP2): The synthesis of substrates via Palladium-catalyzed substitution of the corresponding allyl carbonates is carried out with few modifications of the original procedure reported by Zhao[8] and co-workers as follows. Under a dry nitrogen atmosphere, a mixture of $Pd_2(dba)_3$ (2 mol%) and Xantphos (4 mol%) in dry THF is stirred for 1 hour. To the resultant complex solution, a mixture of the corresponding allyl carbonate (1 equiv.) and diethyl phosphite (1.2 equiv.) is added and the resultant mixture is refluxed for 24 hours. Afterwards, the reaction mixture is cooled down to room-temperature and filtered over a bed of celite. The filtrate is concentrated under reduced pressure and the concentrate is purified using silica-gel chromatography. **Note:** ***GP2*** *is carried out for the preparation of substrates bearing a basic nitrogen or sensitive heterocyclic functional groups. In such cases either the preparation of corresponding allyl bromide isn't straightforward, or the corresponding allyl bromides are very unstable.*

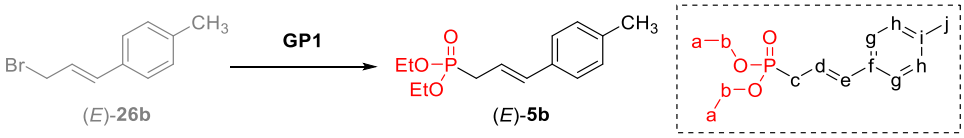


Synthesis of allylic phosphonate (*E*)-5a: Following **GP1**, the allyl bromide (*E*)-**26a** (197 mg, 1.00 mmol) yields alkene substrate (*E*)-**5a** (218 mg, 86%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (2H, d, *J* = 7.5 Hz, g), 7.31-7.27 (2H, m, aryl), 7.23-7.19 (1H, m, aryl), 6.52 (1H, dd, *J* = 15.8, 5.1 Hz, e), 6.21-6.12 (1H, m, d), 4.18-4.05 (4H, m, b), 2.76 (2H, ddd, *J* = 22.4, 7.5, 1.3 Hz, c), 1.31 (6H, t, *J* = 7.08 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.88 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 134.73 (d, $^3J_{C\text{-}P}$ = 14.79 Hz, e), 128.61 (aryl), 127.64 (aryl), 126.28 (d, $^5J_{C\text{-}P}$ = 2.07 Hz, g), 118.91 (d, $^2J_{C\text{-}P}$ = 12.0 Hz, d), 62.08 (d, $^2J_{C\text{-}P}$ = 6.7 Hz, b), 31.16 (d, $^1J_{C\text{-}P}$ = 139.89 Hz, c), 16.55 (d, $^3J_{C\text{-}P}$ = 5.89 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.81 ppm; IR (neat) 3055 (sp^2 C-H), 2979 (sp^3 C-H), 1651 (C=C), 1597 (C=C), 1495 (aromatic C=C), 1448 (aromatic C=C), 1247 (P=O), 1018 (C-O), 955 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{19}O_3P$+Na^+ = 277.0972, found 277.0972 *m/z*.

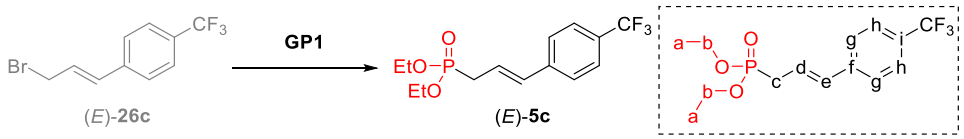


Synthesis of allylic phosphonate (*Z*)-5a: Photoisomerization of the allylic phosphonate (*E*)-**5a** (200 mg, 0.79 mmol; Ref. **5**) yields the diastereomeric substrate (*Z*)-**5a** (178 mg, 89%; Z:E ratio = 9:1) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (5H, m, aryl), 6.67-6.63 (1H, m, e), 5.76-5.68 (1H, m, d), 4.13-4.04

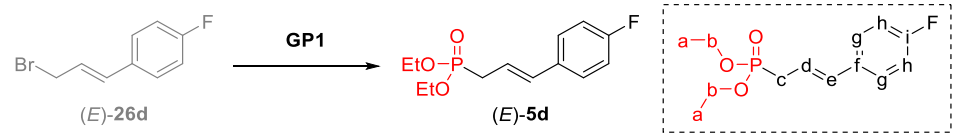
(4H, m, b), 2.84 (2H, ddd, J = 22.4, 8.0, 1.5 Hz, c), 1.29 (6H, t, J = 7 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.40 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, f), 133.17 (d, $^{3}J_{C\text{-}P}$ = 14.5 Hz, e), 128.59 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, g), 128.39 (h), 127.21 (i), 120.45 (d, $^{2}J_{C\text{-}P}$ = 11 Hz, d), 61.98 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b), 26.93 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.45 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.28 ppm; IR (neat) 3025 (sp^2 C-H), 2904 (sp^3 C-H), 1599 (C=C), 1495 (aromatic C=C), 1446 (aromatic C=C), 1247 (P=O), 1021 (C-O), 955 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{19}O_3P$+Na^+ = 277.0970, found 277.0971 *m/z*.



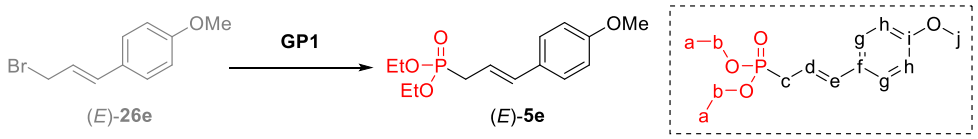
Synthesis of allylic phosphonate (*E*)-5b: Following **GP1**, the allyl bromide (*E*)-**26b** (211 mg, 1.00 mmol) yields alkene substrate (*E*)-**5b** (244 mg, 91%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (2H, d, J = 8.70 Hz, g), 7.13 (2H, d, J = 7.98 Hz, h), 6.51 (1H, dd, J = 15.79, 5.15 Hz, e), 6.17-6.08 (1H, m, d), 4.20-4.07 (4H, m, b), 2.76 (2H, ddd, J = 22.7, 7.6, 1.18 Hz, c), 2.34 (3H, s, j), 1.33 (6H, t, J = 7.06 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.57 (d, $^{7}J_{C\text{-}P}$ = 1.07 Hz, i), 134.71 (d, $^{3}J_{C\text{-}P}$ = 14.93 Hz, e), 134.23 (d, $^{4}J_{C\text{-}P}$ = 3.3 Hz, f), 129.41 (h), 126.29 (d, $^{5}J_{C\text{-}P}$ = 2.05 Hz, g), 117.86 (d, $^{2}J_{C\text{-}P}$ = 12.09 Hz, d), 62.19 (d, $^{2}J_{C\text{-}P}$ = 6.65 Hz, b), 31.25 (d, $^{1}J_{C\text{-}P}$ = 139.92 Hz, c), 21.34 (j), 16.65 (d, $^{3}J_{C\text{-}P}$ = 5.94 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.02 ppm; IR (neat) 2980 (C-H), 1513 (C=C), 1443 (aromatic C=C), 1391 (aromatic C=C), 1247 (P=O), 1019 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_3P$+Na^+ = 291.1129, found 291.1126 *m/z*.



Synthesis of allylic phosphonate (*E*)-5c: Following **GP1**, the allyl bromide (*E*)-**26c** (265 mg, 1.00 mmol) yields alkene substrate (*E*)-**5c** (164 mg, 51%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 8.25 Hz, g), 7.46 (2H, d, J = 8.15 Hz, h), 6.57 (1H, dd, J = 15.5, 5.10 Hz, e), 6.34-6.24 (1H, m, d), 4.22-4.08 (4H, m, b), 2.80 (2H, ddd, J = 22.5, 7.6, 1.2 Hz, c), 1.34 (6H, t, J = 7.05 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.38 (f), 133.52 (d, $^{3}J_{C\text{-}P}$ = 14.5 Hz, e), 129.57 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz, i), 126.55 (d, J = 2 Hz, g), 125.71 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz, h), 124.50 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, CF_3), 122.07 (d, $^{2}J_{C\text{-}P}$ = 11.93 Hz, d), 62.30 (d, $^{2}J_{C\text{-}P}$ = 6.70 Hz, b), 31.36 (d, $^{1}J_{C\text{-}P}$ = 139 Hz, c), 16.65 (d, $^{3}J_{C\text{-}P}$ = 5.78 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.23 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.54 ppm; IR (neat) 2983 (sp^2 C-H), 2933 (sp^3 C-H), 1614 (C=C), 1323 (C-F), 1247 (P=O), 1162 (C-O), 1015 (C-O), 953 (P-O), 789 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{18}F_3O_3P$+Na^+ = 345.0843, found 345.0849 *m/z*.

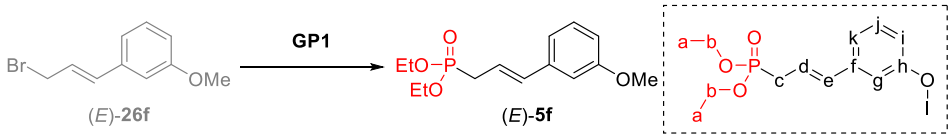


Synthesis of allylic phosphonate (*E*)-5d: Following **GP1**, the allyl bromide (*E*)-**26d** (215 mg, 1.00 mmol) yields alkene substrate (*E*)-**5d** (180 mg, 66%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (2H, m, g), 7.01-6.97 (2H, m, h), 6.49 (1H, dd, *J* = 15.0, 5.5 Hz, e), 6.13-6.03 (1H, m, d), 4.20-4.04 (4H, m, b), 2.75 (2H, ddd, *J* = 22.25, 7.5, 1.0 Hz, c), 7.06 (6H, t, *J* = 7.05 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.45 (d, $^{1}J_{C\text{-}F}$ = 246 Hz, i), 133.62 (d, $^{3}J_{C\text{-}P}$ = 14.9 Hz, e), 127.89 (dd, $^{3}J_{C\text{-}F}$ = 8.0 Hz, $^{6}J_{C\text{-}P}$ = 2.0 Hz, g), 118.77 (dd, $^{2}J_{C\text{-}P}$ = 12 Hz, $^{6}J_{C\text{-}F}$ = 2.0 Hz, d), 115.62 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz, h), 62.20 (d, $^{2}J_{C\text{-}P}$ = 6.75 Hz, b), 31.18 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.64 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.77 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.49 ppm; IR (neat) 2981 (sp^2 C-H), 2909 (sp^3 C-H), 1600 (C=C), 1508 (C-F), 1247 (P=O), 1225 (P=O), 1020 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{18}FO_3P+Na^+$ = 295.0875, found 295.0885 *m/z*.



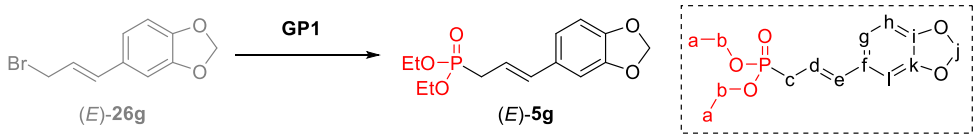
(*E*)-**26e** (*E*)-**5e**

Synthesis of allylic phosphonate (*E*)-5e: Following **GP1**, the allyl bromide (*E*)-**26e** (227 mg, 1.00 mmol) yields alkene substrate (*E*)-**5e** (202 mg, 71%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, d, *J* = 8.5 Hz, g), 6.85 (2H, d, *J* = 8.5 Hz, h), 6.48 (1H, dd, *J* = 15.0, 5.5 Hz, e), 6.08-5.98 (1H, m, d), 4.21-4.08 (4H, m, b), 3.81 (3H, s, j), 2.75 (2H, ddd, *J* = 22.0, 7.5, 1.25 Hz, c), 1.33 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.36 (i), 134.22 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 129.84 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, f), 127.55 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, g), 116.59 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 114.12 (h), 62.16 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b), 55.44 (j), 31.20 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.65 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.15 ppm; IR (neat) 2980 (sp^2 C-H), 2905 (sp^3 C-H), 1606 (C=C), 1510, 1244 (P=O), 1018 (C-O), 958 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_4P+Na^+$ = 307.1075, found 307.1078 *m/z*.

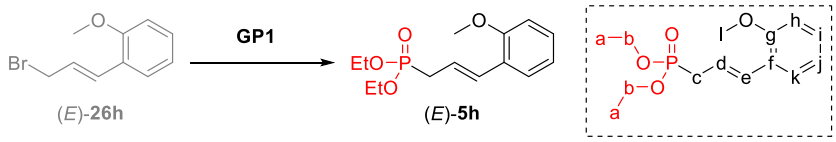


(*E*)-**26f** (*E*)-**5f**

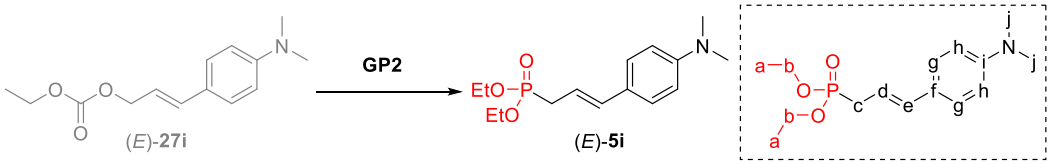
Synthesis of allylic phosphonate (*E*)-5f: Following **GP1**, the allyl bromide (*E*)-**26f** (227 mg, 1.00 mmol) yields alkene substrate (*E*)-**5f** (196 mg, 69%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (1H, m, j), 6.93 (2H, d, *J* = 7.6 Hz, k), 6.87 (1H, s, g), 6.76 (1H, d, *J* = 8.2 Hz, i), 6.47 (1H, dd, *J* = 15.75, 4.75 Hz, e), 6.19-6.09 (1H, m, d), 4.16-4.04 (4H, m, b), 3.77 (3H, s, l), 2.73 (2H, dd, *J* = 22.5, 7.5 Hz, c), 1.30 (6H, td, *J* = 7.0, 2.5 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.82 (h), 138.28 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, f), 134.62 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 129.56 (j), 119.19 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 118.95 (d, $^{5}J_{C\text{-}P}$ = 1.65 Hz, k), 113.25 (i), 111.56 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, g), 62.08 (d, $^{2}J_{C\text{-}P}$ = 7.0 Hz, b), 55.22 (l), 31.08 (d, $^{1}J_{C\text{-}P}$ = 139 Hz, c), 16.51 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.75 ppm; IR (neat) 2981 (sp^2 C-H), 2905 (sp^3 C-H), 1597 (C=C), 1488 (aromatic C=C), 1463 (aromatic C=C), 1241 (P=O), 1019 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_4P+Na^+$ = 307.1075, found 307.1077 *m/z*.



Synthesis of allylic phosphonate (*E*)-5g: Following **GP1**, the allyl bromide (*E*)-**26g** (240 mg, 1.00 mmol) yields alkene substrate (*E*)-**5g** (206 mg, 69%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (1H, s, l), 6.80-6.74 (2H, m, g+h), 6.44 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.04-5.95 (3H, m, d+j), 4.22-4.04 (4H, m, b), 2.74 (2H, ddd, *J* = 22.0, 7.5, 1.5 Hz, c), 1.33 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.18 (i), 147.37 (d, $^6J_{C\text{-}P}$ = 1.0 Hz, k), 134.39 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 131.51 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 121.02 (d, $^5J_{C\text{-}P}$ = 2.25 Hz, g), 117.11 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 108.42 (h), 105.74 (d, $^5J_{C\text{-}P}$ = 2.0 Hz, l), 101.24 (j), 62.20 (d, $^2J_{C\text{-}P}$ = 6.75 Hz, b), 31.12 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.99 ppm; IR (neat) 2980 (sp^2 C-H), 2904 (sp^3 C-H), 1605 (C=C), 1489 (aromatic C=C), 1445 (aromatic C=C), 1240 (P=O), 1018 (C-O), 957 (P-O), 781 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{19}O_5P$+Na^+ = 321.0868, found 321.0869 *m/z*.

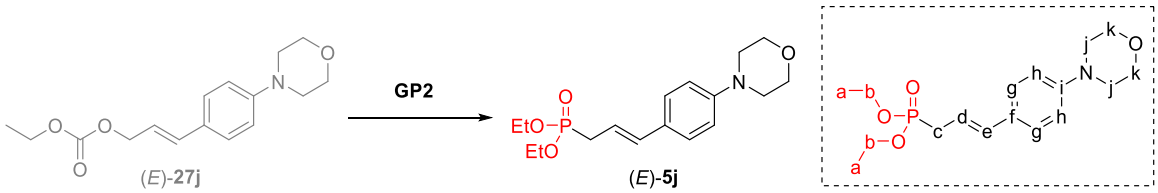


Synthesis of allylic phosphonate (*E*)-5h: Following **GP1**, the allyl bromide (*E*)-**26h** (227 mg, 1.00 mmol) yields alkene substrate (*E*)-**5h** (169 mg, 63%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (1H, t, *J* = 8.0 Hz, aryl), 6.97 (1H, d, *J* = 7.6 Hz, k), 6.91 (1H, br s, h), 6.81 (1H, dd, *J* = 8.25, 2.50 Hz, aryl), 6.52 (1H, dd, *J* = 15.0, 5.5 Hz, e), 6.23-6.14 (1H, m, d), 4.19-4.09 (4H, m, b), 3.83 (3H, s, l), 2.78 (2H, ddd, *J* = 22, 7.5, 1.5 Hz, c), 1.34 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98 (g), 138.45 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 134.72 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 129.72 (aryl), 119.38 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 119.13 (d, $^5J_{C\text{-}P}$ = 2.0 Hz, k), 113.41 (aryl), 111.73 (d, $^6J_{C\text{-}P}$ = 2.0 Hz, h), 62.26 (d, $^2J_{C\text{-}P}$ = 6.75 Hz, b), 55.42 (l), 31.28 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.78 ppm; IR (neat) 2980 (sp^2 C-H), 2904 (sp^3 C-H), 1597 (C=C), 1578 (C=C), 1247 (P=O), 1156 (C-O), 1019 (C-O), 956 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_4P$+Na^+ = 307.1075, found 307.1078 *m/z*.

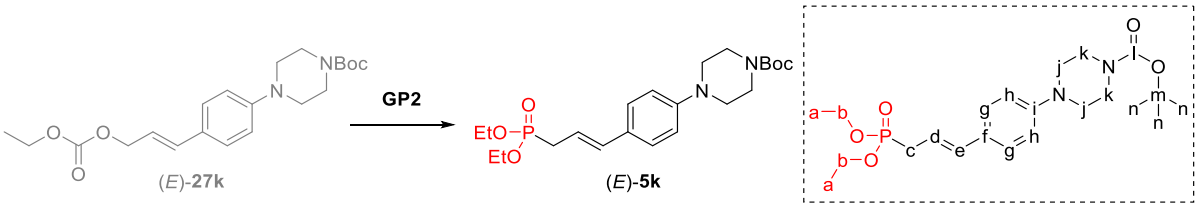


Synthesis of allylic phosphonate (*E*)-5i: Following **GP2**, the allyl carbonate (*E*)-**27i** (249 mg, 1.00 mmol) yields alkene substrate (*E*)-**5i** (110 mg, 37%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (2H, d, *J* = 9 Hz, g), 6.69 (2H, d, *J* = 9 Hz, h), 6.45 (1H, dd, *J* = 15.75, 5.5 Hz, e), 6.01-5.92 (1H, m, d), 4.20-4.07 (4H, m, b), 2.97 (6H, s, j), 2.76 (2H, ddd, *J* = 22, 7.5, 1.5 Hz, c), 1.33 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.25 (i), 134.70 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 127.36 (d, $^5J_{C\text{-}P}$ = 1.6 Hz, g), 125.62

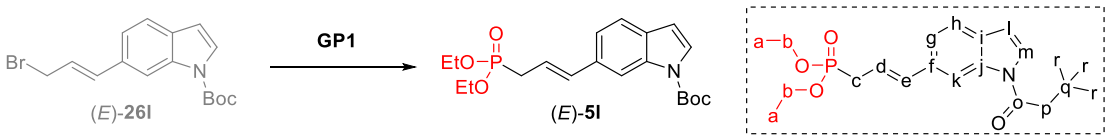
(d, $^{4}J_{C\text{-}P}$ = 3.3 Hz, f), 114.19 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 112.53 (h), 62.17 (d, $^{2}J_{C\text{-}P}$ = 6.8 Hz, b), 40.67 (j), 31.27 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.68 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.50 ppm; IR (neat) 2980 (sp^2 C-H), 2902 (sp^3 C-H), 1608 (C=C), 1520, 1352 (C-N), 1246 (P=O), 1019 (C-O), 944 (P-O), 786 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{24}NO_3P+Na^+$ = 320.1391, found 320.1398 *m/z*.



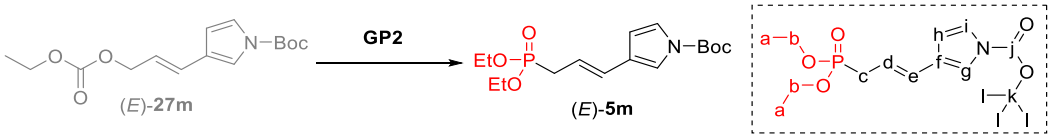
Synthesis of allylic phosphonate (*E*)-5j: Following **GP2**, the allyl carbonate (*E*)-**27j** (291 mg, 1.00 mmol) yields alkene substrate (*E*)-**5j** (139 mg, 41%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* = 8.5 Hz, g), 6.85 (2H, d, *J* = 8.5 Hz, h), 6.46 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.10-5.93 (1H, m, d), 4.18-4.06 (4H, m, b), 3.85 (4H, t, *J* = 4.5 Hz, k), 3.16 (4H, t, *J* = 4.5 Hz, j), 2.75 (2H, dd, *J* = 22.0, 7.5 Hz, c), 1.32 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.79 (i), 134.29 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 128.83 (d, $^{4}J_{C\text{-}P}$ = 3.5, f), 127.28 (d, $^{5}J_{C\text{-}P}$ = 2.0 Hz, g), 115.99 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 115.52 (h), 66.95 (k), 62.13 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz, b), 49.18 (j), 31.18 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.62 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.23 ppm; IR (neat) 2976 (sp^2 C-H), 2823 (sp^3 C-H), 1605 (C=C), 1514, 1449 (aromatic C=C), 1379 (aromatic C=C/C-N), 1234 (P=O), 1120 (C-O), 925 (P-O), 787 cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{26}NO_4P+Na^+$ = 362.1497, found 362.1498 *m/z*.



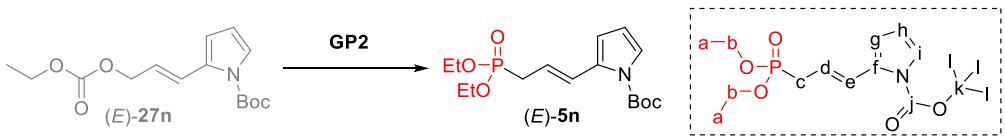
Synthesis of allylic phosphonate (*E*)-5k: Following **GP2**, the allyl carbonate (*E*)-**27k** (195 mg, 0.50 mmol) yields alkene substrate (*E*)-**5k** (99 mg, 45%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (2H, d, *J* = 8.75 Hz, g), 6.85 (2H, d, *J* = 8.75 Hz, h), 6.43 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.05-5.93 (1H, m, d), 4.17-4.04 (4H, m, b), 3.56 (4H, d, *J* = 5.0 Hz, j or k), 3.13 (4H, d, *J* = 5.0 Hz, j or k), 2.73 (2H, ddd, *J* = 22, 7.5, 1.0 Hz, c), 1.47 (9H, s, n), 1.30 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.79 (l), 150.71 (i), 134.25 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 128.96 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, f), 127.25 (d, $^{5}J_{C\text{-}P}$ = 1.8 Hz, g), 116.35 (h), 116.06 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 80.00 (m), 62.11 (d, $^{2}J_{C\text{-}P}$ = 6.8 Hz, b), 49.17 (j or k), 43.58 (j or k), 31.14 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 28.52 (n), 16.59 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.21 ppm; IR (neat) 2979 (sp^2 C-H), 2904 (sp^3 C-H), 1691 (C=O), 1606 (C=C), 1514, 1233 (P=O), 1162 (C-O), 1020 (C-O), 961 (P-O), 751 cm^{-1}; HRMS (ESI) calculated for $C_{22}H_{35}N_2O_5P+Na^+$ = 461.2181, found 461.2180 *m/z*.



Synthesis of allylic phosphonate (*E*)-5l: Following **GP1**, the allyl bromide (*E*)-**26l** (168 mg, 0.50 mmol) yields alkene substrate (*E*)-**5l** (153 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 8.18 (1H, s, k), 7.58 (1H, d, *J* = 3.6 Hz, m), 7.49 (1H, d, *J* = 8.0 Hz, h), 7.30 (1H, d, *J* = 8.0 Hz, g), 6.65 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.54 (1H, dd, *J* = 3.6, 0.5 Hz, l), 6.27-6.17 (1H, m, d), 4.21-4.08 (4H, m, b), 2.81 (2H, ddd, *J* = 22.0, 7.5, 1.5 Hz, c), 1.69 (9H, s, r), 1.34 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.87 (o), 135.78 (i or j), 135.66 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 133.49 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 130.32 (i or j), 126.56 (m), 121.22 (d, $^5J_{C\text{-}P}$ = 2.0 Hz, g), 121.05 (h), 117.92 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 113.49 (d, $^5J_{C\text{-}P}$ = 2.0 Hz, k), 107.41 (l), 83.91 (q), 62.22 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 31.38 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.37 (r), 16.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.05 ppm; IR (neat) 2979 (sp^2 C-H), 2904 (sp^3 C-H), 1729 (C=O), 1612 (C=C), 1335 (C-N), 1250 (P=O), 1125 (C-O), 1020 (C-O), 960 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{28}NO_5P+Na^+$ = 416.1603, found 416.1607 *m/z*.

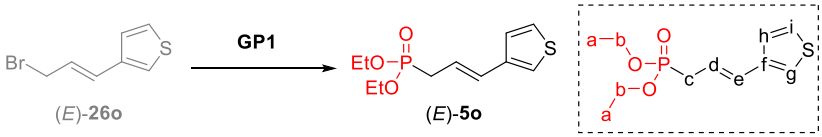


Synthesis of allylic phosphonate (*E*)-5m: Following **GP2**, the allyl carbonate (*E*)-**27m** (295 mg, 1.00 mmol) yields alkene substrate (*E*)-**5m** (151 mg, 44%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.15 (2H, m, g+i), 6.40-6.35 (2H, m, e+h), 5.94-5.85 (1H, m, d), 4.19-4.06 (4H, m, b), 2.72 (2H, dd, *J* = 22, 7.5 Hz, c), 1.60 (9H, s, l), 1.33 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.89 (j), 127.15 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 125.51 (d, $^4J_{C\text{-}P}$ = 3.75 Hz, f), 121.17 (i), 117.88 (d, $^5J_{C\text{-}P}$ = 3 Hz, g), 117.29 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 109.57 (h), 83.93 (k), 62.20 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 31.16 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.17 (l), 16.67 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.13 ppm; IR (neat) 2980 (sp^2 C-H), 2802 (sp^3 C-H), 1738 (C=O), 1352 (C-N), 1251 (P=O), 1154 (C-O), 1021 (C-O), 959 (P-O), 769 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{26}NO_5P+Na^+$ = 366.1446, found 366.1446 *m/z*.



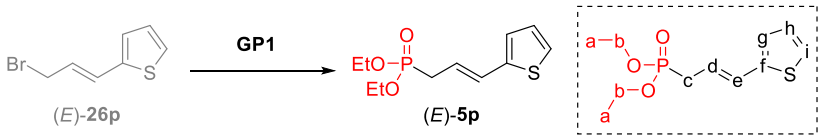
Synthesis of allylic phosphonate (*E*)-5n: Following **GP2**, the allyl carbonate (*E*)-**27n** (295 mg, 1.00 mmol) yields alkene substrate (*E*)-**5n** (134 mg, 39%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 2:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, br s, i), 7.10 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.38 (1H, br s, g), 6.12 (1H, dd, *J* = 3.5, 3.0 Hz, h), 5.99-5.90 (1H, m, d), 4.19-4.07 (4H, m, b), 2.76 (2H, dd, *J* = 22.0, 7.5 Hz, c), 1.60 (9H, s, l), 1.33 (6H, t, *J* = 7.10 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.51 (j), 133.58 (d, $^4J_{C\text{-}P}$ = 3.75 Hz, f), 125.98 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 121.87 (i), 118.70 (d, $^2J_{C\text{-}P}$ = 12.25 Hz, d), 111.12 (d, $^5J_{C\text{-}P}$ = 3.0 Hz, g), 111.00 (h), 83.96 (k), 62.19 (d, $^2J_{C\text{-}P}$ = 6.75 Hz, b), 31.34 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 28.18 (l), 16.65

(d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.85 ppm; IR (neat) 2979 (sp^2 C-H), 2906 (sp^3 C-H), 1739 (C=O), 1320 (C-N), 1246 (P=O), 1122 (C-O), 1022 (C-O), 958 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{26}NO_5P+Na^+$ = 366.1446, found 366.1447 *m/z*.



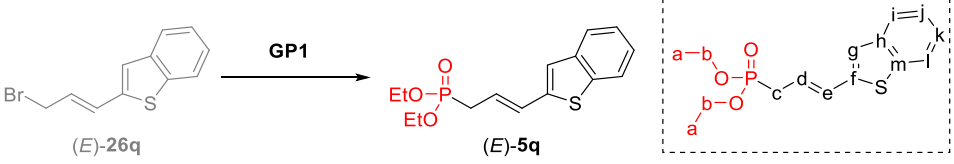
(*E*)-**26o** (*E*)-**5o**

Synthesis of allylic phosphonate (*E*)-5o: Following **GP1**, the allyl bromide (*E*)-**26o** (203 mg, 1.00 mmol) yields alkene substrate (*E*)-**5o** (216 mg, 83%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (1H, dd, *J* = 5.0, 3.0 Hz, h), 7.20 (1H, d, *J* = 5.0 Hz, i), 7.12 (1H, br s, g), 6.54 (1H, dd, *J* = 15.75, 5.5 Hz, e), 6.07-5.97 (1H, m, d), 4.19-4.06 (4H, m, b), 2.72 (2H, ddd, *J* = 22, 7.5, 1.0 Hz, c), 1.32 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.57 (d, $^{4}J_{C\text{-}P}$ = 3.5 Hz, f), 129.02 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 126.16 (h), 125.05 (i), 121.98 (d, $^{5}J_{C\text{-}P}$ = 3.0 Hz, g), 118.76 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 62.16 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz, b), 31.09 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.63 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.88 ppm; IR (neat) 3078 (sp^2 C-H), 2904 (sp^3 C-H), 1477 (aromatic C=C), 1390 (aromatic C=C), 1244 (P=O), 1018 (C-O), 955 (P-O), 765 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{17}O_3PS+Na^+$ = 283.0534, found 283.0534 *m/z*.



(*E*)-**26p** (*E*)-**5p**

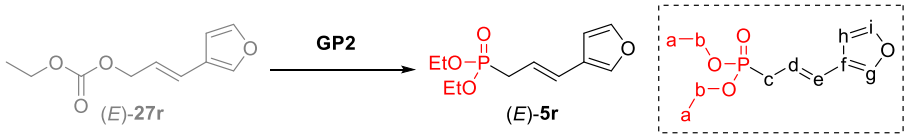
Synthesis of allylic phosphonate (*E*)-5p: Following **GP1**, the allyl bromide (*E*)-**26p** (203 mg, 1.00 mmol) yields alkene substrate (*E*)-**5p** (205 mg, 79%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (1H, m, g or h), 6.96-6.93 (2H, m, g *or* h *and* i), 6.66 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.04-5.94 (1H, m, d), 4.19-4.06 (4H, m, b), 2.73 (2H, ddd, *J* = 22, 7.5, 1.5 Hz, c), 1.35-1.31 (6H, m, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.94 (d, $^{4}J_{C\text{-}P}$ = 4.5 Hz, f), 127.90 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 127.44 (i), 125.55 (d, $^{5}J_{C\text{-}P}$ = 3.0 Hz, g), 124.31 (d, $^{6}J_{C\text{-}P}$ = 1.5 Hz), 118.57 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, d), 62.25 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz, b), 31.06 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.64 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.45 ppm; IR (neat) 3030 (sp^2 C-H), 2904 (sp^3 C-H), 1433 (aromatic C=C), 1391 (aromatic C=C), 1246 (P=O), 1018 (C-O), 950 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{17}O_3PS+Na^+$ = 283.0534, found 283.0533 *m/z*.



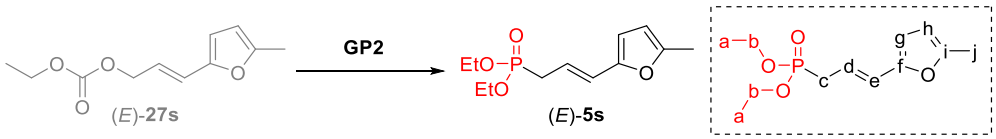
(*E*)-**26q** (*E*)-**5q**

Synthesis of allylic phosphonate (*E*)-5q: Following **GP1**, the allyl bromide (*E*)-**26q** (127 mg, 0.50 mmol) yields alkene substrate (*E*)-**5q** (127 mg, 82%) as a viscous oil: TLC analysis (ethyl acetate/hexanes 4:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (1H, m, aryl), 7.70-7.68 (1H, m, aryl), 7.34-7.27 (2H, m, aryl), 7.13 (1H, s, g), 6.78 (1H, dd, *J* = 15.5, 5.5 Hz, e), 6.15-

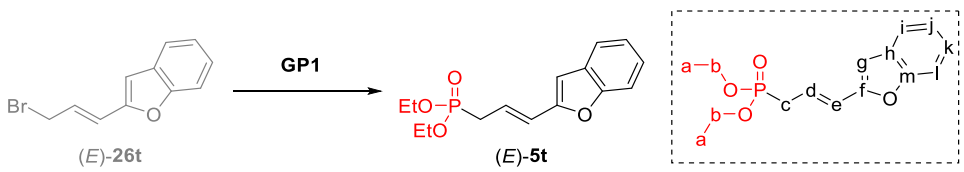
6.05 (1H, m, e), 4.22-4.09 (4H, m, b), 2.79 (2H, ddd, J = 22, 7.5, 1.2 Hz, c), 1.35 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142 (d, $^4J_{C\text{-}P}$ = 4.5 Hz, f), 140.13 (d, $^6J_{C\text{-}P}$ = 1.2 Hz, h), 138.99 (m), 128.65 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 124.88 (aryl), 124.62 (aryl), 123.62 (aryl), 122.73 (d, $^5J_{C\text{-}P}$ = 3.5 Hz, g), 122.36 (aryl), 121.45 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 62.37 (d, $^2J_{C\text{-}P}$ = 6.7 Hz, b), 31.27 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.67 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.06 ppm; IR (neat) 2980 (sp^2 C-H), 2904 (sp^3 C-H), 1245 (P=O), 1017 (C-O), 951 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{19}O_3PS+Na^+$ = 333.0690, found 333.0693 *m/z*.



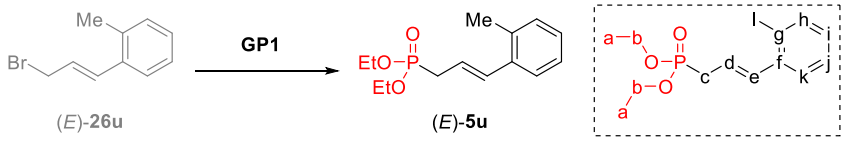
Synthesis of allylic phosphonate (*E*)-5r: Following **GP2**, the allyl carbonate (*E*)-**27r** (785 mg, 4.00 mmol) yields alkene substrate (*E*)-**5r** (288 mg, 30%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, br s, g), 7.34 (1H, dd, J = 1.5, 1.0 Hz, h), 6.52 (1H, d, J = 1.7 Hz, h), 6.38 (1Hh, dd, J = 15.75, 5.0 Hz, e), 5.93-5.83 (1H, m, d), 4.18-4.05 (4H, m, b), 2.71 (2H, ddd, J = 22.0, 7.50, 1.25 Hz, c), 1.32 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.66 (i), 140.32 (d, $^5J_{C\text{-}P}$ = 3.5 Hz, g), 124.55 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 123.98 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 118.40 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 107.64 (h), 62.18 (d, $^2J_{C\text{-}P}$ = 6.7 Hz, b), 31.08 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.62 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.94 ppm; IR (neat) 2981 (C-H), 1507 (aromatic C=C), 1443 (aromatic C=C), 1391 (aromatic C=C), 1246 (P=O), 1161, 1017 (C-O), 955 (P-O), 870, 773 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{17}O_4P+Na^+$ = 267.0757, found 267.0757 *m/z*.



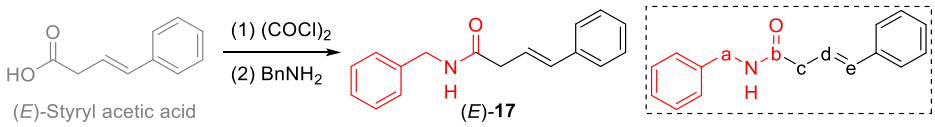
Synthesis of allylic phosphonate (*E*)-5s: Following **GP2**, the allyl carbonate (*E*)-**27s** (210 mg, 1.00 mmol) yields alkene substrate (*E*)-**5s** (119 mg, 46%) as a buff colored oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (1H, dd, J = 15.75, 5.5 Hz, e), 6.09 (1H, dd, J = 2.5, 2.0 Hz, g), 6.07-5.96 (1H, m, d), 5.96-5.95 (1H, m, h), 4.19-4.09 (4H, m, b), 2.72 (2H, ddd, J = 22.5, 7.5, 1.2 Hz, c), 2.31 (3H, s, j), 1.34 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.10 (i), 150.95 (d, $^4J_{C\text{-}P}$ = 4.5 Hz, f), 123.24 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 115.78 (d, $^2J_{C\text{-}P}$ = 12.5 Hz, d), 108.85 (d, $^5J_{C\text{-}P}$ = 3.0 Hz, g), 107.38 (h), 62.17 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b), 30.98 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.62 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a), 13.79 (j) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.78 ppm; IR (neat) 2982 (sp^2 C-H), 2906 (sp^3 C-H), 1592 (C=C), 1534, 1443 (aromatic C=C), 1391 (aromatic C=C), 1248 (P=O), 1017 (C-O), 954 (P-O), 774 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{19}O_4P+Na^+$ = 281.0919, found 281.0922 *m/z*.



Synthesis of allylic phosphonate (*E*)-5t: Following **GP1**, the allyl bromide (*E*)-**26t** (118 mg, 0.50 mmol) yields alkene substrate (*E*)-**5t** (125 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 4:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (1H, d, *J* = 7.5 Hz, i or l), 7.44 (1H, d, *J* = 7.5 Hz, i or l), 7.29-7.18 (2H, m, j+k), 6.56 (1H, br s, g), 6.53-6.37 (2H, m, d+e), 4.23-4.10 (4H, m, b), 2.82 (2H, dd, *J* = 22, 7.5 Hz, c), 1.36 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.93 (m), 154.21 (d, $^4J_{C\text{-}P}$ = 4.5 Hz, f), 129.00 (d, $^6J_{C\text{-}P}$ = 1.35 Hz, h), 124.72 (j or k), 123.29 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 122.99 (j or k), 121.44 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 121.06 (i or l), 111.12 (i or l), 104.45 (d, $^5J_{C\text{-}P}$ = 3.5 Hz, g), 62.36 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 31.29 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.67 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.05 ppm; IR (neat) 2980 (sp^2 C-H), 2904 (sp^3 C-H), 1451 (aromatic C=C), 1391 (aromatic C=C), 1250 (P=O), 1018 (C-O), 944 (P-O), 748 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{19}O_4P$+Na^+ = 317.0919, found 317.0920 *m/z*.

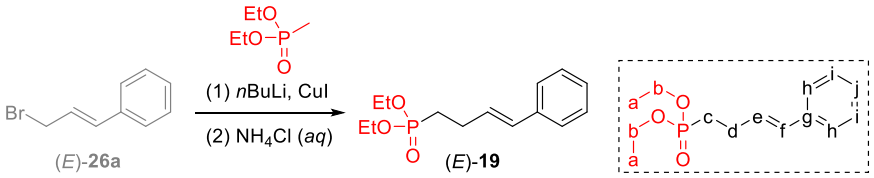


Synthesis of allylic phosphonate (*E*)-5u: Following **GP1**, the allyl bromide (*E*)-**26u** (211 mg, 1.00 mmol) yields alkene substrate (*E*)-**5u** (177 mg, 66%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (1H, m, aryl), 7.23-7.11 (3H, m, aryl), 6.74 (1H, d, *J* = 15.5, 5.5 Hz, e), 6.08-5.99 (1H, m, d), 4.19-4.06 (4H, m, b), 2.79 (2H, dd, *J* = 22.0, 7.50 Hz, c), 2.33 (3H, s, l), 1.33 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.06 (d, $^4J_{C\text{-}P}$ = 3.5 Hz, f), 135.18 (d, $^5J_{C\text{-}P}$ = 2.0 Hz, g), 132.70 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 130.26 (aryl), 127.56 (aryl), 126.16 (aryl), 125.74 (d, $^5J_{C\text{-}P}$ = 2.5 Hz, k), 120.22 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 62.06 (d, $^2J_{C\text{-}P}$ = 6.75 Hz, b), 31.37 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 19.82 (l), 16.54 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.88 ppm; IR (neat) 2979 (sp^2 C-H), 2906 (sp^3 C-H), 1694 (C=C), 1483 (aromatic C=C), 1391 (aromatic C=C), 1247 (P=O), 1019 (C-O), 958 (P-O), 746 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_3P$+Na^+ = 291.1126, found 291.1129 *m/z*.

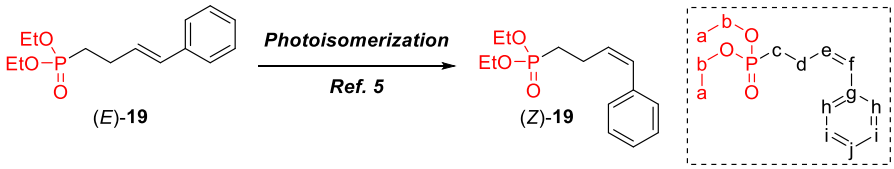


Synthesis of benzylamide substrate (*E*)-17: To a solution of styryl acetic acid (486 mg, 3.00 mmol, 1.00 eq) in dry dichloromethane (15 mL) at 0 ºC is added a drop of dry DMF. To the resultant mixture is added oxalyl chloride (0.38 mL, 4.50 mmol, 1.50 eq) drop wise and the resultant mixture is stirred at room temperature for *ca.* 2 hours. Following this, the reaction mixture is subjected to rotary evaporation to get rid of unreacted oxalyl chloride. The crude mass is redissolved in dry dichloromethane (15 mL) and benzylamine (0.66 mL, 6.00 mmol, 2.00 eq) is added dropwise and the resultant mixture is stirred for *ca.* 2 hours. The mixture is concentrated via rotary evaporation and flash chromatography over silica gel (ethyl-acetate/hexanes/dichloromethane 40:50:10) affords the benzylamide product (*E*)-**17** (580 mg, 77%) as yellowish-white flaky solid: TLC analysis (ethyl acetate/hexanes 1:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.25 (10H, m, aryl), 6.54 (1H, d, *J* = 16 Hz, e), 6.33 (1H, dt, *J* = 15.5, 7.5 Hz, d), 6.17 (1H, br s, NH), 4.46 (2H, d, *J* = 6.0 Hz, a), 3.21 (2H, dd, *J* = 7.5, 1.1

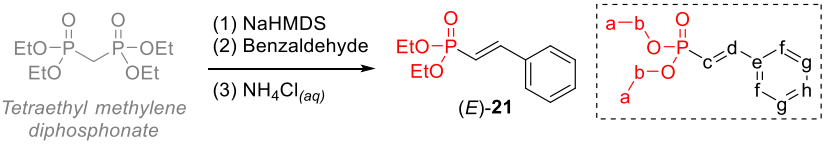
Hz, c) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.75 (b), 138.35 (aryl), 136.71 (aryl), 134.79 (e), 128.86 (aryl), 128.77 (aryl), 127.92 (aryl), 127.67 (aryl), 126.47 (aryl), 122.48 (d), 43.82 (a), 40.95 (c) ppm; IR (neat) 3235 (N-H), 3035 (C-H), 2160 (C=N), 1630 (C=O), 1539 cm^{-1}.



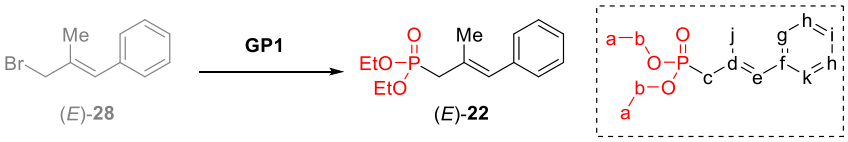
Preparation of disubstituted phosphonate (*E*)-19: This transformation is carried out using our previously reported procedure on the synthesis of homoallyl phosphonate via reaction between allyl bromides and lithiated diethyl methylphosphonate.[9] The allyl bromide (*E*)-**26a** (197 mg, 1.00 mmol) yields alkene substrate (*E*)-**19** (190 mg, 71%) as a colorless oil: TLC analysis (ethyl acetate/hexanes) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.19 (5H, m, aryl), 6.44 (1H, d, *J* = 15.5 Hz, f), 6.23 (1H, dt, *J* = 15.5, 6.5 Hz, e), 4.19-4.06 (4H, m, b), 2.57-2.48 (d), 1.96-1.87 (2H, m, c), 1.34 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.43 (g), 130.79 (f), 129.18 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 128.71 (h or i), 127.38 (j), 126.23 (h or i), 61.72 (d, $^2J_{C\text{-}P}$ = 6 Hz, b), 26.18 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 25.79 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.19 ppm; IR (neat) 3025 (sp^2 C-H), 2980 (sp^3 C-H), 1597 (C=C), 1495 (aromatic C=C), 1442 (aromatic C=C), 1390 (aromatic C=C), 1240 (P=O), 1023 (C-O), 956 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_3P$+Na^+ = 291.1126, found 291.1129 *m/z*.



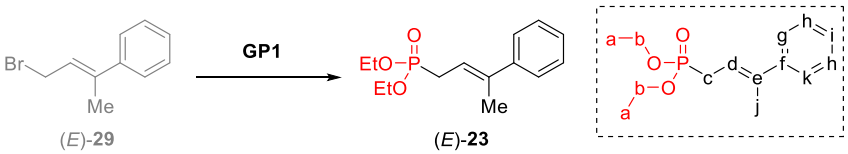
Synthesis of allylic phosphonate (*Z*)-19: Photoisomerization of the allylic phosphonate (*E*)-**19** (200 mg, 0.75 mmol; Ref. **5**) affords the diastereomeric (*Z*)-**19** (170 mg, 84%; Z:E ratio = 4:1) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (5H, m, aryl), 6.48 (1H, d, *J* = 12 Hz, f), 5.68 (1H, dt, *J* = 12, 7.0 Hz, e), 4.18-4.06 (4H, m, b), 2.68-2.62 (2H, m, d), 1.92-1.86 (2H, m, c), 1.32 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.22 (g), 131.12 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 130.11 (f), 128.89 (h or i), 128.45 (h or i), 127.03 (j), 61.76 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b), 26.21 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 21.91 (d, $^2J_{C\text{-}P}$ = 4.8 Hz, d), 16.65 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.05 ppm; IR (neat) 3026 (sp^2 C-H), 2978 (sp^3 C-H), 1597 (C=C), 1496 (aromatic C=C), 1440 (aromatic C=C), 1391 (aromatic C=C), 1237 (P=O), 1023 (C-O), 958 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_3P$+Na^+ = 291.1126, found 291.1127 *m/z*.



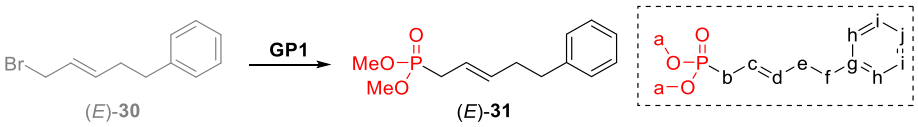
Synthesis of vinyl phosphonate substrate (*E*)-21: To a solution of tetraethyl-methylene-diphosphonate (288 mg, 1.00 mmol, 1.00 eq) in dry THF (10 mL) at 0 °C is added NaHMDS (2M solution in THF; 0.6 mL, 1.2 mmol, 1.2 eq) dropwise, and the resultant solution is stirred for 10 minutes. To the resultant mixture is added benzaldehyde (0.11 mL, 1.10 mmol, 1.10 eq) and the resultant mixture is stirred at room temperature for 3 hours. Following this, a saturated aqueous solution of NH_4Cl (10 mL) is added to the reaction mixture and the layers separated. The aqueous layer is extracted with ethyl acetate (2 x 20 mL) and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. Flash chromatography over silica gel (ethyl acetate) affords the desired vinyl phosphonate (*E*)-**21** (202 mg, 84%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.37 (6H, m, d+f+g+h), 6.27 (1H, dd, *J* = 17.5 Hz, c), 4.21-4.07 (4H, m, b), 1.36 (6H, t, *J* = 7 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.92 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, d), 135.02 (d, $^3J_{C\text{-}P}$ = 23 Hz, e), 130.40 (h), 129.01 (f or g), 127.86 (f or g), 114.12 (d, $^1J_{C\text{-}P}$ = 191 Hz, c), 62.04 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, b), 16.57 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.50 ppm; IR (neat) 2981 (C-H), 1615 (C=C), 1449 (aromatic C=C), 1391 (aromatic C=C), 1242 (P=O), 1018 (C-O), 954 (P-O), 740 cm^{-1}.



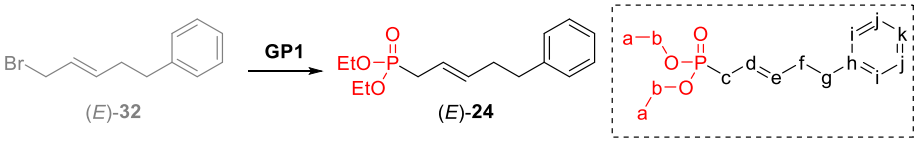
Preparation of trisubstituted allylic phosphonate (*E*)-22: Following **GP1**, the allyl bromide (*E*)-**28** (211 mg, 1.00 mmol) yields alkene substrate (*E*)-**22** (228 mg, 85%) as a colorless oil: TLC analysis (ethyl acetate/hexanes) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (5H, m, aryl), 6.43 (1H, d, *J* = 5.7 Hz, e), 4.21-4.07 (4H, m, b), 2.75 (2H, d, $^2J_{P\text{-}H}$ = 22.5 Hz, c), 2.03 (3H, d, *J* = 3.75 Hz, j), 1.34 (6H, t, *J* = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.83 (d, $^4J_{C\text{-}P}$ = 3.9 Hz, f), 129.79 (d, $^3J_{C\text{-}P}$ = 13 Hz, e), 129.52 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 128.96 (d, $^6J_{C\text{-}P}$ = 3 Hz, g), 128.27 (h), 126.59 (i), 62.11 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b), 38.19 (d, $^1J_{C\text{-}P}$ = 137 Hz, c), 19.31 (d, $^3J_{C\text{-}P}$ = 2.75 Hz, j), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.10 ppm; IR (neat) 2981 (C-H), 1599 (C=C), 1444 (aromatic C=C), 1391 (aromatic C=C), 1247 (P=O), 1019 (C-O), 955 (P-O) cm^{-1}.



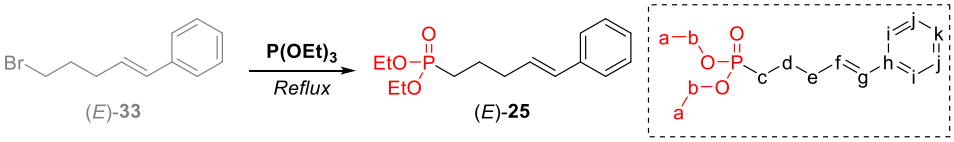
Preparation of trisubstituted allylic phosphonate (*E*)-23: Following **GP1**, the allyl bromide (*E*)-**29** (211 mg, 1.00 mmol) yields alkene substrate (*E*)-**23** (209 mg, 78%) as a colorless oil: TLC analysis (ethyl acetate/hexanes) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (5H, m, aryl), 5.83-5.76 (1H, m, d), 4.18-4.09 (4H, m, b), 2.79 (2H, ddd, *J* = 22.5, 8.0, 0.5 Hz, c), 2.09 (3H, dt, *J* = 4.0, 0.6 Hz, j), 1.34 (6H, t, *J* = 7 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.28 (d, $^4J_{C\text{-}P}$ = 3.6 Hz, f), 139.45 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 128.41 (h), 127.29 (i), 125.95 (d, $^5J_{C\text{-}P}$ = 2.25 Hz, g), 116.36 (d, $^2J_{C\text{-}P}$ = 12 Hz, d), 62.12 (d, $^2J_{C\text{-}P}$ = 7 Hz, b), 27.57 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 16.67 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a), 16.35 (d, $^4J_{C\text{-}P}$ = 2.5 Hz, j) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.65 ppm; IR (neat) 2980 (C-H), 1600 (C=C), 1494 (aromatic C=C), 1444 (aromatic C=C), 1390 (aromatic C=C), 1247 (P=O), 1019 (C-O), 955 (P-O), 757, 695 cm^{-1}.



Preparation of disubstituted allylic phosphonate (*E*)-31: Following **GP1** (with dimethyl phosphite) the allyl bromide (*E*)-**30** (225 mg, 1.00 mmol) yields dimethyl phosphonate alkene substrate (*E*)-**31** (211 mg, 83%) as a colorless oil: TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.17 (5H, m, aryl), 5.76-5.64 (1H, m, e), 5.50-5.41 (1H, m, d), 3.73 (6H, d, $^{3}J_{P\text{-}H}$ = 11 Hz, a), 2.71 (2H, t, J = 7.75 Hz, f), 2.58 (2H, dd, $^{2}J_{C\text{-}P}$ = 22 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, b), 2.42-2.36 (2H, m, e) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.76 (g), 135.58 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, c), 128.61 (h or i), 128.49 (h or i), 126.03 (j), 119.03 (d, $^{2}J_{C\text{-}P}$ = 11 Hz, c), 52.83 (d, $^{2}J_{C\text{-}P}$ = 6.8 Hz, a), 35.69 (d, $^{5}J_{C\text{-}P}$ = 3.5 Hz, f), 34.43 (d, $^{4}J_{C\text{-}P}$ = 2.0 Hz, e), 29.64 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, b) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.27 ppm; IR (neat) 2951 (sp^2 C-H), 2850 (sp^3 C-H), 1603 (C=C), 1496 (aromatic C=C), 1453 (aromatic C=C), 1400 (aromatic C=C), 1251 (P=O), 1022 (C-O), 968 (P-O), 850, 805, 747, 698 cm^{-1}.



Preparation of disubstituted allylic phosphonate (*E*)-24: Following **GP1**, the allyl bromide (*E*)-**32** (225 mg, 1.00 mmol) yields alkene substrate (*E*)-**24** (217 mg, 77%) as a colorless oil: TLC analysis (ethyl acetate/hexanes) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (5H, m, aryl), 5.71-5.63 (1H, m, e), 5.51-5.42 (1H, m, d), 4.15-4.05 (4H, m, b), 2.71 (2H, t, J = 7.8 Hz, g), 2.56 (2H, dd, J = 21.5, 7.5 Hz, c), 2.42-2.37 (2H, m, f), 1.32 (6H, t, J = 7.0 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.83 (h), 135.29 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 128.59 (i or j), 128.49 (i or j), 126.03 (k), 119.43 (d, $^{2}J_{C\text{-}P}$ = 11 Hz, d), 62.02 (d, $^{2}J_{C\text{-}P}$ = 7 Hz, b), 35.76 (d, $^{5}J_{C\text{-}P}$ = 3.5 Hz, g), 34.49 (d, $^{4}J_{C\text{-}P}$ = 2 Hz, f), 30.64 (d, $^{1}J_{C\text{-}P}$ = 140 Hz, c), 16.64 (d, $^{3}J_{C\text{-}P}$ = 6 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.82 ppm; IR (neat) 2981 (sp^2 C-H), 2906 (sp^3 C-H), 1603 (C=C), 1496 (aromatic C=C), 1454 (aromatic C=C), 1391 (aromatic C=C), 1249 (P=O), 1021 (C-O), 957 (P-O), 698 cm^{-1}.



Preparation of disubstituted phosphonate (*E*)-25: This transformation is carried out using our previously reported procedure for phosphonate synthesis via Michaelis-Arbuzov Rearrangement.[9] The allyl bromide (*E*)-**33** (225 mg, 1.00 mmol) yields alkene substrate (*E*)-**25** (184 mg, 65%) as a colorless oil: TLC analysis (ethyl acetate/hexanes) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.20 (5H, m, aryl), 6.42 (1H, d, J = 15.8 Hz, g), 6.18 (1H, dt, J = 15.8, 7.0 Hz, f), 4.18-4.05 (4H, m, b), 2.35-2.30 (2H, m, e), 1.89-1.74 (4H, m, c+d), 1.34 (6H, t, J = 7 Hz, a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.64 (h), 131.26 (g), 129.34 (f), 128.68 (i or j), 127.23 (k), 126.16 (i or j), 61.61 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b), 33.79 (d, $^{3}J_{C\text{-}P}$ = 17 Hz, e), 25.29 (d,

$^{1}J_{C\text{-}P}$ = 141 Hz, c), 22.35 (d, $^{2}J_{C\text{-}P}$ = 5 Hz, d), 16.67 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.21 ppm; IR (neat) 3025 (sp^2 C-H), 2980 (sp^3 C-H), 1701 (C=C), 1493 (aromatic C=C), 1448 (aromatic C=C), 1390 (aromatic C=C), 1236 (P=O), 1022 (C-O), 955 (P-O), 693 cm^{-1}.

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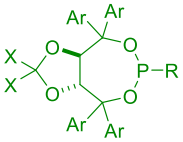
(3) Ligand Screening Data

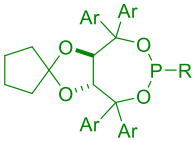
The data presented here is a series of ligands that were screened on the substrate (*E*)-**5a** as part of the initial optimizations. Preliminary screening of boranes demonstrated the superior performance of pinacolborane (pinBH) over tmdBH in forming significant amounts of hydroboration products. With catecholborane (catBH), uncatalyzed background reactions were observed. The yields for the screening data are estimated from the ^{31}P NMR analysis of the crude CAHB mixtures. The enantiomer ratios are obtained after oxidation to the corresponding alcohols via chiral HPLC analysis. BINOL-derived phosphoramidite (*R*)-**B1** was empirically chosen as the ligand of choice for the subsequent development of chemistry because it gave the highest possible enantioinduction for product **6a** as compared to others tested. The major side product in the CAHB of (*E*)-**5a** is the alkene reduction product **8a**. The minor regioisomer **7a** is formed in trace quantities.

Ligands Screened:

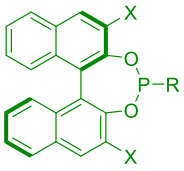


T1: X = Me, Ar = 3,5-Me_2-C_6H_3; R = O(2-Me-C_6H_4)
T2: X = Me; Ar = 3,5-Me_2-C_6H_3; R = OPh
T3: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(C_6F_5)
T4: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(3,4,5-$(OMe)_3$-C_6H_2)
T5: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(1-naphthyl)
T6: X = Me; Ar = 3,5-Me_2-C_6H_3; R = O(2-naphthyl)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

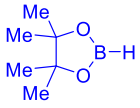


T17: Ar = Ph; R = OPh
T18: Ar = Ph; R = N(Me)Ph

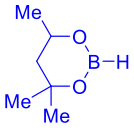


B1: X = Ph; R = N(Bn)Ph
B2: X = H; R = N(Bn)Ph
B3: X = Me; R = N(Bn)Ph
B4: X = $SiMe_3$; R = N(Bn)Ph
B5: X = H; R = OPh

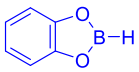
Boranes Screened:



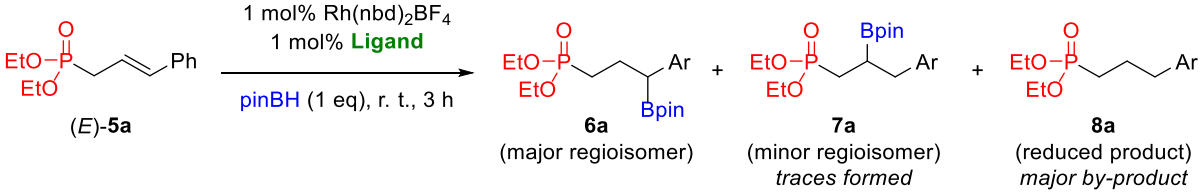
Pinacolborane (pinBH)



tmdBH



Catecholborane (catBH)

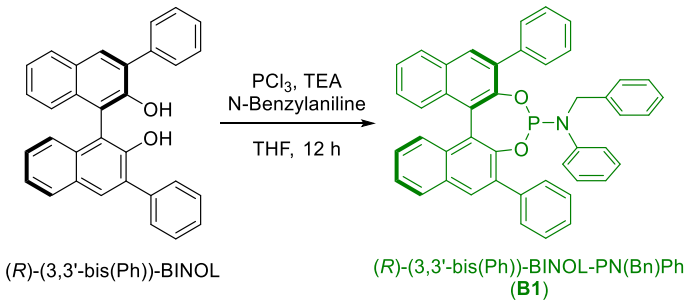


Summary of the small-scale (50 µmol substrate) screening results. (**Note:** Yields are estimated by ^{31}P NMR analysis of the crude reaction mixtures.)

Entry	Ligand Used	Unreacted (*E*)-**5a** (%)	Yield of **6a** (%)	Enantiomer Ratio of **6a**	Yield of **8a** (%)	Ratio of **6a:8a**	Total mass balance
1	**T1**	0	81	64:36	14	6:1	95
2	**T2**	0	82	48:52	9	9:1	91
3	**T3**	27	66	43:57	4	19:1	97
4	**T4**	0	68	40:60	17	4:1	85
5	**T5**	3	77	34:66	17	5:1	97
6	**T6**	0	84	29:71	7	12:1	91
7	**T7**	7	82	79:21	11	7:1	100
8	**T8**	0	91	80:20	6	15:1	97
9	**T9**	0	81	55:45	12	7:1	93
10	**T10**	0	82	29:71	13	6:1	95
11	**T11**	0	86	82:18	7	12:1	93
12	**T12**	0	87	58:42	5	17:1	92
13	**T13**	0	90	60:40	7	13:1	97
14	**T14**	0	86	61:39	8	11:1	94
15	**T15**	0	85	36:64	8	11:1	93
16	**T16**	0	89	59:41	9	10:1	98
17	**T17**	0	89	76:24	8	11:1	97
18	**T18**	0	91	59:41	6	15:1	97
19	**B1**	0	87	97:3	10	9:1	97
20	**B2**	6	86	90:10	4	22:1	96
21	**B3**	0	83	94:6	15	6:1	98
22	**B4**	0	80	95:5	17	5:1	97
23	**B5**	82	9	*Not determined*	9	1:1	100
24	**(*R*)-BINAP**	95	0	--	0	--	95
25	No catalyst	100	0	--	0	--	100

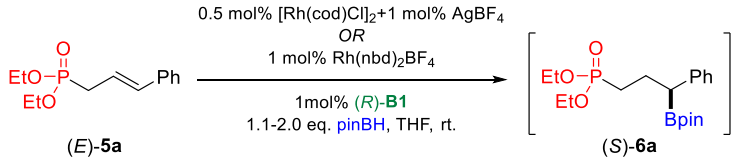
Note: Entry 25 is carried out to look for any background reaction of the substrate with pinacolborane in the absence of chiral rhodium catalyst under standard conditions.

(4) Ligand Synthesis: Preparation of BINOL-Derived Phosphoramidite B1



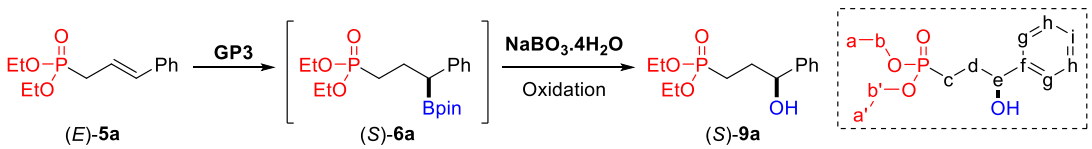
(*R*)-(3,3'-bis(Ph))-BINOL is prepared as previously reported.[10] The chiral cyclic phosphoramidite (*R*)-(3,3'-bis(Ph))-BINOL-PN(Bn)Ph (**B1**) is prepared according to previously reported procedure[11] from our lab as follows: PCl_3 (0.26 mL, 1.1 equiv, 3.00 mmol) is added dropwise to a solution of N-Benzylaniline (549 mg, 1.10 equiv, 3.00 mmol) and triethylamine (TEA; 0.70 mL, 1.85 equiv, 5.00 mmol) in dry THF (20 mL) under nitrogen at room temperature. The resultant mixture is refluxed for 6 hours, then cooled down to room temperature and eventually to -78^{o}C using a dry ice-acetone bath. A solution of (*R*)-(3,3'-bis(Ph))-BINOL (1.20 mg, 2.73 mmol, 1.00 equiv) and TEA (1.36 mL, 9.80 mmol, 3.60 equiv) in THF (20 mL) is then added drop-wise to the reaction mixture. The resultant mixture is allowed to slowly warm up to room temperature and stir for a total of *ca.* 12 hours. Afterwards, the mixture is filtered over a bed of celite, celite bed washed with THF and the combined filtrates were concentrated in vacuum. Flash chromatography over silica gel (dichloromethane/hexanes 20:80) affords the title compound (1.24 g, 70%) as a foamy white solid: TLC analysis (dichloromethane/hexanes 20:80) R_f = 0.5; $[\alpha]_D^{20}$ = -210^{o} (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, d, *J* = 12.5 Hz), 8.01 (2H, d, *J* = 8 Hz), 7.84-7.82 (2H, m), 7.73-7.72 (2H, m), 7.55-7.30 (12H, m), 7.13-7.06 (3H, m), 6.92-6.86 (5H, m), 6.18-6.15 (2H, m), 4.41 (1H, d, *J* = 15.5 Hz), 3.66 (1H, d, *J* = 15.5 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.22, 147.18, 146.98, 143.46, 143.20, 138.73, 138.31, 137.95, 135.34, 135.33, 134.68, 132.72, 132.51, 131.55, 131.11, 138.31, 137.95, 135.35, 135.33, 134.68, 132.72, 132.51, 131.55, 131.11, 130.66, 130.63, 130.49, 130.47, 130.33, 128.66, 128.61, 128.22, 128.07, 127.82, 127.79, 127.63, 127.23, 127.18, 126.70, 126.38, 125.57, 125.53, 125.47, 125.32, 124.78, 124.66, 124.19, 50.72, 50.67 ppm (**Note:** *Peak splitting in the ^{13}C NMR due to J_{C-P} was not feasible to resolve in this case because of the severity of peak overlap*.); ^{31}P NMR (162 MHz, $CDCl_3$) δ 135.99 ppm; HRMS (ESI) calculated for $C_{45}H_{32}NO_2P+Na^+$ = 672.2068, found 672.2082 *m/z.*

(5) General Procedures for Catalytic Asymmetric Hydroboration and Stereospecific Functionalizations of Chiral Secondary Benzylic Boronic Esters



General procedure for catalytic asymmetric hydroboration (GP3): Catalytic Asymmetric Hydroboration (CAHB) is carried out according to our previously reported procedure[7] as follows. In a nitrogen glovebox, a 0.05 M solution of $AgBF_4$ in THF (0.2 mL, 10 μmol, 1.0 mol%) is added to a solution of $[Rh(cod)Cl]_2$ (2.5 mg, 5.0 μmol, 1.0 mol% Rh) in dry dichloromethane (1.2 mL) in a dry 8 mL vial charged with a small teflon coated stir-bar. The resultant mixture is stirred for 10 minutes. Afterwards, the formed AgCl precipitate is filtered through a cotton packed Pasteur pipette into a new 8 mL vial. The filtrate is evaporated to dryness over 30 minutes under high vacuum in the antechamber. Following this, 1.0 mL of a stock solution of (*R*)-**B1** (Prepared by dissolving 7.2 mg of (*R*)-**B1** in 1.1 mL THF) is added to the Rh(I)-precatalyst and the result mixture is stirred for *ca.* 10 minutes. Alternatively, 1.0 mol% of $Rh(nbd)_2BF_4$ can be used in place of $[Rh(cod)Cl]_2/AgBF_4$ mixture for generating the Rh(I)-precatalyst in situ. In a separate dry 8 mL vial charged with a teflon coated stir-bar, substrate (*E*)-**5a** (254 mg, 1.00 mmol, 1.00 equiv) is weighed out and is dissolved in 1.0 mL of dry THF. To the resultant substrate solution, neat pinacolborane (0.16 mL, 1.10 mmol, 1.10 equiv) is added and the resultant mixture is stirred for 15 minutes. To this mixture of substrate and pinacolborane, the chiral rhodium catalyst (rhodium-ligand complex) is added drop-wise under vigorous stirring over *ca.* 5-10 minutes. The reaction vial is capped, taken outside the glovebox and is stirred for *ca.* 3 hours at room temperature. The disappearance of the starting material (^{31}P NMR ~ 27 ppm) indicates completion of the reaction. Afterwards, the reaction mixture is subjected to reduced pressure and the crude mixture is chromatographed on silica gel (ethyl-acetate/hexanes 3:1) to afford an inseparable mixture of the γ-boronate (major regioisomer), the β-boronate (minor regioisomer) and the alkene reduction product in approximately 88:2:10 ratio (identified via ^{31}P NMR analysis).

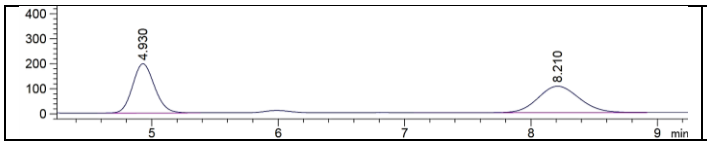
Note: The major regioisomeric boronic ester is not separable from the minor regioisomer and the reduction side products. This purified mixture of products is subjected to oxidation and the benzylic alcohol (major product) is isolated. For other transformations of the chiral boronic ester (*S*)-**6a**, the purified CAHB mixture is directly used assuming 88% purity of the boronic ester for calculations.



General procedure for tandem CAHB and Oxidation (GP4): Catalytic Asymmetric Hydroboration (CAHB) of (*E*)- or (*Z*)-**5a** (76 mg, 0.3 mmol, 1.0 equiv) is carried out according to **GP3**. After purification of CAHB mixture using silica gel chromatography, the inseparable mixture of products is subjected to oxidation as follows. The purified mixture is redissolved in THF (2 mL), $NaBO_3.4H_2O$ (231 mg, 1.50 mmol, 5.00 equiv) and H_2O (1 mL) are sequentially

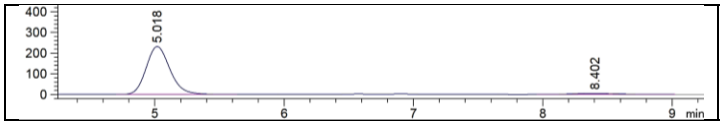
added and the resultant mixture is stirred vigorously at room temperature for *ca.* 12 hours. Afterwards, the reaction mixture is extracted with ethyl acetate (4 mL x 5) and the combined organics are dried, concentrated in vacuum and purified by silica gel chromatography (5% methanol in ethyl acetate) to afford the desired alcohol (*S*)-**9a** (67 mg, 82%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.2; $[\alpha]_D^{20}$ = -29.1° (*c* = 1.0, $CHCl_3$) [**Absolute Configuration Assignment:** *Alcohol **9a** is a previously reported[12] compound in the literature and the negative value of optical rotation obtained for **9a** is expected for the (S)-enantiomer.*]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (5H, m, aryl), 4.80 (1H, dd, *J* = 6.5, 6.0 Hz, e), 4.15-4.06 (4H, m, b+b'), 2.87 (1H, br s, OH), 2.09-2.04 (2H, m, d), 1.94-1.79 (2H, m, c), 1.33 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.04 (f), 128.69 (g or h), 127.82 (i), 125.96 (g or h), 74.02 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 61.89 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.86 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 31.99 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 22.15 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.63 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 32.83 ppm; IR (neat) 3369 (O-H), 3026 (sp^2 C-H), 2928 (sp^3 C-H), 1493 (aromatic C=C), 1452 (aromatic C=C), 1392 (aromatic C=C), 1225 (P=O), 1053 (C-O), 1021 (C-O), 956 (P-O), 700 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{21}O_4P+Na^+$ = 295.1075, found 295.1081 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.0 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

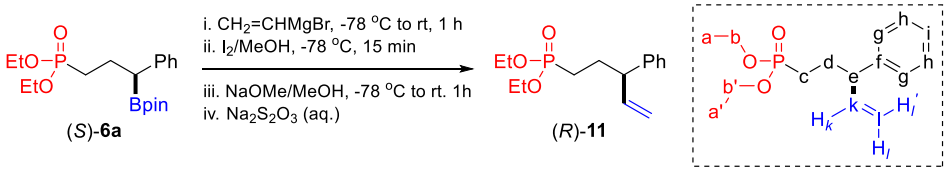


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	4.930	BB	0.1873	2383.36279	50.0002
2	8.210	VB	0.3529	2383.34546	49.9998

(b) R:S = 4:96, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by oxidation



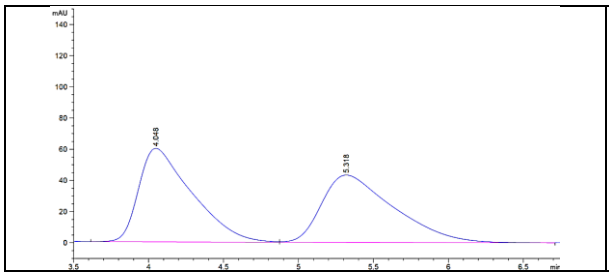
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.018	BB	0.1972	2961.21484	95.7663
2	8.402	BB	0.3608	130.91283	4.2337



General procedure for vinylation of chiral secondary benzylic boronic esters (GP5): This transformation is carried out with slight modifications of the original procedure[13] reported by Aggarwal and coworkers as follows. A solution of (*S*)-**6a** (86 mg of 88% purity containing 76 mg (*S*)-**6a**, 0.2 mmol, 1.0 equiv) in dry THF (3 mL) is cooled down to -78 °C using a dry ice-acetone bath. Vinylmagnesium bromide (1.6 mL of a 1.0 M solution; 1.6 mmol, 8.0 equiv) is added dropwise to the reaction mixture and the resultant solution is stirred at -78°C for 5 minutes. Afterwards, the cooling bath is removed, and the reaction mixture is stirred at room temperature for 1 hour. The reaction mixture is re-cooled to -78 °C and a solution of I_2 (406 mg, 1.60 mmol, 8.00 equiv) in methanol (4.0 mL) is added drop-wise to the reaction mixture and the resultant mass is stirred for 15 minutes. Following this, a solution of sodium methoxide

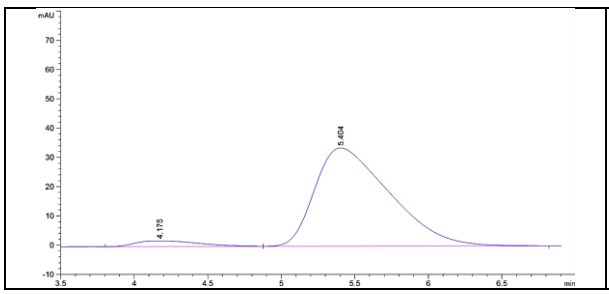
(108 mg, 2.00 mmol, 10.0 equiv.) in methanol (4.0 mL) is added dropwise and the reaction mixture is allowed to warm up to room temperature and stir for a total of 1 hour. Afterwards, the reaction mixture is concentrated to dryness under reduced pressure and 10 mL of a saturated solution of $Na_2S_2O_3$ and 20 mL of ethyl acetate are added. The mixture is vigorously agitated to dissolve all precipitates and then transferred to a separatory funnel. The organic layer is separated, and the aqueous layer is extracted with ethyl acetate (20 mL x 3). The combined organic layers are washed with brine, dried over anhydrous $MgSO_4$ and concentrated under vacuum. Flash chromatography over silica gel (3:1 ethyl acetate/hexanes) affords the desired vinylated product (*R*)-**11** (44.5 mg, 79%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -11.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (2H, m, aryl), 7.23-7.18 (3H, m, aryl), 5.98-5.89 (1H, m, k), 5.10-5.06 (2H, m, l), 4.14-4.00 (4H, m, b+b'), 7.54 (1H, dt, *J* = 7.5 Hz, e), 2.10-1.93 (2H, m, d), 1.81-1.55 (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 143.1750 (f), 141.14 (k), 128.77 (aryl), 127.72 (aryl), 126.70 (aryl), 115.20 (l), 61.60 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 50.48 (d, $^3J_{C\text{-}P}$ = 17.5 Hz, e), 28.07 (d, $^2J_{C\text{-}P}$ = 4.2 Hz, d), 23.99 (d, $^1J_{C\text{-}P}$ = 141.39 Hz, c), 16.60 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.20 ppm; IR (neat) 2982 (sp^2 C-H), 2905 (sp^3 C-H), 1636 (C=C), 1600 (C=C), 1492 (aromatic C=C), 1452 (aromatic C=C), 1391 (aromatic C=C), 1240 (P=O), 1055 (C-O), 1024 (C-O), 954 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{23}O_3P+Na^+$ = 305.1283, found 305.1284 *m/z*. Enantiomer ratio = 95:5, determined by chiral HPLC analysis (**Note:** *The enantiomers of vinylated product **11** are not separable in chiral HPLC. Instead, **11** is treated with BH_3 and H_2O_2 to obtain the alcohol derivative for chiral HPLC analysis. The data given here is for the alcohol derivative*): Stationary phase = CHIRALPAK AS-H; Mobile Phase = 20:80 Isopropanol:Hexanes; Flow rate = 2 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate of the alcohol derivative of **11**.

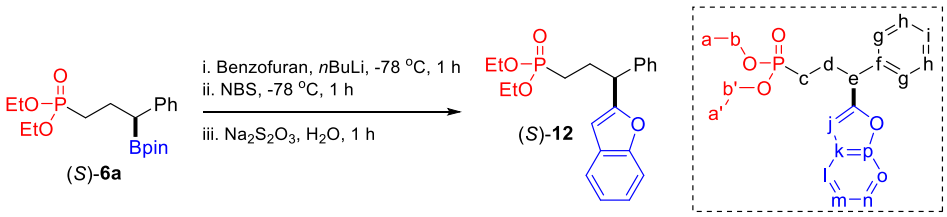


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.048	BV	0.3546	1481.53613	60.00051	50.8014
2	5.318	VB	0.4901	1434.79382	43.18307	49.1986

(b) R:S = 5:95, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by vinylation to obtain (*R*)-**11**. Hydroboration/oxidation of (*R*)-**11** is carried out to obtain the (*S*)-alcohol derivative. **Note:** *The trace below is for the (S)-enriched alcohol derivative obtained from (R)-enriched **11**.*

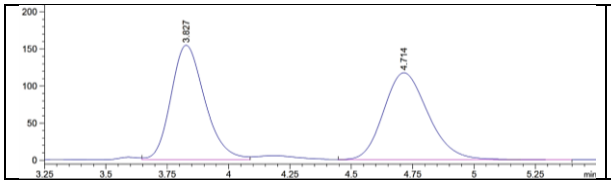


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.175	BB	0.3620	57.41818	1.90327	4.6219
2	5.404	BB	0.5232	1184.89758	33.58085	95.3781



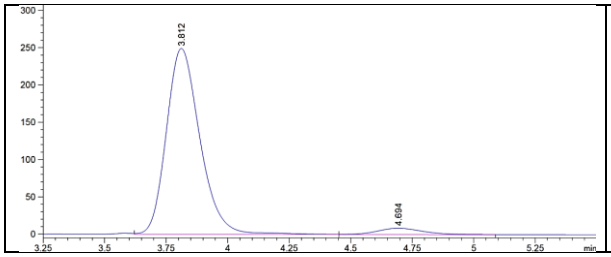
General procedure for transition metal free cross-coupling of chiral secondary benzylic boronic esters with benzofuran (GP6): This transformation is carried out using slight modifications of the original procedure[14] reported by Aggarwal and co-workers as follows. A solution of benzofuran (40 µL, 0.36 mmol, 1.45 equiv) in dry THF (1 mL) is cooled down to -78 °C using a dry ice-acetone bath and *n*BuLi (0.14 mL, 0.35 mmol, 1.41 equiv) is added drop-wise. The resultant mixture is stirred for 30 minutes at -78°C, warm to 0 °C for another 30 minutes and then cooled down to -78 °C again. A solution of (*S*)-**6a** (108 mg of 88% purity containing 95.0 mg (*S*)-**6a**, 0.25 mmol, 1.00 equiv) in dry THF (0.5 mL) is added drop-wise and the resultant mixture is stirred for 1 hour at -78 °C. A solution of NBS (60 mg, 0.34 mmol, 1.37 equiv) in THF (1 mL) is added dropwise and the resultant mixture is stirred for 1 hour at -78 °C. A saturated solution of $Na_2S_2O_3$ (3 mL) is added to the reaction and the mixture is allowed to warm up to room temperature and stirred for a total of 1 hour. Afterwards, the reaction mixture is extracted with ethyl acetate (5 mL x 4) and the combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. Flash chromatography over silica gel (ethyl acetate) affords the desired cross coupling product (*S*)-**12** (63 mg, 68%) as a light yellow oil (**Note:** *The cross-coupling product is expected to form with retention of configuration via 1,2-migration from a boron "ate" complex as demonstrated by Aggarwal.*): TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -15° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.51 (1H, d, *J* = 7.5 Hz, l or o), 7.42 (1H, d, *J* = 8.0 Hz, l or o), 7.36-7.33 (4H, m, aryl), 7.29-7.19 (3H, m, aryl), 6.51 (1H, s, j), 4.15-4.07 (5H, m, b+b'+e), 2.55 (1H, br s, d(1H)), 2.30 (1H, br s, d(1H)), 1.83-1.72 (2H, m, c), 1.34 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.98 (aryl), 155.02 (aryl), 140.92 (aryl), 128.96 (aryl), 128.20 (aryl), 127.39 (aryl), 123.82 (aryl), 122.81 (aryl), 120.78 (aryl), 111.24 (aryl), 103.17 (j), 61.81 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 46.31 (d, $^3J_{C\text{-}P}$ = 17.5 Hz, e), 27.52 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 24.16 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.47 ppm; IR (neat) 2980 (C-H), 2232, 1716, 1454, 1230 (P=O), 1024 (C-O), 957 (P-O), 726, 699, 644 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{25}O_4P$+Na^+ = 395.1388, found 395.1392 *m/z*. Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 60:40 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



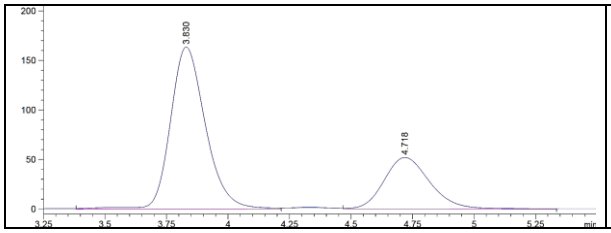
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	3.827	VV	0.1469	1480.80908	49.9775
2	4.714	VB	0.1955	1482.14026	50.0225

(b) R:S = 4:96, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by cross-coupling to form **12**.

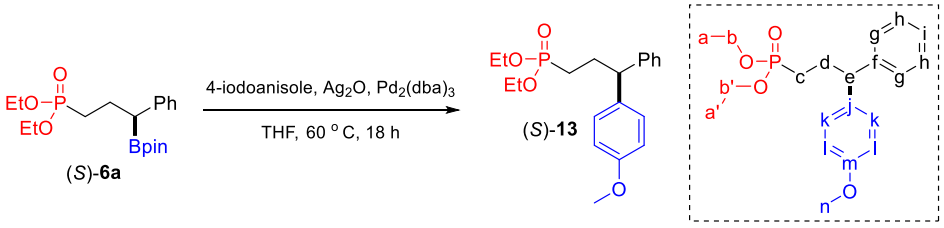


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	3.812	VV	0.1458	2368.21924	95.6756
2	4.694	VB	0.1965	107.04126	4.3244

(c) R:S = 29:71, CAHB of (*E*/*Z*)-**5a** using (*R*)-**B1** followed by cross-coupling using Crudden's Conditions with 2-iodobenzofuran to obtain **12** (**GP7**; *vide infra*)



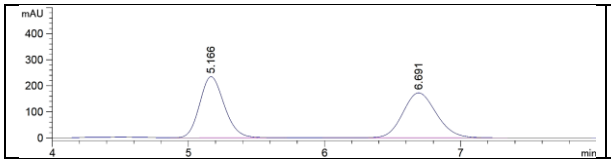
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	3.830	BV	0.1519	1626.69202	70.7161
2	4.718	VB	0.2001	673.62311	29.2839



General procedure for palladium-catalyzed cross coupling of chiral secondary benzylic boronic esters with 4-iodoanisole (GP7): This transformation is carried out with slight modifications of the original procedure[15] reported by Crudden and co-workers as follows. The chiral secondary benzylic boronic ester (*S*)-**6a** (102 mg of 88% purity containing 90.0 mg of (*S*)-**6a**, 0.23 mmol, 1.00 equiv), 4-iodoanisole (73.0 mg, 0.31 mmol, 1.35 equiv), Ag_2O (72.6 mg, 0.31 mmol, 1.35 equiv), PPh_3 (84.0 mg, 0.32 mmol) and $Pd_2(dba)_3$ (11.4 mg, 12.4 µmol, 10.7 mol% Pd) are taken up in dry THF (4 mL) in an oven dry 8 mL vial charged with borosilicate glass beads. The vial is sealed inside the glovebox, taken outside and is vigorously shaken for 18 hours in a shaker-incubator at 60 °C for 18 hours. Afterwards, the reaction mixture is filtered, and the concentrated filtrate is purified via silica gel chromatography (ethyl acetate/hexanes 3:1) to afford the desired cross-coupled product (*S*)-**13** (50 mg, 60%) as a colorless oil (**Note:** *In this procedure, triphenylphosphine oxide is a major side product and it overlaps significantly with the cross-coupling product (S)-**13**. Separating (S)-**13** from triphenylphosphine oxide and the protodeborylated side product isn't trivial and traces of triphenylphosphine oxide peaks can be seen in the NMR's of (S)-**13**.*): TLC analysis (ethyl acetate/hexanes 3:1) R_f = 0.4; $[\alpha]_D^{20}$ = +6.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30-7.28 (2H, m, h), 7.23 (2H, d, *J* = 7.25 Hz, g), 7.20-7.18 (1H, t, *J* = 7.25 Hz, i), 7.16 (2H, d, *J* = 8.65 Hz, k), 6.85 (2H, d, *J* = 8.65 Hz, l), 4.12-4.03 (4H, m, b+b'), 3.90 (1H, t, *J* = 7.9 Hz, e), 3.78 (3H, s, n), 2.36-2.29 (2H, m, d), 1.75-1.65 (2H, m, c), 1.31 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.26 (m), 144.37 (f), 136.07 (j), 128.90 (k),128.71 (g), 127.87 (h), 126.49 (i), 144.10 (l), 61.63 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 55.36 (n), 51.11 (d, $^3J_{C\text{-}P}$ = 18 Hz, e), 28.56 (d, $^2J_{C\text{-}P}$ = 4.0 Hz, d), 24.50 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.62 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.11 ppm; IR (neat) 2985 (C-H), 1458 (aromatic C=C), 1247 (P=O), 1025 (C-O), 959 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{27}O_4P+Na^+$ = 385.1545. found 385.1554 *m/z*. Enantiomer ratio = 77:23, determined by chiral HPLC analysis:

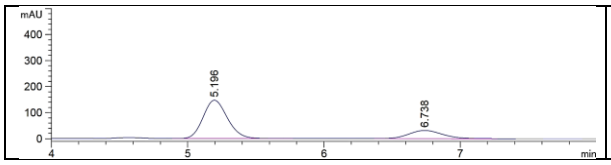
Stationary phase = CHIRALPAK IC; Mobile Phase = 40:60 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



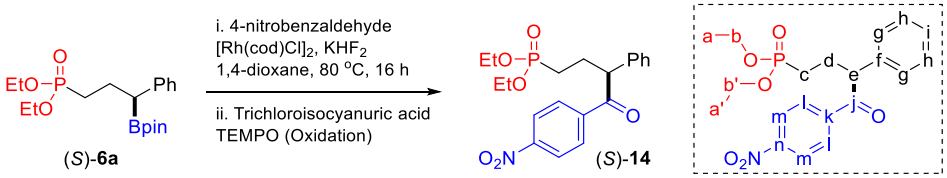
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.166	VB	0.1944	2938.63208	49.9252
2	6.691	BB	0.2658	2947.43970	50.0748

(b) R:S = 23:77, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by cross-coupling with 4-iodoanisole to form **13**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.196	VB	0.1922	1834.83081	77.4636
2	6.738	BB	0.2643	533.80627	22.5364

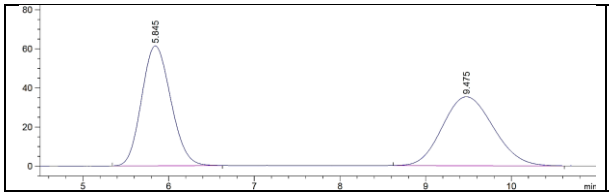
Absolute configuration assignment: The chiral boronic ester (*S*)-**6a** (102 mg of 88% purity containing 90.0 mg of (*S*)-**6a**, 0.23 mmol, 1.00 equiv) is subjected to cross-coupling under Crudden's Conditions (**GP7**) with 2-iodobenzofuran (76.0 mg, 0.31 mmol, 1.35 equiv) to afford (*S*)-**12** (47 mg, 55%; 71:29 er). Matching the HPLC traces of **12** formed from (*S*)-**6a** with **GP6** and **GP7** (see HPLC traces under GP6) shows that **12** is formed with predominant retention of stereochemistry using **GP7**. Hence, **GP7** with (*S*)-**6a** occurs with retention of stereochemistry and the configuration of (*S*)-**13** is assigned based on this analogy.



General procedure for rhodium-catalyzed cross-coupling of chiral secondary benzylic boronic esters with 4-nitrobenzaldehyde/oxidation (GP8): The first step of coupling is carried out according to Tang's modification[16] of the original procedure[17] reported by Aggarwal and co-workers as follows. The chiral secondary benzylic boronic ester (*S*)-**6a** (108 mg of 88% purity containing 95.0 mg of (*S*)-**6a**, 0.25 mmol, 1.00 equiv), 4-nitrobenzaldehyde (50.0 mg, 0.33 mmol, 1.32 equiv) and $[Rh(cod)Cl]_2$ (5.0 mg, 10 μmol, 4 mol%) are taken up in deoxygenated dioxane (2.5 mL) in an oven dry 8 mL vial charged with a stir-bar inside the glovebox. The resultant mixture is stirred vigorously for 10 minutes. Following this, a solution of KHF_2 in deoxygenated H_2O (80 mg KHF_2 dissolved in 1 mL H_2O; 0.35 mL, 0.36 mmol, 1.43 eq) is added drop-wise to the above solution and the resultant mixture is sealed, taken outside the glovebox and is stirred vigorously at 80 °C for 16 hours. Afterwards, the reaction mixture is cooled down to room temperature and saturated aqueous NH_4Cl solution (2 mL) is added and the mixture is extracted with ethyl acetate (3 mL x 5). The combined organics are washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. Flash chromatography over silica gel (1% methanol in ethyl acetate) affords the alcohol product as a sticky liquid (84 mg, 82%) as a mixture of diastereomers. To a cooled (0 °C) solution of the diastereomeric alcohols (84 mg, 0.2 mmol) and trichloroisocyanuric acid (47 mg, 0.2 mmol) in

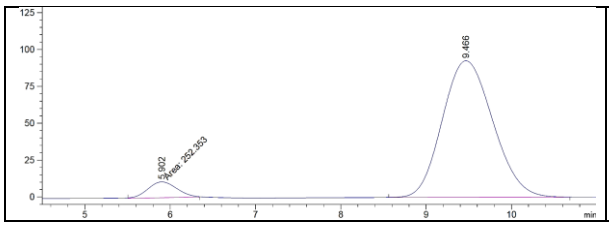
dichloromethane (1.0 mL), TEMPO (6 mg, 20 mol%) is added and the resultant mixture is stirred at room temperature for 2 hours. Afterwards, the reaction mixture is diluted with dichloromethane, washed with water and brine and dried over anhydrous Na_2SO_4. Flash chromatography over silica gel (ethyl acetate) affords the ketone product (*S*)-**14** as a sticky liquid (75 mg, 74% yield over 2 steps): TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +78° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (2H, d, *J* = 9.0 Hz, l or m), 8.09 (2H, d, *J* = 9.0 Hz, l or m), 7.41-7.21 (5H, m, g+h+i), 4.78 (1H, t, *J* = 7.25 Hz, e), 4.17-4.03 (4H, m, b+b'), 2.56-2.40 (1H, m, d(1H)), 2.22-2.10 (1H, m, d(1H)), 1.86-1.65 (2H, m, c), 1.32 (3H, t, *J* = 7.0 Hz, a or a'), 1.31 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.92 (j), 150.24 (n), 141.29 (k), 137.80 (f), 129.92 (l), 129.63 (g or h), 128.49 (g or h), 128.04 (i), 123.93 (m), 61.85 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.81 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 54.19 (d, $^3J_{C\text{-}P}$ = 12.5 Hz, e), 26.68 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 23.31 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.26 ppm; IR (neat) 2981 (C-H), 1687 (C=O), 1524 (N-O), 1344 (N-O), 1223 (P=O), 1052 (C-O), 1022 (C-O), 946 (P-O), 700 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{24}NO_6P+Na^+$ = 428.1239, found 428.1241 *m/z*. Enantiomer ratio = 6:94, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 75:25 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

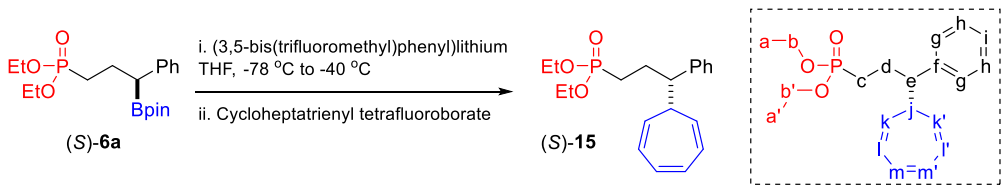


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.845	BB	0.3725	1454.32874	49.9927
2	9.475	BB	0.6524	1454.75562	50.0073

(b) R:S = 6:94, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by cross-coupling with 4-nitrobenzaldehyde, followed by oxidation to yield (*S*)-**14**



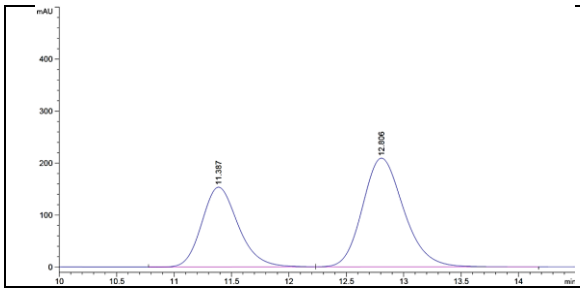
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.902	MM	0.3924	252.35327	6.1992
2	9.466	BB	0.6519	3818.41797	93.8008



General procedure for S$_E$2 reaction of boron-ate complexes of chiral secondary benzylic boronic esters with electrophiles (GP9): This transformation is carried out with slight modifications of the original protocol[18] developed by Aggarwal and co-workers as follows. To a solution of 3,5-bis(trifluoromethyl)bromobenzene (89 mg, 0.3 mmol, 1.5 equiv) in dry THF (3 mL) at -78 °C is added *n*BuLi in hexanes (2.5M solution; 0.12 mL, 0.3 mmol, 1.5 equiv) dropwise. The resultant solution is stirred for 1 hour at -78 °C. A solution of (*S*)-**6a** (86 mg of

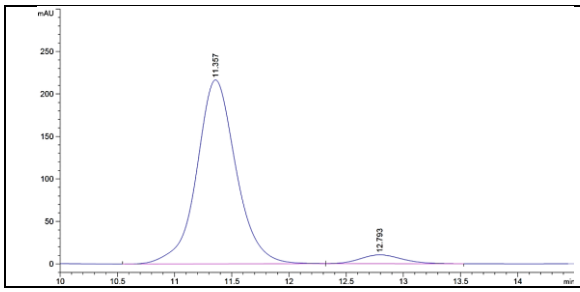
88% purity containing 76 mg (*S*)-**6a**, 0.2 mmol, 1.0 equiv) in dry THF (1 mL) is added drop-wise to the solution of (3,5-bis(trifluoromethyl)phenyl)lithium at -78 ºC. The resultant mixture is stirred for 30 minutes in the dry ice-acetone bath (-78 ºC). Following this, the dry ice-acetone bath is replaced by a dry ice-acetonitrile bath (-40 ºC) and the resultant mixture stirred for another 30 minutes. At this point, solid cycloheptatrienyl tetrafluoroborate (71 mg, 0.4 mmol, 2.0 equiv) is added to the reaction mixture at room temperature and the reaction mixture stirred vigorously for 1 hour. A saturated aqueous solution of $NaHCO_3$ is added and the reaction mixture is extracted with ethyl acetate (20 mL x 3). The combined organics are washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Flash chromatography over silica gel (4:1 ethyl acetate/hexanes) affords the desired product (*S*)-**15** (66 mg, 95%) as a colorless oil: TLC analysis (ethyl acetate) R_f = 0.6; $[\alpha]_D^{20}$ = -64º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (2H, m, aryl), 7.25-7.21 (1H, m, aryl), 7.14-7.12 (2H, m, aryl), 6.72-6.23 (2H, m, m+m'), 6.28 (1H, dd, *J* = 9.5, 5.5 Hz, l or l'), 6.03 (1H, dd, *J* = 9.5, 5.5 Hz, l or l'), 5.39 (1H, dd, *J* = 9.5, 6.0 Hz, k or k'), 4.98 (1H, dd, *J* = 9.5, 6.0 Hz, k or k'), 4.12-3.96 (4H, m, b+b'), 2.90 (1H, td, *J* = 11, 3.5 Hz, e), 2.40-2.30 (1H, m, d(1H)), 1.86-1.73 (2H, m, d(1H)+j), 1.63-1.45 (2H, m, c), 1.29 (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 142.59 (f), 131.11 (m or m'), 130.82 (m or m'), 128.76 (aryl), 128.56 (aryl), 126.89 (aryl), 125.30 (l or l'), 124.81 (k or k'), 124.63 (k or k'), 124.42 (l or l'), 61.56 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 48.80 (d, $^3J_{C\text{-}P}$ = 16.5 Hz, e), 44.55 (j), 27.63 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 23.50 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.57 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.30 ppm; IR (neat) 2981 (C-H), 1584 (C=C), 1494 (aromatic C=C), 1453 (aromatic C=C), 1391 (aromatic C=C), 1237 (P=O), 1054 (C-O), 1022 (C-O), 959 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{27}O_3P+Na^+$ = 369.1596, found 369.1595 *m/z*. Enantiomer ratio = 95:5, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 10:90 Isopropanol:Hexanes; Flow rate = 1.0 mL/min; HPLC UV Detector λ = 210 nm, 25 ºC. HPLC traces:

(a) Racemate

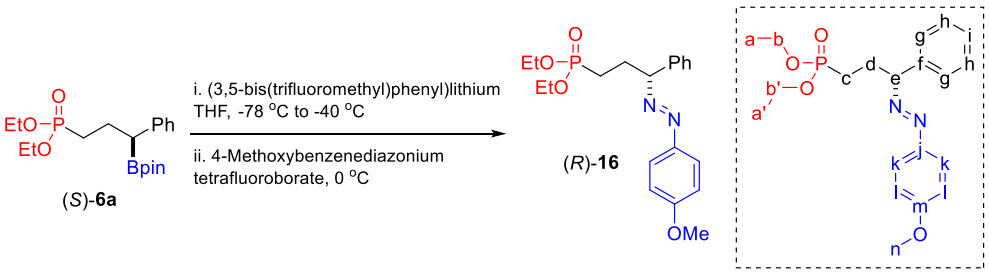


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.387	BV	0.3407	3401.77856	153.40106	39.3958
2	12.806	VB	0.3855	5233.10303	209.06151	60.6042

(b) R:S = 95:5, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by S_E2 to form (*S*)-**15**.

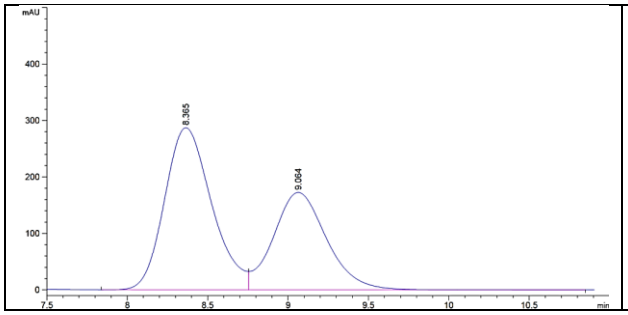


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.357	BB	0.3613	5162.74805	216.40097	95.2596
2	12.793	BB	0.3845	256.91110	10.28351	4.7404



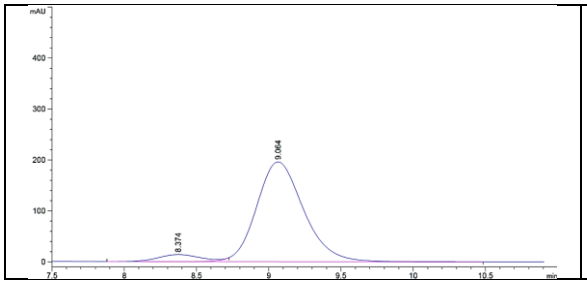
S_E2 reaction with 4-methoxybenzenediazonium tetrafluoroborate: This transformation is carried according to **GP9** with few changes as follows. To a solution of 3,5-bis(trifluoromethyl)bromobenzene (89 mg, 0.3 mmol, 1.5 equiv) in dry THF (3 mL) at -78 °C is added *n*BuLi in hexanes (2.5M solution; 0.12 mL, 0.3 mmol, 1.5 equiv) dropwise. The resultant solution is stirred for 1 hour at -78 °C. A solution of (*S*)-**6a** (86 mg of 88% purity containing 76 mg (*S*)-**6a**, 0.2 mmol, 1.0 equiv) in dry THF (1 mL) is added drop-wise to the solution of (3,5-bis(trifluoromethyl)phenyl)lithium at -78 °C. The resultant mixture is stirred for 30 minutes in the dry ice-acetone bath (-78 °C). Following this, the dry ice-acetone bath is replaced by a dry ice-acetonitrile bath (-40 °C) and the resultant mixture stirred for another 30 minutes. Afterwards the dry ice-acetonitrile bath is removed, and the reaction flask is covered with an aluminum foil and placed in an ice-bath. The lights inside the fume hood are turned off and solid 4-methoxybenzenediazonium tetrafluoroborate (89 mg, 0.4 mmol, 2.0 equiv) is added directly to the reaction mixture under vigorous stirring. The reaction mixture is stirred for 5 minutes at 0°C and is allowed to warm up to room temperature over 30 minutes. A saturated aqueous solution of $NaHCO_3$ is added and the reaction mixture is extracted with ethyl acetate (20 mL x 3). The combined organics are washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure in the rotovap (water bath temperature set at 35 °C). Flash chromatography over silica gel (4:1 ethyl acetate/hexanes) affords the desired product (*R*)-**16** (43 mg, 55%) as a bright orange liquid (**Note:** *The diazo product (R)-**16** is highly light and heat sensitive. Care is taken to rigorously exclude light from the point the electrophile is added to the reaction mixture and through all work-up and purification procedures. The temperature of the water bath in rotovap is kept at 35 °C to concentrate the product. The product decomposed in chloroform within minutes, however, it is found to be stable in dichloromethane, methanol and isopropanol. NMR data for this compound is hence recorded using deuterated dichloromethane.*): TLC analysis (ethyl acetate) R_f = 0.4; $[\alpha]_D^{20}$ = -9.75° (*c* = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75 (2H, d, *J* = 9.0 Hz, k), 7.51 (2H, d, *J* = 7.3 Hz, g), 7.42 (2H, dd, *J* = 7.7, 7.3 Hz, h), 7.34 (1H, t, *J* = 7.3 Hz, i), 6.99 (2H, d, *J* = 9.0 Hz, l), 4.71 (1H, t, *J* = 7.1 Hz, e), 4.13-4.01 (4H, m, b+b'), 3.88 (3H, s, n), 2.54-2.33 (2H, m, d), 1.78-1.62 (2H, m, c), 1.31 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (175 MHz, CD_2Cl_2) δ 161.86 (m), 146.07 (j), 140.12 (f), 128.64 (h), 127.88 (g), 127.64 (i), 124.19 (k), 113.95 (l), 81.85 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 61.49 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 55.53 (n), 28.44 (d, $^2J_{C\text{-}P}$ = 3.5 Hz, d), 22.38 (d, $^1J_{C\text{-}P}$ = 141.5 Hz, c), 16.25 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, CH_2Cl_2) δ 30.96 ppm; IR (neat) 2981 (aromatic C-H), 2832 (aliphatic C-H), 1506 (N=N stretch), 1441 (aromatic C=C), 1391 (aromatic C=C), 1230 (P=O), 1141 (C-N), 1023 (C-O), 959 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{27}N_2O_4P+Na^+$ = 413.1606, found 413.1602 *m/z*. Enantiomer ratio = 95:5, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 30:70 Isopropanol:Hexanes; Flow rate = 1.0 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



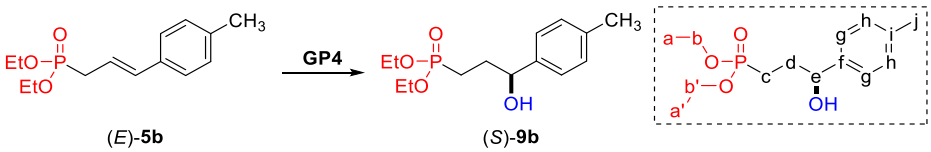
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.365	BV	0.3134	5843.08154	287.09207	59.5381
2	9.064	VB	0.3505	3970.94214	172.56721	40.4619

(b) R:S = 95:5, CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by S_E2 to form (*R*)-**16**.



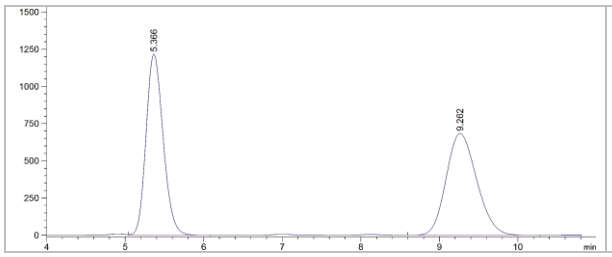
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.374	BV E	0.3090	274.26266	13.88309	5.8206
2	9.064	VB R	0.3476	4437.70410	196.00299	94.1794

(6) Preparation of chiral secondary alcohols via sequential CAHB/Oxidation



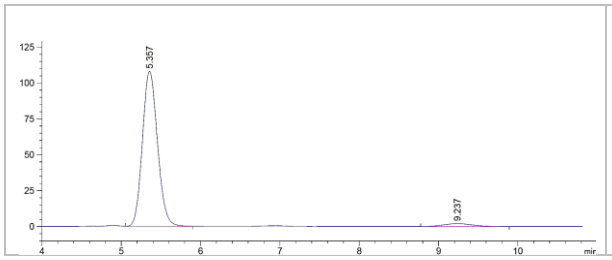
Preparation of chiral secondary benzylic alcohol (*S*)-9b: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*/*Z*)-**5b** (81 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9b** (72 mg, 84%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -37° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (2H, d, *J* = 8.0 Hz, g), 7.13 (2H, d, *J* = 8.0 Hz, h), 4.67 (1H, t, *J* = 6.0 Hz, e), 4.11-3.95 (4H, m, b+b'), 3.57 (1H, br s, OH), 2.32 (3H, s, j), 2.04-1.92 (2H, m, d), 1.90-1.67 (2H, m, c), 1.28 (3H, t, *J* = 7.0 Hz, a or a'), 1.27 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.26 (f), 137.12 (i), 129.14 (h), 125.88 (g), 73.52 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.71 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.68 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 31.86 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.96 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 21.18 (j), 16.51 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a or a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.93 ppm; IR (neat) 3358 (O-H), 2981 (aromatic C-H), 2927 (aliphatic C-H), 1513 (aromatic C=C), 1441 (aromatic C=C), 1392 (aromatic C=C), 1226 (P=O), 1058 (C-O), 1019 (C-O), 954 (P-O), 816, 524 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1242 *m/z*. Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

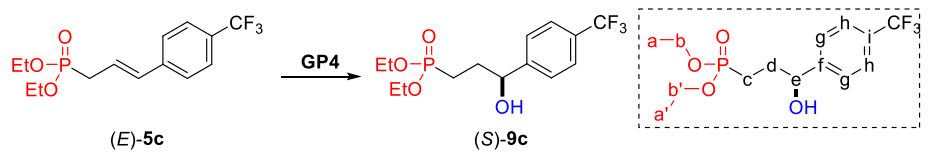


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.366	VB	0.2350	1.83563e4	49.9344
2	9.262	VB	0.4214	1.84046e4	50.0656

(b) R:S = 3:97, CAHB of (*E*)-**5b** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9b**

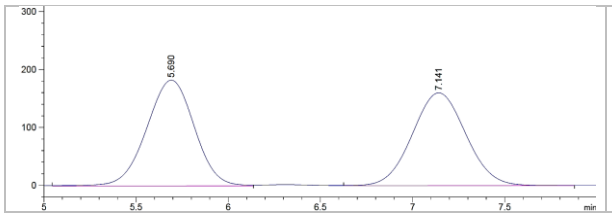


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.357	VB	0.2048	1425.46387	96.5603
2	9.237	BB	0.3767	50.77775	3.4397



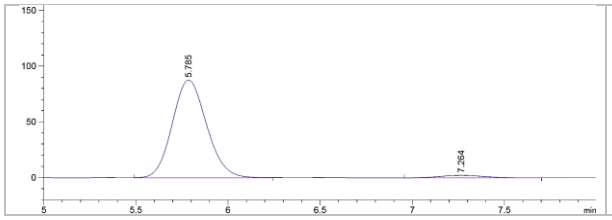
Preparation of chiral secondary benzylic alcohol (*S*)-9c: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5c** (81.0 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9c** (67 mg, 78%) as a colorless oil: TLC analysis (1% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -22° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (2H, d, *J* = 8.2 Hz, h), 7.46 (2H, d, *J* = 8.2 Hz, g), 4.81 (1H, t, *J* = 6.0 Hz, e), 4.30 (1H, br s, OH), 4.11-3.96 (4H, m, b+b'), 2.08-1.75 (4H, m, c+d), 1.28 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.49 (f), 129.70 (q, $^2J_{C\text{-}F}$ = 32.31 Hz, i), 126.27 (g), 125.45 (q, $^3J_{C\text{-}F}$ = 4.0 Hz, h), 124.33 (q, $^1J_{C\text{-}F}$ = 272 Hz, CF_3), 72.88 (d, $^3J_{C\text{-}P}$ = 14 Hz, e), 61.99 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.94 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 32.06 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.83 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.53 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.64 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.48 ppm; IR (neat) 3332 (O-H), 2986 (aromatic C-H), 2932 (aliphatic C-H), 1442 (aromatic C=C), 1413 (aromatic C=C), 1323 (C-F), 1226 (P=O), 1161, 1120, 1064 (C-O), 1016 (C-O), 959 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{20}F_3O_4P+Na^+$ = 363.0949, found 363.0950 *m/z*; Enantiomer ratio = 97:3, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 20:80 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

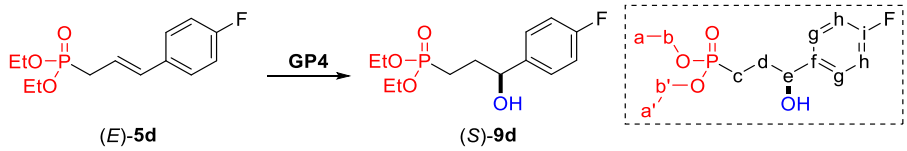


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.690	VV	0.2817	3299.05396	50.3856
2	7.141	VB	0.3156	3248.56299	49.6144

(b) R:S = 3:97, CAHB of (*E*)-**5c** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9c**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.785	VB	0.2017	1140.88721	96.7109
2	7.264	BB	0.2570	38.80151	3.2891

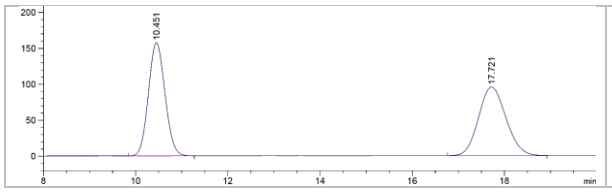


(*E*)-**5d** (*S*)-**9d**

Preparation of chiral secondary benzylic alcohol (*S*)-9d: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5d** (82 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9d** (62 mg, 71%) as a colorless oil: TLC analysis (1% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -34° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m, g), 7.02-6.97 (2H, m, h), 4.70 (1H, t, *J* = 6.0 Hz, e), 4.11-3.95 (4H, m, b+b'), 3.91 (1H, br s, OH), 2.02-1.90 (2H, m, d), 1.88-1.67 (2H, m, c), 1.28 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.21 (d, $^1J_{C\text{-}F}$ = 245 Hz, i), 140.11 (d, $^4J_{C\text{-}P}$ = 3.0 Hz, f), 127.57 (d, $^3J_{C\text{-}F}$ = 8.0 Hz, g), 115.28 (d, $^2J_{C\text{-}F}$ = 21.3 Hz, h), 72.97 (d, $^3J_{C\text{-}P}$ = 15.25 Hz,

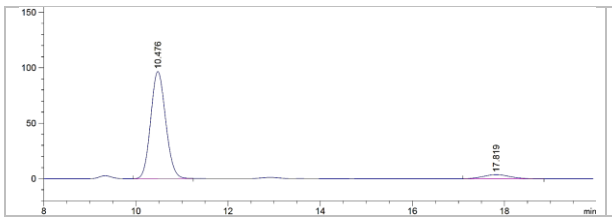
e), 61.85 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.82 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 32.07 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 21.94 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.54 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.75 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.41 ppm; IR (neat) 3356 (O-H), 2982 (aromatic C-H), 2931 (aliphatic C-H), 1508 (C-F), 1218 (P=O), 1054 (C-O), 1021 (C-O), 957 (P-O), 833 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{20}FO_4P+Na^+$ = 313.0981, found 313.0983 *m/z*; Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 20:80 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.451	BB	0.3889	3926.03564	49.8717
2	17.721	BB	0.6473	3946.23096	50.1283

(b) R:S = 6:94, CAHB of (*E*)-**5d** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9d**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	10.476	BB	0.3517	2183.74219	93.6814
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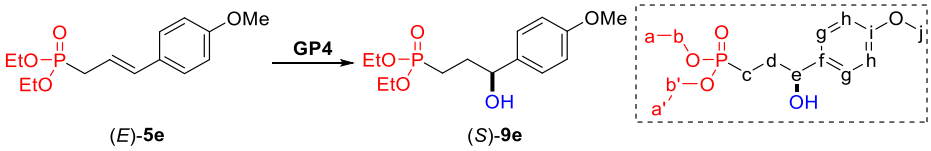
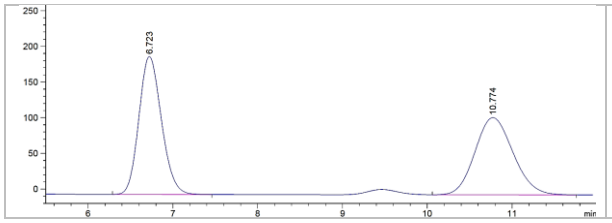


(*E*)-**5e** (*S*)-**9e**

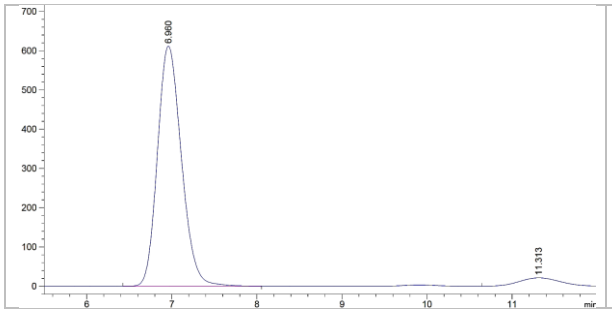
Preparation of chiral secondary benzylic alcohol (*S*)-9e: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5e** (85 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9e** (70 mg, 77%) as a colorless oil: TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -26° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (2H, d, *J* = 8.5 Hz, g), 6.88 (2H, d, *J* = 8.5 Hz, h), 4.70 (1H, t, *J* = 6.25 Hz, e), 4.14-3.99 (4H, m, b+b'), 3.81 (3H, s, j), 3.05 (1H, br s, OH), 2.09-1.94 (2H, m, d), 1.93-1.69 (2H, m, c), 1.31 (6H, t, *J* = 3.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.22 (i), 136.27 (f), 127.21 (g), 114.01 (h), 73.57 (d, $^{3}J_{C\text{-}P}$ = 15.5 Hz, e), 61.83 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.80 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.46 (j), 31.96 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 22.15 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.61 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.85 ppm; IR (neat) 3361 (O-H), 2982 (aromatic C-H), 2836 (aliphatic C-H), 1511, 1442 (aromatic C=C), 1392 (aromatic C=C), 1241 (P=O), 1020 (C-O), 956 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_5P+Na^+$ = 325.1181, found 325.1183 *m/z*; Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

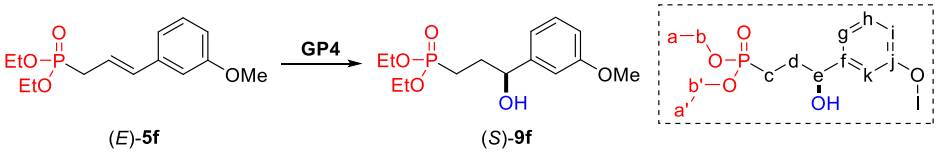


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.723	BB	0.2864	3569.89966	51.3988
2	10.774	VB	0.4850	3375.58862	48.6012

(b) R:S = 6:94, CAHB of (*E*)-**5e** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9e**

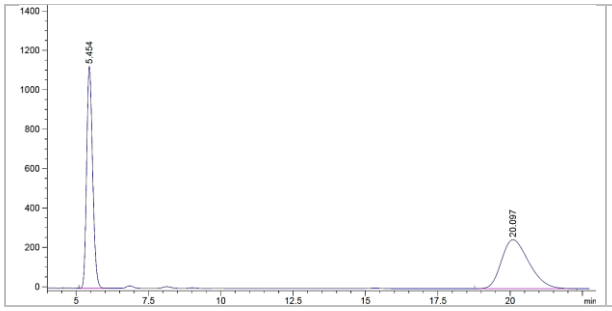


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.960	BB	0.3041	1.19628e4	94.3132
2	11.313	BB	0.5225	721.31665	5.6868



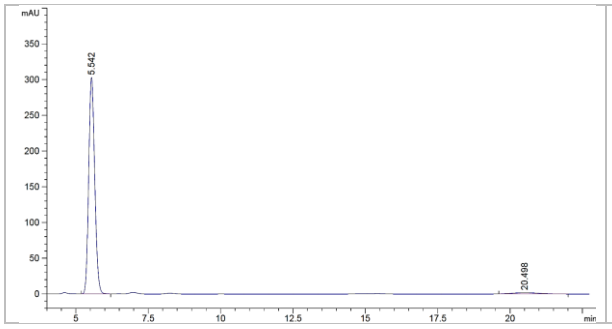
Preparation of chiral secondary benzylic alcohol (*S*)-6f: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5f** (85 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9f** (76 mg, 83%) as a colorless oil: TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -21° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (1H, dd, *J* = 8.25, 7.68 Hz, h), 6.93-6.91 (2H, m, g+k), 6.82-6.79 (1H, m, i), 4.73 (1H, t, *J* = 6.0 Hz, e), 4.13-3.99 (4H, m, b+b'), 3.81 (3H, s, l), 3.33 (1H, br s, OH), 2.08-1.95 (2H, m, d), 1.93-1.72 (2H, m, c), 1.30 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.92 (j), 149.91 (f), 129.63 (h), 118.29 (g), 113.17 (i), 111.45 (k), 73.74 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 61.86 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.82 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 55.39 (l), 31.94 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.02 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.60 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.87 ppm; IR (neat) 3352 (O-H), 2982 (aromatic C-H), 2837 (aliphatic C-H), 1600, 1486 (aromatic C=C), 1436 (aromatic C=C), 1226 (P=O), 1020 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_5P+Na^+$ = 325.1181, found 325.1184 *m/z*. Enantiomer ratio = 98:2, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

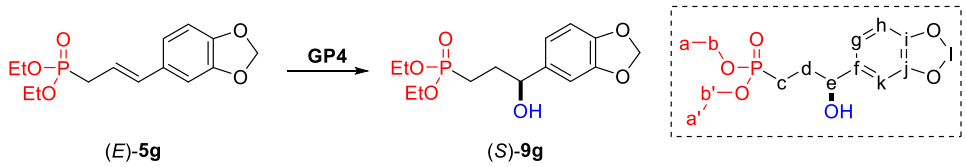


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.454	VB	0.2230	1.62339e4	49.7841
2	20.097	BB	1.0219	1.63747e4	50.2159

(b) R:S = 2:98, CAHB of (*E*)-**5f** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9f**



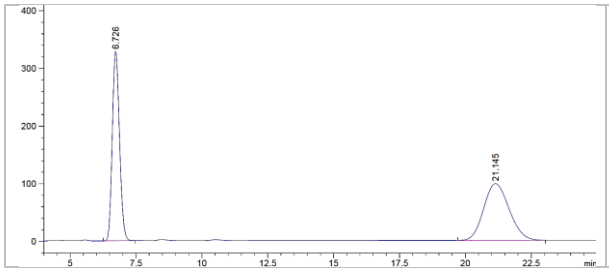
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.542	BB	0.2244	4372.33838	97.5272
2	20.498	BB	0.7239	110.86235	2.4728



(*E*)-**5g** (*S*)-**9g**

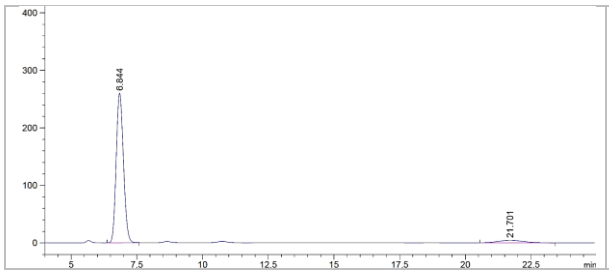
Preparation of chiral secondary benzylic alcohol (*S*)-6g: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5g** (75.0 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9g** (55 mg, 70%) as a colorless oil: TLC analysis (5% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -39° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (1H, d, *J* = 1.25 Hz, k), 6.77-6.71 (2H, m, g+h), 5.92 (2H, s, l), 4.62 (1H, t, *J* = 6.0 Hz, e), 4.13-4.96 (4H, m, b+b'), 3.62 (1H, br s, OH), 2.02-1.62 (4H, m, c+d), 1.28 (3H, t, *J* = 7.0 Hz, a or a'), 1.27 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.85 (i or j), 146.93 (i or j), 138.38 (f), 119.30 (g), 108.13 (h), 106.48 (k), 101.06 (l), 73.54 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.79 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.75 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 31.96 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.99 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.54 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.81 ppm; IR (neat) 3336 (O-H), 2982 (aromatic C-H), 2903 (aliphatic C-H), 1486 (aromatic C=C), 1440 (aromatic C=C), 1234 (P=O), 1020 (C-O), 957 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{21}O_6P+Na^+$ = 339.0973, found 339.0975 *m/z*; Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

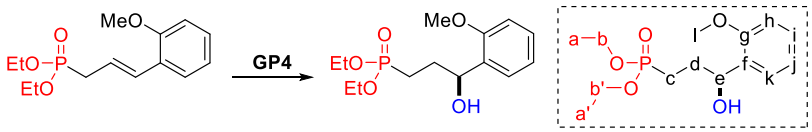


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.726	BB	0.2981	6244.61572	48.5713
2	21.145	BB	1.0529	6611.98193	51.4287

(b) R:S = 6:94, CAHB of (*E*)-**5g** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9g**



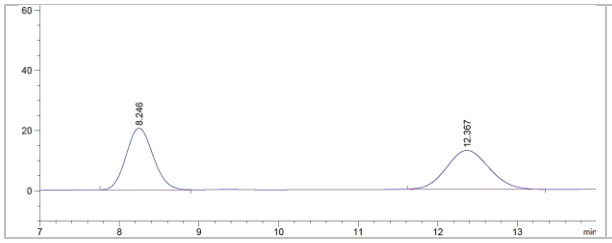
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.844	BB	0.2993	4980.82617	94.4086
2	21.701	BB	0.8190	294.99234	5.5914



(*E*)-**5h** (*S*)-**9h**

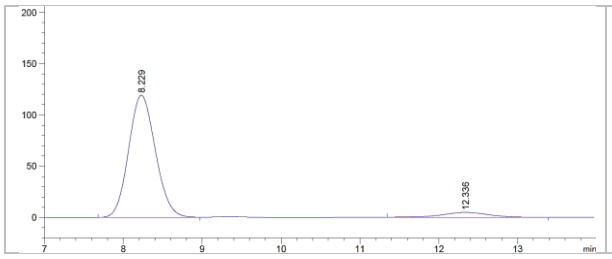
Preparation of chiral secondary benzylic alcohol (*S*)-9h: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: CAHB carried out for 12 hours), the substrate (*E*)-**5h** (71.0 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9h** (54 mg, 72%) as a colorless oil: TLC analysis (4% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -29^o (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (1H, dd, *J* = 7.5, 1.5 Hz, aryl), 7.23 (1H, td, *J* = 8.0, 1.5 Hz), 6.95 (1H, td, *J* = 7.5, 1.0 Hz, aryl), 6.85 (1H, d, *J* = 8.25 Hz, aryl), 4.93 (1H, t, *J* = 6.0 Hz, e), 4.15-3.99 (4H, m, b+b'), 3.82 (3H, s, l), 3.41 (1H, br s, OH), 2.12-1.71 (4H, m, c+d), 1.30 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.37 (g), 131.85 (f), 128.47 (aryl), 126.97 (aryl), 120.84 (aryl), 110.50 (aryl), 70.09 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 61.67 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 55.34 (l), 30.05 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.17 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.55 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.22 ppm; IR (neat) 3367 (O-H), 2981 (aromatic C-H), 2907 (aliphatic C-H), 1489 (aromatic C=C), 1464 (aromatic C=C), 1439 (aromatic C=C), 1235 (P=O), 1048 (C-O), 1022 (C-O), 957 (P-O), 754, 729 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_5P$+Na^+ = 325.1181, found 325.1183 *m/z*; Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 ^{o}C. HPLC traces:

(a) Racemate

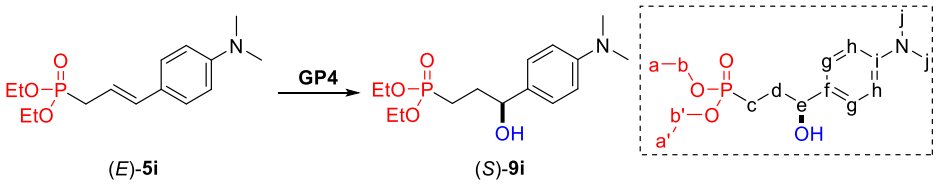


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.246	BB	0.3683	485.50961	50.2144
2	12.367	BB	0.5805	481.36310	49.7856

(b) R:S = 6:94, CAHB of (*E*)-**5h** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9h**



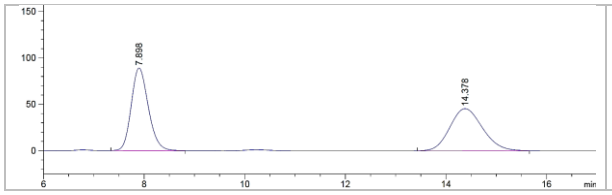
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.229	BB	0.3673	2809.95459	93.5870
2	12.336	BB	0.6071	192.54959	6.4130



(*E*)-**5i** (*S*)-**9i**

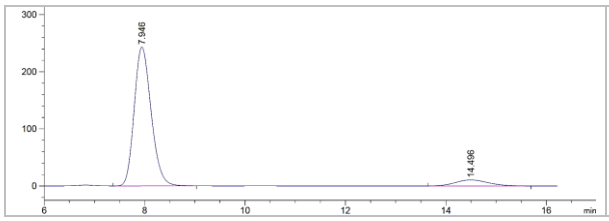
Preparation of chiral secondary benzylic alcohol (*S*)-9i: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used and CAHB carried out for 12 hours), the substrate (*E*)-**5i** (74.0 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9i** (53 mg, 67%) as a colorless oil: TLC analysis (5% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -22° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (2H, d, *J* = 8.75 Hz, g), 6.70 (2H, d, *J* = 8.75 Hz, g), 4.61 (1H, dd, *J* = 7.0, 5.5 Hz, e), 4.14-3.98 (4H, m, b+b'), 2.93 (7H, s, j+OH), 2.08-1.66 (4H, m, c+d), 1.30 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.35 (i), 131.98 (f), 126.94 (g), 112.71 (h), 73.77 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 61.67 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.65 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 40.81 (j), 31.62 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.20 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.57 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.94 ppm; IR (neat) 3351 (O-H), 2980 (aromatic C-H), 2904 (aliphatic C-H), 1617, 1522, 1225 (P=O), 1054 (C-O/C-N), 1022 (C-O/C-N), 945 (P-O), 815, 728 cm^{-1}; Note: *HRMS analysis was not successful on alcohol **9i** in detecting the molecular ion. The structure proof of **9i** is based on the NMR and IR analysis only.* Enantiomer ratio = 92:8, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

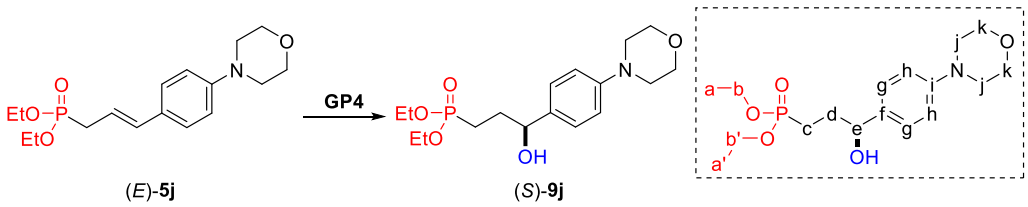


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.898	BB	0.3643	2101.46460	50.6734
2	14.378	BB	0.6987	2045.61108	49.3266

(b) R:S = 8:92, CAHB of (*E*)-**5i** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9i**

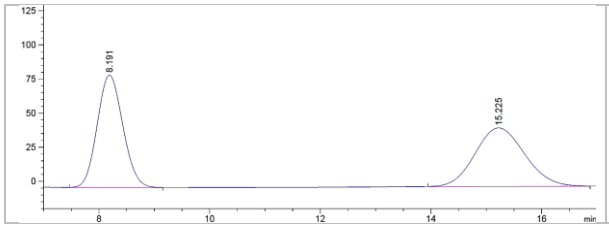


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.946	VB	0.3635	5700.29199	92.1905
2	14.496	BB	0.6915	482.87637	7.8095



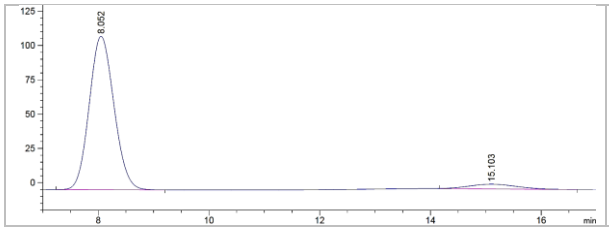
Preparation of chiral secondary benzylic alcohol (*S*)-9j: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used and CAHB carried out for 12 hours), the substrate (*E*)-**5j** (68 mg, 0.2 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9j** (39 mg, 55%) as a colorless oil: TLC analysis (10% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -20° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, *J* = 8.5 Hz, g), 6.91 (2H, d, *J* = 8.5 Hz, h), 4.71 (1H, t, *J* = 6.0 Hz, e), 4.17-4.04 (4H, m, b+b'), 3.88 (4H, t, *J* = 5.0 Hz, k), 3.17 (4H, t, *J* = 5.0 Hz, j), 2.09-1.96 (2H, m, d), 1.94-1.72 (2H, m, c), 1.33 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.08 (i), 135.36 (i), 127.00 (g), 115.85 (h), 73.82 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 67.10 (k), 61.86 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.83 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 49.55 (j), 31.79 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.28 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.68 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.82 ppm; IR (neat) 3355 (O-H), 2995 (aromatic C-H), 2901 (aliphatic C-H), 1525, 1226 (P=O), 1051 (C-O/C-N), 1022 (C-O/C-N), 949 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{17}H_{28}NO_5P$+Na^+ = 380.1603, found 380.1603 *m/z*. Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

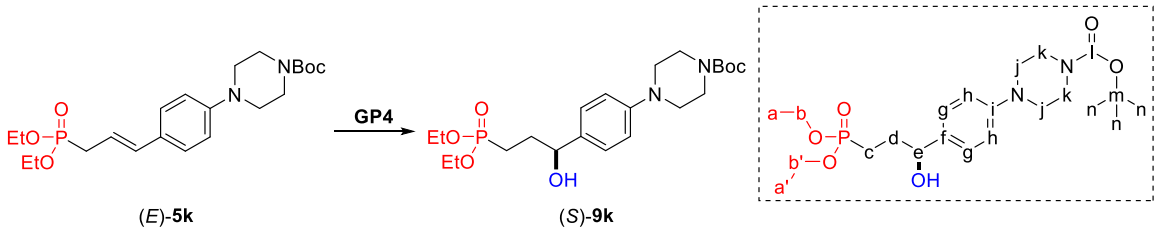


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.191	BB	0.5033	2649.93677	49.7782
2	15.225	BB	0.9745	2673.55615	50.2218

(b) R:S = 6:94, CAHB of (*E*)-**5j** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9j**

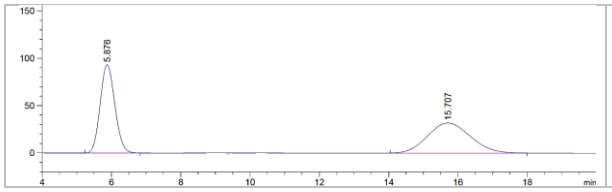


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.052	VB	0.4848	3467.79956	94.4317
2	15.103	BB	0.7068	204.48552	5.5683



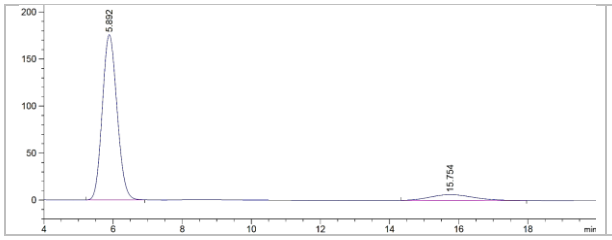
Preparation of chiral secondary benzylic alcohol (*S*)-9k: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used and CAHB carried out for 12 hours), the substrate (*E*)-**5k** (66.0 mg, 0.15 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9k** (47 mg, 68%) as a colorless oil: TLC analysis (6% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -20° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (2H, d, *J* = 8.5 Hz, g), 6.90 (2H, d, *J* = 8.5 Hz, h), 4.67 (1H, t, *J* = 6.0 Hz, e), 4.14-4.00 (4H, m, b+b'), 3.57 (4H, t, *J* = 5.0 Hz, k), 3.12 (4H, t, *J* = 5.0 Hz, j), 2.09-1.94 (2H, m, d), 1.92-1.64 (2H, m, c), 1.49 (9H, s, n), 1.30 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.89 (l), 150.92 (i), 135.75 (f), 126.96 (g), 116.69 (h), 80.09 (m), 73.60 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.80 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.77 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 49.59 (j), 44.00 (k), 31.77 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 28.59 (n), 22.17 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.62 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.86 ppm; IR (neat) 3374 (O-H), 2977 (aromatic C-H), 2818 (aliphatic C-H), 1692 (C=O), 1421 (aromatic C=C), 1227 (P=O), 1022 (C-N/C-O), 959 (P-O), 751 cm^{-1}; HRMS (ESI) calculated for $C_{22}H_{37}N_2O_6P$+Na^+ = 479.2287, found 479.2287 *m/z*. Enantiomer ratio = 91:9, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

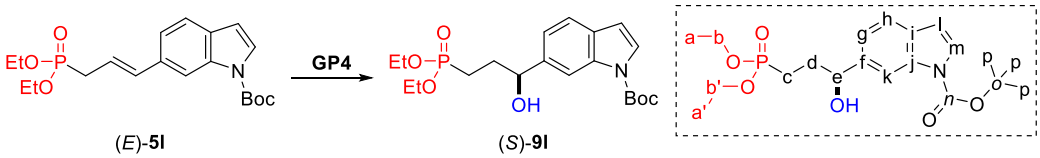


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.876	BB	0.4607	2747.60693	49.9971
2	15.707	BB	1.2837	2747.92358	50.0029

(b) R:S = 9:91, CAHB of (*E*)-**5k** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9k**

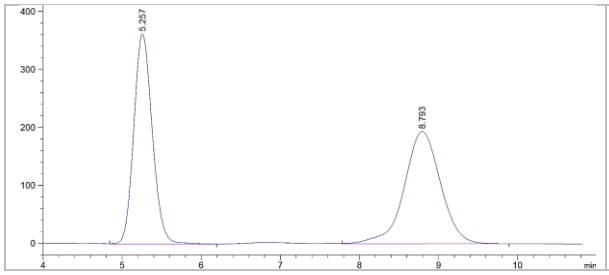


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.892	BB	0.4636	5203.43408	90.7742
2	15.754	BB	1.0301	528.84760	9.2258



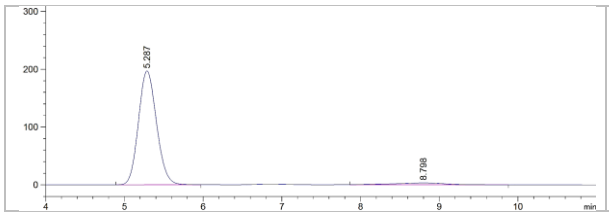
Preparation of chiral secondary benzylic alcohol (*S*)-9l: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used in CAHB), the substrate (*E*)-**5l** (79 mg, 0.2 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9l** (64 mg, 78%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -42° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, br s, k), 7.58 (1H, d, *J* = 3.6 Hz, h), 7.53 (1H, d, *J* = 8.0 Hz, m), 7.25 (1H, dd, *J* = 8.0, 1.0 Hz, l), 6.55 (1H, d, *J* = 3.6 Hz, g), 4.87 (1H, t, *J* = 6.0 Hz, e), 4.13-4.00 (4H, m, b+b'), 2.97 (1H, br s, OH), 2.15-2.05 (2H, m, d), 1.97-1.73 (2H, m, c), 1.68 (9H, s, p), 1.31 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.86 (n),140.48 (j), 135.49 (f), 130.25 (i), 126.35 (h), 121.13 (m), 120.82 (l), 112.95 (k), 107.24 (g), 83.87 (o), 74.67 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.82 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.77 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 32.21 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 28.37 (p), 22.25 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.61 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.85 ppm; IR (neat) 3359 (O-H), 2981 (aromatic C-H), 2930 (aliphatic C-H), 1731 (C=O), 1438 (aromatic C=C), 1341 (aromatic C=C), 1251 (P=O), 1022 (C-O/C-N), 961 (P-O), 726 cm^{-1}; HRMS (ESI) calculated for $C_{20}H_{30}NO_6P$+Na^+ = 434.1708, found 434.1711 *m/z*; Enantiomer ratio = 96:4, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

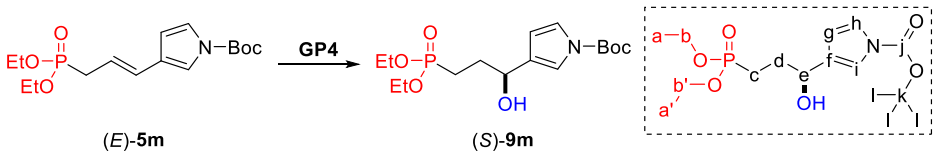


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.257	VB	0.2515	5891.37354	48.7316
2	8.793	BB	0.4900	6198.06885	51.2684

(b) R:S = 4:96, CAHB of (*E*)-**5l** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9l**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.287	BB	0.2484	3145.65259	95.8034
2	8.798	BB	0.5958	137.79367	4.1966

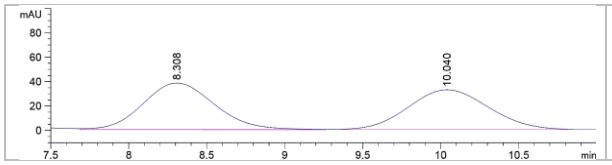


(*E*)-**5m** (*S*)-**9m**

Preparation of chiral secondary benzylic alcohol (*S*)-9m: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used and CAHB carried out for 12 hours), the substrate (*E*)-**5m** (69 mg, 0.2 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9m** (62 mg, 86%) as a colorless oil: TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -23° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.17 (2H,

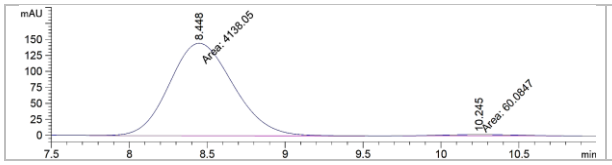
m, h+i), 6.19 (1H, dd, *J* = 3.0, 2.0 Hz, g), 4.68 (1H, t, *J* = 6.0 Hz, e), 4.14-4.01 (4H, m, b+b'), 3.02 (1H, br s, OH), 2.08-1.74 (4H, m, c+d), 1.58 (9H, s, l), 1.31 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (162 MHz, $CDCl_3$) δ 148.96 (j), 130.57 (f), 120.77 (h or i), 116.83 (h or i), 110.25 (g), 83.85 (k), 68.11 (d, $^{3}J_{C\text{-}P}$ = 16 Hz, e), 61.81 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.78 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 30.89 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 28.13 (l), 21.97 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.59 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.92 ppm; IR (neat) 3361 (O-H), 2980 (aromatic C-H), 2932 (aliphatic C-H), 1738 (C=O), 1485 (aromatic C=C), 1395 (aromatic C=C), 1346 (aromatic C=C), 1237 (P=O), 1155 (C-N), 1056 (C-O), 1023 (C-O), 967 (P-O), 729 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{28}NO_6P$+Na^+ = 384.1552, found 384.1553 *m/z*; Enantiomer ratio = 99:1, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 60:40 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 ºC. HPLC traces:

(a) Racemate

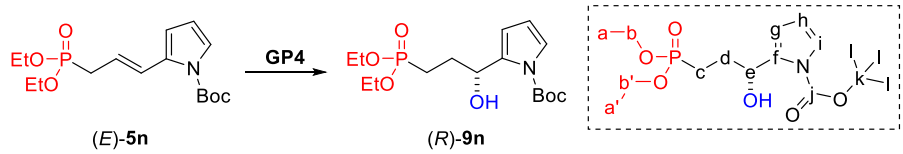


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.308	VB	0.4999	1220.43323	50.7821
2	10.040	BB	0.5680	1182.84241	49.2179

(b) R:S = 1:99, CAHB of (*E*)-**5m** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9m**



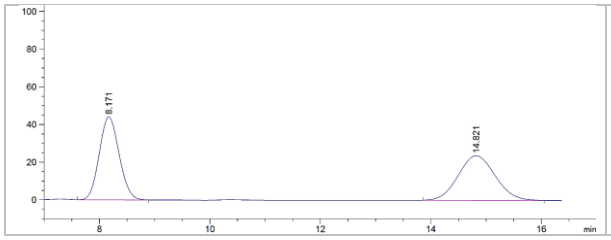
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.448	MM	0.4770	4138.04736	98.5688
2	10.245	MM	0.5194	60.08473	1.4312



(*E*)-**5n** (*R*)-**9n**

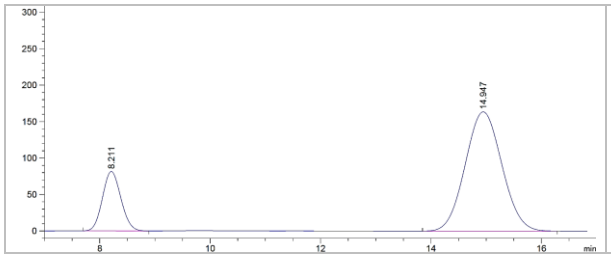
Preparation of chiral secondary benzylic alcohol (*R*)-9n: Following the general procedure for sequential hydroboration-oxidation (**GP4**; Note: 2 eq. of pinBH was used in CAHB), the substrate (*E*)-**5n** (69 mg, 0.2 mmol) affords the chiral secondary benzylic alcohol (*R*)-**9n** (61 mg, 85%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -0.5º (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.14 (1H, m, i), 6.20-6.19 (1H, m, h), 6.08 (1H, t, *J* = 3.5 Hz, g), 4.87 (1H, t, *J* = 6.5 Hz, e), 4.26-4.02 (5H, m, b+b'+OH), 2.20-2.02 (3H, m, c(1H)+d), 1.89-1.74 (1H, m, c(1H)), 1.59 (9H, s, l), 1.31 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.36 (j), 137.38 (f), 122.16 (i), 111.77 (h), 110.49 (g), 84.78 (k), 66.62 (d, $^{3}J_{C\text{-}P}$ = 18 Hz, e), 61.65 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.63 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 28.09 (l), 27.77 (d, $^{2}J_{C\text{-}P}$ = 4.25 Hz, d), 22.58 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.56 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.56 ppm; IR (neat) 3372 (O-H), 2980 (aliphatic C-H), 2933 (aromatic C-H), 1735 (C=O), 1325, 1228 (P=O), 1054 (C-O), 1022 (C-O), 960 (P-O), 722 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{28}NO_6P$+Na^+ = 384.1552, found 384.1555 *m/z*; Enantiomer ratio = 80:20, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 60:40 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 ºC. HPLC traces:

(a) Racemate

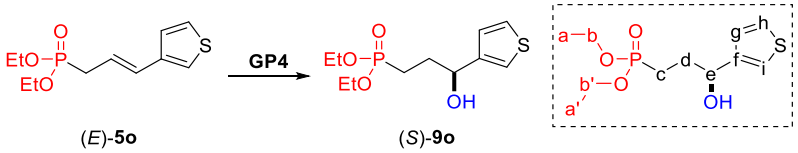


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.171	VB	0.3908	1100.58521	50.0800
2	14.821	BB	0.7195	1097.07043	49.9200

(b) R:S = 80:20, CAHB of (*E*)-**5n** using (*R*)-**B1** followed by oxidation to yield (*R*)-**9n**



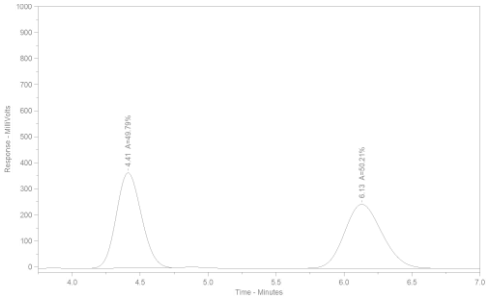
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.211	BB	0.3613	1887.71655	19.9427
2	14.947	BB	0.7241	7577.97021	80.0573



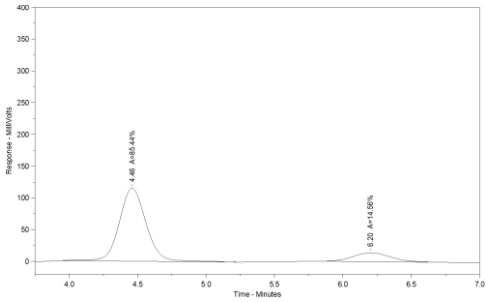
(*E*)-**5o** (*S*)-**9o**

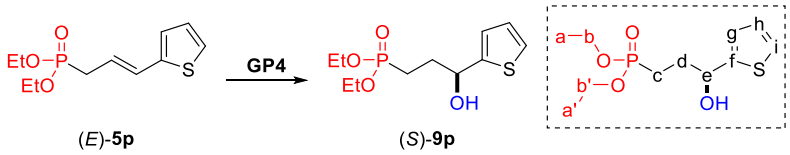
Preparation of chiral secondary benzylic alcohol (*S*)-9o: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5o** (78 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9o** (69 mg, 83%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -20° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (1H, dd, *J* = 5.0, 3.0 Hz, h), 7.24-7.23 (1H, m, i), 7.08 (1H, dd, *J* = 5.0, 1.25 Hz, g), 4.91-4.87 (1H, m, e), 4.17-4.03 (4H, m, b+b'), 3.02 (1H, d, *J* = 4.0 Hz, OH), 2.17-2.02 (2H, m, d), 1.95-1.79 (2H, m, c), 1.34 (3H, t, *J* = 7.0 Hz, a or a'), 1.33 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.56 (f), 126.45 (h), 125.71 (g), 121.09 (i), 70.34 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 61.93 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.90 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 31.37 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.01 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.66 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.85 ppm; IR (neat) 3368 (O-H), 2983 (aromatic C-H), 2905 (aliphatic C-H), 1441 (aromatic C=C), 1391 (aromatic C=C), 1224 (P=O), 1052 (C-O), 1020 (C-O), 956 (P-O), 784 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{19}O_4PS+Na^+$ = 301.0639, found 301.0641 *m/z*; Enantiomer ratio = 85:15, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



(b) R:S = 15:85, CAHB of (*E*)-**5o** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9o**

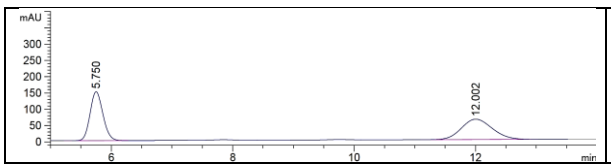




(*E*)-**5p** (*S*)-**9p**

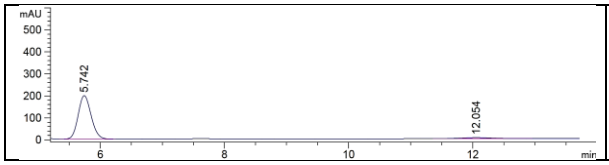
Preparation of chiral secondary benzylic alcohol (*S*)-9p: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5p** (78 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9p** (67 mg, 80%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -13° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (1H, dd, *J* = 4.5, 2.0 Hz, i), 6.95-6.93 (2H, m, g+h), 4.97 (1H, t, *J* = 6.0 Hz, e), 4.11-3.97 (4H, m, b+b'), 2.13-2.04 (2H, m, d), 1.99-1.69 (2H, m, c), 1.29 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.40 (f), 126.75 (h), 124.44 (i), 123.61 (g), 69.69 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.87 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.82 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, b or b'), 32.22 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.88 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.54 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.58 ppm; IR (neat) 3360 (O-H), 2980 (aromatic C-H), 2904 (aliphatic C-H), 1440 (aromatic C=C), 1391 (aromatic C=C), 1219 (P=O), 1017 (C-O), 958 (P-O), 697 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{19}O_4PS+Na^+$ = 301.0639, found 301.0639 *m/z*; Enantiomer ratio = 95:5, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 40:60 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

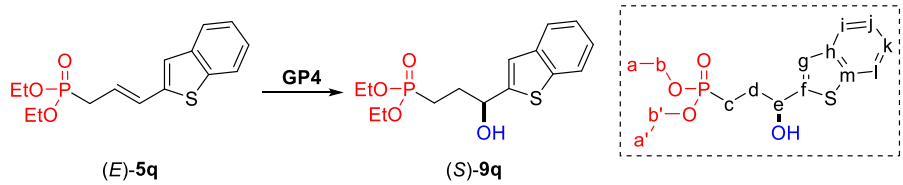


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.750	VB	0.2283	2203.71069	49.8917
2	12.002	BB	0.5534	2213.28174	50.1083

(b) R:S = 5:95, CAHB of (*E*)-**5p** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9p**.



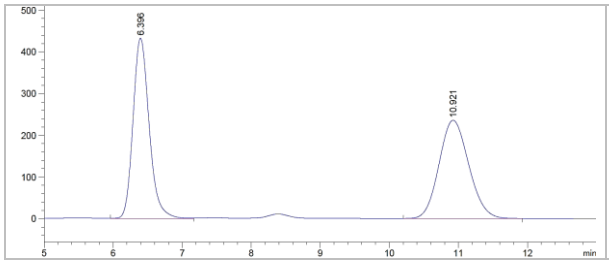
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.742	VB	0.2264	2871.94727	95.0985
2	12.054	BB	0.5312	148.02408	4.9015



(*E*)-**5q** (*S*)-**9q**

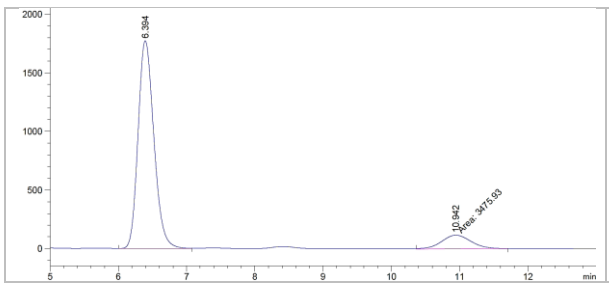
Preparation of chiral secondary benzylic alcohol (*S*)-9q: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5q** (77.6 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9q** (53 mg, 65%) as a waxy solid: TLC analysis (1% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -21° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.79 (2H, m, i or l), 7.71-7.69 (2H, m, i or l), 7.36-7.27 (2H, m, j+k), 7.19 (1H, s, g), 5.07 (1H, t, *J* = 6.0 Hz, e), 4.23-3.99 (5H, m, b+b'+OH), 2.22-2.13 (2H, m, d), 1.98-1.80 (2H, m, c), 1.30 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.07 (f), 139.75 (h), 139.46 (m), 124.38 (j or k), 124.20 (j or k), 123.56 (i or l), 122.56 (i or l), 120.21 (g), 70.17 (d, $^3J_{C-P}$ = 15 Hz, e), 62.00 (d, $^2J_{C-P}$ = 6.0 Hz, b or b'), 61.93 (d, $^2J_{C-P}$ = 6.0 Hz, b or b'), 31.91 (d, $^2J_{C-P}$ = 4.5 Hz, d), 21.77 (d, $^1J_{C-P}$ = 142 Hz, c), 16.56 (d, $^3J_{C-P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.54 ppm; IR (neat) 3252 (O-H), 2979 (aromatic C-H), 2927 (aliphatic C-H), 1219 (P=O), 1027 (C-O), 1011 (C-O), 950 (P-O) cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{21}O_4PS+Na^+$ = 351.0796, found 351.0798 *m/z*; Enantiomer ratio = 89:11, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 40:60 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

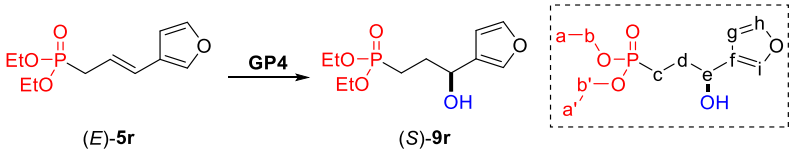


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.396	VB	0.2505	7018.30811	49.9438
2	10.921	BB	0.4663	7034.09570	50.0562

(b) R:S = 11:89, CAHB of (*E*)-**5q** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9q**

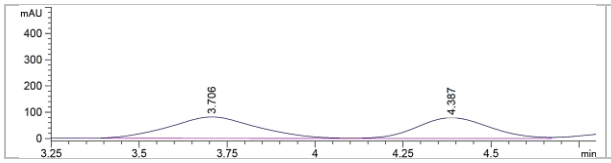


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.394	VV	0.2496	2.85179e4	89.1356
2	10.942	MM T	0.4977	3475.92603	10.8644



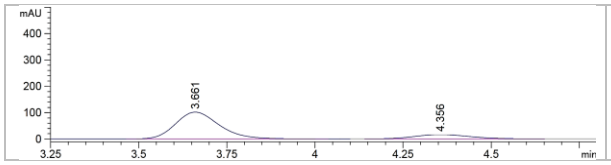
Preparation of chiral secondary benzylic alcohol (*S*)-9r: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5r** (73 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9r** (60 mg, 76%) as a colorless oil: TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -5.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (2H, m, h+i), 6.37 (1H, br s, g), 4.70 (1H, t, *J* = 6.0 Hz, e), 4.12-3.98 (4H, m, b+b'), 3.64 (1H, br s, OH), 2.05-1.72 (4H, m, c+d), 1.29 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.41 (h), 139.27 (i), 128.69 (f), 108.60 (g), 66.55 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 61.84 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.81 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 30.76 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.79 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 16.55 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.85 ppm; IR (neat) 3357 (O-H), 2982 (C-H), 1501 (aromatic C=C), 1442 (aromatic C=C), 1391 (aromatic C=C), 1222 (P=O), 1159, 1016 (C-O), 957 (P-O), 873, 788, 600 cm^{-1}; HRMS (ESI) calculated for $C_{11}H_{19}O_5P$+Na^+ = 285.0862, found 285.0867 *m/z*; Enantiomer ratio = 83:17, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 60:40 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

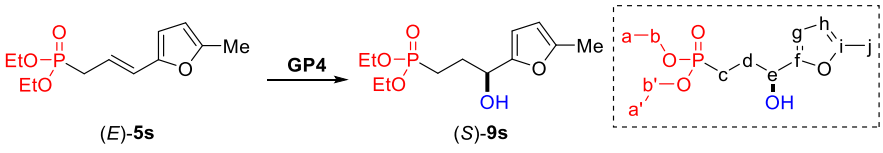


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	3.706	BV	0.2524	1417.37683	55.7812
2	4.387	VV	0.2222	1123.58179	44.2188

(b) R:S = 17:83, CAHB of (*E*)-**5r** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9r**



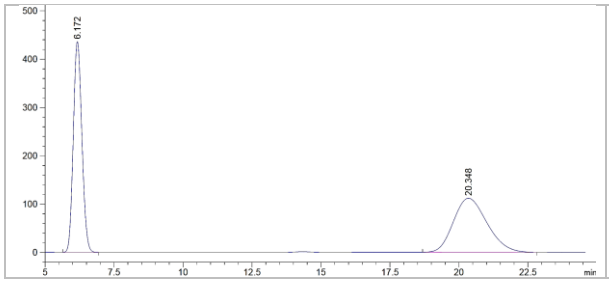
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	3.661	BB	0.1328	876.91345	83.1618
2	4.356	BV	0.1665	177.55312	16.8382



Preparation of chiral secondary benzylic alcohol (*S*)-9s: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5s** (77 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9s** (68 mg, 82%) as a colorless oil: TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -11° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (1H, d, *J* = 3.0 Hz, g), 5.87 (1H, dd, *J* = 3.0, 1.0 Hz, h), 4.65 (1H, t, *J* = 6.5 Hz, e), 4.13-3.99 (4H, m, b+b'), 3.44 (1H, br s, OH), 3.16 (3H, s, j), 2.15-2.00 (2H, m, d), 1.93-1.72 (2H, m, c), 1.29 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.36 (f), 151.73 (i),

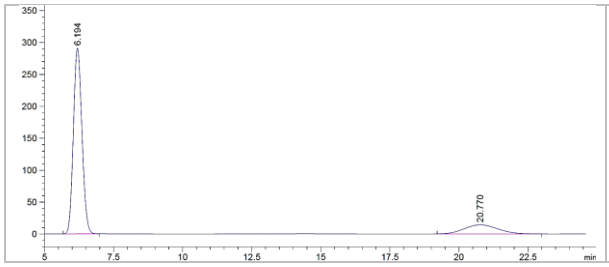
107.01 (g), 106.12 (h), 67.44 (d, $^{3}J_{C\text{-}P}$ = 17 Hz, e), 61.82 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.80 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 28.62 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 21.88 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.54 (d, $^{3}J_{C\text{-}P}$ = 6.0 Hz, a+a'), 13.64 (j) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.63 ppm; IR (neat) 3353 (O-H), 2982 (aromatic C-H), 2925 (aliphatic C-H), 1566, 1442 (aromatic C=C), 1391 (aromatic C=C), 1220 (P=O), 1018 (C-O), 956 (P-O), 784 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{21}O_5P+Na^+$ = 299.1024, found 299.1023 *m/z*; Enantiomer ratio = 84:16, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1.5 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

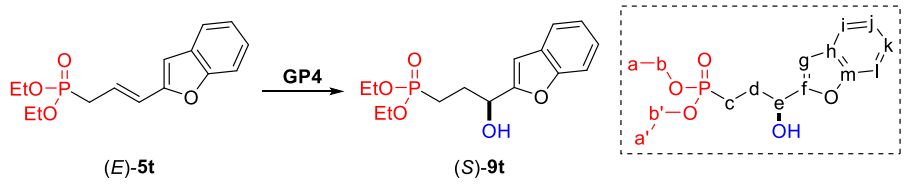


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.172	BB	0.3386	9442.63574	49.9660
2	20.348	BB	1.2935	9455.47266	50.0340

(b) R:S = 16:84, CAHB of (*E*)-**5s** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9s**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	6.194	BB	0.3380	6284.61719	83.9406
2	20.770	BB	1.2673	1202.36584	16.0594

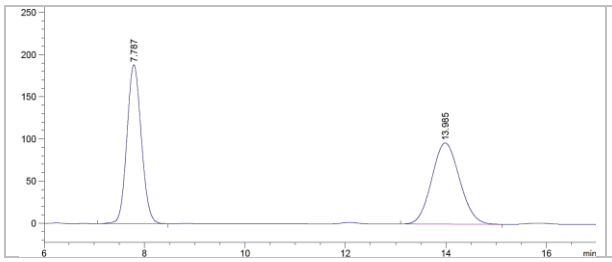


(*E*)-**5t** (*S*)-**9t**

Preparation of chiral secondary benzylic alcohol (*S*)-9t: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5t** (73.6 mg, 0.25 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9t** (43 mg, 55%) as a light yellow oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -18° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (2H, m, i), 7.45-7.43 (2H, m, l), 7.28-7.19 (2H, m, j+k), 6.67 (1H, s, g), 4.90 (1H, dd, *J* = 7.0, 5.5 Hz, d), 4.13-4.02 (5H, m, b+b'+OH), 2.32-2.13 (2H, m, d), 1.99-1.81 (2H, m, c), 1.31 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.13 (f), 154.92 (m), 128.32 (h), 124.16 (j or k), 122.89 (j or k), 121.15 (i), 111.32 (l), 102.98 (g), 67.78 (d, $^{3}J_{C\text{-}P}$ = 15 Hz, e), 62.03 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 61.01 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, b or b'), 28.71 (d, $^{2}J_{C\text{-}P}$ = 4.5 Hz, d), 21.56 (d, $^{1}J_{C\text{-}P}$ = 142 Hz, c), 16.55 (d, $^{3}J_{C\text{-}P}$ = 5.5 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.71 ppm; IR (neat) 3309 (O-H), 2981 (aromatic C-H), 2907 (aliphatic C-H), 1454 (aromatic C=C), 1224 (P=O), 1021 (C-O),

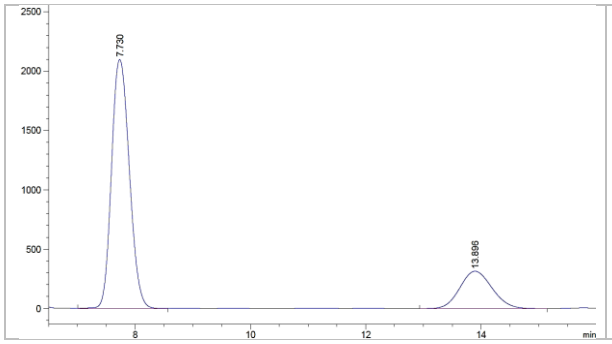
956 (P-O), 804 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{21}O_5P+Na^+$ = 335.1024, found 335.1031 *m/z*; Enantiomer ratio = 89:11, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 40:60 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

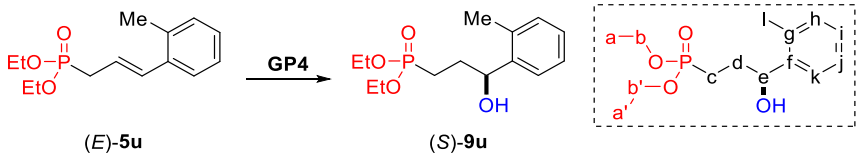


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.787	VB	0.3106	3764.61792	50.2179
2	13.985	BB	0.6036	3731.95068	49.7821

(b) R:S = 21:79, CAHB of (*E*)-**5t** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9t**



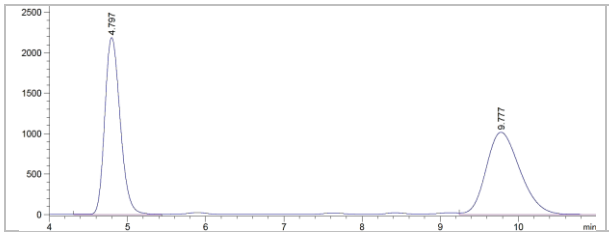
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.730	BB	0.3389	4.51091e4	78.7184
2	13.896	BB	0.6064	1.21953e4	21.2816



(*E*)-**5u** (*S*)-**9u**

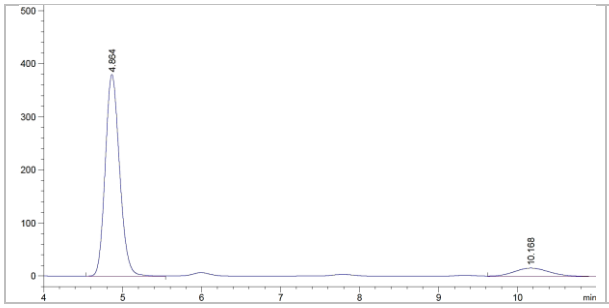
Preparation of chiral secondary benzylic alcohol (*S*)-9u: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**5u** (80 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**9u** (64 mg, 74%) as a colorless oil: TLC analysis (1% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -39° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, d, *J* = 7.5 Hz, h), 7.22-7.11 (3H, m, i+k), 4.97 (1H, dd, *J* = 6.5, 4.5 Hz, e), 4.12-3.98 (4H, m, b+b'), 3.37 (1H, br s, OH), 2.32 (3H, s, l), 2.04-1.79 (4H, m, c+d), 1.30 (3H, t, *J* = 7.0 Hz, a or a'), 1.29 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.38 (f), 134.36 (g), 130.47 (aryl), 127.30 (aryl), 126.33 (aryl), 125.38 (h), 70.03 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 61.79 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 61.73 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b or b'), 30.67 (d, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 22.09 (d, $^1J_{C\text{-}P}$ = 142 Hz, c), 19.14 (l), 16.56 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.95 ppm; IR (neat) 3361 (O-H), 2980 (aromatic C-H), 2930 (aliphatic C-H), 1485 (aromatic C=C), 1441 (aromatic C=C), 1391 (aromatic C=C), 1224 (P=O), 1020 (C-O), 957 (P-O), 755 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1234 *m/z*; Enantiomer ratio = 91:9, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate

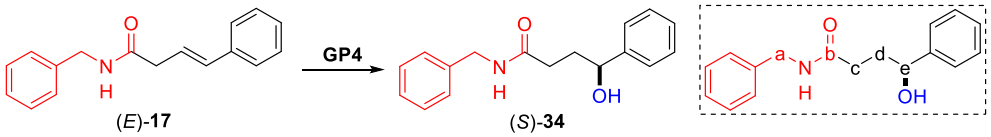


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	4.797	VV	0.2126	2.99077e4	49.4560
2	9.777	VBA	0.4678	3.05656e4	50.5440

(b) R:S = 9:91, CAHB of (*E*)-**5u** using (*R*)-**B1** followed by oxidation to yield (*S*)-**9u**

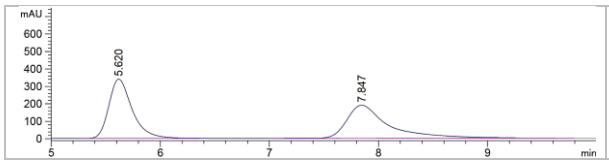


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	4.864	BB	0.1948	4785.50879	90.8853
2	10.168	VB	0.4807	479.92606	9.1147



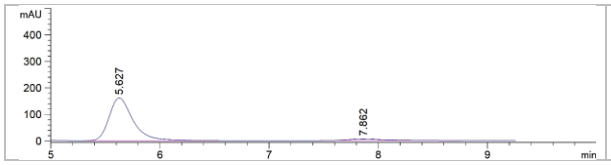
Preparation of chiral secondary benzylic alcohol (*S*)-34: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**17** (75 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**34** (63 mg, 78%) as a white solid (regioisomeric ratio, rr = 7:1): TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -50° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (10 H, m, aryl), 6.39 (1H, br s, NH), 4.72 (1H, br s, e), 4.37 (2H, d, *J* = 5.75 Hz, a), 4.15 (1H, br s, OH), 2.35-2.31 (2H, m, c), 2.11-1.96 (1H, m, d) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.69 (b), 144.58 (aryl), 138.27 (aryl), 128.82 (aryl), 128.51 (aryl), 127.89 (aryl), 127.63 (aryl), 127.46 (aryl), 125.88 (aryl), 73.57 (e), 43.80 (a), 34.58 (d), 32.96 (c) ppm; IR (neat) 3297 (O-H), 3009 (C-H), 1639 (C=O), 1544, 1494 (aromatic C=C), 1453 (aromatic C=C), 1216, 1060 (C-O), 1027 (C-O), 746, 697, 666 cm^{-1}; Enantiomer ratio = 94:6, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 25:75 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



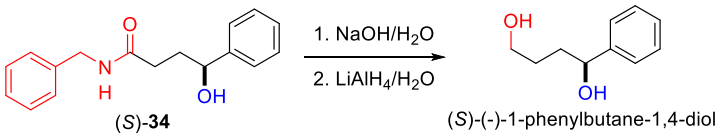
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.620	VB	0.2240	5026.27832	49.9635
2	7.847	BB	0.3842	5033.62109	50.0365

(b) R:S = 6:94, CAHB of (*E*)-**17** using (*R*)-**B1** followed by oxidation to yield (*S*)-**34**

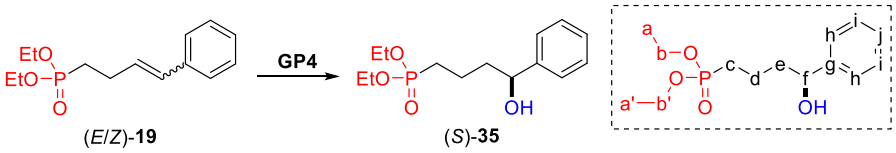


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.627	BB	0.2294	2449.29272	94.0400
2	7.862	BB	0.3625	155.23045	5.9600

Absolute Configuration Assignment: The amide-functionalized chiral secondary benzyl alcohol **34** obtained from (*E*)-**17** via CAHB using (*R*)-**B1** followed by oxidation was converted to 1-phenylbutane-1,4-diol ($[\alpha]_D^{20}$ = -45° (*c* = 1.0, $CHCl_3$)) via sequential hydrolysis ($NaOH/H_2O$) and reduction ($LiAlH_4$). 1-phenylbutane-1,4-diol is a previously reported compound in the literature[19] and the negative value of optical rotation is expected for the (*S*)-enantiomer. Hence, the chiral secondary benzyl alcohol **34** is assigned *"S"*.



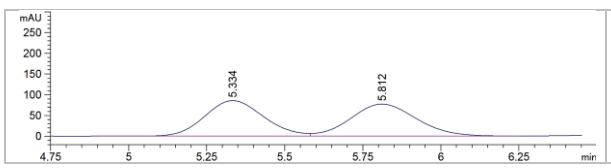
(*S*)-**34** (*S*)-(-)-1-phenylbutane-1,4-diol



(*E*/*Z*)-**19** (*S*)-**35**

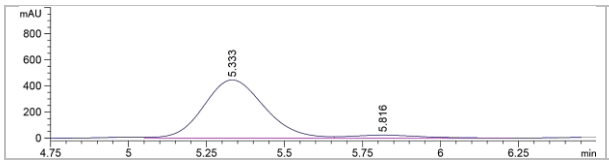
Preparation of chiral secondary alcohol (*S*)-35: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**19** (80 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**35** (68 mg, 79%) as a colorless oil. Alternatively, the substrate (*Z*)-**19** (80 mg, 0.3 mmol) affords the chiral secondary benzylic alcohol (*S*)-**35** (70 mg, 81%) as a colorless oil: (**Note:** >20:1 regioisomeric ratio of benzylic : non-benzylic boronic esters is estimated from ^{31}P NMR of crude CAHB mixture): TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -16° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.13 (5H, m, aryl), 4.61 (1H, dd, *J* = 7.0, 4.5 Hz, f), 4.05-3.92 (4H, m, b+b'), 3.49 (1H, br s, OH), 1.84-1.51 (6H, m, c+d+e), 1.25 (3H, t, *J* = 7.0 Hz, a or a'), 1.24 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.08 (g), 128.39 (h or i), 127.35 (j), 125.91 (h or i), 73.57 (f), 61.54 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 39.84 (d, $^3J_{C\text{-}P}$ = 16 Hz, e), 25.39 (d, $^1J_{C\text{-}P}$ = 140 Hz, c), 18.95 (d, $^2J_{C\text{-}P}$ = 5.0 Hz, d), 16.48 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.24 ppm; IR (neat) 3365 (O-H), 2979 (aromatic C-H), 2905 (aliphatic C-H), 1492 (aromatic C=C), 1452 (aromatic C=C), 1391 (aromatic C=C), 1226 (P=O), 1020 (C-O), 955 (P-O), 700 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{23}O_4P+Na^+$ = 309.1232, found 309.1239; Enantiomer ratio = 95:5, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



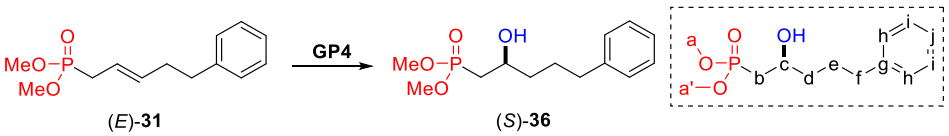
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.334	BV	0.2044	1125.28809	49.7661
2	5.812	VV	0.2276	1135.86536	50.2339

(b) R:S = 5:95, CAHB of (*E*/*Z*)-**19** using (*R*)-**B1** followed by oxidation to yield (*S*)-**35**



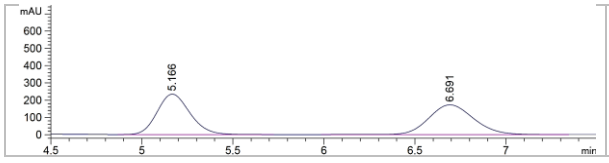
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.333	VV	0.2092	6003.92041	94.5894
2	5.816	VV	0.2342	343.43286	5.4106

Absolute Configuration Assignment: See section 7: Absolute Configuration Assignments via Kinetic Resolution of Chiral Secondary Benzylic Alcohols using Benzotetramisole (BTM).



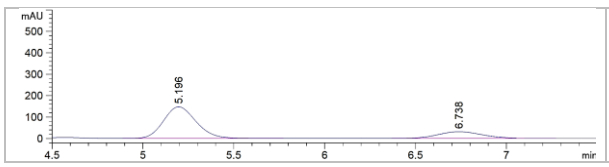
Preparation of chiral secondary alcohol (*S*)-36: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**31** (76 mg, 0.3 mmol) affords the chiral secondary alcohol (*S*)-**36** (38 mg, 47%) as a colorless oil (**Note:** About a 3:1:1 ratio of the β-regioisomer : γ-regioisomer : reduced product is formed in CAHB. Yield after oxidation is low because of the high polarity of the products and the potential hydrolysis of the methyl phosphonate. This example is carried for the absolute configuration assignment of the product (*S*)-**37** (*vide infra*)): TLC analysis (5% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +9.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (5H, m, aryl), 4.05-4.03 (1H, m, c), 3.76 (3H, d, $^3J_{P\text{-}H}$ = 11 Hz, a or a'), 3.74 (3H, d, $^3J_{P\text{-}H}$ = 11 Hz, a or a'), 3.46 (1H, br s, OH), 2.65 (2H, t, *J* = 7.5 Hz, f), 2.01-1.49 (4H, m, d+e) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.32 (g), 128.57 (h or i), 128.47 (h or i), 125.94 (j), 66.48 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, d), 52.62 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a'), 52.59 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, a or a'), 37.92 (d, $^3J_{C\text{-}P}$ = 17 Hz, d), 35.80 (f), 32.72 (d, $^1J_{C\text{-}P}$ = 138 Hz, b), 27.36 (d, $^4J_{C\text{-}P}$ = 1.0 Hz, e) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.08 ppm; IR (neat) 3375 (O-H), 2950 (aromatic C-H), 2852 (aliphatic C-H), 1496 (aromatic C=C), 1453 (aromatic C=C), 1223 (P=O), 1023 (C-O), 842, 817, 749, 699 cm^{-1}; Enantiomer ratio = 77:23, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 60:40 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.166	VB	0.1944	2938.63208	49.9252
2	6.691	BB	0.2658	2947.43970	50.0748

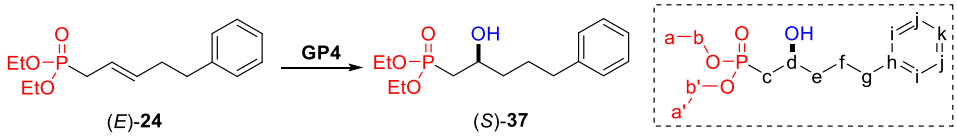
(b) R:S = 23:77, CAHB of (*E*)-**31** using (*R*)-**B1** followed by oxidation to yield (*S*)-**36**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.196	VB	0.1922	1834.83081	77.4636
2	6.738	BB	0.2643	533.80627	22.5364

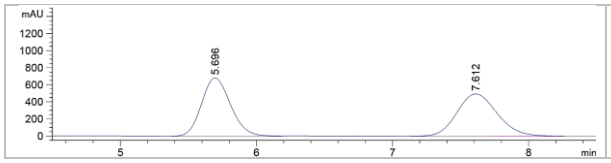
Absolute Configuration Assignment: The dimethyl phosphonate substrate (*E*)-**31** is prepared because the product alcohol **36** is a previously reported compound in the literature.[20] CAHB of

(*E*)-**31** using (*R*)-**B1** followed by oxidation yields **36** with a positive value of optical rotation ($[\alpha]_D^{20}$ = +9.5° (*c* = 1.0, $CHCl_3$)) which is expected for the *"S"* enantiomer. The configuration of chiral secondary alkyl alcohol **37** (*vide infra*) is based on analogy to this assignment.



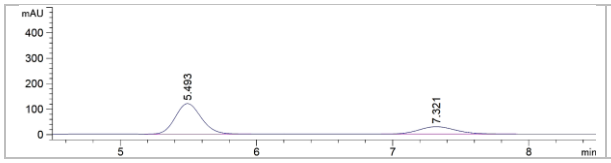
Preparation of chiral secondary alcohol (*S*)-37: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**24** (85 mg, 0.3 mmol) affords the chiral secondary alcohol (*S*)-**37** (54 mg, 60%) as a colorless oil: TLC analysis (2% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +8.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.17 (5H, m, aryl), 4.20-4.02 (5H, m, b+d), 3.58 (1H, br s, OH), 2.65 (2H, t, *J* = 7.5 Hz, g), 2.00-1.49 (c+e+f), 1.34 (3H, t, *J* = 7.0 Hz, a or a'), 1.33 (3H, t, *J* = 7.0 Hz, a or a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.37 (h), 128.57 (i or j), 128.46 (i or j), 125.91 (k), 66.53 (d, $^2J_{C\text{-}P}$ = 5.5 Hz, d), 62.02 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, b+b'), 37.88 (d, $^3J_{C\text{-}P}$ = 17 Hz, e), 35.84 (g), 33.66 (d, $^1J_{C\text{-}P}$ = 138 Hz, c), 27.38 (f), 16.59 (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, $CDCl_3$) δ 30.51 ppm; IR (neat) 3377 (O-H), 2981 (aromatic C-H), 2930 (aliphatic C-H), 1496 (aromatic C=C), 1453 (aromatic C=C), 1391 (aromatic C=C), 1219 (P=O), 1020 (C-O), 957 (P-O), 698 cm^{-1}; Enantiomer ratio = 75:25, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



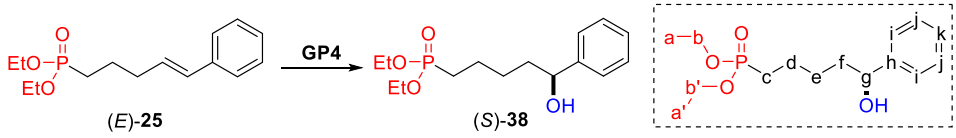
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.696	VV	0.2320	1.02209e4	49.9280
2	7.612	VV	0.3210	1.02504e4	50.0720

(b) R:S = 25:75, CAHB of (*E*)-**24** using (*R*)-**B1** followed by oxidation to yield (*S*)-**37**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.493	VB	0.2041	1582.53699	74.5054
2	7.321	VB	0.2924	541.52081	25.4946

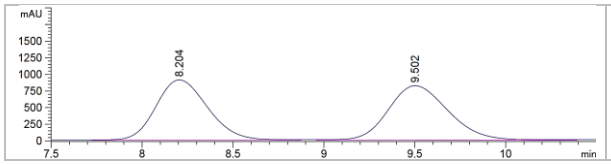
Absolute Configuration Assignment: The absolute configuration of alcohol **37** is based on analogy to the assignment of alcohol **36**.



Preparation of chiral secondary alcohol (*S*)-38: Following the general procedure for sequential hydroboration-oxidation (**GP4**), the substrate (*E*)-**25** (85 mg, 0.3 mmol) affords the

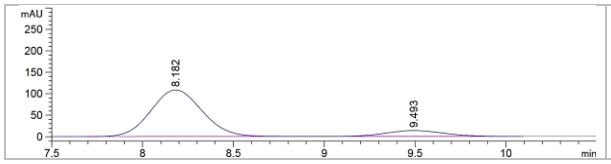
chiral secondary benzylic alcohol (*S*)-**38** (43 mg, 47%) as a colorless oil (**Note:** About a 2.5:1 ratio of benzylic : non-benzylic boronic esters is estimated from ^{31}P NMR of crude CAHB mixture): TLC analysis (3% methanol in ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = -4.5° (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.18 (5H, m, aryl), 4.63 (1H, t, *J* = 6.5 Hz, g), 4.08-3.97 (4H, m, b+b'), 2.99 (1H, br s, OH), 1.83-1.32 (8H, m, c+d+e+f), 1.27 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.20 (h), 128.44 (i or j), 127.44 (k), 125.99 (i or j), 74.06 (g), 61.53 (d, $^2J_{C-P}$ = 6.5 Hz, b+b'), 38.70 (f), 26.90 (d or e), 26.73 (d or e), 25.62 (d, $^1J_{C-P}$ = 141 Hz, c), 16.55 (d, $^3J_{C-P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.31 ppm; IR (neat) 3370 (O-H), 2981 (aromatic C-H), 2932 (aliphatic C-H), 1452 (aromatic C=C), 1391 (aromatic C=C), 1218 (P=O), 1051 (C-O), 1020 (C-O), 956 (P-O), 700 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{25}O_4P+Na^+$ = 323.1388, found 323.1395 *m/z*; Enantiomer ratio = 88:12, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 75:25 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.204	VB	0.3104	1.82104e4	48.9106
2	9.502	BB	0.3593	1.90216e4	51.0894

(b) R:S = 12:88, CAHB of (*E*)-**25** using (*R*)-**B1** followed by oxidation to yield (*S*)-**38**

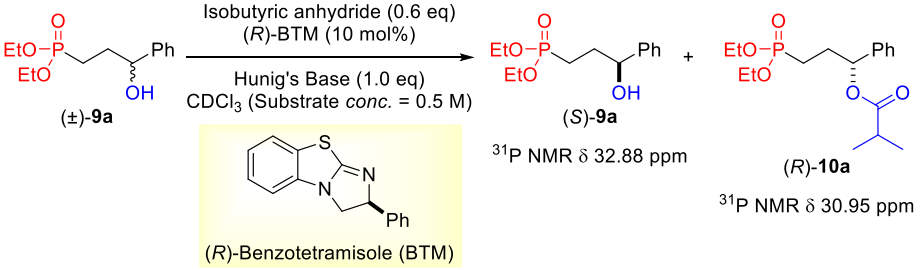


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.182	BB	0.3053	2122.38354	87.7490
2	9.493	BB	0.3435	296.31558	12.2510

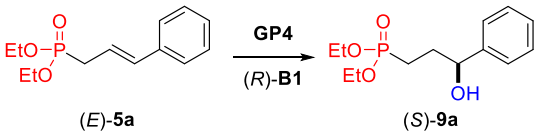
Absolute Configuration Assignment: See section 7: Absolute Configuration Assignments via Kinetic Resolution of Chiral Secondary Benzylic Alcohols using Benzotetramisole (BTM).

(7) Absolute Configuration Assignments via Kinetic Resolution of Chiral Secondary Benzylic Alcohols using Benzotetramisole (BTM)

Benzotetramisole is prepared according to Birman's previously reported procedure.[21] For carrying out enantioselectivity tests, the general guided reaction of kinetic acylation using Benzotetramisole (BTM) for a racemic mixture of chiral secondary benzyl alcohol **9a** is shown below. (*R*)-BTM catalyzes the esterification reaction of (*R*)-enantiomer of the chiral secondary benzylic alcohol with isobutyric anhydride faster than the (*S*)-enantiomer and vice-versa.



General Procedure for Absolute Configuration Assignment via Enantioselectivity Test (GP10): The absolute configuration assignments based on enantioselectivity tests were carried out according to the procedure reported by Birman and coworkers as follows. The stock solution of the kinetic acylation catalyst is prepared by dissolving 0.05 mmol of BTM and 0.75 mmol of Hunig's base in 1 mL $CDCl_3$ (dried over activated molecular sieves). The racemic mixture of the chiral secondary benzylic alcohol (0.25 mmol) is taken in an oven dried glass vial and to this, 0.5 mL of the stock solution of the catalyst is added. To this, propionic anhydride (0.15 mmol, 0.6 eq) is added (stopwatch started at this point), the contents were mixed and transferred to an NMR tube. The reaction is monitored by ^{31}P NMR by comparing the integration values of the peak corresponding to the starting alcohol and the new peak appearing upfield (corresponding to the anhydride). When the relative ratios of the two species are about 1:1, the reaction mixture is quenched by pouring the contents into a vial containing MeOH. Standard workup and HPLC analysis were carried out afterwards.

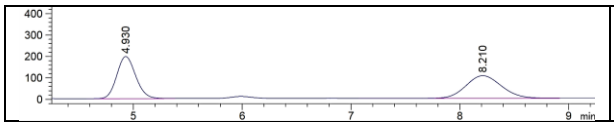


Absolute configuration assignment of alcohol 9a obtained from (*E*)-5a following GP4 using (*R*)-B1: *Rac*-**9a** is subjected to kinetic acylation according to **GP10** using (*R*)-BTM. Matching the HPLC traces of unreacted **9a** after kinetic acylation with that of **9a** obtained from (*E*/*Z*)-**5a** after CAHB/Oxidation sequence (**GP4** using (*R*)-**B1**) suggested that (*S*)-**9a** is forming in the CAHB/Oxidation sequence of **5a** with (*R*)-**B1**.

Alcohol **9a** is also a previously reported compound in the literature. Negative value of optical rotation obtained for **9a** (obtained via CAHB/Oxidation sequence of (*E*/*Z*)-**5a** (**GP4**) using (*R*)-**B1**) is also in lines with what would be expected for the (*S*)-enantiomer.[12]

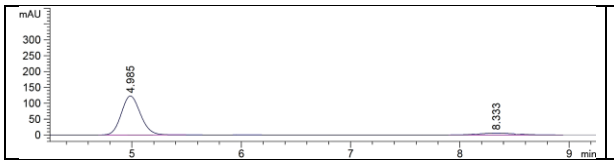
HPLC traces are shown below:

(a) Racemate



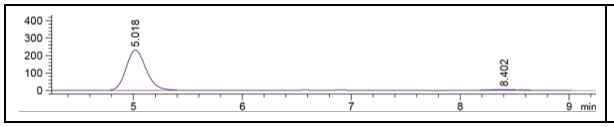
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	4.930	BB	0.1873	2383.36279	50.0002
2	8.210	VB	0.3529	2383.34546	49.9998

(b) After kinetic resolution of *rac*-**9a** using (*R*)-BTM. Major peak corresponds to (*S*)-**9a**.

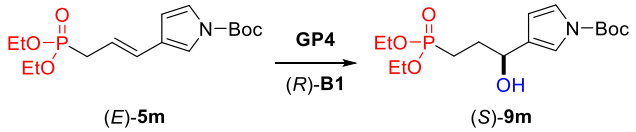


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	4.985	BB	0.1883	1486.30774	92.2252
2	8.333	BB	0.3563	125.29859	7.7748

(c) **9a** formed via CAHB of (*E*/Z)-**5a** using (*R*)-**B1** followed by oxidation (R:S = 4:96). Major peak corresponds to (*S*)-**9a**.



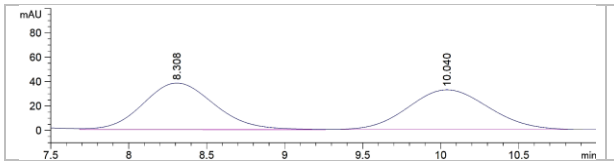
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.018	BB	0.1972	2961.21484	95.7663
2	8.402	BB	0.3608	130.91283	4.2337



(*E*)-**5m** (*S*)-**9m**

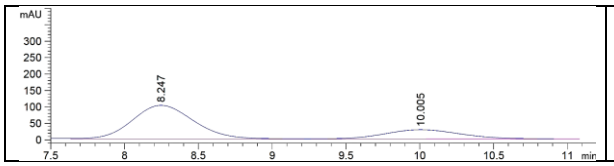
Absolute configuration assignment of alcohol 9m obtained from (*E*)-5m following GP4 using (*R*)-B1: *Rac*-**5m** is subjected to kinetic acylation according to **GP10** using (*R*)-BTM. Matching the HPLC traces of unreacted **9m** after kinetic acylation with that of **9m** obtained from (*E*)-**5m** after CAHB/Oxidation sequence (**GP4** using (*R*)-**B1**) confirmed that (*S*)-**9m** is forming in the CAHB/Oxidation sequence of (*E*)-**5m** with (*R*)-**B1**. HPLC traces are shown below:

(a) Racemate



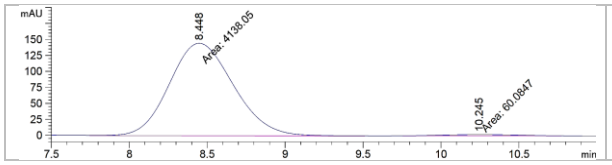
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.308	VB	0.4999	1220.43323	50.7821
2	10.040	BB	0.5680	1182.84241	49.2179

(b) After kinetic resolution of *rac*-**9m** using (*R*)-BTM. Major peak corresponds to (*S*)-**9m**

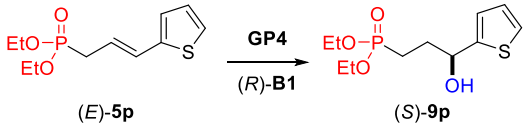


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.247	VB	0.4523	2985.92114	74.8995
2	10.005	BB	0.5597	1000.65094	25.1005

(c) **9m** formed via CAHB of (*E*)-**5m** using (*R*)-**B1** followed by oxidation (R:S = 1:99). Major peak corresponds to (*S*)-**9m**.



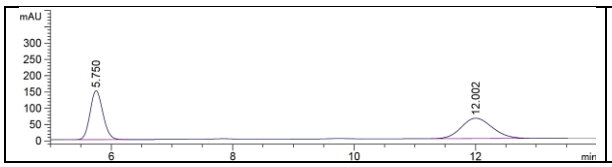
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.448	MM	0.4770	4138.04736	98.5688
2	10.245	MM	0.5194	60.08473	1.4312



(*E*)-**5p** (*S*)-**9p**

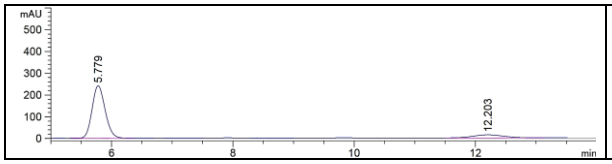
Absolute configuration assignment of alcohol 9p obtained from (*E*)-5p following GP4 using (*R*)-B1: *Rac*-**9p** is subjected to kinetic acylation according to **GP10** using (*R*)-BTM. Matching the HPLC traces of unreacted **9p** after kinetic acylation with that of **9p** obtained from (*E*)-**5p** after CAHB/Oxidation sequence (**GP4** using (*R*)-**B1**) confirmed that (*S*)-**9p** is forming in the CAHB/Oxidation sequence of **5p** with (*R*)-**B1**. HPLC traces are shown below:

(a) Racemate



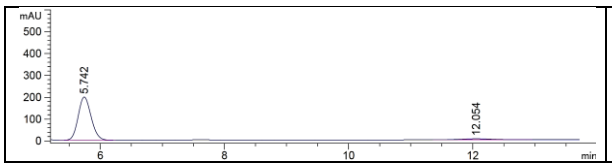
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.750	VB	0.2283	2203.71069	49.8917
2	12.002	BB	0.5534	2213.28174	50.1083

(b) After kinetic resolution of *rac*-**9p** using (*R*)-BTM. Major peak corresponds to (*S*)-**9p**.

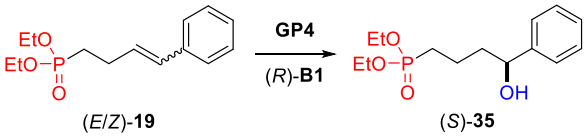


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.779	BB	0.2320	3595.21875	87.9068
2	12.203	BB	0.5500	494.58777	12.0932

(c) **9p** formed via CAHB of (*E*)-**5p** using (*R*)-**B1** followed by oxidation (R:S = 5:95). Major peak corresponds to (*S*)-**9p**.



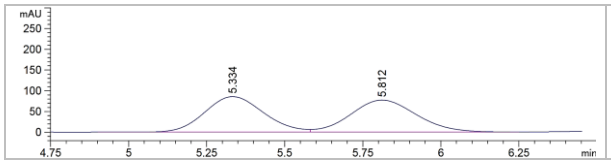
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.742	VB	0.2264	2871.94727	95.0985
2	12.054	BB	0.5312	148.02408	4.9015



(*E*/*Z*)-**19** (*S*)-**35**

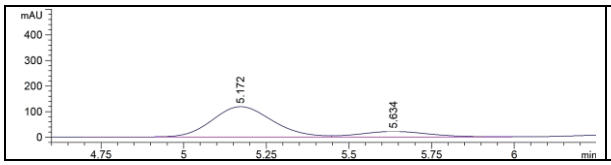
Absolute configuration assignment of alcohol 35 obtained from (*E*)-19 following GP4 using (*R*)-B1: *Rac*-**35** is subjected to kinetic acylation according to **GP10** using (*R*)-BTM. Matching the HPLC traces of unreacted **35** after kinetic acylation with that of **35** obtained from (*E*/*Z*)-**19** after CAHB/Oxidation sequence (**GP4** using (*R*)-**B1**) confirmed that (*S*)-**35** is forming in the CAHB/Oxidation sequence of (*E*/*Z*)-**19** with (*R*)-**B1**. HPLC traces are shown below:

(a) Racemate



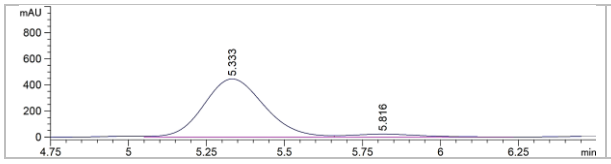
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.334	BV	0.2044	1125.28809	49.7661
2	5.812	VV	0.2276	1135.86536	50.2339

(b) After kinetic resolution of *rac*-**35** using (*R*)-BTM. Major peak corresponds to (*S*)-**35**

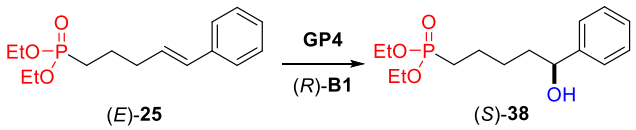


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.172	BV	0.1969	1500.03491	83.1596
2	5.634	VV	0.2183	303.76675	16.8404

(c) **35** formed via CAHB of (*E*/*Z*)-**19** using (*R*)-**B1** followed by oxidation (R:S = 5:95). Major peak corresponds to (*S*)-**35**.



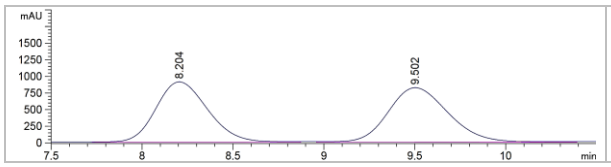
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	5.333	VV	0.2092	6003.92041	94.5894
2	5.816	VV	0.2342	343.43286	5.4106



(*E*)-**25** (*S*)-**38**

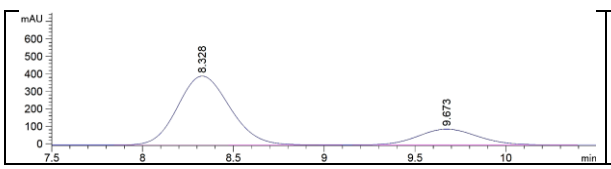
Absolute configuration assignment of alcohol 38 obtained from (*E*)-25 following GP4 using (*R*)-B1: *Rac*-**38** is subjected to kinetic acylation according to **GP10** using (*R*)-BTM. Matching the HPLC traces of unreacted **38** after kinetic acylation with that of **38** obtained from (*E*)-**25** after CAHB/Oxidation sequence (**GP4** using (*R*)-**B1**) confirmed that (*S*)-**38** is forming in the CAHB/Oxidation sequence of (*E*)-**25** with (*R*)-**B1**. HPLC traces are shown below:

(a) Racemate



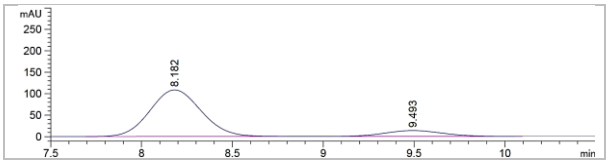
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.204	VB	0.3104	1.82104e4	48.9106
2	9.502	BB	0.3593	1.90216e4	51.0894

(b) After kinetic resolution of *rac*-**38** using (*R*)-BTM. Major peak corresponds to (*S*)-**38**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.328	VB	0.3121	7869.70459	79.2916
2	9.673	BB	0.3552	2055.31274	20.7084

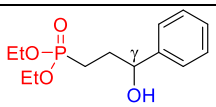
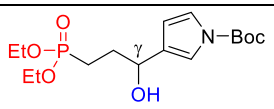
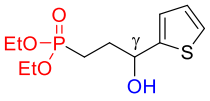
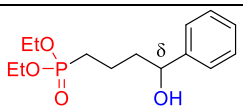
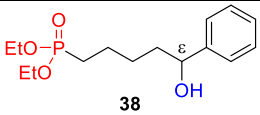
(c) **38** formed via CAHB of (*E*)-**25** using (*R*)-**B1** followed by oxidation (R:S = 12:88). Major peak corresponds to (*S*)-**38**.



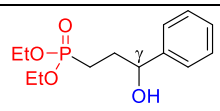
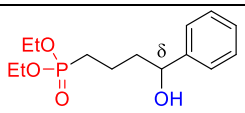
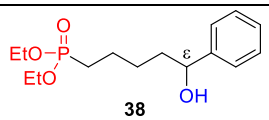
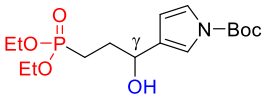
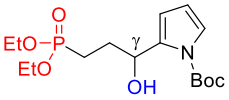
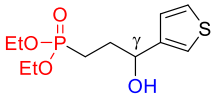
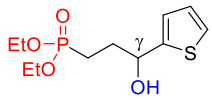
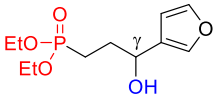
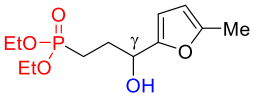
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	8.182	BB	0.3053	2122.38354	87.7490
2	9.493	BB	0.3435	296.31558	12.2510

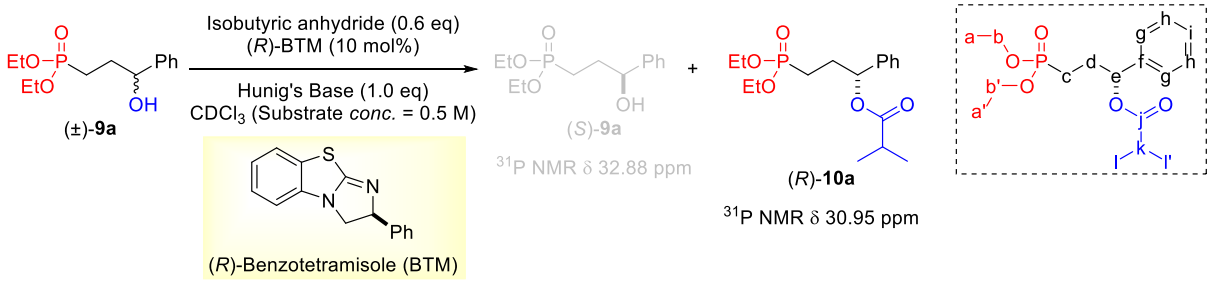
For the above 5 cases, absolute configuration is assigned based on enantioselectivity tests. The conversion (*c*) is estimated via NMR analysis. The selectivity factor (*s*)[22] is calculated using the following formula:

$$s = \ln[(1-c)(1-ee)]/\ln[(1-c)(1+ee)]$$

Entry	Substrate	ee of recovered alcohol	Conversion (via NMR)	Selectivity factor (*s*)
1	 **9a**	84.45%	49%	41.45
2	 **9m**	49.80%	46%	6.15
3	 **9p**	75.81%	47%	29.08
4	 **35**	66.32%	40%	45.38
5	 **38**	58.58%	40%	28.00

General Procedure for Absolute Configuration Assignment based on the Relative Speed of Ester Formation from Chiral Secondary Benzylic Alcohol (Obtained via CAHB/Oxidation sequence) using (*R*)- and (*S*)- BTM (GP11): Two separate stock solutions of (*R*)- and (*S*)-BTM were prepared as follows. 25 μmol of BTM and 0.4 mmol of Hunig's base are taken up in 1 mL $CDCl_3$ (dried over activated molecular sieves). The chiral secondary benzylic alcohol (0.25 mmol; Obtained using **GP4** with (*R*)-**B1**) is weighed in two separate labelled oven dried glass vials and in one vial 0.5 mL of the stock solution of (*R*)-BTM is added. In the second vial, 0.5 mL of the stock solution of (*S*)-BTM is added. To each vial propionic anhydride (0.15 mmol, 0.6 eq) is added and (timer started at this point), the contents were mixed and transferred to an NMR tube. The reactions are monitored by ^{31}P NMR spectroscopy for the appearance of an upfield peak corresponding to the ester. Since (*R*)-BTM catalyzes reaction of (*R*)-enantiomer of a chiral secondary benzylic alcohol with propionic anhydride faster than the (*S*)-enantiomer and vice-versa, the absolute configuration is assigned based on which configuration of BTM leads to the faster formation of the anhydride.

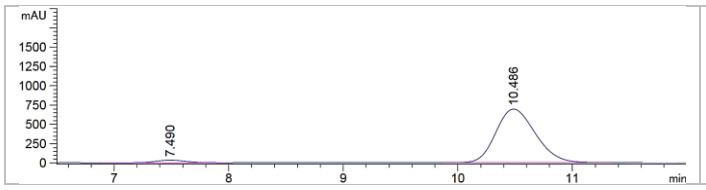
Entry	Alcohol obtained via **GP4** (Using (*R*)-**B1**)	% Ester formation using (*R*)-BTM	% Ester formation using (*S*)-BTM	Absolute Configuration
1	 **9a**	5% in 30 minutes	50% in 30 minutes	*"S"*
2	 **35**	3% in 30 minutes	45% in 30 minutes	*"S"*
3	 **38**	5% in 30 minutes	47% in 30 minutes	*"S"*
4	 **9m**	2% in 12 hours	27% in 12 hours	*"S"*
5	 **9n**	21% in 12 hours	3% in 12 hours	*"R"*
6	 **9o**	4% in 1 hour	30% in 1 hour	*"S"*
7	 **9p**	2% in 1 hour	31% in 1 hour	*"S"*
8	 **9r**	6% in 12 hours	41% in 12 hours	*"S"*
9	 **9s**	3% in 12 hours	14% in 12 hours	*"S"*



Characterization data of **10a**: TLC analysis (ethyl acetate) R_f = 0.5; $[\alpha]_D^{20}$ = +47° (*c* = 1.0, $CHCl_3$; Optical rotation of *"R"* enantiomer); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (5H, m, aryl), 5.76 (1H, dd, *J* = 7.0, 6.0 Hz, e), 4.13-4.00 (4H, m, b+b'), 2.58 (1H, sept, *J* = 7.0 Hz, k),

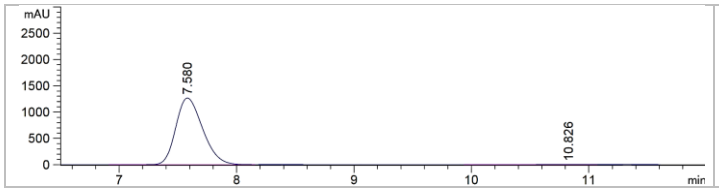
2.23-2.02 (2H, m, d), 1.82-1.62 (2H, m, c), 1.30 (6H, t, J = 7.0 Hz, a+a'), 1.18 (3H, d, J = 7.0 Hz, l or l'), 1.15 (3H, d, J = 7.0 Hz, l or l') ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.08 (l), 139.99 (f), 128.69 (h), 128.19 (i), 126.42 (g), 75.26 (d, $^{3}J_{C\text{-}P}$ = 19 Hz, e), 61.75 (d, $^{2}J_{C\text{-}P}$ = 6.5 Hz, b+b'), 34.27 (k), 29.61 (d, $^{2}J_{C\text{-}P}$ = 4.25 Hz, d), 22.11 (d, $^{1}J_{C\text{-}P}$ = 143 Hz, c), 19.05 (l or l'), 19.00 (l or l'), 16.54 (d, $^{3}J_{C\text{-}P}$ = 5.9 Hz, a+a') ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.95 ppm; IR (neat) 2976 (C-H), 1732 (C=O), 1470 (aromatic C=C), 1455 (aromatic C=C), 1387 (aromatic C=C), 1244 (P=O), 1053 (C-O), 1022 (C-O), 955 (P-O), 699 cm^{-1}. Enantiomer ratio = 99:1, determined by chiral HPLC analysis: Stationary phase = CHIRALPAK IC; Mobile Phase = 50:50 Isopropanol:Hexanes; Flow rate = 1 mL/min; HPLC UV Detector λ = 210 nm, 25 °C. HPLC traces:

(a) R:S = 96:4, Reaction of *rac*-**9a** with 0.6 eq. isobutyric anhydride with (*R*)-BTM. Ester **10a** formed is enriched in *"R"* enantiomer.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.490	VB	0.2798	628.97388	3.6464
2	10.486	BB	0.3750	1.66201e4	96.3536

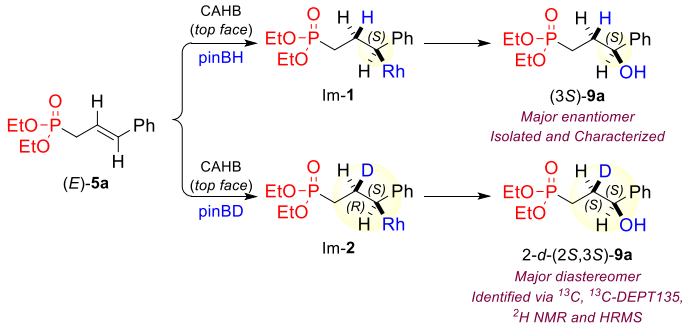
(b) R:S = 1:99, Reaction of *rac*-**9a** with 0.6 eq. isobutyric anhydride with (*S*)-BTM. Ester **10a** formed is enriched in *"S"* enantiomer.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %
1	7.580	VV	0.2481	2.02153e4	99.2186
2	10.826	VV	0.4515	159.21370	0.7814

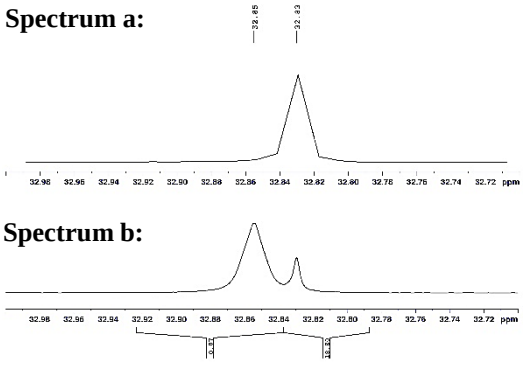
(8) Mechanistic studies

Recall that using the same catalyst system for CAHB, (*E*)- and (*Z*)-**5a** give the same major enantiomer of chiral alcohol **9a** after oxidation. Rhodium-catalyzed pinBH addition to (*E*)-**5a** occurs from the *"top-face"* in the perspective drawn to form (3*S*)-**9a** (Scheme S1). To probe the origin of their stereoconvergent CAHB, we separately carried out deuterium labelling experiments using **GP4** with pinBD for each stereoisomer of the substrate. In analogy to pinBH, CAHB of (*E*)-**5a** with pinBD proceeding via addition to the *"top face"* should yield the 2-*d*-(2*S*,3*S*)-**9a** diastereomer. The site and extent of deuterium incorporated in **9a** were analyzed via ^{1}H, ^{2}H, ^{13}C, ^{13}C-DEPT 135 NMR and MS.



Scheme S1. "Top-face" addition of pinBH and pinBD in CAHB of (*E*)-**5a**.

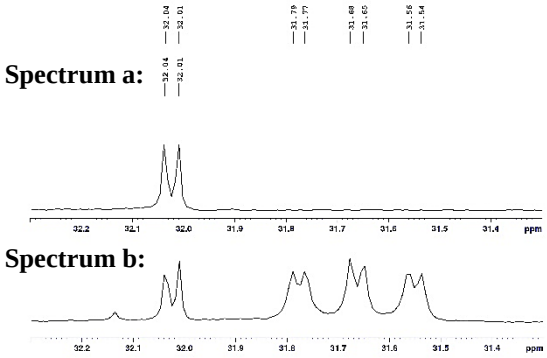
The ^{31}P NMR spectrum of (3*S*)-**9a** shows a single peak at 32.83 ppm (Spectrum a, Scheme S2). The ^{31}P NMR spectrum of **9a** obtained from (*E*)-**5a** after CAHB with pinBD followed by oxidation shows two peaks at 32.85 ppm and 32.83 ppm in about 80:20 ratio (Spectra b, Scheme S2). The peak at 32.85 ppm is assigned to 2-*d*-(2*S*,3*S*)-**9a** and that of 32.83 ppm for (3*S*)-**9a**. The formation of (3*S*)-**9a** must arise from pinBH addition to (*E*)-**5a**; although completely deuterated pinBD is used, we must conclude that some pinBH is formed under the reaction conditions.



Scheme S2. ^{31}P NMR spectra of (3*S*)-**5a** (Spectrum a) and enriched 2-*d*-(2S,3S)-**9a** (Spectrum b).

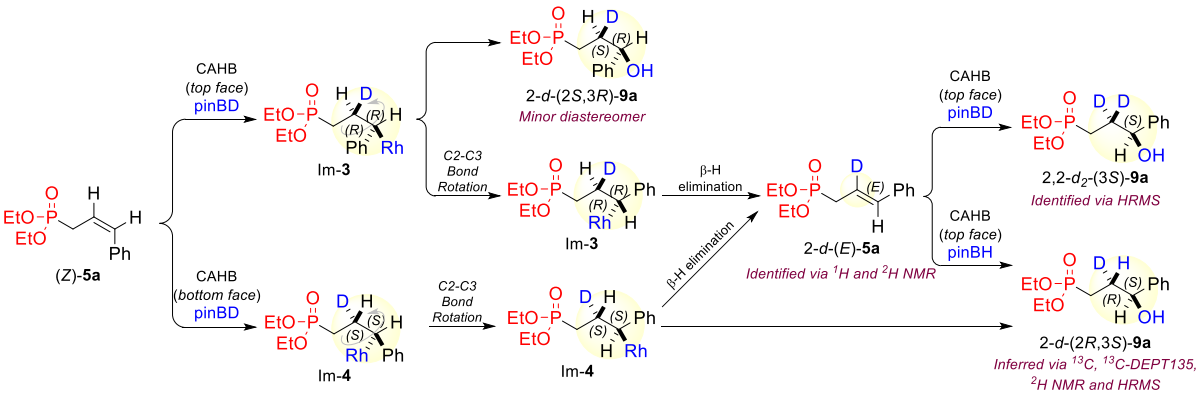
The peak for the β-carbon of (3*S*)-**9a** appears as a doublet at δ 32.02 ($^{2}J_{C\text{-}P}$ = 5.0 Hz; Spectra a, Scheme S3). The ^{13}C NMR spectrum of **9a** obtained from (*E*)-**5a** after CAHB with pinBD followed by oxidation shows two peaks as shown in Scheme S3, spectrum b). The β-carbon atom assigned to 2-*d*-(2*S*,3*S*)-**9a** bonded to deuterium and being two bonds away from phosphorus is identified at δ 31.66 in the ^{13}C NMR spectrum with a splitting pattern of a triplet of doublets ($^{1}J_{C\text{-}D}$ coupling ~ 20 Hz, $^{2}J_{C\text{-}P}$ coupling ~ 4.25 Hz): 31.66 (td, $^{1}J_{C\text{-}D}$ = 20 Hz, $^{2}J_{C\text{-}P}$ = 4.25 Hz) ppm. The peak at d 32.02 (d, $^{2}J_{C\text{-}P}$ = 5.0 Hz) is assigned to the non-deuterated (3*S*)-

9a. The ratio of deuterium to hydrogen in the β-carbon is about 80:20 based on the ^{13}C and ^{31}P NMR spectra obtained.



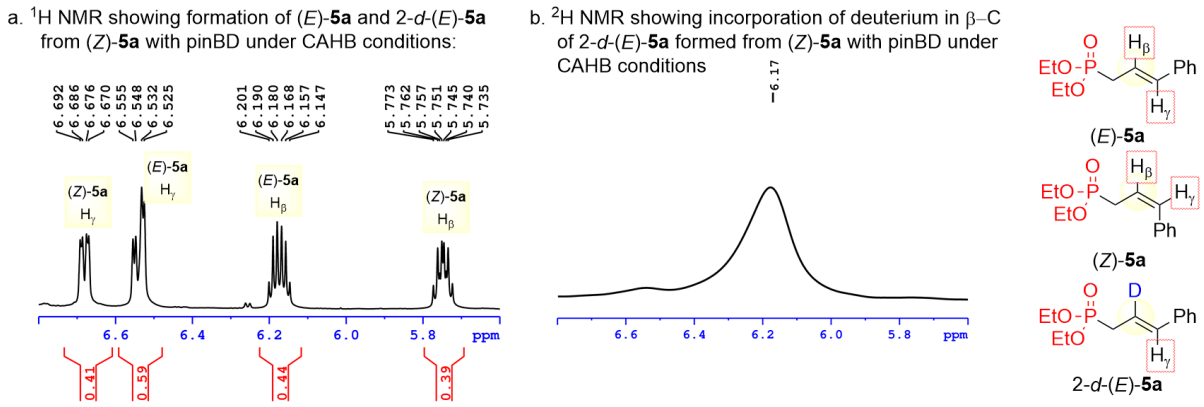
Scheme S3. ^{13}C NMR spectra (zoomed in for β-carbon) of (3*S*)-**5a** (Spectrum a) and enriched 2-*d*-(2S,3S)-**9a** (Spectrum b).

In Scheme S4, we consider the consequences of *"top face"* and *"bottom face"* addition of pinBD to the isomeric (*Z*)-**5a** in light of the fact that it must ultimately produce deuterated (*S*)-**9a**, not deuterated (*R*)-**9a**. Addition of pinBD to the *"top-face"* of (*Z*)-**5a** would give rise to Im-**3**. Alternatively, addition of pinBD to the *"bottom face"* of (*Z*)-**5a** would give rise to Im-**4**. Were subsequent steps in the mechanism leading to C–B bond formation fast, Im-**3** would lead to deuterated (*R*)-**9a**, while Im-**4** would lead to the observed product, deuterated (*S*)-**9a**. But there is an alternative explanation to this (*E/Z*)-alkene geometry induced change in the sense π-facial discrimination; (*E/Z*)-alkene isomerization under the CAHB reaction conditions is supported by our labeling experiments.



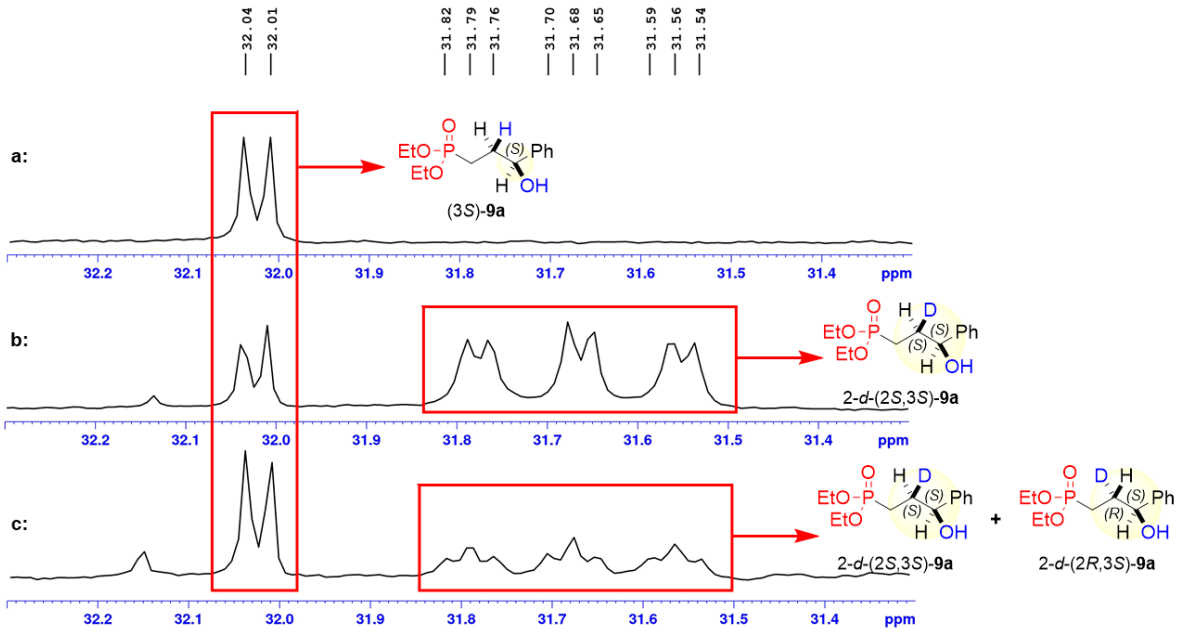
Scheme S4. Top and bottom-face addition of pinBD in CAHB of (*Z*)-**5a**.

The formation of either Im-**3** or Im-**4** followed by rapid β-hydride elimination would form 2-*d*-(*E*)-**5a** which has been identified via ^{1}H and ^{2}H NMR analysis (Scheme S5) from a reaction of (*Z*)-**5a** with pinBD that is quenched early with methanol. We find that isomerization of (*Z*)-**5a** is rapid in the beginning of the reaction; a nearly 1:1 ratio of *E:Z* substrates is identified in the first 5 minutes of the reaction time and then increases more slowly reaching a 2:1 ratio after about 30 minutes.



Scheme S5. ^{1}H and ^{2}H NMR's showing formation of (*E*)-**5a** and 2-*d*-(*E*)-**5a** from (*Z*)-**5a** with pinBD under CAHB conditions.

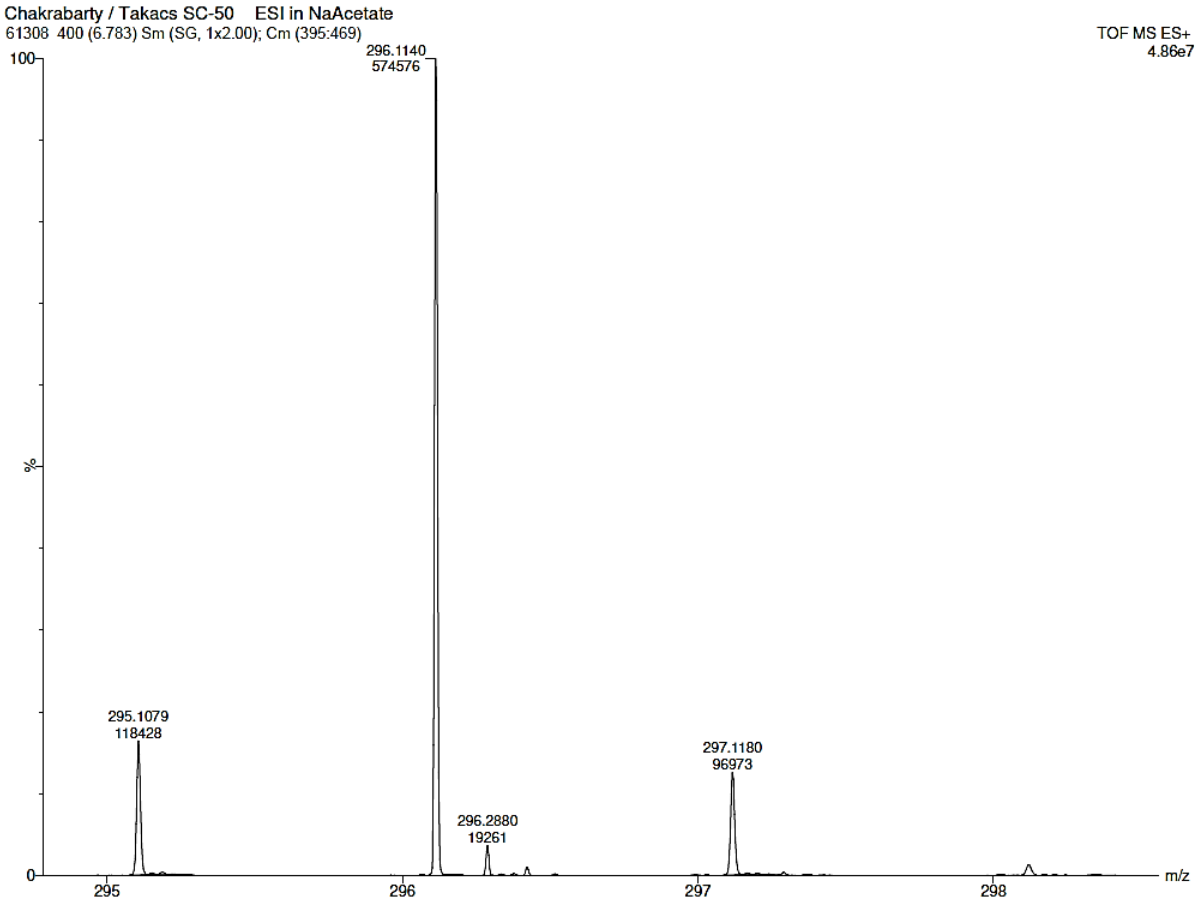
As illustrated in Scheme S4, CAHB of 2-*d*-(*E*)-**5a** with pinBD from the expected *"top-face"* should afford 2,2-d_2-(3*S*)-**9a**, and the latter has been identified via HRMS analysis (vide infra). However, β-hydride elimination from Im-**3** or Im-**4** not only forms 2-*d*-(*E*)-**5a** but generates an equivalent amount of pinBH from pinBD. We also find products resulting from this in situ generated pinBH; its expected addition to the *"top-face"* of 2-*d*-(*E*)-**5a** should afford 2-*d*-(2*R*,3*S*)-**9a** as illustrated above (Scheme S4). Furthermore, isomerization of (*Z*)-**5a** to (*E*)-**5a** via the with the initial addition of pinBH and then followed by pinBD addition should generate the diastereomeric 2-*d*-(2*S*,3*S*)-**9a**. Finally, the addition of pinBH to in situ generated (*E*)-**5a** should generate a small amount of (3*S*)-**9a**. Thus, CAHB of (*Z*)-**5a** with pinBD should potentially lead to the formation of four products: (3*S*)-**9a**, 2-*d*-(2*R*,3*S*)-**9a**, 2-*d*-(2*S*,3*S*)-**9a** and 2,2-d_2-(3*S*)-**9a**. The ^{13}C NMR data shown in Scheme S6 highlight the characteristic signatures for: **a**. (3*S*)-**9a**; **b.** 2-*d*-(2*S*,3*S*)-**9a** (as formed from (*E*)-**5a** with pinBD); and **c**. the mixture of 2-*d*-(2*S*,3*S*)-**9a** and 2-*d*-(2*R*,3*S*)-**9a** formed from (*Z*)-**5a** with pinBD in which the presence of 2-*d*-(2*R*,3*S*)-**9a** is inferred from the overlapping sets of ddd signals for the β-carbon bearing one deuterium from each of the two diastereomers.



Scheme S6. ^{13}C NMR zoomed in for the region of β-carbon: (a) CAHB of (*E*)-**5a** with pinBH, then oxidation to yield (3*S*)-**9a**. (b) CAHB of (*E*)-**5a** with pinBD, then oxidation to yield mixtures of hydro- and deutero

incorporated **9a**. (c) CAHB of (*Z*)-**5a** with pinBD, then oxidation to yield diastereomeric monodeuterated **9a** in addition to hydro-incorporated **9a**.

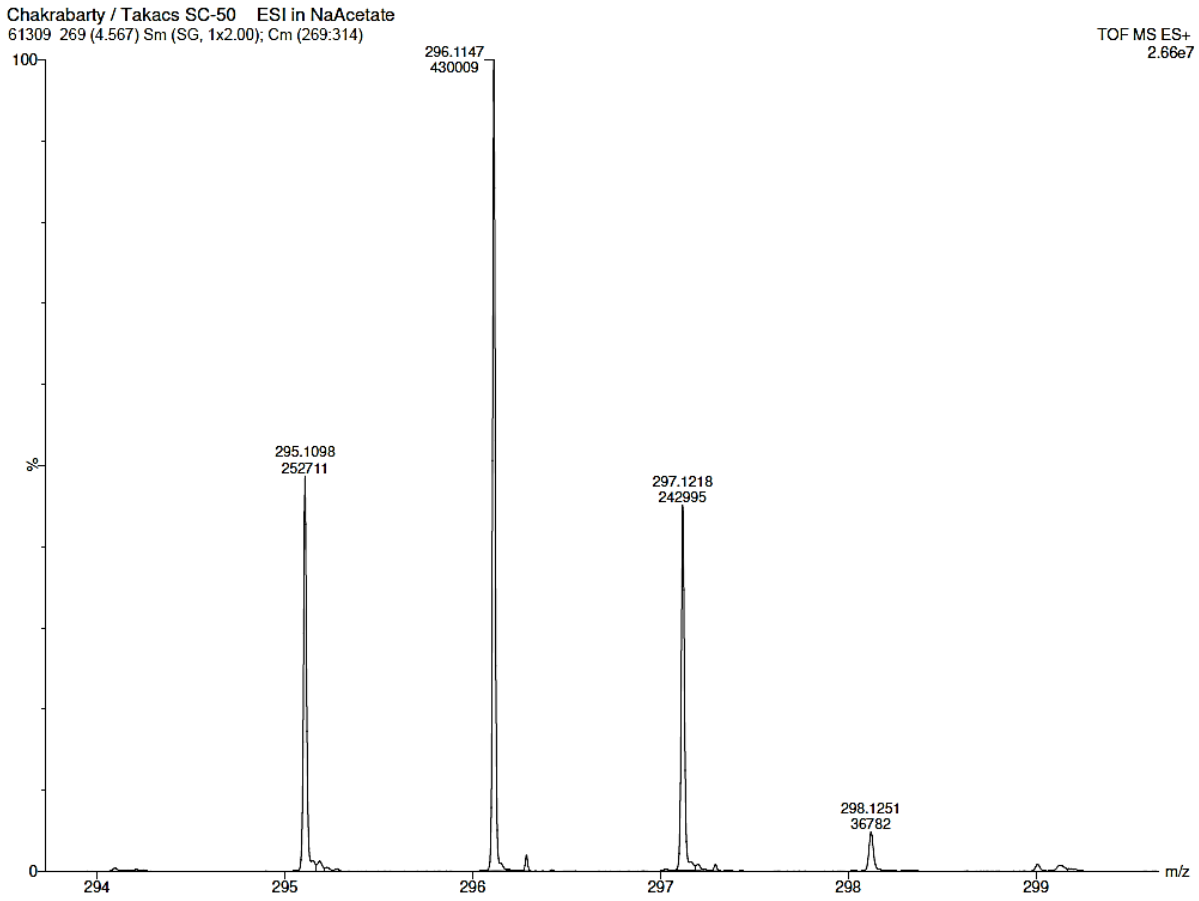
Mass spectral analysis of the products obtained by reaction of pinBD with (*E*)-**5a** and with (*Z*)-**5a** are shown below. The mixture of proteo/mono-deutero alcohols **9a** obtained via CAHB of (*E*)-**5a** with pinBD following **GP4** is subjected to HRMS (Scheme S7). (i) The molecular ion peak for (3*S*)-**9a** (Calculated for $C_{13}H_{21}O_4P+Na^+$ = 295.1075) corresponds to a *m/z* peak at 295.1079 and that of 2-*d*-(2*S*,3*S*)-**9a** (Calculated for $C_{13}H_{20}DO_4P+Na^+$ = 296.1138) corresponds to a *m/z* peak at 296.1140. (ii) Since **9a** contains 13 C atoms and the relative abundance of ^{13}C is 1.1% in nature, 14.3% of the area under the peak corresponding to *m/z* 295.1079 is subtracted from the area under the peak corresponding to *m/z* of 296.1140 to account for the ^{13}C correction. This gives a corrected area of 557640 under the peak corresponding to *m/z* of 296.1140 (molecular ion peak for 2-*d*-(2*S*,3*S*)-**9a**). The ^{13}C correction for area under the peak corresponding to *m/z* of 297.1180 would give a corrected area of 14808. This peak is mainly due to ^{13}C and not due to ^{2}H (See the elemental analysis). (iii) The ratio of (3*S*)-**9a** to 2-*d*-(2*S*,3*S*)-**9a** as obtained from the above HRMS analysis (Sample obtained from CAHB/Oxidation of (*E*)-**5a** with pinBD using **GP4**) is 17:83.



Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
295.1075	16.28	295.1075	0.0	0.0	3.5	-1.$	n/a	1.#R	12C13 1H21 16O4 23Na 31P
		295.1097	-2.2	-7.5	4.5	-1.$	n/a	1.#R	12C12 13C 1H17 16O6 23Na 2H
		295.1099	-2.4	-8.1	12.5	-1.$	n/a	1.#R	12C20 1H16 16O 23Na
		295.1039	3.6	12.2	13.5	-1.$	n/a	1.#R	12C19 13C 1H13 16O 23Na 2H
296.1139	100.00	296.1138	0.1	0.3	3.5	-1.$	n/a	1.#R	12C13 1H20 16O4 23Na 2H 31P
		296.1132	0.7	2.4	12.5	-1.$	n/a	1.#R	12C19 13C 1H16 16O 23Na
		296.1162	-2.3	-7.8	12.5	-1.$	n/a	1.#R	12C20 1H15 16O 23Na 2H
		296.1109	3.0	10.1	3.5	-1.$	n/a	1.#R	12C12 13C 1H21 16O4 23Na 31P
		296.1191	-5.2	-17.6	3.5	-1.$	n/a	1.#R	12C12 13C 1H20 16O6 23Na
297.1177	12.63	297.1171	0.6	2.0	3.5	-1.$	n/a	1.#R	12C12 13C 1H20 16O4 23Na 2H 31P
		297.1195	-1.8	-6.1	12.5	-1.$	n/a	1.#R	12C19 13C 1H15 16O 23Na 2H
		297.1232	-5.5	-18.5	2.5	-1.$	n/a	1.#R	12C13 1H23 16O4 23Na 31P

Scheme S7. HRMS analysis of the mixture of proteo/mono-deutero alcohols **9a** obtained via CAHB of (*E*)-**5a** with pinBD.

The mixture of proteo/mono deutero and dideutero alcohols **9a** obtained via CAHB of (*Z*)-**5a** with pinBD following **GP4** is subjected to HRMS (Scheme S8). (i) The molecular ion peak for (3*S*)-**9a** (Calculated for $C_{13}H_{21}O_4P+Na^+$ = 295.1075) corresponds to a *m/z* peak at 295.1098, that of 2-*d*-(2*S*,3*S*)-**9a** (Calculated for $C_{13}H_{20}DO_4P+Na^+$ = 296.1138) corresponds to a *m/z* peak at 296.1147 and that of 2,2-d_2-(3*S*)-**9a** (Calculated for $C_{13}H_{19}D_2O_4P+Na^+$ = 297.1201) corresponds to a *m/z* peak at 297.1218. (ii) Since **9a** contains 13 C atoms and the relative abundance of ^{13}C is 1.1% in nature, 14.3% of the area under the peak corresponding to *m/z* 295.1098 is subtracted from the area under the peak corresponding to *m/z* of 296.1147 to account for the ^{13}C correction. This gives a corrected area of 393871 under the peak corresponding to *m/z* of 296.1147 (molecular ion peak for 2-*d*-(2*S*,3*S*)-**9a**). 14.3% of the corrected area under the peak corresponding to *m/z* 296.1147 is to be subtracted from the peak corresponding to *m/z* of 297.1218 to account for ^{13}C correction. Thus, the corrected area under *m/z* 297.1218 is 186671. (iii) Thus, the ratio of (3*S*)-**9a**: 2-*d*-(2*S*,3*S*)-**9a**: 2,2-d_2-(3*S*)-**9a** determined from HRMS analysis (Sample obtained from CAHB/Oxidation of (*Z*)-**5a** with pinBD using **GP4**) is 30: 47: 23.

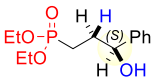
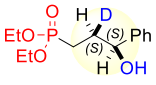
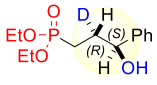
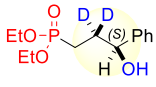
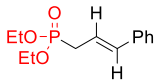
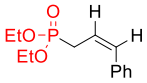


Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
295.1077	48.90	295.1075	0.2	0.7	3.5	-1.$	n/a	1.#R	12C13 1H21 16O4 23Na 31P
		295.1068	0.9	3.0	13.5	-1.$	n/a	1.#R	12C20 1H12 2H2 16O 23Na
		295.1097	-2.0	-6.8	4.5	-1.$	n/a	1.#R	12C12 13C 1H17 2H 16O6 23Na
		295.1099	-2.2	-7.5	12.5	-1.$	n/a	1.#R	12C20 1H16 16O 23Na
		295.1044	3.3	11.2	4.5	-1.$	n/a	1.#R	12C13 1H17 2H2 16O4 23Na 31P
		295.1039	3.8	12.9	13.5	-1.$	n/a	1.#R	12C19 13C 1H13 2H 16O 23Na
		295.1127	-5.0	-16.9	4.5	-1.$	n/a	1.#R	12C13 1H16 2H2 16O6 23Na
296.1138	100.00	296.1138	0.0	0.0	3.5	-1.$	n/a	1.#R	12C13 1H20 2H 16O4 23Na 31P
		296.1132	0.6	2.0	12.5	-1.$	n/a	1.#R	12C19 13C 1H16 16O 23Na
		296.1160	-2.2	-7.4	4.5	-1.$	n/a	1.#R	12C12 13C 1H16 2H2 16O6 23Na
		296.1162	-2.4	-8.1	12.5	-1.$	n/a	1.#R	12C20 1H15 2H 16O 23Na
		296.1109	2.9	9.8	3.5	-1.$	n/a	1.#R	12C12 13C 1H21 16O4 23Na 31P
		296.1101	3.7	12.5	13.5	-1.$	n/a	1.#R	12C19 13C 1H12 2H2 16O 23Na
		296.1191	-5.3	-17.9	3.5	-1.$	n/a	1.#R	12C12 13C 1H20 16O6 23Na
297.1197	44.90	297.1195	0.2	0.7	12.5	-1.$	n/a	1.#R	12C19 13C 1H15 2H 16O 23Na
		297.1201	-0.4	-1.3	3.5	-1.$	n/a	1.#R	12C13 1H19 2H2 16O4 23Na 31P
		297.1171	2.6	8.8	3.5	-1.$	n/a	1.#R	12C12 13C 1H20 2H 16O4 23Na 31P
		297.1224	-2.7	-9.1	12.5	-1.$	n/a	1.#R	12C20 1H14 2H2 16O 23Na
		297.1232	-3.5	-11.8	2.5	-1.$	n/a	1.#R	12C13 1H23 16O4 23Na 31P
		297.1254	-5.7	-19.2	3.5	-1.$	n/a	1.#R	12C12 13C 1H19 2H 16O6 23Na
		297.1255	-5.8	-19.5	11.5	-1.$	n/a	1.#R	12C20 1H18 16O 23Na

Scheme S8. HRMS analysis of mixture of proteo/mono deutero and dideutero alcohols **9a** obtained via CAHB of (*Z*)-**5a** with pinBD.

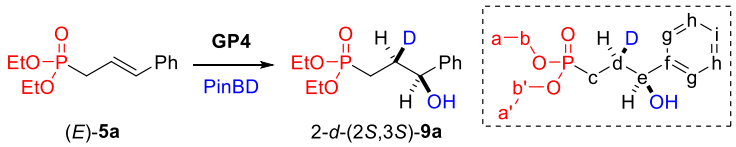
Summary of deuterium-labeling experiments.

Following is the distribution of products that is obtained from (*E*)-**5a** and (*Z*)-**5a** when reacted with pinBD under standard CAHB conditions:

Substrate	Percentages inferred from NMR and HRMS analysis			
	 (3*S*)-**9a**	 2-*d*-(2*S*,3*S*)-**9a**	 2-*d*-(2*R*,3*S*)-**9a**	 2,2-d_2-(3*S*)-**9a**
 (*E*)-**5a**	18	82	--	--
 (*Z*)-**5a**	30	47		21

In conclusion, the same major enantiomer of **9a** is obtained from both (*E*)- and (*Z*)-**5a**. This (*E*/*Z*)-stereoconvergence during CAHB can be simply explained by the rapid isomerization of (*Z*)-**5a** to (*E*)-**5a** via initial addition of borane followed by β-hydride elimination under reaction conditions; this isomerization has been verified by deuterium labelling studies. However, it should be noted that the question of whether the (*E*/*Z*)-alkene geometry induces a change in the sense π-facial discrimination is not answered definitively by our data. We can only conclude it is not necessary to invoke such a change to account for the observed results.

Characterization data for 2-*d*-(2*S*,3*S*)-9a:



(*E*)-**5a** 2-*d*-(2*S*,3*S*)-**9a**

CAHB of (*E*)-5a with pinBD: Following the general procedure for sequential hydroboration-oxidation (**GP4**) with deuterated pinacolborane (pinBD), the substrate (*E*)-**5a** (50 mg, 0.2 mmol) affords the mixture of hydro/deutero γ-alcohol product **9a** (30 mg, ~55%) as a colorless oil: TLC analysis (methanol/ethyl acetate 1:19) R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (5H, m, aryl), 4.79 (1H, d, *J* = 4.7, 6.0 Hz, e), 4.15-4.06 (4H, m, b+b'), 3.20 (1H, br s, OH), 2.09-2.03 (1.2H, m, d), 1.95-1.79 (2H, m, c), 1.34 (6H, t, *J* = 7.0 Hz, a+a') ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.13 (f), 128.65 (g or h), 127.74 (i), 125.98 (g or h), 73.84 (d, $^3J_{C\text{-}P}$ = 15 Hz, e), 61.87 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 61.84 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, b or b'), 31.63 (td, $^1J_{C\text{-}D}$ = 20 Hz, $^2J_{C\text{-}P}$ = 4.5 Hz, d), 21.97 (d, $^1J_{C\text{-}P}$ = 141 Hz, c), 16.61 (d, $^3J_{C\text{-}P}$ = 6.0 Hz, a+a') ppm; ^{31}P NMR (283 MHz, $CDCl_3$) δ 32.85 ppm; HRMS (ESI) calculated for $C_{13}H_{20}DO_4P+Na^+$ = 296.1138, found 296.1139 *m/z*.

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