Concatenated Catalytic Asymmetric Allene Diboration/Allylation/Functionalization

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Supporting Information

General. ^1H NMR spectra were recorded on Bruker DRX 300, 400, or 500 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR was recorded on a Bruker 400 MHz (100 MHz) or 500 MHz (125 MHz) spectrometer with complete proton decoupling. ^{31}P NMR spectra were recorded on a Bruker 400 MHz (161 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl_3 : 77.0 ppm). High-resolution and low resolution mass spectrometry were performed by the University of Minnesota or the University of North Carolina at Chapel Hill Mass Spectrometry Service Laboratory. Infrared (IR) spectra were obtained on an ASI ReactIR 1000. Bands are characterized as broad (br), strong (s), and medium (m).

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2 , 230 X 450 mesh) purchased from EMD Chemicals, Inc. Thin layer chromatography was performed on 250 μm silica gel plates from Sorbent Technologies, Inc. Visualization was achieved using UV light, phosphomolybdic acid in ethanol, potassium permanganate in water, or cerium sulfate and ammonium molybdate in sulfuric acid, each followed by heating.

Analytical gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatography equipped with a CTC Analysis Combi Pal autosampler by Leap Technologies (Carrboro, NC), a split mode capillary injection system, a flame ionization detector and a Supelco β -dex 120 column with helium as the carrier gas. Analytical supercritical fluid chromatography (SFC) was performed on a Berger Instruments supercritical chromatograph equipped with an Alcott autosampler and a Knauer UV detector.

Diboration/allylation reactions were conducted in oven and flame dried glassware under an inert atmosphere of nitrogen or argon. Toluene was distilled over CaH_2 and degassed by freeze-pump-thaw cycles prior to use. Tris(dibenzylideneacetone)dipalladium was purchased from Strem Chemical Company. Allenes were synthesized according to the literature [(a) Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, 94, 112 (b) Myers, A. G.; Zheng, B. *J. Am. Chem. Soc.* **1996**, 118, 4492]. Racemic compounds were prepared by the diboration of allenenes using PCy_3 as the ligand. Isobutyraldehyde, butyraldehyde, benzaldehyde and iodobenzene were freshly distilled prior to use. All other reagents were purchased from Strem, Aldrich, BASF, Cambridge Isotopes, Matrix, or Alfa Aesar Chemical Companies and used directly. Benzoate derivatives of the β -hydroxyketone products for SFC analysis were prepared by treatment of the β -hydroxyketones with benzoyl chloride, pyridine, and 4-dimethylaminopyridine in CH_2Cl_2 followed by silica gel chromatography.

General Procedure for Monitoring Conversion for the Formation of 1,2-Bis(boronate)esters

To a two-dram oven dried vial equipped with magnetic stir was added tris(dibenzylideneacetone)dipalladium(0) (3.47 mg, 0.0038 mmol) and the respective TADDOL-phosphoramidite (0.00912 mmol) in 300 μL toluene- d_8 in an inert atmosphere dry box. This mixture was stirred for 60 min at which time bis(pinacolato)diboron (46.3 mg, 0.1824 mmol, 1.2 equiv) and the respective allene (0.152 mmol) were added. The mixture was transferred to an oven dried J-Young Tube, an additional 700 μL of toluene- d_8 was added, and the reaction was removed from the dry box. After 12 or 24 h, the reaction was charged with trimethoxybenzene and the reaction was monitored by ^1H NMR and the amount of allene consumed was calculated. The isolated yields for 1,2-bis(boronate) esters were determined from reactions using this general procedure but without the addition of internal standard. The allene diboration adducts have been previously characterized (Pelz et. al *J. Am. Chem. Soc.* **2004**, *126*, 16328).

Preparation and Characterization of TADDOLPNMe₂:

Alexakis, A.; Burton, J.; Vastra, J.; Benhaim, C.; Fournioux, X.; Heuvel, A. V. D.; Levêque, J. M.; Mazé, F.; Rosset, S. *Eur. J. Org. Chem.* **2000**, 4011.

Preparation and Characterization of 3,5-Me₂TADDOLPNMe₂:

Boele, M.D.K.; Kamer, P.C.J.; Lutz, M.; Spek, A.L.; de Vries, J.G.; van Leeuwen, P.W. N. M.; vanStrijdonck, G.P.F. *Chem. Eur. J.* **2004**, *10*, 6232.

Procedure for the Preparation of 3,5-(*t*-Bu)₂TADDOLPNMe₂:

To a 250-mL flame-dried round bottom flask equipped with an oven dried magnetic stir bar was added 4Å molecular sieves, followed by 3,5-(*t*-Bu)₂TADDOL (prepared from L-tartaric acid and 1-bromo-3,5-di-*tert*-butyl benzene, see: Seebach, D.; Beck, A.K.; Keckel, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 92-138.) (5.573 g 6.087 mmol, 1 equiv) and tetrahydrofuran (25 mL, 0.25 M). The flask was cooled to 0 °C (ice-water bath) and charged with triethylamine (2.88 mL, 20.69 mmol, 3.4 equiv) and phosphorus trichloride (637 μL , 7.305 mmol, 1.2 equiv). The mixture was allowed to warm to ambient temperature and was stirred for 30 min, at which time it was cooled to 0 °C (ice-water bath) and charged with dimethyl amine (30 mL, 2.0 M in tetrahydrofuran, 10 equiv). The mixture was warmed to ambient temperature and was allowed to stir overnight before it was diluted with diethyl ether and filtered over Celite. The solvent was removed via rotary evaporation and the crude reaction mixture was purified on silica gel (4% ethyl acetate/Hexanes) to afford the desired phosphoramidite (3.95 g, 65% yield).

Dimethyl-[4,4,8,8-tetrakis-(3,5-di-*tert*-butyl-phenyl)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphin-6-yl]-amine. IR (CH_2Cl_2): 3437 (w, br), 3064 (s), 2959 (s), 2900 (s), 2854 (s), 2792 (s), 2753 (s), 2709 (s), 2353 (s), 2326 (s), 2287 (s), 1778 (s), 1592 (s), 1475 (s), 1392 (s), 1366 (s), 1254 (s), 1190 (s), 1053 (s), 968 (s), 894 (s), 870 (s), 785 (s), 734 (s), 696 (s). cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.08 (3H, s, CH_3CO), 1.24 (18H, s, $(\text{CH}_3)_3\text{CAr}$), 1.26 (18H, s, $(\text{CH}_3)_3\text{CAr}$), 1.28 (18H, s, $(\text{CH}_3)_3\text{CAr}$), 1.29 (18H,

s, (CH₃)₃CAr), 1.46 (3H, s, CH₃CO), 2.88 (6H, d, *J* = 10.4 Hz, (CH₃)₂N), 4.76 (1H, d, *J* = 8.8 Hz, OCHC), 5.25 (1H, dd, *J* = 8.4, 2.4 Hz, OCHC), 7.12 (2H, d, *J* = 2 Hz, H-Ar), 7.20-7.25 (4H, m, H-Ar), 7.41 (2H, s, H-Ar), 7.60 (2H, d, *J* = 1.6 Hz, H-Ar), 7.63 (2H, d, *J* = 1.6 Hz, H-Ar). ¹³C NMR (100 MHz, CDCl₃): δ 24.08, 28.23, 31.65, 31.69, 31.7, 34.96, 35.09, 35.17, 35.57, 35.77, 81.52, 81.49, 82.44, 82.50, 83.90, 83.94, 84.11 (the region 81.52-84.11 ppm contains extra carbon peaks, possibly due to C-P coupling, see: Boele, M.D.K.; Kamer, P.C.J.; Lutz, M.; Spek, A.L.; de Vries, J.G.; van Leeuwen, P.W.N.M.; van Strijdonck, G.P.F. *Chem. Eur. J.* **2004**, *10*, 6232), 110.03, 120.11, 120.40, 120.72, 121.62, 123.80, 123.96, 123.99, 141.26, 142.01, 146.20, 146.23, 146.66, 148.89, 149.05, 149.37, 149.76. ³¹P NMR (161 MHz, CDCl₃): δ 141.98. HRMS (ESI) Calc'd for C₆₅H₉₈NO₄P (M+H)⁺: 988.7312 Found (M+H)⁺: 988.7306.

Determination of Enantiopurity of 1,2-Bis(boronate)esters

Enantioselectivity was determined by diimide reduction (2-nitrobenzenesulfonylhydrazide, triethylamine, dioxanes, 95 °C) of the diboron followed by basic hydrogen peroxide oxidation (3M NaOH, H₂O₂, quench with Na₂S₂O₃). The resultant diol was protected as the acetone (pTsOH, 2,2-dimethoxypropane, 60 °C, 10 min). Absolute stereochemistry of the 1,2-bis(boronate)esters was reported in Pelz, N.F.; Woodward, A.R.; Burks, H.E.; Sieber, J.D.; Morken, J.P. *J. Am. Chem. Soc.* **2004**, *126*, 16328.

Representative Procedure for One-Pot, Sequential Diboration/Allylation/Oxidation of Allenes:

An oven-dried 20 mL vial equipped with a stir-bar was charged with 10 mg (0.01 mmol) Pd₂(dba)₃, 18 mg (0.03 mmol) (*R,R*-xylyl-TADDOL)PNMe₂, and 0.86 mL toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 min – 1 h). After this time, 130 mg (0.51 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 min. Next, 50 mg (0.43 mmol) of propa-1,2-dienyl-benzene was added to the solution. The vial was sealed with a screw-cap and allowed to stir for 12 hours at ambient temperature. After this time, 180 μL of a 1.5 M solution of isobutyraldehyde (0.27 mmol) in toluene was added to the solution, and the reaction was allowed to stir for 12 h. The vial was cooled to 0 °C. Subsequently, 1 mL THF and 1 mL 3 M NaOH were added, followed by dropwise addition of 1 mL of a 30% aqueous H₂O₂ solution. The solution was allowed to warm to room temperature and stirred for 5 h. The reaction was quenched with 1 mL of saturated aqueous Na₂S₂O₃ and 1 mL of 1 M NaOH. The mixture was extracted with ethyl acetate (2 x 5 mL). The organic layers were dried over anhydrous Na₂SO₄, filtered, and the solvent removed by rotary evaporation. The crude material was purified by silica gel chromatography (5:1 hexanes:ethyl acetate) to provide 51 mg (93%) of 4-hydroxy-5-methyl-1-phenylhexan-2-one as a clear oil.

Procedure for One-pot Simultaneous Diboration/Allylation:

An oven-dried 20 mL vial equipped with a stir-bar was charged with 10 mg (0.01 mmol) Pd₂(dba)₃, 18 mg (0.03 mmol) (*R,R*-xylyl-TADDOL)PNMe₂, and 0.86 mL toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes – 1 hour). After this time, 130 mg (0.51 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 min. Next, 50 mg (0.43 mmol) of propa-1,2-dienyl-benzene and 180 μL of a 1.5 M solution of isobutyraldehyde (0.27 mmol) in toluene were added to the solution, and the reaction was allowed to stir for 12 h. The vial was cooled to 0 °C. Subsequently, 1 mL THF and 1 mL 3 M NaOH were added, followed by dropwise addition of 1 mL of a 30% aqueous H₂O₂ solution. The solution was allowed to warm to room temperature and stirred for 5 hours. The reaction was quenched with 1 mL of saturated aqueous Na₂S₂O₃ and 1 mL of 1 M NaOH. The mixture was extracted with ethyl acetate (2 x 5 mL). The

organic layers were dried over anhydrous Na_2SO_4 , filtered, and the solvent removed by rotary evaporation. The crude material was purified by silica gel chromatography (5:1 hexanes:ethyl acetate) to provide 44 mg (80%) of 4-hydroxy-5-methyl-1-phenylhexan-2-one as a clear oil.

(R)-4-Hydroxy-1-phenylheptan-2-one. Clear oil. $R_f = 0.25$ in 5:1 hexanes/ethyl acetate. IR (neat) 3454 (br, m), 2960 (m), 1710 (s), 700.4 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.30 (2H, m), 7.28 – 7.24 (1H, m), 7.17 (2H, d, 7.2 Hz), 4.00 (1H, m), 3.69 (2H, s), 2.92 (1H, s), 2.62 (1H, dd, $J = 17.6, 2.8$ Hz), 2.52 (1H, dd, $J = 17.6, 8.8$ Hz), 1.44 – 1.36 (2H, m), 1.33 – 1.24 (2H, m), 0.873 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 209.7, 113.6, 129.4, 128.8, 127.2, 67.3, 50.8, 48.3, 38.5, 18.6, 13.9; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 229.1 Found ($\text{M}+\text{Na}$) $^+$: 229.2.

SFC (Chiracel, AD-H, Supelco, 150 psi, 50 °C, flow = 3.0 mL/min, 2.0% MeOH) analysis of benzoate derivative of allylboration product:

Diboration/Allylboration
Product

Racemic

Diboration/Allylboration
Product + Racemic

(R)-4-Hydroxy-5-methyl-1-phenylhexan-2-one. Clear oil. $R_f = 0.25$ in 5:1 hexanes/ethyl acetate. IR (neat) 3450 (m, br), 2962 (m), 1710 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.31 (2H, m), 7.28 – 7.24 (1H, m), 7.19 – 7.17 (2H, m), 3.75 (1H, m), 3.71 (2H, s), 2.83 (1H, s), 2.62 (1H, dd, $J = 17.4, 2.6$ Hz), 2.52 (1H, dd, $J = 17.6, 9.6$ Hz), 1.62 (1H, m), 0.86 (6H, dd, $J = 13.6, 0.86$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 209.9, 133.7, 129.5, 128.8, 127.2, 72.4, 50.9, 45.4, 33.0, 18.4, 17.7; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 229.1 Found ($\text{M}+\text{Na}$) $^+$: 229.0.

SFC (Chiracel AD-H, Supelco, 150 psi, 50°C, flow = 2.5 mL/min, 2.0% MeOH) analysis of benzoate derivative of allylboration product:

Diboration/Allylboration
Product

Racemic

Diboration/Allylboration
Product + Racemic

CCCCCCCCCCCCCCCC(=O)C[C@H](O)CCCC **(R)-4-Hydroxyheptadecan-6-one.** White solid. $R_f = 0.38$ in 5:1 hexanes/ethyl acetate. IR (CH_2Cl_2) 3056 (m, br), 2929 (s), 2856 (s), 2306 (m), 1704 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 4.03 – 3.99 (1H, m), 2.56 (1H, dd, $J = 17.2, 2.8$ Hz), 2.46 (1H, dd, $J = 17.2, 9.0$ Hz), 2.38 (2H, t, $J = 7.4$ Hz), 1.55 – 1.52 (2H, m), 1.49 – 1.38 (2H, m), 1.36 – 1.28 (2H, m), 1.28 – 1.24 (16H, m), 1.32 (3H, t, $J = 6.6$ Hz), 1.28 (3H, t, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 213.0, 67.7, 49.3, 44.1, 39.0, 32.3, 30.0, 29.8, 29.7, 29.6, 24.0, 23.1, 19.1, 14.5, 14.4; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 293.3 Found ($\text{M}+\text{Na}$) $^+$: 293.3.

SFC (Chiracel AD-H, Supelco, 150 psi, 50 °C, flow = 2.0 mL/min, 2.0% MeOH) analysis of benzoate derivative of allylboration product:

Diboration/Allylboration Product

Racemic

Diboration/Allylboration Product + Racemic

(R)-3-Hydroxy-2-methylhexadecan-5-one. White solid. $R_f = 0.47$ in 5:1 hexanes/ethyl acetate. IR (CH_2Cl_2) 2925 (s), 2858 (s), 1704 (s), 1470 (m), 1370 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.80 (1H, ddd, $J = 9.2, 6.0, 2.4$ Hz), 2.58 (1H, dd, $J = 17.4, 2.4$ Hz), 2.48 (1H, dd, $J = 17.4, 9.2$ Hz), 2.43 (2H, t, $J = 7.4$ Hz), 1.70 – 1.65 (1H, m), 1.59 – 1.55 (2H, m), 1.25 (18H, s, br), 0.92 (6H, dd, $J = 10.8, 6.8$ Hz), 0.88 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 213.3, 72.7, 46.3, 44.2, 33.4, 32.3, 30.0, 29.9, 29.8, 29.7, 29.6, 24.0, 23.1, 18.8, 18.2, 14.5; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 271.3 Found ($\text{M}+\text{H}$) $^+$: 271.3.

Proof of Stereochemistry. Absolute stereochemistry was established in comparison to material prepared by reaction of isobutyraldehyde with the boron enolate-derived from chlorodiisocampheylborane and tridecan-2-one. The reaction provided the methylketone aldol adduct (*S*)-3-Hydroxy-2-methylhexadecan-5-one in 65% *ee* according to literature procedures [(a) Paterson, I.; Goodman, J. M.; Lister, M. A.; Schumann, R. C.; McClure, C. K.; Norcross, R. D. *Tetrahedron* **1990**, 46, 4663. (b) Brown, H. C., Dhar, R. K., Ganesan, K., Singaram, B. *J. Org.Chem.* **1992**, 57, 499.].

SFC (Chiracel AD-H, 150 psi, 50 °C, flow = 3.0 mL/min, 4.0% MeOH) analysis of benzoate derivative of allylboration product (retention times shown in minutes):

Allylboration Product

Racemic

Authentic

Allylboration
Product
+ Racemic

(R)-1-Hydroxy-1-phenyltetradecan-3-one. White solid. $R_f = 0.34$ in 5:1 hexanes/ethyl acetate. IR (CH_2Cl_2) 2927 (s), 2858 (s), 1704 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.33 – 7.30 (4 H, m), 7.29 – 7.23 (1 H, m), 5.13 (1 H, dd, $J = 8.6, 3.6$ Hz), 2.86 – 2.80 (1 H, dd, $J = 17.3, 8.6$ Hz), 2.79 – 2.74 (1 H, dd, $J = 17.4, 3.6$ Hz), 2.40 (2 H, t, $J = 7.4$ Hz), 1.60 – 1.50 (2 H, br m), 1.30 – 1.15 (16 H, br m), 0.87 (3 H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 212.1, 143.3, 128.9, 128.0, 126.0, 70.4, 51.4, 44.2, 32.3, 30.0, 29.8, 29.7, 29.5, 24.0, 23.1, 14.5; LRMS (ESI) Calc'd for $\text{C}_{20}\text{H}_{32}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 327.5 Found ($\text{M}+\text{Na}$) $^+$: 327.3.

SFC (Chiracel AD-H, Supelco, 150 psi, 50°C, flow = 3.0 mL/min, 4.0% MeOH) analysis of benzoate derivative of allylboration product:

Diboration/Allylboration
Product

Racemic

Diboration/Allylboration
Product + Racemic

(R)- 1-Cyclohexyl-4-hydroxyheptan-2-one. White solid. $R_f = 0.23$ in 10:1 hexanes/ethyl acetate. IR (neat) 3317 (m, br), 2919 (s), 1700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 4.01 (1H, m), 3.04 (1H, d, $J = 3.2$), 2.56 (1H, dd, $J = 17.6$, 2.8 Hz), 2.45 (1H, dd, $J = 17.6$, 8.8 Hz), 2.27 (2H, d, $J = 6.8$ Hz), 1.86 – 1.75 (1H, m), 1.69 – 1.59 (5H, m), 1.52 – 1.18 (6H, m), 1.17 – 1.06 (1H, m), 0.96 – 0.85 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 212.5, 67.3, 51.4, 49.6, 38.5, 33.9, 33.2, 26.1, 26.0, 18.6, 14.0; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 235.2 Found ($\text{M}+\text{Na}$) $^+$: 235.1.

Proof of Stereochemistry. Absolute stereochemistry was established in comparison to material prepared by reaction of butyraldehyde with the boron enolate-derived from chlorodiisocampheylborane and 1-cyclohexylpropan-2-one. The reaction provided the methylketone aldol adduct (*S*)-1-cyclohexyl-4-hydroxyheptan-2-one in 48% *ee* according to literature procedures [(a) Paterson, I.; Goodman, J. M.; Lister, M. A.; Schumann, R. C.; McClure, C. K.; Norcross, R. D. *Tetrahedron* **1990**, 46, 4663. (b) Brown, H. C., Dhar, R. K., Ganesan, K., Singaram, B. *J. Org. Chem.* **1992**, 57, 499.].

SFC (Chiracel AD-H, Supelco, 150 psi, 50 °C, flow = 2.5 mL/min, 2.0% MeOH) analysis of benzoate derivative of allylboration product:

(R)-1-Cyclohexyl-4-hydroxy-5-methylhexan-2-one. Clear oil. $R_f = 0.29$ in 10:1 hexanes/ethyl acetate. IR (neat) 3491 (br, m) 2925 (s), 1702 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 3.77 (1H, m) 3.0 (1H, d, $J = 2.4$ Hz) 2.53 (1H, dd, $J = 17.2$, 2.6 Hz), 2.43 (1H, dd, $J = 17.2$, 9.6 Hz), 2.28 (2H, d, $J = 6.8$ Hz), 1.83 – 1.76 (1H, m), 1.66 – 1.59 (6H, m), 1.24 – 1.91 (2H, m), 1.16 – 1.09 (2H, m), 0.94 – 0.87 (8H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 212.6, 72.2, 51.4, 46.6, 33.9, 33.2, 33.0, 26.2, 26.0, 18.4, 17.8; LRMS (ESI) Calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 213.2 Found ($\text{M}+\text{H}$) $^+$: 213.2.

SFC (Chiracel OD-H, Supelco, 150 psi, 50 °C, flow = 2.0 mL/min, 1.0% MeOH) analysis of benzoate derivative of allylboration product:

Allylboration Product

Racemic

Allylboration Product +
Racemic

(R)-1-Cyclohexyl-4-hydroxy-4-phenyl-butan-2-one. Clear oil. $R_f = 0.56$ in 4:1 hexanes/ethyl acetate. IR (neat) 3425 (m, br), 2923 (s), 1708 (s), 700 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.24 (5H, m), 5.11 – 5.14 (1H, m), 3.38 (1H, d, $J = 3.2$ Hz), 2.85 – 2.73 (2H, m), 2.28 (2H, d, $J = 6.8$ Hz), 1.85 – 1.77 (1H, m), 1.68 – 1.62 (5H, m), 1.30 – 1.08 (3H, m), 0.95 – 0.85 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 211.4, 142.8, 128.4, 127.5, 125.6, 69.8, 51.6, 51.4, 33.8, 33.1, 26.1, 26.0; LRMS (ESI) Calc'd for $\text{C}_{16}\text{H}_{22}\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: 269.3 Found ($\text{M}+\text{Na}$) $^+$: 269.1.

SFC (Chiracel AD-H, Supelco, 150 psi, 50 °C, flow = 3.0 mL/min, 2.0% MeOH) analysis of benzoate derivate of allylboration product:

Diboration/Allylboration
Product

Racemic

Diboration/Allylboration
Product + Racemic

4-(2,2-Dimethyl-[1,3]dioxolan-4S-yl)-4R-hydroxy-1-phenylbutan-2-one (4).

Clear oil. $R_f = 0.46$ in 1:1 hexanes/ethyl acetate. IR (CH_2Cl_2): 3570 (s), 2896 (s), 1733 (s), 1497 (m), 1374 (m), 1212 (m), 1065 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.32 (2H, m), 7.29 – 7.25 (1H, m), 7.20 – 7.18 (2H, m), 4.06 – 4.02 (2H, m), 3.98 – 3.94 (1H, m), 3.81 – 3.77 (1H, m), 3.75 (2H, s), 2.71 (1H, dd, $J = 17.0, 8.2$ Hz), 2.59 (1H, dd, $J = 17.0, 3.4$ Hz), 1.37 (6H, d, $J = 30.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 208.2, 134.0, 129.9, 129.2, 127.6, 110.0, 78.1, 66.3, 65.9, 51.3, 45.2, 26.7, 25.5; LRMS (ESI) Calc'd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ ($\text{M}+\text{Na}$) $^+$: 287.1 Found ($\text{M}+\text{Na}$) $^+$: 287.2.

4-(2,2-Dimethyl-[1,3]dioxolan-4S-yl)-4S-hydroxy-1-phenylbutan-2-one (5).

Clear oil. $R_f = 0.51$ in 1:1 hexanes/ethyl acetate. IR (CH_2Cl_2): 3570 (s), 2896 (s), 1725 (s), 1497 (m), 1382 (m), 1206 (m), 1075 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.32 (2H, m), 7.30 – 7.26 (1H, m), 7.21 – 7.19 (2H, m), 4.06 – 4.01 (1H, m), 3.97 – 3.88 (3H, m), 3.74 (2H, s), 2.85 (1H, dd, $J = 17.8, 2.6$ Hz), 2.63 (1H, dd, $J = 18.0, 8.4$ Hz), 1.34 (6H, d, $J = 15.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 209.7, 133.8, 129.9, 129.2, 127.7, 109.9, 69.5, 67.2, 51.2, 45.2, 27.0, 25.6; LRMS (ESI) Calc'd for $\text{C}_{15}\text{H}_{20}\text{O}_4$ ($\text{M}+\text{Na}$) $^+$: 287.1 Found ($\text{M}+\text{Na}$) $^+$: 287.2.

The diastereomer ratio of the reaction products in Scheme 2 was determined by ^1H NMR analysis of the unpurified reaction mixture. The relative configuration was established in analogy to the reaction products described herein and by comparison to similar glyceraldehyde-derived methyl ketone aldol adducts. For comparison, relevant data is below. Note that for the syn diastereomer the downfield indicated methylene proton always has a larger vicinal coupling with the adjacent carbinol (ca. 8 Hz) versus the upfield methylene proton (ca. 3 Hz). For the anti diastereomer, this situation is reversed.

Dondoni, A.; Merino, P. *J. Org. Chem.* **1991**, 56, 5294

Gefflaut *J. Org. Chem.* **2001**, 66, 2296.

Santos et. al *Tetrahedron: Asymm.* **2001**, 12, 3447.

Cubero *Carbohydrate Research*, **1986**, 148, 209.

Garcia et. al *Tetrahedron* **1998**, 54, 6867.
similar data: Cubero *Carbohydrate Research*, **1986**, 148, 209.

Santos et. al *Tetrahedron: Asymm.* **2001**, 12, 3447.

Procedure for Diboration/Allylation/Protiodiboration:

An oven-dried 20 mL vial equipped with a stir-bar was charged with 9 mg (0.01 mmol) $\text{Pd}_2(\text{dba})_3$, 16 mg (0.25 mmol) (*R,R*-xylyl-TADDOL)P NMe_2 , and 0.80 mL toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes – 1 hour). After this time, 121 mg (0.475 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 minutes. Next, 72 mg (0.40 mmol) of trideca-1,2-diene and 167 μL of a 1.5 M solution of isobutyraldehyde (0.250 mmol) were added to the solution, and the reaction was allowed to stir for 12 h. The solvent was removed under reduced pressure and 0.5 mL $\text{CH}_3\text{CO}_2\text{H}$ was added. The reaction was warmed to 100 $^\circ\text{C}$ for 5 hours then allowed to cool to room temperature. The reaction was quenched with 2 mL 1 M NaOH and extracted with ethyl acetate (2 x 5 mL). The organic layers were dried over anhydrous Na_2SO_4 , filtered, and the solvent removed by rotary evaporation. The crude material was purified by silica gel chromatography (10:1 hexanes/ethyl acetate) to provide 52 mg (82%) of 2-methylhexadec-5-en-3-ol as a clear oil.

2-Methylhexadec-5Z-en-3-ol (7). Clear oil. $R_f = 0.45$ in 10:1 hexanes/ethyl acetate. IR (CH_2Cl_2): 2929 (s), 2856 (s), 1735 (m), 1468 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.60 – 5.54 (1H, m), 5.44 – 5.38 (1H, m), 3.39 – 3.34 (1H, m), 2.25 – 2.17 (2H, m), 2.08 – 1.99 (2H, m), 1.74 – 1.63 (1H, m), 1.25 (16H, br s), 0.94 (6H, dd, $J = 6.8, 4.8$ Hz), 0.89 (3H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 134.0, 125.9, 76.6, 33.5, 32.6, 32.3, 30.1, 30.0, 29.9, 29.7, 27.8, 23.1, 19.2, 18.0, 14.5; LRMS (ESI) Calc'd for $\text{C}_{17}\text{H}_{34}\text{O}$ ($\text{M} + \text{Na}$) $^+$: 277.5 Found ($\text{M} + \text{Na}$) $^+$: 277.3.

Olefin geometry was determined by analysis of the vinylic ^1H - ^1H coupling constant after decoupling of the allylic protons ($J=10.8$ Hz). Enantiomeric excess was determined by ^1H NMR analysis of the Mosher ester.

Procedure for Diboration/Allylation/Iodination:

An oven-dried 20 mL vial equipped with a stir-bar was charged with 9 mg (0.01 mmol) $\text{Pd}_2(\text{dba})_3$, 16 mg (0.25 mmol) (*R,R*-xylyl-TADDOL)PNMe₂, and 0.80 mL toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes – 1 hour). After this time, 121 mg (0.475 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 minutes. Next, 72 mg (0.40 mmol) of trideca-1,2-diene and 167 μL of a 1.5 M solution of isobutyraldehyde (0.250 mmol) were added to the solution, and the reaction was allowed to stir for 12 h. The solvent was removed under reduced pressure and the crude material was filtered through a plug of silica with 10:1 hexanes/ethyl acetate. THF (0.5 mL) and 3M NaOH (0.25 mL) were then added. A solution of 0.5 M I₂ (1.0 mL) was added dropwise over 30 minutes. The reaction was diluted with 2 mL H₂O and extracted with ethyl acetate (2 x 5 mL). The organics were dried over Na₂SO₄, filtered, and the solvent was removed by rotary evaporation. The crude material was purified by silica gel chromatography (15:1 hexanes/ethyl acetate) to provide 45 mg (47%) of 5*E*-iodo-2-methylhexadec-5-en-3*R*-ol as a clear oil.

5*E*-Iodo-2-methylhexadec-5-en-3*R*-ol (6). Clear oil. $R_f = 0.47$ in 10:1 hexanes/ethyl acetate. IR (CH_2Cl_2) 3595 (m), 2927 (s), 2858 (s), 563 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 6.38 (1H, t, $J = 7.6$ Hz), 3.68 – 3.63 (1H, m), 2.64 (1H, dd, $J = 14.4, 9.2$ Hz), 2.39 (1H, dd, $J = 14.4, 2.2$ Hz), 2.13 – 2.06 (2H, m), 1.79 – 1.72 (1H, m), 1.37 – 1.33 (2H, m), 1.26 (15 H, br), 0.97 (6H, dd, $J = 6.8, 5.2$ Hz), 0.88 (3H, t, $J = 7.0$); ^{13}C NMR (125 MHz, CDCl_3): δ 144.9, 98.7, 74.8, 43.1, 32.6, 31.8, 31.2, 29.5, 29.4, 29.3, 29.2, 29.0, 22.6, 18.7, 17.6, 14.0; LRMS (ESI) Calc'd for $\text{C}_{17}\text{H}_{33}\text{IO}$ ($\text{M}+\text{Na}$)⁺: 403.3 Found ($\text{M}+\text{Na}$)⁺: 403.3.

Alkene geometry was confirmed by treatment of the vinyl iodide with 3.0 equiv of *n*-butyllithium in hexanes and tetrahydrofuran at -78°C followed by H₂O to give **7**. Analysis of the coupling constant between the vinylic hydrogens ($J = 10.8$ Hz) indicates the *cis*-alkene is present. Mosher's ester analysis was performed on the dehalogenated material and compared to that for **7** above.

Procedure for One-pot Diboration/Allylation/Suzuki Coupling:

An oven-dried 20 mL vial equipped with a stir-bar was charged with 10 mg (0.01 mmol) $\text{Pd}_2(\text{dba})_3$, 18 mg (0.03 mmol) (*R,R*-xylyl-TADDOL)PNMe₂, and 0.86 mL toluene under an inert atmosphere of argon in a dry-box. The purple solution was stirred until it appeared yellow (30 minutes – 1 hour). After this time, 130 mg (0.51 mmol) of bis(pinacolato)diboron was added to the solution. The solution was allowed to stir for 5 minutes. Next, 50 mg (0.43 mmol) of propa-1,2-dienyl-benzene and 180 μL of a 1.5 M solution of isobutyraldehyde (0.27 mmol) in toluene was added to the solution, and the reaction was allowed to stir for 12 h. The cap was removed from the reaction and 60 μL (0.54 mmol) iodobenzene was added followed by 0.90 mL 3 M aqueous KOH. The reaction was heated to 95 °C for 6 hours. It was allowed to cool to room temperature and was quenched with saturated aqueous NH_4Cl . The mixture was extracted with ethyl acetate (2 x 5 mL). The organic layers were dried over anhydrous Na_2SO_4 , filtered, and the solvent removed by rotary evaporation. The crude material was purified by silica gel chromatography (10:1 hexanes:ethyl acetate) to provide 53 mg (74%) of 2-methyl-5,6-diphenylhex-5-en-3-ol as a clear yellow oil.

(*R*)-2-Methyl-5,6-diphenylhex-5-en-3-ol (8). Clear yellow oil. $R_f = 0.47$ in 5:1 hexanes/ethyl acetate. IR (CH_2Cl_2) 2597 (m), 3056 (s), 2964 (m), 1600 (m), 1495 (m), 1447 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.49 (4H, m), 7.43 – 7.26 (6H, m), 6.92 (1H, s), 3.52 – 3.47 (1H, m), 3.04 (1H, dd, $J = 14.4, 10.0$ Hz), 2.85 (1H, dd, $J = 14.4, 2.8$ Hz), 1.76 – 1.71 (1H, m), 0.93 (6H, dd, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 142.6, 139.9, 137.7, 131.6, 129.1, 128.6, 128.3, 127.5, 126.9, 126.7, 74.5, 34.6, 33.6, 18.7, 17.5; LRMS (ESI) Calc'd for $\text{C}_{19}\text{H}_{22}\text{O}$ ($\text{M}+\text{Na}$)⁺: 289.4 Found ($\text{M}+\text{Na}$)⁺: 289.2.

The % ee of the product was determined by ^1H NMR analysis of the Mosher ester.

heb2-233

Current Data Parameters
NAME heb2-233
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050803
Time 10.54
Spect 1H/13C
PULPROG 5mm QNP 1H/13C
TD 2930
FIDRES 32768
AQ 32768
RG 161.3
DE 78.000 usec
TE 293.0 K
D1 1.00000000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SFO1 400.1326008 MHz
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0

7.601
7.597
7.412
7.260
7.249
7.245
7.240
7.224
7.211
7.207
7.203
7.125
7.120

5.266
5.260
5.245
5.239
4.766
4.744

2.893
2.867

1.511
1.456
1.445
1.338
1.328
1.314
1.287
1.277
1.263
1.239
1.225
1.209
0.970
0.912
0.895

141.758

Current Data Parameters
 NAME heb2-233
 EXPNO 6
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20050803
 Time 10.59
 INSTRUM spect
 PROBHD 5mm QNP 1H/13C
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 51282.051 Hz
 FIDRES 0.782502 Hz
 AQ 0.6390358 sec
 RG 5160.6
 DW 9.750 usec
 DE 6.00 usec
 TE 293.0 K
 D1 2.0000000 sec
 d11 0.0300000 sec
 d12 0.0000200 sec
 ===== CHANNEL f1 =====
 NUC1 31P
 P1 5.70 usec
 PL1 0.00 dB
 SFO1 161.9786325 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -6.00 dB
 PL12 14.00 dB
 PL13 14.50 dB
 SFO2 400.1316005 MHz
 F2 - Processing parameters

7.340
7.323
7.304
7.277
7.260
7.253
7.240
7.239
7.183
7.165

5.280

4.010
3.998
3.991
3.982
3.692

2.886
2.878
2.644
2.637
2.600
2.593
2.554
2.532
2.510
2.488
2.235
1.531
1.456
1.443
1.440
1.420
1.407
1.401
1.388
1.365
1.344
1.338
1.327
1.319
1.303
1.295
1.284

741
lc-1-234
Asy(Xy)/Ph/nPr
product
6/2/05

Current Data Parameters
NAME pdtb
EXPNO 231
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050602
Time 19.55
INSTRUM spect
PROBHD 5 mm HR 13C/31
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 161.3
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8623988 MHz

F2 - Processing parameters
SI 32768
SF 399.8000176 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0

1c-1-244
Asy(Xy)/Ph/iPr
6/3/05

7.344
7.341
7.337
7.324
7.320
7.308
7.305
7.280
7.277
7.274
7.265
7.259
7.252
7.240
7.190
7.186
7.169

3.781
3.775
3.767
3.759
3.752
3.744
3.738
3.715
2.833
2.646
2.639
2.602
2.596
2.558
2.534
2.514
2.490
1.664
1.647
1.630
1.616
1.599
1.582
1.558
0.887
0.870
0.853
0.836

Current Data Parameters
NAME pdt
EXPNO 244
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050603
Time 7.20
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.3560319 sec
RG 574.7
DW 78.000 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec

==== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SFO1 400.132608 MHz

F2 - Processing Parameters
SI 32768
SF 400.1300175 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0

1.999
0.860
1.919

1.078
2.000

0.930
2.155

1.120
0.417

6.261

7.260

Current Data Parameters
NAME aw2-62
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050416
Time 15.10
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS * 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101.6
DW 78.000 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 399.7997895 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0

aw 2-62

4.253
4.245
4.234
4.226
3.312
2.901
2.895
2.861
2.854
2.813
2.792
2.772
2.751
2.730
2.713
2.696
2.183
1.937
1.921
1.906
1.877
1.870
1.858
1.839
1.828
1.813
1.793
1.772
1.754
1.736
1.724
1.715
1.703
1.628

7.260

aw 2-54

3.823
3.817
3.809
3.800
3.793
3.785
3.779
2.606
2.600
2.563
2.557
2.512
2.488
2.468
2.450
2.445
2.432
2.413
1.846
1.699
1.682
1.666
1.650
1.587
1.569
1.552
1.252
0.943
0.926
0.916
0.899
0.892
0.875
0.857
0.065

Current Data Parameters
NAME aw2-54
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050407
Time 7.13
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 181
DW 78.000 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SF01 400.1326008 MHz

===== CHANNEL f2 =====
CPDPRG2 off
NUC2 13C
PCPD2 100.00 usec
PL2 0.00 dB

7.330
7.326
7.311
7.307
7.304
7.287
7.276
7.268
7.264
7.261
7.254
7.248
7.240
7.233
7.191
7.137
7.126
7.090
7.057
6.918
6.903
6.872
6.851
6.832
6.572
6.539
5.200
5.148
5.139
5.127
5.118
4.534
4.109
4.091
4.073
3.323
3.080
3.037
3.023
2.977
2.955
2.942
2.936
2.927
2.863
2.841
2.820
2.798
2.790
2.781
2.747
2.737
2.700
2.660
2.632
2.573
2.555
2.536
2.419
2.401
2.382
2.342
2.333
2.307
2.292
2.273
2.255

Current Data Parameters
NAME MW-60
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030416
Time 14.51
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zgpg30
TD 32768
SOLVENT CECI3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.135425 Hz
AQ 2.5580519 sec
RG 128
RW 76.000 usec
TX 6.00 usec
TE 293.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SFO1 400.132608 MHz

F2 - Processing parameters
SI 32768
SF 400.1300172 MHz
WDW EM
SSB 0
LA 0
GB 0
0.30 Hz

1c-1-189
 Asy(Xy)/Cy/Ph
 product
 4/10/05

Current Data Parameters
 NAME pdt
 EXPNO 189
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050410
 Time 18.35
 INSTRUM spect
 PROHD 5mm QNP 1H/13C
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.195625 Hz
 AQ 2.5560319 sec
 RG 128
 DW 78.000 usec
 DE 6.00 usec
 TE 293.0 K
 D1 1.0000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 22.50 usec
 PL1 0.00 dB
 SFO1 400.1326008 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300172 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0

1c-1-190
 Asy(Xy)/Cy/nPr
 6/3/05

Current Data Parameters
 NAME product
 EXPNO 190
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20050604
 Time 1.54
 INSTRUM spect
 PROBHD 5mm QNP 1H/13C
 PULPROG zg30
 TD 32768
 SOLVENT CDC13
 NS 16
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.195625 Hz
 AQ 2.5560319 sec
 RG 574.7
 DW 78.000 usec
 DE 6.00 usec
 TE 293.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 21.50 usec
 PL1 0.00 dB
 SF01 400.1324008 MHz
 F2 - Processing parameters
 SI 32768
 SF 400.1304172 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0

1c-1-209
Asy(Xy)/Cy/iPr
product
4/25/05

7.242

1.256
1.279
1.286
1.295
1.589
1.597
1.601
1.614
1.631
1.647
1.652
1.662
1.763
1.772
1.782
1.791
1.800
1.808
1.817
1.827
2.272
2.289
2.396
2.420
2.439
2.463
2.507
2.514
2.551
2.557
3.013
3.019
3.743
3.749
3.758
3.765
3.773
3.780

Current Data Parameters
NAME product
EXPNO 209
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050425
Time 7.13
INSTRUM spect
PROBHD 5mm QNP 1H/13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5560319 sec
RG 128
DW 78.000 usec
DE 6.00 usec
TE 293.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 22.50 usec
PL1 0.00 dB
SFO1 400.1326008 MHz

F2 - Processing parameters
SI 32768
SF 400.1300165 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0

7.354 7.351 7.346 7.333 7.329 7.318 7.315 7.291 7.288 7.284 7.276 7.270 7.262 7.251 7.204 7.201 7.196 7.183

4.123 4.105 4.087 4.073 4.062 4.058 4.052 4.047 4.044 4.042 4.038 4.032 4.021 3.976 3.960 3.955 3.939 3.810 3.802 3.795 3.789 3.774 3.746 2.738 2.717 2.695 2.675 2.611 2.603 2.569 2.560 2.038 1.409 1.333 1.270 1.252 1.234

Current Data Parameters
NAME aw2-270-fraction2
EXPNO 1
PROCNO 1

aw 2-270 fraction 2

F2 - Acquisition Parameters
Date_ 20050826
Time 16.09
INSTRUM spect
PROBHD 5 mm HR 13C/31
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 80.6
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8023988 MHz

F2 - Processing parameters
SI 32768
SF 399.8000084 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0

Current Data Parameters
NAME awaw2-261-fraction2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050812
Time 16.37
INSTRUM spect
PROBHD 5 mm HR 13C/31
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 71.8
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8023988 MHz

F2 - Processing parameters
SI 32768
SF 399.8000091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0

aw 2-261 fraction 2

7.513 7.508 7.495 7.490 7.430 7.428 7.423 7.411 7.410 7.395 7.392 7.375 7.359 7.356 7.353 7.344 7.339 7.332 7.323 7.320 7.317 7.304 7.296 7.286 7.267 7.263 7.260 6.917

3.517 3.509 3.505 3.495 3.483 3.479 3.471 3.069 3.044 3.033 3.008 2.872 2.869 2.864 2.836 2.834 2.828 1.757 1.743 1.740 1.727 1.724 1.710 1.495 1.297 0.978 0.947 0.929 0.910

aw 2-196 fraction 1

Current Data Parameters
NAME aw2-196-fraction1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20050706
Time 17.25
INSTRUM spect
PROBHD 5 mm HR 13C/31
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 71.8
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.8023988 MHz

F2 - Processing parameters
SI 32768
SF 399.8000091 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0

1.314
 1.330
 1.346
 1.363
 1.443
 1.521
 1.626
 1.661
 1.678
 1.692
 1.695
 1.709
 1.712
 1.726
 1.743
 1.743
 1.994
 2.027
 2.043
 2.061
 2.078
 2.171
 2.187
 2.196
 2.207
 2.225
 2.246
 3.344
 3.357
 3.362
 3.371
 3.376
 3.389
 3.590
 3.376
 3.380
 3.394
 3.399
 4.03
 4.07
 4.13
 4.18
 4.21
 4.41
 4.44
 5.40
 5.55
 5.59
 5.62
 5.68
 5.73
 5.77
 5.82
 5.86
 6.04
 7.260

Current Data Parameters
 NAME aw2-207-pp3
 EXPNO 7
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20050811
 Time 7.46
 INSTRUM spect
 PROBHD 5mm QNP 1H/13C
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 6410.256 Hz
 FIDRES 0.195625 Hz
 AQ 2.5560319 sec
 RG 228.1
 DW 78.000 usec
 DE 6.00 usec
 TE 293.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 22.50 usec
 PL1 0.00 dB
 SFO1 400.1326008 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300095 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0

aw 2-207

ppm

3.123
6.158

16.646

0.847
1.027
1.316

2.190
1.860

0.898

1.000
0.931