RH-CATALYZED ENANTIOSELECTIVE HYDROGENATION OF VINYL BORONATES FOR THE CONSTRUCTION OF SECONDARY BORONIC ESTERS.

Wesley J. Moran and James P. Morken*

Department of Chemistry, Venable and Kenan Laboratories, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Supporting Information

General. $^1$H NMR spectra were recorded on Bruker DRX 300 or 400 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl3: 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and assignment. $^{13}$C NMR was recorded on a Bruker 400 MHz (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl3: 77.0 ppm). Mass spectrometry (m/z) was performed on either a Bruker BioTOF II or a Micromass Quattro II, operating in ESI or APCI mode, with only molecular ions reported. Infrared (IR) spectra were obtained on an ASI ReactIR 1000 or a Nicolet 560 Magna-IR, $\nu_{\text{max}}$ in cm$^{-1}$. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). Flash chromatography was performed on silica gel (SiO$_2$, 230 X 450 mesh) purchased from Sorbent Technologies, Inc. Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60). Visualization was achieved using basic potassium permanganate solution, 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 E-dex 120 column with helium as the carrier gas. All reactions were conducted in oven and flame dried glassware under an inert atmosphere of nitrogen unless otherwise stated. Walphos 1, (R)-1-[2-(2'-diphenylphosphinophenyl)ferrocenyl]ethylid(bis-3,5-trifluoromethylphenyl)phosphine, was kindly donated by Sovias AG. Bis(norbornadiene) rhodium(I) tetrafluoroborate was purchased from Acros Organics. All other reagents were purchased from Aldrich Chemical Companies and used directly. Hydrogenations were performed in a stainless steel high-pressure vessel from Parr Instrument Company. Enantiomeric excesses of the boronate compounds were determined by chiral GC analysis after oxidation of the carbon boron bond followed by acetate derivatization. Absolute configuration of products determined by comparison of GC data of commercial non-racemic chiral alcohols.

A note about NMR spectra: Due to the boron quadrupole, carbons directly attached to this element are often not detected in $^{13}$C spectra. See Wrackmeyer, B. Prog. In NMR Spectroscopy, 1979, 12, 227. In some cases, the $^3$J and $^3$J$^{11}$B/$^1$H and $^{10}$B/$^1$H coupling makes determination of some $^1$H/$^1$H coupling constants difficult.


```
1-Octyne (1.3 ml, 9.1 mmol, 1 equiv) was added dropwise to a 1 M solution of boron tribromide (4.5 ml, 4.5 mmol, 0.5 equiv) at -78 °C. The resulting solution was allowed to warm to room temperature over 3 h. Glacial acetic acid (9 ml) was added to the mixture and stirred for 1 h. This mixture was quenched with water, extracted with DCM and dried over MgSO4. Filtration, followed by (careful) concentration in vacuo and passage through a short silica column (hexanes) provided the desired vinyl bromide sufficiently clean to continue on to the next step. This vinyl bromide was dissolved in THF (15 ml) and cooled to -78 °C. t-BuLi (1.5 M, 12 ml, 18 mmol, 2 equiv) was added dropwise, and the resulting mixture stirred for 0.5 - 1 h at -78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.8 ml, 14 mmol, 1.5 equiv) dissolved in THF (10 ml) was added dropwise via cannula and the mixture allowed to warm to room temperature over 3 h. 1 M HCl solution (20 ml) was added and the mixture was stirred for 0.5 h. Extraction with DCM, followed by drying
```
over MgSO₄, filtration and concentration in vacuo provided the crude oil. Purification by flash chromatography (20:1 hexanes / EtOAc) furnished a colorless oil (1.8 g, 83%). IR (neat): 2975 (s), 2861 (s), 1721 (s), 1615 (s), 1142 (br) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.83 (3H, t, J = 6.4 Hz), 1.15-1.42 (20H, m), 2.11 (2H, t, J = 6.4 Hz), 5.57 (1H, br), 5.72 (1H, br). ¹³C NMR (100.6 MHz, CDCl₃): δ 14.5, 23.0, 25.1, 29.4, 29.6, 32.2, 35.8, 83.7, 129.1.

2-(1-benzyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. IR (neat): 2981 (s), 2931 (s), 1947 (w), 1887 (w), 1887 (w), 1713 (s), 1615 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.21 (12H, s), 3.47 (2H, s), 5.51 (1H, br), 5.82 (1H, br), 7.13-7.25 (5H, m). ¹³C NMR (100.6 MHz, CDCl₃): δ 14.1, 24.9, 26.9, 32.7, 43.0, 83.4, 126.1.

2-(1-cyclohexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. IR (neat): 2979 (s), 2925 (s), 2852 (s), 1611 (m), 1306 (s), 1144 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.10-1.70 (22H, m), 2.00-2.16 (1H, m), 5.55 (1H, br), 5.70 (1H, br). ¹³C NMR (100.6 MHz, CDCl₃): δ 14.1, 24.8, 41.6, 83.7, 125.9, 128.3, 129.4, 130.1, 140.9.

2,2-dimethyl-propionic acid 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-pent-4-enyl ester. IR (neat): 3025 (s), 2900 (s), 1727 (s), 1484 (m) cm -1. ¹H NMR (300 MHz, CDCl₃): δ 1.20 (9H, s), 1.26 (12H, s), 1.67-1.80 (2H, m), 2.22 (2H, t, J = 7.7 Hz), 4.04 (2H, t, J = 6.6 Hz), 5.62 (1H, br), 5.80 (1H, br). ¹³C NMR (75.5 MHz, CDCl₃): δ 22.9, 25.0, 27.4, 28.4, 39.0, 64.1, 83.6, 130.1, 178.3.

2,2-dimethyl-propionic acid 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-but-3-enyl ester. IR (neat): 3025 (s), 2914 (s), 1756 (s), 1360 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.15 (9H, s), 1.24 (12H, s), 2.45 (2H, t, J = 6.8 Hz), 4.13 (2H, t, J = 7.0 Hz), 5.66 (1H, br), 5.84 (1H, br). ¹³C NMR (100.6 MHz, CDCl₃): δ 25.2, 27.6, 35.0, 39.1, 63.8, 83.9, 132.3, 178.9.

2-{1-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-vinyl}-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. IR (neat): 2933 (s), 1723 (s), 1382 (s) cm -1. ¹H NMR (400 MHz, CDCl₃): δ 0.01 (6H, s), 0.87 (9H, s), 1.26 (12H, s), 2.37 (2H, t, J = 7.2 Hz), 3.65 (2H, t, J = 7.2 Hz), 5.65 (1H, br), 5.82 (1H, br). ¹³C NMR (100.5 MHz, CDCl₃): δ -5.2, 18.4, 24.7, 26.0, 39.1, 63.1, 83.3, 131.8.

2-{1-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-vinyl}-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. IR (neat): 3025 (s), 2914 (s), 1756 (s), 1360 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.26 (12H, s), 1.44 (9H, s), 2.30-2.43 (2H, m), 5.61 (1H, br), 5.76 (1H, br). ¹³C NMR (100.5 MHz, CDCl₃): δ 25.0, 28.4, 31.1, 35.3, 80.2, 83.6, 130.0, 173.0.

t-Butyldimethyl(2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enyloxy)silane. IR (neat): 2981 (s), 2929 (s), 2858 (s), 1615 (m), 1472 (s), 1372 (s), 1146 (s), 1092 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.00 (6H, s), 0.81 (3H, d, J = 8.0 Hz), 0.87 (9H, s), 1.23 (12H, s), 1.70-1.90 (2H, m), 2.43-2.52 (1H, dd, J = 12, 8.0 Hz), 3.30 (1H, dd, J = 8.0, 8.0 Hz), 3.45 (1H, dd, J = 12, 8.0 Hz), 5.55 (1H, br), 5.77 (1H, br). ¹³C NMR (100.6 MHz, CDCl₃): δ -5.3, 16.4, 18.1, 24.5, 25.8, 35.4, 39.0, 67.9, 83.1, 130.2.
Synthesis of 4,4,5,5-tetramethyl-2-(1-(R)-methyl-heptyl)-[1,3,2]dioxaborolane.

Reaction in 1,2-dichloroethane: A vial was charged with bis(norbornadiene)rhodium(I) tetrafluoroborate (3.9 mg, 0.010 mmol, 0.05 equiv), Walphos 1 (16 mg, 0.017 mmol, 0.08 equiv) and 1,2-dichloroethane (1 ml) in a dry-box and stirred at room temperature for 1 minute. 2-(1-Hexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (50 mg, 0.21 mmol, 1 equiv) was added to the catalyst solution and the vial was capped and removed from the dry-box. The cap was removed and the vial placed in a Parr Instruments pressure vessel. The vessel was partly submerged in a cryo-bath and cooled to approximately -35 °C, then purged with H₂. The vessel was charged with 30 bar H₂ and then depressurized. The vessel was re-charged with 30 bar H₂ and left stirring for 15 h. The pressure was released and the vessel removed from the cryo-bath. The vial was removed from the pressure vessel, and the volatiles were removed in vacuo. The resulting residue was purified by flash chromatography (20:1 hexanes/ethyl acetate) to furnish a colorless oil (50 mg, >95% yield). IR (neat): 2957 (m), 2927 (s), 2855 (m), 1464 (m), 1371 (s), 1313 (s), 1145 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 0.83 (3H, t, J = 6.6 Hz), 0.94 (3H, brs), 1.1 -1.5 (27 H, m). ¹³C NMR (75.5 MHz, CDCl₃): δ 14.0, 15.4, 22.6, 24.7 (2C), 28.9, 29.5, 31.8, 33.2, 82.7. GC of oxidation/acylation adduct: 85% ee; 100 °C, 25 psi, tₛ=8.8 min, tᵣ=10.0 min.

Reaction in toluene: A vial was charged with bis(norbornadiene)rhodium(I) tetrafluoroborate (3.9 mg, 0.010 mmol, 0.05 equiv), Walphos 1 (16 mg, 0.017 mmol, 0.08 equiv) and toluene (1 ml) in a dry-box and stirred at room temperature for 60 minutes. 2-(1-Hexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (50 mg, 0.21 mmol, 1 equiv) was added to the catalyst solution and the vial was capped and removed from the dry-box. The cap was removed and the vial placed in a Parr Instruments pressure vessel. The vessel was partly submerged in a cryo-bath and cooled to approx. -45 °C, then purged with H₂. The vessel was charged with 30 bar H₂ and then depressurized. The vessel was re-charged with 30 bar H₂ and left stirring for 40 h. The pressure was released and the vessel removed from the cryo-bath. The vial was taken from the pressure vessel, and the volatiles were removed in vacuo. The resulting residue was purified by flash chromatography (20:1 hexanes/ethyl acetate) to furnish a colorless oil (50 mg, >99% yield, 81% ee; GLC as above).

GC conditions: 100 °C, 25 psi, tₛ = 8.8 min, tᵣ = 10.0 min; oxidation/acylation product.

---

(1) Absolute configuration determined by GLC comparison to protected commercially available (R)-(-)-2-octanol.
4,4,5,5-tetramethyl-2-(1-(R)-methyl-2-phenyl-ethyl)-[1,3,2]dioxaborolane\(^2\): IR (neat): 3062 (m), 3027 (m), 2979 (s), 2931 (s), 1457 (s), 1144 (s) cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.94 (3H, d, J = 7.5 Hz), 1.17 (12H, s), 1.35 (1H, m), 2.54 (1H, dd, J = 13.8, 8.2 Hz), 2.78 (1H, dd, J = 13.5, 7.5 Hz), 7.16-7.28 (5H, m). \(^13\)C NMR (75.5 MHz, CDCl\(_3\)): \(\delta\) 15.2, 24.7 (2C), 39.0, 83.0, 125.5, 128.0, 128.0, 142.3.

GC conditions: 120 °C, 25 psi, \(t_s = 17.0\) min, \(t_R = 17.9\) min; oxidation/acylation product.

(2) Absolute configuration determined by GLC comparison to protected commercially available \((R)\)-(-)-1-phenyl-2-propanol.
2-(R)-(1-cyclohexyl-ethyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane<sup>3</sup>: IR (neat): 2979 (s), 2925 (s), 2852 (s), 1449 (s), 1380 (s), 1146 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.9 - 1.40 (19H, s), 1.53-1.74 (6H, m), 1.95-2.05 (2H, m). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): δ 13.5, 25.8, 27.7, 32.8 (2C), 33.7 (2C), 41.5, 83.5. MS (A.P.C.I.+ m/z calc'd for C<sub>14</sub>H<sub>28</sub>BO<sub>2</sub>: 239.2. Found: 239.1.

GC conditions: 100 °C, 25 psi, t<sub>S</sub> = 16.5 min, t<sub>R</sub> = 19.2 min; oxidation/acylation product.

2,2-dimethyl-propionic acid 4-(R)-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolanyl-2-yl)-pentyl ester. IR (neat): 2960 (s), 1723 (s), 1463 (s), 1382 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.90-1.06 (4H, m), 1.15 (9H, s), 1.19 (12H, s), 1.23-1.37 (1H, m), 1.42-1.53 (1H, m), 1.54-1.65 (2H, m), 4.00 (2H, t, J = 6.6 Hz). <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>): δ 15.4, 24.7, 27.2, 28.0, 29.4, 38.7, 64.6, 82.9, 178.8. MS (E.S.I.) m/z calc'd for C<sub>16</sub>H<sub>32</sub>BO<sub>4</sub>: 299.2. Found: 299.2.

GC conditions: 130 °C, 25 psi, t<sub>S</sub> = 13.5 min, t<sub>R</sub> = 14.8 min; oxidation/acylation product.

---

(3) Absolute configuration determined by comparison of derived Mosher’s amide (vide infra) with authentic sample.
2,2-dimethyl-propionic acid 3-(R)-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-butyl ester: IR (neat): 2929 (m), 1723 (m), 1600 (s), 1470 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.96 (3H, d, J = 7.6 Hz), 1.04-1.14 (1H, m), 1.16 (9H, s), 1.20 (12H, s), 1.51-1.63 (1H, m), 1.70-1.82 (1H, m), 3.98-4.10 (2H, m). ¹³C NMR (100.5 MHz, CDCl₃): δ 15.0, 24.4, 24.5, 27.0, 31.4, 38.5, 63.7, 82.8, 178.4. MS (ESI) m/z calc’d for C₁₅H₃₀BO₄: 285.2. Found: 285.2

GC conditions: 120 °C, 25 psi, tₛ = 11.2 min, tᵣ = 11.9 min; oxidation/acylation product.

(4) Absolute configuration determined by chiral GC analysis of protected commercially available (R)-(−)-1,3-butanediol.
(R)-tert-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane

IR (neat): 3072 (s), 2997 (s), 2866 (m), 2306 (s), 1434 (s), 1293 (s) cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.02 (6H, s), 0.86 (9H, s), 0.95 (3H, d, J = 7.6 Hz), 1.04-1.13 (1H, m), 1.20 (12H, s), 1.42-1.52 (1H, m), 1.63-1.74 (1H, m), 3.53-3.65 (2H, m). \(^{13}\)C NMR (100.5 MHz, CDCl\(_3\)): \(\delta\) -4.8, 15.9, 18.8, 23.0, 25.1, 25.2, 26.4, 36.5, 63.0, 83.2. MS (ESI) m/z calc'd for C\(_{16}\)H\(_{36}\)BO\(_3\)Si: 315.2. Found: 315.2.

GC conditions: 110 °C, 25 psi, \(t_S = 14.0\) min, \(t_R = 15.0\) min; oxidation/acylation product.

---

(5) Absolute configuration determined by chiral GC analysis of protected commercially available (R)-(−)-1,3-butanediol.
(R)-tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate. IR (neat): 2979 (s), 2933 (s), 2873 (s), 1735 (s), 1466 (m), 1364 (m), 1146 (m) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 0.94 (3H, s), 1.20 (12H, s), 1.40 (9H, s), 1.47-1.76 (3H, m), 2.20 (2H, t, J = 8.0 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 15.1, 24.5, 24.6, 27.9, 28.1, 34.7, 79.6, 82.7, 173.2. MS (ESI) m/z calc’d for C₁₅H₂₉BO₄Na⁺: 307.2. Found: 307.4.

GC conditions: 120 °C, 20 psi, tₛ = 14.9 min, tᵣ = 16.6 min; oxidation/acylation product.
t-butyldimethyl((2R,4R)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyloxy)silane: IR (neat): 2977 (s), 2929 (s), 2856 (s), 1472 (m), 1387 (s), 1315 (s), 1256 (s), 1146 (s), 1094 (s), 837 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.02 (6H, s), 0.82-1.15 (17H, m), 1.23 (12H, s), 1.45-1.67 (2H, m), 3.25 (1H, dd, J = 9.9, 7.2 Hz), 3.45 (1H, dd, J = 9.6, 5.1 Hz). \(^13\)C NMR (100.5 MHz, CDCl\(_3\)): \(\delta\) -5.5 (2C), 15.1, 16.4, 18.2, 24.5 (2C), 25.8, 34.2, 36.0, 68.5, 82.6. MS (ESI) m/z calc’d for C\(_{18}\)H\(_{39}\)BO\(_3\)SiNa\(^+\): 365.3. Found: 365.4.

Synthesis of (R)-N-benzyl-1-cyclohexylethanamine: A vial was charged with bis(norbornadiene)rhodium(I) tetrafluoroborate (9.5 mg, 0.025 mmol, 0.05 equiv), Walphos 1 (38 mg, 0.041 mmol, 0.08 equiv) and 1,2-dichloroethane (2.4 ml) in a dry-box and stirred at room temperature for 1 minute. 2-(1-Cyclohexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2] dioxaborolane (120 mg, 0.51 mmol, 1 equiv) was added to the catalyst solution and the vial was capped and removed from the dry-box. The cap was removed and the vial placed in a Parr Instruments pressure vessel. The vessel was partly submerged in a cryo-bath and cooled to approx. -35 °C, then purged with H₂. The vessel was charged with 30 bar H₂ and then depressurized. The vessel was re-charged with 30 bar H₂ and left stirring for 15 h. The pressure was released and the vessel removed from the cryo-bath. The vial was taken from the pressure vessel, capped, and allowed to warm to ambient temperature. The vial was then taken back into the dry-box and boron trichloride (1M in CH₂Cl₂, 1.0 ml, 1.0 mmol, 2 equiv) was added. After 3 h, benzyl azide (0.16 ml, 1.3 mmol, 2.5 equiv) was added carefully (nitrogen evolution observed) and the mixture stirred for a further 4 h. The vial was removed from the dry-box and aqueous NaOH solution (2M, 1 ml) was added. The mixture was stirred for 0.5 h at ambient temperature, and then extracted with EtOAc. Evaporation of the volatiles in vacuo provided the crude residue, which was purified by flash chromatography (9:1 hexanes/EtOAc) to provide a colorless oil (91 mg, 82%). Spectral data are in agreement with that reported for this compound.\(^7\) \(^1\)H NMR (400 MHz, CDCl₃):  0.95 (3H, d, J = 5.3 Hz), 1.00-1.32 (7H, m), 1.50-1.72 (5H, m), 2.40-2.44 (1H, m), 3.62 (1H, d, J = 13.2 Hz), 3.76 (1H, d, J = 13.2 Hz), 7.18-7.27 (5H, m). \(^13\)C NMR (100.5 MHz, CDCl₃): 17.1, 27.0, 26.8, 26.9, 28.3, 30.1, 43.2, 51.8, 57.2, 127.0, 128.4, 128.6, 141.3.

\(^1\)H NMR of debenzylated Mosher’s amide; NH resonance:

![racemic](image1.png) ![reaction product](image2.png)

Synthesis of (R)-2-cyclohexylpropan-1-ol: A vial was charged with bis(norbornadiene)rhodium(I) tetrafluoroborate (9.5 mg, 0.025 mmol, 0.05 equiv), Walphos 1 (38 mg, 0.041 mmol, 0.08 equiv) and 1,2-dichloroethane (2.4 ml) in a dry-box and stirred at room temperature for 1 minute. 2-(1-Cyclohexyl-vinyl)-4,4,5,5-tetramethyl-[1,3,2] dioxaborolane (120 mg, 0.51 mmol, 1 equiv) was added to the catalyst solution and the vial was capped and removed from the dry-box. The cap was removed and the vial placed in a Parr Instruments pressure vessel. The vessel was partly submerged in a cryo-bath and cooled to approx. -35 °C, then purged with H₂. The vessel was charged with 30 bar H₂ and then depressurized. The vessel was re-charged with 30 bar H₂ and left stirring for 15 h. The pressure was released and the vessel removed from the cryo-bath. The vial was taken from the pressure vessel and the solvent removed in vacuo. THF (2 ml) was added followed by bromochloromethane (43 μl, 0.66 mmol, 1.3 equiv). The reaction mixture was then cooled to –78 °C and n-BuLi (2.5 M in hexanes, 0.26 ml, 0.66 mmol, 1.3 equiv) added dropwise. The reaction was allowed to warm to ambient temperature overnight and then 30% aqueous hydrogen peroxide solution (0.5 ml) and aqueous NaOH solution (2M, 0.5 ml) were added. After a further 2.5 h, the reaction mixture was extracted with EtOAc and concentrated in vacuo. Purification by flash chromatography (9:1 hexanes/EtOAc) provided the product as a colorless oil (62 mg, 85 %). Spectral data are in agreement with that reported for this compound.\(^8\) ¹H NMR (300 MHz, CDCl₃): δ 0.88 (3H, d, J = 6.9 Hz), 0.90-1.40 (6H, m), 1.40-1.55 (1H, m), 1.60-1.80 (5H, m), 3.43 (1H, dd, J = 10.5, 6.9 Hz), 3.59 (1H, dd, J = 10.5, 5.7 Hz). ¹³C NMR (75 MHz, CDCl₃): δ 13.4, 26.8, 26.9, 27.0, 29.0, 31.2, 39.6, 41.2, 66.5.

Current Data Parameters
NAME       WMZ-181B-C
EXPN0      1
PROCNO

F2 - Acquisition Parameters
Date       20051102
Time       12:24
INSTRUM     spect
PROBID      5mm QNP 1H/13C
POLPROC     zgpg20
TD          6536
SOLVENT     CDCl3
NS          512
DS          2
SNH         26446.719 Hz
FIDRES      0.400492 Hz
AQ          1.2485298 sec
RG          12768
DM          19.050 usec
DS          6.00 usec
TE          300.0 K
D1          0.000000001 sec
d11         0.030000000 sec
d12         0.000020000 sec

============= CHANNEL f1 ==========
NUC1        13C
P1          6.00 usec
PL1         0.00 dB
SPD1        100.6036782 MHz

============= CHANNEL f2 ==========
CPDPROC2     walts16
NUC2        1H
P2D0        80.00 usec
PL2         -6.00 dB
PL12        13.80 dB
PL13        14.50 dB
SPD2        400.0516002 MHz

F2 - Processing parameters
SI          12768
SF          100.5926741 MHz
NDW         no
SSB         0