Electronic Supplementary Material (ESI) for Chemical Communications.

ELECTRONIC SUPPORTING INFORMATION

Studies Towards the Synthesis of Halomon: Asymmetric Hexafunctionalisation of Myrcene

D. Christopher Braddock,* Alison X. Gao, Andrew J. P. White and Mariko Whyte

Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK.

Email Address: c.braddock@imperial.ac.uk

Cover Page and Contents

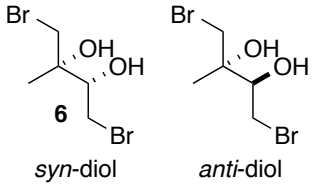
General Experimental.

Solvents and reagents: All reagents were obtained from commercial sources and used as received. All solvents were used as received. MeOH, CH_2Cl_2 and n-hexane were HiPerSolv grade. EtOAc was GPR grade. Petroleum ether refers to BDH AnalR petroleum spirit 40-60 ^oC.

Experimental techniques: Reactions were carried out under nitrogen in oven-dried glassware. The phrase "solvent removed under reduced pressure" refers to rotary evaporation. Brine refers to a saturated aqueous solution of NaCl. Column chromatography was carried out on BDH silica gel 60, grade 40-63 μm using flash techniques. Eluents are given in parentheses. Analytical thin layer chromatography (TLC) was performed using Kieselgel 60 F_{254} pre-coated aluminium-backed plates. These were visualised using ultraviolet light (254 nm) and chemical staining using potassium permanganate or vanillin solution.

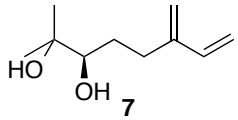
Characterisation: Melting points were obtained using a Stuart SMP30 melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained using a PerkinElmer Spectrum100 FTIR apparatus with automatic background subtraction and carried out neat. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 400 MHz on Bruker DRX-400 spectrometers. Chemical shifts are referenced to the residual solvent peak, 7.26 ppm for $CDCl_3$ and 3.31 ppm for CD_3OD respectively. Coupling constants (*J*) are given in Hertz (Hz). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz on a Bruker DRX-400 spectrometer. Chemical shifts are referenced to 77.0 ppm for $CDCl_3$ and 49.0 ppm for CD_3OD respectively. The following abbreviations are used for the multiplicity of NMR signals: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet. Low and high resolution mass spectra were recorded by Imperial College Mass Spectrometry Service using a Micromass Platform II and Thermo Scientific Q-Exactive spectrometer. Optical Rotation measurements were made using a Bellingham+Stanley ADP410 polarimeter.

(2*S,3*S**)-1,4-Dibromo-2-methyl-butane-2,3-diol (6) and (2*S**,3*R**)-1,4-dibromo-2-methyl-butane-2,3-diol**



According to a modified procedure of Sharpless[2] to a solution of citric acid (3.84 g, 11.6 mmol, 2 equiv.) in *t*-BuOH/H_2O (20 mL of a 1:1 mixture) was added the allyl bromide **5** (1.33 g, 5.8 mmol) at room temperature. $K_2OsO_2(OH)_4$ (44.2 mg, 0.12 mmol, 2 mol%) and *N*-methylmorpholine-*N*-oxide (747 mg, 6.38 mmol, 1.1 equiv.) were then added and the solution turned bright green. The mixture was stirred at ambient temperature for 16 h, after which time it went nearly colourless. The solution was extracted with EtOAc (3 × 20 mL) and the combined organics were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (80:20 – 60:40 petroleum ether : EtOAc) to give the title compound **6** (1.16 g, 77%) as a white solid, and *anti*-diol (70 mg, 5%) as a colourless oil. ***Syn*-6**: m.p. 155 - 157°C; R_f 0.46 (60:40 petroleum ether : EtOAc); IR (neat) ν_{max} 3400 (br), 2932, 1229, 1203, 1163, 1071, 676, 606, 580, 556cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.68 (dd, *J* = 10.4, 2.4 Hz, 1H), 3.61 (d, *J* = 10.2 Hz, 1H), 3.49 (t, *J* = 10.3 Hz, 1H), 3.44 (d, *J* = 10.1 Hz, 1H), 2.68 (br. s, 1H), 2.53 (br. s, 1H), 1.34 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 76.0, 73.5, 40.0, 36.0, 22.0 ppm; MS (CI^+, NH_3) *m/z* 282, 280, 278 $[M + NH_4]^+$; HRMS (CI^+, NH_3) calcd for $C_5H_{14}{}^{79}Br_2NO_2$ 277.9391 $[M + NH_4]^+$, found 277.9378. The *syn*-diol **6** was recrystallised from a mixture of *n*-hexane and CH_2Cl_2 to give a crystals suitable for X-ray crystallography. *Crystal data for* **6**: $C_5H_{10}Br_2O_2$, *M* = 261.95, monoclinic, $P2_1/n$ (no. 14), *a* = 5.56972(10), *b* = 9.61673(17), *c* = 15.4286(3) Å, β = 97.5499(16)°, *V* = 819.23(3) Å^3, *Z* = 4, D_c = 2.124 g cm^{-3}, μ(Cu-Kα) = 12.043 mm^{-1}, *T* = 173 K, colourless blocky needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 1597 independent measured reflections (R_{int} = 0.0231), F^2 refinement,[3] R_1(obs) = 0.0223, wR_2(all) = 0.0519, 1440 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 144°], 91 parameters. CCDC 1017807. ***Anti*-6**: R_f 0.48 (60:40 petroleum ether : EtOAc); IR (neat) ν_{max} 3300 (br), 2936, 1245, 1225, 1065, 647, 575 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (ddd, *J* = 10.3, 3.7, 2.1 Hz, 1H), 3.85 (dd, *J* = 10.3, 2.0 Hz, 1H), 3.81 (d, *J* = 10.7 Hz, 1H), 3.55 (d, *J* = 10.3 Hz, 1H), 3.46 (t, *J* = 10.3 Hz, 1H), 2.61 (d, *J* = 3.5 Hz, 1H), 2.37 (s, 1H), 1.34 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 75.3, 73.0, 43.2, 36.6, 19.9 ppm; MS (CI^+, NH_3) *m/z* 282, 280, 278 $[M + NH_4]^+$; HRMS (CI^+, NH_3) calcd for $C_5H_{14}{}^{79}Br_2NO_2$ 277.9391 $[M + NH_4]^+$, found 277.9378.

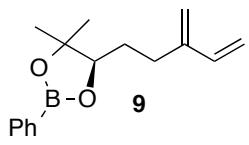
(3*R*)-2-Methyl-6-methylene-oct-7-ene-2,3-diol (7)



7

According to method of Sharpless,[4] to a stirred solution of AD-mix-β (10.2 g) in 1:1 v/v *t*-BuOH/H_2O (72 mL) at ambient temperature was added methanesulfonamide (1.47 g, 15.5 mmol, 1.03 equiv.). The reaction mixture was stirred vigorously at this temperature for 0.5 h until the mixture became a homogeneous orange solution and myrcene (**2**) (685 mg, 2.8 mL, 15.0 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 20 h. The reaction was quenched with Na_2SO_3 (20 g) and stirred for 1 h at ambient temperature. Water (20 mL) was added and two phases were separated. The aqueous phase was extracted with EtOAc (5 × 20 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed (80:20 – 60:40 petroleum ether : EtOAc) to give (*R*)-diol **7** (1.70 g, 67%) as a colourless oil: R_f 0.46 (50:50 petroleum ether : EtOAc); $[\alpha]_D^{25}$ + 34.0 (*c* = 1.0, $CHCl_3$) {lit.[5] $[\alpha]_D^{22}$ + 37.4 (*c* = 1.0, $CHCl_3$)} 91% ee; IR (neat) ν_{max} 3377 (br), 2972, 2934, 2876, 1722, 1245, 1155, 1048, 939 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.27 (d, *J* = 17.6 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 5.06 – 5.02 (m, 3H), 3.41 (dd, *J* = 10.4, 1.9 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.34 – 2.21 (m, 1H), 2.15-1.80 (br s, 2H), 1.74 – 1.62 (m, 1H), 1.57 – 1.44 (m, 1H), 1.21 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.1, 138.7, 116.1, 113.6, 78.2, 73.1, 30.2, 28.5, 26.5, 23.2 ppm; MS (CI^+, NH_3) *m/z* 188 $[M + NH_4]^+$; HRMS (CI^+, NH_3) calcd for $C_{10}H_{22}NO_2$ $[M + NH_4]^+$ 188.1651, found 188.1651.

(3*R*)-4,4-Dimethyl-5-(3-methylene-pent-4-enyl)-2-phenyl-[1,3,2]dioxaborolane (9)



9

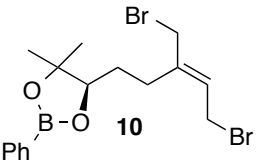
Using a modified method of Muñiz[6] to a solution of containing AD-mix-β (10.2 g), phenylboronic acid (2.19 g, 18 mmol, 1.2 equiv.) in *t*-BuOH/H_2O (50 mL of a 1:1 mixture) was added additional $K_2OsO_2(OH)_4$ (55.3 mg, 0.15 mmol, 1 mol%), $(DHQD)_2PHAL$ (233.7 mg, 0.3 mmol, 2 mol%). The mixture was stirred vigorously at room temperature until all materials had dissolved. Myrcene (**2**) (685 mg, 2.8 mL, 15 mmol) was added in one portion and the mixture was stirred at ambient temperature for 20 h and then quenched with sat. aq. $Na_2S_2O_3$ solution (50 mL). Two phases were separated and the aqueous phase was extracted with diethyl ether (5 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (90:10 petroleum ether : EtOAc) furnished the title compound **9** (2.3 g, 60%) as a colourless oil. R_f 0.30 (90:10 petroleum ether : EtOAc); $[\alpha]_D^{25}$ + 34.0 (*c* = 1.0, $CHCl_3$); IR (neat) ν_{max} 3088, 2976, 1600, 1500, 1270, 1228, 1143, 1097, 1068, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0,

1.3 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.42 – 7.35 (m, 2H), 6.42 (dd, J = 17.6, 10.8 Hz, 1H), 5.33 (d, J = 17.6 Hz, 1H), 5.16 – 5.06 (m, 3H), 4.13 (dd, J = 10.6, 3.0 Hz, 1H), 2.67 (ddd, J = 14.7, 10.2, 4.6 Hz, 1H), 2.43 – 2.31 (m, 1H), 1.87 – 1.75 (m, 1H), 1.73 – 1.63 (m, 1H), 1.45 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 145.8, 138.7, 134.8, 131.3, 127.8, 116.3, 113.6, 85.3, 82.1, 30.4, 28.8, 28.3, 23.5 ppm; MS (CI^+, NH_3) *m/z* 274, 273 $[M + NH_4]^+$; HRMS (CI^+, NH_3) calcd for $C_{16}H_{25}{}^{11}BNO_2$ 274.1978 $[M + NH_4]^+$, found 274.1986.

Deprotection of boronate 9 to diol 7

According to the procedure reported by Sharpless,[7] to a stirred solution of the boronic ester **9** (100 mg, 0.39 mmol) in EtOAc:acetone (6 mL of a 1:1 mixture) at room temperature was added a 30% aqueous solution of hydrogen peroxide (0.11 g, 0.98 mmol, 2.5 equiv.) in one portion. The reaction mixture was stirred at room temperature for 4 h and water (10 mL) was added. The layers were separated and the aqueous layer was extracted with EtOAc (4 × 20 mL), and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (40:60 petroleum ether : EtOAc) to give the title compound **7** (60 mg, 90%) as a colourless oil. R_f 0.40 (50:50 petroleum ether : EtOAc); $[\alpha]_D^{25}$ + 34.0 (c = 1.0, $CHCl_3$) {lit.[5] $[\alpha]_D^{22}$ + 37.4 (c = 1.0, $CHCl_3$)} 91% ee. All other data identical to that reported above for diol **7**.

(3*R*)-5-(5-Bromo-3-bromomethyl-pent-3-enyl)-4,4-dimethyl-2-phenyl-[1,3,2]dioxaborolane (10)

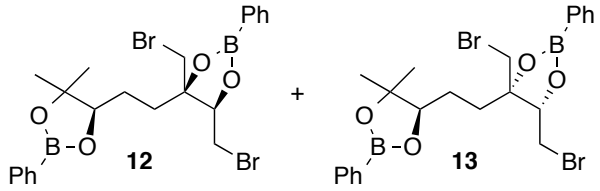


10

According to a modified procedure of Alexakis,[1] to a stirred suspension of diene **9** (260 mg, 1.02 mmol) and K_2CO_3 (14 mg, 0.1 mmol, 0.1 equiv.) in hexane (30 mL) at -78 °C was added a solution of molecular Br_2 (0.06 mL, 1.02 mmol) in hexane (10 mL), dropwise, in the absence of light and the mixture was stirred for 2 h. The reaction mixture was quenched with Na_2SO_3 (5 g) and then allowed to warm to ambient temperature. Water (30 mL) was added and two phases were separated. The aqueous phase was extracted with ether (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo* to provide the title compound **10** (420 mg, 100%) as a pale yellow oil, which was taken on further without purification. R_f = 0.20 (90:10 petroleum ether : EtOAc); $[\alpha]_D^{25}$ + 26.0 (c = 1.0, $CHCl_3$); IR (neat) ν_{max} 3085, 3055, 2973, 2935, 2881, 1603, 1350, 1270, 1203, 1146, 1096, 1068, 1026, 669, 650, 559 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.76 (d, J = 6.8 Hz, 2H), 7.48 (t, J = 7.3 Hz), 7.39 (dd, J = 7.9, 6.8 Hz, 2H), 5.99 (t, J = 8.4 Hz, 1H), 4.11 – 4.03 (m, 5H),

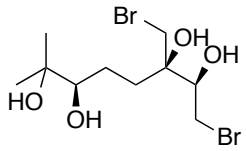
2.69 – 2.63 (m, 1H), 2.58 – 2.49 (m, 1H), 1.79 – 1.69 (m, 2H), 1.45 (s, 3H), 1.29 (s, 3H) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 140.8, 134.8, 131.4, 127.8, 127.7, 84.6, 82.0, 37.1, 29.8, 28.8, 27.2, 25.5, 23.5 ppm; MS (CI^+, NH_3) *m/z* 436, 435, 434, 343, 432, 431 $[M + NH_4]^+$; HRMS (CI^+, NH_3) calcd for $C_{16}H_{25}{}^{11}B^{79}Br_2NO_2$ 432.0345 $[M + NH_4]^+$, found 432.0344.

(3*R*,6*S*,7*S*)- and (3*R*,6*R*,7*R*)-5-[2-(4,5-*Bis*-bromomethyl-2-phenyl-[1,3,2]dioxaborolan-4-yl)-ethyl]-4,4-dimethyl-2-phenyl-[1,3,2]dioxaborolane (12 and 13)



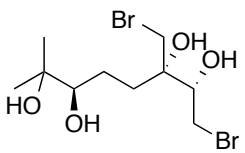
According to a modified method of Sharpless,[2] to a solution of the citric acid (420 mg, 2 mmol, 2 equiv.) in *t*-BuOH/H_2O (10 mL of a 1:1 mixture) was added allyl bromide **10** (416 mg, 1 mmol) at room temperature. $K_2OsO_2(OH)_4$ (29.5 mg, 0.08 mmol, 4 mol%), *N*-methylmorpholine-*N*-oxide (128.9 mg, 1.1 mmol, 1.1 equiv.) and phenylboronic acid (121.9 mg, 1 mmol, 1 equiv.) were then added and the solution turned bright green. The mixture was stirred at ambient temperature for 16 h, after which time it went nearly colourless. The solution was extracted with EtOAc (3 × 20 mL) and the combined organics were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed (80:20 petroleum ether : EtOAc) to give a *ca.* 1:1 inseparable diastereomeric mixture of the title compounds **12** and **13** (450 mg, 85%) as a brown oil which could be used directly in the next step. Further chromatography gave the boronate mixture as a yellow oil: R_f 0.38 (90:10 petroleum ether : EtOAc); IR (neat) ν_{max} 3059, 2935, 1348, 1295, 1267, 1223, 1152, 1026, 669, 646, 620, 537 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 8H), 7.55 – 7.31 (m, 12H), 4.84 – 4.78 (m, 2H), 4.10 (dd, *J* = 5.7, 4.0 Hz, 2H), 3.75 – 3.54 (m, 8H), 2.42 (ddd, *J* = 13.9, 11.7, 4.9 Hz, 1H), 2.36 – 2.25 (m, 1H), 1.99 – 1.81 (m, 4H), 1.80 – 1.62 (m, 2H), 1.47 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H,) ppm; ^{13}C NMR (100 MHz; $CDCl_3$) δ 135.1, 134.8, 132.0, 132.0, 131.4, 131.0, 128.8, 128.0, 127.9, 127.9, 127.8, 85.7, 85.4, 84.4, 84.2, 83.0, 82.7, 82.1, 82.1, 38.1, 37.6, 31.7, 31.2, 29.4, 29.2, 29.0, 28.9, 25.6, 23.6, 23.5, 21.1 ppm; MS (EI^+) *m/z* 538, 537, 536, 535, 534, 533, 532 $[M]^{+\bullet}$; HRMS (EI^+) calcd for $C_{22}H_{26}{}^{11}B_2{}^{79}Br_2O_4$ 534.0384 $[M]^{+\bullet}$, found 534.0397.

(3*R*,6*R*,7*R*)- and (3*R*,6*S*,7*S*)-2-Methyl-6-bromomethyl-8-bromooctane-2,3,6,7-tetrols [(3*R*,6*R*,7*R*)-3 and (3*R*,6*S*,7*S*)-3]



(3*R*,6*R*,7*R*)-**3**

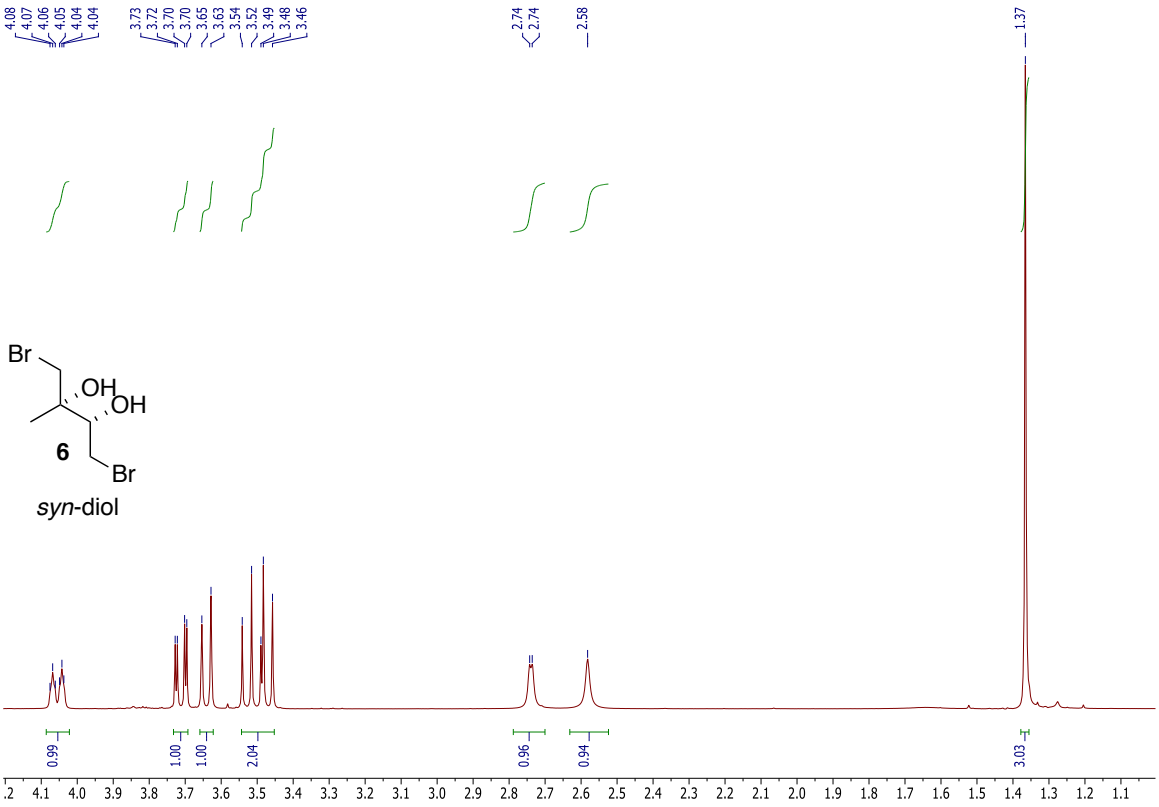
and



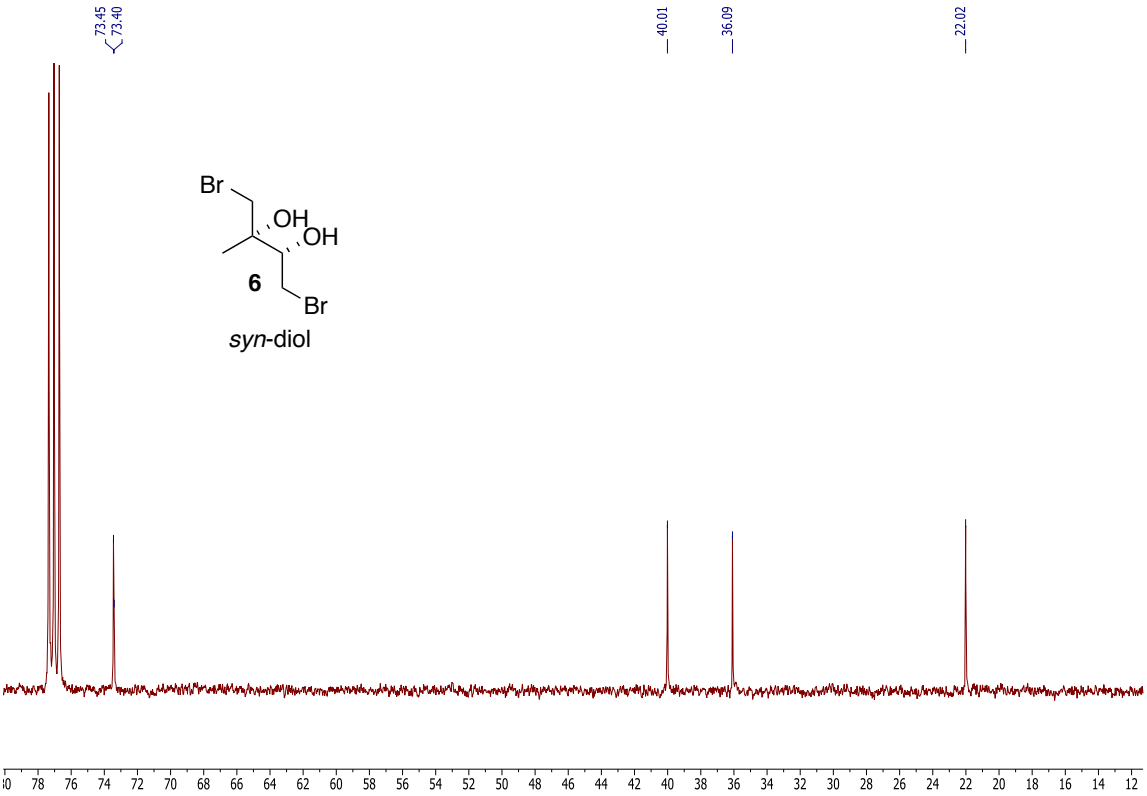
(3*R*,6*S*,7*S*)-**3**

Adapting a method described by Padwa,[8] to a solution of the mixture of diboronates **12** and **13** (158 mg, 0.3 mmol) and AcOH (10 μL, 0.2 mmol, 0.6 eq.) in CH_2Cl_2 (5 mL) was added pinacol (248 mg, 2.1 mmol, 7.0 eq.) and the reaction was stirred at ambient temperature for 72h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (50:50 – 10:90, petroleum ether: EtOAc) to give the two diastereomeric products as off-white crystalline solids (90 mg, 0.25 mmol, 82%) as a *ca.* 1:1 mixture. Analytically pure samples of each could be obtained by further careful chromatography. (3*R,*6*R,*7*R*)-**3**: crystalline white solid, m.p. 102-105 ^{o}C; R_f = 0.49 (10:90, pet. ether : EtOAc); $[\alpha]_D^{25}$ + 21.8 (*c* = 0.3, MeOH);[9] IR (neat) ν_{max} 3379 (br), 2974, 2937, 1433, 1386, 1230, 1159, 1159, 1071 cm^{-1}; ^{1}H NMR (400 MHz, MeOD) δ 3.94 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.82 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.66 (d, *J* = 10.4 Hz, 1H), 3.54 (d, *J* = 10.4 Hz, 1H), 3.43 (t, *J* = 10.4 Hz, 1H), 3.26 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.04-1.94 (m, 1H), 1.79-1.65 (m, 2H), 1.40-1.31 (m, 1H), 1.20 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_3OD) δ 78.6, 75.1, 74.4, 72.4, 37.0 35.0, 32.3, 24.3, 24.1, 23.7 ppm; HRMS (TOF, ES$^-$) *m/z* calcd for $C_{10}H_{19}{}^{79}Br_2O_4$ (M-H)$^-$ 360.9650, found 360.9623. (3*R,*6*S,*7*S*)-**3**: crystalline white solid, m.p. 135-137 ^{o}C; R_f = 0.46 (10:90, pet. ether : EtOAc); $[\alpha]_D^{25}$ + 9.2 (*c* = 0.2, MeOH);[9] IR (neat) ν_{max} 3366 (br), 2974, 1632, 1389, 1431, 1227, 1161, 1077, 971 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 3.95 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.80 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 3.49 (d, *J* = 10.4 Hz, 1H), 3.44 (t, *J* = 10.4 Hz, 1H), 3.26 (dd, *J* = 10.0, 2.0 Hz, 1H), 2.01-1.93 (m, 1H), 1.77-1.68 (m, 2H), 1.48-1.39 (m, 1H), 1.20 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, MeOD) δ 78.5, 75.1, 74.3, 72.4, 36.4, 34.8, 32.1, 24.3, 24.0, 23.6 ppm; HRMS (TOF, ES$^-$) *m/z* calcd for $C_{10}H_{19}{}^{79}Br_2O_4$ (M-H)$^-$ 360.9650, found 360.9654; *Crystal data for* (3*R*,6*S*,7*S*)-**3**: $C_{10}H_{20}Br_2O_4$, *M* = 364.08, orthorhombic, $P2_12_12_1$ (no. 19), *a* = 5.2172(3), *b* = 12.8186(6), *c* = 21.7125(15) Å, *V* = 1452.07(15) Å^3, *Z* = 4, D_c = 1.665 g cm^{-3}, μ(Mo-Kα) = 5.580 mm^{-1}, *T* = 173 K, colourless platy needles, Agilent Xcalibur 3E diffractometer; 2874 independent measured reflections (R_{int} = 0.0264), F^2 refinement,[3] R_1(obs) = 0.0543, wR_2(all) = 0.0830, 2040 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 163 parameters. The absolute structure of (3*R*,6*S*,7*S*)-**3** was determined by use of the Flack parameter [*x* = 0.014(12)]. CCDC 1017806.

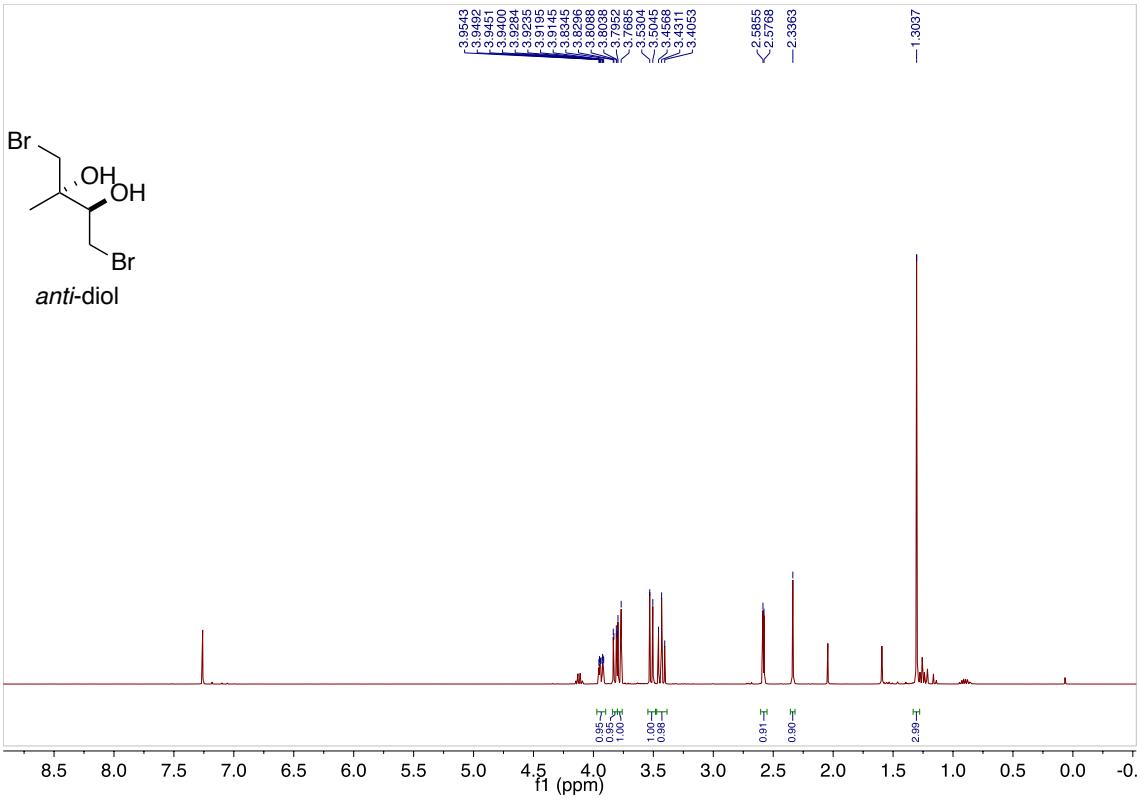
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2*S**,3*S**)-1,4-dibromo-2-methyl-butane-2,3-diol (**6**)



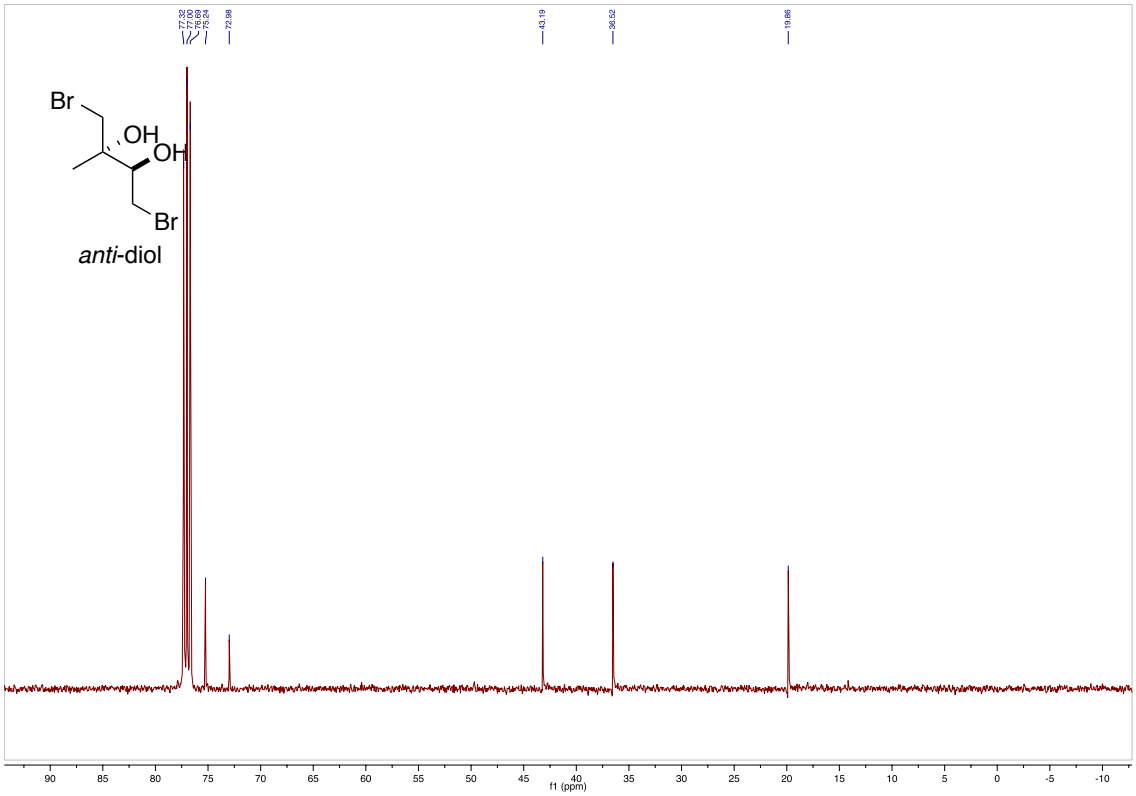
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2*S**,3*S**)-1,4-dibromo-2-methyl-butane-2,3-diol (**6**)



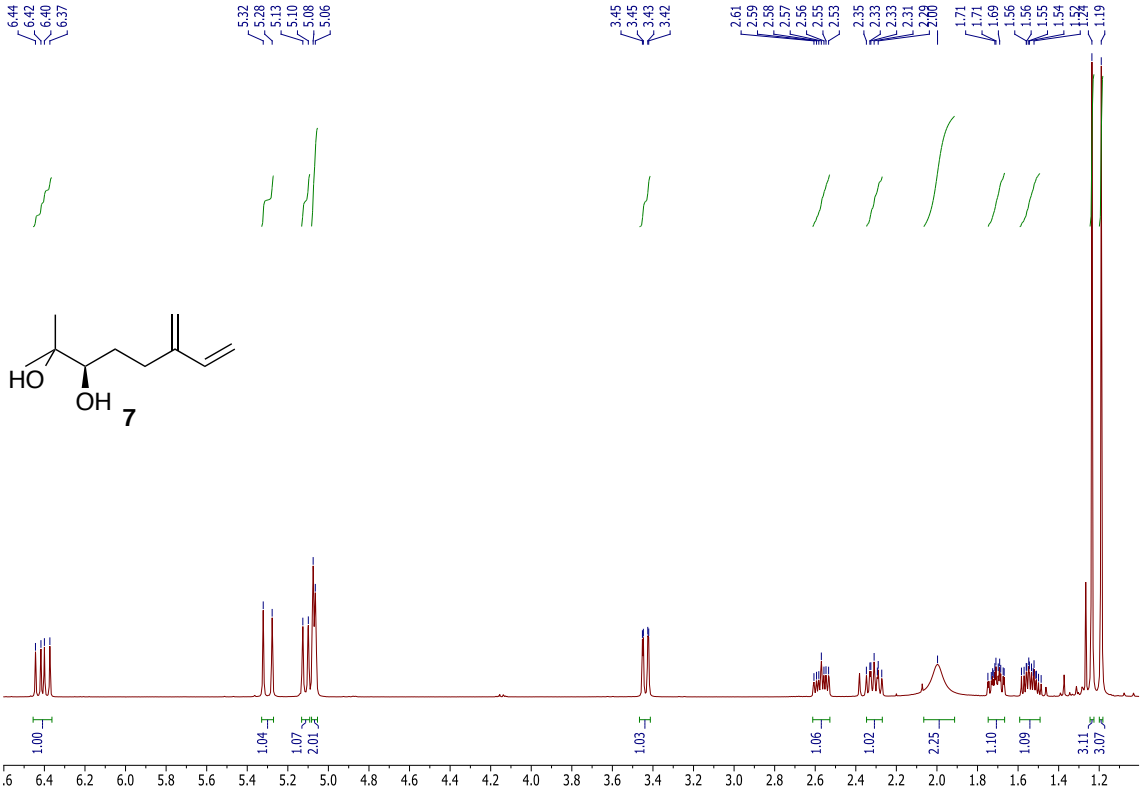
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (2*S**,3*R**)-1,4-dibromo-2-methyl-butane-2,3-diol



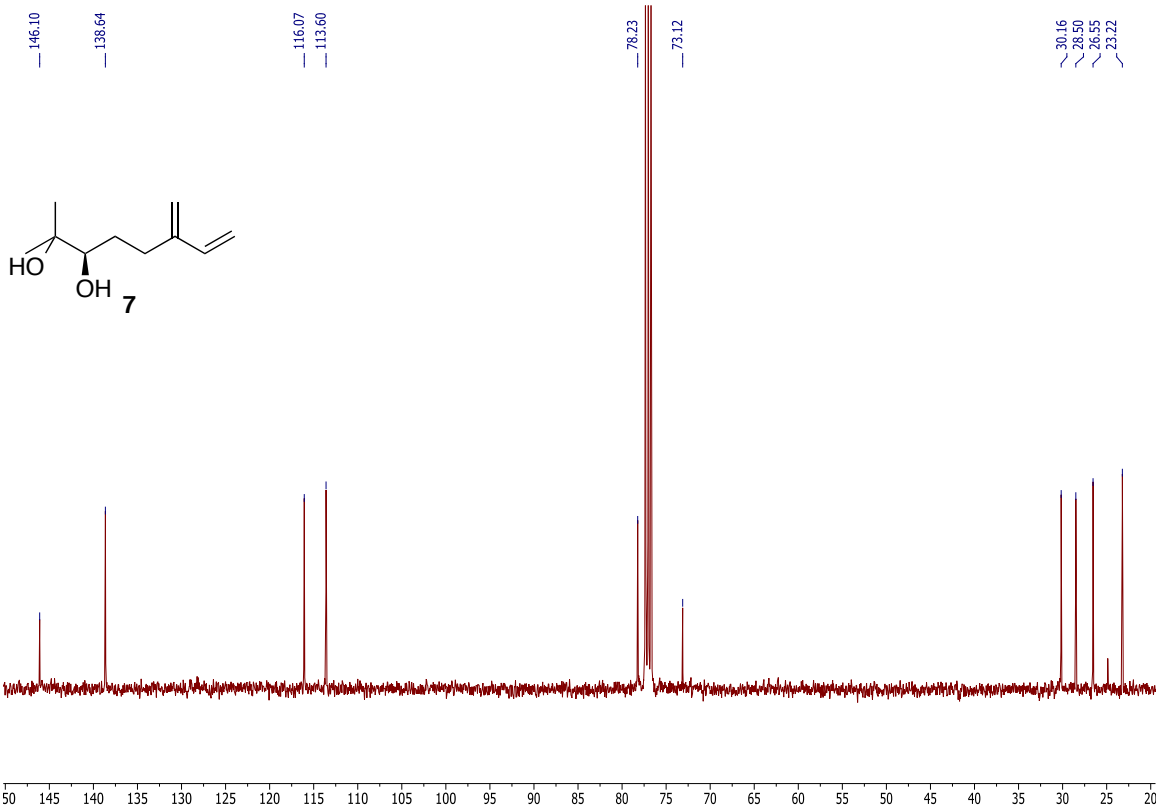
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (2*S**,3*R**)-1,4-dibromo-2-methyl-butane-2,3-diol



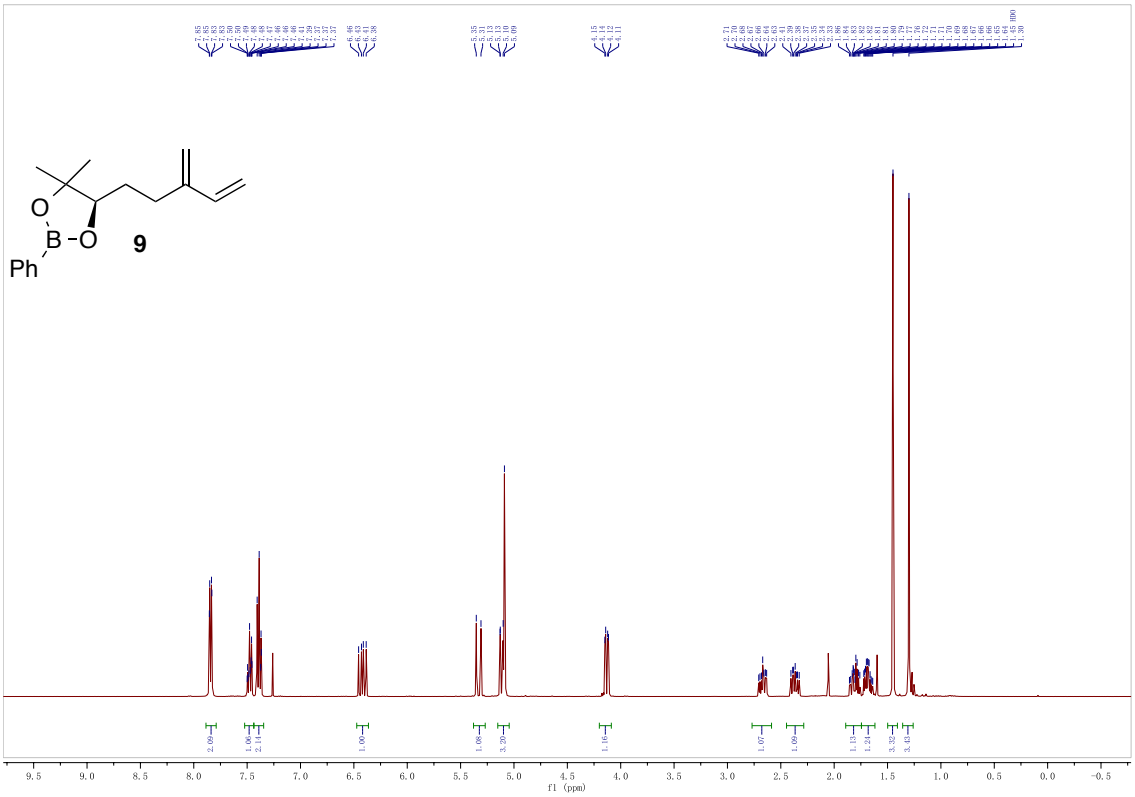
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (3*R*)-2-methyl-6-methylene-oct-7-ene-2,3-diol (**7**)



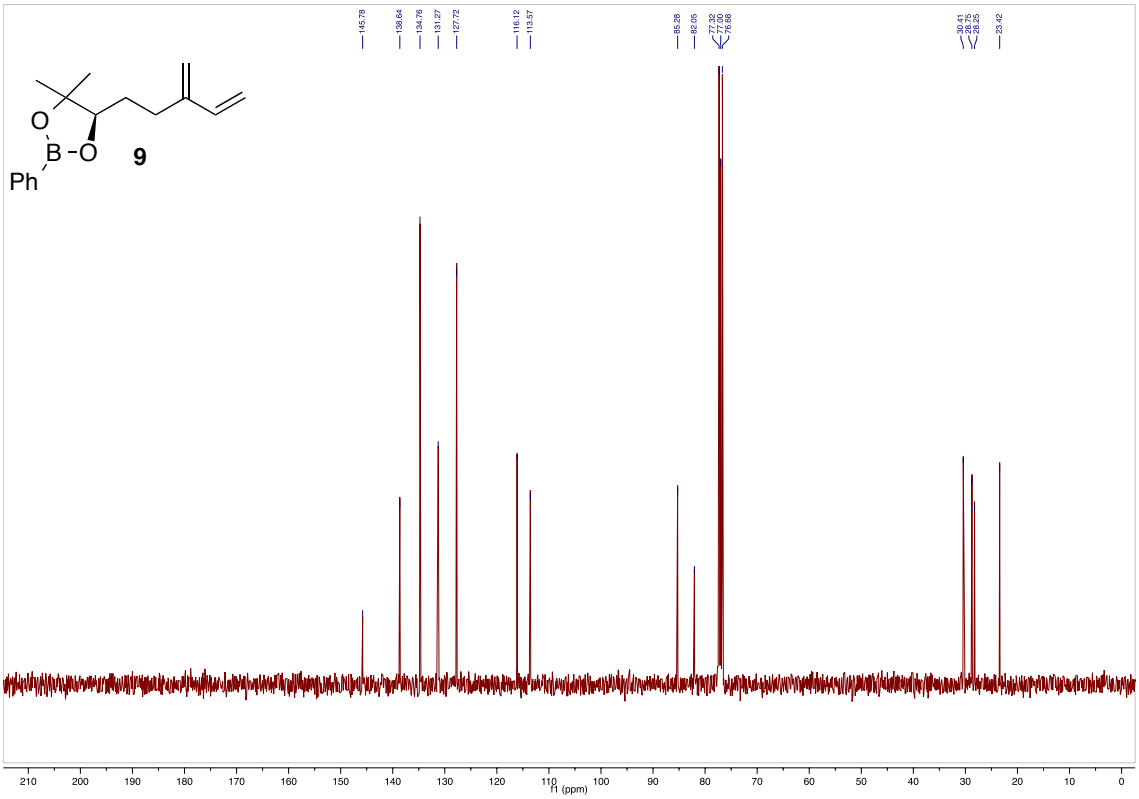
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (3*R*)-2-methyl-6-methylene-oct-7-ene-2,3-diol (**7**)



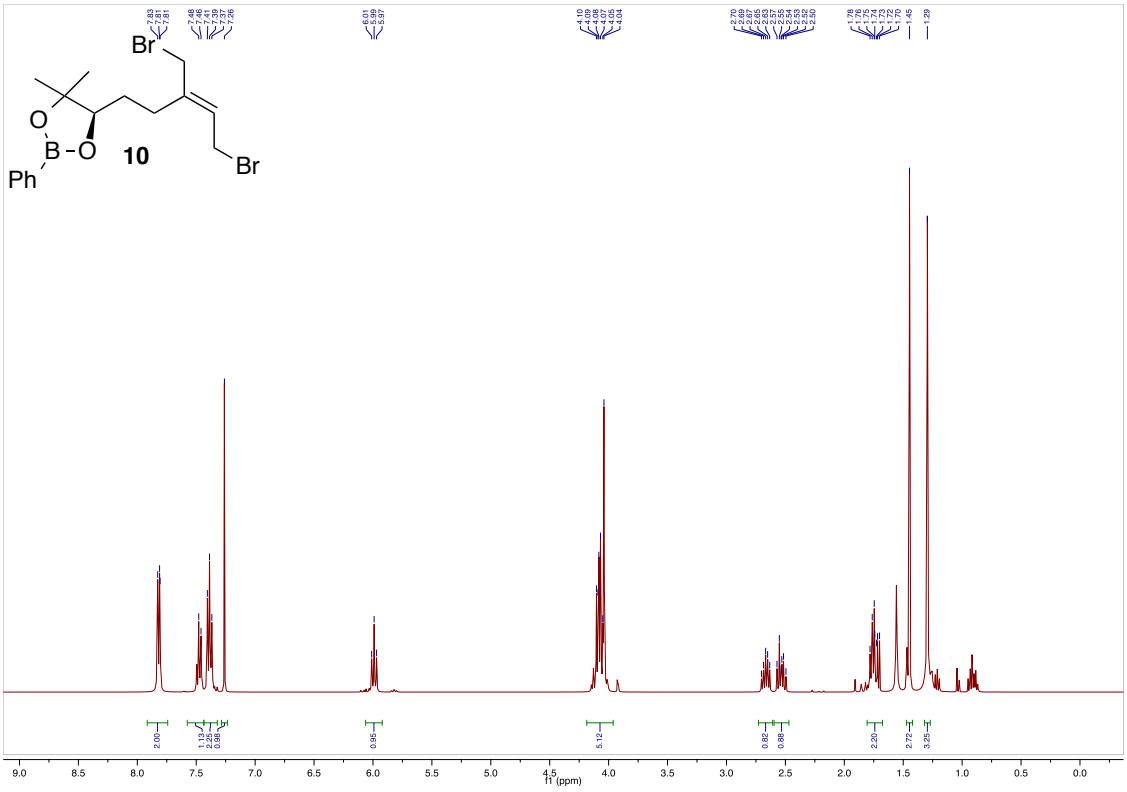
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (3*R*)-4,4-dimethyl-5-(3-methylene-pent-4-enyl)-2-phenyl-[1,3,2]dioxaborolane (**9**)



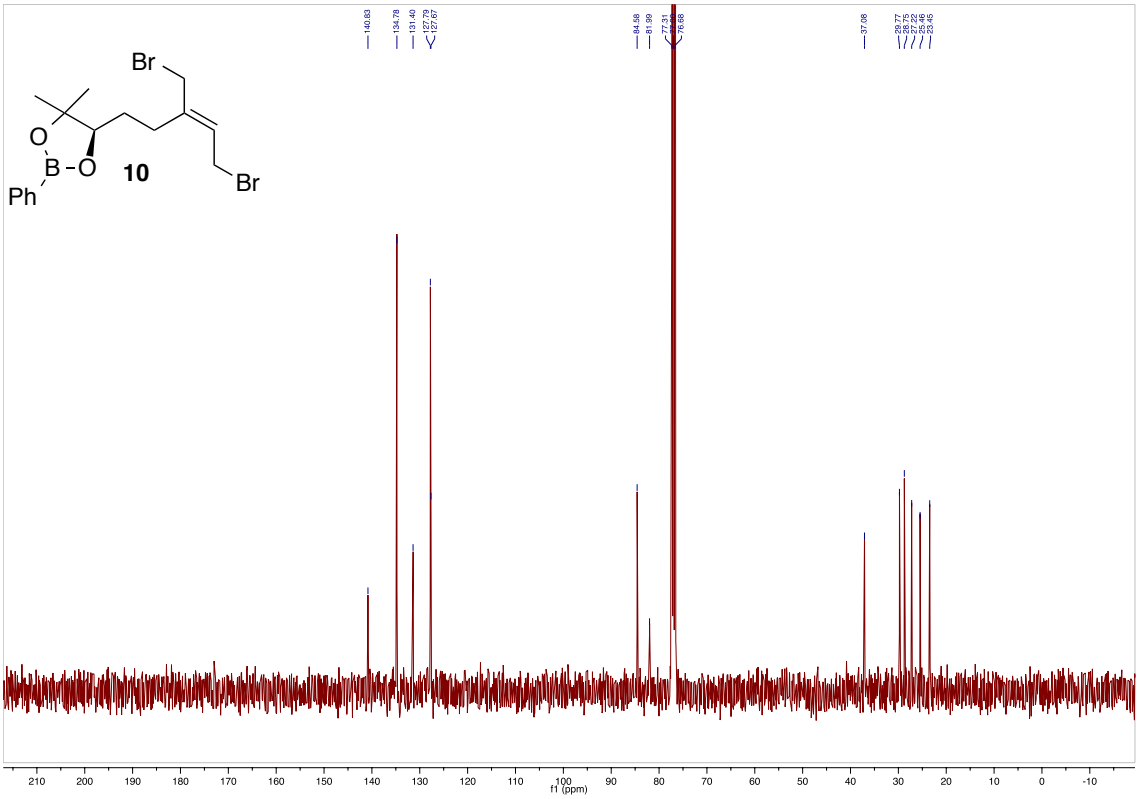
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (3*R*)-4,4-dimethyl-5-(3-methylene-pent-4-enyl)-2-phenyl-[1,3,2]dioxaborolane (**9**)



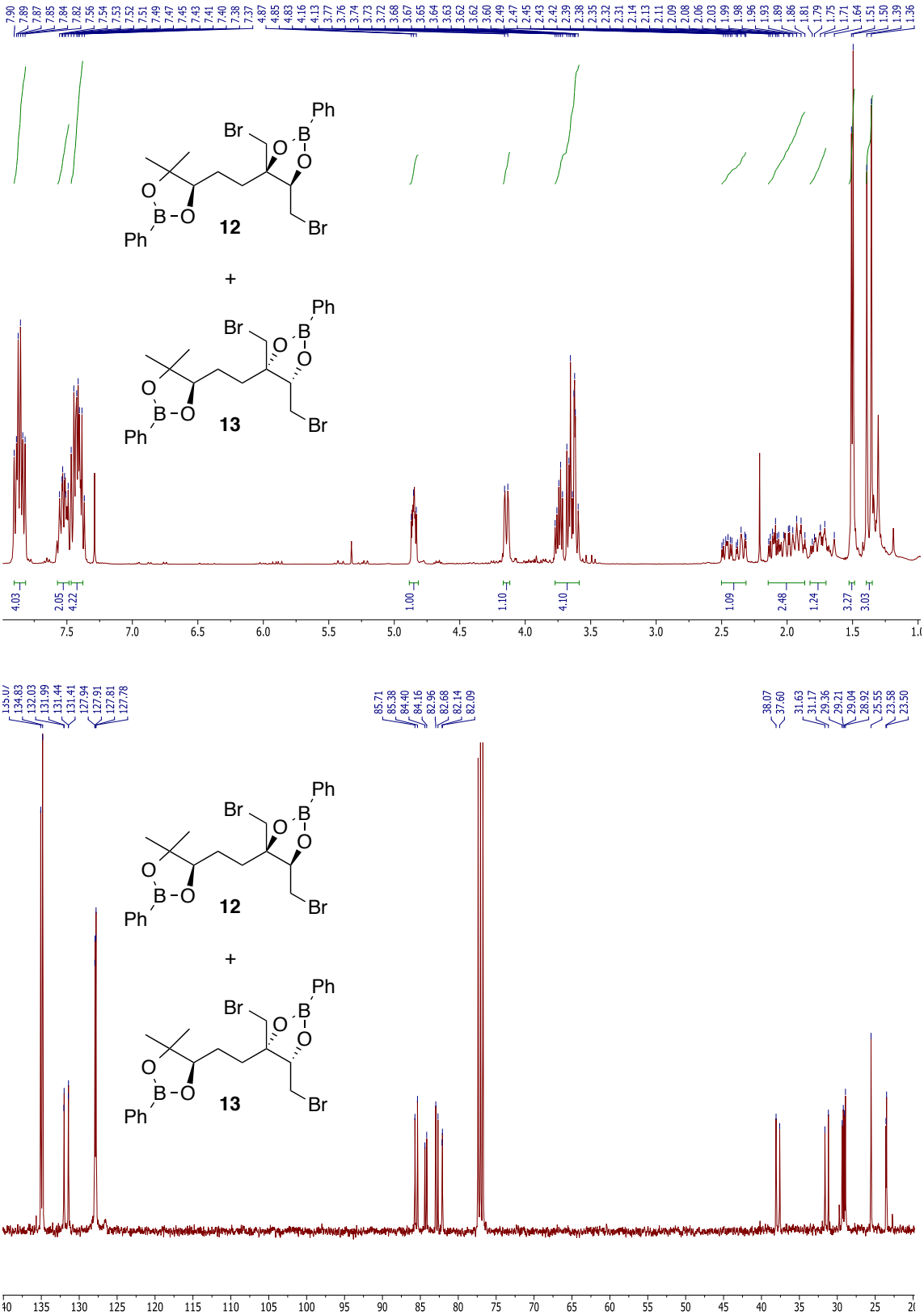
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (3*R*)-5-(5-bromo-3-bromomethyl-pent-3-enyl)-4,4-dimethyl-2-phenyl-[1,3,2]dioxaborolane (**10**)



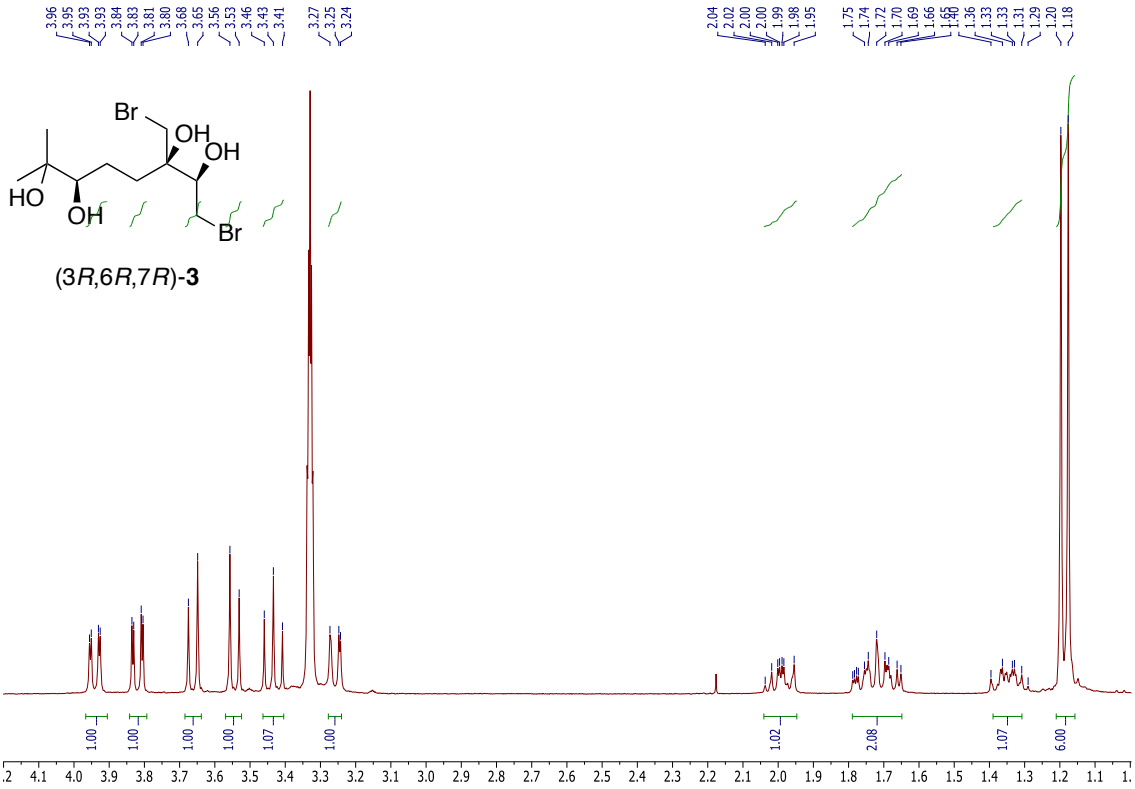
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (3*R*)-5-(5-bromo-3-bromomethyl-pent-3-enyl)-4,4-dimethyl-2-phenyl-[1,3,2]dioxaborolane (**10**)



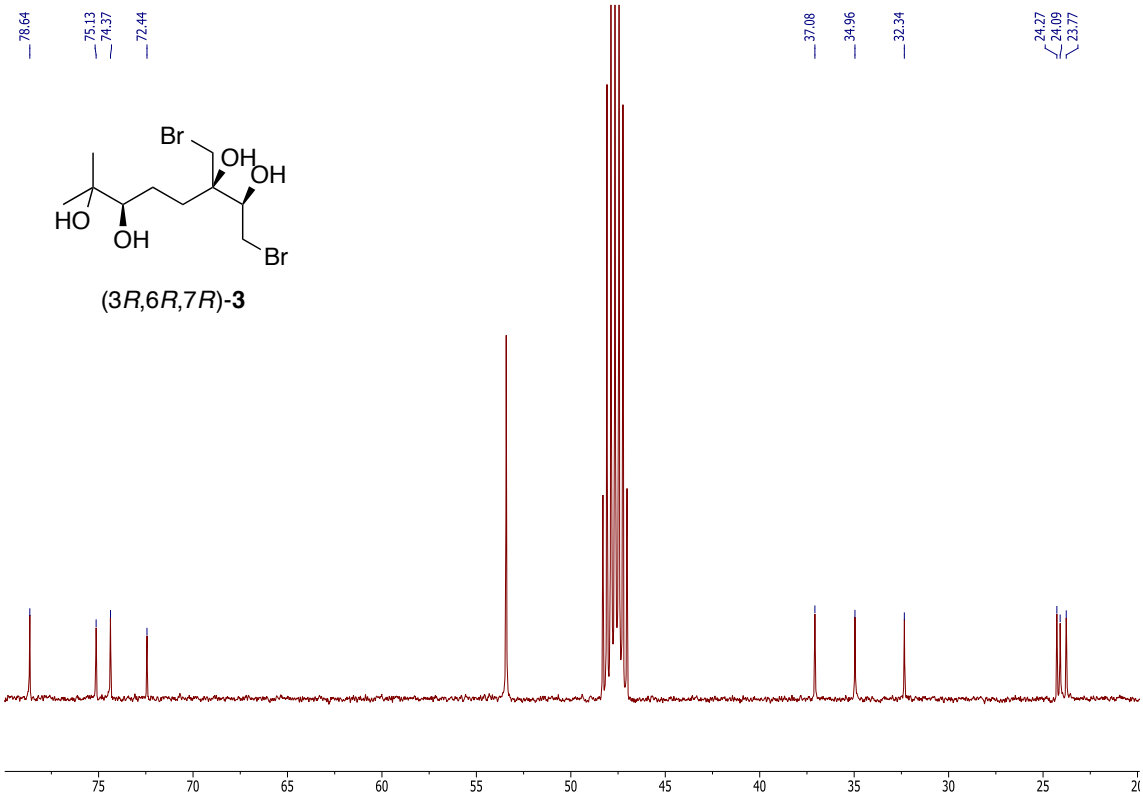
^{1}H NMR spectrum (top) (400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (bottom) (100 MHz, $CDCl_3$) of a *ca.* 1:1 mixture of (3*R*,6*S*,7*S*)- and (3*R*,6*R*,7*R*)-5-[2-(4,5-*bis*-bromomethyl-2-phenyl-[1,3,2]dioxaborolan-4-yl)-ethyl]-4,4-dimethyl-2-phenyl-[1,3,2]dioxaborolanes (**12** and **13**)



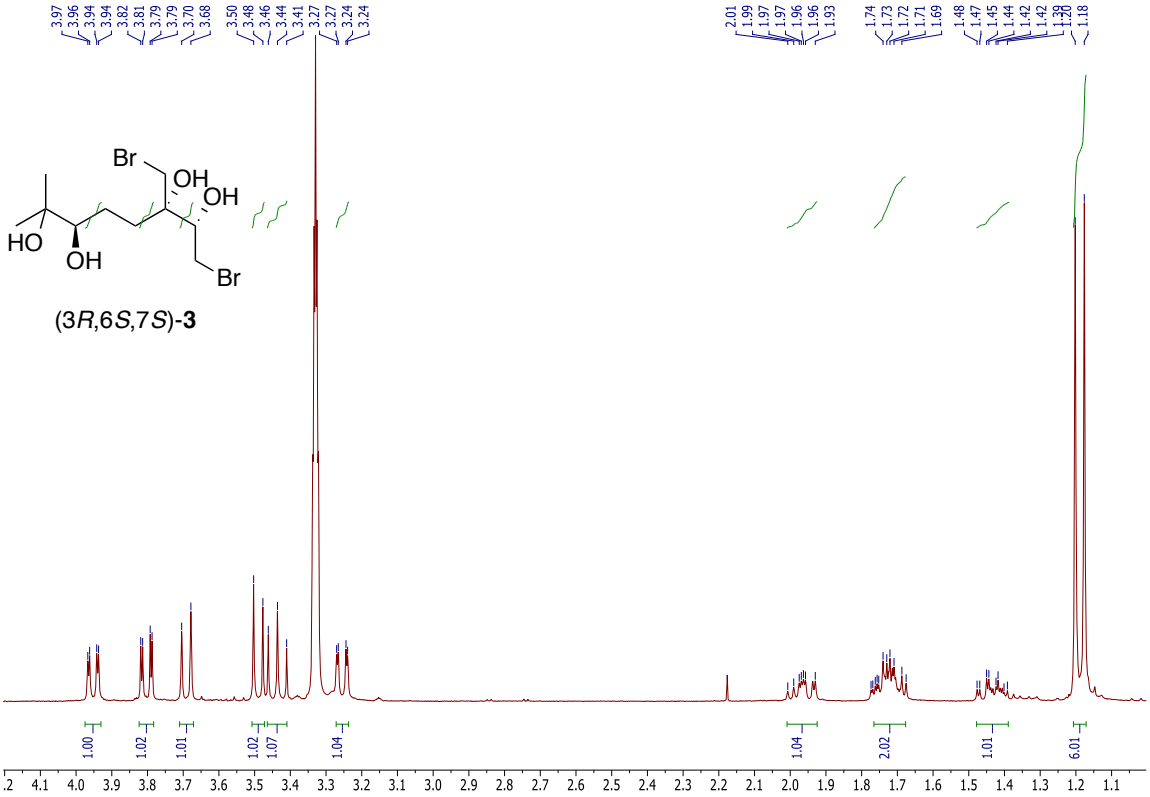
^{1}H NMR spectrum (400 MHz, CD_3OD) of (3*R*,6*R*,7*R*)-2-methyl-6-bromomethyl-8-bromooctane-2,3,6,7-tetrol [(3*R*,6*R*,7*R*)-**3**]



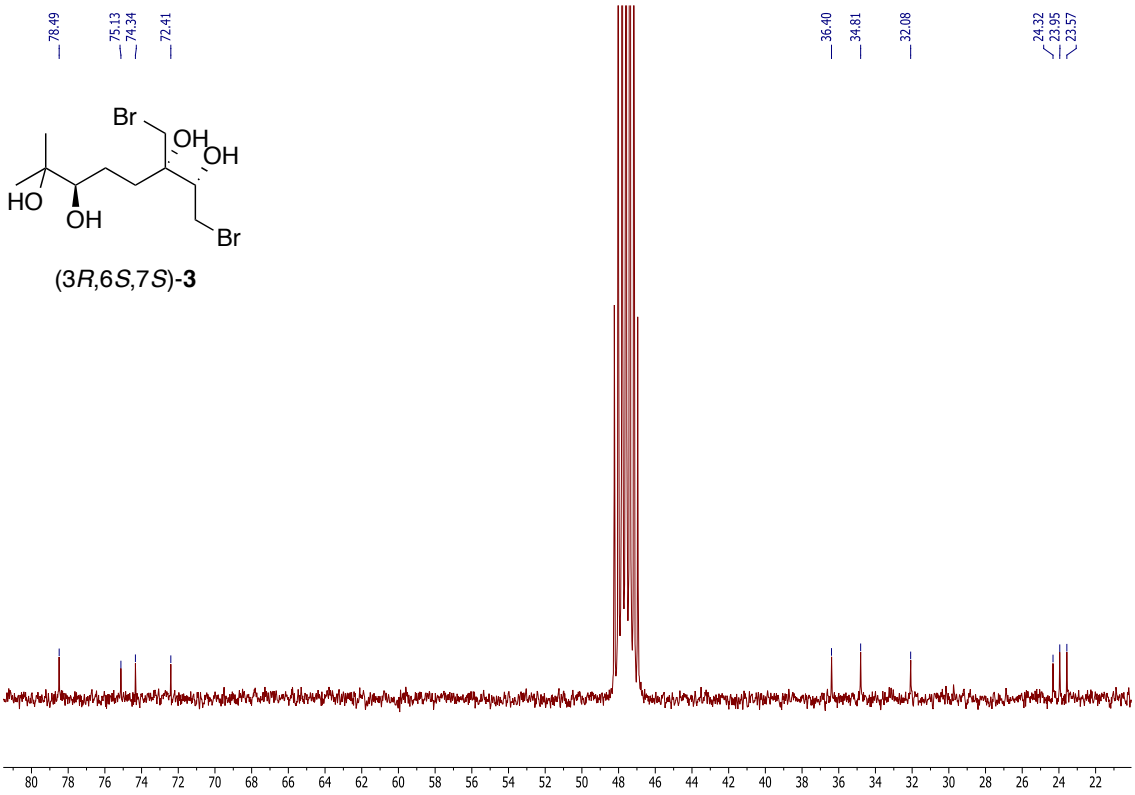
^{13}C NMR spectrum (100 MHz, CD_3OD) of (3*R*,6*R*,7*R*)-2-methyl-6-bromomethyl-8-bromooctane-2,3,6,7-tetrol [(3*R*,6*R*,7*R*)-**3**]



^{1}H NMR spectrum (400 MHz, CD_3OD) of (3*R*,6*S*,7*S*)-2-methyl-6-bromomethyl-8-bromooctane-2,3,6,7-tetrol [(3*R*,6*S*,7*S*)-**3**]



^{13}C NMR spectrum (100 MHz, CD_3OD) of (3*R*,6*S*,7*S*)-2-methyl-6-bromomethyl-8-bromooctane-2,3,6,7-tetrol [(3*R*,6*S*,7*S*)-**3**]



X-Ray Crystallography

The X-ray crystal structure of 6

The two O–H hydrogen atoms in the structure of **6** were both located from Δ*F* maps and refined freely subject to O–H distance constraints of 0.90 Å.

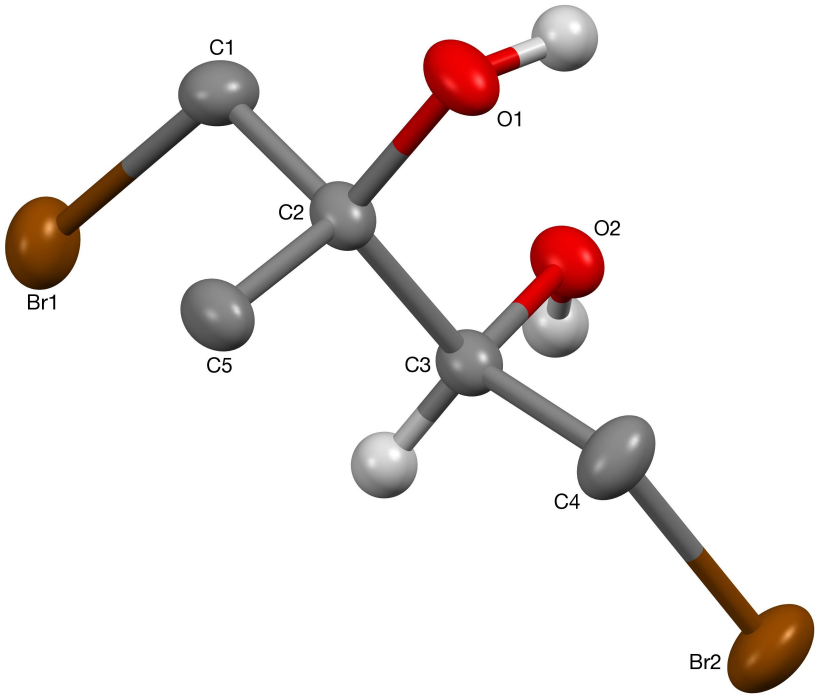


Fig. S1 The crystal structure of **6** (50% probability ellipsoids).

The X-ray crystal structure of (3*R*,6*S*,7*S*)**-3**

The four O–H hydrogen atoms in the structure of (3*R*,6*S*,7*S*)-**3** were all located from Δ*F* maps and refined freely subject to O–H distance constraints of 0.90 Å. The absolute structure of (3*R*,6*S*,7*S*)-**3** was determined by use of the Flack parameter [*x* = 0.014(12)].

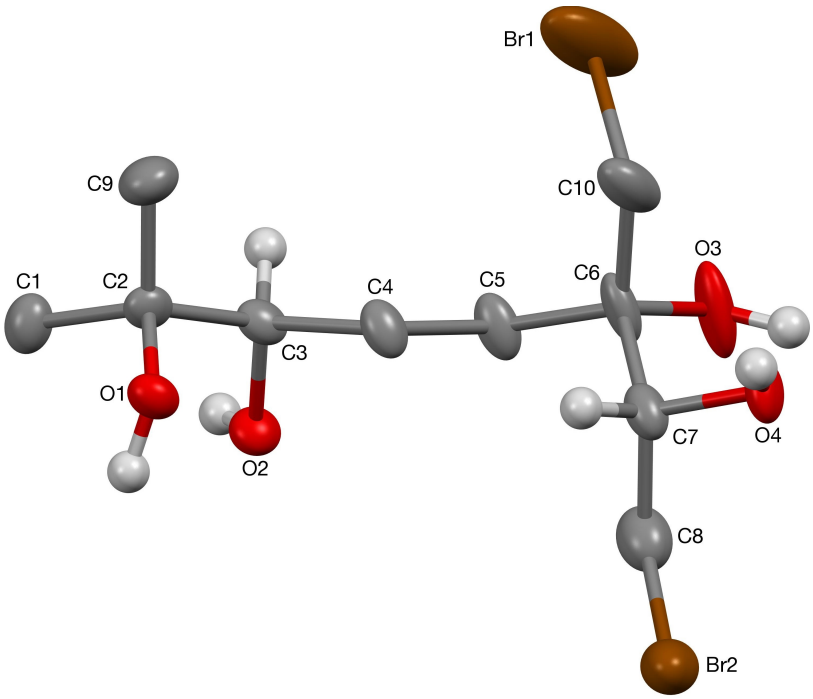


Fig. S2 The crystal structure of (3*R*,6*S*,7*S*)-**3** (50% probability ellipsoids).

References:

1. Falciola, C. A.; Tissot-Crosset, K.; Reyneri, H.; Alexakis, A. *Adv. Synth. Catal.* **2008**, *350*, 1090-1100.

2. Dupau, P.; Epple, R.; Thomas, A. A; Fokin, V. V.; Sharpless, K. B. *Adv. Synth. Catal.* **2002**, *344*, 421-433.

3. SHELXTL, Bruker AXS, Madison, WI; SHELX-97, G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122; SHELX-2013, http://shelx.uni-ac.gwdg.de/SHELX/index.php

4. Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768-2271.

5. Hioki, H.; Ooi, H.; Hamano, M.; Mimura, Y.; Yoshio, S.; Kodama, M.; Ohta, S.; Yanai, M.; Ikegami, S. *Tetrahedron* **2001**, *57*, 1235-1246.

6. Hövelmann, C. H.; Muñiz, K. *Chem. Eur. J.* **2005**, *11*, 3951-3958.

7. Gypser, A.; Michel, D. Nirschl, D. S.; Sharpless, K. B. *J. Org. Chem.* **1998**, *63*, 7322-7327.

8. Padwa, A.; Wang, Q. *J. Org. Chem.* **2006**, *71*, 7391-7402.

9. Optical rotations recorded by Mr James Clarke, Department of Chemistry, Imperial College London.