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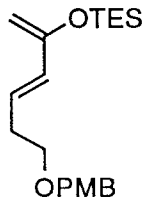
Supporting Information for
Stereoselective Synthesis of the C3-C17 Bis-Oxane Domain of Phorboxazole A

Experimental Procedures and Compound Characterization Data

General Methods. All reactions were carried out under argon or nitrogen in oven dried glassware using standard syringe, cannula, and septa techniques. Tetrahydrofuran and Et_2O were distilled from Na/benzophenone ketyl under nitrogen. CH_2Cl_2, CH_3CN, Et_3N, and $BF_3{\bullet}OEt_2$ were distilled from CaH_2 under nitrogen. DMF was dried over activated 3Å molecular sieves. (*S*)-4-(4-Methoxybenzyloxy)butan-1,2-diol was prepared from (*S*)-malic acid as previously described for (*S*)-4-(benzyloxy)butan-1,2-diol. Flash chromatography was performed using Baker Flash silica gel 60 (40 μm) and the solvent systems indicated. Analytical and preparative TLC was performed with 0.25 mm or 0.50 mm EM silica gel 60 F_{254} plates, respectively, and visualized by fluorescence upon 254 nm irradiation and/or staining with anisaldehyde reagent (450 mL of 95% EtOH, 25 mL of H_2SO_4, 15 mL of HOAc, and 25 mL of anisaldehyde). NMR spectra obtained in $CDCl_3$ are referenced to residual $CHCl_3$ at 7.25 ppm (^1H) and 77.0 ppm (^{13}C). The mass spectrometers used show deviations of less than 5 ppm.



4

Preparation of Diene 4.

3-(4-Methoxybenzyloxy)-propan-1-ol (4a).

To a soln of *p*-anisaldehyde (27.5 g, 202 mmol) in benzene (700 mL) was added 1,3-propanediol (15.22 g, 200.0 mmol), and $TsOH{\bullet}H_2O$ (90 mg, 500 μmol). The flask was equipped with a Dean-Stark trap and the mixture heated at reflux for 18 h. The mixture was cooled to rt, concentrated by rotary evaporation to a volume of 200 mL, and diluted with THF (300 mL). The soln was cooled to 0 °C and $LiAlH_4$ (7.6 g, 0.20 mol) followed by $AlCl_3$ (27 g, 0.20 mol) were added cautiously. The mixture was warmed to rt and stirred for 18 h. The reaction was quenched cautiously with water (150 mL) and 15% aqueous NaOH (150 mL). The mixture was extracted with Et_2O (3 X 200 mL) and the combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. The resultant pale yellow oil was distilled (bp 149-154 °C, 0.9 Torr) to give 3-(4-methoxybenzyloxy)-propan-1-ol (33.44 g, 170.4 mmol, 85%) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.77 (q, J = 5.7 Hz, 2H), 3.63 (t, J = 5.7 Hz, 2H), 2.27 (t, J = 5.7 Hz, 1H), 1.84 (p, J = 5.7 Hz, 2H).

3-(4-Methoxybenzyloxy)-propanal (4b).

To a soln of oxalyl chloride (2.42 mL, 27.7 mmol) in CH_2Cl_2 (75 mL) at -78 °C was added a soln of DMSO (3.94 mL, 55.5 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at -78 °C for 5 min before a soln of **4a** (4.95 g, 25.2 mmol) in CH_2Cl_2 (25 mL) was added. The mixture was stirred at -78 °C for 20 min before Et_3N (17.6 mL, 126 mmol) was added and the mixture allowed to warm to rt. The mixture was diluted with Et_2O (200 mL), washed with water (100 mL) and brine (100 mL), and the combined aqueous phases were extracted with Et_2O (100 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was dried by azeotropic removal of water with benzene to provide crude **4b** as a pale yellow oil which was used without further purification: ^1H NMR ($CDCl_3$, 300 MHz): δ 9.77 (t, J = 1.8 Hz, 1H), 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.78 (t, J = 6.1 Hz, 2H), 2.67 (ddd, J = 6.1, 6.1, 1.8 Hz, 2H).

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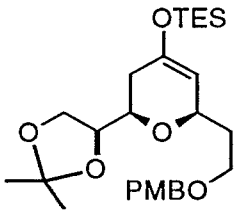
(*E*)-6-(4-Methoxybenzyloxy)-3-hexen-2-one (4c).
To a suspension of LiCl (1.28 g, 30.2 mmol) in CH_3CN (280 mL) was added dimethyl (2-oxopropyl)phosphonate (5.0 g, 30 mmol), *i*-Pr_2NEt (4.40 mL, 25.2 mmol) and crude **4b** (ca. 5 g, 25 mmol). The mixture was stirred at rt for 18 h, then diluted with Et_2O (200 mL), washed with water (70 mL) and brine (70 mL), and the combined aqueous phases were extracted with Et_2O (150 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Flash chromatography (3:1 hexanes-ethyl acetate) provided **4c** (4.88 g, 20.8 mmol, 83% for 2 steps) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.80 (ddd, *J* = 16.1, 6.8, 6.8 Hz, 1H), 6.11 (d, *J* = 16.1 Hz, 1H), 4.44 (s, 2H), 3.80 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.50 (q, *J* = 6.5 Hz, 2H), 2.23 (s, 3H).

(*E*)-2-(Triethylsilyl)oxy-6-(4-methoxybenzyl)oxy-1,3-hexadiene (4).
To a soln of diisopropylamine (6.50 mL, 49.6 mmol) in THF (80 mL) at 0 °C was added a soln of n-BuLi in hexanes (19.2 mL of a 2.58 M soln, 49.5 mmol). The soln was stirred at 0 °C for 15 min then cooled to -78 °C before a soln of **4c** (10.54 g, 44.99 mmol) in THF (10 mL) was added over 15 min. The soln was stirred at -78 °C for 15 min before chlorotriethylsilane (8.30 mL, 49.4 mmol) was added. The resulting soln was stirred at -78 °C for 30 min and then warmed to -20 °C over 2.2 h. The reaction mixture was diluted with pentane (600 mL) and washed with cold, saturated aqueous $NaHCO_3$ (100 mL) and brine (100 mL), and the combined aqueous phases were extracted with pentane (150 mL). The combined pentane phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography on silica gel neutralized with Et_3N (20:1 hexanes-ethyl acetate) afforded **4** (11.64 g, 33.39 mmol, 74%) as a colorless oil: R_f 0.63 (5:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.93-6.04 (m, 2H), 4.48 (s, 2H), 4.27 (s, 1H), 4.24 (s, 1H), 3.83 (s, 3H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.44 (q, *J* = 6.6 Hz, 2H), 1.01 (t, *J* = 8.2 Hz, 9H), 0.74 (q, *J* = 8.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 154.9, 130.5, 129.5, 129.3, 127.6, 113.8, 94.0, 72.6, 69.5, 55.3, 32.6, 6.8, 4.9; HRMS calcd for $C_{20}H_{32}O_3Si$ $[M]^+$: 348.2121, found 348.2108.



5

Enol ether (5).
To a soln of **4** (4.638 g, 13.31 mmol) and (*S*)-glyceraldehyde acetonide (3.52 g, 27 mmol) in Et_2O (90 mL) at -78 °C was added BF_3•OEt_2 (330 μL, 2.7 mmol). The soln was stirred at -78 °C for 30 min then quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was diluted with ethyl acetate (120 mL), washed with water (40 mL) and brine (50 mL), and the combined aqueous phases were extracted with ethyl acetate (2 X 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Filtration through a plug of silica gel, neutralized with Et_3N, and eluting with hexanes and 20:1 hexanes-ethyl acetate afforded **5** as a mixture of diastereomers (5.47 g, 11.4 mmol, 86%) which was used without further separation. Chromatographic purification provided an analytical sample of diastereomerically pure **5** as a colorless oil: R_f 0.48 (5:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.75 (s, 1H), 4.41 (s, 2H), 4.27 (m, 1H), 4.04 (m, 1H), 3.97 (m, 1H), 3.87 (m, 1H), 3.79 (s, 3H), 3.52 (m, 3H), 2.10 (m, 2H), 1.77 (m, 2H), 1.40 (s, 3H), 1.35 (s, 3H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.64 (q, *J* = 7.8 Hz, 6H).

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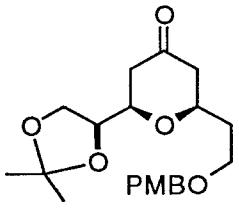
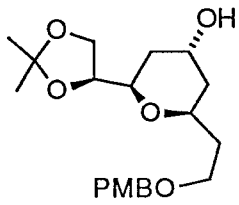


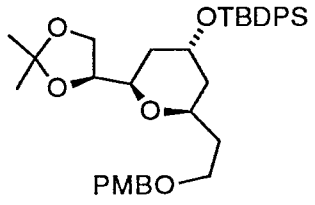
6

Ketone (6).
To a soln of **5** (5.47 g, 11.4 mmol) in THF (90 mL) at 0 °C was added a soln of tetra-*n*-butylammonium fluoride in THF neutralized (as indicated by pH paper) with $TsOH•H_2O$ (11.4 mL of a 1.0 M soln, 11 mmol). The soln was stirred for 10 min then diluted with Et_2O (150 mL), washed with water (2 X 70 mL) and brine (70 mL), and the combined aqueous phases were extracted with Et_2O (75 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (3:1 hexanes-ethyl acetate) afforded **6** (2.903 g, 7.966 mmol, 60% from **4**) as a colorless oil: R_f 0.32 (2:1 hexanes-ethyl acetate); $[\alpha]^{23}_D$ = +16 (*c* 0.78, $CHCl_3$); IR (neat): 2870, 1720, 1610, 1510, 1245 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.39 (d, *J* = 11.8 Hz, 1H), 4.07 (m, 2H), 3.80 (m, 5H), 3.58 (ddd, *J* = 8.8, 8.8, 5 Hz, 1H), 3.51 (m, 2H), 2.55 (ddd, *J* = 14.5, 2.3, 2.3 Hz, 1H), 2.38 (ddd, *J* = 14.5, 2.3, 2.3 Hz, 1H), 2.34 (dd, *J* = 14.5, 11.5 Hz, 1H), 2.27 (dd, *J* = 14.5, 11.5 Hz, 1H), 1.91 (dddd, *J* = 14.1, 8.5, 5.2, 5.2 Hz, 1H), 1.80 (dddd, *J* = 14.2, 8.4, 5.8, 4.1 Hz, 1H), 1.40 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 206.6, 159.2, 130.3, 129.4, 113.8, 109.9, 77.6, 74.3, 72.7, 66.7, 65.5, 55.3, 47.8, 43.8, 36.4, 26.6, 25.1; HRMS calcd for $C_{20}H_{28}O_6$ $[M]^+$: 364.1886, found 364.1895.



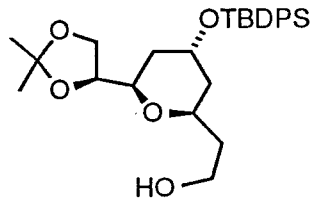
6a

Axial alcohol (6a).
To a soln of **6** (2.850 g, 7.820 mmol) in THF (260 mL) at -78 °C was added a soln of potassium tri-*sec*-butylborohydride in THF (11.7 mL of a 1.0 M soln, 12 mmol). The soln was stirred for 30 min below -70 °C then warmed to -25 °C over 2 h. The reaction was quenched with aqueous NaOH (47 mL of a 1.0 M soln, 47 mmol) and aqueous H_2O_2 (21 mL, 30 wt%) then warmed to 0 °C and stirred for 20 min. The mixture was diluted with water (600 mL) and extracted with CH_2Cl_2 (4 X 90 mL) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (1:1 hexanes-ethyl acetate) afforded **6a** (2.785 g, 7.600 mmol, 97%) as a colorless oil: R_f 0.34 (1:1 hexanes-ethyl acetate); $[\alpha]^{23}_D$ = +15.9 (*c* 1.12, $CHCl_3$); IR (neat): 3450, 2900, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.25 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* =11.6 Hz, 1H), 4.28 (m, 1H), 4.03 (dd, *J* = 8.1, 6.3 Hz, 1H), 3.92 (m, 2H), 3.81 (dd, *J* = 8.1, 5.4 Hz, 1H), 3.80 (s, 3H), 3.69 (ddd, *J* = 11.7, 6.9, 2.1 Hz, 1H), 3.53 (m, 2H), 1.84 (dddd, *J* = 14, 2.4, 2.4, 2.4 Hz, 1H) 1.59-1.76 (m, 3H), 1.42-1.55 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 130.5, 129.3, 113.7, 109.3, 78.1, 72.7, 72.6, 68.8, 67.0, 66.3, 64.1, 55.2, 38.7, 36.2, 34.8, 26.6, 25.3; HRMS calcd for $C_{20}H_{30}O_6$ $[M+H]^+$ 367.2121, found 367.2091.



6b

TBDPS ether (6b).
To a soln of **6a** (2.497 g, 6.814 mmol) in DMF (34 mL) was added imidazole (3.71 g, 54.5 mmol), 4-dimethylaminopyridine (100 mg, 819 μmol) and *t*-butylchlorodiphenylsilane (7.10 mL, 27.3 mmol). The mixture was stirred at rt for 18 h then diluted with water (100 mL) and extracted with CH_2Cl_2 (4 X 75 mL) and the combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (20:1-5:1 hexanes-ethyl acetate) afforded **6b** (3.853 g, 6.370 mmol, 93%) as a colorless oil: R_f 0.32 (5:1 hexanes-ethyl acetate); $[\alpha]^{23}_D$ = +7.9 (*c* 1.26, $CHCl_3$); IR (neat): 3090, 2900, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (m, 4H), 7.33-7.45 (m, 6H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.47 (d, *J* = 11.4 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 4.23 (m, 1H), 3.96-4.15 (m, 2H), 3.88 (m, 3H), 3.81 (s, 3H), 3.54 (m, 2H), 1.51-1.84 (m, 4H), 1.41 (s, 3H), 1.35 (s, 3H), 1.21-1.34 (m, 2H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 135.73, 135.69, 134.2, 134.0, 130.7, 129.67, 129.65, 129.2, 127.6, 113.7, 109.3, 78.2, 72.9, 72.6, 69.4, 66.8, 66.6, 65.7, 55.2, 39.1, 36.3, 35.2, 27.0, 26.7, 25.4, 19.3; HRMS calcd for $C_{36}H_{48}O_6Si$ $[M-H]^+$ 603.3143, found 603.3160.



6c

Alcohol (6c).
To a soln of **6b** (547 mg, 949 μmol) in CH_2Cl_2 (48 mL) was added t-BuOH (4.8 mL), aq. phosphate buffer (480 μL, pH 7) and DDQ (431 mg, 1.90 mmol). The mixture was stirred at rt for 30 min then additional phosphate buffer (400 μL, pH 7) and DDQ (140 mg, 617 μmol) were added and stirring continued for 30 min. The reaction mixture was diluted Et_2O (200 mL), washed with aqueous $NaHCO_3$ (100 mL), water (75 mL) and brine (75 mL), and the combined aqueous phases were extracted with Et_2O (75 mL). The combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. Flash chromatography (3:1-2:1 hexanes-ethyl acetate) afforded **6c** (444 mg, 916 μmol, 97%) as a colorless oil: R_f 0.35 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.64 (m, 4H), 7.39 (m, 6H), 4.21 (m, 2H), 3.90-4.05 (m, 4H), 3.76-3.90 (m, 2H), 2.65 (m, 1H), 1.46-1.78 (m, 4H), 1.43 (s, 3H), 1.35 (s, 3H), 1.22-1.41 (m, 2H), 1.08 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 135.7, 135.6, 134.0, 133.8, 129.75, 129.73, 127.6, 109.3, 77.9, 72.9, 72.6, 66.1, 65.3, 61.6, 38.8, 37.6, 34.9, 27.0, 26.6, 25.2, 19.2; HRMS calcd for $C_{28}H_{40}O_5Si$ $[M+H]^+$ 485.2723, found 485.2734.

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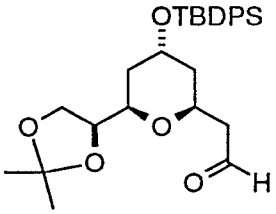
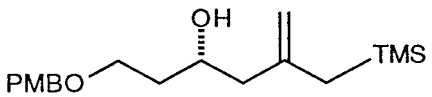


7

Aldehyde (7).
To a soln of **6c** (175 mg, 361 μmol) in CH_2Cl_2 (4 mL) at 0 °C was added $NaHCO_3$ (300 mg, 3.57 mmol) and Dess-Martin periodinane (230 mg, 542 μmol). The mixture was warmed to rt and stirred for 45 min before additional $NaHCO_3$ (150 mg, 1.79 mmol) and Dess-Martin periodinane (230 mg, 542 μmol) were added. Stirring was continued for 1.25 h before the reaction mixture was diluted Et_2O (25 mL), saturated aqueous $NaHCO_3$ (10 mL) and 10% aqueous $Na_2S_2O_3$ (10 mL) and allowed to stir for an additional 30 min. The layers were separated and the organic phase was washed with water (15 mL) and brine (15 mL), and the combined aqueous phases were extracted with Et_2O (20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (6:1 hexanes-ethyl acetate) afforded **7** (139 mg, 288 μmol, 80%) as a colorless oil: R_f 0.64 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 9.79, (t, J = 2.4 Hz, 1H), 7.66, (m, 4H), 7.39 (m, 6H), 4.52 (dddd, J = 11.1, 8.7, 4.5, 2.1 Hz, 1H), 4.26 (m, 1H), 3.85-4.05 (m, 4H), 2.53 (ddd, J = 16.2, 8.6, 2.8 Hz, 1H), 2.38 (ddd, J = 16.2, 4.5, 1.8 Hz, 1H), 1.83 (m, 1H), 1.59 (m, 1H), 1.42 (s 3H), 1.35 (s, 3H), 1.25-1.40 (m, 2H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 201.2, 135.7, 135.6, 133.8, 133.6, 129.8, 127.6, 109.3, 77.9, 73.0, 67.7, 66.6, 65.3, 49.4, 38.5, 34.6, 27.0, 26.6, 25.3, 19.2; HRMS calcd for $C_{28}H_{38}O_5Si$ $[M+H]^+$ 483.2566, found 483.2564.



8a

Hydroxy silane (8a).
To a soln of (*S*)-4-(4-methoxybenzyloxy)butan-1,2-diol (1.076 g, 4.755 mmol) in THF (60 mL) at 0 °C was added NaH (285 mg, 11.9 mmol) and the mixture warmed to rt and stirred for 1 h. The mixture was cooled to 0 °C and *N*-tosylimidazole (1.057 g, 4.755 mmol) was added in three equal portions over 20 min. The mixture was warmed to rt and stirred for 40 min before CuI (90 mg, 470 μmol) was added and the mixture cooled to -40 °C. A soln of Grignard reagent prepared from 2-bromo-3-(trimethylsilyl)propene (2.87 mL, 16.6 mmol), magnesium (520 mg, 21.4 mmol) and THF (25 mL) was added. The mixture was warmed to -10 °C over 1.3 h and then quenched with aqueous $NaHCO_3$ (2 mL). The mixture was diluted with ethyl acetate (150 mL), washed with water (75 mL) and brine (75 mL), and the combined aqueous phases were extracted with ethyl acetate (75 mL). The combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. Flash chromatography (5:1 hexanes-ethyl acetate) afforded **8a** (838 mg, 2.60 mmol, 55%) as a colorless oil: ^1H NMR (C_6D_6, 500 MHz): δ 7.18 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 4.74 (m, 1H), 4.66 (m, 1H), 4.29 (d, J = 11.8 Hz, 1H), 4.26 (d, J = 11.8 Hz, 1H), 4.03 (m, 1H), 3.59 (ddd, J = 9.5, 5.8, 5.8 Hz, 1H), 3.49 (ddd, J = 9.5, 6, 6 Hz, 1H), 3.29 (s, 3H), 2.52 (d, J = 3 Hz, 1H), 2.21 (ddd, J = 13.5, 8, 1 Hz, 1H), 2.14 (ddd, J = 13.5, 5, 1 Hz, 1H), 1.75 (m, 2H), 1.53 (dd, J = 13, 1 Hz, 1H), 1.49 (dd, J = 13, 1 Hz, 1H), 0.01 (s, 9H).

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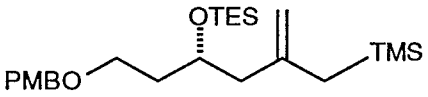
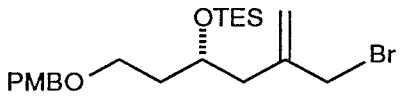


8b

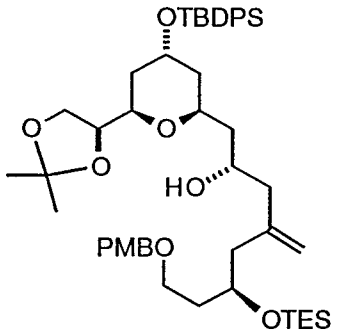
TES ether silane (8b).
To a soln of **8a** (601 mg, 1.86 mmol) in CH_2Cl_2 (15 mL) was added imidazole (387 mg, 5.68 mmol), 4-dimethylaminopyridine (16 mg, 130 μmol), and chlorotriethylsilane (410 μL, 2.44 mmol). The mixture was stirred at rt for 1 h, diluted with Et_2O (80 mL), washed with water (25 mL) and brine (25 mL), and the combined aqueous phases were extracted with Et_2O (20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (20:1 hexanes-ethyl acetate) afforded **8b** (753 mg, 1.72 mmol, 93%) as a colorless oil: ^1H NMR ($CDCl_3$, 300 MHz): δ 7.26 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.61 (m, 1H), 4.56 (m, 1H), 4.44 (d, J = 11.4 Hz, 1H), 4.39 (d, J = 11.4 Hz, 1H), 3.97 (dddd, J = 7.5, 7.5, 5.7, 4.2 Hz, 1H), 3.80 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 2.18 (ddd, J = 13.5, 5.7, 0.9 Hz, 1H), 2.06 (ddd, J = 13.5, 7.5, 0.6 Hz, 1H), 1.88 (dddd, J = 14, 7.1, 7.1, 4.1 Hz, 1H), 1.63 (dddd, J = 14, 7.7, 6.1, 6.1 Hz, 1H), 1.54 (dd, J = 13.5, 0.9 Hz, 1H), 1.48 (dd, J = 13.2, 0.9 Hz, 1H), 0.95 (t, J = 7.8 Hz, 9H), 0.59 (q, J = 7.8 Hz, 6H), 0.01 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 144.0, 130.7, 129.3, 113.7, 110.0, 72.6, 68.5, 66.9, 55.3, 46.9, 36.9, 27.1, 7.0, 5.0, -1.4.



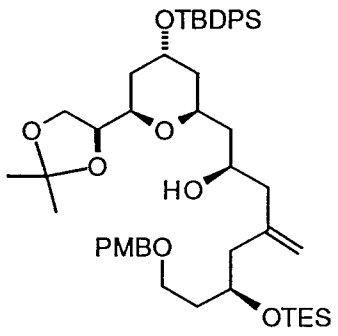
8

TES bromide (8).
To a soln of **8b** (157 mg, 359 μmol) in ethyl acetate (35 mL) at ca. -50 °C was added bromine dropwise until a light yellow color persisted. A soln of imidazole (100 mg, 1.47 mmol) in ethyl acetate (3 mL) was added quickly and the yellow color dissipated. The reaction mixture was warmed to 0 °C, filtered through a plug of silica gel and washed with aqueous $NaHCO_3$ (15 mL) and brine (15 mL), and the combined aqueous phases were extracted with ethyl acetate (15 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (25:1 hexanes-ethyl acetate) afforded **8** (122 mg, 275 μmol, 77%) as a colorless oil: R_f 0.38 (10:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.25 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.23 (d, J = 1.2 Hz, 1H), 4.98 (d, J = 1.2 Hz, 1H), 4.44 (d, J = 11.4 Hz, 1H), 4.39 (d, J = 11.4 Hz, 1H), 3.95-4.05 (m, 3H), 3.81 (s, 3H), 3.51 (t, J = 6.3 Hz, 2H), 2.39 (dd, J = 6.3, 0.9 Hz, 2H), 1.61-1.83 (m, 2H), 0.95 (t, J = 8 Hz, 9H), 0.60 (q, J = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 142.6, 130.6, 129.3, 118.0, 113.7, 72.7, 68.1, 66.6, 55.3, 41.4, 37.4, 36.9, 6.9, 5.0; HRMS calcd for $C_{21}H_{35}O_3SiBr$ $[M-H]^+$ 441.1471, found 441.1453.

Supporting Information for
Stereoselective Synthesis of the C3-C17 Bis-Oxane Domain of Phorboxazole A



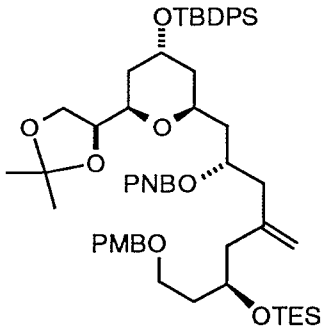
9



10

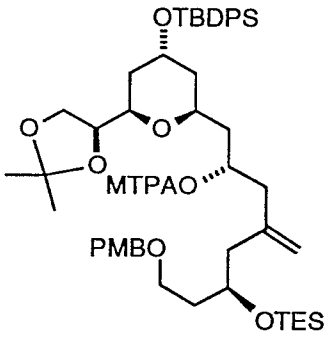
Coupled products (9 and 10).
To a suspension of $CrCl_2$ (containing 1% w/w $NiCl_2$, 370 mg, 3.01 mmol) in THF (2 mL) was added a soln of **8** (446 mg, 1.01 mmol) in THF (4 mL) followed by a soln of **7** (200 mg, 414 μmol) in THF (4 mL). The mixture was stirred for 3.5 h then quenched with saturated aqueous $NaHCO_3$ (2 mL). The mixture was diluted with ethyl acetate (75 mL), washed with water (25 mL) and brine (30 mL), and the combined aqueous phases were extracted with ethyl acetate (2 X 20 mL). The combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. Flash chromatography (10:1-6:1 hexanes-ethyl acetate) afforded **9** (163 mg, 192 μmol, 46%) and and **10** (117 mg, 138 μmol, 33%) as colorless oils. Data for **9**: R_f 0.24 (5:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (m, 4H), 7.39 (m, 6H), 7.26 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.90 (s, 2H), 4.45 (d, J = 11.7 Hz, 1H), 4.40 (d, J = 11.7 Hz, 1H), 4.33 (m, 1H), 4.26 (m, 1H), 3.90-4.06 (m, 6H), 3.80 (s, 3H), 3.53 (t, J = 6.5 Hz, 2H), 2.82 (d, J = 3.3 Hz, 1H), 2.24 (m, 4H), 1.43 (s, 3H), 1.35 (s, 3H), 1.24-1.90 (m, 8H), 1.09 (s, 9H), 0.96 (t, J = 7.9 Hz, 9H), 0.60 (q, J = 7.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 143.6, 135.7, 135.6, 134.0, 133.9, 130.6, 129.68, 129.66, 129.2, 127.6, 114.9, 113.7, 109.3, 78.0, 73.0, 72.6, 69.8, 68.5, 66.6, 66.5, 66.4, 65.6, 55.2, 44.8, 44.2, 41.8, 38.6, 36.9, 34.9, 27.0, 26.6, 25.2, 19.2, 6.9, 5.0; HRMS calcd for $C_{49}H_{74}O_8Si_2$ $[M+H]^+$ 847.5003, found 847.4938.
Data for **10**: R_f 0.19 (5:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (m, 4H), 7.39 (m, 6H), 7.26 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.90 (s, 2H), 4.45 (d, J = 11.4 Hz, 1H), 4.40 (d, J = 11.4 Hz, 1H), 4.23 (m, 2H), 3.88-4.08 (m, 6H), 3.80 (s, 3H), 3.57 (s, 1H), 3.54 (t, J = 6.6 Hz, 2H), 2.10-2.34 (m, 4H), 1.47-1.91 (m, 6H), 1.43 (s, 3H), 1.35 (s, 3H), 1.29 (m, 2H), 1.09 (s, 9H), 0.96 (t, J = 7.8 Hz, 9H), 0.61 (q, J = 7.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 143.3, 135.7, 135.6, 133.9, 133.7, 130.6, 129.75, 129.72, 129.2, 127.63, 127.62, 114.9, 113.7, 109.3, 77.8, 73.4, 72.8, 72.6, 69.9, 68.2, 66.7, 66.3, 65.2, 55.2, 44.5, 42.1, 39.2, 36.7, 34.9, 27.0, 26.6, 25.2, 19.2, 6.9, 5.0; HRMS calcd for $C_{49}H_{74}O_8Si_2$ $[M+H]^+$ 847.5003, found 847.5033.

Supporting Information for
Stereoselective Synthesis of the C3-C17 Bis-Oxane Domain of Phorboxazole A



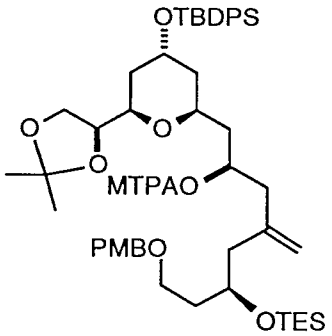
10a

***p*-Nitrobenzoate (10a).**
To a soln of **10** (78 mg, 92 μmol) in benzene (3 mL) was added PPh_3 (121 mg, 461 μmol), 4-nitrobenzoic acid (69 mg, 410 μmol) and diethyl azodicarboxylate (73 μL, 460 μmol). The mixture was stirred for 1.5 h then diluted with ethyl acetate (35 mL), washed with water (10 mL), and brine (10 mL), and the combined aqueous phases were extracted with ethyl acetate (10 mL). The combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. Flash chromatography (7:1 hexanes-ethyl acetate) afforded samples of impure (42 mg) and pure **10a** (60 mg, >100% combined) as colorless oils: R_f 0.70 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.25 (d, J = 8.9 Hz, 2H), 8.19 (d, J = 8.9 Hz, 2H), 7.56 (m, 4H), 7.39 (m, 2H), 7.32 (m, 4H), 7.24 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.60 (m, 1H), 4.85 (s, 1H), 4.82 (s, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.39 (d, J = 11.6 Hz, 1H), 4.23 (m, 1H), 3.82-4.08 (m, 5H), 3.79 (s, 3H), 3.74 (m, 1H), 3.52 (t, J = 6.8 Hz, 2H), 2.16-2.49 (m, 4H), 1.59-1.86 (m, 5H), 1.46 (m, 1H), 1.37 (s, 3H), 1.34 (s, 3H), 1.30 (m, 2H), 0.92 (m, 18H), 0.58 (q, J = 7.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.8, 159.0, 150.3, 142.0, 136.0, 135.6, 135.5, 133.9, 133.7, 130.64, 130.58, 129.71, 129.68, 129.2, 127.6, 123.4, 115.5, 113.7, 109.2, 77.9, 73.5, 72.6, 70.7, 68.5, 68.3, 67.1, 66.7, 65.6, 55.2, 44.3, 42.3, 40.8, 39.1, 36.9, 34.9, 26.8, 26.6, 25.2, 19.1, 6.9, 5.0.
To a soln of impure **10a** (102 mg, ca. 92 μmol) in MeOH (6 mL) and CH_2Cl_2 (600 μL) was added K_2CO_3 (20 mg, 140 μmol). The mixture was stirred for 22 h then diluted with ethyl acetate (60 mL), washed with water (10 mL) and brine (10 mL), and the combined aqueous phases were extracted with ethyl acetate (20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (7:1-6:1 hexanes-ethyl acetate) afforded **9** (59 mg, 70 μmol, 76% from **10**) that matched **9** prepared from **7** and **8** above.



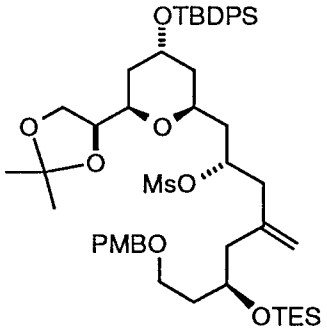
(*R*)-MTPA-9

(*R*)-Mosher Ester of 9 ((*R*)-MTPA-9).
To a soln of **9** (6.1 mg, 7.2 μmol) in CH_2Cl_2 (800 μL) was added 4-dimethylaminopyridine (13 mg, 110 μmol) and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (6 μL, 30 μmol). The mixture was stirred for 30 min and then diluted with ethyl acetate (10 mL), washed with water (3 mL) and brine (3 mL), and the combined aqueous phases were extracted with ethyl acetate (5 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (6:1 hexanes-ethyl acetate) afforded **(*R*)-MTPA-9** (5.0 mg, 4.7 μmol, 65%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.59 (m, 6H), 7.38 (m, 9H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.55 (m, 1H), 4.85 (s, 2H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.17 (m, 1H), 3.90-4.06 (m, 4H), 3.86 (m, 1H), 3.78 (s, 3H), 3.76 (m, 1H), 3.53 (s, 3H), 3.51 (m, 2H), 2.47 (dd, *J* = 13.8, 6.6 Hz, 1H), 2.14-2.31 (m, 3H), 1.79 (m, 2H), 1.64 (m, 3H), 1.45 (m, 1H), 1.41 (s, 3H), 1.34 (s, 3H), 1.26 (m, 2H), 1.02 (s, 9H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H).



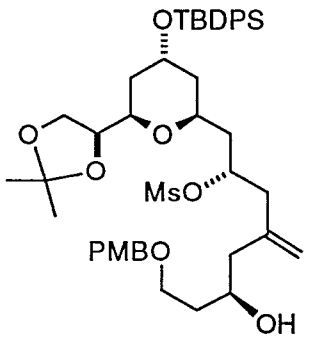
(*R*)-MTPA-10

(*R*)-Mosher Ester of 10 ((*R*)-MTPA-10)
Compound **10** was treated as described above for **9** to afford **(*R*)-MTPA-10** (97%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62 (m, 4H), 7.52 (m, 2H), 7.38 (m, 9H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.40 (m, 1H), 4.76 (s, 2H), 4.43 (d, *J* = 11.4 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.20 (m, 1H), 3.81-4.10 (m, 6H), 3.79 (s, 3H), 3.51 (s, 3H), 3.49 (m, 2H), 2.32 (m, 2H), 2.17 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.09 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.54-1.91 (m, 6H), 1.40 (s, 3H), 1.33 (s, 3H), 1.26 (m, 2H), 1.05 (s, 9H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H).



11

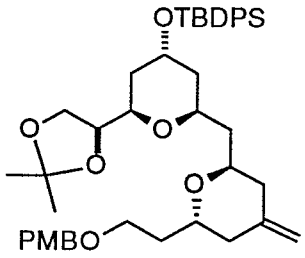
Mesylate (11).
To a soln of **9** (160 mg, 189 μmol) in CH_2Cl_2 (15 mL) at 0 °C was added Et_3N (260 μL, 1.87 mmol) and MsCl (73 μL, 940 μmol). The mixture was stirred at 0 °C for 20 min and then quenched with saturated aqueous $NaHCO_3$ (3 mL). The mixture was diluted with ethyl acetate (70 mL), washed with water (15 mL) and brine (15 mL), and the combined aqueous phases were extracted with ethyl acetate (15 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (7:1 hexanes-ethyl acetate) afforded **11** (168 mg, 182 μmol, 96%) as a colorless oil: R_f 0.64 (2:1 hexanes-ethyl acetate); ^1H NMR (C_6D_6, 300 MHz): δ 7.72 (m, 4H), 7.21 (m, 8H), 6.78 (d, J = 8.4 Hz, 2H), 5.28 (m, 1H), 4.87 (s, 1H), 4.82 (s, 1H), 4.34 (m, 4H), 4.14 (m, 3H), 4.09 (dd, J = 8.4, 6.3 Hz, 1H), 3.89 (m, 1H), 3.44-3.61 (m, 2H), 3.27 (s, 3H), 2.55 (m, 1H), 2.51 (s, 3H), 2.24-2.40 (m, 3H), 1.70-1.98 (m, 3H), 1.54 (m, 1H), 1.45 (s, 3H), 1.30 (s, 3H), 1.16 (s, 9H), 1.01 (t, J = 7.8 Hz, 9H), 0.84-1.39 (m, 4H), 0.64 (q, J = 7.8 Hz, 6H); ^{13}C NMR (C_6D_6, 75 MHz): δ 159.3, 142.2, 135.8, 135.7, 134.3, 134.0, 130.9, 129.7, 129.2, 127.8, 127.7, 115.9, 113.7, 108.9, 78.4, 77.1, 73.0, 72.5, 68.2, 67.1, 66.3, 65.8, 54.4, 44.2, 43.0, 40.9, 39.0, 37.7, 37.5, 35.7, 26.9, 26.6, 25.5, 19.2, 7.0, 5.2; HRMS calcd for $C_{50}H_{76}O_{10}Si_2S$ $[M+Na]^+$ 947.45954, found 947.4560.



11a

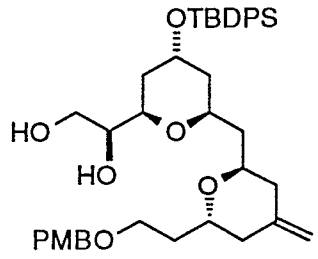
Hydroxy mesylate (11a).
To a soln of **11** (167 mg, 180 μmol) in THF (8 mL) at 0 °C was added a soln of tetra-*n*-butylammonium fluoride in THF (270 μL of a 1.0 M soln, 270 μmol). The soln was stirred at 0 °C for 45 min then diluted with ethyl acetate (60 mL), washed with water (10 mL) and brine (10 mL), and the combined aqueous phases were extracted with ethyl acetate (10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (2:1 hexanes-ethyl acetate) afforded **11a** (137 mg, 169 μmol, 94%) as a colorless oil: R_f 0.55 (1:1 hexanes-ethyl acetate); ^1H NMR (C_6D_6, 300 MHz): δ 7.72 (m, 4H), 7.17 (m, 8H), 6.75 (d, J = 8.4 Hz, 2H), 5.31 (m, 1H), 4.84 (s, 1H), 4.81 (s, 1H), 4.35 (m, 1H), 4.28 (dd, J = 8.4, 6 Hz, 1H), 4.10-4.22 (m, 4H), 4.03 (dd, J = 8.1, 6.6 Hz, 1H), 3.97 (m, 1H), 3.86 (q, J =

6.4 Hz, 1H), 3.36-3.52 (m, 2H), 3.27 (s, 3H), 2.73 (m, 1H), 2.61 (m, 1H), 2.56 (s, 3H), 2.10-2.36 (m, 3H), 1.88 (m, 1H), 1.48-1.70 (m, 3H), 1.46 (s, 3H), 1.28 (s, 3H), 1.15 (s, 9H), 0.84-1.41 (m, 4H); ^{13}C NMR (C_6D_6, 75 MHz): δ 159.4, 142.6, 135.8, 135.7, 134.3, 134.0, 130.4, 129.7, 129.1, 127.8, 127.7, 115.6, 113.8, 108.9, 78.3, 77.4, 72.8, 72.7, 69.0, 68.3, 67.1, 66.8, 65.8, 54.4, 44.1, 42.9, 40.6, 38.9, 37.7, 36.7, 35.7, 26.9, 26.6, 25.4, 19.2; HRMS calcd for $C_{44}H_{62}O_{10}SiS$ $[M+Na]^+$ 833.3731, found 833.3718.



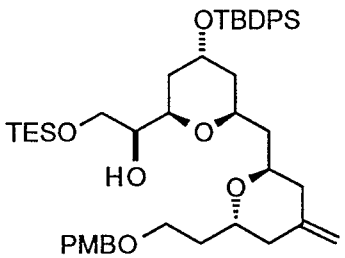
12

Bispyran acetonide (12).
A soln of **11a** (136 mg, 168 μmol) in CH_3CN (11 mL) and Et_3N (1 mL) was heated to reflux for 47 h. The soln was cooled to rt, diluted with ethyl acetate (60 mL), washed with water (10 mL), and brine (10 mL), and the combined aqueous phases were extracted with ethyl acetate (2 X 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography (6:1 hexanes-ethyl acetate) afforded **12** (103 mg, 144 μmol, 86%) as a pale yellow oil: R_f 0.69 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67 (m, 4H), 7.43 (m, 2H), 7.38 (t, J = 7.5 Hz, 4H), 7.25 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.79 (s, 1H), 4.77 (s, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.25 (m, 1H), 4.03 (m, 3H), 3.92 (m, 4H), 3.80 (s, 3H), 3.52 (m, 2H), 2.42 (dd, J = 13.5, 4.5 Hz, 1H), 2.34 (dd, J = 13.0, 4 Hz, 1H), 2.07 (dd, J = 13.5, 5.5 Hz, 1H), 2.02 (dd, J = 13.5, 7.5 Hz, 1H), 1.88 (m, 2H), 1.74 (m, 2H), 1.55 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.31 (m, 2H), 1.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 142.1, 135.7, 134.0, 133.9, 130.6, 129.7, 129.1, 127.6, 113.7, 110.2, 109.2, 78.1, 73.1, 72.6, 69.04, 68.96, 68.92, 66.9, 66.7, 65.7, 55.2, 40.0, 39.1, 38.8, 35.2, 34.1, 27.0, 26.7, 25.3, 19.2; HRMS calcd for $C_{43}H_{58}O_7Si$ $[M+H]^+$ 715.4032, found 715.3990.



12a

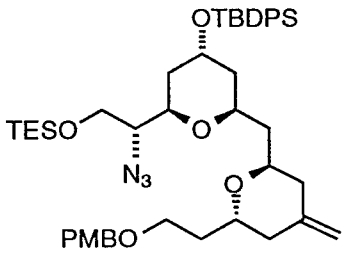
Bispyran diol (12a).
To a soln of **12** (103 mg, 144 μmol) in MeOH (10 mL) was added $TsOH•H_2O$ (5 mg, 30 μmol). The soln was stirred at rt for 7 h, then diluted with ethyl acetate (90 mL), washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL), and brine (10 mL), and the combined aqueous phases were extracted with ethyl acetate (2 X 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (1:1 hexanes-ethyl acetate) afforded **12a** (94.6 mg, 140 μmol, 97%) as a pale yellow oil: R_f 0.03 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, J = 7.5 Hz, 4H), 7.43 (m, 2H), 7.38 (t, J = 7.5 Hz, 4H), 7.25 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.78 (s, 1H), 4.76 (s, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.26 (m, 1H), 4.06 (m, 2H), 3.97 (m, 2H), 3.80 (s, 3H), 3.64 (m, 2H), 3.54 (m, 3H), 2.66 (m, 2H), 2.38 (dd, J = 13.5, 4.5 Hz, 1H), 2.34 (dd, J = 13.5, 4 Hz, 1H), 2.02 (m, 2H), 1.90 (dddd, J = 14, 6.7, 6.7, 6.7 Hz, 1H), 1.80 (ddd, J = 14.3, 7.3, 7.3 Hz, 1H), 1.72 (dddd, J = 13.1, 6.6, 6.6, 6.6 Hz, 1H), 1.59 (m, 2H), 1.47 (ddd, J = 14, 5.8, 5.8 Hz, 1H), 1.39 (ddd, J = 13.5, 11.5, 2.5 Hz, 1H), 1.28 (m, 1H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 141.9, 135.7, 133.9, 130.6, 129.7, 129.2, 127.6, 113.7, 110.3, 74.3, 73.5, 72.5, 69.8, 69.3, 69.2, 66.6, 65.7, 63.5, 55.2, 39.7, 39.4, 39.3, 39.0, 34.3, 33.7, 27.0, 19.2; HRMS calcd for $C_{40}H_{54}O_7Si$ $[M+H]^+$ 675.3719, found 675.3685.



13

Bispyran TES ether (13).
To a soln of **12a** (94.4 mg, 140 μmol) in CH_2Cl_2 (5 mL) was added imidazole (28 mg, 410 μmol). The soln was cooled to -78 °C, chlorotriethylsilane (28 μL, 170 μmol) was added and the mixture was stirred for 30 min. The mixture was diluted with Et_2O (30 mL), washed with water (5 mL) and brine (5 mL), and the combined aqueous phases were extracted with Et_2O (2 X 5 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (6:1 hexanes-ethyl acetate) afforded **13** (91.5 mg, 116 μmol, 83%) as a colorless oil: R_f 0.56 (2:1 hexanes-ethyl acetate); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, J = 8 Hz, 4H), 7.43 (m, 2H), 7.38 (t, J = 8 Hz, 4H), 7.24 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.80 (s, 1H), 4.76 (s, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.27 (m, 1H), 3.90-4.06 (m, 4H), 3.80 (s, 3H), 3.71 (dd, J = 10, 4.5 Hz, 1H), 3.68 (dd, J = 10, 5.5 Hz, 1H), 3.52 (m, 3H), 2.49 (d, J = 5 Hz, 1H), 2.41 (dd, J = 13.5, 4.5 Hz, 1H), 2.34 (dd, J = 13, 4 Hz, 1H), 2.08 (dd, J = 13.5, 5.5 Hz, 1H), 2.04 (dd, J = 13, 7.5 Hz, 1H), 1.86 (m, 2H), 1.73 (m, 2H),

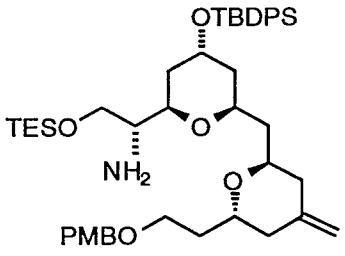
1.55 (m, 2H), 1.39 (ddd, J = 13.5, 11.5, 2.5 Hz, 1H), 1.29 (ddd, J = 13.5, 11.5, 2.5 Hz, 1H), 1.10 (s, 9H), 0.99 (t, J = 8 Hz, 9H), 0.64 (q, J = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 142.2, 135.70, 135.68, 134.2, 134.0, 130.6, 129.6, 129.2, 127.6, 113.7, 110.2, 73.8, 72.6, 71.8, 69.05, 68.97, 68.8, 66.7, 65.9, 62.9, 55.2, 40.0, 39.1, 38.7, 34.5, 34.1, 27.0, 19.3, 6.7, 4.3; HRMS calcd for $C_{46}H_{68}O_7Si_2$ $[M+H]^+$ 789.4584, found 789.4521.



13a

Bispyran azide (13a).
To a soln of **13** (91.3 mg, 116 μmol) in THF (5 mL) was added PPh_3 (152 mg, 580 μmol), diethyl azodicarboxylate (91 μL, 580 μmol), and diphenylphosphoryl azide (120 μL, 557 μmol). The reaction was stirred for 30 min, then concentrated by rotary evaporation, and filtered through a plug of silica gel eluting with 5:1 hexanes-ethyl acetate. The filtrate was concentrated by rotary evaporation and the residue was dissolved in ethyl acetate (40 mL), washed with water (5 mL), and brine (5 mL), and the combined aqueous phases were extracted with ethyl acetate (10 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Flash chromatography (15:1 hexanes-ethyl acetate) afforded **13a** (82.5 mg, 101 μmol, 88%) as a colorless oil: R_f 0.69 (2:1 hexanes-ethyl acetate); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, J = 8 Hz, 4H), 7.44 (m, 2H), 7.39 (t, J = 8 Hz, 4H), 7.25 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.79 (s, 2H), 4.43 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.27 (m, 1H), 4.14 (ddd, J = 11.5, 3.3, 3.3 Hz, 1H), 4.0 (m, 3H), 3.82 (dd, J = 10.5, 4.5 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, J = 10.5, 7.0 Hz, 1H), 3.51 (m, 2H), 3.22 (ddd, J = 6.3, 4.8, 4.8 Hz, 1H), 2.41 (dd, J = 13, 4.5 Hz, 1H), 2.36 (dd, J = 13, 4 Hz, 1H), 2.07 (dd, J = 13, 6 Hz, 1H), 2.03 (dd, J = 13, 6.5 Hz, 1H), 1.91 (m, 1H), 1.79 (ddd, J = 14, 6, 8 Hz, 1H), 1.71 (m, 1H), 1.54 (m, 4H), 1.32 (ddd, J = 13.5, 11.5, 2.5 Hz, 1H), 1.10 (s, 9H), 1.0 (t, J = 8 Hz, 9H), 0.65 (q, J = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 142.1, 135.6, 133.9, 130.6, 129.7, 129.2, 127.6, 113.6, 110.2, 72.6, 71.1, 69.2, 69.1, 68.6, 66.7, 66.6, 65.9, 62.7, 55.2, 39.8, 39.2, 38.8, 38.7, 35.5, 33.6, 27.0, 19.3, 6.7, 4.3.

Supporting Information for
Stereoselective Synthesis of the C3-C17 Bis-Oxane Domain of Phorboxazole A



2

Bispyran amine (2).
To a soln of **13a** (82.3 mg, 101 μmol) in THF (4 mL) was added PPh_3 (53 mg, 200 μmol) and water (18 μL, 1.0 mmol). The soln was heated at reflux for 13 h, cooled to rt, additional water (35 μL, 1.9 mmol) was added and the soln was heated at reflux for an additional 3 h. The soln was cooled to rt and concentrated by rotary evaporation. Flash chromatography on silica gel neutralized with Et_3N (1:1 hexanes-ethyl acetate) afforded **2** (70.3 mg, 89.2 μmol, 88%) as a pale yellow oil: R_f 0.23 (1:2 hexanes-ethyl acetate); $[\alpha]^{23}_D$ = -17.7 (*c* 0.975, $CHCl_3$); IR (neat): 3390, 3080, 2950, 1515, 1245 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.65 (m, 4H), 7.43 (m, 2H), 7.37 (m, 4H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.79 (s, 1H), 4.76 (s, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.25 (m, 1H), 4.06 (m, 1H), 4.0 (m, 1H), 3.92 (m, 2H), 3.79 (s, 3H), 3.60 (dd, *J* = 10, 5 Hz, 1H), 3.52 (m, 2H), 3.47 (dd, *J* = 9.5, 7 Hz, 1H), 2.66 (q, *J* = 5.7 Hz, 1H), 2.41 (dd, *J* = 13, 4.5 Hz, 1H), 2.33 (dd, *J* = 13, 4 Hz, 1H), 2.09 (dd, *J* = 13, 5 Hz, 1H), 2.02 (dd, *J* = 13, 7.5 Hz, 1H), 1.88 (m, 1H), 1.71 (m, 2H), 1.65 (m, 2H), 1.44-1.59 (m, 4H), 1.28 (ddd, *J* = 13.5, 11.5, 2 Hz, 1H), 1.09 (s, 9H), 0.98 (t, *J* = 8 Hz, 9H), 0.62 (q, *J* = 8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 142.2, 135.7, 134.1, 130.6, 129.6, 129.2, 127.6, 113.7, 110.2, 72.6, 72.2, 69.1, 69.0, 68.6, 66.7, 66.1, 64.7, 57.0, 55.2, 40.0, 39.2, 39.1, 38.7, 35.4, 34.1, 27.0, 19.2, 6.8, 4.4; HRMS calcd for $C_{46}H_{69}O_6NSi_2$ $[M+H]^+$ 788.4744, found 788.4777.

STANDARD PROTON PARAMETERS

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np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
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tpwr	58	wtfile	
pw	7.5	proc	ft
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in	n		
dp	y		
hs	yn		
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vs	27		
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wc	210		
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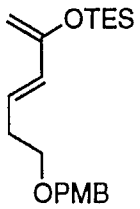
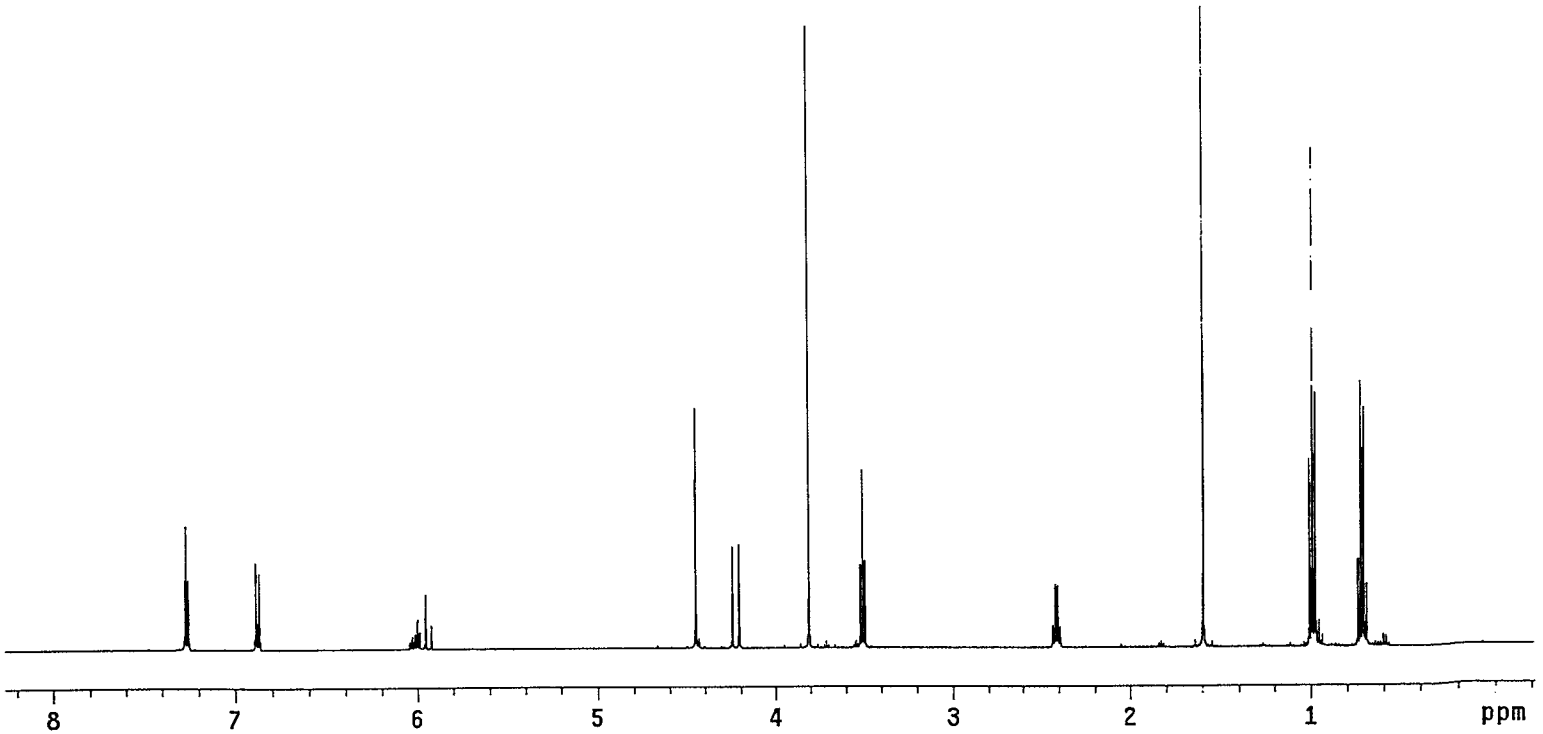
th	7		
ins	100.000		
ai cdc ph			



4



STANDARD PROTON PARAMETERS

exp1 s2pul

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np	40000	dres	1.0
sw	9997.5	homo	n
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tpwr	58	wtfile	
pw	7.5	proc	ft
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tof	1504.1	math	f
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ct	16	werr	
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in	n		
dp	y		
hs	yn		
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sc	0		
wc	210		
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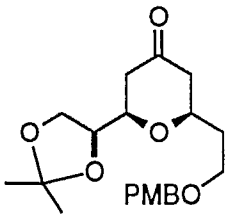
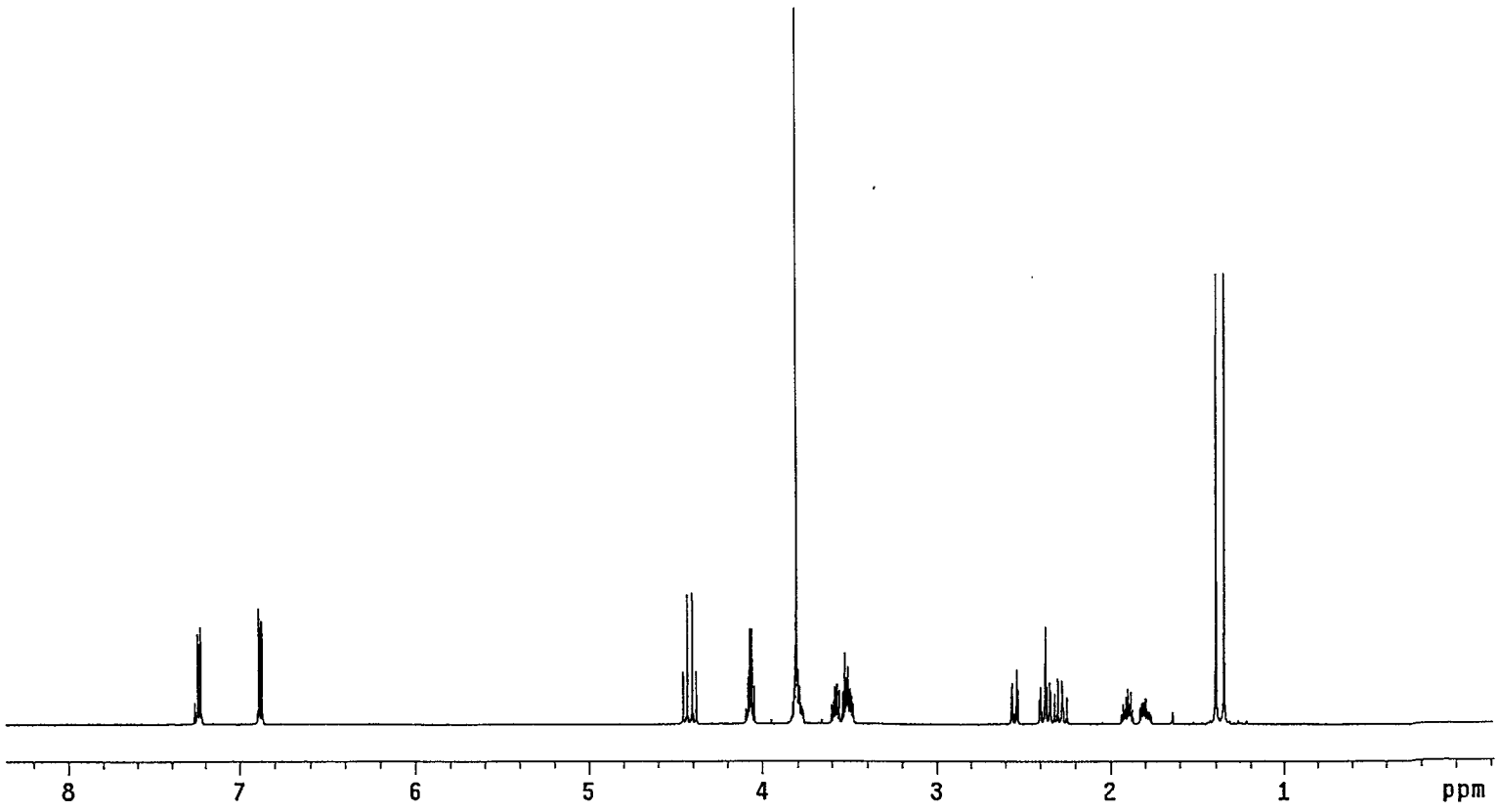
th	7		
ins	100.000		
ai cdc ph			



6



RC-III-18

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np	24000	dres	undefined
sw	5997.9	homo	n
fb	3400	PROCESSING	
bs	16	lb	0.10
tpwr	63	wtfile	
pw	9.5	proc	ft
d1	1.500	fn	131072
tof	1322.9	math	f
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gain	not used		de','h1','c13 glid~
FLAGS			e_c13_acq','dept g~
il	n		lide_dept_acq')
in	n	wbs	
dp	y	wnt	
hs	yn		
DISPLAY			
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vs	60		
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rfl	2771.0		
rfp	2171.2		
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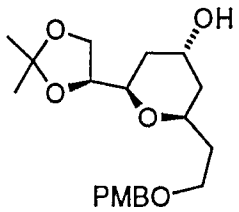
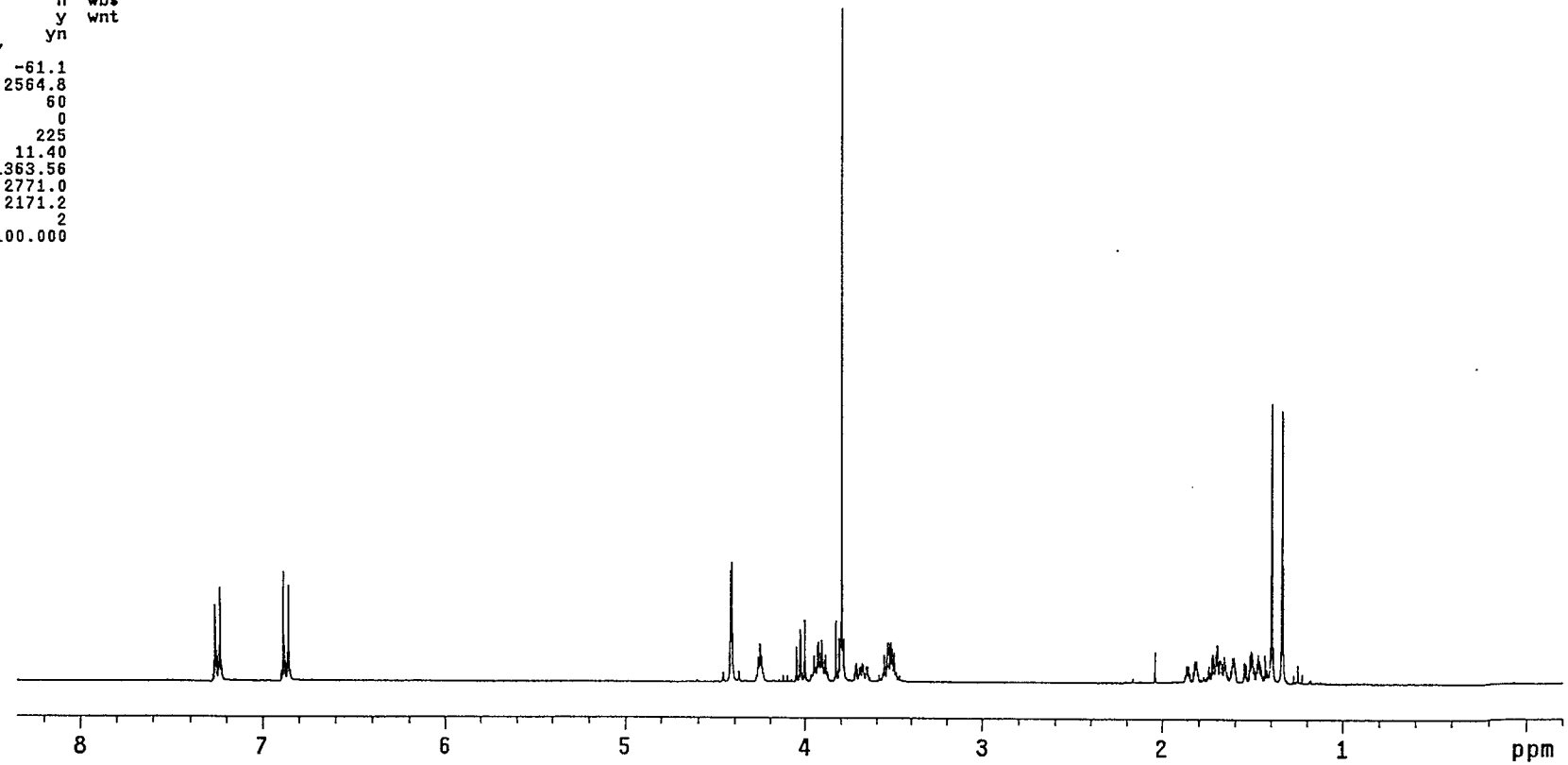
ins	100.000		
ai cdc ph			



6a



RC-III-21

exp1 std1h

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np	24000	dres	undefined
sw	5997.9	homo	n
fb	3400	PROCESSING	
bs	16	lb	0.10
tpwr	63	wtfile	
pw	9.5	proc	ft
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in	n		
dp	y		
hs	yn		
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vs	76		
sc	0		
wc	225		
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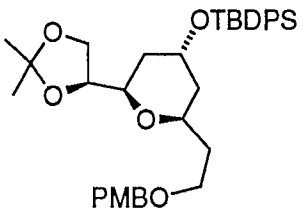
rfp	2171.2		
th	2		
ins	100.000		

ai cdc ph



6b

RC-II-229

exp1 std1h

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sfrq	299.891	dmm	c
tn	H1	dmf	200
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np	24000	dres	undefined
sw	5997.9	homo	n
fb	3400	PROCESSING	
bs	16	lb	0.10
tpwr	63	wtfile	
pw	9.5	proc	ft
d1	1.500	fn	131072
tof	1322.9	math	f
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hs	yn		
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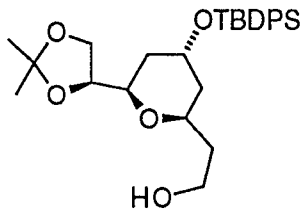
ai cdc ph			



6c

RC-II-251

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np	24000	dres	undefined
sw	5997.9	homo	n
fb	3400	PROCESSING	
bs	16	lb	0.10
tpwr	63	wtfile	
pw	9.5	proc	ft
d1	1.500	fn	131072
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nt	16		
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in	n		
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hs	yn		
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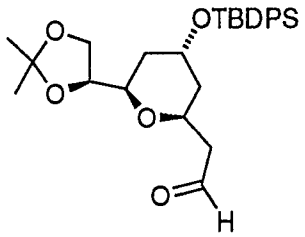
ai cdc ph			



7

STANDARD 1H OBSERVE

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pw	12.2	proc	ft
d1	1.500	fn	65536
tof	1317.4	math	f
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ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
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vs	95		
sc	0		
wc	210		
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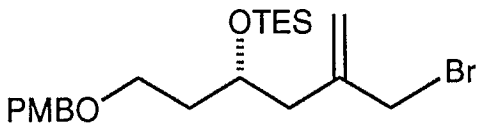
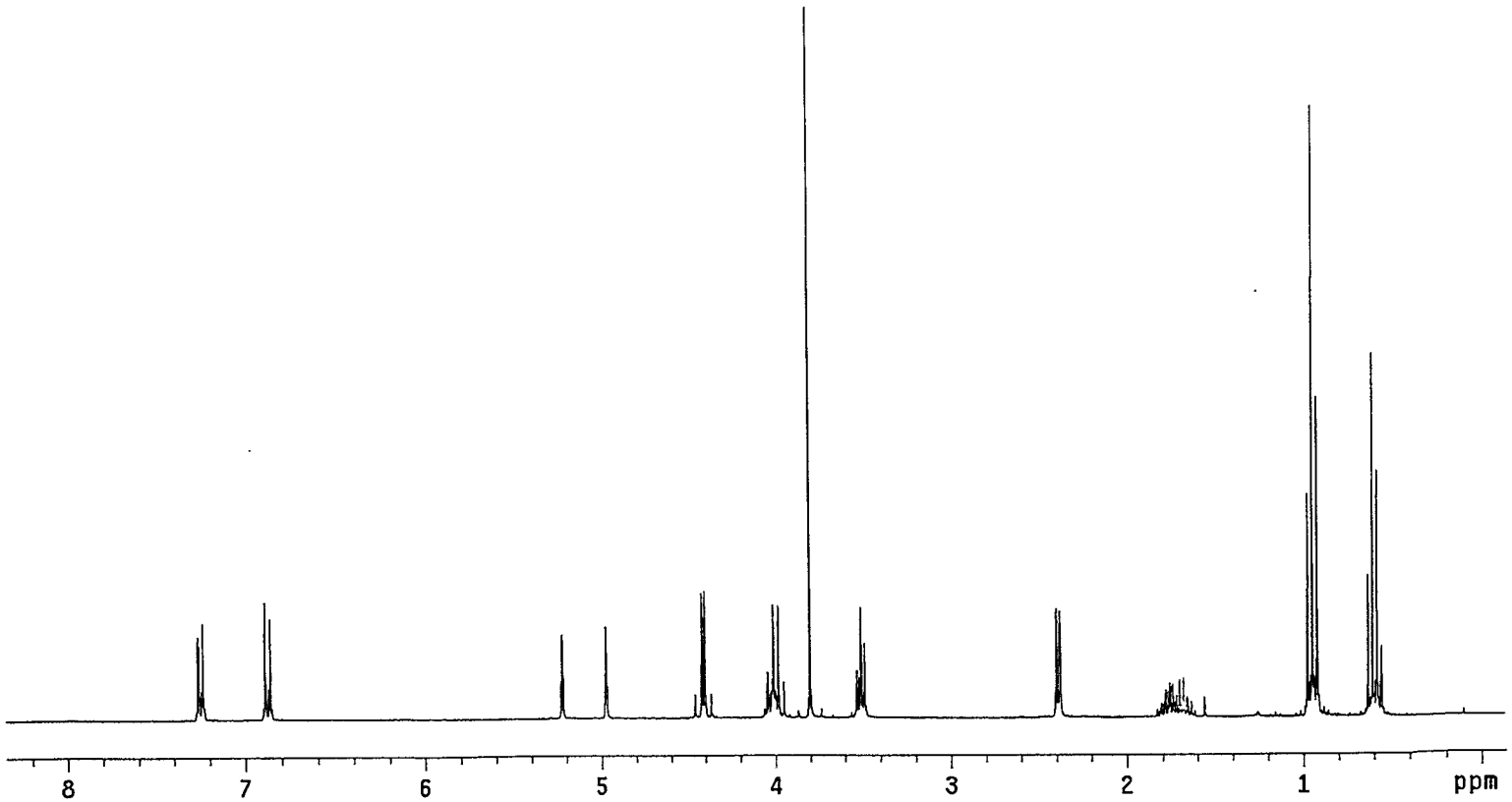
th	20		
ins	100.000		
nm cdc ph			



8



STANDARD 1H OBSERVE

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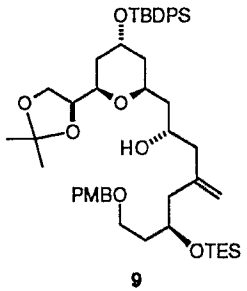
file	/data/cfordc/~	dpwr	30
	rciii168_1h	dof	0
ACQUISITION		dm	nnn
sfrq	300.171	dmm	c
tn	H1	dmf	200
at	1.999	dseq	
np	24000	dres	1.0
sw	6003.3	homo	n
fb	3000	PROCESSING	
bs	16	lb	0.10
tpwr	55	wtfile	
pw	17.0	proc	ft
d1	1.500	fn	131072
tof	900.5	math	f
nt	16		
ct	16	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-79.6		
wp	2618.2		
vs	164		
sc	0		
wc	210		
hzmm	12.47		
is	500.00		
rfl	2773.5		
rfp	2173.2		
th	20		
ins	100.000		
nm cdc ph			

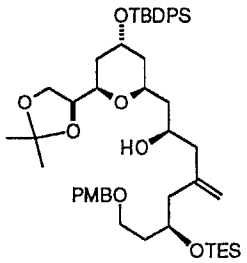


9

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 9 97	dfrq	300.170
solvent	CDCl3	dn	H1
file	/data/cfordc/~	dpwr	30
	rc111168_2h	dof	0
ACQUISITION		dm	nnn
sfrq	300.171	dmm	c
tn	H1	dmf	200
at	1.999	dseq	
np	24000	dres	1.0
sw	6003.3	homo	n
fb	3000	PROCESSING	
bs	16	lb	0.10
tpwr	55	wtfile	
pw	17.0	proc	ft
d1	1.500	fn	131072
tof	900.5	math	f
nt	16		
ct	16	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-50.7		
wp	2574.8		
vs	137		
sc	0		
wc	210		
hzmm	12.26		
is	500.00		
rfl	2773.5		
rfp	2173.2		
th	20		
ins	100.000		
nm cdc ph			



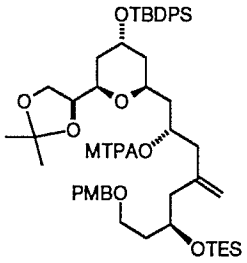
10

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 7 97	dfrq	300.170
solvent	CDCl3	dn	H1
file	/data/cfordc/~rciii173	dpwr	30
ACQUISITION		dof	0
sfrq	300.171	dm	nnn
tn	H1	dmm	c
at	1.999	dmf	200
np	24000	dseq	
sw	6003.3	dres	1.0
fb	3000	homo	n
bs	16	**PROCESSING**	
tpwr	55	lb	0.10
pw	17.0	wtfile	
d1	1.500	proc	ft
tof	900.5	fn	131072
nt	16	math	f
ct	16	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-79.6		
wp	2574.8		
vs	163		
sc	0		
wc	210		
hzmm	12.26		
is	500.00		
rfl	2773.5		
rfp	2173.2		
th	20		
ins	100.000		

nm cdc ph

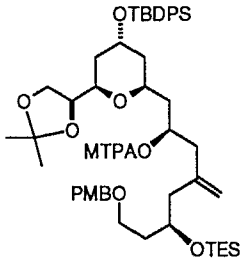


(R)-MTPA-9

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 7 97	dfrq	300.170
solvent	CDCl3	dn	H1
file	/data/cfordc/~ rciii172	dpwr	30
		dof	0
ACQUISITION		dm	nnn
sfrq	300.171	dmm	c
tn	H1	dmf	200
at	1.999	dseq	
np	24000	dres	1.0
sw	6003.3	homo	n
fb	3000	PROCESSING	
bs	16	lb	0.10
tpwr	55	wtfile	
pw	17.0	proc	ft
d1	1.500	fn	131072
tof	900.5	math	f
nt	32		
ct	32	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-79.6		
wp	2589.3		
vs	160		
sc	0		
wc	210		
hzmm	12.33		
is	500.00		
rfl	2773.5		
rfp	2173.2		
th	20		
ins	100.000		
nm cdc ph			

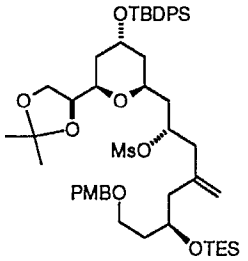


(R)-MTPA-10

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 18 97	dfrq	300.170
solvent	Benzene	dn	H1
file	/data/cfordc/~ rciii183_h	dpwr	30
		dof	0
ACQUISITION		dm	nnn
sfrq	300.171	dmm	c
tn	H1	dmf	200
at	1.999	dseq	
np	24000	dres	1.0
sw	6003.3	homo	n
fb	3000	PROCESSING	
bs	16	lb	0.10
tpwr	55	wtfile	
pw	17.0	proc	ft
d1	1.500	fn	131072
tof	900.5	math	f
nt	32		
ct	32	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-67.2		
wp	2576.7		
vs	164		
sc	0		
wc	210		
hzmm	12.27		
is	500.00		
rfl	2746.5		
rfp	2146.2		
th	20		
ins	100.000		
nm cdc ph			



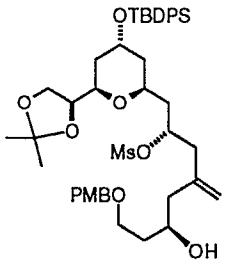
11

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Apr 21 97	dfrq	300.170
solvent	Benzene	dn	H1
file	/data/cfordc/~rc111185_h	dpwr	30
		dof	0
ACQUISITION		dm	nnn
sfrq	300.171	dmm	c
tn	H1	dmf	200
at	1.999	dseq	
np	24000	dres	1.0
sw	6003.3	homo	n
fb	3000	PROCESSING	
bs	16	lb	0.10
tpwr	55	wtfile	
pw	17.0	proc	ft
d1	1.500	fn	131072
tof	900.5	math	f
nt	32		
ct	32	werr	
alock	s	wexp	wft
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-79.6		
wp	2589.3		
vs	162		
sc	0		
wc	210		
hzmm	12.33		
is	500.00		
rfl	2746.5		
rfp	2146.2		
th	20		
ins	100.000		

nm cdc ph

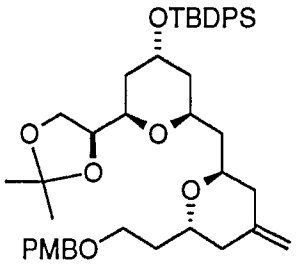


11a

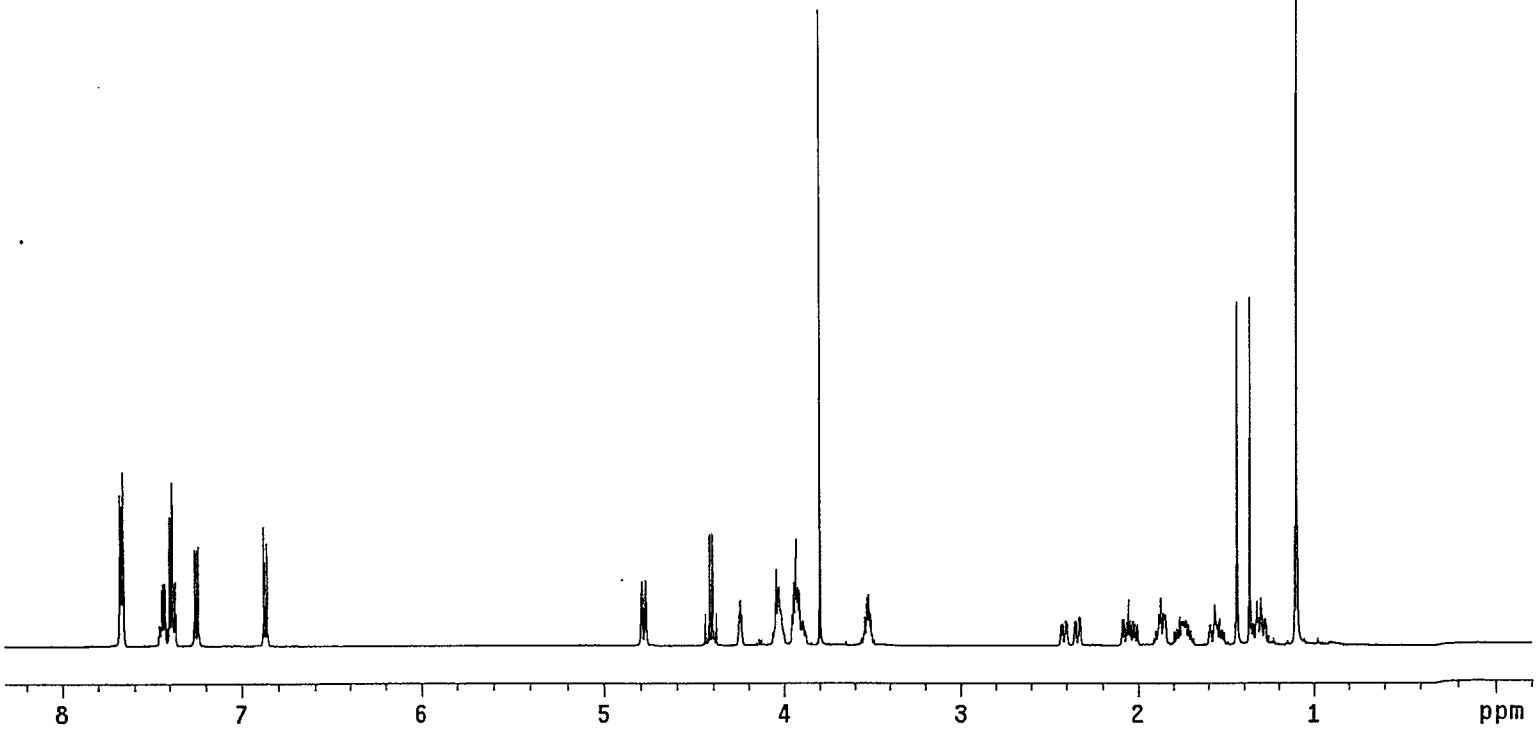
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 23 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~	dpwr	15
	rciii187_h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	-104.1		
wp	4264.0		
vs	41		
sc	0		
wc	210		
hzmm	20.30		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			



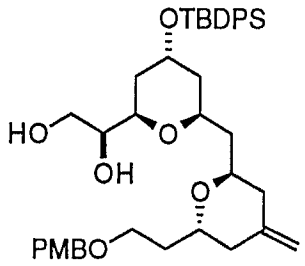
12



STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 25 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~ rciii189_h	dpwr	15
		dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	0	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	-80.0		
wp	4264.0		
vs	39		
sc	0		
wc	210		
hzmm	20.30		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			

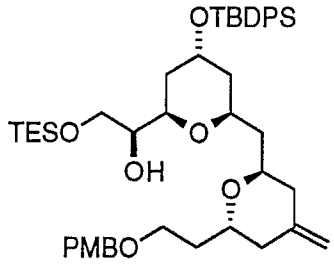


12a

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 28 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~	dpwr	15
	rciii191_h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	-104.1		
wp	4287.9		
vs	39		
sc	0		
wc	210		
hzmm	20.42		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			

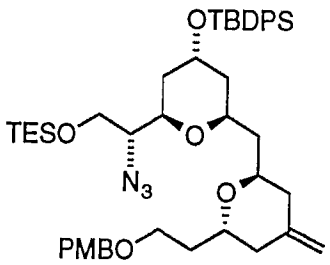


13

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 29 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~	dpwr	15
	rciii193_h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	-80.0		
wp	4239.9		
vs	59		
sc	0		
wc	210		
hzmm	20.19		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			

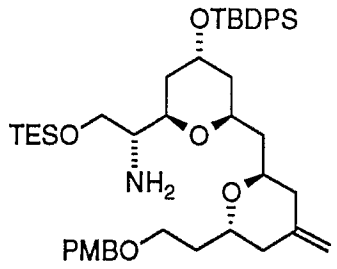


13a

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~ rciii194_h	dpwr	15
		dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	-176.2		
wp	4336.1		
vs	51		
sc	0		
wc	210		
hzmm	20.65		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			



2