Highly Diastereoselective Synthesis of Propargylic 1,2-*anti*-Diol Derivatives Using α-Alkoxypropargylstannanes

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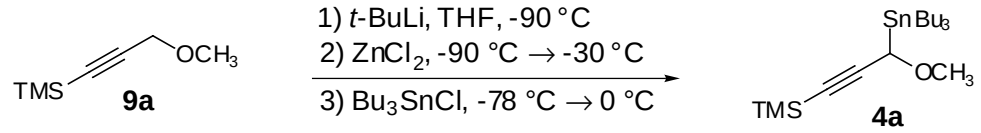
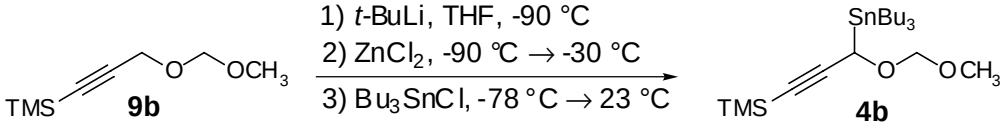
SUPPORTING INFORMATION

Experimental procedures for synthesis of α-alkoxypropargylstannanes **4a** and **4b**; representative procedure for the additions of **4a,b** to aldehydes; tabulated spectroscopic data for *anti*-diol derivatives **2a-e**, **10a-e**, **16** and **17**; and stereochemical assignments for **2a,b** and **3a** (11 pages). This material is available free of charge via the Internet at http://pubs.acs.org.



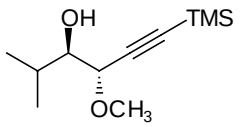
[3-Methoxy-3-(tributylstannyl)-1-propynyl]trimethylsilane (**4a**): A solution of (3-methoxy-1-propynyl)trimethylsilane (6.5 g, 46 mmol) in THF cooled to –90 °C was treated dropwise with *t*-BuLi (1.5 M in pentane, 32 mL, 48 mmol), maintaining the internal temperature below –88 °C. The resulting orange suspension was stirred at –90 °C for 1 h then warmed to –78 °C and treated with a solution of $ZnCl_2$ (6.8 g, 50 mmol) in 30 mL of THF. The yellow suspension was warmed to –30 °C over 90 min, recooled to –78 °C and treated with Bu_3SnCl (13.6 mL, 50 mmol). The solution was warmed to 0 °C over 1 h and quenched by the addition of NH_4Cl (40 mL), diluted with Et_2O (200 mL), and the layers separated. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 22.0 g of crude 4a which was purified on basic alumina (170 g, with a gradient of 0% to 5% Et_2O-hexanes) to provide 16.5 g (84% yield) of **4a** as a pale yellow oil which was used in the subsequent experiments. α-Alkoxypropargylstannane **4a** could be further purified by bulb-to-bulb vacuum distillation (0.5 mm Hg, 140 °C): ^1H NMR ($CDCl_3$, 400 MHz) δ 4.19 (s, 1H), 3.36 (s, 3 H), 1.60-0.80 (m, 27 H) 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 106.9, 94.1, 64.6, 59.2, 29.0, 28.9, 27.3, 13.6, 9.90, 0.16; IR (neat) 2958, 2928, 2872, 2853, 2147, 1720(w), 1463, 1249, 1072, 842 cm^{-1}; HRMS (EI) for $C_{15}H_{31}OSiSn$ $[M - C_4H_9]^+$ calcd. 375.1166, found 375.1172.



[3-(Methoxymethoxy)-3-(tributylstannyl)-1-propynyl] trimethylsilane (**4b**): A solution of (3-(methoxymethoxy)-1-propynyl)trimethylsilane (2.74 g 15.9 mmol) in THF cooled to –90 °C was treated dropwise with *t*-BuLi (1.4 M in pentane, 11.9 mL, 16.7 mmol), maintaining the

internal temperature below –80 °C. The resulting orange suspension was stirred at –90 °C for 30 min then warmed to –78 °C and treated with a solution of $ZnCl_2$ (2.38 g, 17.4 mmol) in 17 mL of THF. The yellow suspension was warmed to –30 °C over 45 min, recooled to –78 °C and treated with Bu_3SnCl (4.74 mL, 17.4 mmol). The solution warmed to 0 °C over 1 h and was quenched by the addition of a saturated NH_4Cl solution (40 mL), diluted with Et_2O (200 ML), and the layers separated. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield 22.0 g of crude **4b**, which was purified on silica gel (60 g, that was made basic by washing with 3% Et_3N in hexanes) using 1.5% EtOAc in hexanes as eluent to provide 6.01 g (82% yield) of **4b** as a clear oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88 (d, J = 6.2 Hz, 1H), 4.54 (s, 1H), 4.52 (d, J = 6.2 Hz, 1H), 3.33 (s, 3 H), 1.70 – 0.80 (m, 27 H), 0.14 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 106.6, 95.4, 93.1, 57.7, 55.5, 28.9, 27.3, 13.7, 9.9, 0.1; IR (neat) 2958, 2929, 2150 (s), 1464, 1249, 1017, 924, 842, 759 cm^{-1}; HRMS (EI) for $C_{16}H_{33}OSiSn$ $[M - C_4H_9]^+$ calcd. 405.1271, found 405.1269.

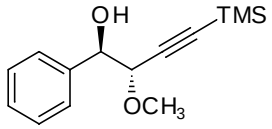
Representative Procedure for the Addition of α-Alkoxypropargyl Stannanes to Lewis Acid Complexed Aldehydes. A -78 °C solution of **4a** (307 mg, 0.71 mmol) and isobutyraldehyde (40 mg, 0.56 mmol) in CH_2Cl_2 was treated dropwise with a solution of $BuSnCl_3$ (0.71 mL, 1.06M in CH_2Cl_2). This mixture was allowed to warm to 0 °C over 1 h. The reaction was quenched by the addition of 0.1 N HCl (1 mL) and diluted with Et_2O (10 mL). The Et_2O layer was separated and treated with KF/Celite® (700 mg/ mmol of **4a**). The solution stirred vigorously for at least 2 h and then filtered through Celite®. The resulting oil was purified on silica gel (6.0 g) to give 115 mg (96% yield) of a 97 : 3 mixture of **2a** and **3a**.



2a

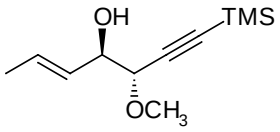
***anti*-3-Methoxy-5-methyl-1-trimethylsilyl-hex-1-yn-4-ol (2a):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.01 (dd, *J* = 4.4, 0.7 Hz, 1H), 3.43 (s, 3 H), 3.39 (ddd, *J* = 7.3, 4.4, 4.0 Hz, 1H),

2.20 (dd, *J* = 4.4, 1.1 Hz, 1H), 1.94-1.82 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 3 H), 0.92 (d, *J* = 6.9 Hz, 3 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 100.8, 93.2, 77.4, 74.2, 56.7, 30.3, 19.0, 18.1, –0.14; IR (neat) 3496(br), 2961, 2876, 2874, 2170, 1466, 1251, 1103, 1074, 878, 844, 760 cm^{-1}; HRMS (CI, NH_3) for $C_{11}H_{22}O_2Si$ $[M+NH_4]^+$ calcd. 232.1732, found 232.1724. *Anal.* Calcd. for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C 61.71; H 10.51.



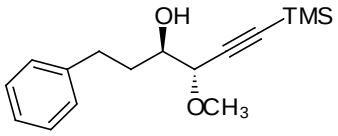
2b

***anti*-2-Methoxy-1-phenyl-4-trimethylsilyl-but-3-yn-1-ol (2b):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.42 (m, 2 H), 7.41-7.28 (m, 3 H), 4.84 (t, *J* = 4.4 Hz ,1H), 4.12 (d, *J* = 4.4 Hz, 1H), 3.44 (s, 3 H), 2.76 (d, *J* = 4.0 Hz, 1H), 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.1, 127.9, 126.9, 100.3, 94.1, 76.9, 74.9, 57.1, -0.30; IR (neat) 3467(br), 3032, 2959, 2899, 2173, 1605, 1453, 1343, 1250, 1189, 1106, 1089, 1027, 884, 844, 760, 737, 699 cm^{-1}; HRMS (CI, NH_3) for $C_{12}H_{24}O_3Si$ $[M+NH_4]^+$ calcd. 266.1576, found 266.1567. *Anal.* Calcd. for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C 67.34; H 8.21.



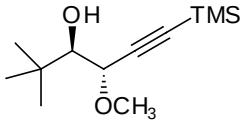
2c

***anti*-3-Methoxy-1-trimethylsilyl-hept-5-en-1-yn-4-ol (2c):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.80 (dq, *J* = 15.4, 6.6 Hz, 1H), 5.66 (ddd, *J* = 15.4, 6.6, 1.5 Hz, 1H), 4.17 (app. dd, *J* = 5.9, 4.4 Hz, 1H), 3.96 (d, *J* = 4.0 Hz, 1H), 3.44 (s, 3 H), 2.27 (d, *J* = 5.9 Hz ,1H), 1.73 (ddd, *J* = 6.6, 0.7, 0.7 Hz, 3 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 129.7, 128.7, 101.0, 93.6, 75.9, 74.0, 57.2, 18.1, 0.05; IR (neat) 3449(br), 2961, 2900, 2824, 2172, 1675, 1450, 1251, 1110, 1086, 1023, 965, 844, 760, 699 cm^{-1}; HRMS (CI, NH_3) for $C_{11}H_{20}O_2Si$ $[M+NH_4]^+$ calcd. 230.1576, found 230.1586. *Anal.* Calcd. for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C 62.10; H 9.46.



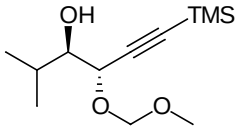
2d

***anti*-3-Methoxy-6-phenyl-1-trimethylsilyl-hex-1-yn-4-ol (2d):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.21 (m, 5 H), 3.96 (d, *J* = 4.0 Hz, 1H), 3.73 (ddd, *J* = 13.2, 5.9, 3.7 Hz, 1H), 2.91 (ddd, *J* = 13.7, 9.5, 5.5 Hz, 1H), 2.74 (ddd, *J* = 13.9, 9.2, 7.3 Hz, 1H), 2.19 (d, *J* = 5.9 Hz, 1H), 2.00-1.86 (m, 2 H), 0.22 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.9, 128.5, 128.3, 125.8, 100.8, 93.4, 75.7, 72.0, 56.9, 34.0, 31.8, -0.14; IR (neat) 3467(br), 3027, 2957, 2170, 1604, 1496, 1454, 1251, 1117, 1088, 1031, 844, 760, 699 cm^{-1}; HRMS (CI, NH_3) for $C_{16}H_{24}O_2Si$ $[M+NH_4]^+$ calcd. 294.1889, found 294.1884; *Anal.* Calcd. for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C 69.60; H 8.87.



2e

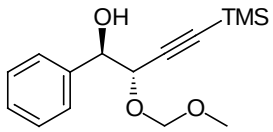
***anti*-5,5-Dimethyl-3-methoxy-1-trimethylsilyl-hex-1-yn-4-ol (2e):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.07 (d, *J* = 3.3 Hz, 1H), 3.41 (s, 3 H), 3.39 (dd, *J* = 5.5, 3.3 Hz, 1H), 2.21 (d, *J* = 5.5 Hz, 1H), 0.99 (s, 9 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 101.2, 94.9, 79.9, 73.6, 56.3, 34.2, 26.4, -0.28; IR (neat) 3498(br), 2958, 2904, 2823, 2172, 1481, 1467, 1363, 1251, 1113, 1087, 1016, 974, 911, 844, 760, 614 cm^{-1}; HRMS (CI, NH_3) for $C_{12}H_{24}O_2Si$ $[M+NH_4]^+$ calcd. 246.1889, found 246.1878.



10a

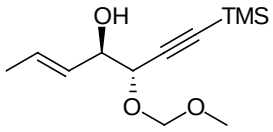
***anti*-3-Methoxymethoxy-5-methyl-1-trimethylsilyl-hex-1-yn-4-ol (10a):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.94 (d, *J* = 6.9 Hz, 1H), 4.62 (d, *J* = 6.6 Hz, 1H), 4.41 (d, *J* = 4.4 Hz, 1H), 3.38 (dd, *J* = 4.4, 4.4 Hz, 1H) 3.36 (s, 3 H), 2.30 (d, *J* = 4.0 Hz, 1H), 1.88 (hept, *J* =

7.0 Hz, 1H), 1.00 (d, *J* = 7.0 Hz, 3 H), 0.92 (d, *J* = 7.0 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 100.5, 94.0, 93.0, 77.6, 68.8, 55.8, 30.3, 19.0, 18.0. –0.21; IR (neat) 3496(br), 2960, 2899, 2171, 1472, 1251, 1155, 1099, 1031, 844, 761 cm^{-1}; HRMS (CI, NH_3) for $C_{12}H_{22}O_3Si$ $[M+NH_4]^+$ calcd. 262.1838, found 262.1847.



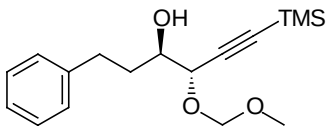
10b

***anti*-2-Methoxymethoxy-1-phenyl-4-trimethylsilyl-but-3-yn-1-ol (10b):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (dd, *J* = 3.6, 1.8 Hz, 1H), 7.21-7.40 (m, 3 H), 4.89 (d, *J* = 6.6 Hz, 1H), 4.82 (app t, *J* = 4.4 Hz, 1H), 4.60 (d, *J* = 6.9 Hz, 1H), 4.48 (d, *J* = 5.1 Hz, 1H), 3.20 (s, 3 H), 2.88 (d, *J* = 3.7 Hz ,1H), 0.16 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.2, 128.0, 126.9, 100.3, 94.2, 93.8, 75.2, 71.8, 55.6, -0.30; IR (neat) 3459(br), 3064, 3033, 2958, 2896, 2175, 1604(w), 1454, 1250, 1151, 1100, 1032, 845, 761, 699 cm^{-1}; HRMS (CI, NH_3) for $C_{12}H_{24}O_3Si$ $[M+NH_4]^+$ calcd. 296.1682, found 296.1681.



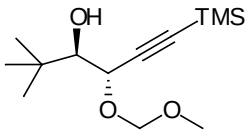
10c

***anti*-3-Methoxymethoxy-1-trimethylsilyl-hept-5-en-1-yn-4-ol (10c):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.81 (ddq, *J* = 15.4, 6.6, 1.1 Hz, 1H), 5.58 (dddd, *J* = 15.4, 6.6, 3.3, 1.8 Hz, 1H), 4.90 (d, *J* = 6.6 Hz, 1H), 4.65 (d, *J* = 7.0 Hz, 1H), 4.32 (d, *J* = 4.0 Hz, 1H), 4.17 (m, 1H), 3.37 (s, 3 H), 2.51 (d, *J* = 6.3 Hz, 1H), 1.73 (ddd, *J* = 6.0, 1.5, 0.7, 3 H), 0.18 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 129.4, 128.6, 100.5, 94.5, 93.1, 73.9, 70.9, 55.8, 17.8, -0.25; IR (neat) 3449(br), 2960, 2896, 2174, 1676(w), 1450, 1251, 1153, 1102, 1031, 844, 760 cm^{-1}; HRMS (CI, NH_3) for $C_{15}H_{22}O_3Si$ $[M+NH_4]^+$ calcd. 260.1682, found 260.1674.



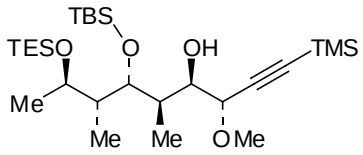
10d

***anti*-3-Methoxymethoxy-6-phenyl-1-trimethylsilyl-hex-1-yn-4-ol (10d):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.15 (m, 5 H), 4.95 (d, *J* = 6.6 Hz, 1 H), 4.66 (d, *J* = 6.9 Hz, 1 H), 4.34 (d, *J* = 4.0 Hz, 1 H), 3.74 (ddd, *J* = 12.8, 5.9 4.0 Hz ,1 H), 3.39 (s 1 H), 2.90 (ddd, *J* = 13.9, 9.5, 5.1 Hz, 1 H), 2.73 (ddd, *J* = 13.9, 9.2, 7.4 Hz, 1 H), 2.40 (d, *J* = 5.9 Hz, 1 H), 2.04-1.85 (m, 2 H), 0.19 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.8, 128.4, 128.3, 125.8, 100.5, 94.3, 93.2, 72.1, 70.7, 55.8, 34.0, 31.7, -0.23; IR (neat) 3467(br), 3027, 2956, 2896, 2173, 1603(w), 1496, 1454, 1251, 1151, 1101, 1030, 845, 760, 699 cm^{-1}; HRMS (CI, NH_3) for $C_{17}H_{26}O_3Si$ $[M+NH_4]^+$ calcd. 324.1994, found 324.1996.



10e

***anti*-5,5-Dimethyl-3-methoxymethoxy-1-trimethylsilyl-hex-1-yn-4-ol (10e):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.95 (d, *J* = 6.9 Hz, 1 H), 4.56 (d, *J* = 6.9 Hz, 1 H), 4.50 (d, *J* = 2.6 Hz, 1 H), 3.40 (dd, *J* = 5.9, 2.6 Hz, 1 H), 3.37 (s, 3 H), 2.34 (d, *J* = 5.9 Hz, 1 H), 0.99 (s, 9 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 100.8, 94.9, 93.7, 80.3, 67.9, 55.8, 34.2, 26.4, -0.36; IR (neat) 3504(br), 2958, 2958, 2174, 1480, 1364, 1251, 1152, 1097, 1033, 844, 761 cm^{-1}; HRMS (CI, NH_3) for $C_{13}H_{26}O_3Si$ $[M+NH_4]^+$ calcd. 276.1995, found 276.2002.



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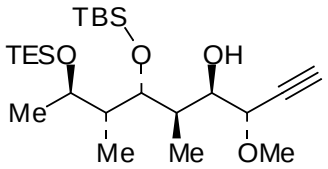
[3*S*,4*R*,5*R*,6*S*,7*R*,8*R*]-6-[(*tert*-Butyldimethylsilyl)oxy]-4-hydroxy-5,7-dimethyl-3-methoxy-8-[(triethylsilyl)oxy]-1-trimethylsilylnon-1-yne (16): $[\alpha]^{26}_D$

+16.3° (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.97 (d, J = 6.8 Hz, 1 H), 3.93 (overlapping ddd, J=10.3, 2.7 Hz, 1 H), 3.90 (dd, *J* = 3.7, 3.7 Hz, 1 H), 3.68 (dq, *J* = 6.1, 7.6 Hz, 1 H), 3.41 (s, 3 H), 3.21 (d, *J* = 2.4 Hz, 1 H), 1.97 (m, 1 H), 1.73 (m, 1 H), 1.08 (d, *J* = 6.1 Hz, 3 H), 1.00 (d, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 8.1 Hz, 9 H), 0.90 (s, 9 H), 0.86 (d, *J* = 7.1 Hz, 3 H), 0.62 (q, *J* = 8.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 102.7, 91.9, 76.4, 73.3, 73.2, 71.0, 56.5, 43.9, 39.2, 26.1, 20.7, 18.3, 11.8, 10.8, 7.0, 5.3, 0.0, -3.7, -3.9; IR (neat) 3483(br), 2957, 2880, 2248(w), 2172, 1463, 1384, 1251, 1104, 1074, 1018, 843, 773, 735 cm^{-1}; HRMS (CI, NH_3) for $C_{27}H_{58}O_4Si3$ $[M+H]^+$ calcd. 531.3721, found 531.3714.

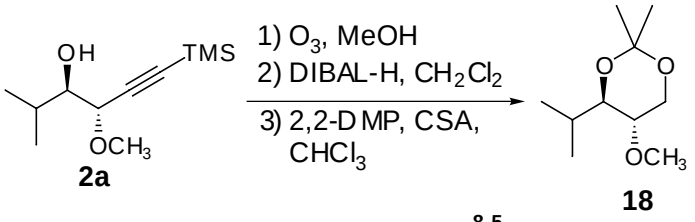


17

[3*S*,4*R*,5*R*,6*S*,7*R*,8*R*]-6-[(*tert*-Butyldimethylsilyl)oxy]-4-hydroxy-5,7-dimethyl-3-methoxy-8-[(triethylsilyl)oxy]non-1-yne (17): $[\alpha]^{26}_D$ +14.6° (*c* 0.95, CH_2Cl_2); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.04 (ddd, J = 7.7, 1.3, 1.3 Hz, 1 H), 3.93 (dd, J=7.7, 1.7 Hz, 1 H), 3.87 (dd, *J* = 4.4, 2.7 Hz, 1 H), 3.70 (dq, *J* = 13.1, 6.0 Hz, 1 H), 3.61 (s, 1 H), 3.42 (s, 3 H), 2.49 (d, *J* = 2.0 Hz, 1 H), 1.95 (m, 1 H), 1.76 (m, 1 H), 1.06 (d, *J* = 6.4 Hz, 3 H), 1.00 (d, *J* = 7.1 Hz, 3 H), 0.95 (m, 9 H), 0.90 (s, 9 H), 0.88 (d, *J* = 7.4 Hz, 3 H), 0.60 (m, 6 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 81.3, 78.0, 74.6, 73.1, 72.4, 70.6, 56.6, 44.3, 38.3, 26.1, 20.4, 18.3, 11.7, 11.2, 6.9, 5.3, -3.8; IR (thin film) 3488(br), 3311, 2937, 2956, 2879, 2858, 2825, 2114, 1463, 1383, 1252, 1103, 1076, 1004, 978, 836, 773, 742 cm^{-1}; HRMS (CI, NH_3) for $C_{24}H_{51}O_4Si2$ $[M+H]^+$ calcd. 459.3326, found 459.3314.

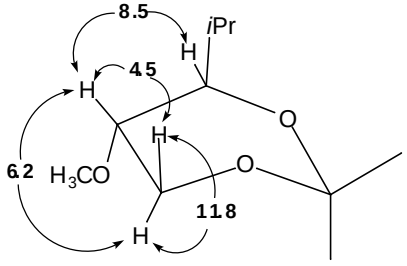
Representative Procedure for the Structure Determination of 2a,b and 3a. A solution of **2b** (150 mg, 0.6 mmol) in MeOH was cooled to 0° C and ozone was bubbled into the solution through a fritted dispersion tube until the solution turned blue (5 min). The mixture was then

purged with nitrogen. The resulting solution was treated with $BF{\bullet}Et_2O$ (0.05 ml) and stirred at 23 ℃ for 14 h. The reaction was diluted with ether, washed with saturated $NaHCO_3$, dried, and concentrated. The crude mixture was purified on 5g silica gel (20-30% EtOAc/Hex) to give 90 mg of the methyl ester. The methyl ester (90 mg, 0.43 mmol) was dissolved in CH_2Cl_2 (5 ml) cooled to –78 °C and treated with DIBAL-H (1.28 ml of 1.0 M solution in hexanes) then slowly warmed to –20 C over one hour. The reaction was quenched by the addition of a saturated Rochelle's salt solution, stirred for 2 h and extracted with ether. The crude diol was dissolved in $CHCl_3$ and treated with 2,2-dimethoxypropane (0.15 ml) followed by camphorsulfonic acid (0.5 mg) and stirred for 12 h. The reaction was quenched by the addition of saturated $NaHCO_3$ and extracted with $CHCl_3$. The crude acetonide was purified on 3g of silica gel (10% EtOAc/Hex) to yield 58 mg of pure **19** (45% from **2b**).

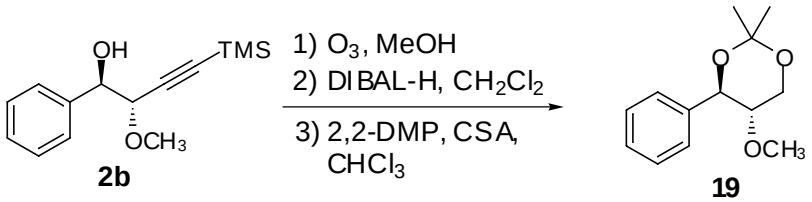


coupling constants (Hz)

18



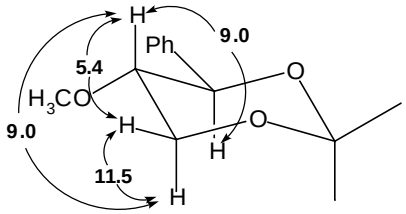
***trans*-2,2-Dimethyl-4-isopropyl-5-methoxy-[1,3]dioxane (18)** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.89 (A of ABX J_{AB} = 11.7 Hz, J_{AX} = 4.5 Hz, 1H), 3.63 (B of ABX, J_{AB} = 11.7 Hz, J_{BX} = 6.2 Hz, 1H), 3.38 (dd, J = 8.5, 4.2 Hz, 1H), 3.34 (s, 3H), 3.21 (ddd, J = 8.7, 6.3, 4.4 Hz, 1H), 1.89 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 0.95 (d, J = 7.1 Hz, 3H), 0.92 (d, J = 7.1 HZ, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 99.0, 76.1, 75.9, 61.8, 56.8, 29.4, 27.2, 20.6, 18.8, 16.7.



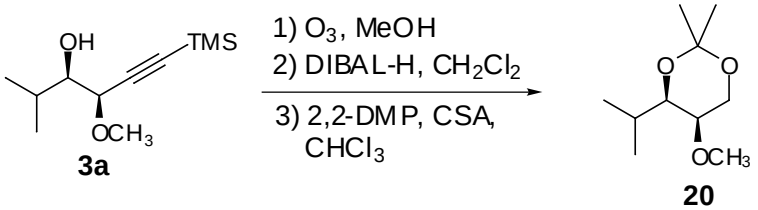
2b **19**

coupling constants (Hz)

19



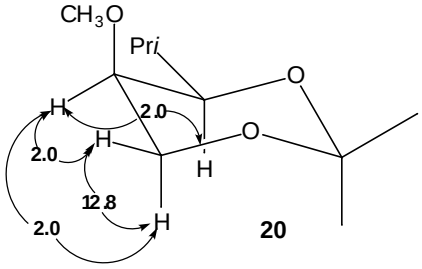
***trans*-4-Benzyl-2,2-dimethyl-5-methoxy-[1,3]dioxane (19)** ^{1}H NMR (CDCl3, 500 MHz) δ 7.47-7.29 (m, 5H) 4.60 (A of ABX J_{AB} = 11.5 Hz, J_{AX} = 5.4 Hz, 1H), 4.06 (B of ABX, J_{AB} = 11.5 Hz, J_{BX} = 9.0 Hz, 1H), 3.77 (ddd, J = 9.0, 9.0, 5.4, 1H), 3.08, (s, 3H), 1.57 (s, 3H), 1.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.8, 128.3, 128.0, 127.2, 99.1, 76.7, 75.4, 62.7, 58.1, 28.5, 19.4.



3a **20**

Coupling constants (Hz)

20



20

***cis*-2,2-dimethyl-4-isopropyl-5-methoxy-[1,3]dioxane (20)** ^{1}H NMR (CDCl3, 500 MHz) δ 4.08 (A of ABX J_{AB} = 12.8 Hz, J_{AX} = 2.0 Hz, 1H), 3.84 (B of ABX, J_{AB} = 12.8 Hz, J_{BX} = 2.0 Hz, 1H), 3.41 (s, 3H), 3.32 (dd, J = 9.5, 2.0 Hz, 1H), 3.05 (m, 1H), 2.00 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H), 0.94 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 98.5, 76.7, 72.2, 60.8, 56.9, 29.2, 28.2, 19.2, 18.8, 17.9.

nOe analysis **20**