## [Suppporting Information]

# Regioselective Alkyl and Alkynyl Substitution Reactions of Epoxy Alcohols by the use of Organoaluminum Ate-Complexes: Regiochemical Reversal of Nucleophilic Substitution Reactions

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### Experimental

General. All reactions were carried out under a dry nitrogen atmosphere. Routine flash column chromatography was achieved with Merck silica gel 60 for purification of products.

Material. Anhydrous $CH_2Cl_2$ was dried by distillation from $P_2O_5$.

Epoxy alcohols **1**[1], **4**[2], and **5**[2] were prepared according to the previously described procedures, respectively. Diols **2a**[1], **11**[3], and **13**[4] were also previously reported by other groups.

**(*2S,3S,4S*)-4-(*tert*-Butyldimethylsiloxy)-2,3-epoxy-1-pentanol 6:** IR (neat) 3450, 1254, 1157, 1103 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.05 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 1.23 (d, $J$ = 6.3 Hz, 3 H), 1.62 (bt, $J$ = 5.4 Hz, 1 H), 2.91 (dd, $J$ = 2.3, 4.1 Hz, 1 H), 3.13 (dt, $J$ = 2.3, 4.3 Hz, 1 H), 3.64 (ddd, $J$ = 4.3, 7.6, 12.6 Hz, 1 H), 3.83 (dq, $J$ = 4.1, 6.3 Hz, 1 H), 3.94 (ddd, $J$ = 2.5, 5.3, 12.6 Hz, 1 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ -4.71, -4.60, 18.21, 20.92, 25.82 (3 C), 55.86, 58.97, 61.49, 66.85; HRMS Calcd for $C_7H_{15}O_3Si$ ([M-$^t$Bu]); 175.0790. Found: 175.0783.

**(*2S,3S,4S*)-5-Benzyloxy-3,4-epoxy-2-pentanol 7:** IR (neat) 3430, 1655, 1560, 1113, 895 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 1.25 (d, $J$ = 6.4 Hz, 3 H), 1.87 (bs, 1 H), 2.96 (dd, $J$ = 2.5, 3.1 Hz, 1 H), 3.26 (dt, $J$ = 2.3, 5.6 Hz, 1 H), 3.50 (dd, $J$ = 5.6, 11.5 Hz, 1 H), 3.78 (dd, $J$ = 2.8, 11.5 Hz, 1 H), 3.96-4.04 (bm, 1 H), 4.57 (d, $J$ = 12.0 Hz, 1 H), 4.59 (d, $J$ = 12.0 Hz, 1 H), 7.27-7.39 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 18.81, 53.53, 58.81, 64.58, 69.71, 73.27, 127.62 (2 C), 127.67, 128.32 (2 C), 137.65; HRMS Calcd for $C_{12}H_{16}O_3$; 208.1099. Found: 208.1094.

**(*2S,3S,4R*)-5-Benzyloxy-2,3-epoxy-4-methyl-1-pentanol 8:** IR (neat) 3450, 1497, 1454, 1207, 1099 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 1.01 (d, $J$ = 6.9 Hz, 3 H), 1.74-1.86 (m, 2 H) 2.95 (dd, $J$ = 2.5, 6.8 Hz, 1 H), 3.00 (dt, $J$ = 2.5, 4.3 Hz, 1 H), 3.45 (dd, $J$ = 5.6, 9.1 Hz, 1 H), 3.50 (dd, $J$ = 5.6, 9.2 Hz, 1 H), 3.57-3.66 (m, 1 H), 3.86-3.95 (m, 1 H), 4.52 (s, 2 H), 7.20-7.38 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 13.43, 35.84, 56.76, 61.83, 72.48, 73.14, 127.44 (3 C), 128.26 (2 C), 138.25; HRMS Calcd for $C_{13}H_{18}O_3$; 222.1256. Found: 222.1219.

**(*2R*,3R**)-2,3-Epoxy-5-phenyl-1-pentanol 9:** IR (neat) 3410, 1603, 1541, 1093, 1030, 880, 700 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 1.53 (b, 1 H), 1.82-1.98 (m, 2 H), 2.68-2.89 (m, 3 H), 2.99 (dt, $J$ = 2.3, 5.8 Hz, 1 H), 3.57 (ddd, $J$ = 4.3, 7.4, 12.5 Hz, 1 H), 3.84 (ddd, $J$ = 2.6, 5.3, 12.5 Hz, 1 H),

7.18-7.33 (m, 5 H); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ 32.24, 33.38, 55.35, 58.63, 61.60, 126.00, 128.26 (2 C), 128.36 (2 C), 140.90; HRMS Calcd for $C_{11}H_{12}O$ ([M-$H_2O$]); 160.0888. Found: 160.0913.

***(2R*,3R*)*-2,3-Epoxy-5-phenylsulfonyl-1-pentanol 10:** IR (neat) 3500, 1655, 1560, 1448, 1308, 1146, 1086, 1026, 881, 689 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 1.81 (b, 1 H), 1.86-2.00 (m, 1 H), 2.10-2.22 (m, 1 H), 2.94-2.98 (bm, 1 H), 3.07 (ddd, *J* = 2.1, 4.6, 6.6 Hz, 1 H), 3.23 (dd, *J* =6.9, 8.1 Hz, 2 H), 3.62-3.70 (b, 1 H), 3.82-3.87 (b, 1 H), 7.55-7.94 (m, 5 H ); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ 25.14, 52.77, 53.58, 58.56, 61.20, 127.91 (2 C), 129.33 (2 C), 133.85, 138.69; HRMS Calcd for $C_{11}H_{12}O_3S$ ([M-$H_2O$]); 224.0507. Found: 224.0470.

**Typical Procedure for the Alkyl Substitution Reaction of 2,3-Epoxy Alcohols. *(2R*,3R*)*-4-Benzyloxy-2-methyl-1,3-butanediol 11:** To a solution of epoxy alcohol **4** (97 mg, 0.5 mmol) in $CH_2Cl_2$ (10 mL) was added a 1.50 M hexane solution of *n*-BuLi (0.37 mL, 0.55 mmol) at 0 ℃. After being stirred for 30 min, a 1.0 M hexane solution of $Me_3Al$ (1.5 mL, 1.5 mmol) was added at 0 ℃, and the mixture was stirred for 30 min. Water followed by aqueous 3 N HCl was added, and the mixture was separated. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine, and dried over $MgSO_4$. Concentration under reduced pressure followed by flash column chromatography afforded 101 mg (96%) of the known diol **11**[3] as a 97:3 mixture of regio isomers.

***(2R*,3R*)*-4-(*tert*-Butyldimethylsiloxy)-2-ethyl-1,3-butanediol 2b:** IR (neat) 3400, 1460, 1256, 1111 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 0.09 (b, 6 H), 0.91 (s, 9 H), 0.95 (t, *J*= 3.6 Hz, 3 H), 1.35-1.50 (m, 3 H), 2.84 (bd, *J* = 2.8 Hz, 1 H), 3.06 (b, 1 H), 3.57 (dd, *J* = 8.6, 10.7 Hz, 1 H), 3.65-3.84 (m, 4 H ); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ -5.28, -5.23, 11.77, 18.35, 21.33, 25.92 (3C), 43.67, 63.71, 65.84, 75.27; HRMS Calcd for $C_8H_{19}O_3Si$ ([M-$^t$Bu]); 191.1103. Found: 191.1104.

***(2R*,3R*)*-4-Benzyloxy-2-ethyl-1,3-butanediol 12:** IR (neat) 3400, 1655, 1560, 1099, 1028, 910, 737 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, *J*= 7.3 Hz, 3 H), 1.29-1.56 (m, 3 H), 2.78 (bd, *J* = 3.1 Hz, 1 H), 2.85 (bt, *J* = 5.9 Hz, 1 H), 3.51 (dd, *J* = 7.7, 9.4 Hz, 1 H), 3.61 (dd, *J* = 3.5, 9.4 Hz, 1 H), 3.69 (dt, *J* = 5.6, 11.4 Hz, 1 H), 3.81 (ddd, *J* = 3.0, 6.1, 11.4 Hz, 1 H), 3.86-3.93 (m, 1 H ), 4.57 (s, 2 H), 7.27-7.64 (m, 5 H); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ 11.76, 21.36, 43.81, 63.63, 73.21, 73.45, 73.84, 127.68 (2 C), 127.81, 128.41 (2 C), 137.58; HRMS Calcd for $C_{13}H_{20}O_3$; 224.1412. Found: 224.1383.

***(2R*,3S*)*-4-benzyloxy-2-ethyl-1,3-butanediol 14:** IR (neat) 3400, 1655, 1560, 1497, 1101, 698 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3 H), 1.29-1.47 (m, 2 H), 1.63-1.73 (m, 1 H), 2.65 (b, 1 H), 2.77 (bd, *J* = 3.1 Hz, 1 H), 3.53-3.61 (m, 2 H), 3.72 (bt, *J* = 4.4 Hz, 2 H), 4.00-4.07 (m, 1 H ), 4.56 (d, *J* = 12.3 Hz, 1 H), 4.57 (d, *J* = 12.3 Hz, 1 H), 7.26-7.39 (m, 5 H); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ 12.23, 19.03, 44.44, 63.37, 71.88, 73.23, 73.54, 127.67 (2 C), 127.80, 128.41 (2 C), 137.58; HRMS Calcd for $C_{13}H_{20}O_3$; 224.1412. Found: 224.1395.

***(2R, 3S, 4S)*-4-(*tert*-Butyldimethylsiloxy)-2-methyl-1,3-pentanediol 15:** IR (neat) 3400, 1385, 1256, 937, 810 cm$^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 3 H), 0.09 (s, 3 H), 0.82 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H), 1.11 (d, *J* = 6.3 Hz, 3 H), 1.73-1.83 (m, 1 H), 2.75 (bd, *J* = 1.6 Hz, 1 H), 3.35-3.43 (b, 1 H), 3.48 (bd, *J* = 8.7 Hz, 1 H), 3.54-3.70 (bm, 2 H), 3.92 (dq, *J* = 3.3, 6.3 Hz, 1 H); $^{13}$C

NMR (67.8 MHz, $CDCl_3$) δ -4.80, -4.40, 13.20, 15.90, 18.12, 25.85 (3 C), 36.53, 68.03, 69.37, 80.19; HRMS Calcd for $C_8H_{19}O_3Si$ ([M-$^t$Bu]); 191.1103. Found: 191.1115.

**(*2S,3R,4S*)-1-Benzyloxy-3-methyl-2,4-pentanediol 16:** IR (neat) 3400, 1655, 1560,1105, 905 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.89 (d, *J* = 7.1 Hz, 3 H), 1.18 (d, *J* = 6.6 Hz, 3 H), 1.74 (dquint, *J* = 2.3, 7.1 Hz, 1 H), 2.89-2.98 (b, 2 H), 3.47 (dd, *J* = 7.7, 9.4 Hz, 1 H), 3.59 (dd, *J* = 3.3, 9.4 Hz, 1 H), 3.86 (dt, *J* = 3.3, 7.4 Hz, 1 H), 3.99-4.08 (b, 1 H), 4.57 (s, 2 H), 7.30-7.36 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 11.57, 19.34, 40.19, 69.29, 72.98, 73.44, 73.70, 127.67 (2 C), 127.79, 128.41 (2 C), 137.66; HRMS Calcd for $C_{13}H_{20}O_3$; 224.1418. Found: 191.1412.

**(*2R,3S,4R*)-5-Benzyloxy-2,4-dimethyl-1,3-pentanediol 17:** IR (neat) 3450, 1456, 1096,1076, 986, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.97 (d, *J* = 6.9 Hz, 3 H), 1.01 (d, *J* = 6.9 Hz, 3 H), 1.85 (dsext, *J* = 3.3, 6.9 Hz, 1 H), 1.98-2.13 (m, 1 H), 3.43-3.54 (m, 3 H involving a dd at 3.50, *J* = 5.9, 9.2 Hz), 3.58-3.67 (m, 1 H), 3.73 (dd, *J* = 3.8, 9.2 Hz, 1 H), 3.77-3.85 (m, 1 H), 4.52 (d, *J* = 11.9 Hz, 1 H), 4.53 (d, *J* = 11.9 Hz, 1 H), 7.20-7.40 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 14.58, 14.76, 35.53, 37.24, 66.98, 73.73, 74.36, 82.69, 127.61 (2 C), 127.83, 128.43 (2 C), 137.28; HRMS Calcd for $C_{14}H_{23}O_3$ ([M+H]); 239.1647. Found: 239.1681.

**(*2R*,3R**)-3-Methyl-5-phenyl-1,2-pentanediol 18:** IR (neat) 3380, 1560, 1497, 1070, 1030, 908, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.97 (d, *J* = 6.6 Hz, 3 H), 1.40-1.70 (m, 2 H), 1.80-1.97 (m, 2 H), 2.08 (bd, *J* = 3.0 Hz, 1 H), 2.55 (ddd, *J* = 6.6, 10.1, 13.7 Hz, 1 H), 2.76 (ddd, *J* = 5.1, 10.4, 13.7 Hz, 1 H), 3.45-3.58 (m, 2 H), 3.64-3.76 (m, 1 H), 7.15-7.30 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 15.28, 33.26, 34.32, 35.75, 64.57, 76.07, 125.62, 128.21(4 C), 142.32; HRMS Calcd for $C_{12}H_{18}O_2$; 194.1307. Found: 194.1314.

**(*2R*,3R**)-2-Methyl-5-(phenylsulfonyl)-1,3-pentanediol 19:** IR (neat) 3450, 1447, 1304, 1146, 1086, 1026, 689 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.9 Hz, 3 H), 1.64-2.17 (m, 3 H), 2.37 (bs, 1 H), 3.23 (ddd, *J* = 5.9, 9.9, 14.2 Hz, 1 H), 3.35 (ddd, *J* = 5.4, 10.1, 14.2 Hz, 1 H), 3.48 (b, 1 H), 3.58-3.82 (bm, 3 H ), 7.54-7.70 (m, 3 H), 7.90-7.95 (m, 2 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 13.61, 28.09, 39.95, 52.97, 67.70, 75.00, 127.86(2 C), 129.23 (2 C), 133.65, 139.06; HRMS Calcd for $C_{12}H_{19}O_4S$; 259.1004. Found: 259.0978.

**Typical Procedure for the Alkynyl Substitution Reaction of 2,3-Epoxy Alcohols. (*2R*,3R**)-4-Benzyloxy-2-[2-(trimethylsilyl)ethynyl]-1,3-butanediol 20:** To a solution of (trimethylsilyl)acetylene (0.17 mL, 1.2 mmol) in $CH_2Cl_2$ (4 mL) was added a 1.5 M hexane solution of *n*-BuLi (0.80 mL, 1.2 mmol) at 0 ℃. After being sttired for 30 min, a 1.0 M hexane solution of $Me_2AlCl$ (1.2 ml, 1.2 mmol) was added at 0 ℃. After being stirred for 30 min, the mixture was cooled to -78 ℃. To this was added a solution of lithium alkoxide, which was prepared from epoxy alcohol **4** (58 mg, 0.3 mmol) in $CH_2Cl_2$ (2 ml) and a 1.5 M hexane solution of *n*-BuLi (0.22 mL, 0.33 mmol) at 0 ℃ for 30 min. After being stirred for 30 min, the mixture was allowed to warm to 0 ℃ and stirring was continued for 1 h. Water followed by aqueous 3 N HCl was added, and the mixture was separated. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine, and dried over $MgSO_4$. Concentration under reduced pressure followed by flash column chromatography afforded 82 mg (94%) of

diol **20** as a 91:9 mixture of regioisomers: IR (neat) 3450, 1454, 1250, 1074, 1030, 900, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 2.51-2.61 (bm, 1 H), 2.69 (bd, *J* = 4.6 Hz, 1 H), 2.77 (dt, *J* = 5.6, 9.2 Hz, 1 H), 3.59 (dd, *J* = 6.3, 9.6 Hz, 1 H), 3.77 (dd, *J* = 3.1, 9.6 Hz, 1 H), 3.80-3.88 (bm, 2 H), 3.89-3.98 (bm, 1 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 7.25-7.40 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 0.09 (3 C), 38.79, 63.97, 72.13, 72.48, 73.46, 89.49, 102.93, 127.67 (2 C), 127.77, 128.37 (2 C), 137.56; HRMS Calcd for $C_{16}H_{24}O_3Si$; 292.1495. Found: 292.1538.

**(*2S*,3R**)-4-Benzyloxy-2-[2-(trimethylsilyl)ethynyl]-1,3-butanediol 21:** IR (neat) 3460, 2341, 1686, 1250, 1094, 1047, 843, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 2.22 (t, *J* = 6.4 Hz 1 H), 2.48 (d, *J* = 5.3 Hz, 1 H), 2.91 (dt, *J* = 3.8, 5.9 Hz, 1 H), 3.59 (dd, *J* = 5.4, 9.6 Hz, 1 H), 3.64 (dd, *J* = 6.3, 9.6 Hz, 1 H), 3.75-3.85 (m, 2 H), 3.96-4.05 (m, 1 H), 4.58 (s, 2 H), 7.26-7.39 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 0.16 (3 C), 39.13, 63.01, 69.79, 72.11, 73.43, 89.98, 102.28, 127.65 (2 C), 127.72, 128.34 (2 C), 137.61; HRMS Calcd for $C_{16}H_{24}O_3Si$; 292.1495. Found: 292.1477.

**(*2R*,3R**)-4-(*tert*-Butyldimethylsiloxy)-2-[2-(trimethylsilyl)ethynyl]-1,3-butanediol 22:** IR (neat) 3460, 2363, 1420, 1252 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.15 (s, 9 H), 0.92 (s, 9 H), 2.65-2.76 (m, 3 H), 3.70-3.93 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ -5.31, -5.24, 0.10 (3 C), 18.44, 25.96 (3 C) 38.54, 64.12, 65.24, 73.40, 89.42, 103.11; HRMS Calcd for $C_{15}H_{33}O_3Si_2$ ([M+H]); 317.1968. Found: 317.1959.

**(*2R,3S,4R*)-5-Benzyloxy-4-methyl-2-[2-(trimethylsilyl)ethynyl]-1,3-pentanediol 23:** IR (neat) 3460, 1686, 1560, 1250, 1078, 1030, 843, 698 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.13 (s, 9 H), 1.18 (d, *J* = 7.3 Hz, 3 H), 2.15-2.25 (m, 1 H), 2.71-2.79 (m, 1 H), 3.12 (bt, *J* = 6.2 Hz, 1 H), 3.54 (dd, *J* = 3.6, 9.4 Hz, 1 H), 3.65-3.72 (m, 2 H), 3.83-3.91 (m, 3 H), 4.49 (d, *J* = 11.9 Hz, 1 H), 4.54 (d, *J* = 11.9 Hz, 1 H), 7.25-7.40 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 0.15 (3 C), 15.56, 35.64, 40.50, 65.22, 72.94, 73.73, 78.93, 89.13, 103.90, 127.56 (2 C), 127.85, 128.44 (2 C), 137.32; HRMS Calcd for $C_{18}H_{26}O_2Si$ ([M-$H_2O$]); 302.1702. Found: 302.1739.

**(*2R*,3R**)-5-phenylsulfonyl-2-[2-(trimethylsilyl)ethynyl]-1,3-pentanediol 24:** IR (neat) 3500, 1717, 1558, 1306, 1250, 1148, 1086, 843, 689 $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 1.85-2.05 (m, 1 H), 2.18-2.34 (m, 1 H), 2.40 (bs, 1 H), 2.61 (ddd, *J* = 4.6, 6.8, 8.2 Hz, 1 H), 3.17 (bd, *J* = 4.1 Hz, 1 H), 3.22-3.43 (m, 2 H), 3.70-3.95 (m, 3 H), 7.53-7.95 (m, 5 H); $^{13}C$ NMR (67.8 MHz, $CDCl_3$) δ 0.08 (3 C), 28.57, 41.81, 52.88, 64.05, 71.40, 90.26, 102.32, 127.94 (2 C), 129.25 (2 C), 133.67, 138.83; HRMS Calcd for $C_{16}H_{25}O_4SSi$ ([M+H]); 341.1243. Found: 341.1241.

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