Supporting Information

General

NMR

^{1}H NMR spectra and ^{13}C NMR spectra were measured with JEOL JNM-ECX 300 /TRH (300MHz/75MHz) and JEOL JNM-ECP 600 (600MHz/150MHz) spectrophotometers. Chemical shifts (^{1}H, ^{13}C) were relative to tetramethylsilane or chloroform (7.26 ppm, 77.0 ppm) as an internal standard. Splitting patterns are designated as an s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Coupling constants were giving in Hz.

IR

Infrared spectra (IR) were recorded on JASCO Model FT/IR-7300 spectrophotometer. Data were given only the significant diagnostic bans.

MS

Mass spectra (MS-EI) were obtained on JEOL JMS-700 spectrometer.

Others

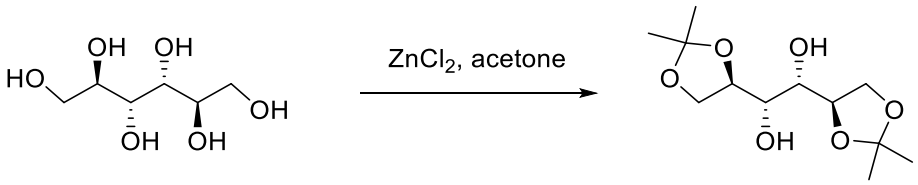
Analytical thin layer chromatography (TLC) was performed by using Merck precoated TLC plate 60F254 (silica gel) with indicator. Visualization of the spots was done by UV light and dipping anisaldehyde-H_2SO_4-EtOH solution and $KMnO_4$-acetone solution. Column chromatography was performed by using silica gel.

Solvents

Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Kanto Kagaku as anhydrous solvents.
Ether (Et_2O) was distilled from sodium benzophenone ketyl.
N, *N*-dimethylformamide (DMF) and acetonitrile(MeCN) were distilled from CaH_2.
Dimethylsulfoxide (DMSO) was distilled from CaH_2
Triethylamine (Et_3N) and pyridine were distilled from KOH.
Ethanol (EtOH) and methanol (MeOH) were distilled from magnesium alcoholate.

Preparation from D-mannitol

1, 2-Bis-(2, 2-dimethyl-[1, 3] dioxolan-4-yl)-ethane-1, 2-diol(Ref1,2)

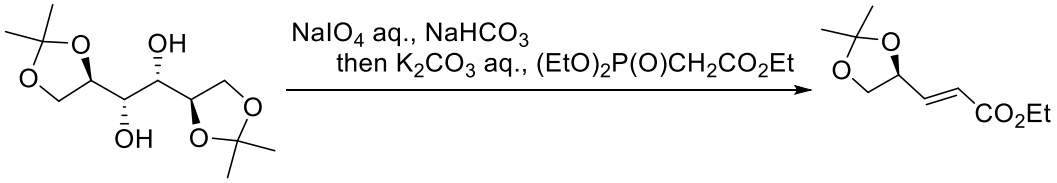


To a suspension of Zinc Chloride (80g, 0.57mol) in acetone (500mL) was added slowly dropwise D-mannitol (50g, 0.27mol) at 0°C under an argon atmosphere and the reaction mixture was stirred for 24 h at room temperature. After quenching with aqueous K_2CO_3(80g/100mLH_2O), the resulting mixture was stirred for 30 min at room temperature. The acetone layer was collected by decantation and the precipitates were extracted with CH_2Cl_2 (5 times). The aqueous NH_3(1 mL) was added to acetone layer, and the resulting mixture was concentrated *in vacuo*. The residue was extracted with CH_2Cl_2 (5 times). The combined organic layers were dried over K_2CO_3. Concentration gave the diol. The crude product was used in the next step subsequently without further purification.

Ref1: Yokoyama, H.; Kobayashi, H.; Miyazawa, M.; Yamaguchi, S.; Hirai, Y. *Heterocycles* (2007)283

Ref2: Li, X.; Tanasova, M.; Vasileiou, C.; Borhan, B. *J. Am. Chem. Soc.* (2008)1885

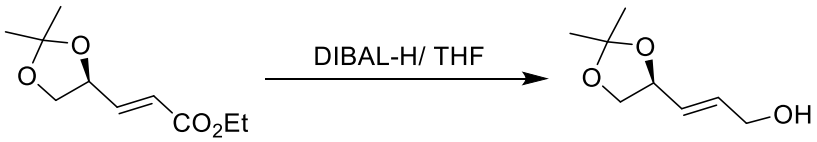
3-(2, 2-Dimethyl-[1, 3] dioxolan-4-yl)-acrylic acid ethyl ester(Ref3)



To a solution of diol (0.27mol) in saturated aqueous $NaHCO_3$ (300 mL) was added aqueous $NaIO_4$ (64.2 g, 0.3mol) and the mixture was stirred for 7 h. After completion of the reaction, the reaction mixture was cooled to 0°C. To the reaction mixture was added diethyl phosphonoacetic acid ethyl ester (132g, 0.59mol) and aqueous potassium carbonate (6M, 100mL) at 0°C, and the mixture was stirred for 12 h. The reaction mixture was filtered through celite and extracted with CH_2Cl_2 (3 times). The extract was washed with H_2O, dried over K_2CO_3. Concentration and chromatography gave the unsaturated ester (67.5g, 60% in 3 steps) as colorless oil.

Ref 3: Schomaker, J.M.; Pulgan, V. R.; Borhan, B. *J. Am. Chem. Soc.* (2004)13600

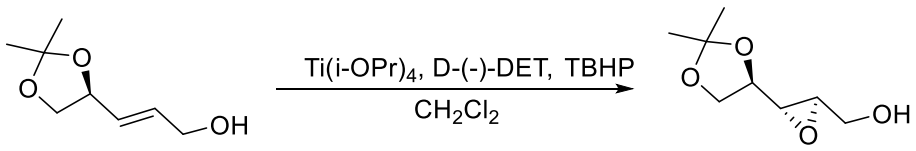
3-(2, 2-Dimethyl-[1, 3] dioxolan-4-yl)-prop-2-en-1-ol(Ref4)



To a stirred solution of unsaturated ester (12g, 59.9mmol) in THF (150mL) was added slowly dropwise diisobutylaluminum hydride (DIBAL-H) (200mL, 210mmol, 1.04M hexane solution) at -78°C under an argon atmosphere. After 1 h, the reaction mixture was quenched with ethyl acetate (3 times). The combined organic phases were dried over Na_2SO_4. Concentration and chromatography gave allyl alcohol (6g, 63%) as colorless oil.

Ref4: Spangenberg, T.; Schoenfelder, A.; Bret, B.; Mann, A. *Eur. J. Org. Chem.* (2010)6005

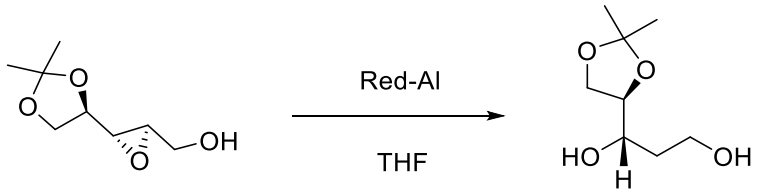
[3-(2, 2-Dimethyl-[1, 3] dioxolan-4-yl)-oxiranyl]-methanol (Ref5)



Activated 3 Å molecular sieves (2.0g) were added to stirred CH_2Cl_2 (200ml) under N_2 atmosphere. The flask was cooled to -20°C, and $Ti(O\text{-}^iPr)_4$ (31.4ml, 114mmol) and (*S,S*)-(-)-diethyl tartrate (D-(-)-DET) (23.5g, 114mmol) were added sequentially with stirring. After 20 min, the allyl alcohol (15g, 94.8mmol) in CH_2Cl_2 (10ml) was added and *t*-butyl hydroperoxide (TBHP) (116ml, 190mmol) was also added slowly. After the addition, the reaction mixture was stirred at -25°C for 24 h. Tartaric acid aqueous solution (56.9g, 0.379mol) was added, and the stirring was continued for 30 min at 0°C. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. To an organic phase was added 3N aqueous NaOH and the mixture was stirred for 1 h at 0°C. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 times). The combined organic phases were washed with brine, dried over $MgSO_4$ and filtered. Concentration and column chromatography gave the epoxy alcohol (13.21g, 80%) as colorless oil.

Ref5: Li, X.; Borhan, B. *J. Am. Chem. Soc.* (2008)16126

1-(2, 2-Dimethyl-[1,3]dioxolan-4-yl)-propane-1,3-diol



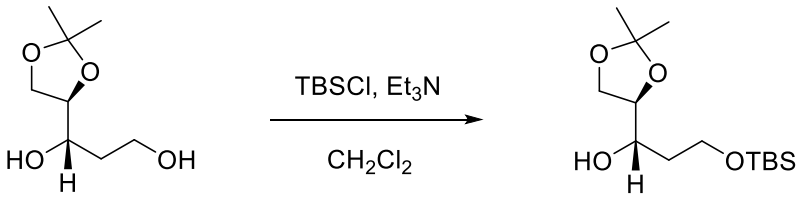
Red-Al (47.3g, 152mmol, 65 wt% toluene solution) was added to epoxy alcohol (13.21 g, 75.8 mmol) in THF (300mL) at 0 ºC in a flame dried flask under an argon atmosphere. After 1 h, the reaction mixture was quenched with saturated aqueous Na_2SO_4. The aqueous layer was extracted with ethyl acetate (3 times) and the organic layers were combined, washed with brine, dried over $MgSO_4$ and filtered. Concentration and column chromatography gave diol (7.52g, 56%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
4.02-4.05 (m, 2H)
3.93-3.96 (m, 2H)
3.87-3.92 (m, 2H)
2.74-2.75 (m, 1H)
2.27-2.30 (m, 1H)
1.81-1.77 (m, 1H)
1.68-1.64 (m, 1H)
1.43 (s, 3H)
1.37 (s, 3H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
109.2, 78.3, 71.6, 65.3, 61.5, 34.4, 26.5, 25.2

IR (neat); 3777-3044

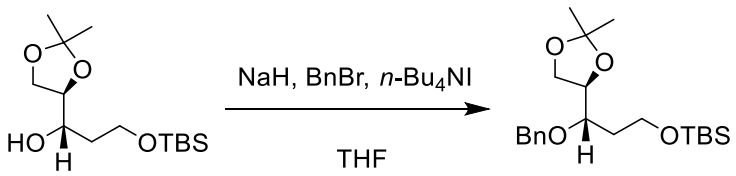
3-(*tert*-Butyl-dimethyl-silanyloxy)-1-(2, 2-dimethyl-[1, 3] dioxolan-4-yl)-propan-1-ol (Ref6)



To a solution of diol (0.67g, 3.80mmol) and triethylamine (0.64mL, 4.56mmol) in di-chloromethane (40mL) was added *t*-butyldimethylsilyl chloride (0.69g, 4.56mmol) at 0°C under an argon atmosphere. The mixture was warmed to room temperature. After 17 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and the resulting mixture was extracted with CH_2Cl_2 twice (3 times). The organic phase was washed with brine, dried over $MgSO_4$ and filtered. Concentration and chromatography gave the TBS ether (0.93g, 84%) as colorless oil.

Ref6: Suzuki, Y.; Ohara, A.; Sugaya, K.; Takao, K.; Tadano, K. *Tetrahedron*(2001)7291

[3-Benzyloxy-3-(2, 2-dimethyl-[1,3]dioxolan-4-yl)-propoxy]-*tert*-butyl-dimethyl-silane



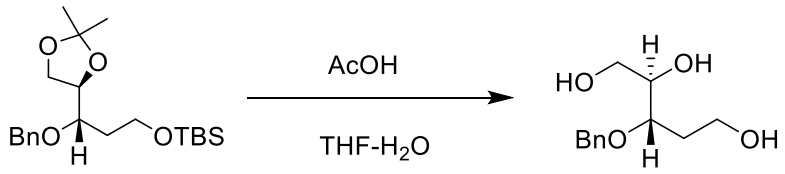
55% Sodium hydride (0.28g, 6.40mmol) was suspended in THF (32mL). The TBS ether (0.93g, 3.20mmol) in THF was added to this mixture at 0°C. The mixture was stirred for 1 h and warmed to room temperature over 1 h. After the mixture was cooled to 0°C, benzyl bromide (0.53ml, 4.48mmol) and tetrabutylammonium iodide was added. The resulting mixture was warmed to room temperature over 12 h. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with ethyl acetate (3 times). The organic phase was washed with brine, dried over $MgSO_4$ and filtered. Concentration and chromatography gave the benzyl ether (1.11g, 91%).

^{1}H NMR (600MHz, $CDCl_3$) δ=:
7.35-7.26 (m, 5H)
4.71 (d, *J*= 11.4Hz, 1H)
4.61 (d, *J*= 11.4Hz, 1H)
4.13 (ddd, *J*= 6.6, 6.6, 5.1Hz, 1H)
4.02 (dd, *J*= 6.6, 8.1Hz, 1H)
3.83 (dd, *J*= 6.6, 8.1Hz, 1H)
3.77-3.71 (m, 1H)
3.73 (t, *J*= 5.3Hz, 2H)
1.81-1.76(m, 1H)
1.67 (ddt, *J*= 5.3, 8.2, 13.4Hz, 1H)
1.43 (s, 3H)
1.36 (s, 3H)
0.89 (s, 9H)
0.04 (s, 6H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
128.3, 127.8, 127.6, 109.04, 78.50, 75.98, 73.30, 65.99, 59.26, 34.91, 26.51, 25.93, 25.33, 18.24, -5.331

IR (neat); 2954, 2930, 1256, 776

3-Benzyloxy-pentane-1, 2, 5-triol



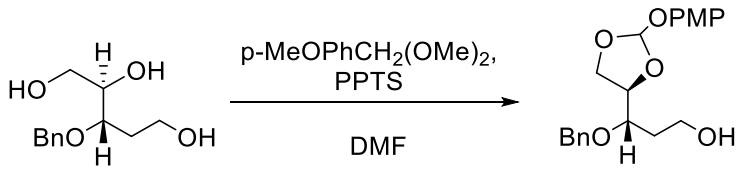
The benzyl ether (14.4g, 37.8mmol) was added to stirred 80%AcOHaq. (380ml) at room temperature. When the reaction was completed, the reaction mixture was concentrated *in vacuo*. This crude product was purified by column chromatography on silica gel using ethyl acetate / hexane mixture as an eluent to afford the triol (5.25g, 61%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
7.37-7.29 (m, 5H)
4.60 (d, J= 11.4Hz, 1H)
4.55 (d, J= 11.4Hz, 1H)
3.85-3.82 (m, 2H)
3.77 (dd, J= 3.5, 11.3Hz, 1H)
3.74-3.71 (m, 1H)
3.69 (dd, J= 6.2, 11.3Hz, 1H)
3.65 (ddd, J= 5.5, 5.5, 5.5Hz, 1H)
1.94-1.83 (m, 2H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
137.8, 128.6, 128.0, 128.0, 78.22, 72.74, 72.12, 63.43, 59.12, 32.42

IR (neat); 3912-3006

3-Benzyloxy-3-[2-(4-methoxy-phenyl)-[1, 3] dioxolan-4-yl]-propan-1-ol



To a stirred solution of triol (5.10g, 22.5mmol) and *p*-anisaldehyde dimethyl acetal (4.46mL, 24.8mmol) in DMF (68mL) was added PPTS (57mg, 0.23mmol) at room temperature under an argon atmosphere. After 2 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and the resulting mixture was extracted with diethyl ether (3 times). The organic phases were washed with brine, dried over $MgSO_4$. Concentration and chromatography gave 4-methoxybenzylidene derivative (6.0g, 77%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
7.41-7.29 (m, 7H)
6.92-6.87 (m, 2H)
5.88 (s, 0.5H)
5.74 (s, 0.5H)
4.73 (d, *J* = 11.4Hz, 0.5H)
4.69 (d, *J* = 11.4Hz, 0.5H)
4.68 (d, *J* = 11.4Hz, 0.5H)
4.65 (d, *J* = 11.4Hz, 0.5H)
4.29-4.25 (m, 1H)
4.12-4.10 (m, 1H)
3.99-3.96 (m, 0.5H)
3.93-3.89 (m, 0.5H)
3.84-3.82 (m, 1H)
3.812 (s, 1.5H)
3.811 (s, 1.5H)
3.80-3.76 (m, 2H)
1.97-1.77 (m, 2H)

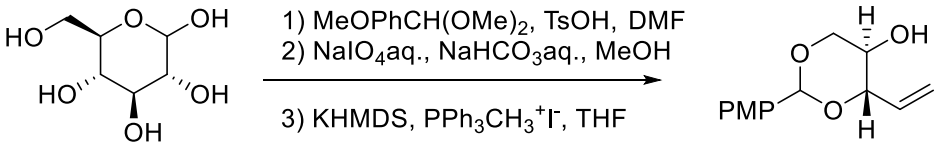
^{13}C NMR (150MHz, $CDCl_3$) δ=:
160.5, 138.0, 137.9, 128.6, 128.5, 128.0, 127.9, 127.8, 113.79, 113.78, 104.2, 103.9, 78.2, 78.1, 77.9, 77.6, 73.0, 72.8, 67.6, 67.4, 59.75, 59.71, 55.3, 33.7, 33.6

IR (neat); 3757-3128

EIMS m/z 344 (M+).
HREIMS m/z calcd. for C20H24O5(M+) 344.1624, found 344.1604.

Preparation from D-glucose

2- (4-Methoxy-phenyl)-4-vinyl-[1, 3] dioxan-5-ol



A suspension of D-glucose (10g, 55.5mmol), *p*-methoxybenzaldehyde dimethylacetal (4.99mL, 27.8mmol) and *p*-TsOH (0.14g, 0.55mmol) in DMF (56ml) was stirred for 1 day at 60°C. The reaction mixture was then quenched by addition of Et_3N, the solvents were removed *in vacuo* and the residue was purified by column chromatography on silica gel to give the product(4.3g, 52%) as colorless solid.

To a solution of 4, 6-*O*-p-methoxybenzylidene-D-glucose(2.3g, 7.71mmol) in MeOH (7.7mL) was added aqueous $NaIO_4$ (4.95 g, 23.13mmol), saturated aqueous $NaHCO_3$ (1.3g, 15.4mmol), and the reaction mixture was stirred for 3 h. The reaction mixture was filtered through celite and extracted with CH_2Cl_2 (5 times). The extract was washed with brine, dried over $MgSO_4$, and concentrated to give the aldehyde, which was used directly without purification.

To a solution of PPh_3CH_3I (7.8g, 19.3mmol) in THF (39ml) was added KHMDS (37mL, 18.5mmol, 0.5M toluene solution) at 0°C. After stirring for 3 h, a solution of the aldehyde (7.71mmol) in THF (5mL) was added and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and filtered through celite. The filtrate was extracted with Et_2O (3 times). The combined extracts were washed with brine, dried ($MgSO_4$). Concentration and column chromatography gave alcohol (1.61g, 46% in 3 steps) as colorless solid.

^1H NMR (600MHz, $CDCl_3$) δ=:

7.44-7.42 (m, 2H)

6.90-6.88 (m, 2H)

5.98 (ddd, *J* = 6.6, 10.6, 17.3Hz, 1H)

5.50 (s, 1H)

5.48 (ddd, *J* = 1.3, 1.3, 17.3Hz, 1H)

5.40 (ddd, *J* = 1.3, 1.3, 10.6Hz, 1H)

4.33-4.29 (m, 1H)

4.00 (m, 1H)

3.79 (s, 1H)

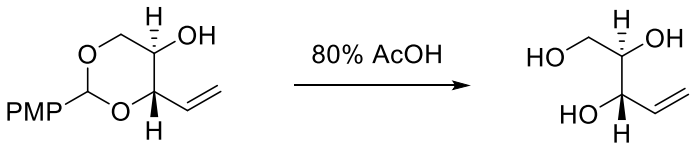
3.65-3.59 (m, 2H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
160.0, 134.6, 130.1, 127.8, 127.5, 119.3, 113.6, 100.9, 83.4, 70.7, 65.2, 55.3

IR (neat): 3100-3600, 2923, 2854

EIMS m/z 236 (M^+).
HREIMS m/z calcd. for C13H16O4(M+) 236.1049, found 236.1045.

Pent-4-ene-1, 2, 3-triol



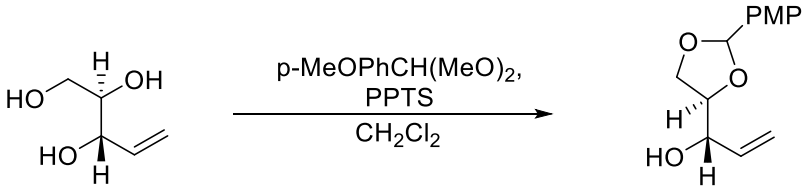
The alcohol (0.56g, 2.37mmol) was added to the solution of AcOH-H_2O (24ml, 4:1) at room temperature. When the reaction was completed, the reaction mixture was concentrated *in vacuo*. This crude product was purified by column chromatography on silica gel using ethyl acetate / hexane mixture as a eluent to afford the triol (0.24g, 86%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
5.93 (ddd, *J* = 6.2, 10.7, 17.2Hz, 1H)
5.39 (ddd, *J* = 1.5, 1.5, 17.2Hz, 1H)
5.29 (ddd, *J* = 1.5, 1.5, 10.7Hz, 1H)
4.32-4.30 (m, 1H)
3.79 (dd, *J* = 5.5, 11.3Hz, 1H)
3.74 (dd, *J* = 3.9, 11.3Hz, 1H)
3.71-3.69 (m, 1H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
136.5, 117.2, 74.8, 73.4, 63.1

IR (neat); 3778-3053

1-[2-(4-Methoxyphenyl)-[1, 3] dioxolan-4-yl]prop-2-en-1-ol



To a stirred solution of triol (0.12g, 1.04mmol) and *p*-anisaldehyde dimethyl acetal (0.22mL, 1.2mmol) in CH_2Cl_2 (10mL) was added PPTS (2mg, 0.01mmol) at 0°C under an argon atmosphere. After 1h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and the resulting mixture was extracted with diethyl ether (3 times). The organic phases were washed with brine, dried over $MgSO_4$. Concentration and chromatography gave 4-methoxybenzylidene derivative (0.104g, 42%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
7.43-7.39 (m, 2H)
6.92-6.88 (m, 2H)
5.96 (s, 0.5H)
5.92-5.85 (m, 1H)
5.77 (s, 0.5H)
5.44 (ddd, *J*= 1.5, 1.5, 17.3Hz, 0.5H)
5.42 (ddd, *J*= 1.5, 1.5, 17.3Hz, 0.5H)
5.27 (ddd, *J*= 1.5, 1.5, 10.6Hz, 1H)
4.48-4.46 (m, 0.5H)
4.42-4.40 (m, 0.5H)
4.25-4.20 (m, 1H)
4.17-4.14 (m, 1H)
4.02-3.99 (m, 1H)
3.82 (s, 1.5H)
3.81 (s, 1.5H)

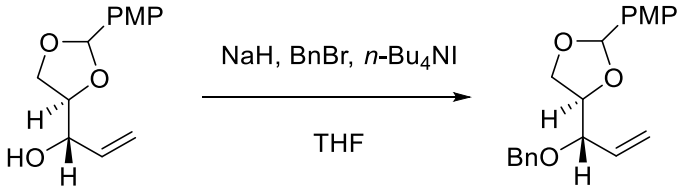
^{13}C NMR (150MHz, $CDCl_3$) δ=:
160.5, 160.3, 135.6, 135.5, 127.9, 127.8, 127.5, 117.1, 113.8, 113.7, 104.4, 104.2, 78.6, 78.1, 72.2, 72.1, 65.9, 65.7, 55.3

IR (neat); 3791-3122

EIMS m/z 235 (M^+-H).

HREIMS m/z calcd. for C13H15O4(M+-H) 235.0970, found 235.0975.

4-(1-Benzyloxy-allyl)-2-(4-methoxy-phenyl)-[1, 3] dioxolane



55% Sodium hydride (0.037g, 0.84mmol) was suspended in THF (5mL). The 4-methoxybenzylidene derivative (0.1g, 0.42mmol) in THF was added to this mixture at 0°C. The mixture was stirred for 1 h and warmed to room temperature over 1 h. After the mixture was cooled to 0°C, the benzyl bromide (0.05ml, 0.46mmol) and tetrabutyl ammonium iodide was added at 0°C. The resulting mixture was warmed to room temperature over 12 h. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with ethyl acetate (3 times). The organic phase was washed with brine, dried over $MgSO_4$ and filtered. Concentration and chromatography gave benzyl ether (0.117g, 85%) as colorless oil.

^1H NMR (600MHz, $CDCl_3$) δ=:

7.43-7.29 (m, 7H)

6.91-6.87 (m, 2H)

5.87 (s, 0.5H)

5.90-5.80 (m, 1H)

5.74 (s, 0.5H)

5.42-5.37 (m, 2H)

4.70-4.56 (m, 2H)

4.47-4.401 (m, 1H)

4.31-4.20 (m, 1H)

4.11-4.06 (m, 1H)

4.00-3.96 (m, 1H)

3.81 (s, 1.5H)

3.80 (s, 1.5H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:

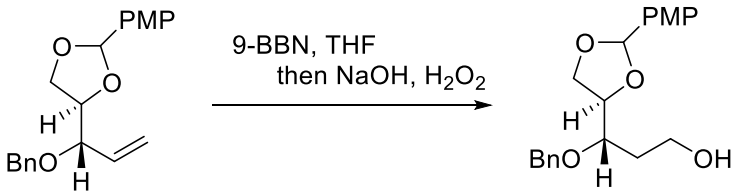
160.4, 160.3, 138.1, 138.0, 135.1, 134.9, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 127.4, 113.7, 113.6, 104.4, 104.1, 81.0, 80.7, 77.9, 77.7, 72.9, 70.6, 70.5, 67.8, 67.5, 55.2

IR (neat); 1615

EIMS m/z 326 (M^+).

HREIMS m/z calcd. for C20H22O4(M+) 326.1518, found 326.1506.

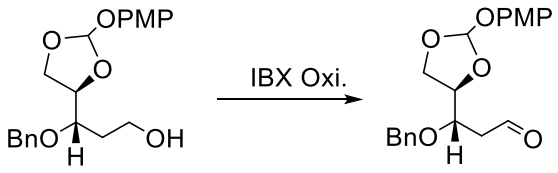
3-Benzyloxy-3-[2-(4-methoxy-phenyl)-[1, 3] dioxolan-4-ylpropan-1-ol



To a stirred solution of benzyl ether (0.117g, 0.36mmol) in THF (1.0mL) was added 9-BBN (2.2ml, 1.08mmol, 0.50M THF solution) at 0°C under an argon atmosphere. The mixture was warmed to room temperature. After 7 h, the reaction mixture was cooled to 0°C and added 3 N aqueous NaOH (1.8mL, 5.4mmol) solution and 30% aqueous solution of H_2O_2 (1.2mL, 9.36mmol). The reaction mixture was stirred for 12 h at room temperature. The reaction mixture was quenched by an addition of aqueous $Na_2S_2O_3$ solution and the aqueous phase was extracted with ethyl acetate (3 times). The combined organic phases were washed with brine, dried ($MgSO_4$). Concentration and chromatography gave the alcohol (0.089g, 72%) as colorless oil.

Synthesis of CD fragment (~ the triol (**5**))

3-Benzyloxy-3-[2-(4-methoxy-phenyl)-[1, 3] dioxolan-4-yl]-propionaldehyde

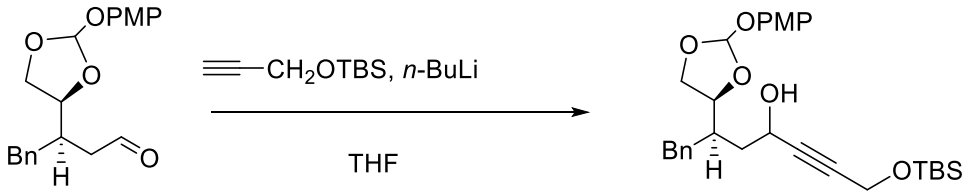


To a stirred solution of alcohol (4.77g, 13.9mmol) in DMSO (140mL) was added *o*-Iodoxybenzoic acid (IBX) (11.6g, 41.6mmol) and the mixture was stirred at room temperature for 3 h under an argon atmosphere. The reaction mixture was quenched by an addition of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$ solution. The aqueous phase was extracted with diethyl ether (3 times). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was used in the next step subsequently without further purification.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
9.84-9.83 (m, 0.5H)
9.80-9.79 (m, 0.5H)
7.37-7.29 (m, 7H)
6.90-6.88 (m, 2H)
5.83 (s, 0.5H)
5.73 (s, 0.5H)
4.67 (d, *J*= 11.4Hz, 0.5H)
4.65 (d, *J*= 11.4Hz, 0.5H)
4.63-4.59 (m, 0.5H)
4.59 (d, *J*= 11.4Hz, 0.5H)
4.27-4.22 (m, 1.5H)
4.21-4.15 (m, 0.5H)
4.11-4.05 (m, 2H)
3.80 (s, 3H)
2.84-2.75 (m, 2H)

IR (neat); 2736, 1729, 1652

1-Benzyloxy-6-(*tert*-Butyl-dimethyl-silanyloxy)-1-[2-(4-methoxy-phenyl)-[1, 3] dioxo-lan-4-yl]-hex-4-yn-3-ol



To a stirred suspension of lithium *tert*-butyldimethylsilyl acetylene (prepared from *tert*-butyldimethylsilyl acetylene (5.2g, 55.6mmol) and *n*-BuLi (16.8mL, 27.8mmol, 1.65M hexane solution) in THF (140mL)) was added a solution of aldehyde (13.9mmol) in THF at -78°C and the resulting mixture was stirred for an additional 20 min at -78°C. The reaction mixture was quenched with saturated aqueous NH_4Cl and filtered through celite. The filtrate was extracted with ethyl acetate (3 times). The combined extracts were washed with brine, dried over $MgSO_4$. Concentration and chromatography gave the alcohol (5.94g, 84% in 2 steps) as colorless oil.

^1H NMR (600MHz, $CDCl_3$) δ=:
7.43-7.27 (m, 7H)
6.91-6.87 (m, 2H)
5.90 (s, 0.25H)
5.89 (s, 0.25H)
5.74 (s, 0.25H)
5.73 (s, 0.25H)
4.82-4.61 (m, 3H)
4.35-4.33 (m, 2H)
4.30-4.22 (m, 2H)
4.14-4.06 (m, 2H)
4.02-3.96 (m, 1H)
3.82-3.81 (m, 3H)
2.12-1.89 (m, 2H)
0.91-0.90 (m, 9H)
0. 12-0.09 (m 6H)

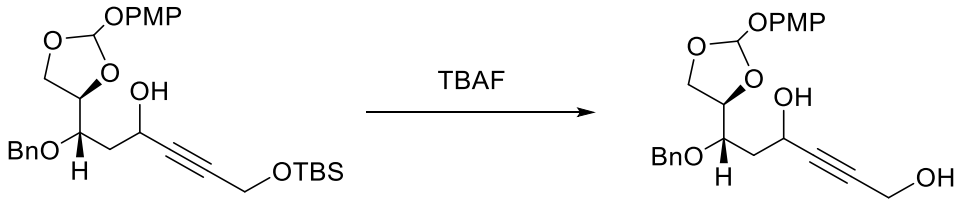
^{13}C NMR (150MHz, $CDCl_3$) δ=:
160.5, 137.8, 137.7, 129.8, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7,

113.8, 113.7, 104.2, 104.1, 103.9, 85.0, 84.0, 78.6, 78.4, 78.3, 78.2, 76.5, 76.4, 73.5, 73.1, 72.9, 67.5, 67.2, 66.9, 66.6, 60.3, 60.2, 59.8, 55.3, 55.2, 51.7, 39.6, 38.6, 38.5, 25.8, 18.3, -0.02, -5.13

IR (neat); 3718-3144, 774

EIMS m/z 512 (M^+).
HREIMS m/z calcd. for C22H33O6Si(M+-Bn) 421.2046, found 421.2029.

1-Benzyloxy-6-hydroxy-1-[2-(4-methoxy-phenyl)-[1, 3] dioxolan-4-yl]-hex-4-yn-3-ol



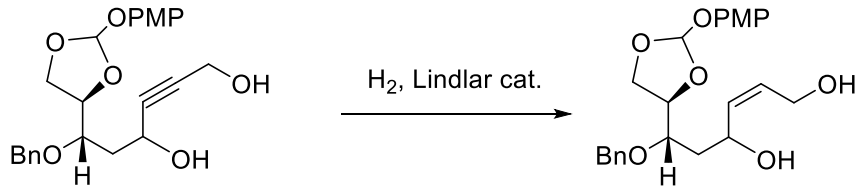
To a solution of silyl ether (7.34g, 14.32mmol) in THF (150mL) was added tetrabutylammonium fluoride (29mL, 28.64mmol) at room temperature. The reaction mixture was stirred for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and the mixture was extracted with ethyl acetate (3 times). The extract was washed with brine, dried over $MgSO_4$. Concentration and chromatography gave the alcohol (4.51g, 79%) as colorless oil.

^1H NMR (600MHz, $CDCl_3$) δ=:
7.31-7.41 (m, 7H)
6.86-6.91 (m, 2H)
5.90 (s, 0.5H)
5.89 (s, 0.5H)
4.60-4.85 (m, 3H)
4.24-4.30 (m, 3H)
4.07-4.15 (m, 2H)
3.97-4.00 (m, 0.5H)
3.89-3.92 (m, 0.5H)
3.81 (s, 3H)
1.90-2.20 (m, 2H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
160.5, 137.8, 128.5, 128.4, 128.4, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.7, 119.5, 113.7, 113.7, 104.2, 78.4, 67.2, 60.1, 55.2, 51.0, 39.4

IR (neat); 3741-3087, 1455, 780
EIMS m/z 398 (M^+).
HREIMS m/z calcd. for C23H26O6 (M+) 398.1729, found 398.1732.

6-Benzyloxy-6-[2-(4-methoxy-phenyl)-[1, 3] dioxolan-4-yl]-hex-2-ene-1,4-diol



A suspension containing Lindlar cat. ($Pd/CaCO_3$, poisoned by lead) (1.55g, 10 wt %) and the alcohol (15.48g, 38.85mmol) in AcOEt (600mL) was placed at room temperature under H_2 atmosphere. After the completed reaction, the reaction mixture was filtered through Silica gel and the filtrate was concentrated *in vacuo*. Concentration and chromatography gave the alcohol (7.8g, 50%) as colorless oil.

^1H NMR (600MHz, $CDCl_3$) δ=:

7.41-7.31 (m, 7H)

6.91-6.89 (m, 2H)

5.90 (s, 0.25H)

5.88 (s, 0.25H)

5.75 (s, 0.25H)

5.74 (s, 0.25H)

5.73-5.69 (m, 1H)

5.60-5.56 (m, 1H)

4.82-4.60 (m, 3H)

4.35-4.0 (m, 4H)

3.89 (s, 0.75H)

3.88 (s, 0.75H)

3.87 (s, 0.75H)

3.81 (s, 0.75H)

1.91-1.73 (m, 2H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:

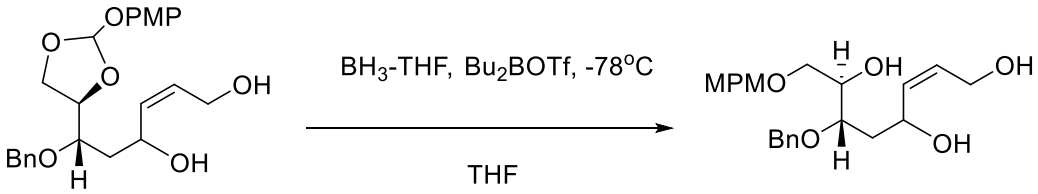
160.4, 160.3, 138.0, 134.7, 134.4, 134.3, 130.6, 130.5, 130.1, 130.0, 129.1, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 113.7, 113.6, 104.1, 104.0, 103.8, 78.8, 78.2, 77.4, 77.3, 73.2, 72.9, 72.6, 67.3, 66.9, 66.7, 65.4, 64.3, 60.4, 58.9, 58.2, 58.2, 55.3, 50.7, 38.7, 38.3, 27.9, 22.6, 21.0, 14.1

IR (neat); 3741-3087

EIMS m/z 400 (M^+).

HREIMS m/z calcd. for C23H28O6 (M+) 400.1886, found 400.1904.

6-Benzyloxy-8-(4-methoxy-benzyloxy)-oct-2-ene-1, 4, 7-triol (**5**)



To a stirred solution of the acetal (1.38g, 3.45mmol) in THF (69mL) was added slowly dropwise borane-THF complex (BH_3-THF) (12.8mL, 1.08M THF solution) at -78°C under an argon atmosphere. After 15 min, the mixture was treated with Bu_2BOTf (8.63mL, 1M CH_2Cl_2 solution) and stirred at -78°C for 8 h. The reaction mixture was then quenched with Et_3N (3.8ml), followed by the dropwise addition of MeOH until effervescence ceased. The mixture was warmed to room temperature and stirred for 30 min. Concentration and chromatography gave the alcohol (**5**) (1.18g, 85%) as colorless oil.

^{1}H NMR (600MHz, $CDCl_3$) δ=:
7.36-7.22 (m, 7H)
6.89-6.86 (m, 2H)
5.72-5.60 (m, 1H)
5.58-5.53 (m, 1H)
4.75-4.71 (m, 1H)
4.70-4.52 (m, 2H)
4.50-4.45 (m, 2H)
4.27-4.19 (m, 1H)
4.15-4.00 (m, 1H)
3.99-3.93 (m, 0.5H)
3.92-3.84 (m, 0.5H)
3.81 (s, 1.5H)
3.80 (s, 1.5H)
3.79-3.71 (m, 1H)
3.69-3.48 (m, 2H)
1.96-1.70 (m, 2H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
159.4, 129.8, 129.7, 129.6, 129.5, 128.6, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.0, 113.9, 113.7, 73.2, 73.1, 72.4, 71.9, 71.6, 71.5, 65.4, 61.5, 60.4, 58.7, 55.3, 21.1,

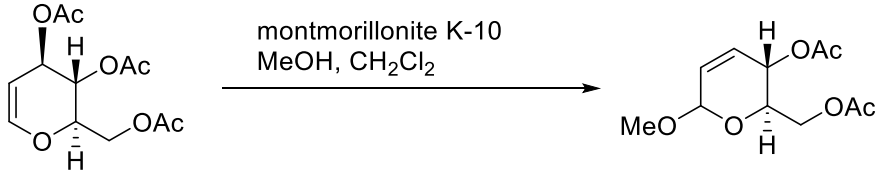
14.2

IR (neat) ; 3750-3055

EIMS m/z 384 (M+-H_2O).
HREIMS m/z calcd. for C23H26O4 (M+-2H_2O) 366.1831, found 366.1817.

Synthesis of JK fragment (~ the aldehyde (**14**))

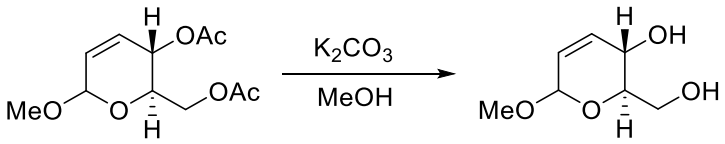
(2*R*,3*S*)-3-Acetoxy-2-acetoxymethyl-6-methoxy-2, 3-dihydro-6*H*-pyran(Ref7)



MeOH (1.11 mL, 27.5 mmol) and montmorillonite K-10 (1.5 g) were added to a solution of tri-*O*-acetyl-D-glucal (5.03g, 18.4 mmol) in CH_2Cl_2 (50 mL) and the reaction mixture was refluxed. After stirring for 3.5 h, the reaction mixture was filtrated through celite pad and the filtrate was concentrated *in vacuo.* The residue was purified by column chromatography (*n*-hexane : AcOEt = 3:1 to 2:1) to afford (2*R*,3*S*)-3-acetoxy-2-acetoxymethyl-5-methoxy-2,3-dihydro-6*H*-pyran (4.60 g, quant) as colorless oil.

Ref7: De, K.; Legros, J.; Crousse, B.; Bonnet-Delpon, D. *Tetrahedron*(2008)64, 10497

(2*R*, 3*S*)-3-Hydroxy-2-hydroxyymethyl-6-methoxy-2, 3-dihydro-6*H*-pyran



A solution containing K_2CO_3 (0.26 g, 1.89 mmol) and (2*R*,3*S*)-3-acetoxy-2-acetoxy-methyl-6-methoxy-2,3-dihydro-6*H*-pyran (4.60 g, 18.9 mmol) in MeOH (102 mL) was stirred for 14.5 h at room temperature. Concentration and column chromatography (AcOEt to AcOEt:MeOH = 1:1) gave (2*R*,3*S*)-3-hydroxy-6-hydroxymethyl-6-methoxy-5,6-dihydro-2*H*-pyran (3.02 g, quant) as colorless oil.

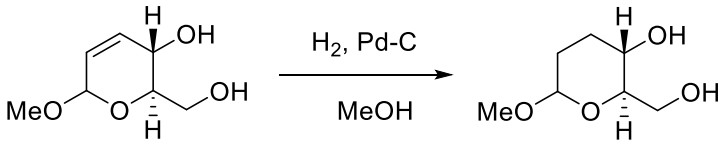
^{1}H NMR (600 MHz, $CDCl_3$) δ=:
5.97 (d, *J* = 10.3 Hz, 1H)
5.80-5.70 (m, 1H)
4.88 (s, 3H)
4.25-4.15 (m, 1H)
3.90-3.80 (m, 2H)
3.71-3.70 (m, 1H)
3.49 (s, 1.5H)
3.45 (s, 1.5H)
2.25-2.15 (m, 1H)
2.15-2.05 (m, 1H)

^{13}C NMR (150 MHz, $CDCl_3$) δ=:
133.4, 132.2, 127.8, 126.2, 97.0, 95.3, 78.2, 71.4, 64.4, 63.5, 63.3, 62.8, 55.9, 55.3

IR (neat): 3394, 2918, 2830, 1450, 1392, 1188, 1094, 1054, 964

EIMS m/z 159 (M+-H).

(2*R*,3*S*)-3-Hydroxy-2-hydroxyymethyl-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran



A suspension containing 10% Pd-C (0.30g) and (2*R*,3*S*)-2-hydroxy-3-hydroxylmethyl-6-methoxy-2,3-di-hydro-2*H*-pyran (3.02 g, 18.9 mmol) in MeOH (102 mL) at room temperature was placed under H_2 atmosphere. After being stirred for 3 h, the reaction mixture was filtered through celite and the filtrate was concentrated *in vacuo.* The residue was purified by column chromatography (*n*-hexane : AcOEt = 3:1 to AcOEt : MeOH = 9:1) to afford (2*R*,3*S*)-3-hydroxy-2-(hydroxylmethyl)-6-methoxy-3,4,5,6-tetra-hydro-2*H*-pyran (2.33 g, 78%) as a colorless oil.

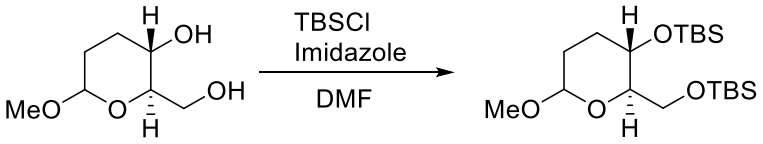
^{1}H NMR (600 MHz, $CDCl_3$) δ=:
4.68 (s, 1H)
3.90-3.75 (m, 2H)
3.66-3.60 (m, 1H)
3.57-3.54 (m, 1H)
3.36 (s, 3H)
1.92-1.67 (m, 4H)

^{13}C NMR (150 MHz, $CDCl_3$) δ=:
102.8, 97.4, 81.6, 78.9, 72.7, 67.7, 67.6, 67.3, 67.0, 63.4, 63.3, 63.2, 56.5, 54.5, 32.6, 30.7, 30.1, 29.2, 27.2, 25.4

IR (neat) : 3394, 2940, 1458, 1219, 1130, 1049, 1003, 979, 948

EIMS m/z 161 (M+-H).

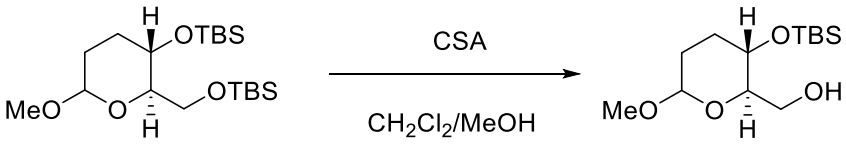
(2*R*, 3*S*)-3-(*tert*-Butyldimethylsiloxy)-2-(*tert*-butyldimethylsiloxymethyl)-6-methoxy-3, 4, 5, 6-tetra-hydro-2*H*-pyran(Ref8)



To a solution containing (2*R*,3*S*)-3-hydroxy-2-hydroxymethyl-5-methoxy-3,4,5,6-tetrahydro-2*H*-pyran (2.69 g, 16.6 mmol) and imidazole (4.53 g, 66.4 mmol) in DMF (17 mL) was added *tert*-butyldimethylsilyl chloride (7.55 g, 49.6 mmol) at room temperature and the reaction mixture was warmed to 50 °C. After stirring for 19 h, MeOH was added to the reaction mixture and the mixture was diluted with ether. The ether layer was washed with brine and then dried over $MgSO_4$. Concentration and column chromatography (*n*-hexane : AcOEt = 19:1) gave (2*R*,3*S*)-3-(*tert*-butyldi-methylsiloxy)-2-(*tert*-butyldimethylsiloxymethyl)-6-methoxy-3,4, 5,6-tetrahydro-2*H*-pyran (5.64 g,87%) as a colorless oil.

Ref8: Rosen, T.; Taschner, M.J.; Heathcock, C. H. *J. Org. Chem.* (1984)3994

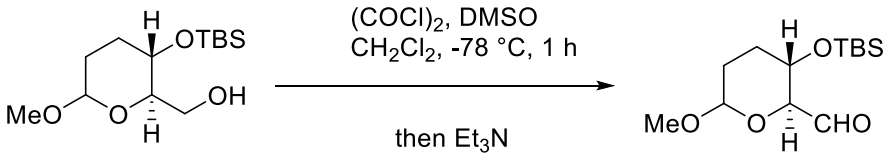
(2*R*,3*S*)-3-(*tert*-Butyldimethylsiloxy)-2-hydroxymethyl-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran(Ref9)



To a solution of (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-2-(*tert*-butyldimethylsiloxymethyl)-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran (5.04 g 12.9 mmol) in MeOH (65 mL) and CH_2Cl_2 (65 mL) was added CSA (0.30 g, 1.29 mmol) at 0 °C under an argon atmosphere and the mixture was stirred for 80 min. After the addition of Et_3N, the resulting mixture was concentrated *in vacuo*. The residue was purified by column chromatography (*n*-hexane:AcOEt = 3:1 to 1:1) to afford (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-2-hydroxymethyl-3, 4, 5, 6-tetrahydro-2*H*-pyran (2.77 g, 78%) as a colorless oil.

Ref9: Matsuo, G.; Kawamura, K.; Hori, N.; Matsukura, H.; Nakata, T. J. Am. Chem. Soc. (2004)14374

(2*R*,3*S*)-3-(*tert*-Butyldimethylsiloxy)-2-formyl-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran



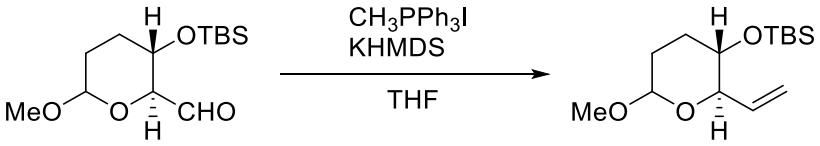
Oxalyl chloride (1.29 mL, 15.0 mmol) was added dropwise to a stirred solution of dimethyl sulfoxide (1.49 mL, 21.0 mmol) in CH_2Cl_2 (20 mL) at -78 °C. After 15 min, (2*R*,3*S*)-3-(*tert*-butyldimethylsiloxy)-2-hydroxymethyl-6-methyl-3,4,5,6-tetrahydro-2*H*-pyran (2.77g, 10.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise and the solution was stirred for 1 h at -78 °C. Et_3N (7.0 mL, 50 mmol) was then added and the reaction mixture was allowed to room temperature. After 105 min, aqueous HCl solution was added to the reaction mixture and the mixture was diluted with Et_2O. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$. Concentration and column chromatography (*n*-hexane: AcOEt = 7:3) afforded (2*R*,3*S*)-3-(*tert*-butyldimethyl-siloxy)-2-formyl-6-methoxy-3,4,5,6-tetrahydro-2*H*-pyran (2.63 g, 96%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ=:
9.82 (s, 1H)
4.76 (d, *J* = 2.9 Hz, 1H)
4.11 (d, *J* = 9.9 Hz, H)
3.77-3.69 (m, 1H)
3.35 (s, 3H)
1.88-1.50 (m, 4H)
0.88 (s, 9H)
0.08 (s, 3H)
0.05 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ=:
199.6, 97.5, 77.3, 67.8, 54.9, 28.4, 28.3, 25.7, 25.6, -4.0, -5.0

IR (neat) : 2931, 2857, 1743, 1472, 1373, 1255, 1105, 1057, 838, 777

(2*R*, 3*S*)-3-(*tert*-Butyldimethylsiloxy)-6-methoxy-2-vinyl-3, 4, 5, 6-tetrahydro-2*H*-pyran



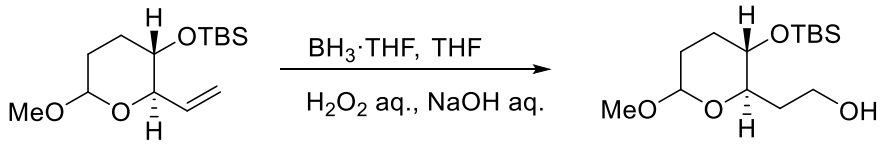
A solution of KHMDS (23.0 mL, 11.5 mmol, 0.5 M toluene solution) was added dropwise to a stirred suspension of methyltriphenylphosphonium iodide (5.81 g, 14.4 mmol) in THF (105 mL) at 0 °C under argon atmosphere. After 15 min, (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-2-formyl-6-methoxy-3,4,5,6-tetrahydro-2*H*-pyran (2.63 g, 9.57 mmol) in THF (10 mL) was added and the reaction mixture was allowed to room temperature. After stirring for 6 h, the reaction mixture was quenched with a saturated aqueous NH_4Cl and filtrated through celite pad. The filtrate was diluted with ether, washed with brine and dried over $MgSO_4$. Concentration and column chromatography (*n*-hexane to *n*-hexane : AcOEt = 19:1) afforded (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-6-methoxy-2-vinyl-3,4,5,6-tetrahydro-2*H*-pyran (1.87 g, 72%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ=:
5.90 (ddd, *J* = 17.4, 10.2, 6.2Hz, 1H)
5.33 (d, *J* = 17.2Hz, 1H)
5.19 (d, *J* = 10.6 Hz, 1H)
4.68 (d, *J* = 2.6 Hz, 1H)
3.93-3.88 (m, 1H)
3.39-3.36 (m, 1H)
3.34 (s, 3H)
1.85-1.43 (m, 4H)
0.86 (s, 9H)
0.04 (s, 3H)
0.02 (s, 3H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
136.7, 116.8, 97.3, 74.1, 70.9, 54.4, 29.2, 28.3, 25.8, 18.0, -4.1, -4.6

IR (neat): 2930, 2894, 2857, 1472, 1373, 1207, 1104, 1060, 1023, 1007, 953, 923, 904, 866, 837, 776

(2*R*,3 *S*)-3-(*tert*-Butyldimethylsiloxy)-2-(2-hydroxyethyl)-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran



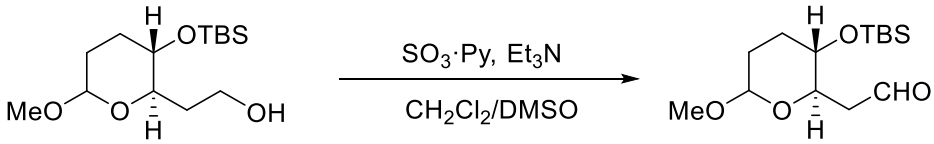
A solution of BH_3•THF (8.2 mL, 7.56 mmol, 0.92M THF solution) was added to a solution of (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-6-methoxy-2-vinyl-3, 4, 5, 6-tetrahydro-2*H*-pyran (1.87 g, 6.87 mmol) in THF at 0 °C. After stirring for 8.5 h at room temperature, to the reaction mixture was added 3M NaOH solution and 30% H_2O_2 solution at 0 °C. After stirring for 10 h at room temperature, the reaction mixture was quenched with H_2O and extracted with AcOEt. The organic phases were washed with brine and dried over $MgSO_4$. Concentration and column chromatography (*n*-hexane : AcOEt = 3 : 1) afforded (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-2-(2-hydroxyethyl)-3, 4, 5, 6-tetrahydro-2*H*-pyran (1.22 g, 61%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ=:
4.63 (s, 1H)
3.82-3.78 (m, 2H)
3.73-3.68 (m, 1H)
3.41-3.37 (m, 1H)
3.36 (s, 3H)
2.10-2.05 (m, 2H)
1.85-1.60 (m, 4H)
0.87 (s, 9H)
0.06 (s, 6H)

^{13}C NMR (150MHz, $CDCl_3$) δ=:
97.3, 74.2, 70.8, 61.8, 54.5, 33.8, 29.2, 27.9, 25.7, -4.0, -4.7

IR (neat): 3448, 2954, 2888, 2857, 1472, 1374, 1256, 1223, 1130, 1100, 1058, 1015, 948, 900, 860, 837, 775

[(2*R*, 3*S*)-3-(*tert*-Butyldimethylsiloxy)-6-methoxy-3, 4, 5, 6-tetrahydro-2*H*-pyran-2-yl] acetaldehyde (**14**)



To a solution of (2*R*, 3*S*)-3-(*tert*-butyldimethylsiloxy)-2-(2-hydroxyethyl)-6-methoxy-3, 4, 5, 6-tetra-hydro-2*H*-pyran (174 mg, 0.63 mmol) in DMSO (3.1 mL) and CH_2Cl_2 (3.1 mL) was added Et_3N (0.44 mL, 3.14 mmol) and SO_3·Py (401 mg, 2.51 mmol) at 0 °C. After stirring for 16.5 h at room temperature, the reaction mixture was quenched with H_2O and diluted with Et_2O. The organic phase was washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$. Concentration and column chromatography (*n*-hexane : AcOEt = 9:1) afforded [(2*R*, 3*S*)-3-(*tert*-butyl-dimethylsiloxy)-3, 4, 5, 6-tetra-hydro-2*H*-pyran-2-yl] acetaldehyde (**14**) (149 mg, 87%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ=:
9.80 (dd, *J* = 3.2, 1.5 Hz, 1H)
4.60 (d, *J* = 3.7 Hz, 1H)
4.07 (td, *J* = 9.3, 3.3 Hz, 1H)
3.42-3.36 (m, 1H)
3.36 (s, 3H)
2.83-2.77 (m, 1H)
2.44 (ddd, *J* = 16.0, 9.5, 3.3 Hz, 1H)
1.90-1.52 (m, 4H)
0.87 (s, 9H)
0.06 (s, 3H)
0.05 (s, 3H)

IR (neat): 2954, 2896, 2857, 1731, 1472, 1389, 1374, 1258, 1224, 1128, 1100, 1056, 1009, 949, 907, 837, 777