**Supporting Information**

# Direct Catalytic Enantio- and Diastereoselective Aldol Reaction Using a Zn-Zn-linked-BINOL Complex: a Practical Synthesis of *syn*-1,2-Diols.

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## Experimental Section

**General**: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for $^{1}H$ NMR and 125.65 MHz for $^{13}C$ NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (= 0) or in the scale relative to $CHCl_3$ (7.24 ppm) for $^{1}H$ NMR. For $^{13}C$ NMR, chemical shifts were reported in the scale relative to $CHCl_3$ (77.0 ppm for $^{13}C$ NMR) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. EI mass spectra were measured on JMS-BU20 GCmate. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; column, DAICEL CHIRALCEL OD; mobile phase, hexane–2-propanol; flow rate, 1.0 mL/min. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. $Et_2Zn$ (1.0 M, in hexanes) was purchased from Aldrich. Other reagents were purified by the usual methods.

**General Procedure for Catalytic Asymmetric Aldol Reaction Promoted by (*S*,*S*)-Zn-Zn-linked-BINOL Complex 2** :

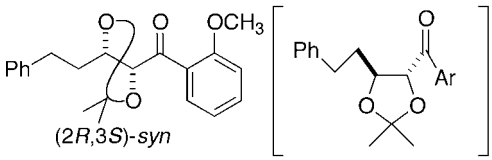
To a stirred solution of (*S*,*S*)-linked-BINOL (6.41 mg, 4.1w/w% diethyl ether and hexane included, 0.02 mmol) in THF (0.3 mL) at –78 ℃, was added $Et_2Zn$ (20 μL, 0.02 mmol, 1.0 M in hexanes). After stirring for 30 min at –20 ℃, a solution of **1d** (322.3 mg, 2.0 mmol) in THF (4.7 mL) was added. The resulting mixture was cooled to –30 ℃, and **3a** (1.0 mmol) was added and stirred at the same temperature. The stirring was continued for 20 h at this temperature and quenched by addition of 1 M HCl (2 mL). The mixture was extracted with ethyl acetate and the combined organic layers were washed with brine and dried over $Na_2SO_4$. Evaporation of solvent gave a crude mixture of the aldol products. The diastereomeric ratios of the aldol products were determined by $^{1}H$ NMR of the crude product. The crude aldol products were converted into the acetonides before purification by flash column chromatography.

**General Procedure for the Conversion of the Aldol Products to the Corresponding**

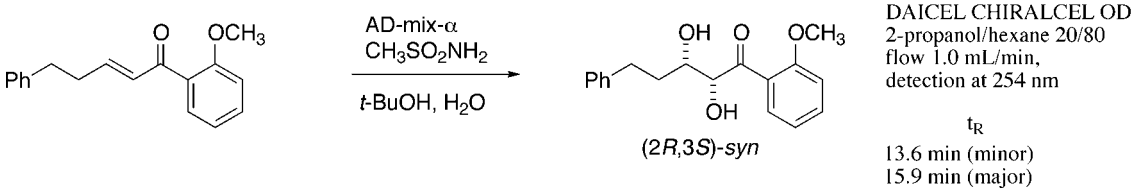
**Acetonides:** The crude mixture of the aldol product obtained by the general procedure described above was treated with *p*-toluenesulfonic acid monohydrate (30 mg) in dimethylformamide/2,2-dimethoxypropane (4.5 mL/4.5 mL) at room temperature for 2 h. Saturated aqueous $NaHCO_3$ (12 mL), $H_2O$ and ether were added to the mixture and the aqueous layer was separated and extracted with ether (×2). The combined organic layers were washed with $H_2O$ and with brine (×2) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the resulting residue was purified by flash silica gel column chromatography to afford the acetonides. The diastereomers were separated by this procedure. The enantiomeric excesses of the acetonides were determined by HPLC after cleavage of the acetonides.

**Synthesis of the Aldol Products**

**(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-6-phenyl-1-pentanone (from *syn*-4a)** :

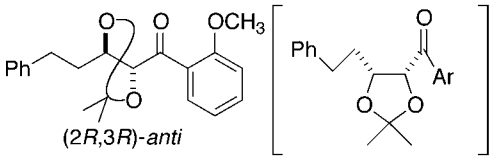



colorless oil; IR (neat) ν 2936, 1685, 1598, 1247 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.34 (s, 3H), 1.49 (s, 3H), 1.87-1.99 (m, 2H), 2.65 (ddd, *J* = 6.9, 9.8, 14.1Hz, 1H), 2.80 (ddd, *J* = 5.5, 10.0, 14.1 Hz, 1H), 3.82 (s, 3H), 4.21-4.23 (m, 1H), 4.95 (d, *J* = 6.7 Hz, 1H), 6.92 (brd, *J* = 8.3 Hz, 1H), 6.99 (ddd, *J* = 0.9, 7.5, 7.5 Hz, 1H), 7.10-7.12 (m, 2H), 7.14-7.17 (m, 1H), 7.22-7.25 (m, 2H), 7.42-7.48 (m, 2H); $^{13}C$ NMR ($CDCl_3$) δ 26.1, 27.5, 31.8, 35.6, 55.6, 77.7, 84.7, 110.3, 111.5, 120.8, 125.8, 127.5, 128.3, 128.3, 130.3, 133.3, 141.5, 157.8, 201.5; EI-MS *m/z* 340 [$M^+$], 135[$ArCO^+$]; $[\alpha]_D^{21}$ –39.4 (*c* 0.52, $CH_2Cl_2$) (92% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 13.6 min (minor) and 15.9 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4a** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.

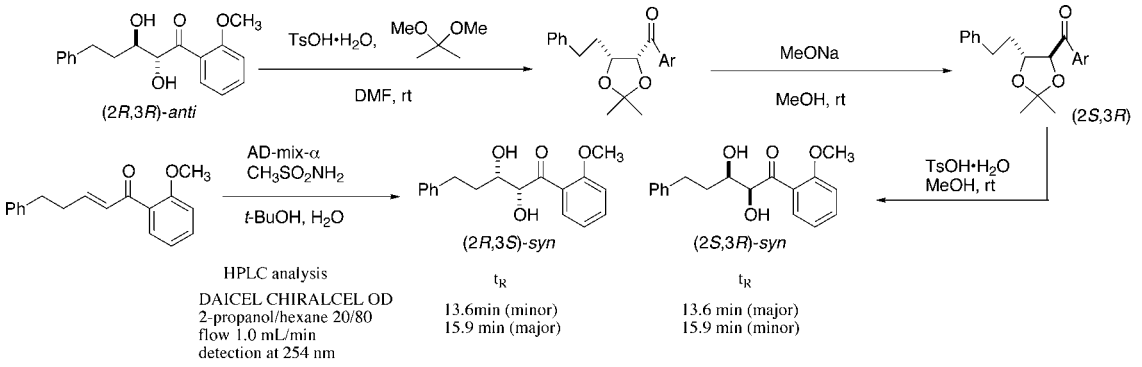



**(2*R*,3*R*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-5-phenyl-1-**

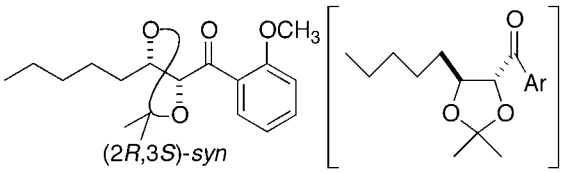
**pentanone (from *anti*-4a):**



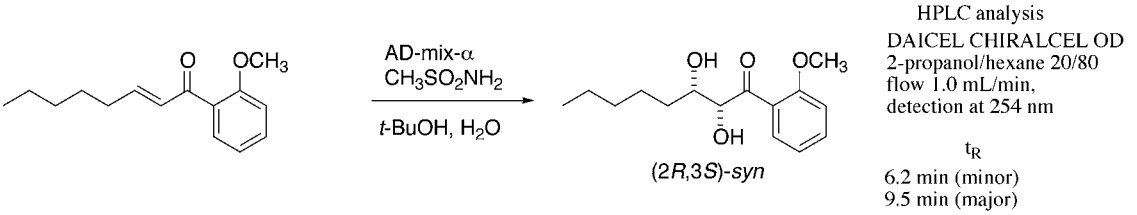

colorless oil; IR (neat) 2937, 2683, 1598, 1245 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.41 (s, 3H), 1.48-1.56 (m,1H), 1.63 (s, 3H), 1.69-1.77 (m, 1H), 2.54-2.61 (m, 1H), 2.73-2.80 (m, 1H), 3.69 (s, 3H), 4.45 (ddd, *J* = 2.8, 7.4, 10.1 Hz, 1H), 5.49 (d, *J* = 7.4 Hz, 1H), 6.89 (brd, *J* = 8.3 Hz, 1H ), 7.01 (ddd, *J* = 0.9, 7.9, 7.9 Hz, 1H), 7.04-7.22 (m, 5H), 7.47 (ddd, *J* = 1.8, 7.0, 8.3 Hz, 1H), 7.81 (dd, *J* = 1.8, 7.9 Hz, 1H) ; $^{13}C$ NMR ($CDCl_3$) δ 25.4, 27.4, 32.2, 32.9, 55.3, 76.7, 82.5, 109.5, 111.5, 121.1, 125.8, 126.5, 128.2, 128.6, 131.1, 134.4, 141.5, 158.5, 196.7; EI-MS *m/z* 340 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{22}$ +49.7 (*c* 0.56, $CH_2Cl_2$) (91% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 10.9 min (minor) and 17.0 min (major). Ee was determined after cleavage of acetonide. An authentic sample was prepared by using AD-mix-α. The absolute configuration of *anti*-**4a** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below.



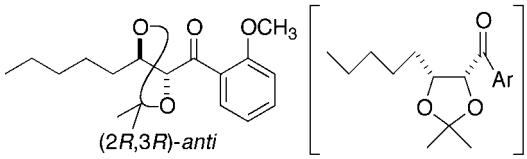

**(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-octanone (from *syn*-4b)** :



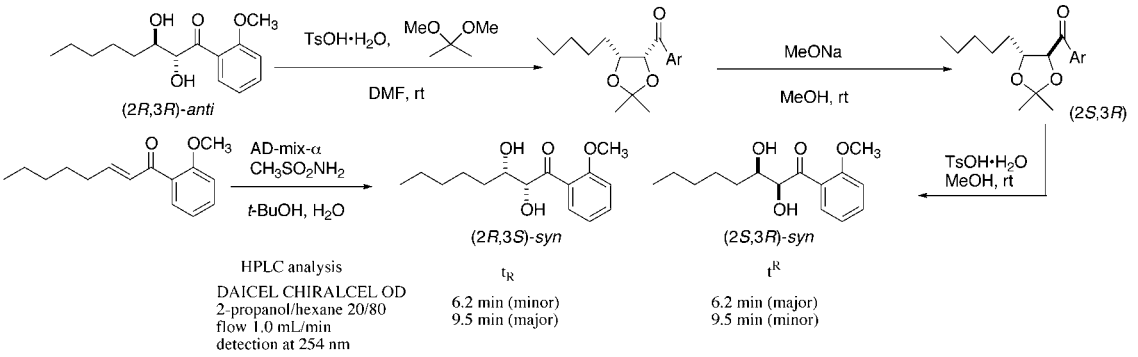

colorless oil; IR (neat) ν 2934, 1686, 1598, 1247, 1024 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.9 Hz, 3H), 1.18-1.47 (m, 6H), 1.53-1.65 (m, 2H), 1.31 (s, 3H), 1.44 (s, 3H), 3.86 (s, 3H), 4.20 (ddd, *J* = 4.6, 7.1, 7.1 Hz, 1H), 4.89 (d, *J* = 7.1 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.99 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.44 (ddd, *J* = 1.8, 7.4, 8.3 Hz, 1H), 7.49 (ddd, *J* = 1.8, 7.4, 7.4 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 14.0, 22.5, 25.3, 26.1, 27.5, 31.7, 33.9, 55.6, 78.5, 84.8, 110.1, 111.5, 120.8, 127.7, 130.1, 133.3, 157.9, 201.8.; EI-MS *m/z* 306 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ –21.6 (*c* 0.83, $CHCl_3$) (95% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.2 min (minor) and 9.5 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4b** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



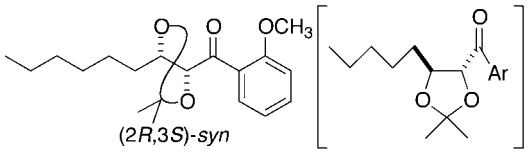

**(2*R*,3*R*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-octanone (from *anti*-4b)**:




colorless oil; IR (neat) ν 2934, 1683, 1598, 1245, 1023 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.79 (t, *J* = 7.0 Hz, 3H), 1.09-1.27 (m, 6H), 1.33-1.47 (m, 2H), 1.40 (s, 3H), 1.59 (s, 3H), 3.90 (s, 3H), 4.46 (ddd, *J* = 2.9, 7.1, 9.8 Hz, 1H), 5.54 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 7.02 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.47 (ddd, *J* = 1.7, 7.9, 8.5 Hz, 1H), 7.79 (dd, *J* = 1.7, 7.9 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 13.9, 22.4, 25.7, 26.1, 27.4, 31.2, 31.5, 55.5, 78.1, 82.7, 109.3, 111.6, 121.1, 126.9, 131.0, 134.2, 158.4, 197.3; EI-MS *m/z* 306 [$M^+$], 135 [ArCO]; $[\alpha]_D^{24}$ +50.3 (*c* 1.24, $CHCl_3$) (91% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.7 min (minor) and 8.1 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *anti*-**4b** was determined by HPLC analysis after emiperization of the acetonide as shown below.

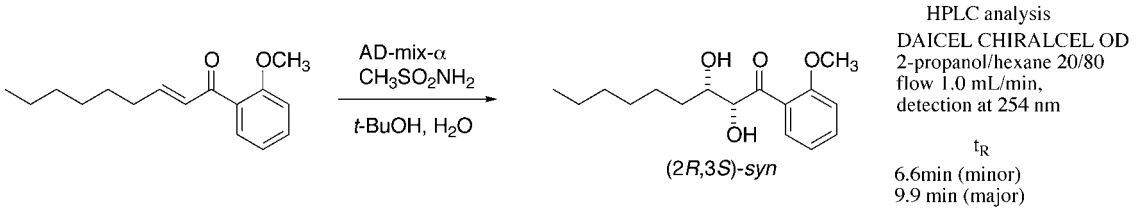



**(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-nonanone ( from *syn*-4c)** :

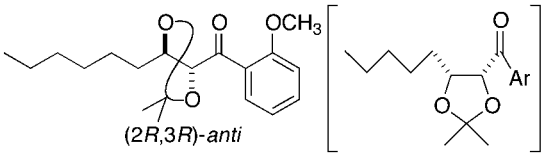



colorless oil; IR (neat) ν 2932, 1685, 1599, 1246, 1163 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.14-1.32 (m, 7H), 1.30 (s, 3H), 1.34-1.45 (m, 1H), 1.42 (s, 3H), 1.52-1.64 (m, 2H), 3.83 (s, 3H), 4.18 (ddd, *J* = 4.6, 7.0, 7.0 Hz, 1H), 4.88 (d, *J* = 7.0, 1H), 6.91 (brd, *J* = 8.5 Hz, 1H), 6.96 (ddd, *J* = 0.9, 7.6, 7.6 Hz, 1H), 7.41 (ddd *J* = , 1.8, 7.0, 7.6 Hz, 1H), 7.47 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 14.0, 22.4, 25.5, 26.0, 27.4, 29.0, 31.6, 33.8, 55.5, 78.4, 84.7, 110.0, 111.4, 120.7, 127.6, 130.0, 133.3, 157.8, 201.7; EI-MS *m/z* 320 [$M^+$] ,135 [$ArCO^+$];

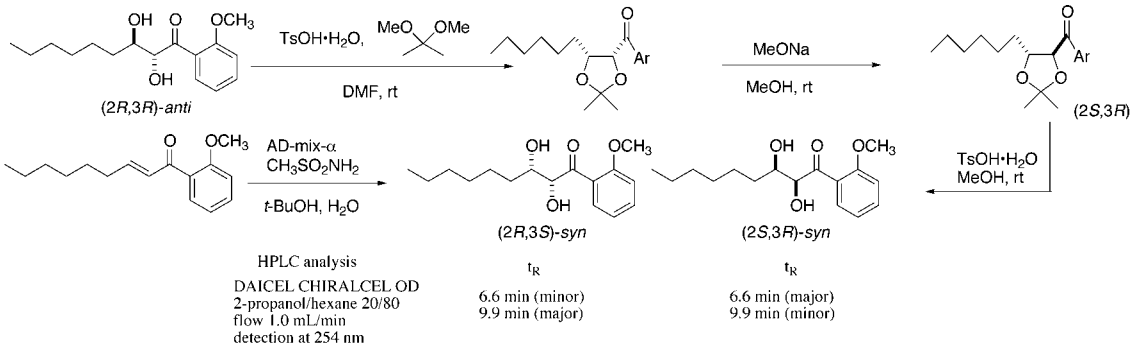
$[\alpha]_D^{22}$ –20.8 (*c* 0.38, $CHCl_3$) (96% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.6 min (minor) and 9.9 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4c** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



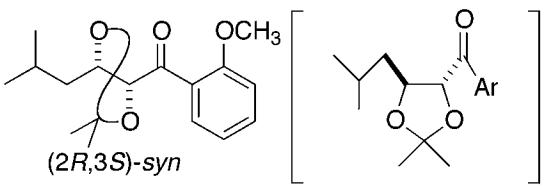

**(2*R*,3*R*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-5-methyl-1-(2-methoxyphenyl)-1-nonanone (from *anti*-4c)** :




colorless oil; IR (neat) ν 2930, 1685, 1598, 1245, 1164 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.79 (t, *J* = 7.2 Hz, 3H), 1.08, 1.42 (m, 10H), 1.39 (s, 3H), 1.59 (s, 3H), 3.89 (s, 3H), 4.46 (ddd, *J* = 3.1, 7.0, 10.1 Hz, 1H), 5.54 (d, *J* = 7.0 Hz, 1H), 6.94 (brd, *J* = 8.2 Hz, 1H), 7.01 (ddd, *J* = 0.8, 7.6, 7.6 Hz, 1H), 7.47 (ddd, *J* = 1.8, 7.6, 8.2 Hz, 1H), 7.78 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 14.0, 22.5, 25.7, 26.3, 27.3, 28.9, 31.2, 31.6, 55.5, 78.0, 82.6, 109.3, 111.6, 121.1, 126.8, 131.0, 134.2, 158.4, 197.2; EI-MS *m/z* 320 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{22}$ +41.4 (*c* 0.29, $CHCl_3$) (87% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.5 min (major) and 7.9 min (minor). Ee was determined after cleavage of the acetonide. An authentic sample was prepared by using AD-mix-α. The absolute configuration of *anti*-**4c** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below.

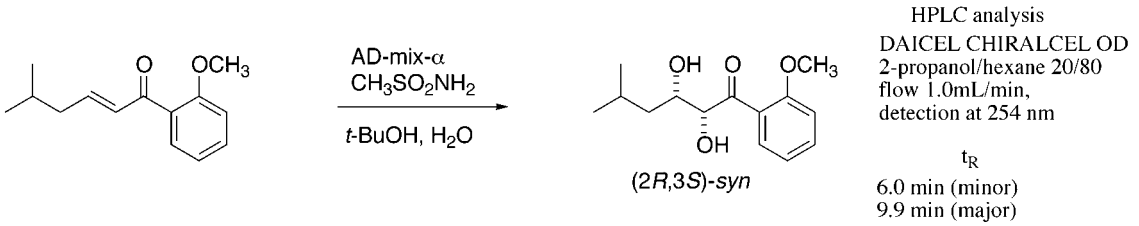



**(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-5-methyl-1-hexanone (from *syn*-4d)** :

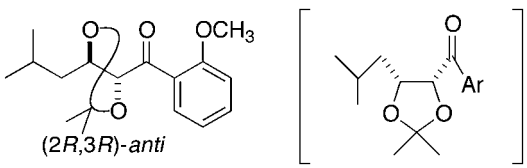



colorless oil; IR (neat) ν 2956, 1685, 1598,

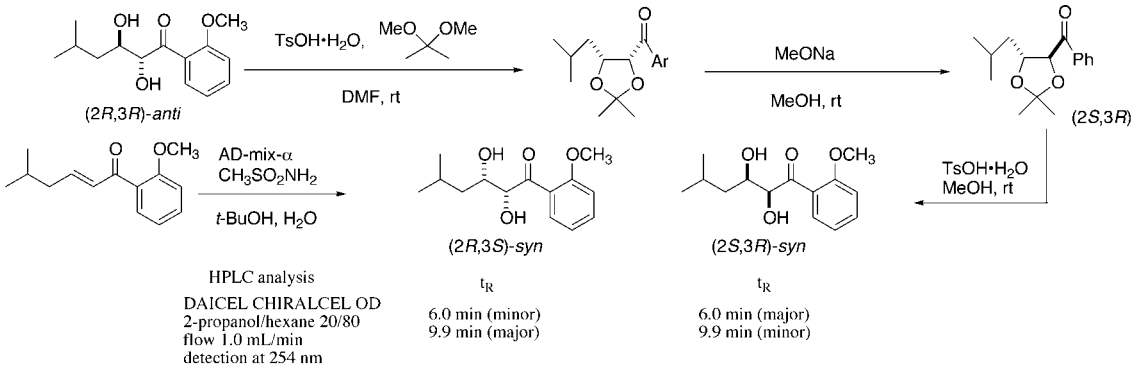
1246, 1097 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.83 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H) 1.30-1.35 (m, 1H), 1.32 (s, 3H), 1.44 (s, 3H), 1.61 (ddd, *J* = 5.4, 9.2, 14.1 Hz, 1H), 1.68-1.79 (m, 1H), 3.85 (s, 3H), 4.26 (ddd, *J* = 3.7, 7.0, 9.2 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 6.93 (brd, *J* = 8.4 Hz, 1H), 6.99 (ddd, *J* = 0.9, 7.5, 7.5 Hz, 1H), 7.44 (ddd, *J* = 1.9, 7.5, 8.4 Hz, 1H), 7.49 (dd, *J* = 1.9, 7.5 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 21.8, 23.4, 25.2, 26.1, 27.6, 43.2, 55.6, 76.9, 85.3, 110.2, 111.5, 120.8, 127.7, 130.0, 133.3, 157.9, 201.7; EI-MS *m/z* 293[($M^+$+1)], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ –29.9 (*c* 0.83, $CHCl_3$) (93% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.0 min (minor) and 9.9 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4d** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



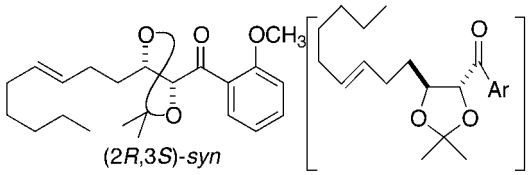

**(2*R*,3*R*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-5-methyl-1-hexanone (from *anti*-4d)** :




colorless oil; IR (neat) ν 2956,1684, 1598, 1245, 1088 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.81 (d, *J* = 6.7 Hz, 6H), 0.95 (ddd, *J* = 2.8, 9.5, 13.4 Hz, 1H), 1.40 (ddd, *J* = 4.3, 10.8, 13.4 Hz, 1H), 1.40 (s, 3H), 1.56 (s, 3H), 1.66-1.76 (m, 1H), 3.90 (s, 3H), 4.58 (ddd, *J* = 2.8, 7.0, 10.8 Hz, 1H), 5.52 (d, *J* = 7.0 Hz, 1H), 6.95 (brd, *J* = 8.3 Hz, 1H), 7.02 (ddd, *J* = 0.9, 7.3, 7.6 Hz, 1H), 7.48 (ddd, *J* = 1.8, 7.3, 8.3 Hz, 1H), 7.81 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 21.2, 23.6, 25.0, 25.7, 27.4, 40.0, 55.4, 76.2, 82.6, 109.4, 111.6, 121.1, 126.7, 131.1, 134.3, 158.4, 197.2; EI-MS *m/z* 292 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ +51.4 (*c* 0.65, $CHCl_3$) (87% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.5 min (minor) and 8.0 min (major). Ee was determined after cleavage of the acetonide. An authentic sample was prepared by using AD-mix-α. The absolute configuration of *anti*-**4d** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below.

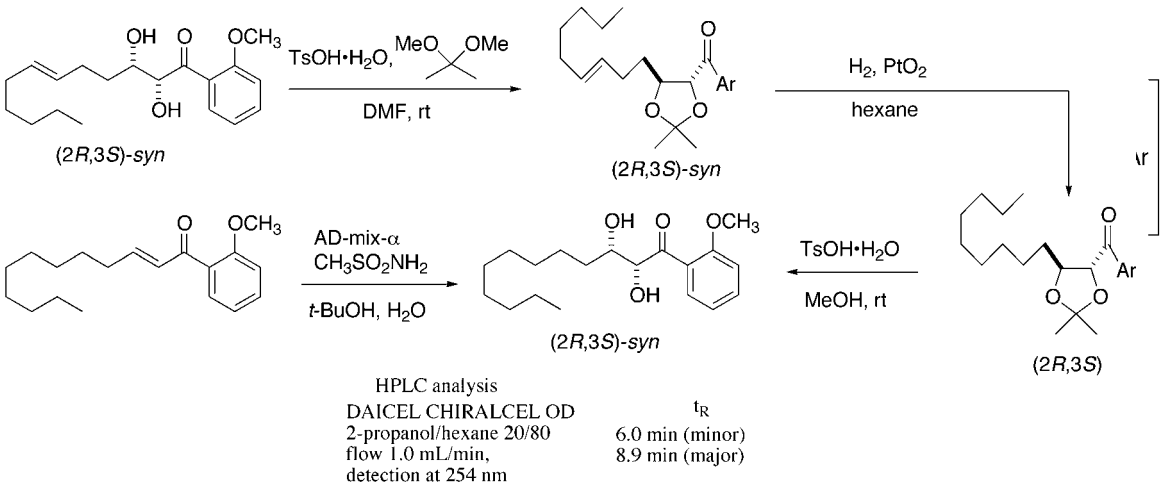



**(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-6-dodecene-1-one (from *syn*-4e)** :

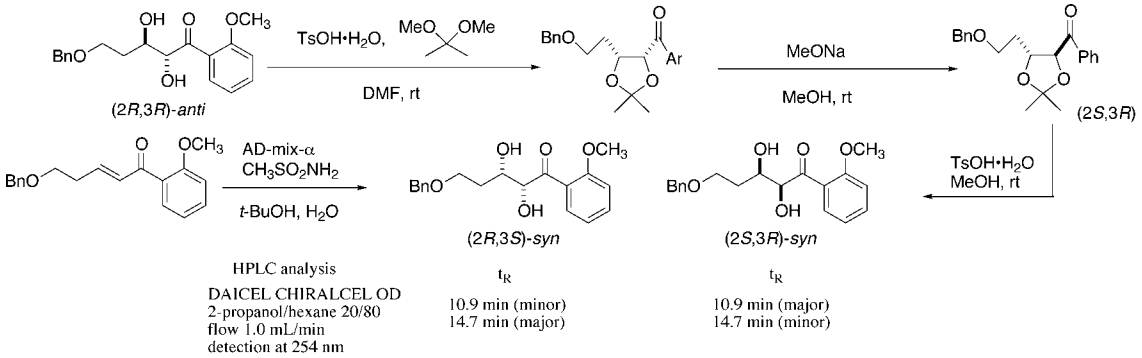



colorless oil; IR (neat) ν 2927, 1686, 1599 1247, 1096 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.2 Hz, 3H), 1.15-1.32 (m, 6H), 1.43 (s, 3H), 1.58-1.72 (m, 2H), 1.87-1.95 (m, 2H), 1.96-2.05 (m, 1H), 2.08-2.15 (m, 1H), 3.84 (s, 3H), 4.18-4.22 (m, 1H), 4.91 (d, *J* = 6.7 Hz, 1H), 5.27-5.39 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.97 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.42 (ddd, *J* = 1.5, 7.5, 8.5 Hz, 1H), 7.48 (d, *J* = 1.5, 7.5 Hz, 1H).; $^{13}C$ NMR ($CDCl_3$) δ 14.0, 22.5, ,26.0, 27.4, 28.5, 29.1, 31.3, 32.5, 33.8, 55.6, 77.9, 84.6, 110.1, 111.4, 120.7, 127.5, 128.8, 130.1, 131.1, 133.3, 157.9, 201.5; EI-MS *m/z* 360 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ –19.6 (*c* 0.78, $CHCl_3$) (87% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.3min (minor) and $t_R$ 10.3 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4e** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.

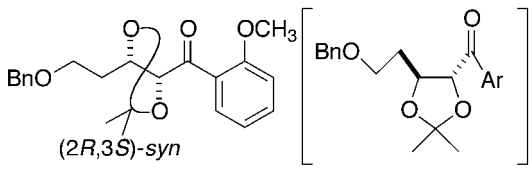
**(2*R*,3*R*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-6-dodecene-1-one (from *anti*-4e)** :



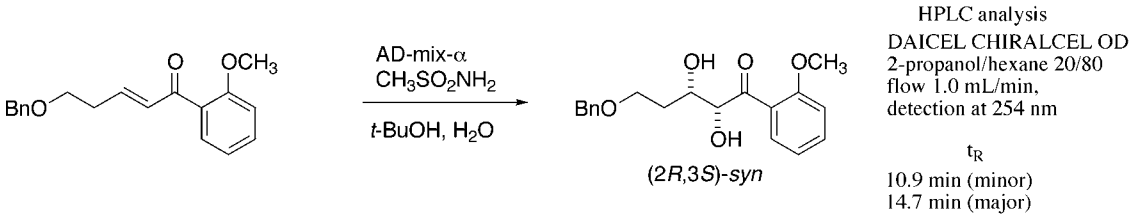
colorless oil; IR (neat) ν 2927, 1684, 1245, 1090 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.15-1.31 (m, 7H), 1.39 (s, 3H), 1.38-1.48 (m, 1H), 1.59 (s, 3H), 1.86-1.96 (m, 3H), 2.04-2.14 (m, 1H), 3.88 (s, 3H), 4.47 (ddd, *J* = 3.1, 7.0, 10.1 Hz, 1H), 5.20-5.34 (m, 2H), 5.53 (d, *J* = 7.0 Hz, 1H), 6.94 (brd, *J* = 8.2 Hz, 1H), 7.00 (ddd,, *J* = 0.8, 7.6, 7.6 Hz, 1H), 7.46 (ddd, *J* = 1.8, 7.6, 8.2 Hz, 1H), 7.79 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 14.0, 22.4, 25.6, 27.3, 29.1, 29.1, 31.0, 31.3, 32.4, 55.5, 77.2, 82.5, 109.3, 111.6, 121.1, 126.7, 128.8, 131.0, 131.2, 134,2, 158.4, 197.2; EI-MS *m/z* 360 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ +42.1 (*c* 1.32, $CHCl_3$) (92% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.6 min (minor) and 8.2 min (major). Ee was determined after cleavage of the acetonide. An authentic sample was prepared by using AD-mix-α. The absolute configuration of *anti*-**4e** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below.



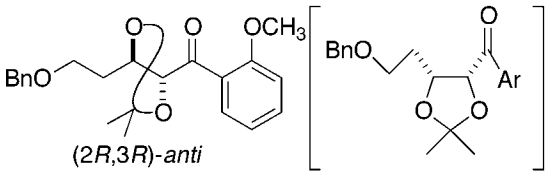

**(2*R*,3*S*)-5-Benzyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-pentanone (from *syn*-4f)**:



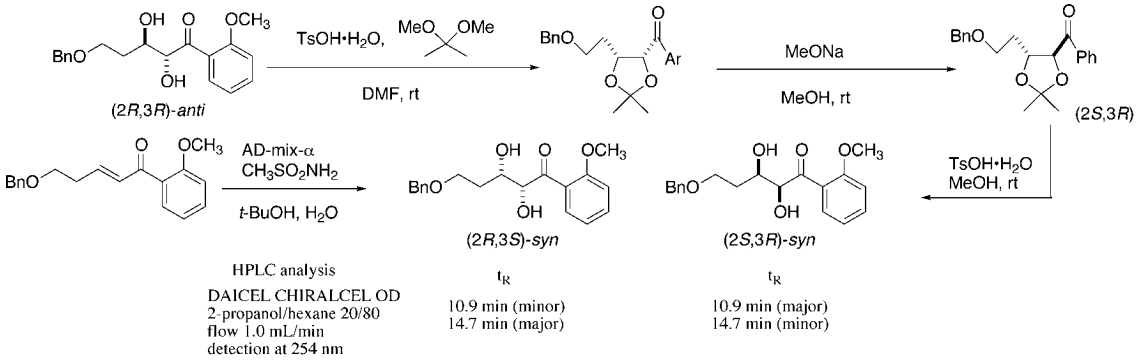

IR (neat) ν 2936, 1685, 1248, 1097 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.43 (s, 3H), 1.90-2.00 (m, 2H), 3.51-3.61 (m, 2H), 3.79 (s, 3H), 4.36-4.40 (m, 1H), 4.40 (s, 2H), 5.02, d, *J* = 6.7 Hz, 1H), 6.87 (brd, *J* = 8.2 Hz, 1H), 6.96 (ddd, *J* = 0.9, 7.6, 7.6 Hz, 1H), 7.19-7.29 (m, 5H), 7.41 (ddd, *J* = 1.8, 7.6, 8.2 Hz, 1H), 7.51 (dd, *J* = 1.8, 7.6 Hz, 1H) ; $^{13}C$ NMR ($CDCl_3$) δ 26.1, 27.4, 34.1, 55.5, 66.8, 72.8, 75.8, 84.6, 110.1, 111.5, 120.7, 127.3, 127.4, 127.5, 128.2, 130.2, 133.4, 138.3, 158.0, 200.9; EI-MS *m/z* 370 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ –16.1 (*c* 1.5, $CHCl_3$) (95% ee); HPLC (for diol) (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 10.9 min (minor) and 14.7 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4f** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



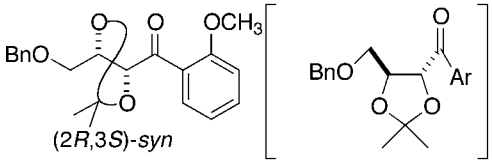

**(2*R*,3*R*)-5-benzyloxy-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-pentanone (from *anti*-4f)**:




colorless oil; IR (neat) ν 2933, 1683, 1598, 1246, 1091 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.41 (s, 3H), 1.59 (s, 3H), 1.57-1.67 (m, 2H), 3.48-3.58 (m, 2H), 3.86 (s, 3H), 4.41 (d, *J* = 6.9 Hz, 1H), 4.43 (d, *J* = 6.9Hz, 1H), 4.71 (ddd, *J* = 3.7, 7.0, 10.1 Hz, 1H), 5.58 (d, *J* = 7.0 Hz, 1H), 6.93 (brd, *J* = 8.6 Hz, 1H), 7.01 (ddd, *J* = 0.9, 7.9, 7.9 Hz, 1H), 7.22-7.31 (m, 5H), 7.47 (ddd, *J* = 1.8, 7.9, 8.6 Hz, 1H), 7.81 (dd, *J* = 1.8, 7.9 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 25.4, 27.4, 31.7, 55.5, 67.2, 72.9, 74.8, 82.4, 109.5, 111.7, 121.1, 126.5, 127.5, 127.5, 128.3, 131.1, 134.4, 138.5, 158.6, 196.9; EI-MS *m/z* 370 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ +35.0 (*c* 0.17 $CHCl_3$) (90% ee); HPLC (for diol) (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 12.6 min (minor) and 15.0 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *anti*-**4f** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.

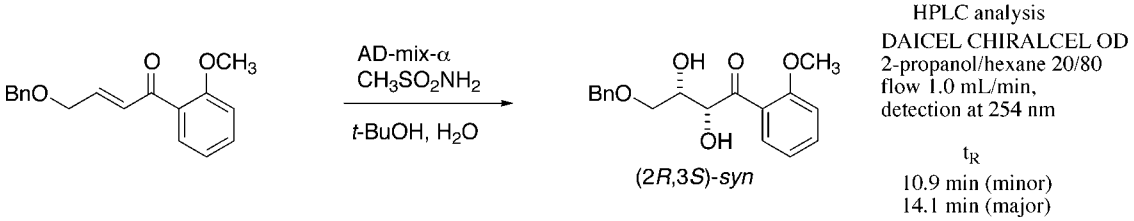



**(2*R*,3*S*)-4-Benzyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-butanone (from *syn*-4g)**:

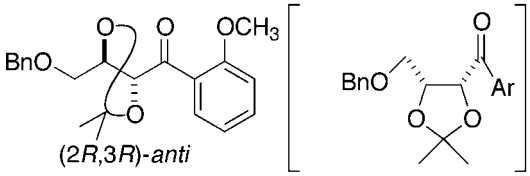



colorless oil; IR (neat) ν 2936, 1684, 1598, 1247, 1096 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.33 (s, 3H), 1.47 (s, 3H), 3.56 (dd, *J* = 5.8, 10.7 Hz, 1H), 3.63 (dd, *J* = 3.4, 10.7 Hz, 1H), 3.77 (s, 3H), 4.45 (ddd, *J* = 3.4, 5.8, 6.7 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H),

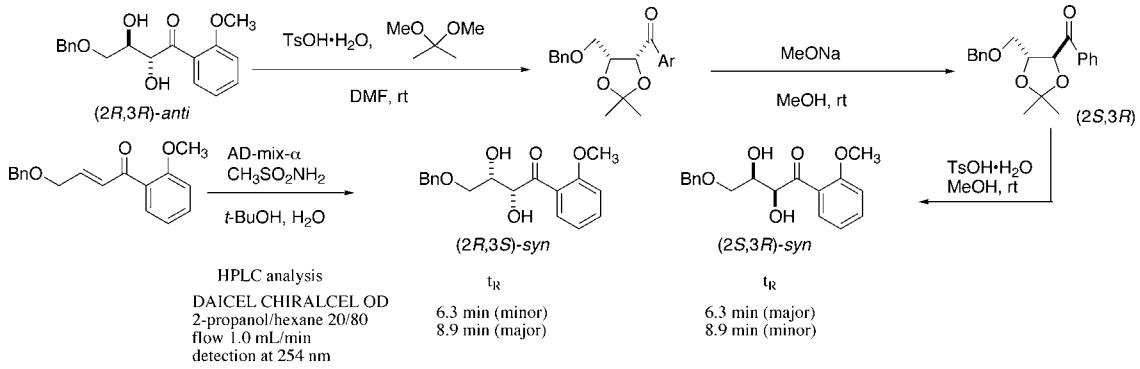
4..56 (d, *J* = 7.8 Hz, 1H), 5.09 (d, *J* = 6.7 Hz, 1H), 6.89 (brd, *J* = 8.5 Hz, 1H), 6.97 (ddd, *J* = 0.8, 7.6, 8.5 Hz, 1H), 7.24-7.36 (m, 5H), 7.43 (ddd, *J* = 1.8, 7.6, 8.5 Hz, 1H), 7.50 (dd, *J* = 1.8, 7.6 Hz, 1H) ; $^{13}$C NMR ($CDCl_3$) δ 26.1, 27.2, 55.6, 70.6, 73.4, 77.9, 81.7, 111.1, 111.5, 120.8, 127.3, 127.6, 127.7,128.3, 130.2, 133.5, 138.0, 158.0, 201.3; EI-MS *m/z* 356 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{23}$ –19.3 (*c* 0.36, $CH_2Cl_2$) (96% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 10.9 min (minor) and 14.1 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4g** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



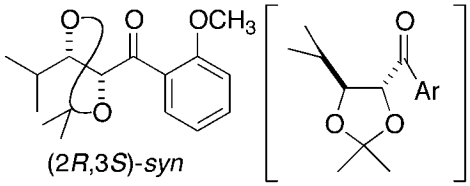

**(2*R*,3*R*)-4-Benzyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-butanone (from *anti*-4g)**:



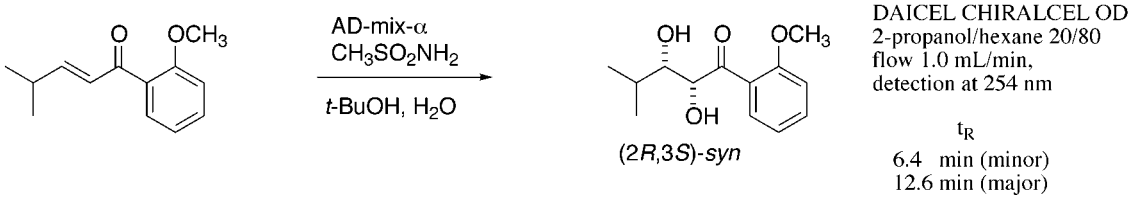

colorless oil; IR (neat) ν 2963, 1686, 1599, 1247 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.50 (s, 3H), 1.68 (s, 3H), 3.44 (dd, *J* = 6.4, 9.8 Hz, 1H), 3.48 (dd, *J* = 5.2, 9.8 Hz, 1H), 3.87 (s, 3H), 4.30 (d, *J* = 6.9 Hz, 1H), 4.40 (d, *J* = 6.9 Hz, 1H), 4.81 (ddd, *J* = 5.2, 6.4, 7.0 Hz, 1H), 5.65 (d, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.09-7.13 (m, 2H), 7.22-7.27 (m, 3H), 7.52 (ddd, *J* = 1.5, 7.6, 8.5 Hz, 1H), 7.90 (dd, *J* = 1.5, 7.6 Hz, 1H) ; $^{13}$C NMR ($CDCl_3$) δ 25.4, 27.3, 55.5, 69.1, 72.9, 76.8, 81.2, 109.2, 111.6, 120.9, 126.2, 127.2, 127.4, 128.0, 130.9, 134.3, 137.7, 158.6, 195.0; EI-MS *m/z* 356 [$M^+$], 135 [$ArCO^+$]; $[\alpha]_D^{25}$ +59.0 (*c* 0.65, $CHCl_3$) (93% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane, flow 1.0 mL/min, detection at 254 nm) $t_R$ 10.8 min (minor) and 13.3 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *anti*-**4g** was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.



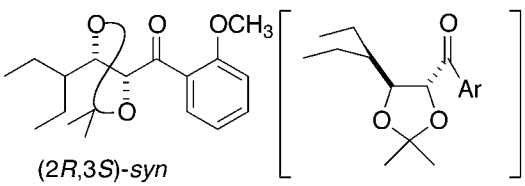

**(2*R*,3*S*)-2,3-dihydroxy-2,3-*O*-isopropylidene-4-methyl-1-(2-methoxyphenyl)-1-pentanone (from *syn*-4h)**:




colorless oil; IR (neat) ν 2963, 1686, 1598, 1247cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.87 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 1.24 (s, 3H), 1.40 (s, 3H), 1.78 (dtt, *J* = 6.4, 6.7, 6.7 Hz, 1H), 3.84 (s, 3H), 4.13 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.93 (d, *J* = 6.4 Hz, 1H), 6.92 (brd, *J* = 8.6 Hz, 1H), 6.96 (ddd, *J* = 0.9, 7.6, 7.6 Hz, 1H), 7.41 (ddd, *J* = 1.8, 7.6, 8.6 Hz, 1H), 7.45 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 17.5, 18.9, 25.8, 27.1, 31.1, 55.7, 82.5, 82.9, 110.0, 111.5, 120.6, 127.9, 130.1, 133.1, 157.9, 202.7; EI-MS *m/z* 279 [($M^+$+1)], 135 [$ArCO^+$]; $[\alpha]_D^{24}$ –40.0 (*c* 0.43, $CHCl_3$ ) (98% ee); HPLC ((for diol) DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.4 min (minor) and 12.6 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4h** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.

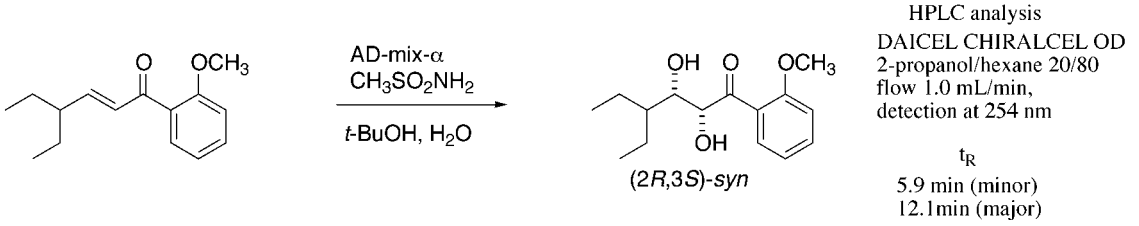



**(2*R*,3*S*)-4-Ethyl-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-hexanone (from *syn*-4i)**:

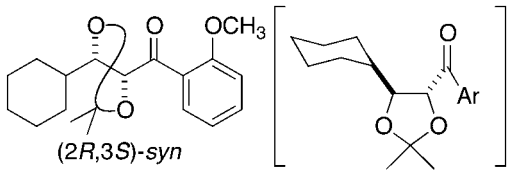



colorless oil; IR (neat) ν 2963, 1686, 1599, 1247 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.78 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H), 1.23 (s, 3H), 1.20-1.47 (m, 5H), 1.38 (s, 3H), 3.81 (s, 3H), 4.33 (dd, *J* = 4.8, 6.7 Hz, 1H), 4.95 (d, *J*

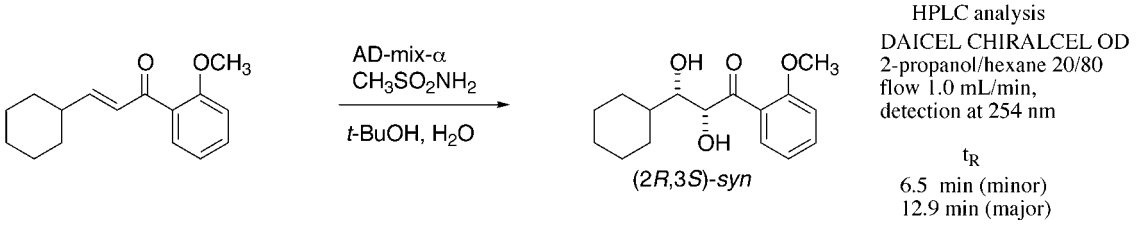
= 6.7 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.94 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.39 (ddd, *J* = 1.8, 7.6, 8.2 Hz, 1H), 7.42 (dd, *J* = 1.8, 7.6 Hz, 1H) ; $^{13}$C NMR ($CDCl_3$) δ 11.2, 11.2, 21.1, 22.3, 25.6, 27.0, 43.6, 55.6, 79.5, 82.4, 109.8, 111.4, 120.6, 127.9, 129.9, 133.0, 157.7, 202, 7; EI-MS *m/z* 307 [$M^+$]; $[\alpha]_D^{24}$ –29.7 (*c* 0.81 $CHCl_3$) (99% ee); HPLC (for diol) (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 5.9 min (major) and 12.1 min (minor). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4i** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.




**(2*R*,3*S*)-3-Cyclohexyl-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-propanone (from *syn*-4j)**:



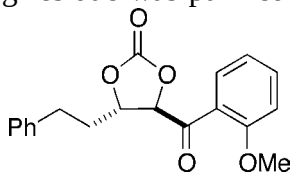

colorless oil; IR (neat) ν 2926, 1684, 1598, 1247 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ 0.99-1.25 (m, 5H), 1.22 (s, 3H), 1.38 (s, 3H), 1.40-1.75 (m, 5H), 1.81-1.88 (m, 1H), 3.83 (s, 3H), 4.13 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 6.91 (brd, *J* = 8.5 Hz, 1H), 6.95 (ddd, *J* = 0.6, 7.6, 7.6 Hz, 1H), 7.40 (ddd, *J* = 1.5, 7.6, 8.5 Hz, 1H), 7.45 (dd, *J* = 1.5, 7.6 Hz, 1H) ; $^{13}$C NMR ($CDCl_3$) δ 25.8, 25.8, 26.0, 26.3, 27.0, 28.1, 29.5, 40.9, 55.7, 82.1, 82.2, 109.9, 111.5, 120.6, 127.9, 130.1, 133.1, 157.9, 202.4; EI-MS *m/z* 318 [$M^+$], 135 [$ArCO^+$] ; $[\alpha]_D^{24}$ –28.6 (*c* 1.0, $CHCl_3$) (98% ee); HPLC (for diol) (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) $t_R$ 6.5 min (minor) and 12.9 min (major). Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**4j** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix-α.




**(2*R*,3*S*)-2,3-Carbonyldioxy-1-(2-methoxyphenyl)-5-phenyl-1-pentanone (6a)**

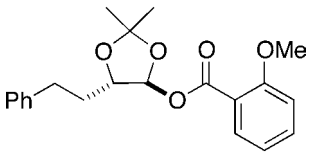
To a stirred solution of **4a** (162.2 mg, 0.540 mmol) in $CH_2Cl_2$ (3.5 ml) was added pyridine (0.0572 mL, 0.702 mmol) at room temperature. After cooling to –20 ℃,

triphosgene (0.351mL, 2.0 M in $CH_2Cl_2$, 0.702 mmol) was added slowly and stirred for 1 h at room temperature. The resulting solution was quenched with saturated aqueous $NH_4Cl$ and extracted with ether (4 mL x 3). The combined organic extracts were washed successively with 1M HCl, saturated aqueous $NaHCO_3$ and brine and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 3/1) to give **6a** (164.4 mg, 0.504 mmol, yield 93 %) as a colorless oil : IR (neat) ν 1810, ,1681 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 2.22-2.31 (m, 2H), 2.82 (ddd, *J* = 7.9, 8.5, 14.0 Hz, 1H), 2.95 (ddd, *J* = 5.1, 9.4, 14.7 Hz, 1H), 3.88 (s, 3H), 4.73 (ddd, *J* = 3.0, 4.2, 8.0 Hz, 1H), 5.35 (d, *J* = 4.2 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 7.10 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.21-7.27 (m, 3H), 7.30-7.36 (m, 2H), 7.59 (ddd, *J* = 1.8, 7.6, 8.5 Hz, 1H), 7.77 (dd, *J* = 1.8, 7.6 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 30.6, 36.6, 55.6, 78.1, 82.6, 111.5, 121.6, 124.1, 126.5, 128.4, 128.7, 131.3, 135.5, 139.9, 154.3, 158.6, 194.9; EI-MS *m/z* 326 [$M^+$] ; $[\alpha]_D^{25}$ –120 (*c* 0.40, $CHCl_3$).




**(4*S*,5*S*)-2,2-Dimethyl-5-(2-phenylethyl)-1,3-dioxolan-4-yl 2-methoxybenzoate (7a).**

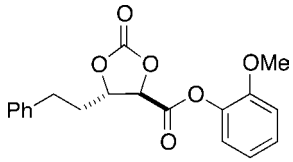
To a stirred solution of **5a** (29.0 mg, 0.0847 mmol) in dichloroethane (0.5 mL) at room temperature were added $NaH_2PO_4$_$2H_2O$ (40.0 mg, 0.254 mmol) and *m*-chloroperbenzoic acid (41.2 mg, 0.167 mmol, >70%). After being stirred for 1h at 50 ℃, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$. The resulting mixture was extracted with diethyl ether (2 mL x 3). The combined organic extracts were washed with ice-cooled saturated aqueous $NaHCO_3$ (2 mL x 2 ) and brine, and then dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate 10/1) to give **7a** (27.0 mg, 0.0754 mmol, yield 89%) as a colorless solid : IR (KBr) ν 2940, 1719, 1240, 1070 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.57 (s, 3H), 1.60 (s, 3H), 1.96-2.12 (m, 2H), 2.37-2.87 (m, 2H), 3.90 (s, 3H), 4.37 (ddd, *J* = 2.1, 5.5, 7.9 Hz, 1H), 6.29 (d, *J* = 2.1 Hz, 1H), 6.97-7.03 (m, 2H), 7.19-7.25 (m, 3H), 7.26-7.32 (m, 2H), 7.51 (ddd, *J* = 1.5, 7.9, 7.9 Hz, 1H), 7.84 (dd, *J* = 1.5, 7.9 Hz, 1H); $^{13}C$ NMR ($CDCl_3$) δ 26.7, 27.9, 31.4, 34.7, 55.8, 81.9, 99.6, 112.0, 112.5, 119.3, 120.1, 126.0, 128.4, 131.9, 134.0, 141.2, 159.6, 165.4; EI-MS *m/z* 356 [$M^+$], 201 [$M^+$–ArCOO], $[\alpha]_D^{24}$ 62.3 (*c* 0.47, $CHCl_3$).




**2-Methoxyphenyl (2*R*,3*S*)-2,3-carbonyldioxy-5-phenylpentanoate (8a)**

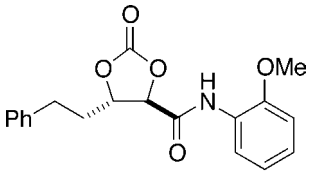
To a stirred solution of **6a** (20.2 mg, 0.0619 mmol) in dichloroethane (0.5 ml) at room temperature were added $NaH_2PO_4$_$2H_2O$ (29.0 mg, 0.186 mmol) and *m*-chloroperbenzoic acid (30.6 mg, 0.124 mmol, >70%). After being stirred for 2 h at 50 ℃, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$. The resulting mixture was extracted with diethyl ether (2 mL x 3). The combined organic extracts were washed with ice-cooled saturated aqueous $NaHCO_3$ (2 mL x 2 ) and brine, and then dried over $Na_2SO_4$.

The solvent was evaporated under reduced pressure, and the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate 6/1) to give **8a** (19.7 mg, 0.0575 mmol, yield 93%) as acolorless solid : IR (KBr) ν 2927, 1796, 1772 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 2.25 (ddd *J* = 1.8 5.5, 7.6 Hz, 2H), 2.82-2.97 (m, 2H), 3.67 (s, 3H), 4.85 (ddd, *J* = 1.8, 5.5, 5.5 Hz, 1H), 4.92 (d, *J* = 5.5 Hz, 1H), 6.96 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.04 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.22-7.26 (m, 4H), 7.30-7.33 (m, 2H) ; $^{13}C$ NMR ($CDCl_3$) δ 30.5, 36.0, 55.8, 76.9, 78.6, 112.4, 120.9, 122.2, 126.6, 127.8, 128.5, 128.7, 138.5, 139.2, 150.4, 153.3, 165.1; EI-MS *m/z* 342 [$M^+$]; $[\alpha]_D^{25}$ –112 (*c* 0.44, $CHCl_3$ ).



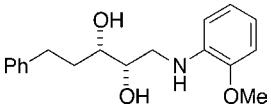

**(2*R*,3*S*)-2,3-Carbonyldioxy-2´-methoxy-5-phenylpentanilide** (**9a**)

To a stirred solution of **6a** (83.2 mg, 0.243 mmol) in $CH_2Cl_2$ was added *O*-mesitylenesulfonylhydroxylamine (MSH, prepared by the procedure of a literature cited in ref 20) (104 mg, 0.485 mmol) at room temperature. After stirring for 4 h at the same temperature, the reaction mixture was concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 6/1) to give **9a** (80.6 mg, 0.236 mmol, yield 97%) as a colorless oil : IR (neat) ν 2939, 1813, 1693, 1255 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 2.16-2.26 (m, 1H), 2.27-2.36 (m, 1H), 2.78-2.88 (m, 1H), 2.79-2.87 (m, 1H), 2.93 (ddd, *J* = 5.8, 9.7, 14.6 Hz, 1H), 3.90 (s, 3H), 4.71 (d, *J* = 6.4, Hz, 1H), 4.78-4.84 (m, 1H), 6.89-7.00 (m, 2H), 7.12 (ddd, *J* = 1.5, 7.9, 7.9 Hz, 1H), 7.20-7.33 (m, 5H), 8.26 (dd, *J* = 1.2, 7.9 Hz, 1H), 8.64 (brs, 1H).; $^{13}C$ NMR ($CDCl_3$) δ 30.7, 36.6, 55.8, 78.0, 79.9, 110.2, 120.0, 120.9, 125.3, 125.7, 126.5, 128.4, 128.7, 139.5, 148.4, 152.6, 164.3; EI-MS_*m/z* 341 [$M^+$]; $[\alpha]_D^{24}$ –75.0 (*c* 0.96, $CHCl_3$).




**(2*R*,3*S*)-1-*o*-anisidino-5-phenyl-2,3-pentanediol** (**10a**)

To a stirred solution of **9a** (18.4 mg, 0.054 mmol) in $CH_2Cl_2$ (0.3 ml) at – 78 °C was added diisobutylaluminum hydride (DIBAL, 0.216 ml, 0.216 mmol, 1.01 M in toluene). The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature and then quenched with saturated aqueous $NH_4Cl$. (2mL) , followed by addition of potassium sodium (+)-tartrate tetrahydrate (Rochelle salt, 30mg). After stirring for 2h at room temperature, the resulting mixture was extracted with diethyl ether (2 mL x 3) and the combined organic extracts were washed with brine and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 3/1) to afford **10a** (15.3 mg, 0.051 mmol, yield 94%) as a colorless oil : IR (neat) ν 3409, 1602, 1510, 1456, 1222 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 1.75-1.90 (m, 2H), 2.62-2.70 (m, 1H), 2.78 (ddd, *J* = 5.7, 9.7, 14.0 Hz, 1H), 3.16 (dd, *J* = 7.6, 13.1 Hz, 1H), 3.23 (dd, *J* = 3.9, 13.1 Hz, 1H), 3.55 (ddd, *J* = 3.9, 3.9,



8.5 Hz, 1H), 3.68 (ddd, *J* = 3.9, 3.9, 7.6 Hz, 1H), 3.76 (s, 3H), 6.58 (dd, *J* = 1.2, 7.9 Hz, 1H), 6.65 (ddd, *J* = 7.9, 7.9 Hz, 1H), 6.71 (dd, *J* = 1.2, 7.9 Hz, 1H), 6.80 (ddd, *J* = 1.2, 7.9, 7.9 Hz, 1H), 7.10-7.16 (m, 3H), 7.19-7.24 (m, 2H); $^{13}$C NMR ($DCl_3$) δ 31.9, 35.6, 47.3, 55.4, 72.1, 72.2, 109.6, 110.6, 117.5, 121.2, 125.9, 128.5, 128.5, 137.9, 141.7, 147.3; EI-MS_*m/z* 301 [$M^+$]; $[\alpha]_D^{24}$ –20.7 (*c* 0.54, $CHCl_3$).