Supporting Information

Direct Catalytic Asymmetric Aldol Reaction of Hydroxyketones: Asymmetric Zn Catalysis with a Et₂Zn/linked-BINOL Complex (1)

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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 ¹H NMR and 125.65 MHz for ¹³C NMR. Chemical shifts in CDCl₃ were reported downfield from TMS (= 0) or in the scale relative to CHCl₃ (7.24 ppm) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to CHCl₃ (77.0 ppm) for ¹³C NMR as an internal reference. Chemical shifts in THF-*d*₆ were reported in the scale relative to THF (3.58 ppm for ¹H NMR and 67.4 ppm for ¹³C NMR). Optical rotations were measured on a JASCO P-1010 polarimeter. EI and FAB mass spectra were measured on JMS-BU20 GCmate. ESI mass spectra were measured on Waters-ZQ4000. 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, OD-H, OJ, OJ-H, CHIRALPAK AS, AS-H, AD, AD-H; 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. Et₂Zn (1.0 M, in hexanes) was purchased from Aldrich. Other reagents were purified by the usual methods.

(A) First generation Et₂Zn/linked-BINOL 1 = 2/1 system:

General Procedure for Catalytic Asymmetric Aldol Reaction of Ketone 7d Promoted by Et₂Zn/(*S,S*)-linked-BINOL = 2/1 System:

To a stirred solution of (*S,S*)-linked-BINOL (6.41 mg, 4.1 w/w% diethyl ether and hexane included, 0.01 mmol) in THF (0.3 mL) at –78 °C, was added Et₂Zn (20 μL, 0.02 mmol, 1.0 M in hexanes). After stirring for 30 min at –20 °C, a solution of **7d** (322.3 mg, 2.0 mmol) in THF (4.7 mL) was added. The resulting mixture was cooled to –30 °C, and aldehyde **6a** (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 Na₂SO₄. Evaporation of solvent gave a crude mixture of the aldol products. The diastereomeric ratios of the aldol products were determined by ¹H 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 NaHCO₃ (12 mL), H₂O 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 H₂O and with brine (×2) and dried over Na₂SO₄. 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

(*2R, 3S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-6-phenyl-1-pentanone
(from *syn*-8a) :

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, $J = 6.9, 9.8, 14.1\text{ Hz}$, 1H), 2.80 (ddd, $J = 5.5, 10.0, 14.1\text{ Hz}$, 1H), 3.82 (s, 3H), 4.21-4.23 (m, 1H), 4.95 (d, $J = 6.7\text{ Hz}$, 1H), 6.92 (brd, $J = 8.3\text{ Hz}$, 1H), 6.99 (ddd, $J = 0.9, 7.5, 7.5\text{ Hz}$, 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^+]; $[\alpha]_{\text{D}}^{21} -39.4$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_4$, 341.1753; found, 341.1743. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**8a** 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*-8a**):**

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, $J = 2.8, 7.4, 10.1\text{ Hz}$, 1H), 5.49 (d, $J = 7.4\text{ Hz}$, 1H), 6.89 (brd, $J = 8.3\text{ Hz}$, 1H), 7.01 (ddd, $J = 0.9, 7.9, 7.9\text{ Hz}$, 1H), 7.04-7.22 (m, 5H), 7.47 (ddd, $J = 1.8, 7.0, 8.3\text{ Hz}$, 1H), 7.81 (dd, $J = 1.8, 7.9\text{ Hz}$, 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^+]; HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_4$, 341.1753; found, 341.1743; $[\alpha]_{\text{D}}^{22} +49.7$ (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*-**8a** 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*-8b**):**

colorless oil; IR (neat) ν 2934, 1686, 1598, 1247, 1024 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84 (t, $J = 6.9\text{ Hz}$, 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^+]; HRMS (FAB) (for diol) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{23}\text{O}_4$, 267.1596; found, 267.1595; $[\alpha]_{\text{D}}^{23} -21.6$ (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-8b* 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-8b*):

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]; $[\alpha]_{\text{D}}^{24} +50.3$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{27}\text{O}_4$, 307.1904; found, 307.1902. Ee was determined after cleavage of the acetonide. The absolute configuration of *anti-8b* was determined by HPLC analysis after emipерization of the acetonide.

as shown below.

(2*R*,3*S*)-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-nonanone (from *syn-8c*):

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^+]; $[\alpha]_{\text{D}}^{22} -20.8$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$,

321.2060; found, 321.2066. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn-8c* 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-nonanone (from *anti-8c*) :

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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$, 321.2060; found, 321.2065. Ee was determined after cleavage of the acetonide. An authentic sample was prepared by using AD-mix- α . The absolute configuration of *anti-8c* 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-8d*) :

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^+], 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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{O}_4$, 293.1747; found, 293.1752. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn-8d* was determined by HPLC

analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

(2R, 3R)-2,3-Dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-5-methyl-1-hexanone (from *anti*-8d) :

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) HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{25}\text{O}_4$, 293.1747; found, 293.1746. Ee was determined after cleavage of the acetonide. An authentic sample was prepared by using AD-mix- α . The absolute configuration of *anti*-8d was determined by HPLC analysis after emiperization of the acetonide as shown in the scheme below.

(2R, 3S)-2,3-Carbonyldioxy-1-(2-methoxyphenyl)-1,6-heptan-dione

(from *syn*-8e)

colorless solid; IR (KBr) ν 1807, 1715, 1678, 1598 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.00-2.07 (m, 1H), 2.16 (s, 3H), 2.16-2.25 (m, 1H), 2.69 (dd, $J = 6.1, 7.9$ Hz, 2H), 3.97 (s, 3H), 4.67 (ddd, $J = 3.6, 9.5, 9.5$ Hz, 1H), 5.38 (d, $J = 3.6$ Hz, 1H), 7.00 (d, $J = 8.2$ Hz, 1H), 7.05 (dd, $J = 7.3, 7.6$ Hz, 1H), 7.55 (ddd, $J = 1.8, 7.3, 8.2$ Hz, 1H), 7.78 (dd, $J = 1.8, 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 28.2, 30.0, 37.7, 55.8, 78.1, 82.6, 111.6, 121.5, 123.7, 131.4, 135.7, 154.2, 158.9, 194.0, 206.7; EI-MS m/z 292 [M^+], 135 [ArCO^+]; HRMS [M^+], calcd for $\text{C}_{15}\text{H}_{16}\text{O}_6$ 292.0947, found 292.0941; $[\alpha]_D^{25} -23.9$ (c 1.06, CHCl_3) (95% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 50/50, flow 1.0 mL/min, detection at 254 nm) t_R 12.4 min (minor) and 22.1 min (major).

(2R, 3S)-2,3-Dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-6-dodecene-1-one
(from *syn*-8f) :

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^+]; HRMS (FAB) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$, 321.2066; found, 321.2070; $[\alpha]_{\text{D}}^{23}$ -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*-**8f** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

(2R, 3R)-2,3-Dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-6-dodecene-1-one (from *anti*-8f**) :**

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^+]; HRMS (FAB) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4$, 321.2066; found, 321.2068; $[\alpha]_{\text{D}}^{23}$ $+42.1$ (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*-**8e** was determined by HPLC analysis after emipерization of the acetonide as shown in the scheme below.

(2*R*, 3*S*)-5-Benzoyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-pentanone (from *syn*-8*g*):

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^+]; HRMS (FAB)(for diol) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$, 331.1545; found, 331.1542; $[\alpha]_{\text{D}}^{23} -16.1$ (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*-8*g* 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-benzoyloxy-2,3-Dihydroxy-2,3-*O*-isopropylidene-1-(2-methoxyphenyl)-1-pentanone (from *anti*-8*g*):

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, $J = 6.9$ Hz, 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^+]; HRMS (FAB)(for diol) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$, 331.1545; found, 331.1540; $[\alpha]_{\text{D}}^{23} +35.0$ (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*-8*g* 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-Benzoyloxy-2,3-dihydroxy-2,3-*O*-

isopropylidene-1-(2-methoxyphenyl)-1-butanone (from *syn-8h*):

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^+]; $[\alpha]_{\text{D}}^{23} -19.3$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5$, 357.1697; found, 357.1698. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn-8h* was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

(2R,3R)-4-Benzyloxy-2,3-dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-1-butanone (from *anti-8h*):

colorless oil; IR (neat) ν 2963, 1686, 1599, 1247 cm^{-1} ; ^1H 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^+]; $[\alpha]_{\text{D}}^{25} +59.0$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5$, 357.1697; found, 357.1694. Ee was determined after cleavage of the acetonide. The absolute configuration of *anti-8h* 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 .

(2R,3S)-5-Benzyloxymethoxy-2,3-dihydroxy-1-(2-methoxyphenyl)-1-pentanone (*syn-8i*)

colorless oil; IR (neat) ν 3444, 2942, 1666, 1598 cm^{-1} ; ^1H NMR (CDCl_3)

δ 1.90-2.04 (m, 2H), 3.71-3.78 (m, 2H), 3.85 (s, 3H), 4.08 (dd, $J = 0.9, 3.9$ Hz, 1H), 4.54 (s, 2H), 4.71 (s, 2H), 5.03 (d, $J = 0.9$ Hz, 1H), 6.95 (d, $J = 8.2$ Hz, 1H), 7.03 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.21-7.33 (m, 5H), 7.41 (ddd, $J = 1.8, 7.6, 8.2$ Hz, 1H), 7.84 (dd, $J = 1.8, 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 34.9, 55.5, 65.0, 69.3, 69.4, 79.2, 94.5, 111.5, 121.2, 124.0, 127.6, 127.8, 128.3, 131.4, 134.7, 137.7, 158.5, 201.0; ESI-MS m/z 397 $[\text{M}+\text{Na}]^+$; HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{O}_6$, 361.1651; found, 361.1649; $[\alpha]_{\text{D}}^{28} +41.0$ (c 3.37, CHCl_3) (90% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 11.4 min (minor) and 17.1 min (major).

(2R,3R)-5-Benzyloxymethoxy-2,3-dihydroxy-1-(2-methoxyphenyl)-1-pentanone (anti-8i)

colorless oil; IR (neat) ν 3453, 2942, 1667, 1598 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.37-1.44 (m, 1H), 1.63-1.72 (m, 1H), 3.58-3.63 (m, 1H), 3.64-3.70 (m, 1H), 3.91 (s, 3H), 4.06 (ddd, $J = 2.7, 3.4, 7.6$ Hz, 1H), 4.45 (d, $J = 11.6$ Hz, 1H), 4.48 (d, $J = 11.6$ Hz, 1H), 4.60 (s, 2H), 5.33 (d, $J = 3.4$ Hz, 1H), 6.97 (d, $J = 8.5$ Hz, 1H), 7.01 (dd, $J = 7.3, 7.6$ Hz, 1H), 7.25-7.34 (m, 5H), 7.51 (ddd, $J = 1.8, 7.3, 8.5$ Hz, 1H), 7.73 (dd, $J = 1.8, 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 30.8, 55.7, 65.1, 69.3, 70.8, 80.1, 94.3, 111.8, 121.2, 124.9, 127.7, 127.9, 128.4, 131.0, 134.9, 137.7, 158.8, 200.9; ESI-MS m/z 383 $[\text{M}+\text{Na}]^+$; HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{O}_6$, 361.1651; found, 361.1662; $[\alpha]_{\text{D}}^{27} +26.8$ (c 0.84, CHCl_3) (84% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 13.0 min (minor) and 16.0 min (major).

(2R,3S)-2,3-dihydroxy-2,3-O-isopropylidene-4-methyl-1-(2-methoxyphenyl)-1-pentanone (from syn-8j):

colorless oil; IR (neat) ν 2963, 1686, 1598, 1247 cm^{-1} ; ^1H 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 $[\text{M}^+ + 1]$, 135 $[\text{ArCO}]^+$; $[\alpha]_{\text{D}}^{24} -40.0$ (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); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$, 279.1591; found, 279.1591. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn-8j* was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

HPLC analysis
DAICEL CHIRALCEL OD
2-propanol/hexane 20/80
flow 1.0 mL/min,
detection at 254 nm

t_{R}
6.4 min (minor)
12.6 min (major)

(2R,3S)-4-Ethyl-2,3-Dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-1-hexanone (from syn-8k):

colorless oil; IR (neat) ν 2963, 1686, 1599, 1247 cm^{-1} ; ^1H 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 $[M]^+$; HRMS (FAB) $[M+H]^+$ calcd for $C_{18}H_{27}O_4$, 307.1909; found, 307.1901; $[\alpha]_D^{24}$ -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*-**8k** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

(2R, 3S)-3-Cyclohexyl-2,3-Dihydroxy-2,3-O-isopropylidene-1-(2-methoxyphenyl)-1-propanone (from *syn*-8l**):**

colorless oil; IR (neat) ν 2926, 1684, 1598, 1247 cm^{-1} ; 1H 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); HRMS (FAB) $[M+H]^+$ calcd for $C_{19}H_{27}O_4$, 319.1904; found, 319.1908. Ee was determined after cleavage of the acetonide. The absolute configuration of *syn*-**8l** was determined by HPLC analysis as shown in the scheme below. An authentic sample was prepared by using AD-mix- α .

(B) Mechanistic studies

(B-1) X-ray Crystallographic Analysis of Preformed Complex **9:**

Preparation of X-ray grade single crystal **9.**

To a solution of (*S,S*)-linked-BINOL **1** (32.94 mg, 6.7w/w% diethyl ether and hexane included, 0.05 mmol) in THF (0.2 mL) at -20 °C in a flame-dried glass tube, was added Et_2Zn (100 μ L, 0.1 mmol, 1.0 M in hexanes). The resulting mixture was vigorously shaken by vortex mixer, and left at -20 °C for several hours. After some needle like crystal emerged in the glass tube, the solvent was evaporated to the dryness. The residue was recrystallized from THF (0.25 mL, 0.2M in Linked-BINOL) at room temperature for a few days to give clear prisms **9**.

X-ray Crystallographic Data Collections and Refinement of the Structures.

Crystals suitable for X-ray analysis were obtained from the procedure described above. The crystals were selected under ambient conditions, attached to the tip of a glass fiber, and transferred to a Bruker SMART CCD diffractometer equipped with use of the SADABS program. The data were collected at -100 ± 1 °C to a maximum 2θ value of 56.9° . The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystal data	
Empirical Formula	C ₁₁₆ H ₁₁₈ O ₁₈ Zn ₃
Formula Weight	1996.34
Crystal Color, Habit	clear, prism
Crystal Dimensions	0.30 X 0.20 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 14.304(2) Å b = 18.552(2) Å c = 36.827(4) Å V = 9772.7(16) Å ³
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)
Z value	4
D _{calc}	1.357 g/cm ³
F ₀₀₀	4192.00
m(MoKa)	8.01 cm ⁻¹

B. Intensity Measurements

Diffractometer	CCD
Radiation	MoKa (λ = 0.71069 Å) graphite monochromated
Detector Aperture	94 mm x 94 mm
Data Images	1265 exposures @ 10.0 seconds
Detector Position	50.00 mm
Detector Swing Angle	-28.00°
2θ _{max}	56.9°
No. of Reflections Measured	Total: 58829 Unique: 12661 (R _{int} = 0.150)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.5847 - 0.8156)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	S w (F _o - F _c) ²
Least Squares Weights	1/s ² (F _o) = 4F _o ² /s ² (F _o ²)
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 1.50σ(I))	6913
No. Variables	1235
Reflection/Parameter Ratio	5.60
Residuals: R; R _w	0.077 ; 0.084
Goodness of Fit Indicator	2.08
Max Shift/Error in Final Cycle	9.56
Maximum peak in Final Diff. Map	0.84 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.39 e ⁻ /Å ³

Figure S(B-1)-1. The ortep diagram of the crystal **9**.

The crystal **9** consists of linked-BINOL **1** and Zn in a ratio 2:3($\text{Zn}_3(\text{linked-binol})_2\text{thf}_3$) with C_2 -symmetry. Three Zn atoms are aligned in an almost straight line, and each Zn center are penta-coordinated. Two phenolic hydrogens exist, and which are involved in hydrogen bonding. Thus, the acidity of these hydrogens seemed to decrease enough to resist deprotonation in the presence of small excess EtZn -species. See, the results of NMR and ethane gas emission experiments described in the section (B-2) and (B-3) of this Supporting Information.

(B-2) NMR Experiments to Verify the Structure of Preformed Complex **9 in Solution Phase:**

Freshly opened Et_2Zn (1.0 M in hexanes, Aldrich) was always used with titration prior to use. ^1H NMR spectra of the mixture solutions of linked-BINOL **1** and Et_2Zn in $\text{THF-}d_8$ are shown in Chart S(B-2)-1 ((*S,S*)-linked-BINOL **1** only), S(B-2)-2 ($\text{Et}_2\text{Zn}/\mathbf{1} = 1/1$), S(B-2)-3 ($\text{Et}_2\text{Zn}/\mathbf{1} = 1.5/1$) and S(B-2)-4 ($\text{Et}_2\text{Zn}/\mathbf{1} = 2/1$). ^1H NMR spectrum of crystal **9** in $\text{THF-}d_8$ is shown in Chart S(B-2)-5.

Chart S(B-2)-1. ^1H NMR spectrum of linked-BINOL **1** in $\text{THF-}d_8$.

Chart S(B-2)-2. ^1H NMR spectrum of $\text{Et}_2\text{Zn/linked-BINOL 1}$ = 1/1 mixture in $\text{THF-}d_8$.

Chart S(B-2)-3. ^1H NMR spectrum of Et_2Zn /linked-BINOL **1** = 1.5/1 mixture in $\text{THF}-d_8$.

Chart S(B-2)-4. ^1H NMR spectrum of Et_2Zn /linked-BINOL **1** = 2/1 mixture in $\text{THF}-d_8$.

Chart S(B-2)-5. ^1H NMR spectrum of the crystal **9** in THF- d_8 .

In Chart S(B-2)-4 ($\text{Et}_2\text{Zn}/\mathbf{1} = 2/1$), single species was observed, which is same as the major species in Chart S(B-2)-5 (crystal **9**). Four different benzylic protons (ArCH) were observed in the NMR spectrum of Chart S(B-2)-4, suggesting the non- C_2 -symmetric environment around one linked-BINOL unit. The observed results in NMR spectrum matched well with the observed X-ray single crystal structure. In Chart S(B-2)-5 (crystal **9**), linked-BINOL **1** (<10%) and other minor species were observed, probably because some of the crystal **9** was hydrolyzed during operation.

The NMR experiments indicated that ≥ 2 mol eq of Et_2Zn was necessary for the complete complexation of linked-BINOL **1** and Zn to form preformed complex **9**. The existence of remaining Et_2Zn in $\text{Et}_2\text{Zn}/\mathbf{1} = 2/1$ were confirmed by measuring ethane gas emission, which is described in the section (B-3) of this Supporting Information. The two remaining phenolic protons (ArOH) seemed to be stabilized by hydrogen bonding, which was observed in X-ray crystal structure of preformed complex **9**.

In S(B-2)-2 ($\text{Et}_2\text{Zn}/\mathbf{1} = 1/1$) and S(B-2)-3 ($\text{Et}_2\text{Zn}/\mathbf{1} = 1.5/1$), free (*S,S*)-linked-BINOL **1** and **9** ($\text{Zn}_2(\text{linked-binol})_3$) were observed as main peaks. The results indicated that the formation of **9** is thermodynamically favorable, thus desirable preformed complex **9** exists even in shortage of Zn source.

(B-3) Ethane Gas Emission Measurement:

Freshly opened Et_2Zn (1.0 M in hexanes, Aldrich) was always used with titration prior to use. Ethane gas emission was measured by following the procedure in the literature. (Ref. Brown, H. C., *Organic Synthesis via Boranes*, Wiley-Interscience, **1975**, pp241.)

To a stirred solution of linked-BINOL **1** (131.8 mg, 0.2 mmol) in THF (6 mL) at 21 °C was successively added portions of Et_2Zn (1.0 M in hexanes), (a) 0.3 mL (0.3 mmol) and (b) 0.1 mL (0.1 mmol). After addition of Et_2Zn , ethane gas emission was measured. In (a) ($\text{Et}_2\text{Zn}/\text{linked-BINOL } \mathbf{1} = 1.5/1$), ethane 0.37 mmol was detected, in (b) ($\text{Et}_2\text{Zn}/\text{linked-BINOL } \mathbf{1} = 2/1$), additional ethane 0.11 mmol was detected (subtotal: 0.48 mmol). To the resulting mixture ($\text{Et}_2\text{Zn}/\text{linked-BINOL } \mathbf{1} = 2/1$) was added conc. H_2SO_4 (0.1 mL) to afford further ethane (0.22 mmol) emission.

Scheme S(B-3)-1. Ethane Gas Emission Measurement.

The results suggested that Et₂Zn remains in the Et₂Zn/linked-BINOL **1** = 2/1 solution. Total gas emission was 0.70 mmol (theoretically 0.80 mmol), it is probably due to technical error. Another ethane gas measurements by adding excess Et₂Zn revealed that ≥3 mol eq Et₂Zn was necessary for complete deprotonation of all four ArOH groups in linked-BINOL **1** at room temperature.

(B-4) CSI-MS (Coldspray Ionization Mass Spectrometry) Experiments:

Preparation of CSI-MS sample of Figure S(B-4)-1.

To a stirred solution of (*S,S*)-linked-BINOL (16.47 mg, 6.7w/w% diethyl ether and hexane included, 0.025 mmol) in THF (0.5 mL) at −20°C, was added Et₂Zn (50 μL, 0.05 mmol, 1.0 M in hexanes). After stirring for 30 minutes at this temperature, the resulting mixture was diluted with dry THF to give CSI-MS sample (THF solution, 2 mM on linked-BINOL).

Figure S(B-4)-1. CSI-MS spectrum of Et_2Zn linked-BINOL **1** = 2/1.

In addition to linked-BINOL **1**:Zn =2:3 (m/z = 1418.8), fragment peaks assigned as linked-BINOL **1**:Zn =1:2 were also observed. Ion distribution pattern depending on Zn isotopes matched nicely for all assigned peaks. The existence of linked-BINOL **1**:Zn =2:3 complex was confirmed by this CSI-MS and NMR (section (B-2) of this Supporting Information) analyses.

Preparation of CSI-MS sample in Figure S(B-4)-2

To a stirred solution of (*S,S*)-linked-BINOL **1** (16.47 mg, 6.7w/w% diethyl ether and hexane included, 0.025 mmol) in THF (0.5 mL) at -20°C , was added Et_2Zn (37.5 μL , 0.0375 mmol, 1.0 M in hexanes). After stirring for 30 minutes at this temperature, the resulting mixture was diluted with dry THF to give CSI-MS sample (THF solution, 2 mM on linked-BINOL).

Figure S(B-4)-2. CSI-MS spectrum of Et_2Zn linked-BINOL **1** = 1.5/1.

Peaks corresponding to linked-BINOL: Et_2Zn = 3:4 and 4:6 may form under conditions to take CSI-MS.

Preparation of CSI-MS sample of Figure S(B-4)-3–S(B-4)-5.

To a THF solution of (*S,S*)-linked-BINOL : Zn = 1:2 mixture (2 mM in linked-BINOL) prepared by the procedure described above, was added appropriate amount of 2-hydroxy-2'-methoxyacetophenone (**7d**) (1.0 M in THF) at room temperature.

Figure S(B-4)-3. CSI-MS spectrum of linked-BINOL **1** : Et_2Zn : ketone **7d** = 1:2:1

<ion distribution pattern>

linked-BINOL : Zn : ketone 7d = 3:7:4 10

Figure S(B-4)-4. CSI-MS spectrum of linked-BINOL : Et₂Zn : ketone 7d = 1:2:5

Figure S(B-4)-5. CSI-MS spectrum of linked-BINOL **1**: Et₂Zn : ketone **7d** = 1:2:10

Preparation of CSI-MS sample in Figure S(B-4)-6.

To a THF solution of Zn/ (*S,S*)-linked-BINOL **1** = 1.5/1 mixture (2 mM in linked-BINOL) prepared by the procedure described above, was added appropriate amount of 2-hydroxy-2'-methoxyacetophenone (**7d**) (1.0 M in THF) at room temperature.

Figure S(B-4)-6. CSI-MS spectrum of linked-BINOL : Et₂Zn ketone **7d** = 1:1.5:10

(B-5) Kinetic Study:

(B-5) –A: Initial rate kinetics in various catalyst amount.

Procedure for the reaction with 1 mol % of linked-BINOL **1** and 2 mol % of Et₂Zn.

To a stirred solution of (*S,S*)-linked-BINOL **1** (6.58 mg, 6.7w/w% diethyl ether and hexane included, 0.01 mmol) in THF (0.3 mL) at –20 °C, was added Et₂Zn (20 µL, 0.02 mmol, 1.0 M in hexanes). After stirring for 30 min at the same temperature, a solution of **7d** (322.3 mg, 2.0 mmol) in THF (4.7 mL) was added. The resulting mixture was cooled to –30 °C, and **6a** (1.0 mmol) was added. The reaction mixture was stirred at –30 °C. Samples were taken at recorded times according to the following procedure: 0.2 mL of the reaction mixture was taken with a syringe filled with 0.3 mL of saturated aqueous NH₄Cl solution and was immediately poured onto saturated aqueous NH₄Cl (2.0 mL). The resulting mixture was extracted with ether. After evaporating solvents, the crude residue was analyzed by ¹H NMR. Yields of the products **8a** were measured by comparison of integrated area of methylene proton of **7d** (4.75 ppm) and a proton at C-2 position of the **8a** (4.99 ppm). Numerical data for determining initial rate are summarized in each section.

$$f(x) = 9.699884E-1 \cdot x + -1.290900E+0$$

$$R^2 = 9.998010E-1$$

Figure S(B-5)-3. Initial rate kinetics on catalyst concentration ($x = 1, 3$ and 5)

Table S(7)-1. Numerical Data for Plots in Figure S(B-5)-1, S(B-5)-2, and S(B-5)-3.

x = 1: linked-BINOL (1 mol %), Et_2Zn (2 mol %)

time (min)	5	10	15	20	30
yield (%)	2.9	4.5	5.5	7.1	9.7

$f(x) = 2.691081\text{E-}1 \cdot x + 1.620270\text{E+}0$
 $R^2 = 9.978689\text{E-}1$

x = 3: linked-BINOL (3 mol %), Et_2Zn (6 mol %)

time (min)	5	10	15	20	30
yield (%)	8.9	13.5	16.4	21.3	28.7

$f(x) = 7.885946\text{E-}1 \cdot x + 5.136486\text{E+}0$
 $R^2 = 9.971096\text{E-}1$

x = 5: linked-BINOL (5 mol %), Et_2Zn (10 mol %)

time (min)	3	5	7	10	15	20	30
yield (%)	13.4	15.6	18.1	22.4	29.1	35.1	44.6

$f(x) = 1.183913\text{E+}0 \cdot x + 1.024540\text{E+}1$
 $R^2 = 9.938757\text{E-}1$

x = 10: linked-BINOL (10 mol %), Et_2Zn (20 mol %)

time (min)	3	5	7	10	15	20
yield (%)	16.3	18.8	22.8	27.1	33.9	40.4

$f(x) = 1.428942\text{E+}0 \cdot x + 1.226058\text{E+}1$
 $R^2 = 9.969986\text{E-}1$

x = 20: linked-BINOL (20 mol %), Et_2Zn (40 mol %)

time (min)	5	10	15	20	30
yield (%)	13.9	19.1	25.0	32.9	43.1

$f(x) = 1.194800\text{E+}0 \cdot x + 7.689000\text{E+}0$
 $R^2 = 9.950462\text{E-}1$

x = 40: linked-BINOL (40 mol %), Et_2Zn (80 mol %)

time (min)	5	10	15	20	30
yield (%)	13.9	19.1	24.8	32.3	42.9

$f(x) = 1.180318\text{E+}0 \cdot x + 7.727570\text{E+}0$
 $R^2 = 9.967889\text{E-}1$

x = 100: linked-BINOL (100 mol %), Et_2Zn (200 mol %)

time (min)	5	10	15	20	30
yield (%)	4.5	6.7	9.0	11.4	15.5

$f(x) = 4.437649\text{E-}1 \cdot x + 2.298162\text{E+}0$
 $R^2 = 9.991626\text{E-}1$

As long as catalyst amount was less than *x* = 10 (linked-BINOL **1** = 10 mol %, Et_2Zn = 20 mol %), the higher amount of catalyst was used (*x* = 1, 3, 5 to 10), the faster reaction rate was observed ($v_{x=1} = 8.97 \times 10^{-6} < v_{x=3} = 2.63 \times 10^{-5} < v_{x=5} = 3.95 \times 10^{-5} < v_{x=10} = 4.76 \times 10^{-5}$). In contrast, the reaction rate decreased

by increasing x from 10, 20, 40, to 100 ($v_{x=10} = 4.76 \times 10^{-5} > v_{x=20} = 3.98 \times 10^{-5} > v_{x=40} = 3.93 \times 10^{-5} > v_{x=100} = 1.48 \times 10^{-5} \text{ Ms}^{-1}$). This result was consistent with the observation in CSI-MS analysis. According to the CSI-MS spectra, excess ketone **7d** compared to preformed complex **9** was required to form active catalyst linked-BINOL : Zn : ketone **7d** = 3:7:4 complex **10**. When the aldol reaction was performed with low catalyst loading (1-5 mol %), ketone **7d** exists in sufficiently excess amount compared to the preformed complex **9**. **9** would be almost completely converted to **10**, and first-order rate dependency was observed on linked-BINOL **1** concentration. On the other hand, more than 10 mol % of catalyst loading (based on linked-BINOL **1**) caused prevention of sufficient formation of **10**.

(B-5) –B: Initial rate kinetics using the crystal 9 as a catalyst.

The crystals were prepared under argon atmosphere by the procedure described in section (B-1). The solvent was removed from the glass tube and the crystal **9** was washed with dry THF (1.0 mL) x 4 times. After drying under reduced pressure, the crystal **9** was weighed in dry-box and was transferred into a test tube.

(a) [crystal 9 alone (1.5 mol %) as a catalyst]

To the crystal **9** (7.0 mg, 0.0035 mmol) at 0°C in a test tube under argon atmosphere, was added THF (0.5 mL) and ketone **7d** (77.4 mg, 0.466 mmol, in 0.665 mL THF). After the crystal dissolved completely, the mixture was cooled to –30°C. To the stirred solution of resulting mixture, was added **6a** (28.7 µL, 0.233 mmol) and the mixture was stirred at –30°C. Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-A.

(b) [crystal 9 (1.5 mol %) with additional Et₂Zn (1.5 mol %) as a catalyst]

To the crystal **9** (7.0 mg, 0.0035 mmol) at 0°C in a test tube under argon atmosphere, was added THF (0.5 mL), Et₂Zn (3.5 µL, 0.0035 mmol, 1.0 M in hexanes) and ketone **7d** (77.4 mg, 0.466 mmol, in 0.665 mL THF). After the crystal dissolved completely, the mixture was cooled to –30°C. To the stirred solution of resulting mixture, was added **6a** (28.7 µL, 0.233 mmol) and the mixture was stirred at –30°C. Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-A. Background reaction with free Et₂Zn is negligible, because only trace aldol adduct (<9%) was obtained by using as much as 10 mol % of Et₂Zn alone at –20 °C for 10 h.

Figure S(B-5)-4. Reaction profile with (a) crystal **9** alone (1.5 mol %) (b) crystal **9** (1.5 mol %) + additional Et₂Zn (1.5 mol %)

Table S(B-5)-2. Numerical Data for Plots in Figure S(B-5)-4.

(a) [crystal **9** alone (1.5 mol %)]

time (min)	30	60	90	120	150
yield (%)	4.0	7.3	11.8	15.0	18.5

$f(x) = 1.218333E-1 \cdot x + 3.610000E-1$
 $R^2 = 9.970544E-1$

(b) [crystal **9** (1.5 mol %) + additional Et₂Zn (1.5 mol %)]

time (min)	30	60	90	120	150
yield (%)	6.3	13.6	19.5	24.5	32.1

$f(x) = 2.084000E-1 \cdot x + 4.720000E-1$
 $R^2 = 9.953906E-1$

(B-5)-C: Rate difference between the reaction catalyzed by crystal **9 and the reaction with standard condition.**

C-1: reaction with standard condition. (10 mol % of ligand)

To a stirred solution of (*S,S*)-linked-BINOL **1** (32.94 mg, 6.7 w/w% diethyl ether and hexane included, 0.05 mmol) in THF (1.0 mL) at -20 °C, was added Et₂Zn (100 μL, 0.1 mmol, 1.0 M in hexanes). After stirring for 30 min at -20 °C, a solution of **7d** (166.17 mg, 1.0 mmol) in THF (1.5 mL) was added. The resulting mixture was cooled to -30 °C, and **6b** (0.5 mmol) was added. The reaction mixture was stirred at -30 °C. Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-A.

C-2: reaction catalyzed by crystal **9** (10 mol % based on ligand).

The crystals were prepared under argon atmosphere by the procedure described in section (B-1). The solvent was removed from the glass tube and the crystal **9** was washed with dry THF (1.0 mL) x 4 times. After drying under reduced pressure, the crystal **9** was weighed in dry-box and was transferred into a test tube.

To the crystal **9** (24.0 mg, 0.012 mmol, (0.024 mmol of **1**)) at 0°C in a test tube under argon atmosphere, was added THF (0.72 mL) and ketone **7d** (79.8 mg, 0.48 mmol, in 0.48 mL THF) and the resulting mixture was stirred at room temperature. After the crystal dissolved completely, the mixture was cooled to -30°C. To the stirred solution of resulting mixture, was added **6b** (0.24 mmol) and the mixture was stirred at -30°C. Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-A.

Figure S(B-5)-5. Rate difference between the reaction catalyzed by crystal alnoe and the reaction with standard conditions.

Table S(B-5)-3. Numerical Data for Plots in Figure S(B-5)-5.

C-1: standard condition **1** 10 mol %
 Et_2Zn 20 mol %

time (min)	5	10	20	30	40
yield (%)	12.3	18.2	30.5	45.6	58.8

$$f(x) = 1.341817\text{E}+0 \cdot x + 4.913841\text{E}+0$$

$$R^2 = 9.984358\text{E}-1$$

C-2: 5 mol % of crystal (10 mol % of ligand **1**)
as a catalyst

time (min)	5	10	20	30	40
yield (%)	7.9	12.4	21.3	30.4	38.4

$$f(x) = 8.775427\text{E}-1 \cdot x + 3.654604\text{E}+0$$

$$R^2 = 9.994700\text{E}-1$$

The reaction catalyzed by crystal **9** ($v = 2.92 \times 10^{-5} \text{ Ms}^{-1}$) proceeded slightly slower than the reaction with standard condition ($v = 4.47 \times 10^{-5} \text{ Ms}^{-1}$).

(B-5)-D: Initial rate kinetics on ketone **1** concentration.

Procedure for the aldol reaction with 0.4 M ketone **7d** concentration.

To a stirred solution of (*S,S*)-linked-BINOL (19.74 mg, 6.7w/w% diethyl ether and hexane included, 0.03 mmol) in THF (0.9 mL) at -20°C , was added Et_2Zn (60 μL , 0.02 mmol, 1.0 M in hexanes). After stirring for 30 min at -20°C , a solution of **7d** (322.3 mg, 2.0 mmol) in THF (4.7 mL) was added. The resulting mixture was cooled to -30°C , and **6a** (1.0 mmol) was added. The reaction mixture was stirred at -30°C . Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-(A).

Figure S(B-5)-6. Reaction profile in various ketone concentration.

Table S(B-5)-4. Numerical Data for Plots in Figure S(B-5)-6.

Ketone **7d** 0.1M

time (min)	5	10	15	20	30
yield (%)	2.9	4.3	5.3	6.1	8.1

$f(x) = 2.037297E-1 \cdot x + 2.084324E+0$
 $R^2 = 9.922099E-1$

Ketone **7d** 0.2M

time (min)	5	10	15	20	30
yield (%)	4.5	7.4	9.8	12.3	15.3

$f(x) = 4.310811E-1 \cdot x + 2.942703E+0$
 $R^2 = 9.794171E-1$

Ketone **7d** 0.3M

time (min)	5	10	15	20	30
yield (%)	7.1	10.1	13.2	16.0	20.9

$f(x) = 5.531351E-1 \cdot x + 4.617838E+0$
 $R^2 = 9.968595E-1$

Ketone **7d** 0.4M

time (min)	5	10	15	20	30
yield (%)	8.9	13.5	16.4	21.3	28.7

$f(x) = 7.885946E-1 \cdot x + 5.136486E+0$
 $R^2 = 9.971096E-1$

Ketone **7d** 0.5M

time (min)	5	10	15	20	30
yield (%)	13.9	19.1	24.8	32.3	42.6

$f(x) = 9.967838E-1 \cdot x + 5.859459E+0$
 $R^2 = 9.986959E-1$

(B-5)-E: Initial rate kinetics on aldehyde concentration.

Procedure for the aldol reaction with 0.2 M aldehyde **6a** concentration.

To a stirred solution of (S,S)-linked-BINOL **1** (19.74 mg, 6.7w/w% diethyl ether and hexane included,

0.03 mmol) in THF (0.9 mL) at $-20\text{ }^{\circ}\text{C}$, was added Et_2Zn (60 μL , 0.06 mmol, 1.0 M in hexanes). After stirring for 30 min at $-20\text{ }^{\circ}\text{C}$, a solution of **7d** (322.3 mg, 2.0 mmol) in THF (4.7 mL) was added. The resulting mixture was cooled to $-30\text{ }^{\circ}\text{C}$, and **6a** (1.0 mmol) was added. The reaction mixture was stirred at $-30\text{ }^{\circ}\text{C}$. Sampling and determination of chemical yields were carried out by the same procedure as described in section (B-5)-(A).

Figure S(B-5)-7. Reaction profile in various aldehyde **6a** concentration.

Table S(B-5)-5. Numerical Data for Plots in Figure S(B-5)-7.

aldehyde **6a** 0.1M

time (min)	5	10	20	30	60
product (mM)	11.54	15.68	22.3	30.9	57.1

$f(x) = 8.290789\text{E-}1 \cdot x + 6.783026\text{E+}0$
 $R^2 = 9.979334\text{E-}1$

aldehyde **6a** 0.2M

time (min)	5	10	20	30	60
product (mM)	13.0	17.1	23.8	33.0	58.8

$f(x) = 8.347105\text{E-}1 \cdot x + 8.256237\text{E+}0$
 $R^2 = 9.983519\text{E-}1$

aldehyde **6a** 0.4M

time (min)	5	10	20	30	60
product (mM)	13.4	13.8	24.6	34.1	59.9

$f(x) = 8.485789\text{E-}1 \cdot x + 8.697526\text{E+}0$
 $R^2 = 9.988500\text{E-}1$

aldehyde **6a** 0.6M

time (min)	5	10	20	30	60
product (mM)	14.8	18.9	26.7	36.2	62.0

$f(x) = 8.626316\text{E-}1 \cdot x + 1.015021\text{E+}1$
 $R^2 = 9.994864\text{E-}1$

aldehyde **6a** 0.8M

time (min)	5	10	20	30	60
product (mM)	17.1	21.0	29.0	39.0	65.0

$f(x) = 9.100000\text{E-}1 \cdot x + 1.190600\text{E+}1$
 $R^2 = 9.988273\text{E-}1$

(C) Second generation Et₂Zn/linked-BINOL = 4/1 system:

General Procedure for Catalytic Asymmetric Aldol Reaction of Ketone 7d Promoted by Et₂Zn/(*S,S*)-linked-BINOL = 4/1 with MS 3A System (For aldehyde 6a and 6l):

MS 3A (200 mg) in a test tube was activated prior to use under reduced pressure (ca. 0.7 kPa) at 160 °C for 3h. After cooling, a solution of (*S,S*)-linked-BINOL (1.6 mg, 4.1w/w% diethyl ether and hexane included, 0.0025 mmol) in THF (0.6 mL) was added under Ar. The mixture was cooled down to –20 °C. To the mixture was added Et₂Zn (10 µL, 0.01 mmol, 1.0 M in hexanes) at –20 °C. After stirring for 10 min at –20 °C, a solution of **7d** (182.8 mg, 1.1 mmol) in THF (1.1 mL) was added. Aldehyde **6a** (1.0 mmol) was added and stirred at –20 °C. The stirring was continued for 18 h at –20 °C 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 *sat. aq* NaHCO₃, brine and dried over MgSO₄. Evaporation of solvent gave a crude mixture of the aldol products. The diastereomeric ratios of the aldol products were determined by ¹H NMR of the crude product. After purification by silica gel flash column chromatography (hexane/acetone 8/1–4/1), **8a** was obtained (269.6 mg, 0.898 mmol, y. 90%, dr: *syn/anti* = 89/11, 96% ee(*syn*)).

The general procedure was applied to aldehyde **6a** and **6l**. In the case of aldehyde **6m**, aldol adduct was directly converted into acetone without aqueous work-up, because aldol adduct was unstable.

Procedure for aldehyde 6m:

MS3A (50 mg) in a test tube tube was activated prior to use under reduced pressure (ca. 0.7 kPa) at 160 °C for 3h. After cooling down to room temperature, argon gas was refilled to the test tube and a solution of (*S,S*)-linked-BINOL **1** (16.96 mg, 9.44 w/w% diethyl ether and hexane included, 0.025 mmol) in THF (0.4 mL) was charged. The resulting mixture was cooled to –20 °C, and was added Et₂Zn (100 µL, 0.1 mmol, 1.0M in hexanes). After stirring for 20 min at this temperature, a solution of **7d** (166.2 mg, 1.0 mmol) in THF (2.1 mL) and **6m** (98.0 µL, 0.5 mmol) was added successively. The stirring was continued for 15 h at this temperature and was added TsOH·H₂O (0.2 mg) in dimethoxypropane (8.0 mL) to the reaction mixture and warmed up to room temperature. After stirring for 11 h at this temperature, quenched with saturated aqueous NaHCO₃. The mixture was extracted with ethyl acetate and was added 1N aqueous HCl (10 mL) to the combined organic layers, then concentrated to half volume under reduced pressure (acetone and dimethoxypropane was removed). The resulting residue was washed with saturated aqueous NaHCO₃ and brine and dried over MgSO₄. Evaporation of solvent gave a crude mixture of aldol products. The resulting crude residue was purified by flash silica gel column chromatography (ethyl acetate/hexane = 1/15) to afford *syn*-**8m** (148.9 mg, y. 75%, 92% ee).

(2*R*, 3*S*)-5-Benzyloxy-2,3-dihydroxy-2,3-*O*-isopropylidene-4,4-dimethyl-1-(2-methoxyphenyl)-1-pentanone (*syn*-8m**):**

colorless oil; IR (neat) ν 1644, 1240, 1149, 1049 cm⁻¹; ¹H NMR (CDCl₃) δ 0.96 (s, 3H), 0.97 (s, 3H), 1.18 (s, 3H), 1.38 (s, 3H), 3.27 (s, 2H), 3.77 (s, 3H), 4.37 (s, 2H), 4.50 (d, *J* = 6.1 Hz, 1H), 5.18 (d, *J* = 6.1 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.94 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.19–7.32 (m, 5H), 7.40 (ddd, *J* = 1.8, 7.6, 8.2 Hz, 1H), 7.50 (dd, *J* = 1.8, 7.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 20.1, 21.3, 25.5, 26.7, 37.1, 55.8, 73.1, 76.9, 79.9, 82.0, 109.4, 111.7, 120.5, 127.2, 127.3, 128.1, 130.4, 133.1, 138.8, 158.2, 202.5; ESI-MS *m/z* 421 [M+Na]⁺; [α]_D²⁵ –31.5 (c 1.4, CHCl₃) (92% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t*_R 5.2 min (minor) and 7.1 min (major); HRMS (FAB) [M+H]⁺ calcd for C₂₄H₃₁O₅, 399.2165; found, 399.2160.

(D) Construction of chiral tetrasubstituted carbon stereocenter:

General Procedure for Catalytic Asymmetric Aldol Reaction of Ketone *rac*-12 Promoted by Et₂Zn/(*S,S*)-linked-BINOL **1 = 4/1 with MS 3A System:**

MS 3A (30 mg) in a test tube was activated prior to use under reduced pressure (ca. 0.7 kPa) at 160 °C for 3h. After cooling, a solution of (*S,S*)-linked-BINOL (9.6 mg, 4.1w/w% diethyl ether and hexane included, 0.015 mmol) in THF (0.2 mL) was added under Ar. The mixture was cooled down to –20 °C. To the mixture was added Et₂Zn (60 µL, 0.06 mmol, 1.0 M in hexanes) at –20 °C. After stirring for 10 min at –20 °C, a solution of *rac*-**12** (270.3 mg, 1.5 mmol) in THF (0.24 mL) was added. After 5 min at –20 °C, aldehyde **6a** (40 µL, 0.304 mmol) was added and stirred at –20 °C. The stirring was continued for 16 h at

–20 °C 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 *sat. aq* NaHCO₃, brine and dried over MgSO₄. Evaporation of solvent gave a crude mixture of the aldol products. The diastereomeric ratios of the aldol products were determined by ¹H NMR of the diastereomixture. After purification by silica gel flash column chromatography (hexane/acetone 8/1–4/1), **13a** was obtained (92.5 mg, 0.294 mmol, y. 97%, dr: *syn/anti* = 62/38, 87% ee(*syn*), 95% ee(*anti*)). Ee was determined by chiral HPLC analysis.

(2R, 3S)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-5-phenyl-1-pentanone (*syn*-13a)

colorless oil; IR (neat) ν 3474, 1699, 1599 cm⁻¹; ¹H NMR (C₆D₆) δ 1.26 (s, 3H), 1.81–1.94 (m, 2H), 2.35 (brd, *J* = 8.8 Hz, 1H), 2.58 (ddd, *J* = 7.3, 9.1, 13.7 Hz, 1H), 2.92 (ddd, *J* = 4.8, 9.4, 13.7 Hz, 1H), 3.08 (s, 3H), 3.93–4.00 (m, 1H), 4.20 (s, 1H), 6.36 (brd, *J* = 8.3 Hz, 1H), 6.73 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.96–7.07 (m, 2H), 7.11–7.16 (m, 4H), 7.47 (dd, *J* = 1.5, 7.3 Hz, 1H); ¹³C NMR (C₆D₆) δ 14.2, 21.4, 32.5, 32.9, 55.2, 60.1, 74.4, 83.1, 111.4, 121.1, 126.1, 128.6, 128.7, 128.9, 129.7, 131.2, 142.7, 156.2, 170.2, 210.0; ESI-MS *m/z* 337 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₁₉H₂₃O₄, 315.1596; found, 315.1595; [α]_D²⁸ –24.3 (c 1.4, CH₂Cl₂) (74% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t*_R 11.1 min (major) and 12.4 min (minor).

(2R, 3R)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-5-phenyl-1-pentanone (*anti*-13a)

colorless solid; IR (KBr) ν 3490, 1672 cm⁻¹; ¹H NMR (C₆D₆) δ 1.52 (s, 3H), 1.87–1.93 (m, 2H), 2.35 (brs, 1H), 2.73 (ddd, *J* = 8.3, 8.3, 13.7 Hz, 1H), 2.93 (s, 3H), 2.88–2.96 (m, 1H), 3.90–3.97 (m, 1H), 3.99 (brs, 1H), 6.26 (brd, *J* = 8.3 Hz, 1H), 6.65 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.93–6.98 (m, 1H), 7.02–7.07 (m, 1H), 7.11–7.20 (m, 5H); ¹³C NMR (C₆D₆) δ 22.3, 32.8, 34.1, 55.1, 75.2, 83.0, 111.4, 121.5, 126.0, 128.7, 129.1, 129.4, 131.7, 142.7, 156.2, 210.0; ESI-MS *m/z* 337 [M+Na]⁺; [α]_D²⁹ +9.1 (c 0.88, CH₂Cl₂) (85% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t*_R 10.4 min (minor) and 13.2 min (major); HRMS (FAB) [M+H]⁺ calcd for C₁₉H₂₃O₄, 315.1596; found, 315.1591.

(2R, 3S)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-6-phenyl-1-hexanone (*syn*-13o)

colorless oil; IR (neat) ν 3475, 1699, 1599 cm⁻¹; ¹H NMR (C₆D₆) δ 1.28 (s, 3H), 1.50–1.59 (m, 3H), 1.88–1.94 (m, 1H), 1.97 (d, *J* = 9.5 Hz, 1H), 2.45–2.52 (m, 2H), 3.07 (s, 3H), 3.90–3.95 (m, 1H), 4.12 (s, 1H), 6.36 (brd, *J* = 8.2 Hz, 1H), 6.73 (ddd, *J* = 0.9, 7.6, 7.6 Hz, 1H), 6.99 (ddd, *J* = 1.6, 7.6 Hz, 1H), 7.04–7.08 (m, 3H), 7.14–7.18 (m, 2H), 7.50 (dd, *J* = 1.6, 7.6 Hz, 1H); ¹³C NMR (C₆D₆) δ 21.5, 28.0, 30.4, 36.1, 55.2, 74.9, 83.0, 111.4, 121.1, 126.0, 128.5, 128.6, 128.7, 129.7, 131.0, 142.7, 156.1, 209.9; ESI-MS *m/z* 351 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₂₀H₂₅O₄, 329.1753; found, 329.1750; [α]_D²⁹ +8.7 (c 0.85, CH₂Cl₂) (78% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t*_R 9.2 min (minor) and 11.9 min (major).

(2R, 3R)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-6-phenyl-1-hexanone (*anti*-13o)

colorless oil; IR (neat) ν 3457, 1683, 1599 cm⁻¹; ¹H NMR (C₆D₆) δ 1.56 (s, 3H), 1.58–1.64 (m, 2H), 1.64–1.75 (m, 1H), 1.95–2.03 (m, 1H), 2.18 (brd, *J* = 8.0 Hz, 1H), 2.48–2.58 (m, 2H), 2.96 (s, 3H), 3.88 (s, 1H), 3.93 (ddd, *J* = 3.4, 8.0, 8.6 Hz, 1H), 6.28 (brd, *J* = 8.2 Hz, 1H), 6.71 (ddd, *J* = 0.6, 7.2, 7.3 Hz, 1H), 6.97 (ddd, *J* = 1.5, 7.2, 8.2 Hz, 1H), 7.04–7.08 (m, 3H), 7.13–7.17 (m, 2H), 7.24 (dd, *J* = 1.5, 7.3 Hz, 1H); ¹³C NMR (C₆D₆) δ 22.5, 28.6, 31.8, 36.0, 55.1, 76.5, 83.0, 111.3, 121.5, 125.9, 128.6, 128.8, 129.5, 130.6, 131.6, 142.8, 156.1, 210.5; ESI-MS *m/z* 351 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₂₀H₂₅O₄, 329.1753; found, 329.1756; [α]_D²⁹ –2.0 (c 0.49, CH₂Cl₂) (90% ee); HPLC (DAICEL CHIRALPAK AD–H, 2-propanol/hexane 20/80, flow 0.8 mL/min, detection at 254 nm) *t*_R 12.5 min (major) and 14.2 min (minor).

(2R, 3S)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-pentanone

(syn-13p)

colorless oil; IR (neat) ν 3465, 1687, 1599 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.95 (t, $J = 7.5$ Hz, 3H), 1.30 (s, 3H), 1.44-1.56 (m, 2H), 1.98 (d, $J = 9.5$ Hz, 1H), 3.08 (s, 3H), 3.81 (ddd, $J = 3.5, 9.5, 9.5$ Hz, 1H), 4.12 (s, 1H), 6.37 (brd, $J = 8.6$ Hz, 1H), 6.73 (ddd, $J = 0.6, 7.6, 7.6$ Hz, 1H), 7.00 (ddd, $J = 1.8, 7.6, 8.6$ Hz, 1H), 7.51 (dd, $J = 1.8, 7.6$ Hz, 1H); ^{13}C NMR (C_6D_6) δ 10.6, 21.5, 23.8, 55.2, 76.5, 83.0, 111.4, 121.1, 128.5, 129.8, 131.0, 156.2, 210.0; ESI-MS m/z 261 $[\text{M}+\text{Na}]^+$; HRMS (FAB)(for carbonate) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5$, 265.1076; found, 265.1084; $[\alpha]_{\text{D}}^{29} +3.6$ (c 0.56, CH_2Cl_2) (68% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} xx 7.6 (minor) and 9.7 min (major).

(2R, 3R)-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-penanone
(anti-13p)

colorless oil; IR (neat) ν 3465, 1698, 1599 cm^{-1} ; ^1H NMR (C_6D_6) δ 1.05 (t, $J = 7.5$ Hz, 3H), 1.51-1.67 (m, 2H), 1.55 (s, 3H), 2.16 (d, $J = 7.9$ Hz, 1H), 2.99 (s, 3H), 3.77-3.81 (m, 1H), 3.87 (s, 1H), 6.29 (brd, $J = 8.6$ Hz, 1H), 6.70 (ddd, $J = 0.9, 7.4, 7.4$ Hz, 1H), 6.97 (ddd, $J = 1.8, 7.4, 8.2$ Hz, 1H), 7.28 (dd, $J = 1.8, 7.4$ Hz, 1H); ^{13}C NMR (C_6D_6) δ 11.3, 22.5, 25.3, 55.1, 78.2, 83.0, 111.4, 121.5, 129.4, 130.6, 131.5, 156.1, 210.4; ESI-MS m/z 261 $[\text{M}+\text{Na}]^+$; HRMS (FAB)(for carbonate) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{25}\text{O}_5$, 265.1076; found, 265.1077; $[\alpha]_{\text{D}}^{29} +4.4$ (c 0.39, CH_2Cl_2) (86% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 6.7 min (major) and 8.0 min (minor).

(2R, 3S)-2,3-Carbonyldioxy-1-(2-methoxyphenyl)-2,5-dimethyl-1-hexanone (from syn-13d)

colorless oil; IR (neat) ν 1810, 1687, 1599 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.98 (d, $J = 6.4$ Hz, 3H), 1.01 (d, $J = 6.4$ Hz, 3H), 1.47-1.53 (m, 1H), 1.57 (s, 3H), 1.69-1.77 (m, 1H), 1.85-1.93 (m, 1H), 3.86 (s, 3H), 4.89 (dd, $J = 2.8, 11.0$ Hz, 1H), 6.94 (brd, $J = 8.6$ Hz, 1H), 7.01 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.27 (dd, $J = 1.5, 7.6$ Hz, 1H), 7.46 (ddd, $J = 1.5, 7.6, 8.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 18.7, 21.5, 23.3, 25.1, 38.4, 55.6, 79.5, 88.3, 111.1, 121.1, 126.9, 129.2, 133.3, 153.7, 157.1, 210.4; ESI-MS m/z 315 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{28} -4.4$ (c 0.49, CHCl_3) (72% ee); HPLC (for diol)(DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 0.6 mL/min, detection at 254 nm) t_{R} 12.6 min (major) and 14.4 min (minor); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{21}\text{O}_5$, 293.1384; found, 293.1381..

(2R, 3R)-2,3-Carbonyldioxy-1-(2-methoxyphenyl)-2,5-dimethyl-1-hexanone (from anti-13d)

colorless oil; IR (neat) ν 1809, 1692, 1599 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (d, $J = 6.5$ Hz, 3H), 0.96 (d, $J = 6.8$ Hz, 3H), 1.51-1.56 (m, 1H), 1.59-1.67 (m, 1H), 1.69 (s, 3H), 1.82-1.92 (m, 1H), 3.83 (s, 3H), 4.54 (dd, $J = 2.8, 11.3$ Hz, 1H), 6.91 (brd, $J = 8.3$ Hz, 1H), 7.00 (ddd, $J = 0.6, 7.6, 7.6$ Hz, 1H), 7.23 (dd, $J = 1.8, 7.6$ Hz, 1H), 7.45 (ddd, $J = 1.8, 7.6, 8.3$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 21.3, 23.4, 25.2, 25.6, 39.4, 55.1, 84.3, 88.9, 110.8, 121.1, 127.0, 129.2, 133.4, 153.5, 155.7, 202.6; ESI-MS m/z 315 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{28} +64.9$ (c 0.59, CHCl_3) (87% ee); HPLC (for diol) (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 0.6 mL/min, detection at 254 nm) t_{R} 11.7 min (minor) and 13.4 min (major); HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5$, 293.1384; found, 293.1387.

(2R, 3S)-2,3-dihydroxy-5-(4-methoxy-benzyloxy)-1-(2-methoxyphenyl)-2-methyl-1-penanone (syn-13q)

colorless oil; IR (neat) ν 3472, 1700, 1599 cm^{-1} ; ^1H NMR (C_6D_6) δ 1.35 (s, 3H), 1.72-1.78 (m, 1H), 1.85-1.93 (m, 1H), 3.11 (s, 3H), 3.16 (d, $J = 5.8$ Hz, 1H), 3.29 (s, 3H), 3.40 (ddd, $J = 4.6, 6.7, 9.2$ Hz, 1H), 3.51 (ddd, $J = 4.6, 6.7, 9.2$ Hz, 1H), 4.10 (s, 1H), 4.20 (d, $J = 11.5$ Hz, 1H), 4.21 (d, $J = 11.5$ Hz, 1H), 4.23 (ddd, $J = 2.5, 5.8, 10.1$ Hz, 1H), 6.38 (d, $J = 8.3$ Hz, 1H), 6.72-6.78 (m, 3H), 6.98-7.02 (m, 1H), 7.10-7.15 (m, 2H), 7.61 (dd, $J = 1.7, 7.3$ Hz, 1H); ^{13}C NMR (C_6D_6) δ 21.3, 30.6, 54.8, 55.2, 68.4, 73.0, 74.6, 82.7, 111.3, 114.2, 120.9, 128.4, 128.4, 129.5, 130.2, 130.7, 156.4, 159.8, 210.2; ESI-MS m/z 397 $[\text{M}+\text{Na}]^+$; $[\alpha]_{\text{D}}^{25} +5.4$ (c 0.88,

CHCl₃) (86% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t_R* 18.5 min (minor) and 23.5 min (major); HRMS (FAB) [M+H]⁺ calcd for C₂₁H₂₇O₆, 507.0778; found, 507.0775.

(2*R*, 3*R*)-2,3-dihydroxy-5-(4-methoxy-benzyloxy)-1-(2-methoxyphenyl)-2-methyl-1-penanone (*anti*-13q)

colorless oil; IR (neat) ν 3472, 1694, 1599 cm⁻¹; ¹H NMR (C₆D₆) δ 1.62 (s, PMBO 3H), 1.85-1.93 (m, 2H), 2.96 (brd, *J* = 3.6 Hz, 1H), 3.06 (s, 3H), 3.30 (s, 3H), 3.46 (ddd, *J* = 4.9, 6.4, 9.2 Hz, 1H), 3.60 (ddd, *J* = 4.6, 7.3, 9.2 Hz, 1H), 3.95 (s, 1H), 4.23 (s, 2H), 4.25-4.30 (m, 1H), 6.32 (brd, *J* = 8.3 Hz, 1H), 6.69-6.72 (m, 1H), 6.73-6.80 (m, 2H), 6.96-7.00 (m, 1H), 7.15-7.13 (m, 2H), 7.41 (dd, *J* = 1.5, 7.6 Hz, 1H); ¹³C NMR (C₆D₆) δ 22.3, 32.3, 54.8, 55.2, 68.4, 73.0, 75.1, 82.7, 111.4, 114.2, 121.2, 129.0, 129.5, 130.9, 131.3, 156.3, 159.3, 210.4; ESI-MS *m/z* 397 [M+Na]⁺; HRMS (FAB)(for carbonate) [M+H]⁺ calcd for C₂₂H₂₅O₇, 401.1600; found, 401.1603; [α]_D²⁵ -5.2 (c 0.54, CHCl₃)(95% ee); HPLC (DAICEL CHIRALCEL OJ, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t_R* 31.5 min (major) and 39.0 min (minor).

(2*R*, 3*S*)-5-benzyloxymethoxy-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-penanone (*syn*-13i)

colorless oil; IR (neat) ν 3468, 2938, 1700, 1598 cm⁻¹; ¹H NMR (C₆D₆) δ 1.37 (s, 3H), 1.79-1.83 (m, 2H), 2.82 (d, *J* = 7.6 Hz, 1H), 3.10 (s, 3H), 3.58 (ddd, *J* = 5.5, 5.5, 10.6 Hz, 1H), 3.70-3.75 (m, 1H), 4.20 (s, 1H), 4.28 (ddd, *J* = 3.6, 7.6, 8.6 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.52 (s, 2H), 6.38 (d, *J* = 8.3 Hz, 1H), 6.72 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.99 (ddd, *J* = 1.5, 7.6, 8.3 Hz, 1H), 7.05-7.09 (m, 1H), 7.13-7.18 (m, 2H), 7.26-7.30 (m, 2H), 7.57 (dd, *J* = 1.5, 7.6 Hz, 1H); ¹³C NMR (C₆D₆) δ 21.3, 30.7, 55.2, 65.5, 69.4, 73.3, 82.9, 94.7, 111.4, 120.9, 127.7, 128.1, 128.3, 128.5, 129.9, 130.9, 138.7, 156.3, 210.0; ESI-MS *m/z* 397 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₂₁H₂₇O₆, 375.1807; found, 375.1811; [α]_D²⁵ -2.7 (c 0.41, CHCl₃) (87% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t_R* 11.8 min (minor) and 14.5 min (major).

(2*R*, 3*R*)-5-benzyloxymethoxy-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-penanone (*anti*-13i)

colorless solid; IR (KBr) ν 3496, 1679, 1596 cm⁻¹; ¹H NMR (C₆D₆) δ 1.60 (s, 3H), 1.79-1.86 (m, 1H), 1.96 (dddd, *J* = 2.1, 5.5, 8.2, 17.5 Hz, 1H), 2.68 (d, *J* = 6.7 Hz, 1H), 3.04 (s, 3H), 3.65 (ddd, *J* = 5.5, 5.5, 9.2 Hz, 1H), 3.79 (ddd, *J* = 4.5, 8.2, 9.2 Hz, 1H), 3.94 (s, 1H), 4.22 (ddd, *J* = 1.8, 6.7, 8.2 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.56 (s, 2H), 6.31 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 6.7, 7.6 Hz, 1H), 6.98 (ddd, *J* = 1.8, 6.7, 8.6 Hz, 1H), 7.06-7.09 (m, 1H), 7.13-7.17 (m, 2H), 7.28-7.30 (m, 2H), 7.38 (dd, *J* = 1.8, 7.6 Hz, 1H); ¹³C NMR (C₆D₆) δ 22.3, 32.3, 55.1, 65.8, 69.3, 74.5, 82.7, 94.7, 111.3, 121.3, 127.7, 128.3, 128.5, 129.2, 130.5, 131.4, 138.7, 156.2, 210.3; ESI-MS *m/z* 397 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₂₁H₂₇O₆, 375.1807; found, 375.1804; [α]_D²⁵ -0.3 (c 0.77, CHCl₃) (97% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t_R* 11.7 min (major) and 14.5 min (minor).

(2*R*, 3*S*)-4-benzyloxy-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-butanone (*syn*-13h)

colorless oil; IR (neat) ν 3466, 1703, 1599 cm⁻¹; ¹H NMR (C₆D₆) δ 1.38 (s, 3H), 3.07 (d, *J* = 5.8 Hz, 1H), 3.13 (s, 3H), 3.60 (dd, *J* = 6.7, 9.7 Hz, 1H), 3.63 (dd, *J* = 4.3, 9.7 Hz, 1H), 4.16 (s, 1H), 4.23 (s, 2H), 4.27-4.30 (m, 1H), 6.39 (d, *J* = 8.3 Hz, 1H), 6.74 (dd, *J* = 7.4, 7.6 Hz, 1H), 6.99-7.09 (m, 2H), 7.10-7.16 (m, 4H), 7.50 (dd, *J* = 1.6, 7.4 Hz, 1H); ¹³C NMR (C₆D₆) δ 21.7, 55.3, 71.1, 73.5, 74.3, 81.7, 111.4, 120.9, 127.9, 128.5, 128.6, 128.6, 130.0, 131.0, 138.5, 156.5, 209.7; ESI-MS *m/z* 353 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₁₉H₂₃O₅, 331.1545; found, 331.1542; [α]_D²⁵ +1.3 (c 0.51, CH₂Cl₂)(85% ee); HPLC (DAICEL CHIRALPAK AD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) *t_R* 12.0 min (minor)

and 15.6 min (major).

(2*R*,3*R*)-4-benzyloxy-2,3-dihydroxy-1-(2-methoxyphenyl)-2-methyl-1-butanone (anti-13h)

colorless oil; IR (neat) ν 3445, 1685, 1599 cm^{-1} ; ^1H NMR (C_6D_6) δ 1.63 (s, 3H), 2.72 (brd, $J = 7.3$ Hz, 1H), 3.08 (s, 3H), 3.64 (dd, $J = 4.6, 10.5$ Hz, 1H), 3.70 (dd, $J = 5.5, 10.6$ Hz, 1H), 4.04 (s, 1H), 4.15 (d, $J = 11.9$ Hz, 1H), 4.19 (d, $J = 11.9$ Hz, 1H), 4.25–4.28 (m, 1H), 6.36 (brd, $J = 8.3$ Hz, 1H), 6.71 (ddd, $J = 0.8, 7.4, 7.6$ Hz, 1H), 6.98–7.12 (m, 6H), 7.36 (dd, $J = 1.8, 7.6$ Hz, 1H); ^{13}C NMR (C_6D_6) δ 22.8, 55.1, 72.0, 73.5, 74.6, 82.2, 111.4, 120.9, 127.9, 128.3, 128.5, 129.3, 130.2, 131.3, 138.3, 156.7, 209.6; ESI-MS m/z 353 $[\text{M}+\text{Na}]^+$; HRMS (FAB) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$, 331.1545; found, 331.1540; $[\alpha]_{\text{D}}^{24} -2.6$ (c 0.87, CH_2Cl_2)(92% ee); HPLC (DAICEL CHIRALCEL OD, 2-propanol/hexane 20/80, flow 1.0 mL/min, detection at 254 nm) t_{R} 9.7 min (minor) and 10.8 min (major).

Determination of the absolute configuration of the aldol product from hydroxyketone 12.

The absolute configuration of the aldol product *syn*-13h (from (*S,S*)-linked-BINOL) was determined after conversion to known compound **S(D)-1** ((2*R*,3*R*)-4-*O*-benzyl-2-methylbutane-1,2,3,4-tetraol) which was reported in *Tetrahedron Asymmetry*, **1997**, 8, 559–577. The transformation was performed by following the scheme S(D)-1, and *enant*-**S(D)-1** (2*S*,3*S*) was obtained. Therefore, absolute configuration of *syn*-13h was determined to be 2*R*,3*S*. Absolute configuration of the other aldol product from hydroxyketone 12 was deduced to be 2*R*,3*S* by analogy.

Scheme S(D)-1. Determination of the absolute configuration of aldol product from hydroxypropionophenone 12.

General Procedure for Catalytic Asymmetric Aldol Reaction of Ketone *rac*-12 Promoted by $\text{Et}_2\text{Zn}/(\text{S,S})$ -Sulfur-linked-BINOL **2 = 4/1 with MS 3A System:**

MS 3A (30 mg) in a test tube was activated prior to use under reduced pressure (ca. 0.7 kPa) at 160 °C for 3h. After cooling, a solution of (*S,S*)-Sulfur-linked-BINOL **2** (10.4 mg, 11.8 μmol) in THF (0.3 mL) was added under Ar. The mixture was cooled down to -20 °C. To the mixture was added Et_2Zn (60 μL , 0.06 mmol, 1.0 M in hexanes) at -20 °C. After stirring for 10 min at -20 °C, a solution of *rac*-12 (270.3 mg, 1.5 mmol) in THF (0.24 mL) was added. After 5 min at -20 °C, aldehyde **6a** (20 μL , 0.152 mmol) was added and stirred at -20 °C. The stirring was continued for 45 h at -20 °C 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 *sat. aq.* NaHCO₃, brine and dried over MgSO₄. Evaporation of solvent gave a crude mixture of the aldol products. The diastereomeric ratios of the aldol products were determined by ¹H NMR of the diastereomixture. After purification by silica gel flash column chromatography (hexane/acetone 8/1–4/1), **13a** was obtained (38.8 mg, 0.129 mmol, y. 85%, dr: *syn/anti* = 35/65, 60% ee(*syn*), 92% ee(*anti*)). Ee was determined by chiral HPLC analysis.

Synthesis of (S,S)-Sulfur linked-BINOL **2**:

Synthetic procedure for 3-bromomethyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**14**) was reported. See, ref. 15a in the text (Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 2252).

3-Thioacetoxymethyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**15**)

To a dark green solution of potassium thioacetate (1.14 g, 10 mmol) in DMF (20 mL) at 0 °C was added 3-bromomethyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**14**) (2.34 g, 5.0 mmol). The mixture was stirred at 0 °C for 10 min, then was diluted with diethyl ether. The organic layer was washed with H₂O, brine and was dried over MgSO₄. After evaporation of solvent, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10/1 to 6/1) to afford **15** as colorless foam (2.23 g, 4.83 mmol, y. 97%). IR (neat) ν 2953, 1688, 1240, 1149 cm⁻¹; ¹H NMR (CDCl₃) δ 2.37 (s, 3H), 3.01 (s, 3H), 3.17 (s, 3H), 4.47 (s, 2H), 4.49 (d, *J* = 5.8 Hz, 1H), 4.61 (d, *J* = 5.8 Hz, 1H), 5.03 (d, *J* = 7.1 Hz, 1H), 5.09 (d, *J* = 7.1 Hz, 1H), 7.11–7.15 (m, 2H), 7.18 (ddd, *J* = 7.9, 6.7, 1.3 Hz, 1H), 7.34 (ddd, *J* = 7.9, 6.7, 1.3 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), 7.25 (ddd, *J* = 6.7, 6.7, 1.3 Hz, 1H), 7.36 (ddd, *J* = 6.7, 6.7, 1.3 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.83–7.86 (m, 2H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.99 (s, 1H); ¹³C NMR (CDCl₃) δ 29.4, 30.4, 56.0, 56.9, 94.8, 99.3, 116.4, 120.5, 124.2, 125.1, 125.3, 125.4, 125.6, 126.2, 126.8, 127.8, 129.6, 129.8, 130.0, 130.8, 131.0, 133.5, 133.9, 152.5, 152.8, 195.6; EI-MS *m/z* 485 [M+Na]⁺; HRMS (FAB) [M+H]⁺ calcd for C₂₇H₂₇O₅S, 463.1579; found, 463.1580.

3,3''-(Thiodimethylene)-di-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**16**)

To a stirred solution of **15** (1.91 g, 4.13 mmol) in THF (12 mL)/CH₃OH (12 mL) at 0 °C was added NaOCH₃ (500 mg, 11.4 mmol). The mixture was stirred at 0 °C for 5 min, and then was quenched by adding *sat. aq.* NH₄Cl. The mixture was extracted with ethyl acetate (100 mL x 3). The combined organic layer was washed with brine, dried over MgSO₄. After evaporation of solvent, the residue was obtained as colorless solid. Because the intermediate thiol was not stable, the crude material was quickly subjected to the next step without further purification.

All the crude solid was dissolved in anhydrous THF (25 mL) and cooled down to 0 °C. To a solution at 0 °C was added NaH in oil (200 mg, 5 mmol as 60% purity), and then 3-bromomethyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (**14**) (2.0 g, 4.28 mmol). The mixture was stirred at 0 °C for 30 min, then was quenched by adding *sat. aq.* NH₄Cl. The mixture was extracted with ethyl acetate. The combined organic layer was washed with brine and was dried over MgSO₄. After evaporation of solvent, the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 5/1 to 2/1) to afford **16** as colorless foam (2.49 g, 3.08 mmol, y. 75% (2 steps)). IR (neat) ν 2927, 1240, 1149, 1049 cm⁻¹; ¹H NMR (CDCl₃) δ 2.80 (s, 6H), 3.15 (s, 6H), 4.14 (d, *J* = 13.6 Hz, 2H), 4.17 (d, *J* = 13.6 Hz, 2H), 4.54 (d, *J* = 5.5 Hz, 2H), 4.62 (d, *J* = 5.5 Hz, 2H), 5.01 (d, *J* = 7.0 Hz, 2H), 5.10 (d, *J* = 7.0 Hz, 2H), 7.13–7.24 (m, 8H), 7.31–7.34 (m, 4H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 8.01 (s, 2H); ¹³C NMR (CDCl₃) δ 31.8, 55.9, 56.6, 94.9, 99.3, 116.5, 120.8, 124.1, 125.0, 125.5, 125.6, 125.7, 125.9, 126.7, 127.7, 127.9, 129.6, 129.8, 129.8, 130.9, 131.8, 133.3, 134.0,

152.5, 152.9; EI-MS m/z 829 $[M+Na]^+$; HRMS (FAB) $[M+H]^+$ calcd for $C_{50}H_{47}O_8S$, 807.2991; found, 807.3017.

3,3''-(Thiodimethylene)-di-1,1'-bi-2-naphthol (2)

To a stirred solution of **16** (698.6 mg, 0.866 mmol) in CH_2Cl_2 (3 mL)/ CH_3OH (3 mL) was added $TsOH \cdot H_2O$ (32 mg, 0.168 mmol). The mixture was stirred at 40 °C for 12 h. The mixture was then diluted with ethyl acetate, washed with *sat. aq* $NaHCO_3$, brine, dried over $MgSO_4$. After evaporation, the residue was purified by silica gel flash column chromatography (hexane/ diethyl ether = 2/1 to 1/1) to afford **2** as pale yellow solid (534.6 mg, containing 9.9 w/w% diethyl ether and hexane as determined by 1H NMR, 0.764 mmol, y. 88%). IR (neat) ν 3499, 3057, 1383, 1210 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.04 (d, J = 13.9 Hz, 2H), 4.08 (d, J = 13.9 Hz, 2H), 4.98 (s, 2H), 5.54 (s, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.20 (dd, J = 7.9, 7.9 Hz, 2H), 7.24 (dd, J = 7.9, 7.9 Hz, 2H), 7.29-7.35 (m, 6H), 7.79 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.9 Hz, 2H), 7.94 (d, J = 9.2 Hz, 2H), 7.96 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 31.6, 111.4, 112.0, 117.8, 123.9, 124.2, 124.2, 124.3, 126.5, 127.2, 127.4, 128.0, 129.1, 129.4, 131.0, 131.2, 132.9, 133.4, 151.4, 152.5, 128.3; EI-MS m/z 653 $[M+Na]^+$; HRMS (FAB) $[M+H]^+$ calcd for $C_{42}H_{31}O_4S$, 631.1943; found, 631.1943. $[\alpha]_D^{25} +90.2$ (c 1.0, $CHCl_3$).

(E) Transformation of aldol adducts:

(2R, 3S)-2,3-Carbonyldioxy-1-(2-methoxyphenyl)-5-phenyl-1-pentanone (18a)

To a stirred solution of **8a** (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 °C, triphosgene (0.351 mL, 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 **18a** (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, $CHCl_3$).

(4S, 5S)-2,2-Dimethyl-5-(2-phenylethyl)-1,3-dioxolan-4-yl 2-methoxybenzoate (19a).

To a stirred solution of **17a** (29.0 mg, 0.0847 mmol) in dichloroethane (0.5 mL) at room temperature were added $NaH_2PO_4 \cdot 2H_2O$ (40.0 mg, 0.254 mmol) and *m*-chloroperbenzoic acid (41.2 mg, 0.167 mmol, >70%). After being stirred for 1h at 50 °C, 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 **19a** (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 $[M^+-ArCOO]$; HRMS (FAB) $[M+H]^+$ calcd for $C_{21}H_{25}O_5$, 357.1702; found, 357.1703; $[\alpha]_D^{24} 62.3$ (c 0.47, $CHCl_3$).

2-Methoxyphenyl (2R, 3S)-2,3-carbonyldioxy-5-phenylpentanoate (20a)

To a stirred solution of **18a** (20.2 mg, 0.0619 mmol) in dichloroethane (0.5 mL) at room temperature were

added $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (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 °C, the reaction mixture was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. 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 **20a** (19.7 mg, 0.0575 mmol, yield 93%) as a colorless 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^+]; $[\alpha]_{\text{D}}^{25} -112$ (c 0.44, CHCl_3).

(2R, 3S)-2,3-Carbonyldioxy-2'-methoxy-5-phenylpentanilide (21a)

To a stirred solution of **18a** (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 **21a** (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^+]; HRMS (FAB) [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_5$, 342.1341; found, 342.1340; $[\alpha]_{\text{D}}^{24} -75.0$ (c 0.96, CHCl_3).

(2R, 3S)-1-*o*-anisidino-5-phenyl-2,3-pentandiol (22a)

To a stirred solution of **21a** (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, 1.0 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 (2 mL), followed by addition of potassium sodium (+)-tartrate tetrahydrate (Rochelle salt, 30 mg). After stirring for 2 h 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 **22a** (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 (CDCl_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^+]; $[\alpha]_{\text{D}}^{24} -20.7$ (c 0.54, CHCl_3).