Supplemental Materials for

Entropy-Controlled Asymmetric Synthesis. How Differential Activation Entropy is Induced in the Chiral Tethered Reactions

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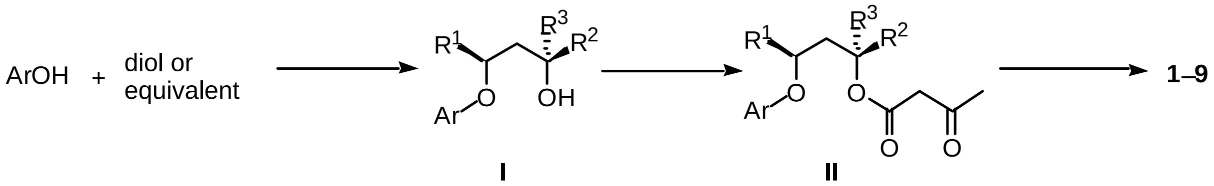
General. All temperatures are uncorrected. ^{1}H-NMR (400MHz) and ^{13}C-NMR (100MHz) were recorded on a JEOL GX-400 spectrometer in $CDCl_3$ as a solvent and internal standard (7.24 ppm and 77.1 ppm). IR spectra were obtained on a JASCO FT/IR-410 spectrometer. Mass spectra were obtained on a JEOL JMS-AX-505HA. Optical rotations were measured on a Perkin-Elmer 243B polarimeter. Analytical GLC was conducted with a Shimadzu gas chromatograph GC-17A using capillary columns. MPLC was carried out by using an FMI pump (10ml/min) and a Lobar column (MERCK Si-60 type B). All solvents were purified by distillation. All reactions were carried out under dry nitrogen atmosphere.

Preparation of substrates 1–9. The substrates were prepared by the following procedure.



For **I-1**, **I-5**, and **I-6** to **I-9**: To a solution of (2*R*,4*R*)-2,4-pentanediol or 1,3-propanediol (1.2 eq), phenol or cresol (2 g, 1.0 eq), and triphenylphosphine (1.2 eq) in THF (100 ml) was added dropwise a THF (50 ml) solution of diethyl azodicarboxylate or diisopropyl azodicarboxylate (1.2 eq). After stirring for 10–15 hours at room temperature, the solution was concentrated, then purified by column chromatography on silica gel (elution with 25% ethyl acetate in hexane) to give 3.0–3.5 g of diastereo- and enantiomerically pure phenyl or tolyl mono-ether.

I-1 (99% yield): colorless oil, $[\alpha]^{D}_{20}$ = +14.97 (c 1.00, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.28–7.23 (m, 2H), 6.95–6.90 (m, 3H), 4.58 (m, 1H), 4.04 (m, 1H), 2.58 (brs, 1H), 1.93 (ddd, *J* = 14.2, 8.8, 5.9 Hz, 1H), 1.66 (ddd, *J* = 14.2, 4.3, 3.0 Hz, 1H), 1.31 (d, *J* = 6.0, Hz, 3H), 1.23 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 127.10, 129.44, 121.09, 116.23, 73.68, 66.84, 45.56, 23.79, 19.97. IR (neat, cm^{-1}) 3400, 2940, 1600, 1500, 1380, 1250, 1120, 760, 700. Anal. calcd for $C_{11}H_{16}O_2$: C: 73.30, H: 8.95. Found: C: 72.03, H: 8.67.

I- 5 (95.0% yield): colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.31–7.27 (m, 2H), 6.98–6.89 (m, 3H), 4.13 (t, *J* = 5.9 Hz, 2H), 3.87 (t, *J* = 5.9 Hz, 2H), 2.05 (quint, *J* = 5.9 Hz, 2H), 1.71 (brs, 1H). IR (neat, cm^{-1}) 3350, 2950, 2900, 1600, 1500, 1250, 1180, 1060, 760, 700. Anal. calcd for $C_9H_{12}O_2$: C: 71.03, H: 7.95. Found: C: 70.35, H: 8.18.

I- 6 (90.2% yield): colorless oil, $[\alpha]^D_{20}$ = +13.46 (c 1.00, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.12 (m, 1H), 6.77–6.63 (m, 3H), 4.57 (m, 1H), 4.06 (m, 1H), 2.32 (s, 3H), 1.93 (ddd, *J* = 14.4, 8.8, 8.8 Hz, 1H), 1.69 (ddd, *J* = 14.4, 4.4, 3.2 Hz, 1H), 1.30 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 139.54, 129.19, 122.02, 117.22, 113.06, 100.53, 73.84, 67.04, 45.63, 23.79, 20.57, 20.07. IR (neat, cm^{-1}) 3430, 2940, 1590, 1460, 1260, 1120, 1050, 950, 880, 700. HRMS, *m*/*z* (M+) calcd for $C_{12}H_{18}O_2$, 194.1307; found, 194.1309.

I- 7 (87.5% yield): colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.15 (t like, *J* = 7.8, 7.3 Hz, 1H), 6.76 (d, *J* = 7.3 Hz, 1H), 6.73–6.70 (m, 2H), 4.08 (t like, *J* = 6.3, 5.9 Hz, 2H), 3.83 (t like, *J* = 6.3, 5.9 Hz, 2H), 2.32 (s, 3H), 2.01 (quint like, *J* = 6.3, 5.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 158.58, 139.32, 129.04, 121.53, 115.25, 111.22, 65.45, 60.26, 32.00, 21.47. IR (neat, cm^{-1}) 3365, 2951, 1712, 1602, 1491, 1263, 1158, 1064, 774, 690. HRMS, *m*/*z* (M+) calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.1019.

I- 8 (79.3% yield): colorless oil, $[\alpha]^D_{20}$ = +25.13 (c 1.02, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.16–7.13 (m, 2H), 6.90–6.85 (m, 2H), 4.62 (m, 1H), 4.07 (m, 1H), 2.74 (brs, 1H), 2.25 (s, 3H), 1.98 (ddd, *J* = 14.4, 9.0, 8.8 Hz, 1H), 1.73 (ddd, *J* = 14.4, 4.2, 2.9 Hz, 1H), 1.29 (d, *J* = 6.1 Hz, 3H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 155.07, 130.89, 127.78, 126.61, 120.76, 113.35, 73.84, 67.04, 45.66, 23.68, 20.05, 16.49. IR (neat, cm^{-1}) 3400, 1500, 1460, 1380, 1290, 1240, 1120, 1050, 960, 750. HRMS, *m*/*z* (M+) calcd for $C_{12}H_{18}O_2$, 194.1307; found, 194.1275.

I- 9 (95.0% yield): colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.17–7.13 (m, 2H), 6.89–6.82 (m, 2H), 4.11 (t like, *J* = 5.9, 5.4 Hz, 2H), 3.87 (t, *J* = 5.9 Hz, 2H), 2.23 (s, 3H), 2.06 (quint like, *J* = 5.9, 5.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 156.70, 130.53, 126.69, 126.44, 120.39, 110.82, 65.72, 60.59, 32.10, 16.26. IR (neat, cm^{-1}) 3375, 2950, 1602, 1496, 1245, 1121, 1061, 750. HRMS, *m*/*z* (M+) calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0966.

The Mitsunobu reaction of **I-1** with benzoic acid gave benzoate of **I-2** in 99.5% yield. Solvolysis of this with KOH in ethanol under reflux resulted in **I-2** in 94.1% yield. $[\alpha]^D_{20}$ =

+86.6 (c 1.0, methanol), ^{1}H NMR ($CDCl_3$) δ 7.25 (dd, *J* = 7.3, 6.3 Hz, 2H), 6.92 (m, 3H), 4.67 (m, 1H), 4.12 (m, 1H), 1.95 (brs, 1H), 1.82 (ddd, *J* = 14.3, 8.3, 2.9 Hz, 1H), 1.72 (ddd, *J* = 14.3, 9.3, 3.4 Hz, 1H), 1.3 (d, *J* = 5.9 Hz, 3H), 1.22 (d, *J* = 5.8 Hz, 3H). IR (neat, cm^{-1}) 3380, 2950, 2930, 1600, 1500, 1380, 1250, 1180, 1120, 1050, 750, 700. HRMS, *m*/*z* (M+) calcd for $C_{11}H_{16}O_2$, 180.1150; found, 180.1185.

For **I-3** and **I-4**, (3*R*)-1-benzolyoxybutane-3-ol and (3*R*)-3-tetrahydropylanoyl-1-butanol were employed instead of the diol for the Mitsunobu reaction with phenol (80.0% and 89.2% yields). After solvolysis, **I-3** and **I-4**, were obtained (98.6% and 69.1% yields).

I-3: colorless oil, $[\alpha]^D_{20}$ = +61.89 (c 0.98, MeOH). ^{1}H NMR (CDCl3) δ 7.30–7.25 (m, 2H), 6.96–6.90 (m, 3H), 4.62 (m, 1H), 3.86–3.79 (m, 2H), 2.04–1.85 (m, 3H), 1.33 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 157.48, 129.24, 120.57, 115.76, 71.43, 59.10, 39.00, 19.62. IR (neat, cm^{-1}) 3400, 2950, 1600, 1500, 1380, 1300, 1240, 1180, 1140, 1060, 760, 700. MS (M+), *m*/*z* (%) 166 (17.8), 149 (18.3), 121 (2.9), 94 (100), 77 (5.7), 66 (7.1). HRMS, *m*/*z* (M+) calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.0983.

I-4: colorless oil, $[\alpha]^D_{20}$ = –40.6 (c 1.2, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.30–7.25 (m, 2H), 6.97–6.89 (m, 3H), 4.20–4.07 (m, 3H), 2.07 (brs, 1H), 1.95–1.90 (m, 2H), 1.27 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 158.45, 129.23, 120.61, 114.28, 65.66, 65.36, 38.04, 23.51. IR (neat, cm^{-1}) 3400, 2950, 1600, 1500, 1480, 1240, 750, 700. MS (M+), *m*/*z* (%) 166 (30.4), 150 (10.4), 149 (32.6), 95 (15.8), 94 (100), 77 (20.6), 57 (11.8), 55 (26.7). HRMS, *m*/*z* (M+) calcd for $C_{10}H_{14}O_2$, 166.0994; found, 166.1006.

A typical procedure for **II** is as follows: To a solution of **I** (1.5 g), diketene (1.2 eq) in CH_2Cl_2 (60 ml) was added Et_3N (1.0eq) slowly at room temperature. After stirring for 2 hours, the mixture was quenched with water, then extracted with CH_2Cl_2 (50 ml x 3), and washed with water (100 ml) and brine (100 ml). Drying over Na_2SO_4, concentration, and column chromatography on silica gel (elution with 30% ethyl acetate in hexane) afforded 1.7–2.2 g of **II** as a light-brownish to colorless oil.

II-1 (99.3% yield): $[\alpha]^D_{20}$ = +22.8 (c 1.04, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.25 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.91 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.86 (dd, *J* = 8.8, 1.0 Hz, 2H), 5.17 (m, 1H), 4.46 (sextet like, *J* = 6.3 Hz, 1H), 3.41 (s, 2H), 2.23 (s, 3H), 2.15 (ddd, *J* = 14.2, 7.8, 6.3 Hz, 1H), 1.71 (ddd, *J* = 14.2, 6.3, 5.4 Hz, 1H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). IR (neat, cm^{-1}) 1750, 1720, 1600, 1500, 1240, 1160, 1100, 760. MS (M+), *m*/*z* (%) 264 (12.1), 121 (98.2), 85 (89.6), 77 (92.3), 43 (100). HRMS, *m/z* (M+) calcd for $C_{15}H_{20}O_4$, 264.1362; found, 264.1354.

II-2 (99.2% yield): $[\alpha]^{D}_{20}$ = +78.0 (c 1.0, methanol), IR (neat, cm^{-1}) 2980, 1750, 1720, 1600, 1500, 1240, 1150, 1110, 760. ^{1}H NMR ($CDCl_3$) δ 7.24 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.90 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.8, 1.0 Hz, 2H), 5.18 (m, 1H), 4.44 (m, 1H), 3.32 (s, 2H), 2.14 (s, 3H), 1.94–1.81 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 5.4 Hz, 3H). HRMS, *m/z* (M+) calcd for $C_{15}H_{20}O_4$, 264.1362; found, 264.1314.

II-3 (80% yield): $[\alpha]^{D}_{20}$ = +49.6 (c 0.87, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.26–7.22 (m, 2H), 6.92–6.87 (m, 3H), 5.20 (m, 1H), 4.50 (m, 1H), 3.98 (t, *J* = 5.9, 2H), 3.38 (s, 2H), 2.17 (s, 3H), 2.05–1.94 (m, 2H), 1.30 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 199.76, 166.40, 157.26, 128.93, 120.29, 115.41, 69.96, 61.48, 49.35, 35.00, 29.52, 19.30. IR (neat, cm^{-1}) 2976, 1717, 1599, 1494, 1241, 755, 694.

II-4 (97.1% yield): $[\alpha]^{D}_{20}$ = –36.5 (c 1.04, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.24 (t-like, *J* = 8.3, 7.3 Hz, 2H), 6.90 (td, *J* = 7.3, 1.0 Hz, 1H), 6.86 (d *J* = 8.3 Hz, 2H), 5.20 (m, 1H), 4.28–4.23 (m, 2H), 3.38 (s, 2H), 2.14 (s, 3H), 2.03 (m, 1H), 1.93 (m, 1H), 1.29 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 200.07, 166.24, 158.39, 129.14, 120.62, 114.23, 69.33, 63.74, 50.08, 35.21, 29.83, 19.92. IR (neat, cm^{-1}) 2979, 1716, 1600, 1497, 1360, 1245, 1049, 756, 693.

II-5 (78.9% yield): ^{1}H NMR ($CDCl_3$) δ 7.28–7.24 (m, 2H), 6.93 (t like, *J* = 7.8, 7.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 4.34 (t , *J* = 6.3 Hz, 2H), 4.03 (t like, *J* = 6.3, 5.9 Hz, 2H), 3.44 (s, 2H), 2.24 (s, 3H), 2.13 (quintet like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2968, 1742, 1600, 1497, 1361, 1244, 1152, 1052, 757, 693. HRMS, *m/z* (M+) calcd for $C_{13}H_{16}O_4$, 236.1049; found, 236.1043.

II-6 (94.7% yield): $[\alpha]^{D}_{20}$ = +24.8 (c 1.02, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.13 (t like, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.3 Hz, 1H), 6.68–6.66 (m, 2H), 5.16 (m, 1H), 4.44 (m, 1H), 3.41 (s, 2H), 2.30 (s, 3H), 2.23 (s, 3H), 2.14 (m, 1H), 1.70 (dt like, *J* = 14.2, 5.9 Hz, 1H), 1.30 (d, *J* = 5.9 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 166.47, 157.46, 139.47, 129.15, 121.51, 116.66, 112.45, 70.28, 69.80, 50.41, 42.41, 30.20, 21.57, 20.28, 19.84. IR (neat, cm^{-1}) 2980, 1740, 1710, 1260, 1150, 1100. HRMS, *m/z* (M+) calcd for $C_{16}H_{22}O_4$, 278.1518; found, 278.1521.

II-7 (93.1% yield): ^{1}H NMR ($CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.3 Hz, 2H), 6.70–6.67 (m, 2H), 4.33 (t, *J* = 6.3 Hz, 2H), 4.01 (t like, *J* = 6.3, 5.9 Hz, 2H), 3.44 (s, 2H), 2.31 (s, 3H), 2.24 (s, 3H), 2.11 (quintet like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2964, 1743, 1602, 1261, 1157, 1057, 777, 691. HRMS, *m/z* (M+) calcd for $C_{14}H_{18}O_4$, 250.1205; found, 250.1159.

II-8 (93.2% yield): $[\alpha]^D{}_{20}$ = +25.16 (c 0.95, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.13–7.09 (m, 2H), 6.84–6.79 (m, 2H), 5.19 (m, 1H), 4.46 (m, 1H), 3.40 (s, 2H), 2.23 (s, 3H), 2.19 (s, 3H), 2.17 (m, 1H), 1.74 (ddd, *J* = 14.2, 5.9, 5.4 Hz, 1H), 1.31 (d, *J* = 5.9 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 200.09, 166.30, 155.43, 130.65, 127.43, 126.46, 120.11, 112.23, 70.27, 69.52, 50.18, 42.39, 29.97, 20.09, 19.75, 16.34. IR (neat, cm^{-1}) 2979, 1717, 1601, 1493, 1360, 1239, 1119, 1038, 958, 751. HRMS, *m*/*z* (M+) calcd for $C_{16}H_{22}O_4$, 278.1518; found, 278.1517.

II-9 (99.6% yield): ^{1}H NMR (CDCl$_3$) δ 7.17–7.13 (m, 2H), 6.87 (t like, *J* = 7.3, 6.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.39 (t , *J* = 6.3 Hz, 2H), 4.06 (t like, *J* = 6.3, 5.9 Hz, 2H), 3.47 (s, 2H), 2.26 (s, 3H), 2.22 (s, 3H), 2.11 (quintet like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2963, 1743, 1602, 1496, 1245, 1123, 1051, 754. HRMS, *m*/*z* (M+) calcd for $C_{14}H_{18}O_4$, 250.1205; found, 250.1188.

A typical experiment for the preparation of **1–9** is as follows: To a solution of **II** (1.5 g, 1.0 eq), TsN$_3$ (1.5 eq) in CH$_3$CN (30 ml) was added dropwise Et$_3$N (3.0 eq) at 0 °C. After stirring for 2–3 hours, the mixture was added to 1N-NaOH (15ml). After 15–20 hours, the mixture was extracted with ether (50 ml, 3 times) and washed with water (100 ml). Drying over Na$_2$SO$_4$, concentration, and column chromatography on silica gel (elution with 20% ethyl acetate in hexane) afforded 0.5–1.7 g of the substrate as deep yellow oil (37–83 % yield).

1 (82.5% yield): $[\alpha]^D{}_{20}$ = +10.4 (c 1.11, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.25 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.91 (t like, *J* = 7.3 Hz, 1H), 6.86 (dd, *J* = 8.8, 1.0 Hz, 2H), 5.18 (m, 1H), 4.70 (brs, 1H), 4.44 (m, 1H), 2.15 (ddd, *J* = 14.2, 8.3., 5.9 Hz, 1H), 1.70 (ddd, *J* = 14.2, 6.3, 4.9 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). IR (neat, cm^{-1}) 2980, 2120, 1700, 1600, 1500, 1390, 1250, 1200, 1100, 760. MS (*m*/*z*) 148 (M+, 37 %), 220 (100).

2 (83.4% yield): $[\alpha]^D{}_{20}$ = +88.4 (c 1.1, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.24 (t-like, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 5.18 (m, 1H), 4.64 (brs, 1H), 4.41 (m, 1H), 1.91 (ddd, *J* = 14.2, 8.3, 4.4 Hz, 1H), 1.85 (ddd, *J* = 14.2, 8.8, 4.4 Hz, 1H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). IR (neat, cm^{-1}) 3100, 2980, 2110, 1700, 1600, 1500, 1380, 1250, 1190, 1110. MS (*m*/*z*) 148 (M+, 8.2%), 220 (100).

3 (72.0% yield): $[\alpha]^D{}_{20}$ = +45.6 (c 1.13, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.23 (t-like, *J* = 8.3, 7.3

Hz, 2H), 6.90 (t, J = 7.3, Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 4.71 (brs, 1H), 4.45 (m, 1H), 4.35–4.22 (m, 2H), 2.01 (m, 1H), 1.91 (m, 1H), 1.29 (d, J = 6.4 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 157.39, 129.05, 120.42, 115.51, 70.20, 61.23, 45.75, 35.43, 19.48. IR (neat, cm-1) 2975, 2111, 1694, 1599, 1494, 1361, 1241, 754, 693.

4 (90.7% yield): $[\alpha]^{D}_{20}$ = –58.5 (c 1.13, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.23 (dd, J = 8.3, 7.3 Hz, 2H), 6.90 (t, J = 7.3, Hz, 1H), 6.86 (d J = 8.3 Hz, 2H), 5.20 (m, 1H), 4.69 (brs, 1H), 3.97–3.94 (m, 1H), 2.05–1.93 (m, 2H), 1.30 (d, J = 6.4 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 158.35, 129.04, 120.35, 114.14, 68.64, 63.77, 45.87, 35.31, 20.19. IR (neat, cm^{-1}) 2979, 2110, 1686, 1599, 1497, 1379, 1245, 756, 692.

5 (58.9% yield): ^{1}H NMR (CDCl$_3$) δ 7.29–7.25 (m, 2H), 6.85–6.87 (m, 3H), 4.73 (brs, 1H), 4.36 (t , *J* = 6.3 Hz, 2H), 4.03 (t like, *J* = 6.3, 5.9 Hz, 2H), 2.12 (quint-like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2112, 1695, 1600, 1496, 1398, 1364, 1244, 1054, 755, 692.

6 (72.6% yield): $[\alpha]^{D}_{20}$ = +25.13 (c 1.02, MeOH). ^{1}H–NMR (CDCl$_3$) δ 7.12 (t like, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.67–6.64 (m, 2H), 5.17 (m, 1H), 4.70 (brs, 1H), 4.40 (m, 1H), 2.30 (s, 3H), 2.23 (s, 3H), 2.14 (m, 1H), 1.69 (ddd, *J* = 14.2, 6.6, 5.2 Hz, 1H), 1.30 (d, *J* = 5.9 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 157.44, 139.40, 129.08, 121.45, 116.61, 112.36, 70.32, 69.14, 46.33, 42.60, 21.61, 20.72, 19.93. IR (neat, cm^{-1}) 2980, 2120, 1680, 1380, 1260, 1190, 1160, 960.

7 (37.1% yield): ^{1}H NMR (CDCl$_3$) δ 7.15 (t, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.71–6.68 (m, 2H), 4.73 (brs, 1H), 4.35 (t , *J* = 6.3 Hz, 2H), 4.01 (t like, *J* = 6.3, 5.9 Hz, 2H), 2.31 (s, 3H), 2.11 (quint-like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2962, 2111, 1695, 1602, 1491, 1364, 1187, 1058, 741, 691.

8 (45.1% yield): $[\alpha]^{D}_{20}$ = +12.97 (c 1.02, MeOH). ^{1}H NMR (CDCl$_3$) δ 7.13–7.09 (m, 2H), 6.83–6.78 (m, 2H), 5.20 (m, 1H), 4.71 (brs, 1H), 4.43 (m, 1H), 2.19 (m,1H), 2.19 (s, 3H), 1.73 (ddd, *J* = 14.2, 6.6, 5.1 Hz, 1H), 1.31 (d, *J* = 5.9 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 155.49, 130.69, 127.52, 126.43, 120.10, 112.14, 70.29, 69.01, 46.20, 42.58, 20.52, 19.83, 16.38. IR (neat, cm^{-1}) 2979, 2110, 1692, 1492, 1379, 1238, 1191, 742.

9 (37.1% yield): ^{1}H NMR (CDCl$_3$) δ 7.15–7.11 (m, 2H), 6.85 (t like, *J* = 7.8, 7.8 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 4.73 (brs, 1H), 4.38 (t , *J* = 6.3 Hz, 2H), 4.03 (t like, *J* = 6.3, 5.9 Hz, 2H), 2.21 (s, 3H), 2.15 (quint-like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2962, 2111, 1695, 1602, 1496, 1364, 1244, 1123, 1052, 752.

Rhodium catalyzed cycloaddition of 1–9

Preparative procedure. To a solution of $Rh_2(OAc)_4$ (ca. 1 mg) in CH_2Cl_2 (80 ml) was added dropwise a solution of **1** (1.2 g, 4.83 mmol) in CH_2Cl_2 (80 ml) for 3 hours at room temperature. Immediately after dropping, the mixture was concentrated, and then purified by column chromatography on silica gel (elution with 20% ethyl acetate in hexane) to give a cycloheptatriene. The other substrates **2–9** were also treated by the same procedure. The structure of the product was determined by the NOE study as well as spin decoupling for the peak assignment on the ^{1}H NMR. A part of the reaction mixture was analyzed by GLC to determine the stereochemical purity.

Cycloheptatriene from **1**: colorless oil, $[\alpha]^D{}_{20}$ = +63.3 (c 1.04, MeOH). ^{1}H NMR ($CDCl_3$) δ 6.55 (dd, $J_{3,4}$ = 10.7, $J_{4,5}$ = 5.4 Hz, 1H, H-4), 6.42 (dd, $J_{3,4}$ = 10.7, $J_{2,3}$ = 6.3 Hz, 1H, H-3), 6.22 (dd, $J_{5,6}$ = 9.5, $J_{4,5}$ = 5.4 Hz, 1H, H-5), 6.00 (dd, $J_{5,6}$ = 9.5, $J_{6,7}$ = 5.4 Hz, 1H, H-6), 5.94 (d, $J_{2,3}$ = 6.3 Hz, 1H, H-2), 4.83 (m, 1H, PD), 4.33 (m, 1H, PD), 2.95 (d, $J_{6,7}$ = 5.4 Hz, 1H-7), 2.04 (s, 3H, H-8), 2.00 (ddd, J = 15.3, 11.2, 9.3 Hz, 1H, PD), 1.83 (dd like, J = 15.3, 3.9 Hz, 1H, PD), 1.34 (d, J = 4.9 Hz, 3H), 1.33 (d, J = 4.9 Hz, 3H, PD). ^{13}C NMR ($CDCl_3$) δ 169.75, 149.04, 129.10, 127.19, 125.49, 120.47, 111.40, 84.57, 73.34, 47.44, 45.42, 22.67, 22.28. IR (neat, cm^{-1}) 1740, 1390, 1330, 1210, 1190, 1140, 1090, 1050, 720. MS (M+), *m/z* (%) 220 (14.9), 176 (16.5), 134 (21.9), 107 (100), 70 (12.2), 44 (19.3). HRMS, *m/z* (M+) calcd for $C_{13}H_{16}O_3$, 220.1099; found, 220.1132. ^{1}H NMR NOE enhancement; H-7 to H-2' = 10.9%.

Cycloheptatriene from **2**: colorless oil, ^{1}H NMR δ 6.54 (m, 2H, H-3,4), 6.36 (dd, $J_{5,6}$ = 8.8, $J_{4,5}$ = 3.4 Hz, 1H, H-5), 5.86 (dd, $J_{5,6}$ = 8.8, $J_{6,7}$ = 7.3 Hz, 1H, H-6), 5.80 (d, $J_{2,3}$ = 3.4 Hz, 1H, H-2), 5.16 (m, 1H, PD), 4.51 (dd, J = 10.7, 3.4 Hz, 1H, PD), 2.29 (d, $J_{6,7}$ = 7.3 Hz, 1H, H-7), 2.08 (ddd, J = 14.2, 10.7, 3.4 Hz, 1H, PD), 1.87 (ddd, J = 14.2, 11.2, 1.5 Hz, 1H, PD), 1.35 (d, J = 5.9 Hz, 3H, PD), 1.24 (d, J = 4.9 Hz, 3H, PD). ^{13}C NMR δ 171.3, 142.5, 129.3, 128.3, 126.2, 125.4, 116.7, 104.3, 70.1, 69.1, 46.3, 45.9, 21.1. ^{1}H-NMR NOE enhancement; H-7 to H-4' = 5.5%.

Cycloheptatriene from **3**: colorless oil, ^{1}H NMR ($CDCl_3$) δ 6.55 (dd, J 3,4= 11.0, J 4,5= 5.4 Hz, 1H, H-4), 6.41 (dd, $J_{3,4}$ = 11.0, $J_{2,3}$ = 6.3 Hz, 1H, H-3), 6.22 (dd, $J_{5,6}$ = 9.3, $J_{4,5}$ = 5.4 Hz, 1H, H-5), 5.93 (d, $J_{2,3}$ = 6.3 Hz, 1H, H-2), 5.92 (dd, $J_{5,6}$ = 9.3, $J_{6,7}$ = 5.4 Hz, 1H, H-6), 4.42 (m, 1H), 4.38–4.25 (m, 2H), 3.00 (d, $J_{6,7}$ = 5.4 Hz, 1H, H-7), 2.12 (m, 1H), 1.92 (m, 1H), 1.35 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.71, 148.72, 129.34, 129.12, 127.27, 125.65, 115.73, 83.65, 64.65, 47.31, 38.01, 22.76. ^{1}H-NMR NOE enhancement; H-7 to H-3' = ca. 5.0%.

Cycloheptatriene from **4**: colorless oil, $[\alpha]^{D}_{20}$ = –1.7 (c 1.03, MeOH). ^{1}H NMR ($CDCl_3$) δ 6.56 (dd, $J_{3,4}$ = 10.9, $J_{4,5}$ = 5.4 Hz, 1H, H-4), 6.50 (dd, $J_{3,4}$ = 10.9, $J_{2,3}$ = 5.9 Hz, 1H, H-3), 6.32 (dd, $J_{5,6}$ = 9.3, $J_{4,5}$ = 5.4 Hz, 1H, H-5), 5.90 (dd, $J_{5,6}$ = 9.3, $J_{6,7}$ = 6.3 Hz, 1H, H-6), 5.86 (d, $J_{2,3}$ = 5.9 Hz, 1H, H-2), 5.01 (m, 1H), 4.35 (m, 1H), 4.01 (m, 1H), 2.50 (d, $J_{6,7}$ = 6.3 Hz, 1H, H-7), 2.16 (m, 1H), 1.97 (m, 1H), 1.37 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.95, 144.91, 127.85, 127.27, 125.43, 117.95, 106.95, 71.13, 66.92, 46.22, 38.48, 21.53.1H-NMR NOE enhancement; H-7 to H-2' = 6.0%.

Cycloheptatriene from **5**: colorless oil, ^{1}H NMR ($CDCl_3$) δ ^{1}H NMR ($CDCl_3$) δ 6.56 (dd, $J_{3,4}$ = 10.7, $J_{4,5}$ = 5.4 Hz, 1H, H-4), 6.46 (dd, $J_{3,4}$ = 10.7, $J_{2,3}$ = 6.3 Hz, 1H, H-3), 6.29 (dd, $J_{5,6}$ = 9.3, $J_{4,5}$ = 5.4 Hz, 1H, H-5), 5.91 (d, $J_{2,3}$ = 6.3 Hz, 1H, H-2), 5.86 (dd, $J_{5,6}$ = 9.3, $J_{6,7}$ = 6.3 Hz, 1H, H-6), 4.54 (ddd, J = 12.7, 5.9, 2.9 Hz, 1H), 4.45–4.36 (m, 2H), 4.05 (dm, J = 12.7 Hz, 1H), 2.78 (d, J6,7 = 6.3 Hz, 1H-7), 2.33 (m, 1H), 2.04 (m, 1H).

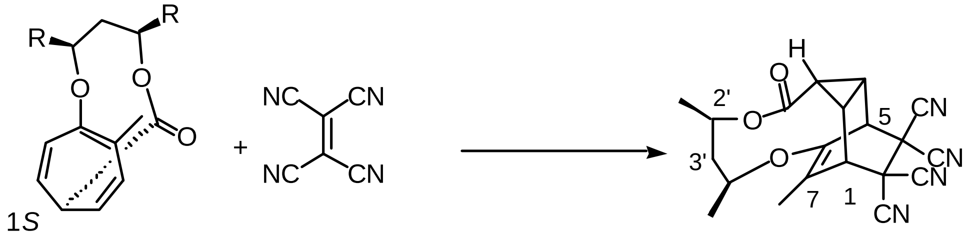
Cycloheptatriene from **6**: colorless solid, $[\alpha]^{D}_{20}$ = +40.18 (c 0.55, CH_2Cl_2). mp 61.9–68.0 °C. ^{1}H NMR ($CDCl_3$) δ 6.34 (d, $J_{4,5}$ = 5.9 Hz, 1H, H-4), 6.13 (dd, $J_{5,6}$ = 9.4, $J_{4,5}$ = 5.9 Hz, 1H, H-5), 5.91 (d, $J_{5,6}$ = 9.4, $J_{6,7}$= 5.3 Hz, 1H, H-6), 5.78 (s, 1H, H-2), 4.84 (m, 1H, PD), 4.32 (m, 1H, PD), 3.02 (d, $J_{6,7}$ = 5.3 Hz, 1H, H-7), 2.04 (s, 3H, H-8), 1.99 (m, 1H, PD), 1.85 (m, 1H, PD), 1.35 (d, J = 6.3 Hz, 3H, PD), 1.33 (d, J = 6.3 Hz, 3H, PD). ^{13}C NMR ($CDCl_3$) δ 170.00, 148.47, 136.20, 126.59, 125.67, 118.76, 114.59, 84.65, 73.31, 47.36, 45.53, 24.61, 22.69, 22.31. IR (neat, cm^{-1}) 1720, 1630, 1240, 1080, 720. HRMS, *m/z* (M+) calcd for $C_{14}H_{18}O_3$, 234.1256; found, 234.1259. ^{1}H NMR NOE enhancement; H-7 to H-4’ = 3.7%, H-7 to H-2’ = 9.2%.

Cycloheptatriene from **7**: colorless oil, ^{1}H NMR ($CDCl_3$) δ 6.34 (d, $J_{4,5}$ = 5.6 Hz, 1H, H-4), 6.17 (dd, $J_{5,6}$ = 9.3, $J_{4,5}$ = 5.6 Hz, 1H, H-5), 5.76 (dd, $J_{5,6}$ = 9.3, $J_{6,7}$ = 5.9 Hz, 1H, H-6), 5.74 (s, 1H, H-2), 4.54 (ddd, J = 12.2, 5.9, 3.4 Hz, 1H), 4.42–4.32 (m, 2H), 4.02 (ddd, J = 12.2, 5.8, 3.4 Hz, 1H), 2.89 (d, J = 5.9 Hz, 1H, H-7), 2.31 (m, 1H), 2.06 (s, 3H), 2.02 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 177.78, 146.52, 136.78, 125.96, 117.29, 117.22, 112.75, 70.23, 63.61, 46.93, 30.88, 24.64. IR (neat, cm^{-1}) 2971, 1732, 1631, 1209, 845, 724. HRMS, *m/z* (M+) calcd for $C_{12}H_{14}O_3$, 206.0943; found, 206.0969.

Cycloheptatriene from **8** with $Rh_2(OAc)_4$: colorless solid, mp 62–63 °C, $[\alpha]^{D}_{20}$ = –47.1 (c 1.47, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 6.19 (d, $J_{4,5}$ = 9.3 Hz, 1H, H-4), 6.06 (d, $J_{2,3}$ = 9.3 Hz, 1H, H-3), 5.86 (t-like, $J_{2,3}$ = 9.3, $J_{1,2}$ = 8.3, Hz, 1H, H-2), 5.69 (t-like, $J_{4,5}$ = 9.3, $J_{1,5}$ = 8.8, Hz, 1H, H-5), 4.08–4.03 (m, 2H, PD), 2.05 (ddd, J = 15.6, 12.2, 2.9 Hz, 1H, PD), 1.95 (s, 3H, 1H, H-6), 1.47 (d, J = 5.8 Hz, 3H, PD), 1.41 (d, J = 6.3 Hz, 3H, PD), 1.32 (m, 1H, PD). ^{13}C NMR

(CDCl$_3$) δ 173.92, 153.37, 129.85, 128.20, 125.34, 125.00, 122.47, 78.60, 76.94, 45.22, 42.33, 23.90, 20.93, 15.81. IR (neat, cm^{-1}) 2976, 1722, 1378, 1206, 11896, 1167, 1120, 1042, 756. HRMS, *m/z* (M+) calcd for $C_{14}H_{18}O_3$, 234.1256; found, 234.1232.

Stereochemistry of this compound was determined to be 1*S* by the NOE analysis of the product of the stereospecific Diels-Alder reaction: The obtained cycloheptatriene (9.1 mg) was treated with TCNE (12 mg, 2.4 eq.) in chloroform at 50 °C for 1 d. Silica gel purification gave a colorless solid (3.1 mg) in 23.6% yield. mp 185–186 °C. $[\alpha]^{D}_{20}$ = 27.7 (c 0.1, CH_2Cl_2), ^{1}H-NMR δ 4.16 (m, 1H, H-2'), 4.10 (m, 1H, H-4'), 3.81 (m, 1H, H-1), 3.79 (m, 1H, H-5), 2.23 (ddd, *J* = 16.4, 12.9, 3.9 Hz, 1H, H-3'), 2.00–1.85 (m, 3H, H-2,3,4), 1.75 (s, 3H, CH3-7), 1.69 (d, t-like, *J* = 16.1, 2.9 Hz, 1H, H-3'), 1.55 (d, $J_{4',5'}$ = 6.8 Hz, 3H, H-5'), 1.35 (d, $J_{1',2'}$ = 6.8 Hz, 3H, H-1'). ^{13}C NMR δ 166.0, 145.0, 121.8, 111.1, 110.9, 110.4, 77.9, 77.2, 75.5, 47.3, 44.8, 44.6, 43.8, 43.7, 23.7, 19.7, 15.5, 15.4, 13.6. ^{1}H NMR NOE enhancement; CH_3-7 to H-1, and H-5 to H-2'.



Cycloheptatriene from **8** with $Rh_2(OCOCF_3)_4$: The reaction was carried out with $Rh_2(OCOCF_3)_4$ at rt for 2 h. Silica gel column purification eluted with 20% ethyl acetate in hexane gave colorless oil in 75% yield. $[\alpha]^{D}_{20}$ = +35.5 (c 0.2, CH_2Cl_2). IR (neat, cm^{-1}) 2977, 1731, 1273, 1186, 1130, 1081. ^{1}H NMR δ 6.38 (dd, $J_{2,3}$ = 5.9 Hz, $J_{3,4}$ = 5.4 Hz, 1H, H-3), 6.25 (dd, $J_{3,4}$ = 4.9 Hz, $J_{4.5}$ = 6.4 Hz, 1H, H-4), 6.13 (d, $J_{2,3}$ = 5.9 Hz, H-2), 5.08 (m, 1H, H-2'), 4.35 (m, 1H, H-4'), 3.15 (s, 1H, H-7), 2.11 (s, 3H, CH_3-6), 2.07 (m, 1H, H-3'), 1.78 (d, *J* = 2.7 Hz, 1H, H-3'), 1.39 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR d 171.4, 145.2, 127.7, 127.5, 124.8, 124.6, 110.6, 78.6, 75.4, 51.5, 45.7, 23.0, 22.6, 22.4. HRMS, *m/z* (M+) calcd for $C_{14}H_{18}O_3$, 234.1256; found 234.1213. ^{1}H NMR NOE enhancement; H-7 to H-2'= 5.9%, and H-7 to CH_3-2 = 8.4%.

Determination of diastereomeric and regioisomeric purities. Stereoselectivity of the all rhodium-catalyzed reactions are over 90% judging by the ^{1}H and ^{13}C NMR after and before the silica gel column purification. The diastereomeric excesses at the 6a-position (7-position of the cycloheptatriene unit) were confirmed by the capillary GLC analysis after the derivation of the reaction mixture.

For example, when the reaction mixture of **1** (50–100 mg) was treated with excess $LiAlH_4$ in dry ether at –78 °C followed by treatments with acetic anhydride/pyridine, the produced diacetate showed a single peak on the GLC analysis (OV-1, 0.25 mm x60 m, 30 cm/min, 145 °C) at 56 min. When the reaction product of **1** after purification was treated with K_2CO_3 in methanol at rt, transesterification took place and gave a mixture of the methyl esters, where the stereochemical purity at the 7 position of the cycloheptatriene unit was completely lost. After the reduction and acetylation, GLC analysis showed two separated peaks at 56 and 58 min in a 1 to 1 ratio. Judging from the detection limit of these GLC conditions, production of the diastereomer in the reaction of **1** was determined to be less than 0.2%, and thus, the product diastereomeric excess is concluded to be over 99.6%. Results of GLC analysis with a chiral column (Chirasil-DEX-CB, GL Science, 0.25mm x 25m, 30 cm/min) also supported this value.

Similar analyses were conducted for the reactions of the other substrates. Since small amounts of dimmeric compounds through intramolecular additions are possible in the reactions of the substrates having lower effective molarities, the stereoselectivities might be underestimated. In addition, there is a possibility to overestimate amounts of the epimers due to other products on the GLC analyses even though the two different columns were employed. Regioselectivity in the reaction of **6–8** was determined to be over 90% by ^1H NMR.

Determination of the effective molarities. A solution of the substrate (20 mM) in a mixture of CH_2Cl_2 and benzene (= 0 : 1 to 1 : 0.03) was added to the $Rh_2(OAc)_4$ at 20 ± 1 °C. The product ratios were determined by the integration of the corresponding peaks on ^1H NMR. The results are shown in Table A. The competitive reaction of benzene and isopropoxybenzene with ethyl diazoacetate was carried out similarly. The reaction of ethyl diazoacetate (4.4 mM) with isopropoxybenzene (44 mM) and benzene (0.13–1.1 M) in the presence of $Rh_2(OAc)_4$ was carried out in dichloromethane. The results are shown in Table B.

Table A.

Substrate	concentration of benzene (M)	intramolecular vs. intermolecular addition ratio	*k*(intra)/*k*(inter)
1	11.25	31 : 69	5.05
	2.81	70 : 30	6.55
	1.61	79 : 21	6.05
	1.12	85 : 15	6.34
average			**6.00 ±0.58**
2	11.25	<2 : > 98	—
	2.81	47 : 53	2.49
	1.61	66 : 34	3.13
	1.12	69 : 31	2.94
average			**2.85 ± 0.27**
3	1.12	27 : 73	0.414
	0.56	41 : 59	0.389
	0.38	52 : 48	0.412
average			**0.406 ± 0.012**
4	1.12	21 : 79	0.316
	0.56	50 : 50	0.560
	0.38	57 : 43	0.504
average			**0.460 ± 0.104**
5	1.12	7 : 93	0.091
	0.56	16 : 84	0.107
	0.38	19 : 81	0.089
average			**0.0957 ± 0.0081**
6	11.25	46 : 54	9.583
	1.16	91 : 9	11.73
	1.12	92 : 8	12.88
average			**11.40 ± 1.37**
7	11.25	12 : 88	0.153
	0.38	35 : 65	0.200
average			**0.177 ± 0.02**
8	0.56	16: 84	0.107
	0.38	33 : 76	0.165
average			**0.130 ± 0.03**

Table B.

[PhH] /M	Product ratio from PhH / iPrOPh	*k*(iPrOPh)/*k*(PhH)
1.10	3.15	7.94
0.731	1.74	9.55
0.550	1.43	8.74
0.504	1.17	9.79
0.441	1.09	9.20
0.221	0.562	8.94
0.127	0.259	11.14
average		**9.33 ± 0.92**

Data for the intermolecular adducts with benzene

From **1**: colorless oil, $[\alpha]^{D}_{20}$ = –3.3 (c 0.93, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.26–7.22 (m, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.64 (t like, *J* = 3.4, 2.9 Hz, 2H), 6.24 (ddm, *J* = 9.3, 2.4 Hz, 2H), 5.41 (dd, *J* = 8.8, 5.9 and 5.4 Hz, 2H), 5.21 (m, 1H), 4.44 (m, 1H), 2.55 (t like, *J* = 5.9, 5.4 Hz, 1H), 2.19 (ddd, *J* = 14.2, 6.3, 5.8 Hz, 1H), 1.73 (ddd, *J* = 14.2, 6.3, 4.9 Hz, 1H), 1.32 (d, *J* = 5.9 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (CDCl3) δ 172.26, 157.41, 130.79, 129.39, 125.55, 120.63, 117.25, 115.72, 70.54, 69.21, 44.32, 42.47, 20.45, 19.95. IR (neat, cm^{-1}) 2978, 1735, 1598, 1494, 1239, 1029, 752, 693. HRMS, *m/z* (M+) calcd for $C_{19}H_{22}O_3$, 298.1569; found, 298.1534.

From **2**: colorless oil, ^{1}H NMR δ 7.25 (dd, *J* = 7.8, 7.3 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 2.9 Hz, 2H), 5.93 (tm, *J* = 9.3 Hz, 2H), 5.34 (dd, *J* = 9.3, 5.3 Hz, 2H), 5.21 (m, 1H), 4.43 (m, 1H), 2.43 (t, *J* = 5.3 Hz, 1H), 1.94–1.85 (m, 2H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.29 (d, *J* = 5.8 Hz, 3H).

From **3**: colorless oil, $[\alpha]^{D}_{20}$ = +39.5 (c 0.53, MeOH). ^{1}H NMR (CDCl3) δ 7.27–7.22 (m, 2H), 6.92 (t *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.63 (t-like, *J* = 3.4, 2.9 Hz, 2H), 6.23 (dd-like, *J* = 9.3, 3.4 and 2.9 Hz, 2H), 5.37 (dd-like, *J* = 9.3, 5.9 and 5.4 Hz, 2H), 4.51 (m, 1H), 4.37–4.28 (m, 2H), 2.53 (t like, *J* = 5.9, 5.4 Hz, 1H), 2.07 (m, 1H), 2.04 (m, 1H), 1.33 (d, *J* = 5.9 Hz, 2H).

From **4**: colorless oil, $[\alpha]^{D}_{20}$ = –60.0 (c 0.57, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.27–7.23 (m, 2H), 6.92 (t *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.63 (t, *J* = 2.9 Hz, 2H), 6.23 (m, 2H), 5.40 (dm, *J* = 8.8 Hz, 2H), 5.26 (m, 1H), 4.02–3.98 (m, 2H), 2.53 (t like, *J* = 5.9, 5.4 Hz, 1H), 2.12–2.00 (m, 2H), 1.34 (d, *J* = 6.4 Hz, 3H).

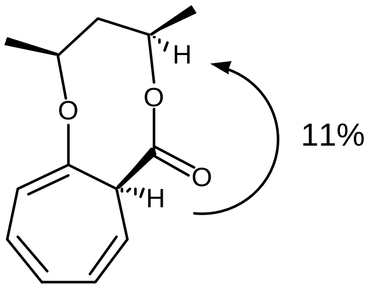
From **5**: colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.28–7.25 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.63 (t-like, *J* = 3.4, 2.9 Hz, 2H), 6.23 (dm, *J* = 9.3 Hz, 2H), 5.39 (dd, *J* = 8.8, 5.9 Hz, 2H), 4.39 (t, *J* = 6.3 Hz, 2H), 4.05 (t like, *J* = 6.3, 5.9 Hz, 2H), 2.55 (t like, *J* = 5.8, 5.4 Hz, 1H), 2.15 (quint like, *J* = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2963, 2926, 1737, 1600, 1496, 1246, 1052, 754, 692, 593. HRMS, *m/z* (M+) calcd for $C_{17}H_{18}O_3$, 270.1256; found, 270.1284.

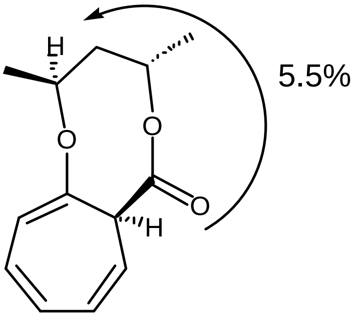
From **6**: colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.67–6.64 (m, 1H), 6.64 (t like, *J* = 3.4, 2.9 Hz, 2H), 6.24 (dd, *J* = 9.3, 2.9 Hz, 2H), 5.41 (ddd, *J* = 8.8, 5.4, 3.4 Hz, 2H), 5.23 (m, 1H), 4.45 (m, 1H), 2.54 (t like, *J* = 5.9, 5.4 Hz, 1H), 2.22 (m, 1H), 2.18 (s, 3H), 1.72 (m, 1H), 1.32 (d, *J* = 5.9 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 172.2, 157.4, 130.8, 130.7, 129.0, 128.2, 121.4, 117.4, 116.5, 112.4, 70.3, 69.1, 44.3, 42.5, 21.6, 20.5, 20.0. HRMS, *m/z* (M+) calcd for $C_{20}H_{24}O_3$, 312.1725; found, 312.1677.

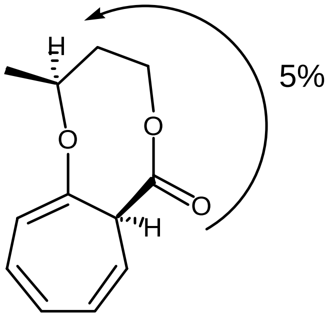
From **7**: colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.14 (t like, J = 7.3, 7.8 Hz, 1H), 6.74 (d, J = 7.3 Hz, 1H), 6.70–6.67 (m, 2H), 6.63 (t, J = 2.9 Hz, 2H), 6.24 (dm, J = 8.8 Hz, 2H), 5.40 (dd, J = 8.8, 5.9 and 5.4 Hz, 2H), 4.38 (t, J = 6.3 Hz, 2H), 4.03 (t like, J = 6.3, 5.9 Hz, 2H), 2.55 (t like, J = 5.8, 5.4 Hz, 1H), 2.30 (s, 3H), 2.14 (quint like, J = 6.3, 5.9 Hz, 2H). IR (neat, cm^{-1}) 2961, 1738, 1602, 1491, 1262, 1158, 1057, 691. HRMS, *m/z* (M+) calcd for $C_{18}H_{20}O_3$, 284.1412; found, 284.1400.

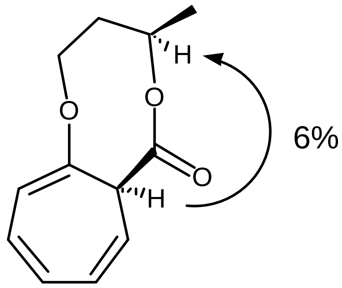
From **8**: colorless oil, $[\alpha]^D{}_{20}$ = +7.0 (c 0.93, MeOH). ^{1}H NMR ($CDCl_3$) δ 7.11 (t, J = 7.3 Hz, 2H), 6.82 (t like, J = 7.8, 7.3 Hz, 2H), 6.65 (t like, J = 3.4, 2.9 Hz, 2H), 6.25 (dd, J = 9.3, 2.9 Hz, 2H), 5.41 (ddd, J = 8.8, 5.4, 3.4 Hz, 2H), 5.40 (m, 1H), 4.42 (m, 1H), 2.55 (t like, J = 5.9, 5.4 Hz, 1H), 2.22 (m, 1H), 2.19 (s, 3H), 1.76 (ddd, J = 14.2, 6.3, 5.4 Hz, 1H), 1.32 (d, J = 5.9 Hz, 3H), 1.29 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 172.14, 155.49, 130.72, 130.68, 127.50, 126.46, 125.47, 120.14, 117.10, 112.23, 70.38, 69.06, 44.18, 42.49, 20.26, 19.92, 16.43. IR (neat, cm^{-1}) 2978, 1735, 1492, 1239, 1119, 747, 700. HRMS, *m/z* (M+) calcd for $C_{20}H_{24}O_3$, 312.1725; found, 312.1700.

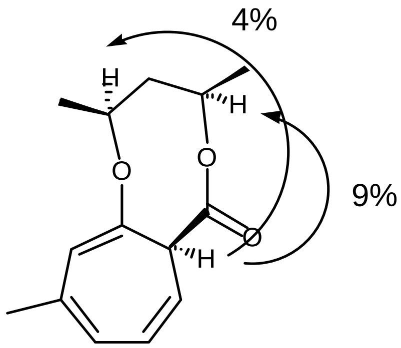
NOE table to determin the stereochemistry

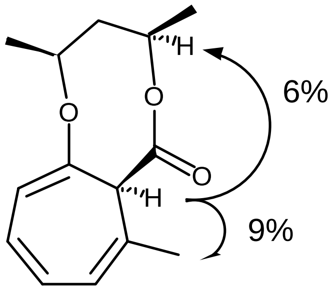


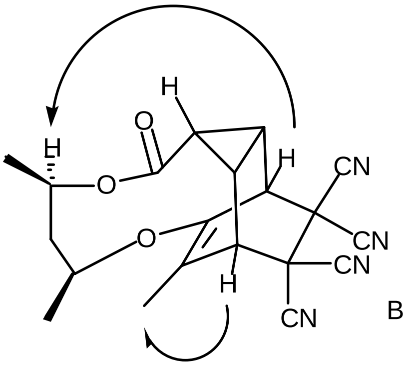












By differential NOE