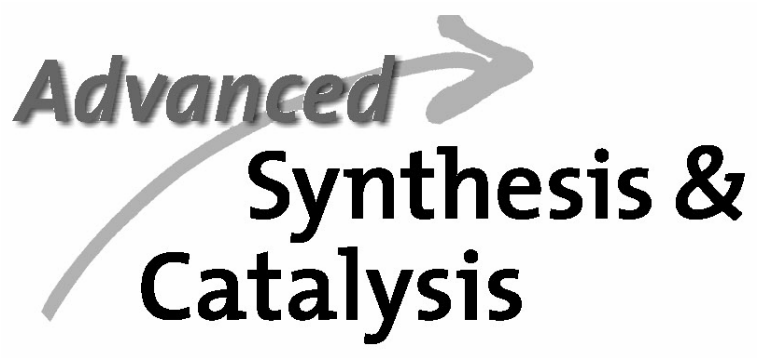

Supporting Information

Supporting Information:

Asymmetric 1,4-Addition of Organoboron Reagents to Quinone Monoketals Catalyzed by a Chiral Diene/Rhodium Complex: A New Synthetic Route to Enantio-enriched 2-Aryltetralones**

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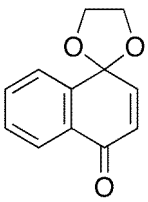
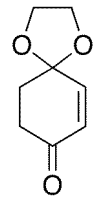
Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-*d* (δ 77.05) for ^{13}C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. 1,4-Dioxane was distilled from benzophenone-ketyl under nitrogen prior to use. THF and toluene were purified by passing through a neutral alumina column under nitrogen. Ethylene glycol, methanol, and *p*-toluenesulfonyl chloride were used as received. $[RhCl(C_2H_4)_2]_2$,[11] (1*R*,4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene ((*R*,*R*)-Ph-bod*),[12] (1*R*,4*R*)-2,5-dibenzylbicyclo[2.2.2]octa-2,5-diene ((*R*,*R*)-Bn-bod*),[2] naphthoquinone monoketal **1a**,[3] and dihydrobenzoquinone monoketal **1c**[4] were prepared according to the reported procedures.

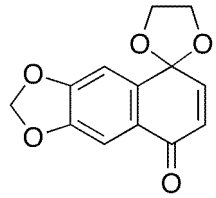


4,4-Ethylenedioxy-1-oxo-1,4-dihydronaphthalene (1a): [CAS:6541-89-5] ^{1}H NMR ($CDCl_3$) δ 4.24-4.32 (m, 2H), 4.34-4.42 (m, 2H), 6.36 (d, *J* = 10.3 Hz, 1H), 6.84 (d, *J* = 10.3 Hz, 1H), 7.50 (dd, *J* = 6.1, 2.5 Hz, 1H), 7.58-7.67 (m, 2H), 8.06 (d, *J* = 7.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 65.90, 99.92, 126.27, 126.63, 128.71, 129.44, 130.75, 133.28, 140.77, 142.76, 184.02.



4,4-Ethylenedioxy-2-cyclohexen-1-one (1c): [CAS:4683-24-3] ^{1}H NMR ($CDCl_3$) δ 2.21 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 3.96-4.12 (m, 4H), 6.00 (d, *J* = 10.2 Hz, 1H), 6.62 (d, *J* = 10.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 32.86, 35.25, 65.04, 103.92, 130.49, 146.34, 198.68.

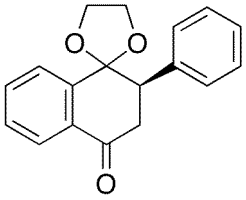
Preparation of 4,4-Ethylenedioxy-6,7-methylenedioxy-1-oxo-1,4-dihydronaphthalene (1b).



According to the reported procedure,[3] $PhI(OAc)_2$ (3.41 g, 10.6 mmol, 2.0 equiv) was added to a solution of 6,7-methylenedioxy-1-naphthol[5] (1.00 g, 5.31 mmol) in ethylene glycol (40 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. After quenched by addition of saturated $NaHCO_3$ aq., the solution was extracted with Et_2O, and the extracts were dried over $MgSO_4$. Evaporation of the solvent followed by silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 2/1) gave the product **1b** (549 mg, 2.23 mmol, 38% yield, white solid).

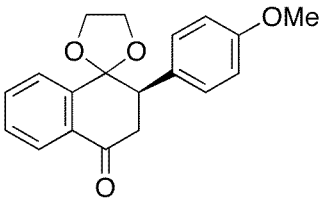
^1H NMR ($CDCl_3$) δ 4.23-4.30 (m, 2H), 4.31-4.38 (m, 2H), 6.05 (s, 2H), 6.29 (d, *J* = 10.2 Hz, 1H), 6.78 (d, *J* = 10.2 Hz, 1H), 6.99 (s, 1H), 7.45 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 65.81, 100.16, 101.98, 105.54, 106.36, 126.49, 128.45, 137.16, 142.03, 148.93, 152.01, 182.79. Anal. Calcd for $C_{13}H_{10}O_5$: C, 63.42; H, 4.09. Found: C, 63.60; H, 3.95.

A Typical Procedure for the Rhodium-Catalyzed Asymmetric 1,4-Addition of Organoboron Reagents to Monoketals (Table 2, Entry 1): To a solution of $[RhCl(C_2H_4)_2]_2$ (1.8 mg, 0.0045 mmol, 3 mol % Rh) and (*R*,*R*)-Ph-bod* (2.6 mg, 0.0099 mmol, 1.1 equiv to Rh) in 1,4-dioxane (0.60 mL) was added KOH aq. (30 μL, 2.0 M, 20 mol % KOH) at room temperature and the mixture was stirred for 5 min. Monoketal **1a** (60.2 mg, 0.30 mmol) and $PhB(OH)_2$ (**2m**) (55.3 mg, 0.45 mmol, 1.5 equiv to **1a**) was added to this catalyst solution with 1,4-dioxane (1.5 mL) and H_2O (0.18 mL) at room temperature. After 20 h stirring at 20 °C, water was added and the mixture was extracted with Et_2O, and the extracts were dried over $MgSO_4$. Evaporation of the solvent followed by preparative thin-layer chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 2/1) gave 79.9 mg (0.29 mmol, 96% yield) of **3am** as a white solid. The enantiomeric excess of **3am** was determined to be 98% ee on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10).

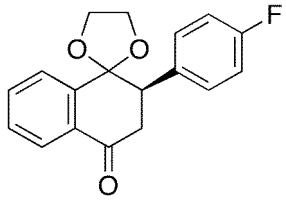


(*R*)-4,4-Ethylenedioxy-1-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene (3am): 3 mol % Rh, 20 °C: 96% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^1H NMR ($CDCl_3$) δ 2.98 (dd, *J* = 17.1, 4.0 Hz, 1H), 3.13 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.53 (dd, *J* = 17.1, 12.9 Hz, 1H), 3.71 (td, *J* = 7.5, 3.8 Hz, 1H), 3.74 (dd, *J* = 12.9, 4.0 Hz, 1H), 3.85 (dd, *J* = 14.8, 8.0 Hz, 1H), 4.07 (td, *J* = 6.8, 3.8 Hz, 1H), 7.26-7.35 (m, 3H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 41.76, 49.57, 64.86, 66.95, 107.50, 124.95,

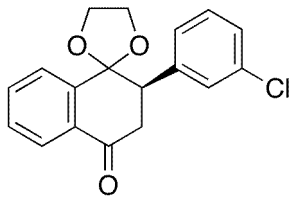
127.12, 127.43, 128.07, 129.13, 129.68, 131.66, 134.01, 138.02, 143.91, 197.10. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 8.1 min [(*R*)-enantiomer], 10.4 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ –41.8 (*c* 1.3, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.96; H, 5.81.



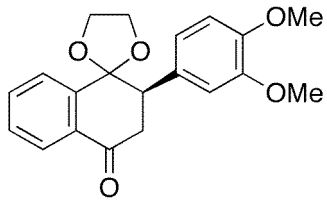
(*R*)-4,4-Ethylenedioxy-3-(4-methoxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3an): 3 mol % Rh, 20 °C: 94% yield, 99% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 2.95 (dd, *J* = 17.0, 3.9 Hz, 1H), 3.18 (dd, *J* = 15.5, 7.6 Hz, 1H), 3.47 (dd, *J* = 17.0, 12.8 Hz, 1H), 3.68 (dd, *J* = 12.8, 3.9 Hz, 1H), 3.71 (td, *J* = 6.3, 3.6 Hz, 1H), 3.81 (s, 3H), 3.86 (dd, *J* = 14.6, 7.9 Hz, 1H), 4.08 (td, *J* = 6.7, 3.9 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 42.00, 48.79, 55.24, 64.92, 66.96, 107.53, 113.48, 125.00, 127.10, 129.09, 130.13, 130.59, 131.70, 133.99, 143.98, 158.97, 197.22. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 11.4 min [(*R*)-enantiomer], 14.1 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ –25.0 (*c* 1.1, $CHCl_3$) for 99% ee. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.42; H, 6.00.



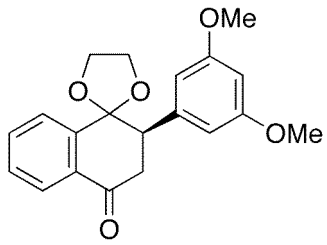
(*R*)-4,4-Ethylenedioxy-3-(4-fluorophenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3ao): 6 mol % Rh, 30 °C: 93% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 2.96 (dd, *J* = 17.1, 3.6 Hz, 1H), 3.15 (dd, *J* = 14.6, 8.2 Hz, 1H), 3.47 (dd, *J* = 17.1, 13.7 Hz, 1H), 3.70-3.78 (m, 2H), 3.86 (dd, *J* = 14.3, 7.9 Hz, 1H), 4.10 (td, *J* = 6.7, 3.6 Hz, 1H), 7.03 (t, *J* = 8.2 Hz, 2H), 7.35 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 41.87, 48.82, 64.78, 67.00, 107.38, 114.94 (d, *J* = 21 Hz), 124.96, 127.21, 129.22, 131.15 (d, *J* = 7.7 Hz), 131.61, 133.73 (d, *J* = 3.6 Hz), 134.07, 143.76, 162.28 (d, *J* = 246 Hz), 196.78. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 9.2 min [(*R*)-enantiomer], 12.2 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ –39.3 (*c* 1.4, $CHCl_3$) for 99% ee. Anal. Calcd for $C_{18}H_{15}O_3F$: C, 72.47; H, 5.07. Found: C, 72.33; H, 5.27.



(*R*)-3-(3-Chlorophenyl)-4,4-ethylenedioxy-1-oxo-1,2,3,4-tetrahydronaphthalene (3ap): 6 mol % Rh, 20 °C: 95% yield, 99% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 2.96 (dd, *J* = 17.1, 4.3 Hz, 1H), 3.21 (dd, *J* = 15.2, 7.9 Hz, 1H), 3.47 (dd, *J* = 17.1, 12.8 Hz, 1H), 3.72 (dd, *J* = 12.8, 4.3 Hz, 1H), 3.75-3.80 (m, 1H), 3.87 (dd, *J* = 14.6, 8.2 Hz, 1H), 4.12 (td, *J* = 6.7, 3.6 Hz, 1H), 7.24-7.30 (m, 3H), 7.40 (s, 1H), 7.50 (td, *J* = 7.9, 0.9 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.63 (td, *J* = 7.9, 0.9 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 41.61, 49.30, 64.79, 67.08, 107.36, 124.91, 127.26, 127.66, 127.89, 129.27, 129.29, 129.87, 131.59, 133.98, 134.08, 140.13, 143.67, 196.48. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 8.4 min [(*R*)-enantiomer], 11.5 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –41.2 (*c* 1.0, $CHCl_3$) for 99% ee. Anal. Calcd for $C_{18}H_{15}O_3Cl$: C, 68.68; H, 4.80. Found: C, 68.51; H, 4.91.

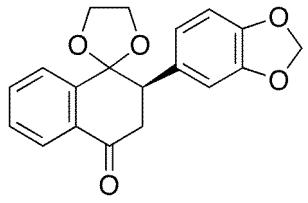


(*R*)-3-(3,4-Dimethoxyphenyl)-4,4-ethylenedioxy-1-oxo-1,2,3,4-tetrahydronaphthalene (3aq): 6 mol % Rh, 30 °C: 94% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 1/1). ^{1}H NMR ($CDCl_3$) δ 2.97 (dd, *J* = 17.0, 4.2 Hz, 1H), 3.24 (dd, *J* = 15.2, 7.9 Hz, 1H), 3.47 (dd, *J* = 17.0, 12.8 Hz, 1H), 3.68 (dd, *J* = 12.8, 4.2 Hz, 1H), 3.74 (td, *J* = 7.6, 4.0 Hz, 1H), 3.85-3.92 (m, 1H), 3.87 (s, 3H), 3.89 (s, 3H), 4.10 (td, *J* = 6.7, 3.6 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.90-6.95 (m, 2H), 7.49 (td, *J* = 8.5, 1.2 Hz, 1H), 7.58 (dd, *J* = 6.4, 1.5 Hz, 1H), 7.62 (td, *J* = 7.9, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 42.09, 49.17, 55.88, 55.98, 64.97, 66.99, 107.57, 110.82, 113.08, 121.75, 124.95, 127.11, 129.13, 130.68, 131.70, 134.01, 143.95, 148.45, 148.52, 197.08. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 19.1 min [(*R*)-enantiomer], 25.0 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –26.2 (*c* 1.1, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.37; H, 6.03.

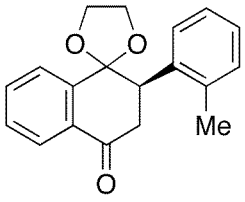


(*R*)-3-(3,5-Dimethoxyphenyl)-4,4-ethylenedioxy-1-oxo-1,2,3,4-tetrahydronaphthalene (3ar): 6 mol % Rh, 30 °C: 86% yield, 97% ee (white solid, eluent: *n*-hexane/ethyl acetate = 1/1). ^{1}H NMR ($CDCl_3$) δ 2.97 (dd, *J* = 17.1, 3.9 Hz, 1H), 3.34 (dd, *J* = 14.6, 7.3 Hz, 1H), 3.46 (dd, *J* = 17.1, 12.8 Hz, 1H), 3.68 (dd, *J* = 12.8, 3.9 Hz, 1H), 3.78 (s, 6H), 3.83 (td, *J* = 6.4, 3.6 Hz, 1H), 3.89 (dd, *J* = 14.3, 7.9 Hz, 1H), 4.13 (td, *J* = 6.7, 4.0 Hz, 1H), 6.41 (t, *J* = 2.1 Hz, 1H), 6.55 (d,

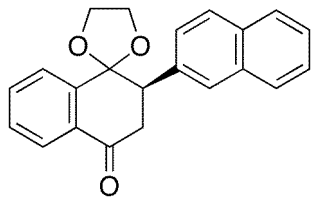
J = 2.1 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 42.04, 49.83, 55.38, 65.00, 67.08, 99.38, 107.55, 107.96, 124.88, 127.13, 129.17, 131.65, 134.04, 140.55, 143.92, 160.43, 196.98. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 11.8 min [(*R*)-enantiomer], 16.1 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –29.8 (*c* 1.0, $CHCl_3$) for 97% ee. Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.40; H, 6.00.



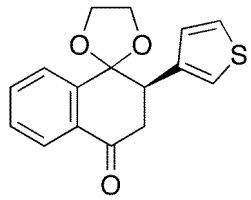
(*R*)-4,4-Ethylenedioxy-3-(3,4-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3as): 6 mol % Rh, 30 °C: 95% yield, 96% ee (white solid, eluent: *n*-hexane/ethyl acetate = 1/1). ^1H NMR ($CDCl_3$) δ 2.94 (dd, J = 17.1, 4.0 Hz, 1H), 3.30 (dd, J = 15.8, 8.5 Hz, 1H), 3.42 (dd, J = 17.1, 12.8 Hz, 1H), 3.66 (dd, J = 12.8, 4.0 Hz, 1H), 3.77-3.84 (m, 1H), 3.88 (dd, J = 14.3, 7.9 Hz, 1H), 4.13 (td, J = 6.4, 3.6 Hz, 1H), 5.96 (s, 2H), 6.78 (d, J = 7.9 Hz, 1H), 6.82 (dd, J = 8.2, 1.5 Hz, 1H), 6.90 (s, 1H), 7.49 (td, J = 8.5, 1.2 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.62 (td, J = 7.6, 1.2 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 42.20, 49.26, 64.88, 67.04, 101.01, 107.48, 107.94, 109.92, 123.00, 124.97, 127.15, 129.15, 131.63, 131.91, 134.02, 143.89, 146.87, 147.40, 196.99. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 13.9 min [(*R*)-enantiomer], 19.0 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –15.3 (*c* 1.2, $CHCl_3$) for 96% ee. Anal. Calcd for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97. Found: C, 70.54; H, 5.18.



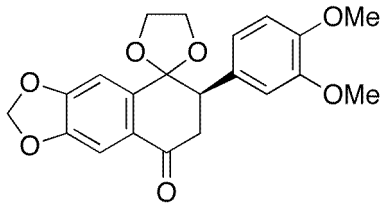
(*R*)-4,4-Ethylenedioxy-3-(2-methylphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3at): 3 mol % Rh, 30 °C: 96% yield, 99% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.85 (dd, J = 17.0, 3.9 Hz, 1H), 3.03 (dd, J = 15.8, 7.0 Hz, 1H), 3.56 (dd, J = 17.0, 13.4 Hz, 1H), 3.73 (td, J = 7.6, 3.3 Hz, 1H), 3.84 (dd, J = 14.9, 8.2 Hz, 1H), 4.04-4.12 (m, 2H), 7.17-7.22 (m, 3H), 7.43-7.46 (m, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.0 Hz, 1H), 7.63 (t, J = 7.3 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 20.50, 42.29, 44.32, 64.83, 67.21, 108.16, 124.86, 125.71, 127.13, 127.18, 128.43, 129.08, 130.23, 131.68, 134.00, 136.66, 137.98, 144.40, 197.51. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 6.4 min [(*R*)-enantiomer], 7.4 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –49.5 (*c* 1.3, $CHCl_3$) for 99% ee. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.59; H, 6.39.



(*R*)-4,4-Ethylenedioxy-3-(2-naphthyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3au): 6 mol % Rh, 20 °C: 97% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 3.07 (dd, *J* = 17.1, 4.0 Hz, 1H), 3.10 (dd, *J* = 15.2, 7.6 Hz, 1H), 3.68 (dd, *J* = 17.1, 12.8 Hz, 1H), 3.68-3.75 (m, 1H), 3.86 (dd, *J* = 14.3, 7.9 Hz, 1H), 3.94 (dd, *J* = 12.8, 4.0 Hz, 1H), 4.06 (td, *J* = 6.7, 3.6 Hz, 1H), 7.47-7.53 (m, 2H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1H), 7.56-7.63 (m, 2H), 7.66 (td, *J* = 7.9, 1.2 Hz, 1H), 7.81-7.89 (m, 4H), 8.13 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 41.92, 49.70, 64.87, 67.04, 107.71, 124.96, 125.96, 126.04, 127.20, 127.48, 127.57, 127.93, 128.03, 128.54, 129.19, 131.70, 132.79, 133.19, 134.07, 135.66, 143.99, 197.04. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 11.6 min [(*R*)-enantiomer], 17.0 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –34.9 (*c* 1.1, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 81.28; H, 5.40.

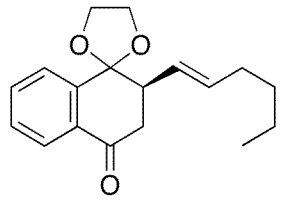


(*R*)-4,4-Ethylenedioxy-1-oxo-3-(3-thienyl)-1,2,3,4-tetrahydronaphthalene (3av): 6 mol % Rh, 30 °C: 87% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 3.29 (dd, *J* = 17.1, 4.3 Hz, 1H), 3.41 (dd, *J* = 17.1, 11.9 Hz, 1H), 3.43-3.50 (m, 1H), 3.76 (td, *J* = 6.4, 4.5 Hz, 1H), 3.86 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.92 (dd, *J* = 14.3, 7.6 Hz, 1H), 4.13 (td, *J* = 7.0, 4.2 Hz, 1H), 7.12-7.18 (m, 2H), 7.25-7.32 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 42.19, 45.15, 65.17, 66.86, 107.27, 123.20, 124.83, 124.98, 127.13, 128.86, 129.19, 131.69, 134.04, 139.03, 143.56, 196.68. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 11.8 min [(*R*)-enantiomer], 13.7 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ –26.2 (*c* 1.1, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93. Found: C, 67.23; H, 5.16.

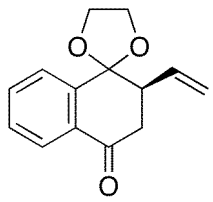


(*R*)-3-(3,4-Dimethoxyphenyl)-4,4-ethylenedioxy-6,7-methylenedioxy-1-oxo-1,2,3,4-tetrahydronaphthalene (3bq): 10 mol % Rh, 20 °C: 95% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 1/1). ^{1}H NMR ($CDCl_3$) δ 2.91 (dd, *J* = 17.1, 3.9 Hz, 1H), 3.20 (dd, *J* = 14.9, 7.6 Hz, 1H), 3.40 (dd, *J* = 17.1, 12.5 Hz, 1H), 3.63 (dd, *J* = 12.5, 3.9 Hz, 1H), 3.72 (td, *J* = 6.4, 3.6 Hz, 1H), 3.86 (dd, *J* = 14.6, 7.3 Hz, 1H), 3.88 (s, 3H), 3.89 (s, 3H), 4.06 (td, *J* = 7.6, 3.9 Hz, 1H), 6.04

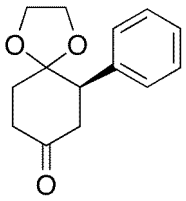
(d, *J* = 1.2 Hz, 1H), 6.05 (d, *J* = 1.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.87-6.92 (m, 2H), 6.98 (s, 1H), 7.48 (s, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 41.77, 49.36, 55.88, 56.00, 65.07, 66.92, 102.02, 104.88, 106.26, 107.65, 110.82, 113.08, 121.76, 127.25, 130.67, 141.14, 148.47, 148.52, 148.61, 152.54, 195.39. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 80/20, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 23.9 min [(*R*)-enantiomer], 39.0 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ –29.5 (*c* 1.0, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24. Found: C, 65.38; H, 5.46.



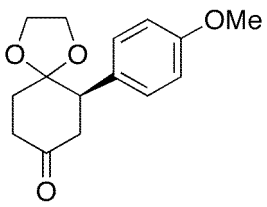
(*R*)-4,4-Ethylenedioxy-3-((*E*)-1-hexenyl)-1-oxo-1,2,3,4-tetrahydro naphthalene (5am): 3 mol % Rh, 30 °C: 94% yield, 99% ee (colorless oil, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.1 Hz, 3H), 1.17-1.35 (m, 4H), 1.93-2.07 (m, 2H), 2.93-2.99 (m, 2H), 3.10 (q, *J* = 6.9 Hz, 1H), 4.07-4.18 (m, 3H), 4.21-4.29 (m, 1H), 5.47 (dd, *J* = 15.5, 6.9 Hz, 1H), 5.59 (dt, *J* = 15.5, 6.6 Hz, 1H), 7.45 (td, *J* = 7.2, 1.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.60 (td, *J* = 7.1, 1.3 Hz, 1H), 8.01 (dd, *J* = 7.8, 0.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 13.90, 22.07, 31.33, 32.40, 41.75, 46.92, 65.49, 66.40, 107.45, 125.08, 126.66, 126.89, 129.03, 131.81, 133.84, 134.40, 142.81, 196.92. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 254 nm, flow rate = 1.0 mL/min, retention times: 5.5 min [(*R*)-enantiomer], 6.2 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ +10.3 (*c* 1.0, $CHCl_3$) for 99% ee. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.75; H, 7.97.



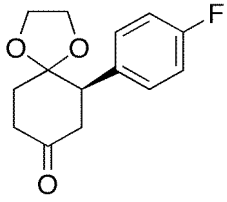
(*R*)-3-Ethenyl-4,4-ethylenedioxy-1-oxo-1,2,3,4-tetrahydronaphthalene (5an): 3 mol % Rh, 30 °C, 3 equiv of potassium vinyltrifluorobotate[6]: 92% yield, 96% ee (colorless oil, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 2.98 (dd, *J* = 17.5, 7.9 Hz, 1H), 3.01 (dd, *J* = 17.5, 5.4 Hz, 1H), 3.16 (dddt, *J* = 7.9, 6.9, 5.4, 1.3 Hz, 1H), 4.10-4.20 (m, 3H), 4.23-4.29 (m, 1H), 5.18 (dt, *J* = 10.4, 1.3 Hz, 1H), 5.21 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.92 (ddd, *J* = 17.1, 10.4, 6.9 Hz, 1H), 7.47 (td, *J* = 7.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.61 (td, *J* = 7.8, 1.3 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 40.99, 47.67, 65.53, 66.39, 107.30, 118.11, 125.06, 127.00, 129.18, 131.79, 133.92, 135.33, 142.59, 196.55. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 98/2, wavelength = 254 nm, flow rate = 0.5 mL/min, retention times: 38.9 min [(*R*)-enantiomer], 41.1 min [(*S*)-enantiomer]). $[\alpha]^{20}_{D}$ +5.6 (*c* 0.64, $CHCl_3$) for 96% ee. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.87; H, 6.42.



(*R*)-4,4-Ethylenedioxy-3-phenylcyclohexanone (3cm): [CAS:446312-13-6] 6 mol % Rh, 20 °C: 82% yield, 98% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 2.00-2.11 (m, 2H), 2.45-2.53 (m, 1H), 2.56 (ddd, *J* = 14.3, 4.4, 2.4 Hz, 1H), 2.78 (dddd, *J* = 14.9, 11.5, 8.1, 0.9 Hz, 1H), 3.09 (dd, *J* = 13.6, 7.2 Hz, 1H), 3.14 (dd, *J* = 14.3, 13.2 Hz, 1H), 3.32 (dd, *J* = 13.2, 4.4 Hz, 1H), 3.61-3.67 (m, 1H), 3.76-3.81 (m, 1H), 3.82-3.87 (m, 1H), 7.23-7.33 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 34.60, 38.62, 44.26, 50.02, 65.22, 65.37, 108.60, 127.21, 127.97, 129.28, 138.55, 209.99. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 210 nm, flow rate = 0.5 mL/min, retention times: 13.6 min [(*R*)-enantiomer], 14.5 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ +8.4 (*c* 1.4, $CHCl_3$) for 98% ee.



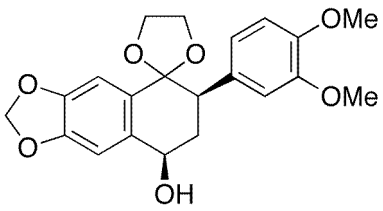
(*R*)-4,4-Ethylenedioxy-3-(4-methoxyphenyl)cyclohexanone (3cn): 6 mol % Rh, 20 °C: 80% yield, 96% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 1.98-2.10 (m, 2H), 2.43-2.52 (m, 1H), 2.54 (ddd, *J* = 14.3, 4.4, 2.4 Hz, 1H), 2.75 (ddd, *J* = 14.9, 11.9, 7.6 Hz, 1H), 3.09 (t, *J* = 14.0 Hz, 1H), 3.15 (dd, *J* = 13.7, 7.0 Hz, 1H), 3.26 (dd, *J* = 13.1, 4.4 Hz, 1H), 3.61-3.67 (m, 1H), 3.76-3.81 (m, 1H), 3.80 (s, 3H), 3.82-3.87 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 34.46, 38.61, 44.48, 49.26, 55.21, 65.22, 65.37, 108.63, 113.37, 130.17, 130.70, 158.80, 209.98. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 210 nm, flow rate = 0.5 mL/min, retention times: 16.1 min [(*R*)-enantiomer], 18.2 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ +7.5 (*c* 1.8, $CHCl_3$) for 96% ee. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.40; H, 6.66.



(*R*)-4,4-Ethylenedioxy-3-(4-fluorophenyl)cyclohexanone (3co): 6 mol % Rh, 20 °C: 75% yield, 97% ee (white solid, eluent: *n*-hexane/ethyl acetate = 2/1). ^{1}H NMR ($CDCl_3$) δ 1.99-2.17 (m, 2H), 2.44-2.53 (m, 1H), 2.54 (ddd, *J* = 14.3, 4.6, 2.4 Hz, 1H), 2.76 (ddd, *J* = 14.6, 12.5, 7.3 Hz, 1H), 3.09 (t, *J* = 13.4 Hz, 1H), 3.13 (dd, *J* = 13.7, 7.0 Hz, 1H), 3.31 (dd, *J* = 13.4, 4.6 Hz, 1H), 3.60-3.68 (m, 1H), 3.77-3.93 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 7.26 (dd, *J* = 8.5, 5.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 34.43, 38.54, 44.35, 49.27, 65.21, 65.34, 108.43, 114.78 (d, *J* = 21 Hz), 130.71 (d, *J* = 7.7 Hz), 134.21 (d, *J* = 3.1 Hz), 162.11 (d, *J* = 245 Hz), 209.54. The ee was determined on a Chiralpak AD-H column (eluent: *n*-hexane/2-propanol = 90/10, wavelength = 210 nm, flow rate = 0.5 mL/min, retention times: 13.7 min [(*R*)-enantiomer], 14.6 min [(*S*)-enantiomer]). $[\alpha]^{20}_D$ +2.1 (*c* 1.7, $CHCl_3$) for 97% ee. Anal. Calcd for $C_{14}H_{15}O_3F$: C, 67.19; H, 6.04. Found: C, 67.14; H, 6.13.

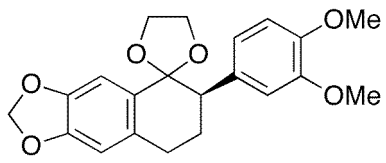
Transformation of 3bq into 9 (Scheme 3.)

1) Synthesis of 6 from 3bq



(1*R*,3*R*)-3-(3,4-Dimethoxyphenyl)-4,4-ethylenedioxy-1-hydroxy-6,7-methylenedioxy-1,2,3,4-tetrahydronaphthalene (6): To a solution of **3bq** (101 mg, 0.263 mmol: 98% ee, obtained by the reaction catalyzed by Rh/(*R*,*R*)-Ph-bod*) in THF (1.5 mL), was added $LiAlH_4$ (10.0 mg, 0.263 mmol, 1.0 equiv) at 0 °C, and the mixture was stirred at the same temperature for 1 h. After quenched by careful addition of cold water at 0 °C, the solution was extracted with Et_2O, and the extracts were dried over $MgSO_4$. Evaporation of the solvent followed by preparative thin-layer chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 1/1) gave the product **6** as a *syn* isomer exclusively (95.9 mg, 0.250 mmol, 94% yield, white solid).
^{1}H NMR ($CDCl_3$) δ 2.00 (broad s, 1H), 2.37-2.53 (m, 2H), 3.16 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.23 (dd, *J* = 14.3, 7.3 Hz, 1H), 3.35 (dd, *J* = 11.9, 6.7 Hz, 1H), 3.84 (dd, *J* = 14.3, 7.3 Hz, 1H), 3.89 (s, 6H), 4.02 (dd, *J* = 11.6, 6.7 Hz, 1H), 4.65-4.87 (m, 1H), 5.94 (s, 1H), 5.96 (s, 1H), 6.84 (t, *J* = 8.2 Hz, 2H), 6,87-6.98 (m, 2H), 7.07 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 37.68, 48.42, 55.88, 55.99, 65.32, 67.00, 69.23, 101.21, 105.32, 106.54, 108.93, 110.73, 113.13, 121.84, 132.43, 132.77, 134.55, 147.35, 148.17, 148.36, 148.45. The ee of **6** was 98% ee (Chiralpak AD-H, eluent: *n*-hexane/2-propanol = 50/50, flow rate = 0.5 mL/min, wavelength = 210 nm, retention times: 19.9 min [(1*S*,3*S*)-enantiomer], 22.6 min [(1*R*,3*R*)-enantiomer]). $[\alpha]^{20}_D$ –81.0 (*c* 0.71, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.07; H, 5.62.

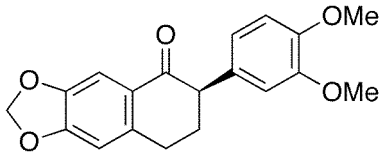
2) Synthesis of 8 from 6 (through 7)



(*R*)-2-(3,4-Dimethoxyphenyl)-1,1-ethylenedioxy-6,7-methylenedioxy-1,2,3,4-tetrahydronaphthalene (8): To a solution of **6** (81.5 mg, 0.211 mmol) in THF (1.5 mL), was added *n*-BuLi (200 μL, 0.316 mmol, 1.58 M in *n*-hexane, 1.5 equiv) at 0 °C, and the mixture was stirred at the same temperature for 0.5 h. To this reaction solution was added *p*-toluenesulfonyl chloride (68.4 mg, 0.359 mmol, 1.7 equiv) at 0 °C and the mixture was stirred at room temperature for 12 h. After addition of water, the solution was quickly extracted with Et_2O, and the extracts were dried over $MgSO_4$. Evaporation of the solvent gave the crude chlorinated product **7**, which was used immediately

for the next reaction without further purification because **7** was easily aromatized on silica gel. To a solution of the crude **7** in toluene (1.5 mL), was added $NaBHEt_3$ (2.10 mL, 2.11 mmol, 1.0 M in toluene, 10 equiv) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. After quenched by addition of water at 0°C, the solution was extracted with Et_2O, and the extracts were dried over $MgSO_4$. Evaporation of the solvent followed by preparative thin-layer chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 1/1) gave the product **8** (47.7 mg, 0.129 mmol, 61% yield in 2 steps, white solid).
^{1}H NMR ($CDCl_3$) δ 2.01-2.08 (m, 1H), 2.42-2.53 (m, 1H), 2.83-2.92 (m, 2H), 3.14 (dd, *J* = 12.8, 2.4 Hz, 1H), 3.26 (q, *J* = 7.3 Hz, 1H), 3.40 (dd, *J* = 11.8, 7.0 Hz, 1H), 3.82-3.97 (m, 1H), 3.87 (s, 3H), 3.88 (s, 3H), 4.03 (dd, *J* = 11.8, 7.0 Hz, 1H), 5.91 (s, 1H), 5.92 (s, 1H), 6.58 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6,86-6.97 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 27.38, 29.43, 49.89, 55.87, 55.96, 65.38, 66.70, 100.92, 105.75, 107.98, 109.22, 110.72, 113.17, 121.73, 131.57, 132.68, 133.60, 146.22, 147.81, 147.94, 148.39. The ee of **8** was 98% ee (Chiralpak AD-H, eluent: *n*-hexane/2-propanol = 50/50, flow rate = 0.5 mL/min, wavelength = 210 nm, retention times: 15.0 min [(*S*)-enantiomer], 27.3 min [(*R*)-enantiomer]). $[\alpha]^{20}_D$ –54.7 (*c* 0.65, $CHCl_3$) for 98% ee. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 68.25; H, 5.78.

3) Synthesis of 9 from 8



(*R*)-2-(3,4-Dimethoxyphenyl)-6,7-methylenedioxy-1-oxo-1, 2,3,4-tetrahydronaphthalene (9): [CAS:41303-46-2] To a solution of **8** (30.2 mg, 0.0815 mmol) in methanol (1.5 mL), 10% HCl aq. (200 μL) was slowly added at –15 °C and the mixture was stirred at the same temperature for 1 h. After addition of cold water, the solution was quickly extracted with Et_2O, and the extracts were dried over Na_2SO_4. Evaporation of the solvent followed by flash silica gel column chromatography (eluent: *n*-hexane/ethyl acetate = 2/1) gave the product **9** (21.5 mg, 0.0660 mmol, 81% yield, white solid).
^{1}H NMR ($CDCl_3$) δ 2.32-2.42 (m, 2H), 2.91-3.07 (m, 2H), 3.68 (t, *J* = 7.9 Hz, 1H), 3.85 (s, 3H), 3.86 (s, 3H), 6.01 (s, 2H), 6.65-6.75 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 1H), 7.52 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.04, 31.50, 53.44, 55.92, 55.97, 101.69, 106.81, 107.91, 111.40, 111.97, 120.41, 127.70, 132.48, 140.98, 147.11, 148.10, 149.01, 152.18, 196.68. The ee of **9** was 98% ee (Chiralpak AD-H, eluent: *n*-hexane/2-propanol = 50/50, flow rate = 0.5 mL/min, wavelength = 210 nm, retention times: 31.4 min [(*S*)-enantiomer], 37.1 min

[(*R*)-enantiomer]). $[\alpha]^{20}_D$ –20.6 (*c* 0.26, CH_2Cl_2) for (*R*) isomer (lit.[7] $[\alpha]^{20}_D$ +20.6 (*c* 0.3, CH_2Cl_2) for (*S*) isomer with >99% ee).

References

[1] R. Cramer, *Inorg. Synth.* **1974**, *15*, 14.
[2] Y. Otomaru, K. Okamoto, R. Shintani, T. Hayashi, *J. Org. Chem.* **2005**, *70*, 2503.
[3] F. Farina, M. C. del Paredes, J. J. Soto, *An. Quim.* **1995**, *91*, 50.
[4] R. C. Larock, T. R. Hightower, G. A. Kraus, P. Hahn, D. Zheng, *Tetrahedron Lett.* **1995**, *36*, 2423.
[5] F. Dallacker, P. Schneider, *Chem. Ztg.* **1986**, *110*, 455.
[6] G. A. Molander, M. R. Rivero, *Org. Lett.* **2002**, *4*, 107.
[7] J. L. Vicario, D. Badía, E. Domínguez, L. Carrillo, *Tetrahedron: Asymmetry*, **2000**, *11*, 1227.