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# Supporting Information

for

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# Supporting Information for "A New Dirhodium(II) Carboxamidate Complex as a Chiral Lewis Acid Catalyst for Enantioselective Hetero-Diels–Alder Reactions"

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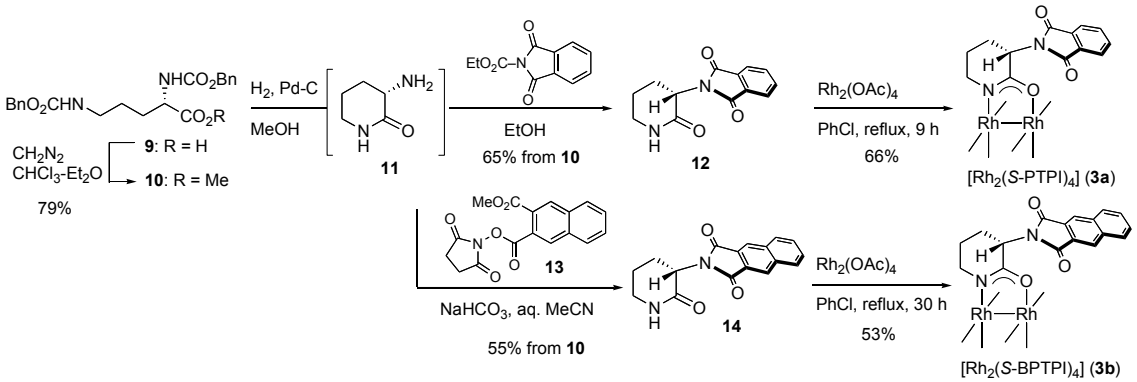
## Experimental Section

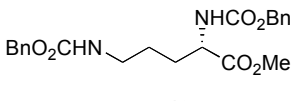
**General**. Melting points were determined on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer and absorbance bands are reported in wavenumber ($cm^{-1}$). $^1H$ NMR spectra were recorded on JEOL JNM-EX 270 (270 MHz) spectrometer or JEOL JNM-AL 400 (400 MHz) spectrometer. Chemical shifts are reported relative to internal standard (tetramethylsilane; $\delta_H$ 0.00, $CDCl_3$; $\delta_H$ 7.26, $C_6D_6$; $\delta_H$ 7.20 or DMSO-$d_6$; $\delta_H$ 2.49). Data are presented as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant and integration. $^{13}C$ NMR spectra were recorded on JEOL JNM-EX 270 (67.8 MHz) spectrometer or JEOL JNM-AL 400 (100 MHz) spectrometer. The following internal references were used: $CDCl_3$ (δ 77.0), $C_6D_6$ (δ 128.6) and DMSO-$d_6$ (δ 40.5). Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). EI-MS spectra were obtained on a JEOL FAB-mate spectrometer, operating with an ionization energy of 70 eV. FAB-MS spectra were obtained on a JEOL JMS-HX 110 spectrometer. Column chromatography was carried out on Merck Kieselgel 60 (70–230 mesh) or Kanto silica gel 60 N (63–210 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 $F_{254}$ plates with visualization by ultraviolet, anisaldehyde stain solution or phosphomolybdic acid stain solution. Analytical high performance liquid chromatography (HPLC) was performed on a JASCO PU-1580 intelligent HPLC pump with JASCO UV-1575 intelligent UV/VIS detector. Detection was performed at 254 nm. Chiralcel OD-H and OJ, Chiralpak AD, AD-H and AS columns (0.46 cm×25 cm) from Daicel were used. Retention times ($t_R$) and peak ratios were determined with Shimadzu C-R6A chromatopac integrator.

All non aqueous reactions were carried out in flame-dried glassware under Ar atmosphere unless otherwise noted. Reagents and solvents were purified by standard means. $CH_2Cl_2$ was distilled from $P_2O_5$ and then $CaH_2$.

**Preparation of Chiral Dirhodium(II) Carboxamidates 3a and 3b**

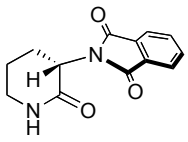



***N*,*N*'-Bis(benzyloxycarbonyl)-L-ornitine methyl ester (10).** To a solution of *N*,*N*'-bis(benzyloxycarbonyl)-L-ornitine (**9**)[1] (10 g, 25.0 mmol) in $CHCl_3$ (80 mL) was added diazomethane in ether (ca. 80 mmol) at 0 °C, and the mixture was stirred until the yellow color of the diazomethane disappeared. Evaporation followed by chromatography (silica gel, 1:1 hexane/EtOAc) and recrystallization from 20:1 ether/hexane (200 mL) afforded **10** (7.9 g, 79%) as colorless plates; mp 74–76 °C; Rf = 0.47 (1:1 hexane/EtOAc); $[\alpha]_D^{24}$ +10.8° (*c* 1.03, $CHCl_3$); IR (KBr) ν: 3328, 1753, 1689, 1537, 1263 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$, 60 °C) δ 1.47–1.74 (m, 3H), 1.85 (m, 1H), 3.19 (q, *J* = 6.5 Hz, 2H), 3.71 (s, 3H), 4.35 (dd, *J* = 6.8, 13.0 Hz, 1H), 4.73 (br-s, 1H), 5.02–5.16 (m, 4H), 5.25 (br-s, 1H), 7.22–7.38 (m, 10H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 25.9, 30.0, 40.5, 52.5, 53.5, 66.7, 67.0, 128.0, 128.1, 128.4, 136.0, 136.4, 155.8, 156.3, 172.5; EI-HRMS *m/z* calcd for $C_{22}H_{26}N_2O_6$ ($M^+$) 414.1790, found 414.1786; Anal. Calcd for $C_{22}H_{26}N_2O_6$ C, 63.76; H, 6.32; N, 6.76. Found: C, 63.68; H, 6.44; N, 6.87.

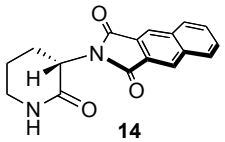


**10**

**(*S*)-3-Phthalimido-2-piperidinone (12)**. A solution of **10** (5.20 g, 12.5 mmol) in MeOH (50 mL) was stirred with 10% Pd/C (520 mg) under 1 atm of $H_2$ at rt for 12 h. The catalyst was removed by filtration, and the filtrate was concentrated *in vacuo* to afford (*S*)-3-amino-2-piperidin one (**11**) (1.42 g), which was dissolved in EtOH (25 mL) and *N*-ethoxycarbonylphthalimide (3.43 g, 15.6 mmol) was added. The mixture was stirred at rt for 30 min, evaporated, and partitioned between EtOAc (320 mL) and water (80 mL). The organic layer was washed with brine (2 × 80 mL), and dried over $Na_2SO_4$. Filtration and evaporation *in vacuo* followed by column chromatography (silica gel, 80:1 $CHCl_3$/MeOH) provided **12** (9.5 g) as a white solid, which was recrystallized from MeOH (200 mL) afforded colorless needles (8.07 g, 65%); mp 169–171 °C (dec); $[\alpha]_D^{22}$ –46.7° (*c* 1.11, $CHCl_3$) [lit.,[2] mp 167 °C (dec), $[\alpha]_D^{22}$ –36.5° (*c* 1.11, $CHCl_3$)]; Rf = 0.40 (50:1 $CHCl_3$/MeOH); $^1H$ NMR (270 MHz, $CDCl_3$) δ

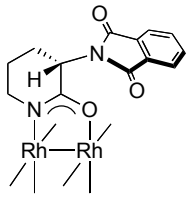

**12**

1.93–2.23 (m, 3H), 2.46 (m, 1H), 3.43 (m, 1H), 3.58 (m, 1H), 4.86 (dd, *J* = 6.0, 12.0 Hz, 1H), 5.91 (br-s, 1H), 7.69 (m, 2H), 8.05 (m, 2H), 8.34 (s, 2H). The homochirality of **12** was established by comparison of retention time in HPLC (Chiralpak AD column, 3:1 hexane/*i*-PrOH, 1.0 mL/min) with the racemic sample: $t_R$ = 13.7 min for (*R*)-enantiomer; $t_R$ = 30.7 min for (*S*)-enantiomer.



**14**

**(3*S*)-3-(1,3-Dioxobenzo[f]isoindol-2-yl)-2-piperidinone (14).** Methyl 3-[(succinimidooxy)carbonyl]-2-naphthoate (**13**)[3] (16.3 g, 50.0 mmol) was added to a solution of crude **11** (prepared from 20.7 g of **10**) in MeCN (600 mL) at rt followed by a solution of $NaHCO_3$ (21.0 g, 250 mmol) in water (400 mL). After 48 h of stirring at this temperature, the whole was partitioned between $CHCl_3$ (600 mL) and water (200 mL). The seprated aqueous layer was extracted with $CHCl_3$ (3 × 200 mL), and the combined organic extracts was washed with brine (2 × 100 mL), dried over $Na_2SO_4$. Filtration and evaporation *in vacuo* followed by column chromatography (silica gel, 80:1 $CHCl_3$/MeOH) provided **14** (10.6 g) as a white solid, which was recrystallized from EtOH (1000 mL) afforded colorless needles (8.09 g, 55%); mp >280 °C; Rf = 0.43 (10:1 $CHCl_3$/MeOH); $[\alpha]_D^{23}$ –77.2° (*c* 1.22, $CHCl_3$); IR (KBr) ν: 3382, 1765, 1713, 1676, 1644, 1379, 770 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.93–2.23 (m, 3H), 2.46 (dq, J = 3.2, 12.8 Hz, 1H), 3.43 (m, 1H), 3.58 (dt, J = 4.4, 11.6 Hz, 1H), 4.86 (dd, *J* = 6.0, 12.0 Hz, 1H), 5.91 (br-s, 1H), 7.69 (m, 2H), 8.05 (m, 2H), 8.34 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 22.4, 26.3, 42.5, 49.5, 124.8, 127.7, 129.1, 130.2, 135.4, 167.2, 167.9; FAB-HRMS *m/z* calcd for $C_{17}H_{15}N_2O_3$ ($MH^+$) 295.1083, found 295.1094; Anal. Calcd for $C_{17}H_{14}N_2O_3$ C, 69.38; H, 4.79; N, 9.52. Found: C, 69.53; H, 4.96; N, 9.50. The homochirality of **14** was established by comparison of retention time in HPLC (Chiralpak AS column, 3:1 hexane/$^i$PrOH, 1.0 mL/min) with the racemic sample: $t_R$ = 44.6 min for (*R*)-enantiomer; $t_R$= 56.0 min for (*S*)-enantiomer.

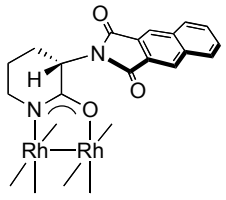


[$Rh_2$(*S*-PTPI)$_4$] (**3a**)

**Dirhodium(II) tetrakis[(*S*)-3-phthalimido-2-piperidinonate] [$Rh_2$(*S*-PTPI)$_4$] (3a).** A mixture of $Rh_2(OAc)_4$·2MeOH (760 mg, 1.50 mmol) and **12** (5.86 g, 24.0 mmol) in 65 mL of chlorobenzene, contained in a round-bottome flask fitted with a Soxlet extraction apparatus was heated at reflux with vigorous stirring under Ar. The thimble in the Soxlet extraction apparatus was charged with an oven-dried mixture (3 g) of two parts sodium carbonate and one-part sand. After completion of the reaction (monitored by TLC, 9 h), the deep-purple mixture was cooled to rt, and evaporated. Chromatography (silica gel, 60 g, EtOAc) followed by recrystallization from THF–MeCN (1:1, 20 mL) afforded THF-MeCN adduct of **3a** (1.20 g, 66%) as red fine needles, which was dried *in vacuo* at 100 °C for 24 h to give the axial ligand free complex; mp > 300 °C; Rf = 0.37 (20:1 $CHCl_3$/MeOH); $[\alpha]_D^{25}$ +234.3° (*c* 0.11, MeCN); IR ($CHCl_3$) ν: 1712, 1620, 1392 $cm^{-1}$;

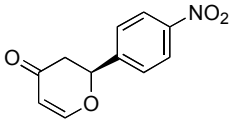
$^1$H NMR (270 MHz, $CDCl_3$) δ 1.71–2.21 (m, 14H), 2.68–3.41 (m, 10H), 4.69 (dd, *J* = 7.0, 10.2 Hz, 2H), 5.27 (dd, *J* = 5.5, 11.7 Hz, 2H), 7.61–8.12 (m, 16H); $^{13}$C NMR (67.8 MHz, $CDCl_3$) δ 22.8, 24.1, 26.2, 27.1, 48.2, 49.7, 51.2, 51.3, 122.6, 123.6, 132.2, 132.7, 133.3, 133.5, 167.3, 167.4, 172.8, 173.8; FAB-HRMS *m/z* calcd for $C_{52}H_{44}N_8O_{12}Rh_2$ ($M^+$) 1178.1189, found 1178.1182; Anal. Calcd for $C_{52}H_{44}N_8O_{12}Rh_2{\cdot}2H_2O$ C, 51.41; H, 3.98; N, 9.22. Found: C, 51.32; H, 3.91; N, 9.02.

**Dirhodium(II) tetrakis[(3*S*)-3-(1,3-dioxobenzo[f]isoindol-2-yl)-2-piperidinonate] $Rh_2$(*S*-BPTPI)$_4$ (3b).** By following the procedure for preparation of **3a**, a mixture of $Rh_2(OAc)_4{\cdot}2MeOH$ (760 mg, 1.50 mmol) and **14** (7.06 g, 24.0 mmol) in chlorobenzene (200 mL) was heated at reflux with vigorous stirring for 30 h. After the mixture was cooled to rt, the unreacted excess of **14** precipitated. Filtration and evaporation *in vacuo* provided the crude product (3.91 g). Chromatography (silica gel, 150 g, EtOAc) followed by recrystallization from $CH_2Cl_2$–MeCN (4:1, 20 mL) afforded acetonitrile adduct of **3b** (1.12 g, 53%) as red fine needles, which turned tris(hydrate) as red purple fine needles after standing; mp > 300 °C; Rf = 0.67 (EtOAc); $[\alpha]_D^{25}$ +61.7° (*c* 0.11, $CH_3CN$); IR (KBr) ν: 3399, 2938, 1767, 1705, 1615, 1377, 766 cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$, 100 °C) δ 1.71–2.03 (m, 12H), 2.19 (m, 2H), 2.49 (m, 2H), 3.24–3.31 (m, 4H), 3.38–3.46 (m, 4H), 4.63 (dd, *J* = 7.2, 10.0 Hz, 2H), 4.85 (dd, *J* = 7.2, 11.6 Hz, 2H), 7.75 (m, 4H), 7.81 (m, 4H), 8.25 (m, 4H), 8.30 (m, 4H), 8.46 (br-s, 4H), 8.51 (br-s, 4H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, 25 °C) δ 24.0, 24.4, 26.2, 26.6, 49.4, 50.3, 53.0, 53.6, 124.7, 125.2, 127.8, 128.1, 129.7, 130.0, 130.9, 131.1, 135.6, 135.7, 166.8, 175.0; FAB-HRMS *m/z* calcd for $C_{68}H_{52}N_8O_{12}Rh_2$ ($M^+$) 1378.1815, found 1378.1820; Anal. Calcd for $C_{68}H_{52}N_8O_{12}Rh_2{\cdot}3H_2O$ C, 56.99; H, 4.08; N, 7.82. Found: C, 56.84; H, 4.31; N, 7.67.



[$Rh_2$(*S*-BPTPI)$_4$] (**3b**)

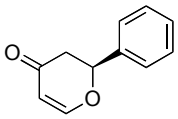
**Typical procedure for Rh$^{II}$-catalyzed enantioselective hetero-Diels–Alder reaction (Table 1, entry 5): (2*S*)-2-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (7aa).**[4] To a solution of **3a** (3.6 mg, 0.003 mmol, 1 mol %) and 4-nitrobenzaldehyde (**5a**) (45 mg, 0.30 mmol) in $CH_2Cl_2$ (0.3 mL) was added a solution of *trans*-1-methoxy-3-(triethylsilyloxy)-1,3-butadiene (**4a**) (96 mg, 0.45 mmol) in $CH_2Cl_2$ (0.2 mL) at 23 °C. After 2 h of stirring at this temperature, a 10% solution of trifluoroacetic acid in $CH_2Cl_2$ (ca. 0.1 mL) was added and the mixture was stirred for an additional 0.5 h. The whole was partitioned between EtOAc (20 mL) and satd. $NaHCO_3$ (2 mL), and the organic layer was washed with water (3 mL) and brine (2 x 3 mL), and dried over $Na_2SO_4$. Filtration and concentration *in vacuo* followed by column chromatography (silica gel, 2:1 hexane/EtOAc) afforded **7aa** (59.8 mg, 91%) as a white



**7aa**

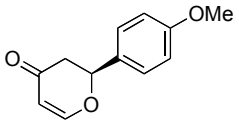
solid; mp 100–102 °C; Rf = 0.37 (1:1 hexane/EtOAc); $[\alpha]_D^{25}$ +59.8° (*c* 1.01, $CH_2Cl_2$) for 94% ee [lit.,[4] $[\alpha]_D$ +59° (c 0.39, $CH_2Cl_2$) for (*S*)-enantiomer]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.73 (ddd, *J* = 1.1, 3.8, 16.7 Hz, 1H), 2.85 (dd, *J* = 14.1, 16.7 Hz, 1H), 5.56 (dd, *J* = 3.8, 14.1 Hz, 1H), 5.59 (dd, *J* = 1.1, 6.0 Hz, 1H), 7.52 (d, *J* = 6.0 Hz, 1H), 7.60 (d, *J* = 6.0 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H). Enantiomeric excess of **7aa** was determined to be 94% by HPLC with a Chiralcel OD-H column (3:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 19.2 min for major enantiomer; $t_R$ = 26.9 min for minor enantiomer.

**(2*S*)-2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (7ab).**[5] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol) and benzaldehyde (**5b**) (32 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7ab** (48.1 mg, 92%) as a colorless oil; Rf = 0.34 (2:1 hexane/EtOAc); $[\alpha]_D^{23}$ +106° (*c* 1.13, $CHCl_3$) for 95% ee [lit.,[5] $[\alpha]_D^{23}$ –96.3° (*c* 0.87, $CHCl_3$) for (*R*)-enantiomer]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.65 (ddd, *J* = 1.3, 3.6, 16.9 Hz, 1H), 2.92 (dd, *J* = 14.5, 16.9 Hz, 1H), 5.43 (dd, *J* = 3.6, 14.5 Hz, 1H), 5.53 (dd, *J* = 1.3, 6.0 Hz, 1H), 7.37-7.45 (m, 5H), 7.48 (d, *J* = 6.0 Hz, 1H). Enantiomeric excess of **7ab** was determined to be 95% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 11.5 min for major enantiomer; $t_R$ = 13.6 min for minor enantiomer.



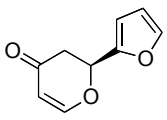
**7ab**

**(2*S*)-2-(4-Methoxyphenyl)-2,3-dihydro-4*H*-pyran-4-one (7ac).**[6] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol) and *p*-anisaldehyde (**5c**) (41 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 8:1 toluene/EtOAc) to provide **7ac** (50.9 mg, 83%) as a white solid; Rf = 0.28 (8:1 toluene/EtOAc); mp 50–51 °C; $[\alpha]_D^{23}$ +124° (*c* 1.15, $CHCl_3$) for 96% ee [lit.,[6] $[\alpha]_D$ –121 (*c* 0.397, $CHCl_3$) for 92% ee of (*R*)-enantiomer]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 3.2, 16.7 Hz, 1H), 2.93 (dd, *J* = 14.5, 16.7 Hz, 1H), 3.83 (s, 3H), 5.37 (dd, *J* = 3.2, 14.5 Hz, 1H), 5.51 (d, *J* = 6.0 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 1H). Enantiomeric excess of **7ac** was determined to be 96% by HPLC with a Chiralcel OD-H column (19:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 23.2 min for major enantiomer; $t_R$ = 26.9 min for minor enantiomer.



**7ac**

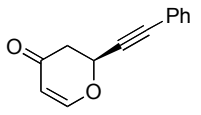
**2-(2-Furyl)-2,3-dihydro-4*H*-pyran-4-one (7ad).**[7] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol) and furfural (**5d**) (29 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 8:1 toluene/EtOAc) to provide **7ad** (46.3 mg,



**7ad**

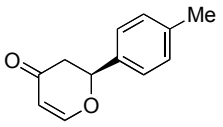
94%) as a white solid; Rf = 0.43 (4:1 toluene/EtOAc); mp 66–67 °C; $[\alpha]_D^{24}$ +337° (*c* 1.08, $CHCl_3$) for 93% ee [lit.,[7] $[\alpha]_D$ –255° (c 0.5, $CHCl_3$) for 66% ee of **7ad**]; mp 66–67 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.74 (ddd, *J* = 1.1, 4.0, 16.9 Hz, 1H), 3.09 (dd, *J* = 12.8, 16.9, 1H), 5.48 (dd, *J* = 4.0, 12.8 Hz, 1H), 5.50 (dd, *J* = 1.1, 6.0 Hz, 1H), 6.41 (m, 1H), 6.45 (m, 1H), 7.37 (d, *J* = 6.0 Hz, 1H), 7.48 (m, 1H). Enantiomeric excess of **7ad** was determined to be 93% by HPLC with a Chiralcel OD-H column (50:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 22.0 min for minor enantiomer; $t_R$ = 23.3 min for major enantiomer. The absolute configuration was not determined.

**(2*S*)-2-(2-Phenylethynyl)-2,3-dihydro-4*H*-pyran-4-one (7ae).**[8] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), phenylpropargyl aldehyde (**5e**) (39 mg, 0.30 mmol) and **3b** (4.3 mg, 0.003 mmol, 1 mol %). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **7ae** (54.1 mg, 91%) as a colorless oil; Rf = 0.37 (4:1 hexane/EtOAc); $[\alpha]_D^{24}$ +388° (*c* 0.94, $CHCl_3$) for 92% ee; IR (neat) ν: 3061, 2236, 1680, 1597, 1267, 1221, 1032, 758 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.84 (dd, *J* = 5.1, 16.9 Hz, 1H), 2.90 (dd, *J* = 9.6, 16.9 Hz, 1H), 5.42 (dd, *J* = 5.1, 9.6 Hz), 5.50 (d, *J* = 6.2 Hz, 1H), 7.31-7.37 (m, 4H), 7.45-7.47 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 42.0, 69.1, 83.5, 87.4, 107.3, 121.0, 128.1, 128.9, 131.6, 161.5, 189.9; EI-HRMS *m/z* calcd for $C_{13}H_{10}O_2$ ($M^+$) 198.0681, found 198.0660; Anal. Calcd for $C_{13}H_{10}O_2$ C, 78.77; H, 5.09. Found: C, 78.75; H, 5.26. Enantiomeric excess of **7ae** was determined to be 92% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 11.9 min for major enantiomer; $t_R$ = 15.0 min for minor enantiomer. The absolute configuration of **7ae** was determined to be *S* by chemical correlation (*vide infra*).

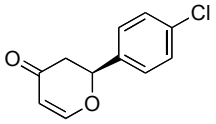


**7ae**

**2-(4-Methylphenyl)-2,3-dihydro-4*H*-pyran-4-one (7af).**[9] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), *p*-tolualdehyde (**5f**) (36 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7af** (54.8 mg, 97%) as a white solid; Rf = 0.35 (2:1 hexane/EtOAc); mp 80–81 °C; $[\alpha]_D^{26}$ +129° (*c* 1.10, $CHCl_3$) for 96% ee [lit.,[9] $[\alpha]_D^{25}$ –27.5° (*c* 0.26, $CHCl_3$) for 92% ee of **7af**]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.64 (ddd, *J* = 0.8, 3.2, 16.8 Hz, 1H), 2.92 (dd, *J* = 14.0, 16.8 Hz, 1H), 5.40 (dd, *J* = 3.2, 14.0 Hz, 1H), 5.52 (dd, *J* = 0.8, 6.0 Hz, 1H), 7.23 (m, 2H), 7.29 (m, 2H), 7.47 (d, *J* = 6.0 Hz, 1H). Enantiomeric excess of **7af** was determined to be 96% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 10.8 min for major enantiomer; $t_R$ = 12.4 min for minor enantiomer. The absolute configuration of **7af** was not determined.

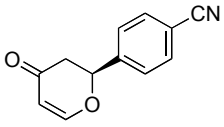


**7af**



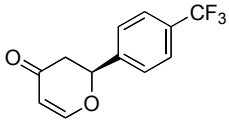
**7ag**

**2-(4-Chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (7ag).**[10] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), 4-chlorobenzaldehyde (**5g**) (42 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7ag** (56.5 mg, 95%) as a white solid; Rf = 0.34 (2:1 hexane/EtOAc); mp 69–71 °C; $[\alpha]_D^{25}$ +106° (*c* 1.29, $CHCl_3$) for 95% ee [lit.,[10] $[\alpha]_D^{23}$ +91.2° (*c* 0.548, $CHCl_3$) for 91% ee of **7ag**]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 3.2, 16.9 Hz, 1H), 2.86 (dd, *J* = 14.3, 16.9 Hz, 1H), 5.41 (dd, *J* = 3.2, 14.3 Hz, 1H), 5.53 (d, *J* = 6.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 6.0 Hz, 1H). Enantiomeric excess of **7ag** was determined to be 95% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 13.0 min for major enantiomer; $t_R$ = 15.9 min for minor enantiomer. The absolute configuration of **7ag** was not determined.



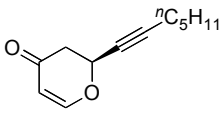
**7ah**

**2-(4-Cyanophenyl)-2,3-dihydro-4*H*-pyran-4-one (7ah).**[10] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), 4-cyanobenzaldehyde (**5h**) (39 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7ah** (55.6 mg, 93%) as a white solid; Rf = 0.31 (1:1 hexane/EtOAc); mp 70–72 °C; $[\alpha]_D^{20}$ +79.1° (*c* 1.24, $CH_2Cl_2$) for 95% ee [lit.,[10] $[\alpha]_D^{28}$ –74.1° (*c* 0.30, $CH_2Cl_2$) for 95% ee of **7ah**]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.70 (dd, *J* = 3.8, 16.7 Hz, 1H), 2.82 (dd, *J* = 14.1, 16.7 Hz, 1H), 5.50 (dd, *J* = 3.8, 14.1 Hz, 1H), 5.57 (d, *J* = 6.0 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 7.52 (m, 2H), 7.73 (m, 2H). Enantiomeric excess of **7ah** was determined to be 95% by HPLC with a Chiralcel OD-H column (3:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 15.9 min for major enantiomer; $t_R$ = 19.7 min for minor enantiomer. The absolute configuration of **7ah** was not determined.



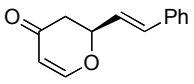
**7ai**

**2-[(4-Trifluoromethyl)phenyl]-2,3-dihydro-4*H*-pyran-4-one (7ai).**[9] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), 4-trifluoromethylbenzaldehyde (**5i**) (52 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **7ai** (67.6 mg, 93%) as a white solid; Rf = 0.26 (2:1 hexane/EtOAc); mp 48–49 °C; $[\alpha]_D^{20}$ +50.6° (*c* 1.00, $CHCl_3$) for 95% ee [lit.,[9] $[\alpha]_D^{28}$ +44.4° (*c* 0.63, $CHCl_3$) for 91% ee of **7ai**]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.70 (ddd, *J* = 0.9, 3.6, 16.7 Hz, 1H), 2.85 (dd, *J* = 14.3, 16.7 Hz, 1H), 5.50 (dd, *J* = 3.6, 14.3 Hz, 1H), 5.56 (dd, *J* = 0.9, 6.0 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 7.54 (m, 2H), 7.69 (m, 2H). Enantiomeric excess of **7ai** was determined to be 95% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 11.3 min for major enantiomer; $t_R$ = 15.7 min for minor enantiomer. The absolute configuration of **7ai** was not determined.



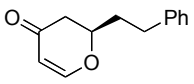
**7aj**

**2-(1-Heptynyl)-2,3-dihydro-4*H*-pyran-4-one (7aj).** The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), 2-octynal (**5j**) (37 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 pentane/$Et_2O$) to provide **7aj** (40.1 mg, 71%) as a colorless oil; Rf = 0.30 (9:1 hexane/EtOAc); $[\alpha]_D^{24}$ +265° (*c* 1.01, $CHCl_3$) for 93% ee; IR (neat) ν: 2934, 2245, 1684, 1597, 1267, 1221, 1034 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.25-1.39 (m, 4H), 1.52 (m, 2H), 2.24 (dt, *J* = 2.4, 7.2 Hz, 2H), 2.71 (dd, *J* = 5.2, 16.8 Hz, 1H), 2.76 (dd, *J* = 9.6, 16.8 Hz, 1H), 5.17 (ddt, *J* = 2.4, 5.2, 9.6 Hz, 1H), 5.46 (d, *J* = 6.0 Hz, 1H), 7.30 (d, *J* = 6.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 14.0, 18.7, 22.2, 27.9, 31.0, 42.7, 69.3, 75.1, 89.3, 107.4, 161.8, 190.8; EI-HRMS *m/z* calcd for $C_{12}H_{16}O_2$ ($M^+$) 192.1150, found 192.1166. Enantiomeric excess of **7aj** was determined to be 93% by HPLC with a Chiralcel OD-H column (200:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 17.2 min for major enantiomer; $t_R$ = 18.5 min for minor enantiomer. The absolute configuration of **7ai** was not determined.



**7ak**

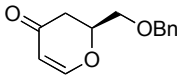
**(2*S*)-2-[(*E*)-2-Phenylethenyl]-2,3-dihydro-4*H*-pyran-4-one (7ak).**[11] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), (*E*)-cinnamaldehyde (**5k**) (40 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 8:1 toluene/EtOAc) to provide **7ak** (51.7 mg, 86%) as a white solid; Rf = 0.41 (4:1 toluene/EtOAc); mp 48–50 °C; $[\alpha]_D^{23}$ +170° (*c* 1.04, $CH_2Cl_2$) for 96% ee [lit.,[11] $[\alpha]_D^{26}$ –215° (c 0.36, $CH_2Cl_2$) for 99% ee of **7ak**]; $^1H$ NMR (400 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 4.0, 16.7 Hz, 1H), 2.74 (dd, *J* = 12.8, 16.7 Hz, 1H), 5.08 (ddd, *J* = 4.0, 6.0, 12.8 Hz 1H), 5.48 (d, *J* = 6.0 Hz, 1H), 6.30 (dd, *J* = 6.6, 16.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 7.26–7.42 (m, 6H). Enantiomeric excess of **7ak** was determined to be 96% by HPLC with a Chiralcel OD-H column (3:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 10.9 min for major enantiomer; $t_R$ = 20.1 min for minor enantiomer. The absolute configuration of **7ak** was determined to be *S* by chemical correlation (*vide infra*).



**7al**

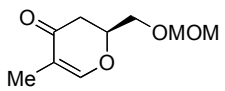
**(2*R*)-2-(2-Phenylethyl)-2,3-dihydro-4*H*-pyran-4-one (7al).**[7] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), 3-phenylpropanal (**5l**) (40 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7al** (54.0 mg, 89%) as a colorless oil; Rf = 0.33 (2:1 hexane/EtOAc); $[\alpha]_D^{25}$ +108° (*c* 1.26, $CHCl_3$) for 94% ee [lit.,[7] $[\alpha]_D^{25}$ –69° (c 0.5, $CHCl_3$) for 69% ee of (*S*)-enantiomer]; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.96 (m, 1H), 2.17 (m, 1H), 2.43 (m, 1H), 2.56 (m, 1H), 2.71–2.88 (m, 2H), 4.40 (m, 1H), 5.41 (m, 1H), 7.17–7.40 (m, 6H). Enantiomeric excess of **7al** was determined to be 94% by HPLC with a Chiralcel OD-H column (3:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 10.7 min for major enantiomer; $t_R$ = 18.9 min for minor enantiomer.

**(2*S*)-2-Benzyloxymethyl-2,3-dihydro-4*H*-pyran-4-one (7am).**[12] The product was prepared following the procedure for the preparation of **7aa** using diene **4a** (96 mg, 0.45 mmol), benzyloxyacetaldehyde (**5m**) (45 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 toluene/EtOAc) to provide **7am** (54.3 mg, 83%) as a colorless oil; Rf = 0.41 (2:1 toluene/EtOAc); $[\alpha]_D^{24}$ +127° (*c* 0.92, $CHCl_3$) for 91% ee [lit.,[12] $[\alpha]_D^{24}$ +75.8° (*c* 0.455, $CHCl_3$) for (*S*)-enantiomer]; $^1$H NMR (400 MHz, $CDCl_3$) δ 2.34 (dd, *J* = 2.4, 16.8 Hz, 1H), 2.67 (dd, *J* = 14.4, 16.8 Hz, 1H), 3.61 (dd, *J* = 5.1, 10.8 Hz, 1H), 3.65 (dd, *J* = 3.8, 10.8 Hz, 1H), 4.50–4.58 (m, 3H), 5.35 (d, *J* = 6.0 Hz, 1H), 7.16–7.32 (m, 6H). Enantiomeric excess of **7am** was determined to be 91% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 14.7 min for major enantiomer; $t_R$ = 17.0 min for minor enantiomer.



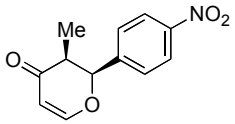
**7am**

**2-(Methoxymethoxymethyl)-5-methyl-2,3-dihydro-4*H*-pyran-4-one (7bn)**.[13] The product was prepared following the procedure for the preparation of **7aa** using diene **4b** (103 mg, 0.45 mmol), methoxymethoxyacetaldehyde (**5n**) (31 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 1:1 pentane/$Et_2O$) to provide **7bn** (48.0 mg, 86%) as a colorless oil; Rf = 0.30 (2:1 hexane/EtOAc); $[\alpha]_D^{24}$ +85.9° (*c* 1.05, $CHCl_3$) for 93% ee; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.68 (s, 3H), 2.44 (dd, *J* = 3.4, 16.7 Hz, 1H), 2.71 (dd, *J* = 14.5, 16.7 Hz, 1H), 3.39 (s, 3H), 3.74 (dd, *J* = 5.2, 11.2 Hz, 1H), 3.77 (dd, *J* = 4.0, 11.2 Hz, 1H), 4.56 (m, 1H), 4.69 (s, 2H), 7.26 (s, 1H). Enantiomeric excess of **7bn** was determined to be 93% by HPLC with a Chiralpak AD column (19:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 13.9 min for minor enantiomer; $t_R$ = 20.0 min for minor enantiomer. The absolute configuration was not determined.



**7bn**

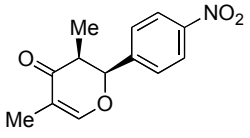
**2,3-*cis*-3-Methyl-2-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (7ca)**. The product was prepared following the procedure for the preparation of **7aa** using diene **4c** (103 mg, 0.45 mmol), **5a** (45 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 2:1 hexane/EtOAc) to provide **7ca** (67.9 mg, 97%) as a white solid; Rf = 0.24 (2:1 hexane/EtOAc); mp 146–147 °C; $[\alpha]_D^{22}$ –13.5° (*c* 0.90, $CHCl_3$) for 96% ee; IR (KBr) ν: 1676, 1589, 1520, 1350, 1267, 1219 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, *J* = 7.4 Hz, 3H), 2.65 (dq, *J* = 2.8, 7.4 Hz, 1H), 5.53 (d, *J* = 6.0 Hz, 1H), 5.62 (d, *J* = 2.8 Hz, 1H), 7.52-7.57 (m, 3H), 8.30 (d, *J* = 6.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 10.0, 45.7, 82.0, 106.2, 123.8, 126.3, 143.4, 147.6, 161.8, 195.8; EI-HRMS *m/z* calcd for $C_{12}H_{11}NO_4$ ($M^+$) 233.0688, found 233.0692; Anal. Calcd for $C_{12}H_{11}NO_4$ C, 61.80; H, 4.75; N, 6.01. Found: C, 61.83; H, 4.85; N, 5.98. Enantiomeric excess of **7ca** was determined to be 96% by HPLC with a Chiralcel OD-H column (3:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$



**7ca**

= 11.2 min for major enantiomer; $t_R$ = 16.6 min for minor enantiomer. The absolute configuration of **7ca** was not determined.

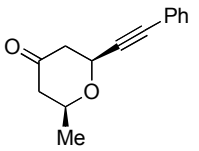
**2,3-*cis*-3,5-Dimethyl-2-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (7da)**.



**7da**

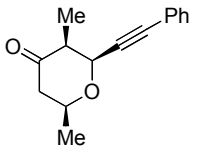
The product was prepared following the procedure for the preparation of **7aa** using diene **4d** (109 mg, 0.45 mmol), **5a** (45 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **7da** (68.2 mg, 92%) as a white solid; Rf = 0.20 (4:1 hexane/EtOAc); mp 150–151 °C; $[\alpha]_D^{22}$ –17.3° (*c* 1.08, $CHCl_3$) for 97% ee; IR (KBr) ν: 3083, 2976, 1671, 1624, 1607, 1522, 1348, 1169, 912, 851, 735 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J* = 7.2 Hz, 3H), 1.73 (s, 3H), 2.63 (dq, *J* = 2.8, 7.2 Hz, 1H), 5.54 (d, *J* = 2.8 Hz, 1H), 7.38 (s, 1H), 7.53 (m, 2H), 8.25 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 9.92, 10.6, 45.2, 81.8, 112.9, 123.7, 126.2, 143.9, 147.4, 157.9, 196.2; EI-HRMS *m/z* calcd for $C_{13}H_{13}NO_4$ ($M^+$) 247.0844, found 247.0846; Anal. Calcd for $C_{13}H_{13}NO_4$ C, 63.15; H, 5.30; N, 5.67. Found: C, 63.01; H, 5.38; N, 5.56. Enantiomeric excess of **7da** was determined to be 97% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 11.8 min for major enantiomer; $t_R$ = 24.2 min for minor enantiomer. The absolute configuration of **7da** was not determined.

**(2*S**,6*S**)-6-methyl-2-(2-phenylethynyl)tetrahydropyran-4-one (8ee).**



**8ee**

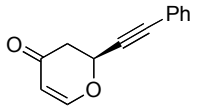
The product was prepared following the procedure for the preparation of **7aa** using diene **4e** (89 mg, 0.45 mmol), **5e** (39 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **8ee** (55.9 mg, 87%) as a white solid; Rf = 0.33 (4:1 hexane/EtOAc); mp 76-77 °C; $[\alpha]_D^{23}$ –33.4° (*c* 1.31, $CHCl_3$) for 99% ee; IR (KBr) ν: 2238, 1725, 1345, 1057 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.0 Hz, 3H), 2.33 (dd, *J* = 11.2, 14.8 Hz, 1H), 2.43 (ddd, *J* = 2.0, 2.8, 14.8 Hz, 1H), 2.67 (ddd, *J* = 2.0, 3.2, 14.8 Hz, 1H), 2.75 (dd, *J* = 11.2, 14.8 Hz, 1H), 3.82 (ddq, *J* = 2.8, 6.0, 11.2 Hz, 1H), 4.62 (dd, *J* = 3.2, 11.2 Hz, 1H), 7.28–7.47 (m, 5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 22.1, 47.5, 49.1, 67.3, 73.4, 85.9, 86.2, 121.8, 128.2, 128.7, 131.8, 204.9; EI-HRMS *m/z* calcd for $C_{14}H_{14}O_2$ ($M^+$) 214.0994, found 214.0983; Anal. Calcd for $C_{14}H_{14}O_2$ C, 78.48; H, 6.59. Found: C, 78.37; H, 6.74. Enantiomeric excess of **8ee** was determined to be 99% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 0.5 mL/min): $t_R$ = 17.2 min for minor enantiomer; $t_R$ = 21.2 min for major enantiomer. The absolute configuration of **8ee** was not determined.

**(2*S**,3*S**,6*S**)-2,6-Dimethyl-2-(2-phenylethynyl)tetrahydropyran-4-one (8fe).** 

**8fe**

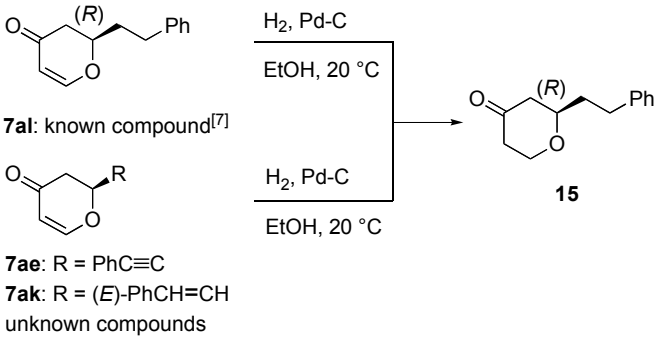
The product was prepared following the procedure for the preparation of **7aa** using diene **4f** (96 mg, 0.45 mmol) and **5e** (39 mg, 0.30 mmol). The crude product was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to provide **8fe** (55.5 mg, 81%) as a colorless oil; Rf = 0.21 (4:1 hexane/EtOAc); $[\alpha]_D^{24}$ +17.0° (*c* 0.58, $CHCl_3$) for 97% ee; IR (neat) ν: 2239, 1727 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.0 Hz, 3H), 1.42 (d, *J* = 7.2 Hz, 3H), 2.30 (dd, *J* = 1.2, 14.8 Hz, 1H), 2.51 (dd, *J* = 11.2, 14.8 Hz, 1H), 2.60 (dq, *J* = 2.8, 7.2 Hz, 1H), 3.84 (ddq, *J* = 2.8, 6.0, 11.2 Hz, 1H), 4.72 (d, *J* = 2.8 Hz, 1H), 7.31–7.46 (m, 5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 12.7, 22.2, 45.5, 49.1, 70.8, 73.6, 84.5, 87.3, 122.0, 128.2, 128.7, 131.8, 209.5; EI-HRMS *m/z* calcd for $C_{15}H_{16}O_2$ ($M^+$) 228.1150, found 228.1161. Enantiomeric excess of **8fe** was determined to be 97% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 0.5 mL/min): $t_R$ = 17.2 min for minor enantiomer; $t_R$ = 21.3 min for major enantiomer. The absolute configuration was not determined.

**HDA reaction of 4a with phenylpropargyl aldehyde (5e) catalyzed by 3b (0.002 mol %) (Table 2, entry 16)**: To an ice-cooled solution of **3b** ($0.5 \times 10^{-3}$ M in $CH_2Cl_2$, 0.40 mL, 0.0002 mmol, 0.002 mol %) and **5e** (1.30 g, 10.0 mmol) in $CH_2Cl_2$ (17 mL) was added a solution of **4a** (2.57 g, 12.0 mmol) in $CH_2Cl_2$ (2.6 mL). After 64 h of stirring at this temperature, a 10% solution of trifluoroacetic acid in $CH_2Cl_2$ (ca. 0.5 mL) was added and the mixture was stirred at 23 °C for an additional 0.5 h. The whole was partitioned between EtOAc (100 mL) and satd. $NaHCO_3$ (10 mL), and the separated organic layer was successively washed with water and brine, and dried over $Na_2SO_4$. Filtration and concentration *in vacuo* followed by column chromatography on silica gel (60 g, 2:1 hexane/EtOAc) afforded **7ae** (1.46 g, 96%) as a pale yellow oil; $[\alpha]_D^{24}$ +377° (*c* 1.00, $CHCl_3$) for 91% ee; Enantiomeric excess of **7ae** was determined to be 91% by HPLC with a Chiralcel OD-H column (9:1 hexane/$^i$PrOH, 1.0 mL/min): $t_R$ = 13.0 min for major enantiomer; $t_R$ = 16.6 min for minor enantiomer.



**7ae**

**Determination of absolute configuration of 7ae and 7ak. Chemical correlation of 7ae and 7ak with 7al.**




**7al**: known compound[7]

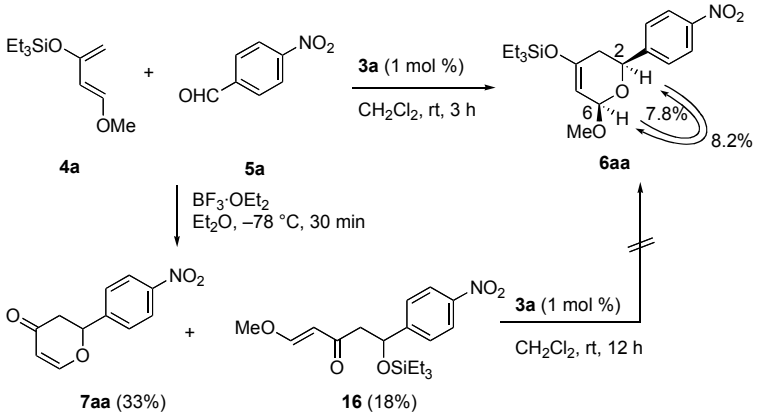
**7ae**: R = PhC≡C
**7ak**: R = (*E*)-PhCH=CH
unknown compounds

**(2*R*)-2-(2-phenylethyl)tetrahydropyran-4-one (15) from (*R*)-7al.** A solution of (*R*)-**7al** (50 mg, 0.25 mmol, 94% ee) in EtOH (5 mL) was stirred with 10% Pd/C (10 mg) under 1 atm of $H_2$ at rt for 2 h. The catalyst was removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, 8:1 toluene/EtOAc) to afford **15** (37.9 mg, 75%) as a colorless oil; Rf = 0.41 (4:1 hexane/EtOAc); $[\alpha]_D^{23}$ –5.62° (*c* 1.08, $CHCl_3$); IR (neat) ν: 2928, 2859, 1717, 1603, 1377, 1254, 1152, 1086, 750, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 1.79 (m, 1H), 1.98 (m, 1H), 2.29–2.42 (m, 3H), 2.60 (ddd, *J* = 7.2, 12.4, 13.6 Hz, 1H), 2.71 (ddd, *J* = 7.2, 9.2, 14.0 Hz, 1H), 2.82 (ddd, *J* = 5.6, 9.6, 14.0 Hz, 1H), 3.57 (ddd, J = 4.0, 7.2, 11.6 Hz, 1H), 3.65 (dt, *J* = 2.8, 11.6 Hz, 1H), 4.32 (ddd, *J*= 1.2, 7.2, 11.2 Hz, 1H), 7.17–7.30 (m, 5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 31.5, 38.0, 42.3, 48.4, 66.5, 77.0, 125.9, 128.3, 128.4, 141.3, 206.7; HRMS (EI) *m/z* calcd for $C_{13}H_{16}O_2$ ($M^+$) 204.1150, found 204.1140; Anal. Calcd for $C_{13}H_{16}O_2$ C, 76.44; H, 7.90;. Found: C, 76.33; H, 7.79.

Following the above procedure, **7ae** (50 mg, 0.25 mmol, 92% ee) was hydrogenated to provide **15** (45.3 mg, 88%, a colorless oil); $[\alpha]_D^{24}$ –5.40° (*c* 1.20, $CHCl_3$). Absolute configuration of **7ae** was determined to be *S* by comparison of the optical rotation of **15** with that of **15** from (*R*)-**7al**.

Following the above procedure, **7ak** (50 mg, 0.25 mmol, 96% ee) was hydrogenated to provide **15** (42.3 mg, 83%, a colorless oil); $[\alpha]_D^{23}$ –5.79° (*c* 0.98, $CHCl_3$). Absolute configuration of **7ak** was determined to be *S* by comparison of the optical rotation of **15** with that of **15** from (*R*)-**7al**.

**Experiments demonstrating that Rh(II)-catalyzed HDA reaction proceeds *via* [4+2] mechanism in an *endo*-mode.**




**(2*S*,6*R*)-6-Methoxy-2-(4-nitrophenyl)-4-triethylsiloxy-3,6-dihydro-2*H*-pyran (6aa).** To a solution of **3a** (1.8 mg, 0.0015 mmol, 1 mol %) and **5a** (23 mg, 0.15 mmol) in $CH_2Cl_2$ (0.3 mL) was added a solution of **4a** (32 mg, 0.15 mmol) in $CH_2Cl_2$ (0.2 mL) at 23 °C. After 2 h of stirring at this temperature, the mixture was concentrated *in vacuo* to furnish the crude **6aa** (53 mg) as a purple oil; $^1$H NMR (400 MHz, $C_6D_6$) δ 0.68 (q, *J* = 8.1 Hz, 6H), 1.01 (t, *J* = 8.1 Hz, 9H), 2.03 (ddd, *J* = 1.9, 3.8, 16.4 Hz, 1H), 2.20 (ddd, *J* = 2.4, 10.5, 16.4 Hz, 1H), 3.44 (s, 3H), 4.35 (dd, *J* = 3.8, 10.5 Hz, 1H), 5.04 (s, 1H), 5.24 (dd, *J* = 1.9, 2.4 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 5.36, 6.96, 37.9, 54.4, 72.4, 99.8, 103.6, 123.6, 126.2, 147.5, 148.6, 152.5; In order to assign the stereochemistry at C2 and C6, NOE studies were performed on **6aa**. Irradiation of C2-H showed NOE with C6-H (8.2%) and the ortho proton of the 4-nitrophenyl group (6.1%). Additionally, irradiation of C6-H exhibited NOE with the C2-H (7.8%). These data revealed *cis* relationship between C2-H and C6-H.

**(*E*)-1-Methoxy-5-(4-nitrophenyl)-5-triethylsiloxy-1-penten-3-one (16).** The following procedure is similar to that reported by Danishefsky.[14] To a solution of **4a** (322 mg, 1.50 mmol) and **5a** (227 mg, 1.50 mmol) in $Et_2O$ (20 mL) at –78 °C was added $BF_3{\cdot}OEt_2$ (0.19 mL, 1.50 mmol) dropwise. After 30 min of stirring at this temperature, the dark-red reaction mixture was quenched with saturated $NaHCO_3$ solution (10 mL). The mixture was partitioned between EtOAc (30 mL) and water (5 mL), and the organic layer was washed with brine (2 x 10 mL) and dried over $Na_2SO_4$. Filtration and evaporation provided crude product, which was purified by column chromatography (silica gel, 4:1 hexane/EtOAc) to give **16** (87.6 mg, 16%) as a pale yellow oil, along with **7aa** (105 mg, 32%).

Siloxyenone **16**: IR (neat) ν: 2957, 1684, 0595, 1522, 1346, 1090 cm$^{-1}$; $^1$H NMR (400 MHz, $C_6D_6$) δ 0.62 (q, J = 8.0 Hz, 6H), 0.96 (t, *J* = 8.0 Hz, 9H), 2.30 (dd, *J* = 4.0, 15.6 Hz, 1H), 2.75 (dd, *J* = 8.6, 15.6 Hz, 1H), 2.89 (s, 3H), 5.40 (d, *J* = 12.8 Hz, 1H), 5.43 (dd, *J* = 4.0, 8.6 Hz, 1H), 7.13 (m, 2H),

7.44 (d, $J$ = 12.8 Hz, 1H), 7.91 (m, 2H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 5.20, 7.14, 51.9, 56.9, 70.9, 106.7, 123.7, 126.3, 147.5, 152.4, 162.9, 194.7; HRMS (FAB) *m/z* calcd for $C_{18}H_{28}NO_5Si$ ($MH^+$) 366.1737, found 366.1742.

A mixture of **16** (10 mg, 0.027 mmol) and **3a** (0.3 mg, 0.00027 mmol, 1 mol %) in $CH_2Cl_2$ (0.1 mL) was stirred at 23 °C for 12 h and concentrated *in vacuo*. No detectable peaks of the cyclized product (**5aa** or **6aa**) was observed in $^1$H NMR spectrum.

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## X-ray crystallographic analysis of bis(acetonitrile) adduct of $Rh_2(PTPI)_4$ (3a)

*Data Collection*

A red prismatic crystal of $C_{56}H_{54}N_{10}O_{14}Rh_2$ having approximate dimensions of 0.30 × 0.15 × 0.10 mm, recrystallized from a tetrahydrofuran/acetonitrile solution, was mounted in a glass capillary. All measurements were made on a Rigaku RAXIS II imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from three 1.0° oscillations which were exposed for 4.0 minutes. The crystal-to-detector distance was 125.0 mm. The detector swing angle was 0.0°. Readout was performed in the 100 μm pixel mode.

Cell constants and an orientation matrix for data collection corresponded to a trigonal hexagonal cell (laue class: $\bar{3}$,3) with dimensions:

a = 24.687(6) Å

c = 31.998(5) Å

V = 16888(9) $Å^3$

For Z = 9 and F.W. = 1296.91, the calculated density is 1.15 $g/cm^3$. Based on the systematic absences of:

hkl: $-h+k+l \neq 3n$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

R3 (#146)

The data were collected at a temperature of 25 ± 1°C to a maximum 2θ value of 50.1°. A total of forty-five 4.0° oscillation images were collected, each being exposed for 30.0 minutes. The crystal-to-detector distance was 125.00 mm. The detector swing angle was 0.0°. Readout was performed in the 100 μm pixel mode.

*Data Reduction*

Of the 13541 reflections which were collected, 5588 were unique ($R_{int}$ = 0.082); equivalent reflextions were merged.

The linear absorption coefficient, μ, for Mo-Kα radiation is 5.0 $cm^{-1}$. The data were corrected for Lorentz and polarization effects.

*Structure Solution and Refinement*

The structure was solved by direct methods[1] and expanded using Fourier techniques[2]. In an asymmetric unit, two water molecules are contained. The phthalimide moieties were refined as rigid groups using individual isotropic temperature factors. Hydrogen atoms, excluding those of

waters, were included but not refined. The final cycle of full-matrix least-squares refinement[3] on F was based on 3245 observed reflections ($I > 3.00\sigma(I)$) and 374 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.070$$

$$R_w = [ \, \Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2 ]^{1/2} = 0.089$$

The standard deviation of an observation of unit weight[4] was 1.37. The weighting scheme was based on counting statistics and included a factor ($p = 0.100$) to downweight the intense reflections. Plots of $\Sigma \, w \, (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.58 and -0.37 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[5]. Anomalous dispersion effects were included in Fcalc[6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[7]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[8]. All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation.

**References**


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[3] Least Squares function minimized:

$$\Sigma w(|F_o|-|F_c|)^2$$

[4] Standard deviation of an observation of unit weight:

$$[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$$

where: $N_o$ = number of observations

$N_v$ = number of variables

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[9] teXsan for Windows: Crystal Structure Analysis Package, Molecular Structure Corporation, 1997.

*EXPERIMENTAL DETAILS*

**Crystal Data**

| | |
|---|---|
| Empirical Formula | $C_{56}H_{54}N_{10}O_{14}Rh_2$ |
| Formula Weight | 1296.91 |
| Crystal Color, Habit | red, prismatic |
| Crystal Dimensions | 0.30 × 0.15 × 0.10 mm |
| Crystal System | trigonal |
| Lattice Type | R-centered |
| Indexing Images | 3 exposures @ 4.0 minutes |
| Detector Position | 125.0 mm |
| Detector Swing Angle | 0.0° |
| Pixel Size | 100 μm |
| Lattice Parameters | a = 24.687(6) Å |
| | c = 31.998(5) Å |
| | V = 16888(9) Å$^3$ |
| Space Group | R3 (#146) |
| Z value | 9 |
| $D_{calc}$ | 1.148 g/cm$^3$ |
| $F_{000}$ | 5958.00 |
| μ(MoKα) | 4.95 cm$^{-1}$ |

**Intensity Measurements**

| | |
|---|---|
| Diffractometer | RAXIS IV |
| Radiation | MoKα (λ = 0.71070 Å) |
| | graphite monochromated |
| Detector Aperture | 200 mm × 200 mm |
| Data Images | 45 exposures @ 30.0 minutes |
| Oscillation Range | 4.0° |
| Detector Position | 125.0 mm |
| Detector Swing Angle | 0.0° |
| Pixel Size | 100 μm |
| $2\theta_{max}$ | 50.1° |
| No. of Reflections Measured | Total: 13541 |
| | Unique: 5588 ($R_{int}$ = 0.082) |
| Corrections | Lorentz-polarization |

**Structure Solution and Refinement**

| | |
|---|---|
| Structure Solution | Direct Methods (SHELXS86) |
| Refinement | Full-matrix least-squares |
| Function Minimized | $\Sigma\ w\ (\|Fo\| - \|Fc\|)^2$ |
| Least Squares Weights | $w = 1/\sigma^2(Fo) = [\sigma_c^2(Fo)+p^2/4\ Fo^2]^{-1}$ |
| p-factor | 0.1000 |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I>3.00σ(I)) | 3245 |
| No. Variables | 374 |
| Reflection/Parameter Ratio | 8.68 |
| Residuals: R; Rw | 0.070 ; 0.089 |
| Goodness of Fit Indicator | 1.37 |
| Max Shift/Error in Final Cycle | 0.01 |
| Maximum peak in Final Diff. Map | 0.58 $e^-/Å^3$ |
| Minimum peak in Final Diff. Map | -0.37 $e^-/Å^3$ |

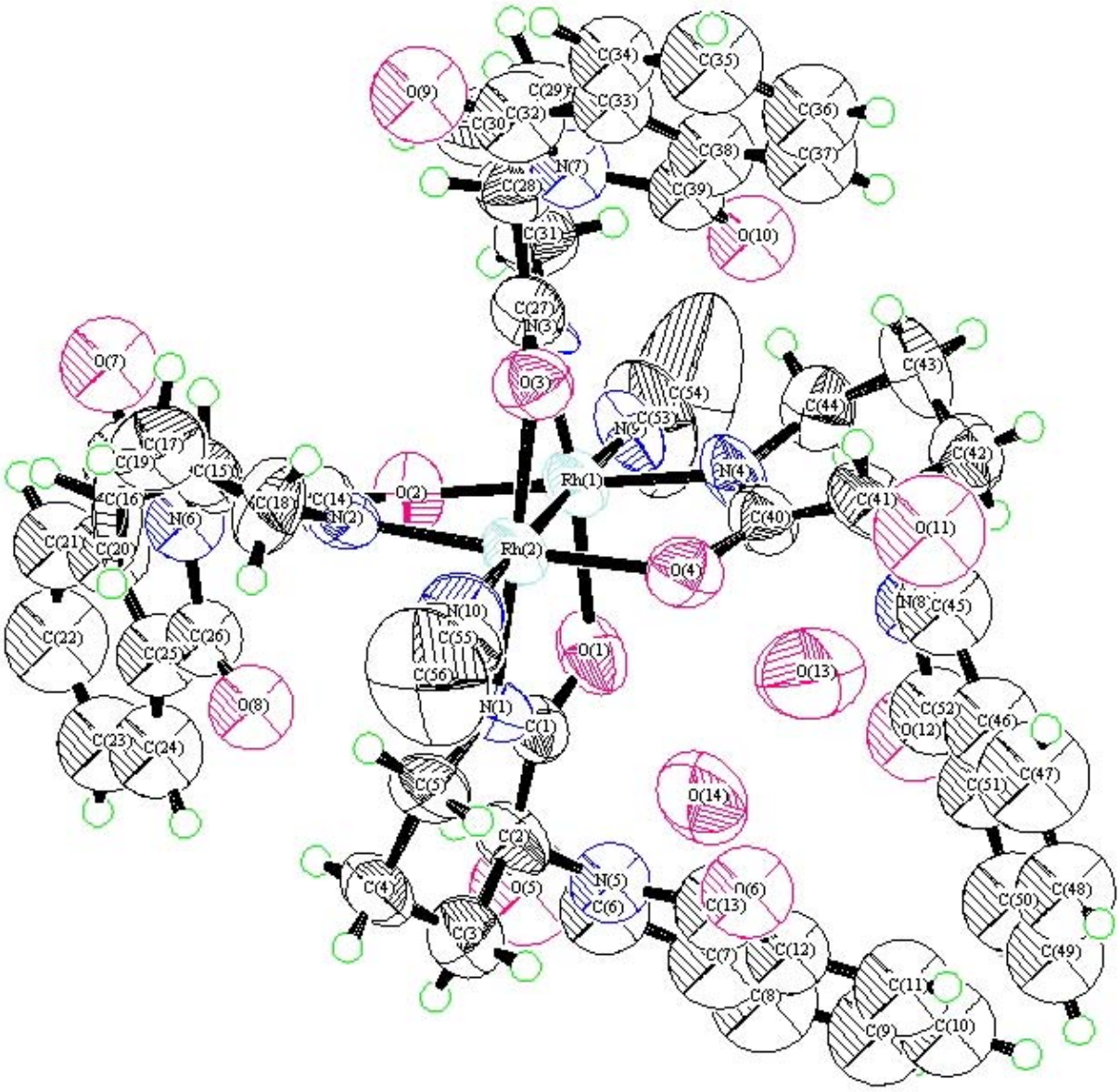


**Figure 1.** ORTEP drawing of bis(acetonitrile) adduct of **3a**. Thermal ellipsoids are drawn at 50% probability level.