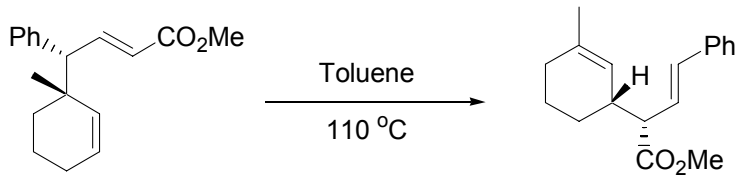
Supporting Information

General

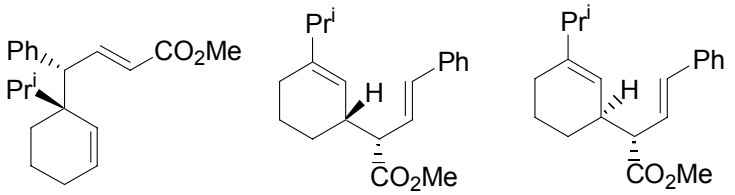
^{1}H NMR spectra were run at 500 MHz, and ^{13}C NMR at 125 MHz with the sample solvent being $CDCl_3$ unless otherwise noted. Mass spectral determinations were carried out at GC-MS (electron impact, EI) or LC-MS (electrospray ionization, ESI), and high-resolution mass spectral (HRMS) determination was performed by the Instrument Center in University at Buffalo. Melting points are uncorrected. IR spectra were obtained by using a Nicolet Impact series 420 Fourier transform (FT)IR. Optical rotations were measured by using a Jasco DIP-370 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Enantiomeric excess (ee) was determined either by chiral GC or HPLC using a Chiralcel OD-H, Chiralpak AD-RH (Chiral Technologies), or (*R,R*)-Whelk-O 1 (Regis Technologies) chiral analytical column (UV detection at 254 nm).

Glassware was dried in an oven overnight then flame dried before use. Reactions were conducted under an atmosphere of argon. Degassing was carried out by bubbling argon through the solution for 20-30 min. Column chromatography was performed on Merck silica gel 60 (230-400 mesh). α,α,α-Trifluorotoluene was purchased from Aldrich as anhydrous grade and used without further purification. Acetonitrile and toluene were purified by Mbraun solvent purifier. 2,2-Dimethylbutane was purified by passing through dry silica gel (heated for 6 h then cooled under an argon atmosphere) then distilled from sodium.



13a **14a (major)**

A solution of **13a** (40 mg, 99% ee) in toluene (3 ml) was refluxed for 24 h. The solvent was evaporated to provide **14a** (**major**) (40 mg, 100% yield, 99% ee) as a pale yellow oil: mp 38-39°C (pentane/ether); R_f 0.65 (5:1 pentane/ether); $[\alpha]_D^{25}$ –106.1° (*c* 2.00, $CHCl_3$); FTIR (CH_2Cl_2) 3026, 2927, 2858, 1734, 1449, 1434, 1158 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.17 (dd, *J* = 15.8, 9.8 Hz, 1H), 5.20 (s, 1H), 3.72 (s, 3H), 2.97 (t, *J* = 9.8 Hz, 1H), 2.56 (br m, 1H), 1.96-1.83 (m, 2H), 1.75-1.67 (m, 2H), 1.65 (s, 3H), 1.56-1.47 (m, 1H), 1.27-1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 136.7, 136.4, 133.0, 128.5, 127.5, 126.7, 126.3, 122.4, 55.8, 51.7, 38.0, 30.0, 26.2, 24.0, 21.1; LC-MS (EI) *m/z* (relative intensity): 249 (100), 271 (M^+ + H, 38), 293 (M^+ + Na, 25); HPLC analysis: 99% ee (Chiralcel OD-H, 1% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 7.7 min, major; t_R = 9.8 min, minor). Analysis. Calculated for $C_{17}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.74; H, 8.23.



13b **14b (major)** **14b (minor)**

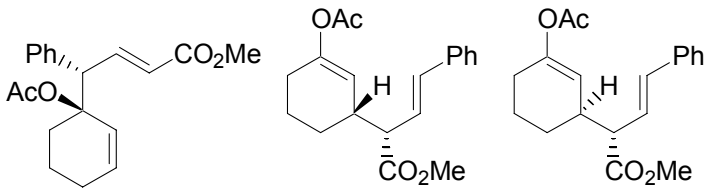
To a solution of 1-isopropyl-1-cyclohexene (**11b**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of syringe-pump. The solvent was evaporated and the residue (**13b**:**14b** = 0.8:1, diastereomeric ratio of **14b** = 1.9:1 by crude ^1H NMR) was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **13b** (46 mg, 31% yield) and **14b** (59 mg, 39% yield).

13b. Colorless oil; R_f 0.36 (10:1 pentane/ether); $[\alpha]_D^{25}$ -74.4° (*c* 4.40, $CHCl_3$); FTIR (film) 3025, 2952, 2836, 1724, 1650, 1600, 1495, 1454, 1435, 1321, 1268, 1245, 1211, 1166 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 15.4, 9.9 Hz, 1H), 7.26-7.18 (m,

5H), 5.93 (ddd, J = 10.4, 4.6, 3.4 Hz, 1H), 5.78 (d, J = 15.4 Hz, 1H), 5.58 (d, J = 10.4 Hz, 1H), 3.69 (s, 3H), 3.56 (d, J = 9.9 Hz, 1H), 1.78-1.65 (m, 2H), 1.65-1.57 (m, 1H), 1.52 (ddd, J = 14.0, 11.0, 4.3 Hz, 1H), 1.43 (dt, J = 14.0, 4.9 Hz, 1H), 1.22-1.15 (m, 1H), 0.93 (d, J = 6.7 Hz, 3H), 0.82 (d, J = 7.0 Hz, 3H), 0.44-0.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 149.8, 140.9, 131.0, 130.0, 129.7, 127.9, 126.6, 121.8, 56.7, 51.4, 44.2, 33.8, 26.6, 24.3, 19.1, 18.3, 16.4; MS (EI) *m/z* (relative intensity): 67.0 (57), 81.0 (45), 123.1 (100), 176.0 (42), 239.2 (15), 298.2 (M^+, 5); HRMS (EI) Calculated for $[C_{20}H_{26}O_2]^+$: 298.1927. Found: 298.1936; ee was determined by converting to **14b (major)**, HPLC analysis: 95% ee (Chiralcel OD-H, 1.0% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 7.2 min, major; t_R = 9.7 min, minor).

14b (major). Colorless oil; R_f 0.45 (10:1 pentane/ether); $[\alpha]_D^{25}$ -105.3° (*c* 1.10, $CHCl_3$); FTIR (film) 2957, 1736, 1434, 1258, 1234, 1152, 1025, 968 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.19 (dd, J = 15.9, 9.5 Hz, 1H), 5.20 (s, 1H), 3.72 (s, 3H), 2.98 (t, J = 9.5 Hz, 1H), 2.58 (br s, 1H), 2.16 (hept, J = 6.7 Hz, 1H), 1.97-1.85 (m, 2H), 1.76-1.67 (m, 2H), 1.54-1.45 (m, 1H), 1.31-1.22 (m, 1H), 0.97 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.1, 145.8, 136.8, 132.9, 128.5, 127.5, 126.8, 126.3, 119.7, 55.8, 51.7, 38.0, 35.3, 26.6, 25.8, 21.4, 21.33, 21.30; MS (EI) *m/z* (relative intensity): 67.0 (52), 81.0 (41), 123.1 (100), 176.0 (45), 239.2 (5), 298.2 (M^+, 2); HRMS (EI) Calculated for $[C_{20}H_{26}O_2]^+$: 298.1927. Found: 298.1931; HPLC analysis: 93% ee (Chiralcel OD-H, 1.0% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 7.2 min, major; t_R = 9.7 min, minor).

14b (**minor**) (contaminated with **14b major**). Colorless oil; R_f 0.45 (10:1 pentane/ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.22 (dd, J = 15.9, 9.5 Hz, 1H), 5.36 (s, 1H), 3.70 (s, 3H), 2.99 (t, J = 9.0 Hz, 1H), 2.62-2.52 (m, 1H), 2.16 (hept, J = 6.7 Hz, 1H), 1.97-1.85 (m, 2H), 1.81-1.73 (m, 2H), 1.54-1.45 (m, 1H), 1.31-1.22 (m, 1H), 0.96 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 145.7, 136.9, 133.3, 128.5, 127.5, 126.6, 126.3, 119.2, 55.6, 51.7, 38.2, 35.4, 27.5, 25.6, 21.9, 21.5, 21.3.



13c **14c (major)** **14c (minor)**

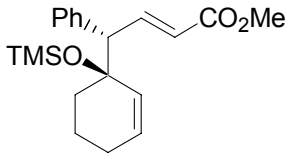
To a solution of 1-cyclohexen-1-yl acetate (**11c**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45 min period by means of a syringe-pump. The solvent was evaporated and the residue (**13c**:**14c** = 2.2:1 by crude ^{1}H NMR) was purified by flash chromatography on silica gel (5:1-2:1 pentane/ether eluent) to provide **13c** (87 mg, 55% yield) and **14c** (44 mg, 28% yield).

13c. Colorless oil; R_f 0.31 (5:1 pentane/ether); $[\alpha]_D^{25}$ +36.5° (*c* 1.10, $CHCl_3$); FTIR (film) 3031, 2941, 1725, 1650, 1436, 1365, 1244, 1202, 1167, 1017 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.28-7.20 (m, 3H), 7.25 (dd, *J* = 15.8, 7.3 Hz, 1H), 6.04 (d, *J* = 10.1 Hz, 1H), 5.98 (dt, *J* = 10.1, 4.0 Hz, 1H), 5.85 (dd, *J* = 15.8, 1.2 Hz, 1H), 4.51 (d, *J* = 8.2 Hz, 1H), 3.71 (s, 3H), 2.12-2.04 (m, 2H), 2.02-1.93 (m, 1H), 1.90 (s, 3H), 1.73-1.65 (m, 2H), 1.63-1.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4 (C), 166.8 (C), 147.1 (CH), 138.1 (C), 133.0 (CH), 129.6 (CH), 128.4 (CH), 128.2 (CH), 127.2 (CH), 123.5 (CH), 81.8 (C), 54.0 (CH), 51.5 (CH_3), 29.9 (CH_2), 24.6 (CH_2), 22.2 (CH_3), 18.0 (CH_2); MS (EI) *m/z* (relative intensity): 97.1 (60), 115.1 (35), 176.1 (100), 195.1 (35), 218.1 (22), 254.2 (34), 282.2 (21); HRMS (ESI) Calculated for $[C_{19}H_{22}NaO_4]^+$ (M^+ + Na): 337.1410. Found: 337.1423; HPLC analysis: 98% ee (Chiralcel OD-H, 2.0% *i*-PrOH in hexane, 0.5 ml/min, λ = 254 nm, t_R = 14.3 min, major; t_R = 21.6 min, minor).

14c (major). Colorless oil; R_f 0.25 (5:1 pentane/ether); FTIR (film) 3026, 2948, 2864, 1758, 1734, 1687, 1496, 1449, 1435, 1367, 1220, 1168, 1148, 1130, 970, 751, 693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J*

= 7.3 Hz, 1H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 9.6 Hz, 1H), 5.25 (s, 1H), 3.71 (s, 3H), 3.06 (pseudo t, *J* = 9.6 Hz, 1H), 2.80-2.73 (m, 1H), 2.21-2.08 (m, 2H), 2.11 (s, 3H), 1.85-1.73 (m, 2H), 1.70-1.62 (m, 1H), 1.36-1.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.5, 169.2, 150.0, 136.6, 133.6, 128.6, 127.7, 126.4, 126.0, 115.5, 55.2, 51.9, 37.1, 26.8, 25.7, 21.1, 20.8; MS (EI) *m/z* (relative intensity): 97.0 (100), 115.0 (37), 144.0 (22), 176.1 (75), 218.1 (20), 314.1 (M^+, 2); HRMS (ESI) Calculated for $[C_{19}H_{22}NaO_4]^+$ (M^+ + Na): 337.1410. Found: 337.1407; HPLC analysis: 97% ee (Chiralpak AD-RH, 5.0% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 7.6 min, major; t_R = 9.0 min, minor).

14c (minor) (contaminated with **13c**). Signals can be identified from mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 9.6 Hz, 1H), 5.37 (s, 1H), 3.71 (s, 3H), 3.05 (pseudo t, *J* = 9.3 Hz, 1H), 2.80-2.73 (m, 1H), 2.09 (s, 3H), 1.59 (s, 3H), 1.36-1.28 (m, 1H).

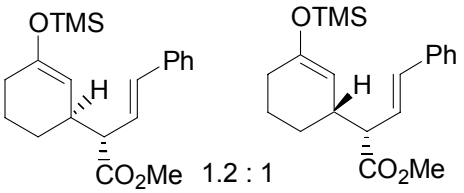


13d

(TMS, trimethylsilyl) To a solution of 1-cyclohexenyloxyltrimethylsilane (**11d**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of (*E*)-methyl phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue (**13d**:**14d** = 2.2:1 by crude ^{1}H NMR) was purified by flash chromatography on silica gel (20:1-10:1 pentane/ether/0.5% Et_3N eluent) to provide **13d** (76 mg, 44% yield) as a colorless oil.

13d. R_f 0.50 (10:1 pentane/ether); $[\alpha]_D^{25}$ -24.4° (*c* 2.25, $CHCl_3$); FTIR (film) 3028, 2950, 2872, 2834, 1726, 1650, 1452, 1435, 1328, 1261, 1249, 1165, 1095, 1029, 989, 900, 839, 738, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 15.5, 9.5 Hz, 1H), 7.26-7.15

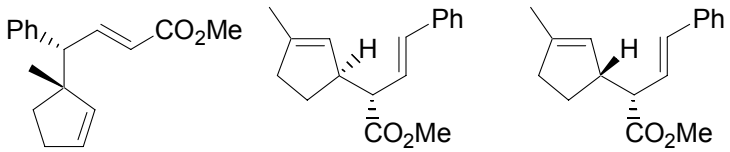
(m, 5H), 5.76 (d, J = 15.5 Hz, 1H), 5.70 (dt, J = 10.3, 3.7 Hz, 1H), 5.33 (d, J = 10.3 Hz, 1H), 3.68 (s, 3H), 3.39 (d, J = 9.5 Hz, 1H), 2.02-1.86 (m, 2H), 1.77-1.59 (m, 3H), 1.58-1.44 (m, 1H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 149.1, 139.5, 131.8, 129.9 (2C), 127.8, 126.7, 122.4, 74.7, 59.3, 51.4, 35.3, 24.8, 19.2, 2.4; MS (fast atom bombardment, FAB) *m/z* (relative intensity): 169.1 (100), 367.2 (M^+ + Na, 18); HPLC analysis: 99% ee (Chiralcel OD-H, 0.5% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 5.7 min, major; t_R = 12.5 min, minor). Analysis. Calculated for $C_{20}H_{28}O_3Si$: C, 69.72; H, 8.19. Found: C, 69.54; H, 8.19.



14d (major) **14d (minor)**

To a solution of 1-cyclohexenyloxyltrimethylsilane (**11d**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (20:1-10:1 pentane/ether eluent) to provide a mixture of **13d** and **14d** (total 104 mg, 60% yield) as a colorless oil.

14d (a mixture of two diastereomers and contaminated with **13d**). Signals can be identified from mixture: **major**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (d, J = 15.9 Hz, 1H), 6.24 (d, J = 6.23 Hz, 1H), 4.91 (s, 1H), 3.74 (s, 3H), 3.04 (t, J = 9.5 Hz, 1H), 2.74-2.68 (m, 1H), 0.20 (s, 9H); **minor**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 (d, J = 15.9 Hz, 1H), 6.22 (dd, J = 15.9, 9.9 Hz, 1H), 4.76 (m, 1H), 3.74 (s, 3H), 3.04 (pseudo t, J = 9.2 Hz, 1H), 2.74-2.68 (m, 1H), 0.21 (s, 9H).



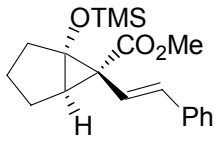
16 **17 (major)** **17 (minor)**

To a solution of 1-methyl-1-cyclopentene (**15**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at -20°C (dry ice/acetone bath) over a 45 min period via syringe-pump. The solvent was evaporated and the residue (**16:17** = 1.2:1, d.r of **17** = 1.2:1 by crude ^{1}H NMR) was purified by flash chromatography on silica gel (20:1 pentane/ether eluent) to provide **16** (66 mg, 51% yield) and **17** (57 mg, 44% yield).

16. Colorless oil; R_f 0.46 (5:1 pentane/ether); $[\alpha]_D^{25}$ –24.9 (*c* 1.35, $CHCl_3$); FTIR (film) 3032, 2952, 2854, 1723, 1650, 1447, 1438, 1269, 1247, 1166 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 15.6, 9.0 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.28-7.17 (m, 3H), 5.78 (dd, *J* = 15.6, 0.9 Hz, 1H), 5.68 (dt, *J* = 5.6, 2.1 Hz, 1H), 5.50 (dt, *J* = 5.6, 2.1 Hz, 1H), 3.71 (s, 3H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.31-2.23 (m, 1H), 2.04 (dddd, *J* = 18.6, 9.2, 4.9, 2.4 Hz, 1H), 1.93 (ddd, *J* = 12.8, 9.2, 5.5 Hz, 1H), 1.56 (ddd, *J* = 12.8, 9.8, 4.9 Hz, 1H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 149.6, 140.4, 137.9, 130.5, 129.2, 128.0, 126.6, 122.3, 58.0, 52.8, 51.4, 35.1, 31.7, 25.2; MS (EI) *m/z* (relative intensity): 81.1 (100), 115.1 (50), 144.1 (32), 176.1 (66), 197.1 (6); HRMS (EI) Calculated for $[C_{17}H_{20}O_2]^+$: 256.1458. Found: 256.1451; HPLC analysis: 96% ee (Chiralcel OD-H, 5% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 6.2 min, major; t_R = 11.6 min, minor). Analysis. Calculated for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.60; H, 7.96.

17 (mixture of two diastereomers). Colorless oil; R_f 0.50 (5:1 pentane/ether); FTIR (film) 3029, 2948, 2848, 1735, 1653, 1440, 1262, 1156 cm^{-1}; **Minor:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 9.2 Hz, 1H), 5.20 (s, 1H), 3.70 (s, 3H), 3.17-3.06

(m, 1H), 2.97 (t, J = 9.3 Hz, 1H), 2.29-2.14 (m, 2H), 2.02 (m, 1H), 1.71 (s, 3H), 1.68-1.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.10, 142.5, 136.8, 132.6, 128.5, 127.5, 126.6, 126.28, 125.6, 55.5, 51.7, 48.51, 36.1, 28.6, 16.7; **Major:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 15.9 Hz, 1H), 6.21 (dd, J = 15.9, 9.5 Hz, 1H), 5.29 (s, 1H), 3.69 (s, 3H), 3.17-3.06 (m, 1H), 3.02 (t, J = 9.0 Hz, 1H), 2.29-2.14 (m, 2H), 2.08 (m, 1H), 1.71 (s, 3H), 1.68-1.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.06, 142.4, 136.9, 132.7, 128.5, 127.5, 126.5, 126.31, 125.3, 55.4, 51.7, 48.54, 36.3, 28.1, 16.7; MS (EI) *m/z* (relative intensity) (mixture of two diastereomers): 81.1 (100), 115.1 (61), 144.1 (42), 176.1 (89), 197.1 (27), 256.2 (M^+, 9); HRMS (EI) Calculated for $[C_{17}H_{20}O_2]^+$ (mixture of two diastereomers): 256.1458. Found: 256.1449. Analysis. Calculated for $C_{17}H_{20}O_2$ (mixture of two diastereomers): C, 79.65; H, 7.86. Found: C, 79.61; H, 7.88.



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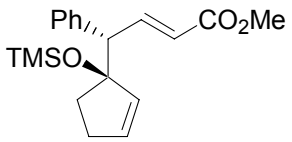

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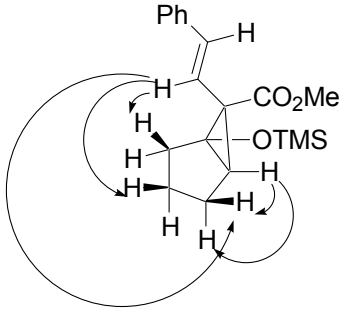
To a solution of 1-trimethylsilyloxy-cyclopentene (**18**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue (**19**:**20**:**21** = 87:7:6 by crude ^{1}H NMR) was purified by flash chromatography on silica gel (20:1-10:1 pentane/ether eluent) to provide **19** (79 mg, 48% yield) and **20** (5 mg, 3% yield).

19. Pale yellow oil; R_f 0.33 (10:1 pentane/ether); $[\alpha]_D^{25}$ +85.5° (*c* 2.60, $CHCl_3$); FTIR (film) 3025, 2953, 2865, 1729, 1448, 1433, 1383, 1302, 1251, 1205, 1135, 1086, 966, 917, 900, 875, 843, 744, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 16.2 Hz, 1H), 6.25 (d, J = 16.2 Hz, 1H), 3.68 (s, 3H), 2.58 (d, J = 5.2 Hz, 1H), 2.24-2.04 (m, 3H), 1.71-1.60 (m,

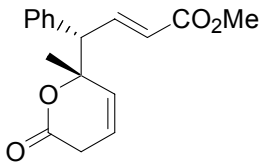
2H), 1.14 (d5, J = 13.7, 9.5 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 137.1, 134.8, 128.5, 127.5, 126.2, 120.9, 75.4, 52.1, 39.4, 35.3, 32.8, 25.0, 21.9, 0.87; GC-MS (EI) *m/z* (relative intensity): 73 (100), 330 (M^+, 20); HPLC analysis: 95% ee (Chiralcel OD-H, 0.3% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 7.4 min, major; t_R = 8.5 min, minor). Analysis. Calculated for $C_{19}H_{26}O_3Si$: C, 69.05; H, 7.93. Found: C, 69.02; H, 7.89. nOe, nuclear Overhauser effect.



nOe of **19**

20. Colorless oil; R_f 0.41 (10:1 pentane/ether); FTIR (film) 3029, 2953, 2853, 1728, 1653, 1454, 1436, 1356, 1324, 1250, 1169, 1082, 840 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 15.9, 8.9 Hz, 1H), 7.33-7.20 (m, 5H), 5.86-5.80 (m, 2H), 5.46 (dt, J = 5.8, 2.0 Hz, 1H), 3.72 (s, 3H), 3.35 (d, J = 8.9 Hz, 1H), 2.44-2.35 (m, 1H), 2.16-2.08 (m, 2H), 1.88-1.80 (m, 1H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 149.2, 139.8, 135.2, 134.1, 129.6, 127.9, 126.8, 122.4, 89.9, 59.6, 51.4, 37.2, 30.9, 1.9; MS (EI) *m/z* (relative intensity): 155.1 (100), 180.1 (22), 240.1 (12), 330.2 (M^+, 2); HRMS (EI) *m/z*: Calculated for $[C_{19}H_{26}O_3Si]^+$: 330.1646. Found: 330.1639.

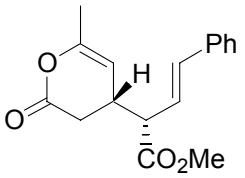
21. Decomposed during the flash chromatography.



23a

To a solution of 3,4-dihydro-6-methyl-2*H*-pyran-2-one (**22**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-phenylvinyldiazoacetate (**12a**) (203 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (1:1-1:2 pentane/ether eluent) to provide **23a** (125 mg, 87% yield).

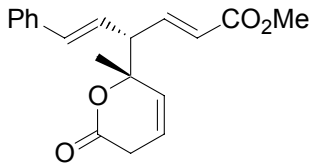
23a. White solid, mp 63-66°C; R_f 0.23 (1:1 pentane/ether); $[\alpha]_D^{25}$ -124.2° (*c* 1.95, $CHCl_3$); FTIR (CH_2Cl_2) 3061, 3030, 2983, 2951, 1723, 1739, 1655, 1453, 1436, 1328, 1279, 1238, 1171, 1085, 742, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 5H), 7.22 (dd, *J* = 15.5, 9.5 Hz, 1H), 5.94 (dd, *J* = 15.5, 0.6 Hz, 1H), 5.85 (ddd, *J* = 10.4, 2.4, 0.9 Hz, 1H), 5.80 (ddd, *J* = 10.4, 4.0, 2.7 Hz, 1H), 3.73 (s, 3H), 3.72 (d, *J* = 9.5 Hz, 1H), 2.75 (ddd, *J* = 22.3, 4.0, 0.9 Hz, 1H), 2.13 (dt, *J* = 22.3, 2.5 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0 (C), 166.2 (C), 144.6 (CH), 136.6 (C), 129.8 (CH), 128.3 (CH), 127.6 (CH), 127.4 (CH), 124.6 (CH), 122.7 (CH), 86.0 (C), 59.2 (CH), 51.6 (CH_3), 28.6 (CH_2), 26.9 (CH_3); MS (FAB) *m/z* (relative intensity): 136.0 (81), 154.0 (100), 287.1(M^+ + H, 5); HPLC analysis: 99% ee (Chiralpak AD-RH, 3% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 18.0 min, minor; t_R = 22.4 min, major). Analysis. Calculated for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.51; H, 6.36.



24a (major)

24a. Colorless oil; R_f 0.30 (2:1 pentane/ether); FTIR (film) 3027, 2925, 2922, 1766, 1733, 1697, 1435, 1264, 1236, 1192, 1161, 1090, 972, 751, 695 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.07 (dd, *J* = 15.9, 9.5 Hz, 1H), 4.97 (d, *J* = 4.3 Hz, 1H), 3.73 (s, 3H), 3.08 (t, *J* = 9.2 Hz, 1H), 2.96-2.89 (m, 1H), 2.66 (dd, *J* = 16.2, 7.0 Hz, 1H),

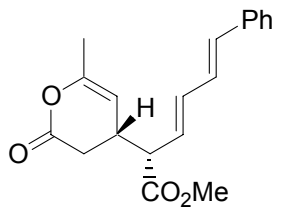
2.59 (dd, J = 16.2, 6.2 Hz, 1H), 1.90 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 168.0, 150.7, 136.0, 135.4, 128.6, 128.1, 126.5, 123.4, 101.5, 53.8, 52.2, 33.4, 31.8, 18.8; MS (EI) *m/z* (relative intensity): 77.0 (37), 103.1 (25), 131.1 (83), 145.1 (55), 173.1 (34), 205.1 (100); HRMS (EI) Calculated for $[C_{17}H_{18}O_4]^+$: 286.1205. Found: 286.1213.



23b

To a solution of 3,4-dihydro-6-methyl-2*H*-pyran-2-one (**22**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*,*E*)-2-diazo-6-phenyl-3,5-hexadienoate (**12b**) (229 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (1:1-1:2 pentane/ether eluent) to provide **23b** (129 mg, 82% yield).

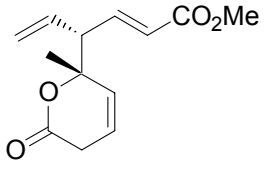
23b. White solid (greenish due to contamination with Rh_2(*S*-DOSP)$_4$ catalyst), mp 74.5-75.0°C (pentane/ether); R_f 0.30 (1:2 pentane/ether); $[\alpha]_D^{25}$ -57.3° (*c* 2.00, $CHCl_3$); FTIR ($CHCl_3$) 3025, 2985, 2950, 1728, 1654, 1489, 1325, 1278, 1230, 1173, 1071, 1000, 982 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.25 (t, J = 7.0 Hz, 1H), 6.99 (dd, J = 15.6, 8.2 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 9.2 Hz, 1H), 5.97 (d, J = 15.6 Hz, 1H), 5.88 (dt, J = 10.2, 3.4 Hz, 1H), 5.82 (d, J = 10.2 Hz, 1H), 3.73 (s, 3H), 3.28 (t, J = 8.6 Hz, 1H), 3.01 (ddd, J = 12.6, 3.4, 1.5 Hz, 1H), 2.93 (dt, J = 12.6, 2.5 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 166.3, 144.6, 136.3, 135.2, 128.6, 128.1, 127.9, 126.3, 124.1, 123.9, 121.7, 85.7, 56.5, 51.6, 29.2, 26.4; GC-MS (EI) *m/z* (relative intensity): 83 (53), 111 (100), 141 (51), 169 (23), 202 (37), 281 (3); HPLC analysis: 99% ee (Chiralpak AD-RH, 5% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 18.0 min, minor; t_R = 20.3 min, major). Analysis. Calculated for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.77; H, 6.45.



24b (major)

A solution of **23b** (74 mg) in toluene (3 ml) was refluxed for 24 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (3:2 pentane/ether eluent) to provide **24b** (**major**) (37 mg, 50% yield) as a colorless oil.

24b (major). R_f 0.35 (1:2 pentane/ether); $[\alpha]_D^{25}$ -78.2° (*c* 1.80, $CHCl_3$); FTIR (film) 3024, 2952, 2922, 1766, 1734, 1698, 1448, 1435, 1269, 1228, 1191, 1161, 1093 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.72 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.34 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.66 (dd, *J* = 15.2, 9.6 Hz, 1H), 4.95 (d, *J* = 4.6 Hz, 1H), 3.72 (s, 3H), 3.00 (pseudo t, *J* = 9.2 Hz, 1H), 2.90-2.83 (m, 1H), 2.64 (dd, *J* = 16.2, 6.7 Hz, 1H), 2.55 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 167.9, 150.6, 136.7, 135.7, 133.7, 128.6, 127.8, 127.4, 127.0, 126.4, 101.6, 53.5, 52.1, 33.3, 31.7, 18.7; MS (ESI) *m/z* (relative intensity): 224 (13), 238 (11), 253 (16), 313 (M^+ + H, 34), 335 (M^+ + Na, 100); HRMS (ESI) *m/z* Calculated for $[C_{19}H_{20}NaO_4]^+$ (M^+ + Na): 335.1254. Found: 335.1262.

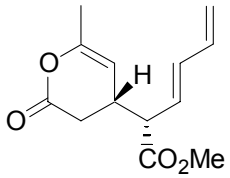


23c

To a solution of 3,4-dihydro-6-methyl-2*H*-pyran-2-one (**22**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in 2,2-dimthylbutane (2 ml) was added a solution of methyl (*E*)-2-diazo-3,5-hexadienoate (**12c**) (153 mg, 1.0 mmol) in 2,2-dimethylbutane (5 ml) at room temperature over a 45-min period by means of a syringe-pump. The solvent was

evaporated and the residue was purified by flash chromatography on silica gel (1:1-1:2 pentane/ether eluent) to provide **23c** (65 mg, 55% yield).

23c. Colorless oil [greenish due to contamination with Rh_2(*S*-DOSP)$_4$ catalyst]: R_f 0.28 (1:2 pentane/ether); $[\alpha]_D^{25}$ -151.9° (*c* 2.54, $CHCl_3$); FTIR (film) 2983, 2952, 1724, 1655, 1437, 1329, 1275, 1241, 1200, 1139, 1103, 1070, 1006 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.92 (dd, *J* = 15.9, 8.1 Hz, 1H), 5.92 (dd, *J* = 15.7, 1.1 Hz, 1H), 5.87 (dt, *J* = 10.2, 3.4 Hz, 1H), 5.83 (dtd, *J* = 17.1, 8.7, 1.5 Hz, 1H), 5.79 (dt, *J* = 10.2, 2.1 Hz, 1H), 5.27 (dd, *J* = 10.1, 0.9 Hz, 1H), 5.21 (d, *J* = 17.1 Hz, 1H), 3.74 (s, 3H), 3.13 (pseudo t, *J* = 8.4 Hz, 1H), 3.03 (dd, *J* = 3.4, 2.1 Hz, 2H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 168.1, 166.3, 144.4, 132.9, 128.1, 124.1, 121.5, 120.6, 85.4, 57.2, 51.6, 29.2, 26.3; MS (EI) *m/z* (relative intensity): 83.0 (29), 111.0 (100), 126.1 (7); HRMS (ESI) *m/z* Calculated for $[C_{13}H_{16}NaO_4]^+$ (M^+ + Na): 259.0941. Found: 259.0941; HPLC analysis: 99% ee (Chiralpak AD-RH, 2% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 15.5 min, minor; t_R = 17.2 min, major).

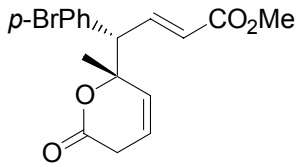


24c (major)

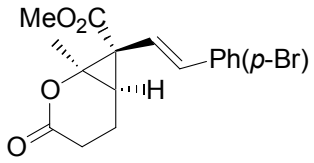
A solution of **23c** (21 mg) in toluene (3 ml) was refluxed for 24 h. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (1:1 pentane/ether eluent) to provide **24c** (**major**) (16 mg, 75% yield) as a colorless oil.

24c (major). R_f 0.32 (1:2 pentane/ether); $[\alpha]_D^{25}$ +17.5° (*c* 1.60, $CHCl_3$); FTIR (film) 2998, 2954, 2923, 1766, 1734, 1697, 1435, 1262, 1233, 1196, 1161, 1143, 1093, 1005 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.30 (dt, *J* = 16.8, 10.4 Hz, 1H), 6.18 (dd, *J* = 15.0, 10.7 Hz, 1H), 5.56 (dd, *J* = 15.3, 9.5 Hz, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 4.3 Hz, 1H), 3.71 (s, 3H), 2.95 (t, *J* = 9.2 Hz, 1H), 2.87-2.81 (m, 1H), 2.63 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.52 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.89 (s, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 172.6 (C), 168.2 (C), 150.8 (C), 136.4 (CH), 135.9 (CH), 127.5 (CH), 119.0 (CH_2), 101.8 (CH), 53.6 (CH), 52.4 (CH_3), 33.4 (CH), 32.0 (CH_2), 19.0 (CH_3); MS (ESI) *m/z* (relative intensity): 177.1 (13), 259.0 (M^+ + Na, 100); HRMS (ESI) *m/z* Calculated for $[C_{13}H_{16}NaO_4]^+$ (M^+ + Na): 259.0941. Found: 259.0930.



23d



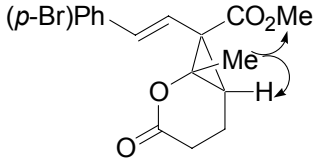
25d

To a solution of 3,4-dihydro-6-methyl-2*H*-pyran-2-one (**22**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in trifluorotoluene (2 ml) was added a solution of methyl (*E*)-*para*-bromophenyldiazoacetate (**12d**) (281 mg, 1.0 mmol) in trifluorotoluene (5 ml) at 0°C over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (1:2 pentane/ether eluent) to provide **23d** (135 mg, 74% yield) and **25e** (35 mg, 19% yield).

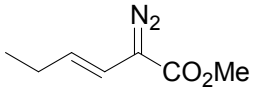
23d. White solid, mp 100-101°C (THF/hexane); R_f 0.23 (1:2 pentane/ether); $[\alpha]_D^{25}$ -78.4° (*c* 1.00, $CHCl_3$); FTIR (CH_2Cl_2) 2987, 2949, 1729, 1655, 1488, 1437, 1325, 1277, 1237, 1171, 1075, 1008, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.15 (dd, *J* = 15.3, 9.3 Hz, 1H), 5.91 (d, *J* = 15.3 Hz, 1H), 5.87-5.81 (m, 2H), 3.73 (s, 3H), 3.67 (d, *J* = 9.3 Hz, 1H), 2.84 (dd, *J* = 22.0, 2.5 Hz, 1H), 2.33 (d, *J* = 22.0 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 166.0, 144.0, 135.8, 131.42, 131.37, 127.3, 124.9, 122.7, 121.8, 85.8, 58.3, 51.6, 28.7, 26.8; MS (chemical ionization, CI) *m/z* (relative intensity): 110.1 (100), 151.1 (28), 183.0 (27), 211.0 (11), 237.0 (33), 269.0 (66), 365.0 (9, M^+ + H); HRMS (CI) *m/z* Calculated for $[C_{17}H_{18}BrO_4]^+$ (M^+ + H): 365.0383. Found: 365.0369; HPLC analysis: 99% ee (Chiralpak AD-RH, 5% *i*-PrOH in hexane, 1.0 ml/min, λ = 254 nm, t_R = 15.4 min, minor; t_R = 22.4 min, major).

25d. Pale yellow oil; R_f 0.27 (1:2 pentane/ether); FTIR (film) 3030, 2953, 1757, 1724, 1644, 1588, 1488, 1435, 1402, 1300, 1240, 1221, 1153, 1102, 1072, 1009 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 16.5 Hz, 1H), 6.05 (d, *J* = 16.5 Hz, 1H), 3.74 (s, 3H), 2.42-2.28 (m, 4H), 1.83-1.75 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.8, 137.2, 135.3, 131.7, 127.8, 122.0, 119.6, 68.5, 52.8, 39.3, 27.9, 26.0, 19.2, 17.2; MS (EI) *m/z* (relative intensity): 170.9 (71), 207.0 (100), 281 (46), 363.9 (M^+, 24); HRMS (EI) *m/z* Calculated for $[C_{17}H_{17}BrO_4]^+$ (M^+): 364.0305. Found: 364.0299.

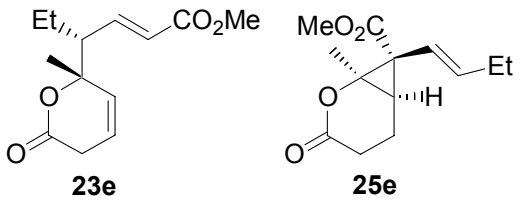


nOe of **25d**



12e

Methyl (*E*)-2-diazo-3-hexenoate (12e). To a solution of methyl (*E*)-3-hexenate (8.04 g) and *p*-ABSA (*para*-acetamidobenzenesufonyl azide) (22.6 g) in acetonitrile (100 ml) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 14 ml) in one portion at 0°C. The resulting mixture was stirred overnight (20 h). Saturated ammonium chloride aqueous solution (50 ml) and water (50 ml) were added. Two layers were separated and the aqueous layer was extracted with ether (twice, 50 ml each). The combined organic phases were washed with brine then dried over $MgSO_4$. The crude product was purified by silica gel chromatography (20:1 pentane/ether eluent) to give **12e** (5.8 g, 60% yield) as a red oil: R_f 0.42 (10:1 pentane/ether); FTIR (film) 2964, 2934, 2874, 2848, 2131, 2081, 1713, 1647, 1437, 1335, 1311, 1273, 1240, 1139, 1099, 952, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.72 (d, *J* = 15.9 Hz, 1H), 5.37 (dt, *J* = 15.9, 6.5 Hz, 1H), 3.80 (s, 3H), 2.19 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H). GC-MS (EI) *m/z* (relative intensity) 122 (100), 139 (22), 154 (M^+, 58); HRMS (EI) *m/z* Calculated for $[C_7H_{10}N_2O_2]^+$: 154.0737. Found: 154.0735.



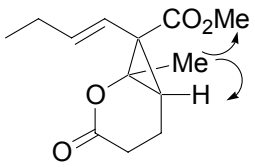
23e **25e**

To a solution of 3,4-dihydro-6-methyl-2*H*-pyran-2-one (**22**) (0.5 mmol) and Rh_2(*S*-DOSP)$_4$ (19 mg, 0.01 mmol) in 2,2-dimthylbutane (2 ml) was added a solution of methyl (*E*)-2-diazo-3-hexenate (**12e**) (155 mg, 1.0 mmol) in 2,2-dimethylbutane (5 ml) at room temperature over a 45-min period by means of a syringe-pump. The solvent was evaporated and the residue was purified by flash chromatography on silica gel (1:1-1:2 pentane/ether eluent) to provide **23e** (26 mg, 20% yield) and **25e** (80 mg, 67% yield).

23e. Colorless oil [greenish due to contaminated with Rh_2(*S*-DOSP)$_4$ catalyst], R_f 0.20 (1:1 pentane/ether); $[\alpha]_D^{25}$ -76.6° (*c* 1.90, $CHCl_3$); FTIR (film) 2966, 2934, 2876, 1724, 1655, 1272, 1238, 1100 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.66 (dd, *J* = 15.6, 10.5 Hz, 1H), 5.92 (d, *J* = 15.6 Hz, 1H), 5.84 (dt, *J* = 10.4, 3.4 Hz, 1H), 5.78 (dt, *J* = 10.4, 1.9 Hz, 1H), 3.76 (s, 3H), 3.06 (dd, *J* = 3.4, 1.9 Hz, 2H), 2.35 (ddd, *J* = 10.5, 10.5, 3.0 Hz, 1H), 1.67 (dqd, *J* = 13.4, 7.5, 3.0 Hz, 1H), 1.43 (s, 3H), 1.33 (ddq, *J* = 13.4, 10.5, 7.5 Hz, 1H), 0.82 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 166.3, 146.1, 127.9, 124.9, 121.0, 86.3, 55.2, 51.6, 29.2, 27.0, 20.9, 11.9; MS (ESI) *m/z* (relative intensity): 179 (12.7), 207 (11.1), 239 (M^+ + H, 33.8), 261 (M^+ + Na, 100); HRMS (ESI) *m/z* Calculated for $[C_{13}H_{18}NaO_4]^+$ (M^+ + Na): 261.1097. Found: 261.1089; HPLC analysis: 98% ee (Chiralpak AD-RH, 2% *i*-PrOH in hexane, 0.8 ml/min, λ = 254 nm, t_R = 15.3 min, minor; t_R = 16.9 min, major).

25e. Pale yellow oil; R_f 0.30 (1:1 pentane/ether); $[\alpha]_D^{25}$ +32.7° (*c* 2.40, $CHCl_3$); FTIR (film) 2962, 2934, 2875, 1758, 1724, 1437, 1435, 1240, 1220, 1167, 1102, 1063 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.30 (dt, *J* = 15.9, 1.0 Hz, 1H), 3.72 (s, 3H), 2.39-2.26 (m, 3H), 2.18 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.12 (pseudo 5d, *J* = 7.0, 1.0 Hz, 2H), 1.82-1.74 (m, 1H), 1.59 (s, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5 (C), 171.0 (C), 142.2 (CH), 117.7 (CH), 68.0 (C), 52.5 (CH_3), 38.8

(C), 27.8 (CH_2), 26.1 (CH_2), 24.9 (CH), 19.2 (CH_3), 17.0 (CH_2), 13.3 (CH_3); GC-MS (EI) *m/z* (relative intensity): 151 (100), 196 (61), 238 (M^+, 2); HRMS (ESI) *m/z* Calculated for $[C_{13}H_{19}O_4]^+$ (M^+ + H): 239.1278. Found: 239.1285. GC analysis: 42% ee (Chiraldex B-DM, 1.0 ml/min, 200°C, t_R = 16.55 min, minor; t_R = 16.63 min, major).



nOe of **25e**

X-Ray Structure for Compound 23d

X-ray diffraction data on **23d** were collected at 90(1) K by using a Bruker SMART1000 charge-coupled device diffractometer installed at a rotating anode source (MoKα radiation, λ = 0.71073 Å), and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.3° frame-width (ω scan) and 20-sec exposure time per frame. Four sets of data (600 frames in each set) were collected, nominally covering half of reciprocal space. The data were integrated, scaled, sorted, and averaged by using the SMART software package (1). The structure was solved by direct methods by using SHELXTL NT Version 5.10 (2). The structure was refined by full-matrix least squares against F^2. Data are summarized in Table 1.

Non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were found by the difference electron density Fourier synthesis. Subsequently, the positions of hydrogen atoms were refined as idealized CH_3 groups with $U_{iso} = 1.5U_{eq}$ of the connected non-hydrogen atom, and the remaining hydrogens were refined by using the "riding" model with $U_{iso} = 1.2U_{eq}$.

Atomic coordinates, anisotropic displacement parameters, and bond lengths and angles are given in Tables 2, 3, and 4, respectively.

Results and Discussion

Table 1. Crystallographic data

Compound	**23d**
Formula	$C_{17}H_{17}O_4Br$
M_r, g•mol^{-1}	365.22
Crystal shape	Colorless parallelepipeds
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	5.6520(2)
b, Å	12.3008(3)
c, Å	11.7762(3)
α, °	90
β, °	100.591(1)
γ, °	90
Volume, Å^3	804.78(4)
Z	2
ρ_{calc}, g/cm^3	1.507
μ, mm^{-1}	2.569
T, K	90(1)
Max. 2θ, °	50.0
Absorption correction method	SADABS (ref. 1)
No. of reflections measured	9,068
No. of unique reflections (R_{int})	2842 (0.056)
No. of reflections $I > 4\sigma(I)$	2,702
Parameters refined	199
R [$I > 2\sigma(I)$]	0.043
wR_2	0.066
Goodness of fit	1.021
Absolute structure parameter (Flack parameter) (ref. 3)	0.036(8)
Extinction coefficient	None

Table 2. Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*(eq)
Br(1)	6715(1)	11317(1)	14367(1)	24(1)
O(1)	9172(3)	7015(2)	11641(2)	14(1)
O(2)	10967(4)	7493(2)	13383(2)	21(1)
O(3)	-759(4)	8198(2)	8028(2)	35(1)
O(4)	1216(4)	8708(2)	6634(2)	22(1)
C(1)	9240(5)	7078(2)	12792(2)	16(1)
C(2)	7223(5)	6584(2)	13296(2)	19(1)
C(3)	5207(5)	6127(2)	12425(3)	18(1)
C(4)	5056(4)	6278(3)	11311(2)	16(1)
C(5)	6946(5)	6866(2)	10797(2)	14(1)
C(6)	6196(5)	8031(2)	10346(2)	14(1)
C(7)	3811(5)	8063(2)	9536(2)	16(1)
C(8)	3523(6)	8341(3)	8444(3)	16(1)
C(9)	1110(6)	8402(2)	7709(3)	19(1)
C(10)	-1040(6)	8696(3)	5827(3)	30(1)
C(11)	7663(5)	6180(3)	9844(2)	19(1)
C(12)	6240(5)	8839(2)	11321(2)	14(1)
C(13)	8063(5)	9613(2)	11532(3)	16(1)
C(14)	8202(5)	10355(2)	12428(3)	17(1)
C(15)	6469(5)	10321(2)	13122(2)	17(1)
C(16)	4637(5)	9562(2)	12934(2)	17(1)
C(17)	4510(5)	8829(2)	12030(2)	15(1)

Table 3. Anisotropic displacement parameters ($Å^2 \times 10^3$)

Atom	U11	U22	U33	U23	U13	U12
Br(1)	33(1)	14(1)	23(1)	-6(1)	5(1)	-1(1)
O(1)	12(1)	14(1)	17(1)	0(1)	3(1)	0(1)

O(2)	20(1)	23(1)	18(1)	2(1)	0(1)	-3(1)
O(3)	16(1)	61(2)	26(1)	11(1)	1(1)	1(1)
O(4)	23(1)	23(1)	18(1)	3(1)	0(1)	2(1)
C(1)	18(2)	8(1)	22(2)	2(1)	4(1)	6(1)
C(2)	21(2)	18(2)	19(1)	4(1)	8(1)	1(1)
C(3)	17(1)	9(2)	32(2)	3(1)	11(1)	1(1)
C(4)	13(1)	8(1)	26(1)	-5(2)	4(1)	-1(2)
C(5)	15(1)	11(1)	15(1)	-1(1)	1(1)	2(1)
C(6)	16(2)	11(1)	15(1)	1(1)	4(1)	-3(1)
C(7)	14(1)	12(1)	23(2)	-3(1)	4(1)	1(1)
C(8)	16(2)	11(2)	21(2)	1(1)	4(1)	-2(1)
C(9)	23(2)	13(2)	22(2)	-2(1)	6(1)	2(1)
C(10)	34(2)	32(2)	20(2)	1(1)	-6(1)	5(2)
C(11)	20(1)	14(2)	22(1)	-4(1)	5(1)	4(1)
C(12)	14(2)	7(2)	20(2)	1(1)	0(1)	3(1)
C(13)	13(2)	12(1)	22(2)	3(1)	2(1)	1(1)
C(14)	14(2)	10(1)	27(2)	0(1)	0(1)	0(1)
C(15)	23(2)	9(1)	19(1)	-1(1)	0(1)	3(1)
C(16)	18(2)	14(1)	19(1)	3(1)	6(1)	4(1)
C(17)	14(1)	11(1)	20(1)	3(1)	4(1)	1(1)

Table 4. Bond lengths and angles

Bond	Length, Å		
Br(1)-C(15)	1.895(3)	C(5)-C(6)	1.560(4)
O(1)-C(1)	1.351(3)	C(6)-C(7)	1.502(4)
O(1)-C(5)	1.465(3)	C(6)-C(12)	1.514(4)
O(2)-C(1)	1.203(4)	C(7)-C(8)	1.312(4)
O(3)-C(9)	1.211(4)	C(8)-C(9)	1.477(5)
O(4)-C(9)	1.333(4)	C(12)-C(13)	1.392(4)
O(4)-C(10)	1.444(4)	C(12)-C(17)	1.398(4)
C(1)-C(2)	1.507(4)	C(13)-C(14)	1.386(4)
C(2)-C(3)	1.495(4)	C(14)-C(15)	1.387(4)
C(3)-C(4)	1.313(4)	C(15)-C(16)	1.382(4)
C(4)-C(5)	1.506(4)	C(16)-C(17)	1.387(4)
C(5)-C(11)	1.517(4)		

Bond	Angle, º
C(1)-O(1)-C(5)	123.4(2)
C(9)-O(4)-C(10)	115.7(2)
O(2)-C(1)-O(1)	118.3(3)
O(2)-C(1)-C(2)	122.4(3)
O(1)-C(1)-C(2)	119.2(2)
C(3)-C(2)-C(1)	114.7(2)
C(4)-C(3)-C(2)	122.3(2)
C(3)-C(4)-C(5)	123.3(3)
O(1)-C(5)-C(4)	111.8(2)
O(1)-C(5)-C(11)	105.0(2)
C(4)-C(5)-C(11)	109.6(2)
O(1)-C(5)-C(6)	105.2(2)
C(4)-C(5)-C(6)	114.2(2)
C(11)-C(5)-C(6)	110.6(2)
C(7)-C(6)-C(12)	110.6(2)
C(7)-C(6)-C(5)	113.3(2)
C(12)-C(6)-C(5)	112.3(2)
C(8)-C(7)-C(6)	124.4(3)
C(7)-C(8)-C(9)	121.5(3)
O(3)-C(9)-O(4)	123.2(3)
O(3)-C(9)-C(8)	124.9(3)
O(4)-C(9)-C(8)	111.9(3)
C(13)-C(12)-C(17)	118.4(3)
C(13)-C(12)-C(6)	119.5(3)
C(17)-C(12)-C(6)	122.1(3)
C(14)-C(13)-C(12)	121.5(3)
C(13)-C(14)-C(15)	118.8(3)
C(16)-C(15)-C(14)	121.0(3)
C(16)-C(15)-Br(1)	120.5(2)
C(14)-C(15)-Br(1)	118.5(2)
C(15)-C(16)-C(17)	119.6(3)
C(16)-C(17)-C(12)	120.6(3)

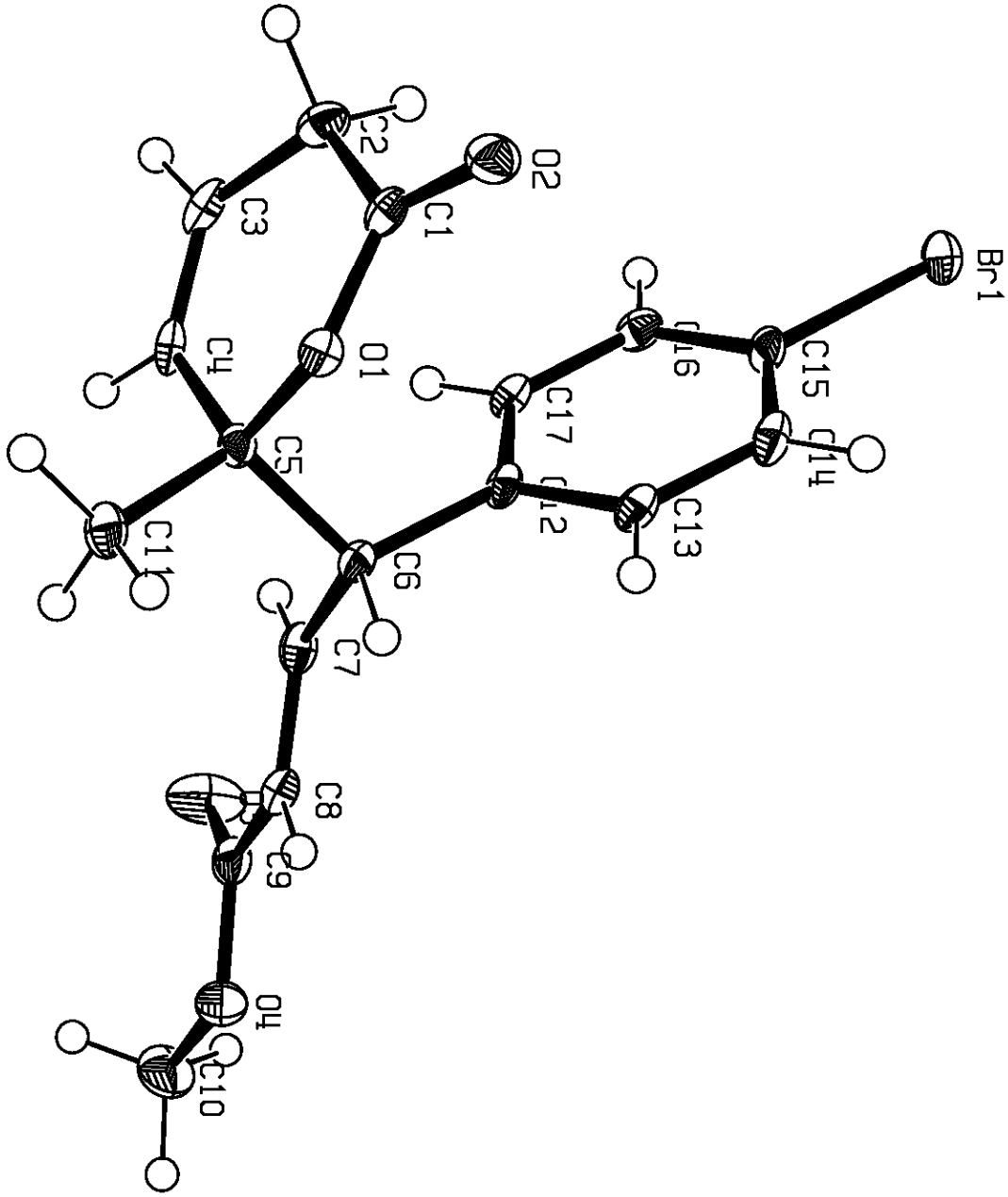


Fig. 1. X-ray structure for compound **23d.**

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