Experimental Section

General Information: 

1H NMR spectra were run at either 400 or 500 MHz, and 13C NMR at 125 MHz with the sample solvent being CDCl$_3$ unless otherwise noted. Mass spectral determinations were carried out at 70 eV. IR spectra were obtained using a Nicolet Impact series 420 IR. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. Column chromatography was carried out on silica gel 60 (230-400) mesh. Enantiomeric excess was determined by HPLC using chiral analytical columns. Reactions were carried out under an atmosphere of argon. Degassing was carried out by bubbling Ar gas through the solution for 5-10 minutes.

Starting materials:

Compound 1$^1$, 5$^1$, 6a$^2$, 6b$^2$, 8b$^1$, 12c$^4$ were prepared according to the literature. Dichloromethane was distilled from CaH$_2$ before use. Dimethylbutane was used directly. Cyclohexene, 8a, 8c, 8d, 8e, 8f 12a, 12b, (+)-15, (-)-15 and (±)-15 are commercially available from Aldrich and used without further purification.

General Procedure for C-H Activation reactions:

To a stirring and degassed solution of alkene (5.0 mmol) and Rh$_2$(S-DOSP)$_4$ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl p-bromophenyldiazoacetate (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (6-10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel to give the product.

Methyl 2-(cyclohexen-1-yl)-phenylacetate (2)$^5$:

To a stirring and degassed solution of cyclohexene (5.0 mmol) and Rh$_2$(S-DOSP)$_4$ (20 mg, 0.01 mmol) in 2,2-dimethylbutane (5 mL) was added a degassed solution of methyl phenyldiazoacetate 1 (96 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo
and the crude product was purified by flash chromatography on silica gel (25:1 then 10:1 pentane/ether) to give 74.6 mg (59% yield) of 2 as a mixture of two diastereomers with a ratio of 1:1 and 18 mg (14% yield) of 3, R<sub>2</sub>:3 = 79:21 (by <sup>1</sup>H NMR of crude product).

**Methyl (R)-α-cyclohexylphenylacetate (4)**<sup>1</sup>: To a stirred solution of 2 (60 mg) in MeOH (10 mL) was added Pd/C (10%, 28 mg). The mixture was stirred under H₂ at room temperature overnight. The solid was filtered and the filtrate was concentrated to give 55.2 mg (91% yield) of 4 as a colorless oil. 93% ee (Chiralcel OD, 0.2% i-PrOH in hexane, 0.8 mL/min, λ = 254 nm, tᵣ = 9.8 min, major; tᵣ = 13.5 min, minor), stereochemistry was determined by HPLC (Lit.<sup>1</sup>: Chiralcel OD, 0.6% i-PrOH in hexane, 0.6 mL/min, λ = 254 nm, tᵣ = 8.6 min, major; tᵣ = 10.4 min, minor)

**Methyl (αR, 1R)-α-(3-trimethylsilyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (7a):** To a stirring and degassed solution of 1-trimethylsilylcyclohexene (2.5 mmol) and Rh₄(S-DOSP)<sub>₄</sub> (20 mg, 0.01 mmol) in 2,2-dimethylbutane (5 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (135 mg, 0.53 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 45.9 mg (23% yield) of 7a as a colorless oil, 29 mg (14%) of both diastereomers, and 19.1 mg (10% yield) of the minor diastereomer. 7a:minor diastereomer = 70:30 (by <sup>1</sup>H NMR of crude product). 7a: R<sub>t</sub> 0.49 (10:1 pentane/ether); [α]<sub>25</sub> = -75.9° (c 0.66, CHCl₃); FTIR (CDCl₃): 2950, 2928, 2857, 1737, 1613, 1488, 1446, 1407, 1335, 1360, 1258, 1246 cm⁻¹; <sup>1</sup>H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 5.41 (br, s, 1H), 3.66 (s, 3H), 3.29 (d, J = 11.0 Hz, 1H), 2.80-2.75 (m, 1H), 2.04-1.93 (m, 2H), 1.80-1.84 (m, 1H), 1.77-1.72 (m, 1H), 1.56-1.48
(m, 1H), 1.31-1.21 (m, 1H), -0.09 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.5, 141.3, 136.4, 135.1, 131.5, 130.5, 121.3, 56.7, 51.9, 39.7, 27.6, 26.6, 21.5, -2.4; Anal. Calcd for C$_{18}$H$_{25}$BrO$_2$Si: C, 56.69; H, 6.61. Found: C, 56.48; H, 6.60; MS (EI) m/z 380 (M$^+$); HPLC analysis: 88% ee (R,R-whelk-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, $\lambda$ = 254 nm, $t_\text{R}$ = 15.18 min, major; $t_\text{R}$ = 18.84 min, minor). **Minor diastereomer:** $R$, 0.54 (10:1 pentane/ether); [$\alpha$]$_D^{25}$ -34.9$^\circ$ (c 0.95, CHCl$_3$). FTIR (CDCl$_3$): 2950, 2926, 1736, 1488, 1446, 1434, 1406, 1340, 1246 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 8.2 Hz, 2H), 7.21 (d, $J$ = 8.2 Hz, 2H), 5.81 (br, s, 1H), 3.68 (s, 3H), 3.27 (d, $J$ = 11.3 Hz, 1H), 2.80-2.76 (m, 1H), 2.05-1.93 (m, 2H), 1.66-1.60 (m, 1H), 1.46-1.32 (m, 2H), 1.02-0.95 (m, 1H), 0.03 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.8, 141.3, 136.6, 136.0, 131.6, 130.1, 121.3, 56.7, 51.9, 39.6, 26.7, 26.3, 21.2, -2.3; HRMS (EI) m/z Calcd for [C$_{18}$H$_{25}$BrO$_2$Si]$^+$: 380.0807. Found: 380.0814; HPLC analysis: 82% ee (R,R-whelk-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, $\lambda$ = 254 nm, $t_\text{R}$ = 17.83 min, major; $t_\text{R}$ = 25.37 min, minor).

**Methyl ($\alpha R$, 1R)- $\alpha$- (3-tert-butyldiphenylsilyl-2-cyclohexen-1-yl)-(4-bromophenyl) acetate (7b):** To a stirring and degassed solution of 1-tert-butyldiphenylsilylcyclohexene (1.65 mmol) and Rh$_2$(S-DOSP)$_4$ (15.6 mg, 0.008 mmol) in 2,2-dimethylbutane (5 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (105 mg, 0.41 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. Solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (25:1 pentane/ether eluent) to give 129.4 mg (58% yield) of 7b as a colorless oil and 14.4 mg (6% yield) of minor diastereomer (not identified). 7b:minor diastereomer = 94:6 (by $^1$H
NMR of crude product). 7b: Rf 0.39 (10:1 pentane/ether); \([\alpha]^{25}\)D = -43.6° (c 1.06, CHCl₃); FTIR (CDCl₃): 3069, 3048, 2928, 2856, 1736, 1488, 1427, 1265, 1194, 1160, 1104 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, \(J = 7.0\) Hz, 2H), 7.37-7.21 (m, 10H), 7.11 (d, \(J = 8.5\) Hz, 2H), 5.56 (br, s, 1H), 3.64 (s, 3H), 3.33 (d, \(J = 10.7\) Hz, 1H), 2.91-2.87 (m, 1H), 2.17-2.08 (m, 2H), 1.94-1.90 (m, 1H), 1.77-1.74 (m, 1H), 1.61-1.55 (m, 1H), 1.41-1.36 (m, 1H), 1.03 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 142.3, 136.3, 163.1, 136.02, 136.00, 134.5, 134.4, 131.5, 130.3, 128.9, 128.8, 127.5, 127.4, 121.2, 56.9, 51.9, 40.3, 29.2, 28.8, 27.6, 21.7, 18.2; HRMS (EI) \(m/z\) Calcd for \([C_{27}H_{26}BrO_2Si]\)⁺ (M - C₄H₉, loss of tert-butyl): 489.0885. Found: 489.0862; HPLC analysis: 95% ee (R,R-whelk-O1, 0.3% i-PrOH in hexane, 1.0 mL/min, \(\lambda = 254\) nm, \(t_R = 12.36\) min, major; \(t_R = 20.08\) min, minor).

Methyl (αR, 1S)-α-(3-methyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (9a) and Methyl (αR, 1R)-α-(3-methyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (10a): To a stirring and degassed solution of 1-methylcyclohexene (4 mmol) and Rh₂(S-DOSP)₄ (15 mg, 0.008 mmol) in 2,2-dimethylbutane (5 mL) was added a degassed solution of methyl 4-bromophenylidiaoacetate 5 (102 mg, 0.4 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 31.3 mg (24% yield) of 10a as a colorless oil and 37.4 mg (29% yield) of a mixture of 9a and 10a. 9a can be separated from the mixture by using preparative TLC as a colorless oil. 9a: Rf 0.54 (10:1 pentane/ether); FTIR (film) 2931, 1743, 1491, 1440, 1406, 1343, 1274 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, \(J = 8.2\) Hz, 2H), 7.23 (d, \(J = 8.5\) Hz, 2H), 4.84 (br, s, 1H), 3.65 (s, 3H), 3.25 (d, \(J = 11.0\) Hz, 1H), 2.80-2.78 (m, 1H), 1.93-1.74 (m,
4H), 1.62-1.56 (m, 1H), 1.54 (s, 3H), 1.25-1.21 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.7, 136.6, 136.5, 131.6, 130.5, 121.4, 121.3, 57.0, 51.9, 38.8, 30.0, 27.7, 23.9, 21.4; HRMS (EI) m/z Calcd for [C$_{16}$H$_{19}$BrO$_2$]$^+$: 322.0568. Found: 322.0561; HPLC analysis: 94% ee (R,R-whelk-O1, 0.2% i-PrOH in hexane, 1.0 mL/min, $\lambda$ = 254 nm, t$_R$ = 10.84 min, major; t$_R$ = 14.67 min, minor).

10a: $R_f$ 0.56 (10:1 pentane/ether); [$\alpha$]$^D_{25}$ = -58.33° (c 0.60, CHCl$_3$); FTIR (film) 3000, 2928, 2860, 2831, 1736, 1488, 1434, 1406, 1336, 1273, 1211, 1193, 1159 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, $J$ = 8.2 Hz, 2H), 7.20 (d, $J$ = 8.5 Hz, 2H), 5.29 (br, s, 1H), 3.68 (s, 3H), 3.24 (d, $J$ = 11.3 Hz, 1H), 2.77-2.76 (m, 1H), 1.92-1.85 (m, 2H), 1.67 (s, 3H), 1.65-1.61 (m, 1H), 1.48-1.40 (m, 1H), 1.34-1.28 (m, 1H), 0.97-0.90 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.8, 136.8, 136.7, 131.6, 130.1, 122.7, 121.2, 57.1, 52.0, 38.7, 30.1, 26.1, 24.0, 21.0; HRMS (EI) m/z Calcd for [C$_{16}$H$_{19}$BrO$_2$]$^+$: 322.0568. Found: 322.0568; HPLC analysis: 98% ee (R,R-whelk-O1, 0.3% i-PrOH in hexane, 1.0 mL/min, $\lambda$ = 254 nm, t$_R$ = 11.6 min, minor; t$_R$ = 12.5 min, major).

Methyl ($\alpha$R, 1S)-$\alpha$-(3-ethyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (9b) and Methyl ($\alpha$R, 1R)-$\alpha$-(3-ethyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (10b): To a stirring and degassed solution of 1-ethylcyclohexene (5 mmol, contaminated with 13% ethylidenecyclohexane) and Rh$_2$(S-DOSP)$_4$ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (7 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (100:1 pentane/ether eluent) to give 19.6 mg (12% yield, contaminated) of 9b as colorless oil and 57.9 mg (34% yield) of 10b as a colorless oil. 9b: $R_f$ 0.41 (20:1...
pentane/ether); [\alpha]_D^{25} -64.0^\circ \text{ (c 0.45, CHCl}_3)\text{; FTIR (film) 2931, 1736, 1488, 1433, 1269, 1155, 1011, 819, 761 cm}^{-1}; ^1H NMR (500 MHz, CDCl}_3) \delta 7.50 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 4.84 (s, 1H), 3.65 (s, 3H), 3.26 (d, J = 11.0 Hz, 1H), 2.83-2.75 (m, 1H), 1.90 (br m, 2H), 1.84 (q, J = 7.5 Hz, 2H), 1.88-1.70 (m, 2H), 1.60-1.51 (m, 1H), 1.28-1.20 (m, 1H), 0.86 (t, J = 7.5 Hz, 3H); ^13C NMR (125 MHz, CDCl}_3) \delta 173.7 \text{ (C), 142.0 (C), 136.6 (C), 131.5 (CH), 130.5 (CH), 121.2 (CH), 121.0 (CH), 57.1 (CH), 51.9 (CH}_3), 38.7 (CH), 30.6 (CH}_2), 28.2 (CH}_2), 27.9 (CH}_2), 21.4 (CH}_2), 12.4 (CH}_3); HRMS (EI) m/z Calcd for [C17H21BrO2]+: 336.0725. Found: 336.0723; HPLC analysis: 90% ee (R,R-Whel-k-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, \lambda = 254 nm, t_R = 11.14 min, major; t_R = 14.06 min, minor). 10b: R, 0.48 (20:1 pentane/ether); [\alpha]_D^{25} -52.9^\circ \text{ (c 0.9, CHCl}_3)\text{; FTIR (film) 2932, 1736, 1488, 1433, 1159, 1150, 1011, 821, 762 cm}^{-1}; ^1H NMR (500 MHz, CDCl}_3) \delta 7.44 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.28 (s, 1H), 3.68 (s, 3H), 3.25 (d, J = 11.0 Hz, 1H), 2.78 (br m, 1H), 1.96 (q, J = 7.5 Hz, 2H), 1.90 (br m, 2H), 1.68-1.60 (m, 1H), 1.49-1.39 (m, 1H), 1.36-1.29 (m, 1H), 0.98 (t, J = 7.5 Hz, 3H), 1.01-0.91 (m, 1H); ^13C NMR (125 MHz, CDCl}_3) \delta 173.8 \text{ (C), 142.1 (C), 136.8 (C), 131.6 (CH), 130.1 (CH), 121.2 (CH), 121.0 (CH), 57.2 (CH), 51.9 (CH}_3), 38.6 (CH), 30.6 (CH}_2), 28.3 (CH}_2), 26.4 (CH}_2), 21.0 (CH}_2), 12.4 (CH}_3); HRMS (EI) m/z Calcd for [C17H21BrO2]+: 336.0725. Found: 336.0718; HPLC analysis (ee determined from its enantiomer): 94% ee (R,R-Whel-k-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, \lambda = 254 nm, t_R = 12.90 min, minor; t_R = 13.58 min, major). The acyclic C-H insertion product 11 could not be cleanly separated from 9b, 10b. Distinctive signals for its structure could be observed in the ^1H NMR. Major: 5.55 (br, 1H), 3.59 (s, 3H), 3.50 (d, J = 11.5 Hz, 1H), 2.71 (dq, J = 11.5, 6.7 Hz, 1H), 0.75 (d, J = 6.7 Hz, 3H). Minor: 5.24 (br, 1H), 3.47 (d, J = 11.5 Hz, minor) (1H), 2.71 (dq, J = 11.5, .6.7 Hz, 1H), 1.10 (d, J = 6.7 Hz, 1H).
Methyl (αR, 1S)-α-(3-iso-propyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (9c) and Methyl (αR, 1R)-α-(3-iso-propyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (10c): To a stirring and degassed solution of 1-isopropylcyclohexene (5 mmol) and Rh$_2$(S-DOSP)$_4$ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syring-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 41.4 mg (24% yield) of 9c as a white solid and 73.1 mg (42% yield) of 10c as a white solid. 9c: R, 0.40 (20:1 pentane/ether); [α]$_D^{25}$ -75.5° (c 0.97, CHCl$_3$); FTIR (CHCl$_3$) 2953, 2932, 1736, 1659, 1487, 1335, 1267, 1193, 1156, 1073, 1011, 819, 761 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, $J$ = 8.0 Hz, 2H), 7.23 (d, $J$ = 8.0 Hz, 2H), 4.86 (s, 1H), 3.65 (s, 3H), 3.27 (d, $J$ = 10.5 Hz, 1H), 2.82-2.75 (m, 1H), 2.05 (7, $J$ = 7.0 Hz, 1H), 1.90 (br, m, 2H), 1.85-1.72 (m, 2H), 1.57-1.48 (m, 1H), 1.27-1.20 (m, 1H), 0.87 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.7, 146.0, 136.6, 131.6, 131.5, 130.5, 121.2, 118.8, 57.1, 51.9, 38.7, 35.3, 28.0, 25.6, 21.5, 21.3, 21.1; Anal. Calcd for C$_{18}$H$_{23}$BrO$_2$: C, 61.54; H, 6.60. Found: C, 62.01; H, 6.78; HRMS (EI) m/z Calcd for [C$_{18}$H$_{23}$BrO$_2$]$^+$: 350.0881. Found: 350.0856; HPLC analysis: 90% ee (R,R-Whelk-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t$_r$ = 14.52 min, major; t$_r$ = 21.84 min, minor). 10c: R, 0.46 (20:1 pentane/ether); [α]$_D^{25}$ -47.7° (c 1.48, CH$_3$Cl); FTIR (CHCl$_3$) 2952, 2933, 1736, 1487, 1153, 1012, 820 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, $J$ = 8.2 Hz, 2H), 7.21 (d, $J$ = 8.2 Hz, 2H), 5.29 (s, 1H), 3.68 (s, 3H), 3.24 (d, $J$ = 11.0 Hz, 1H), 2.78 (br, m, 1H), 2.18 (7, $J$ = 7.0 Hz, 1H), 1.97-1.85 (m, 2H), 1.68-1.60 (m, 1H), 1.46-1.38 (m, 1H), 1.37-1.29 (m, 1H), 0.98 (d, $J$ = 7.0 Hz, 6H), 1.01-0.95 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.8 (C), 146.1 (C), 136.8 (C), 131.6 (CH), 130.1 (CH), 121.2 (C), 120.0 (CH), 75.2 (CH), 51.9 (CH$_3$), 38.6 (CH), 35.3 (CH), 26.6 (CH$_2$), 25.8 (CH$_3$), 21.4 (CH$_3$), 21.24 (CH$_3$), 21.15 (CH$_3$); Anal. Calcd for C$_{18}$H$_{23}$BrO$_2$: C, 61.54; H, 6.60. Found: C, 61.84; H, 6.73. MS (El) m/z: 123.2, 350.3 (M$^+$); HPLC analysis: 93% ee (R,R-Whelk-O1, 0.2% i-PrOH in hexane, 0.8 mL/min, λ = 254 nm, t$_r$ = 19.10 min, major; t$_r$ = 25.36 min, minor).
Methyl (αR, 1S)-α-(3-tert-butyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (9d) and Methyl (αR, 1R)-α-(3-tert-butyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (10d):

To a stirring and degassed solution of 1-t-butylcyclohexene (5 mmol) and Rh₂(S-DOSP)₄ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 29.6 mg (16% yield) of 9d as a white solid, 24.2 mg (13% yield) of 10d as a white solid and 30.1 mg (17% yield) of a mixture of 9d and 10d (total 46% yield). 9d: Rf 0.38 (20:1 pentane/ether); [α]D²⁵ -74.4° (c 1.1, CH₃Cl); FTIR (CHCl₃) 1736, 1650 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.92 (s, 1H), 3.65 (s, 3H), 3.27 (d, J = 10.8 Hz, 1H), 2.82-2.74 (m, 1H), 2.05-1.86 (m, 2H), 1.85-1.70 (m, 2H), 1.56-1.44 (m, 1H), 1.28-1.17 (m, 1H), 0.89 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.7 (C), 148.0 (C), 136.6 (C), 131.4 (CH), 130.5 (CH), 121.2 (C), 117.9 (CH), 57.3 (CH), 51.8 (CH₃), 39.1 (CH), 35.4 (C), 28.9 (CH₃), 27.7 (CH₂), 24.5 (CH₂), 21.8 (CH₂); Anal. Calcd for C₁₉H₂₅BrO₂: C, 62.47; H, 6.90. Found: C, 62.44; H, 6.96; MS (El) m/z: 137.2, 364.3 (M⁺). HPLC analysis: 91% ee (Chiralcel OD, 0.1% i-PrOH in hexane, 0.6 mL/min, λ = 254 nm, tᵣ = 12.95 min, major; tᵣ = 14.99 min, minor). 10d: Rf 0.45 (20:1 pentane/ether); [α]D²⁵ -41.0° (c 0.97, CH₃Cl). FTIR (CHCl₃) 1736, 1650 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.34 (s, 1H), 3.68 (s, 3H), 3.25 (d, J = 11.0 Hz, 1H), 2.84-2.76 (m, 1H), 2.05-1.89 (m, 2H), 1.68-1.60 (m, 1H), 1.45-1.30 (m, 2H), 1.01 (s, 9H), 0.98-0.88 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 173.9 (C), 148.2 (C), 136.8 (C), 131.6 (CH), 130.1 (CH), 121.2 (C), 118.9 (CH), 57.3
Methyl \((\alpha R, 1S)-\alpha-(3-phenyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate\) (9e) and Methyl \((\alpha R, 1R)-\alpha-(3-phenyl-2-cyclohexen-1-yl)-(4-bromophenyl)acetate\) (10e): To a stirring and degassed solution of 1-phenylcyclohexene (5 mmol) and \(\text{Rh}_2(\text{S-DOSP})_4\) (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed \textit{in vacuo} and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 20.7 mg (11% yield) of 9e as a white solid, 76.0 mg (39% yield) of 10e as a white solid and 29.2 mg (15% yield) of a mixture of 9e and 10e (total 65% yield). 9e: \(R_f\) 0.29 (20:1 pentane/ether); \([\alpha]_D^{25} -85.3^\circ\) (c 0.9, CHCl₃); FTIR (CH₂Cl₂) 2930, 1735, 1643, 1488, 1438, 1337, 1267, 1193, 1156, 1073, 1011, 819, 756, 696 cm⁻¹; \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.47 (d, \(J = 8.2\) Hz, 2H), 7.30-7.22 (m, 4H), 7.22-7.16 (m, 3H), 5.54 (s, 1H), 3.68 (s, 3H), 3.38 (d, \(J = 11.0\) Hz, 1H), 3.01 (br m, 1H), 2.45-2.33 (m, 2H), 1.98-1.89 (m, 2H), 1.77-1.67 (m, 1H), 1.41-1.32 (m, 1H); \(^1^3\)C NMR (125 MHz, CDCl₃) \(\delta\) 173.4, 142.0, 138.9, 136.3, 131.7, 130.5, 128.2, 127.0, 125.1, 124.6, 121.5, 56.9, 52.0, 39.3, 27.6, 27.5, 21.5; Anal. Calcd for C_{19}H_{25}BrO₂: C, 62.47; H, 6.90. Found: C, 62.63; H, 7.02; MS (EI) \(m/z\): 137.2, 364.3 (M⁺); HPLC analysis: 81% ee (R,R-Whelk-O1, 0.2% i-PrOH in hexane, 1.0 mL/min, \(\lambda = 254\) nm, \(t_R = 10.59\) min, major; \(t_R = 15.31\) min, minor). 10e: \(R_f\) 0.32 (20:1 pentane/ether)}
pentane/ether); $[\alpha]^\circ_{D_25} = -98.7^\circ$ (c 1.4, CH$_2$Cl$_2$); FTIR (CH$_2$Cl$_2$) 2947, 2923, 1734, 1486, 1146, 1010, 750, 696 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 8.5$ Hz, 2H), 7.37 (d, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.26-7.22 (m, 3H), 5.97 (s, 1H), 3.68 (s, 3H), 3.36 (d, $J = 11.3$ Hz, 1H), 3.04-2.96 (m, 1H), 2.40 (br m, 2H), 1.84-1.78 (m, 1H), 1.65-1.56 (m, 1H), 1.47-1.44 (m, 2H), 1.12-1.03 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.6, 142.1, 139.1, 136.5, 131.7, 130.0, 128.2, 127.0, 125.8, 125.3, 121.4, 56.8, 52.0, 39.1, 27.7, 26.0, 21.1; Anal. Calcd for C$_{21}$H$_{21}$BrO$_2$: C, 65.46; H, 5.49. Found: C, 65.34; H, 5.59; MS (EI) $m/z$: 157.1, 384.1 (M$^+$); HPLC analysis: 95% ee (Chiral Cel OD, 0.3% i-PrOH in hexane, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 14.45$ min, minor; $t_R = 15.57$ min, major).

Methyl ($\alpha R$, 1$R$)-$\alpha$-(3-chloro-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (9f) and Methyl ($\alpha R$, 1$S$)-$\alpha$-(3-chloro-2-cyclohexen-1-yl)-(4-bromophenyl)acetate (10f): To a stirring and degassed solution of 1-chlorocyclohexene (4 mmol) and Rh$_2$(S-DOSP)$_4$ (15 mg, 0.008 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (102 mg, 0.4 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (25:1 pentane/ether eluent) to give 51.6 mg (37% yield) of 9f and 28.8 mg (21% yield) of 10f (total 58% yield). 9f: $R_f$ 0.33 (10:1 pentane/ether); $[\alpha]^\circ_{D_25} = -94.0^\circ$ (c 1.4, CHCl$_3$); FTIR (CDCl$_3$) 2936, 2859, 1736, 1650, 1487, 1436, 1337, 1268 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 5.29 (br, s, 1H), 3.66 (s, 3H), 3.31 (d, $J = 11.3$ Hz, 1H), 2.95-2.90 (m, 1H), 2.34-2.23 (m, 2H), 1.90-1.83 (m, 2H), 1.76-1.67 (m, 1H), 1.33-1.26 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.0, 135.6, 134.3, 131.9, 130.3, 124.7, 121.8, 56.2, 52.1, 40.0, 32.7, 26.7, 22.1; HRMS (EI) $m/z$ Calcd for [C$_{15}$H$_{16}$BrClO$_2$]$^+$: 342.0022. Found: 342.0022; HPLC analysis: 96% ee (R,R-Whelk-O1, 0.2% i-PrOH in hexane, 0.8 mL/min,
$\lambda = 254$ nm, $t_R = 22.77$ min, major; $t_R = 27.03$ min, minor.  

$10f$: R, 0.43 (10:1 pentane/ether); $[\alpha]_D^{25} = -63.4^\circ$ (c 1.4, CHCl$_3$); FTIR (CDCl$_3$) 2944, 2861, 1734, 1650, 1487, 1436, 1337, 1271, 1209 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 2H), 5.76 (d, $J = 1.2$ Hz, 1H), 3.68 (s, 3H), 3.31 (d, $J = 11.3$ Hz, 1H), 2.92-2.89 (m, 1H), 2.30-2.27 (m, 2H), 1.75-1.71 (m, 1H), 1.61-1.56 (m, 1H), 1.37-1.32 (m, 1H), 1.02-0.98 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.0, 160.0, 134.6, 131.9, 129.9, 126.0, 121.6, 56.1, 52.2, 39.7, 32.8, 25.1, 21.6; HRMS (EI) $m/z$: Calcd for [C$_{15}$H$_{16}$BrClO$_2$]$^+$: 342.0022. Found: 342.0019; HPLC analysis: 91% ee (R,R-Whelk-O1, 0.3% i-PrOH in hexane, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 14.02$ min, minor; $t_R = 18.46$ min, major).

**Methyl (2R)-2-(4-bromophenyl)-3,5-dimethyl-4-hexenate (13a+14a):**

To a stirring and degassed solution of 2-methyl-2-pentene (7.5 mmol) and Rh$_2$(S-DOSP)$_4$ (14 mg, 0.0075 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyl diazoacetate 5 (191 mg, 0.75 mmol) in 2,2-dimethylbutane (10 mL) by syring-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (25:1 pentane/ether eluent) to give 163 mg (70% yield) of a mixture of 13a and 14a as a colorless oil, 13a:14a = 75:25 (by $^1$H NMR of crude product).  

$13a+14a$: R, 0.47 (10:1 pentane/ether); FTIR (CDCl$_3$): 2963, 2931, 2871, 1736, 1487, 1438, 1378, 1338, 1270, 1209, 1155 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) Major 13a: $\delta$ 7.37 (d, $J = 7.9$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 4.69 (dd, $J = 1.0$, 9.8 Hz, 2H), 3.66 (s, 3H), 3.26 (d, $J = 10.4$ Hz, 1H), 3.10-3.01 (m, 1H), 1.49 (s, 3H), 1.36 (s, 3H), 1.02 (d, $J = 6.7$ Hz, 3H); Minor 14a: $\delta$ 7.44 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 4.95 (dd, $J = 1.0$, 9.8 Hz, 1H), 3.58 (s, 3H), 3.24 (d, $J = 10.4$ Hz, 1H), 3.10-3.01 (m, 1H), 1.69 (s, 3H), 1.66 (s, 3H), 0.72 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) Major 13a: $\delta$ 173.8, 137.1, 132.3, 131.1, 130.3, 126.9, 120.9, 57.9, 51.9, 36.4, 25.5, 20.0, 17.8;
Minor 14a: δ 173.5, 136.7, 132.6, 131.5, 130.4, 127.4, 121.2, 58.2, 51.7, 36.6, 25.8, 18.6, 17.9; Anal. Calcd for C_{15}H_{19}BrO_{2}: C, 57.89; H, 6.15. Found: C, 58.05; H, 6.19. The primary C-H insertion product could not be cleanly separated from the other products, but compound had a distinctive ^1H NMR. ^1H NMR (500 MHz, CDCl$_3$): δ 7.45-7.15 (4H, superimposed), 5.10 (t, J = 7.2 Hz, 1H), 3.72 (dd, J = 8.7, 7.0 Hz, 1H), 3.64 (s, 3H), 2.73 (dd, J = 13.7, 8.7 Hz, 1H), 2.35 (dd, J = 13.7, 7.0 Hz, 1H), 1.92 (qd, J = 7.5, 7.2 Hz, 1H), 1.59 (s, 3H), 0.84 (t, J = 7.5 Hz, 3H).

Reduction of 13a+14a: Dibal-H (4 equiv.) was added to a stirring solution of 13a+14a (56 mg) in Toluene (5 mL) at 0 °C. The ice-water bath was removed after the addition and the result mixture was stirred for 1h at RT before 5mL of NH$_4$Cl solution was added. 50 mL ether was added and organic layer was separated and washed with brine the dried over anhydrous Na$_2$SO$_4$. The solvent was removed at reduced pressure and crude product was purified by flash chromatography on silica gel (5:1 pentane/ether eluent) to provide 12.5 mg minor product as colorless oil and 41 mg major product as colorless oil. Major: R$_f$ 0.27 (2:1 pentane/ether); [α]$^25_D$ = +42.1° (c 0.53, CHCl$_3$); FTIR (CDCl$_3$): 3355, 2962, 2923, 2877, 1486, 1449, 1406, 1376, 1068, 1009 cm$^{-1}$; ^1H NMR (500 MHz, CDCl$_3$) δ 7.41 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 4.75 (d, J = 9.8 Hz, 1H), 3.89-3.80 (m, 2H), 2.78-2.66 (m, 2H), 1.59 (s, 3H), 1.52 (s, 3H), 1.20 (s, 1H), 0.94 (d, J = 6.7 Hz, 3H); ^13C NMR (125 MHz, CDCl$_3$) δ 140.0, 131.5, 131.4, 131.0, 128.1, 120.6, 64.9, 54.1, 34.1, 26.0, 19.6, 18.2; HRMS (EI) m/z Calcd for [C$_{14}$H$_{19}$BrO]$^+$: 282.0619, Found: 282.0613; HPLC analysis: 86% ee (R,R-whelk-O1, 2% i-PrOH in hexane, 1.0 mL/min, λ = 254 nm, t$_R$ = 11.49 min, minor; t$_R$ = 13.69 min, major). Minor: R$_f$ 0.34 (2:1 pentane/ether); [α]$^25_D$ = +45.3 (c 0.49, CHCl$_3$); FTIR (film) 3365, 2963, 2923, 2873, 1652, 1487, 1452, 1377, 1068, 1009 cm$^{-1}$; ^1H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 5.02 (d, J = 9.8 Hz, 1H), 3.84-3.82 (m, 1H), 3.68-3.64 (m, 1H), 2.60 (tq, J = 10.0, 6.5 Hz, 1H), 2.52-2.47 (m, 1H), 1.73 (s, 3H), 1.66 (s, 3H), 1.56 (s, 1H), 0.71 (d, J
\[ \delta = 6.7 \text{ Hz, 3H}; \] ¹³C NMR (125 MHz, CDCl₃) \( \delta \) 141.0, 131.74, 131.65, 130.3, 129.2, 120.4, 66.2, 54.9, 35.2, 25.8, 19.6, 18.1; HRMS (EI) \( m/z \) Calcd for \([\text{C}_{14}\text{H}_{19}\text{BrO}]^+\): 282.0619, Found: 282.0616; HPLC analysis: 66% ee (R,R-whelk-O1, 2% i-PrOH in hexane, 1.0 mL/min, \( \lambda = 254 \text{ nm, } t_R = 14.37 \text{ min, major}; t_R = 16.29 \text{ min, minor}).

Methyl (2R)-2-(4-bromophenyl)-3-methyl-4-heptenate (13b+14b) : To a stirring and degassed solution of \((E)\)-3-hexene (5 mmol) and Rh₂(S-DOSP)₄ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenylidiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to provide 86.3 mg (56% yield) of a mixture of 13b and 14b as a colorless oil, \( 13b:14b = 56:44 \) (by ¹H NMR): \( R \), 0.31 (20:1 pentane/ether); FTIR (film) 2962, 2931, 1737, 1488, 1161, 1011 cm⁻¹; Major: ¹H NMR (500 MHz, CDCl₃) \( \delta \) 7.40 (d, \( J = 8.5 \text{ Hz, 2H} \)), 7.15 (d, \( J = 8.5 \text{ Hz, 2H} \)), 5.23 (dt, \( J = 15.2, 6.4 \text{ Hz, 1H} \)), 5.00 (dd, \( J = 15.2, 8.2 \text{ Hz, 1H} \)), 3.66 (s, 3H), 3.28 (d, \( J = 10.6 \text{ Hz, 1H} \)), 2.84-2.72 (m, 1H), 1.84-1.76 (m, 2H), 1.08 (d, \( J = 6.7 \text{ Hz, 3H} \)), 0.76 (t, \( J = 7.5 \text{ Hz, 3H} \)). ¹³C NMR (125 MHz, CDCl₃) \( \delta \) 173.6 (C), 136.9 (C), 133.3 (CH), 131.3 (CH), 130.52 (CH), 130.50 (CH), 57.8 (CH), 51.9 (CH₃), 40.2 (CH), 25.4 (CH₂), 19.3 (CH₃), 13.7 (CH₃). Minor: ¹H NMR (500 MHz, CDCl₃) \( \delta \) 7.44 (d, \( J = 8.2 \text{ Hz, 2H} \)), 7.24 (d, \( J = 8.5 \text{ Hz, 2H} \)), 5.57 (dt, \( J = 15.3, 6.4 \text{ Hz, 1H} \)), 5.32 (dd, \( J = 15.3, 8.2 \text{ Hz, 1H} \)), 3.60 (s, 3H), 3.26 (d, \( J = 10.6 \text{ Hz, 1H} \)), 2.84-2.72 (m, 1H), 2.03-1.96 (m, 2H), 0.96 (t, \( J = 7.5 \text{ Hz, 3H} \)), 0.77 (d, \( J = 6.7 \text{ Hz, 3H} \)); ¹³C NMR (125 MHz, CDCl₃) \( \delta \) 173.4 (C), 136.6 (C), 133.1 (CH), 131.6 (CH), 131.4 (CH), 130.3 (CH), 58.2 (CH), 51.6 (CH₃), 40.6 (CH), 25.5 (CH₂), 18.3 (CH₃), 13.9 (CH₃); HRMS (EI) \( m/z \) Calcd for \([\text{C}_{15}\text{H}_{19}\text{BrO}_2]^+\): 310.0568. Found: 310.0554.
Reduction of 13b+14b: Dibal-H (4 equiv.) was added to a solution of 13b+14b (70 mg) in Toluene (5 mL) at 0 °C. The ice-water bath was removed after the addition and the result mixture was stirred for 1 h at RT before 5mL of NH₄Cl solution was added. 50 mL ether was added and organic layer was separated and washed with brine the dried over anhydrous Na₂SO₄. The solvent was removed at reduced pressure and crude product was purified by flash chromatography on silica gel (3:1 pentane/ether eluent) to provide 28.8 mg major product as colorless oil, 24.2 mg minor product as colorless oil and 15.2 mg of mixture of major and minor products (total 100% yield). **Major**: Rₙ 0.30 (2:1 pentane/ether); [α]ᵦ₂₅ +26.1 (c 1.4, CHCl₃); FTIR (film) 3354, 2961, 1488, 1073, 1010, 819 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 5.34 (dt, J = 15.3, 6.4 Hz, 1H), 5.09 (dd, J = 15.3, 8.2 Hz, 1H), 3.88 (dd, J = 10.7, 5.8 Hz, 1H), 3.82 (dd, J = 10.7, 8.5 Hz, 1H), 2.72-2.67 (m, 1H), 2.53-2.44 (m, 1H), 1.95-1.88 (m, 2H), 0.98 (d, J = 6.7 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.5, 132.5, 131.4, 131.2, 130.8, 120.4, 64.6, 53.4, 38.2, 25.5, 18.8, 13.8; HRMS (EI) m/z Calcd for [C₁₄H₁₉BrO]⁺: 282.0619. Found: 282.0611; HPLC analysis: 92% ee (Chiralcel OD, 2% i-PrOH in hexane, 1.0 mL/min, λ = 254 nm, tᵣ = 11.64 min, minor; tᵣ = 13.10 min, major). **Minor**: Rₙ 0.45 (2:1 pentane/ether); [α]ᵦ₂₅ +40.2 (c 1.1, CHCl₃); FTIR (film) 3384, 2960, 2927, 2872, 1725, 1487, 1288, 1073, 1010, 970, 820 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 5.57 (dt, J = 15.3, 6.4 Hz, 1H), 5.32 (dd, J = 15.3, 8.8 Hz, 1H), 3.86 (dd, J = 11.0, 5.0 Hz, 1H), 3.69 (dd, J = 11.0, 8.2 Hz, 1H), 2.55-2.48 (m, 1H), 2.40-2.31 (m, 1H), 2.08-2.00 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H), 0.77 (d, J = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.8, 133.1, 132.4, 131.6, 130.0, 120.4, 66.0, 53.9, 40.0, 25.5, 19.7, 13.8; HRMS (EI) m/z Calcd for [C₁₄H₁₉BrO]⁺: 282.0619. Found: 282.0624; HPLC analysis: 80% ee
(Chiralcel OD, 1% i-PrOH in hexane, 1.0 mL/min, λ = 254 nm, $t_R = 15.26$ min, minor; $t_R = 16.76$ min, major).

Methyl (2$R$, 3$S$)-2-(4-bromophenyl)-(5,5-diphenyl-3-methyl-4-butenate (13c) and Methyl (2$R$, 3$R$)-2-(4-bromophenyl)-(5,5-diphenyl-3-methyl-4-butenate (14c): To a stirring and degassed solution of 1,1-diphenyl-1-butene (2 mmol) and Rh$_2$(S-DOSP)$_4$ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (50:1 pentane/ether eluent) to give 5.4 mg of 13c as a white solid, 5.9 mg of 14c as a white solid and 62.8 mg of a mixture of 13c and 14c (total 33% yield), 13c:14c = 85:15 (by $^1$H NMR of crude product). 13c: R$_f$ 0.27 (20:1 pentane/ether); FTIR (CH$_2$Cl$_2$) 2960, 1735, 1595, 1489, 1442, 1157, 1073, 1010, 765, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35-7.30 (m, 5H), 7.19-7.15 (m, 3H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.95-6.92 (m, 2H), 6.84 (dd, $J = 7.5$, 1.5 Hz, 2H), 5.61 (d, $J = 11.0$ Hz, 1H), 3.61 (s, 3H), 3.40 (d, $J = 10.5$ Hz, 1H), 3.08-3.00 (m, 1H), 1.18 (d, $J = 11.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.1, 142.4, 142.3, 139.6, 131.5, 131.3, 130.4, 129.5, 128.1, 128.0, 127.10, 127.06, 121.2, 57.9, 52.0, 37.5, 20.0; Anal. Calcd for C$_{25}$H$_{23}$BrO$_2$: C, 68.97; H, 5.33. Found: C, 69.31; H, 5.46. MS (EI) m/z: 207.1, 434.1 (M$^+$); HPLC analysis: 96% ee (R,R-Whelk-O1, 0.2% i-PrOH in hexane, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 12.33$ min, minor; $t_R = 28.87$ min, major). 14c: R$_f$ 0.31 (20:1 pentane/ether); FTIR (CH$_2$Cl$_2$) 2955, 2925, 1735, 1660, 1595, 1488, 1442, 1157, 1072, 1010, 764, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40-7.36 (m, 4H), 7.29-7.23 (m, 4H), 7.21-7.18 (m, 2H), 7.14-7.11 (m, 4H), 5.97 (d, $J = 10.4$ Hz, 1H), 3.60 (s, 3H), 3.43 (d, $J = 9.8$ Hz, 1H),
3.02-2.95 (m, 1H), 0.88 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.0, 142.5, 142.4, 139.7, 136.1, 131.5, 131.4, 130.4, 129.6, 128.2, 128.1, 127.3, 127.2, 127.1, 121.4, 58.0, 51.9, 37.9, 19.0; HRMS (EI) $m/z$ Calcd for [C$_{25}$H$_{23}$BrO$_2$]$^+$: 434.0881. Found: 434.0868; HPLC analysis: 30% ee (R,R-Whelk-O1, 0.2% $i$-PrOH in hexane, 1.0 mL/min, $\lambda$ = 254 nm, $t_R$ = 11.07 min, minor; $t_R$ = 22.22 min, major).

Matched reaction: Rh$_2$(S-DOSP)$_4$ catalyzed decomposition of diazo (5) in the presence of (+)-$\alpha$-pinene (15):

Methyl ($\alpha R$, 1$R$, 4$R$, 6$S$)-$\alpha$-(3,5,5-trimethylbicyclo[3,1,1]hept-2-en-1-yl)-(4-bromophenyl)acetate 16: To a stirring and degassed solution of (+)-$\alpha$-pinene 15 (0.5 mmol) and Rh$_2$(S-DOSP)$_4$ (19 mg, 0.01 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyl diazoacetate 5 (255 mg, 1.0 mmol) in 2,2-dimethylbutane (10 mL) by syring-pump over 2 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (100:1 pentane/ether eluent) to provide 169.2 mg (93% yield) 16 and 17 as a white solid (ratio 16:17 = 98:2); m.p. 118-119 °C; R$_f$ 0.5 (20:1 pentane/ether); [$\alpha$]$_D^{25}$ +10.8° (c 1.0, CHCl$_3$); FTIR (CHCl$_3$) 2926, 2871, 1736, 1657, 1486, 1437, 1158, 1073, 1010, 820, 763 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 5.16 (s, 1H), 3.68 (s, 3H), 3.42 (d, J = 11.3 Hz, 1H), 2.92-2.87 (m, 1H), 2.13-2.09 (m, 1H), 1.98-1.94 (m, 1H), 1.69 (s, 3H), 1.51-1.47 (m, 1H), 1.20 (d, J = 8.9 Hz, 1H), 1.16 (s, 3H), 0.83 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.8 (C), 147.1 (C), 136.6 (C), 131.7 (CH), 130.0 (CH), 121.2 (C), 117.5 (CH), 54.3 (CH), 52.0 (CH$_3$), 47.3 (CH), 43.7 (CH), 42.1 (CH), 40.7 (C), 27.2 (CH$_2$), 26.3 (CH$_3$), 23.0 (CH$_3$), 20.4 (CH$_3$); Anal. Calcd for C$_{19}$H$_{23}$BrO$_2$: C, 62.82; H, 6.38. Found: C, 62.55; H, 6.35. MS (EI) $m/z$: 93.1, 362.3 (M$^+$).
The stereochemistry of 16 was determined by conversion of 16 to 3-(4-bromophenyl)-7,9,9-trimethyl-5-oxa-tricyclo[6,1,1,0²,6]decane: Following the literature\(^6\) procedure, a solution of borane THF complex (0.3 mL, 1 M in THF ) was added to a solution of 16+17 (100 mg) in THF (2 mL) at 0 °C. The ice-water bath was removed after the addition and the reaction mixture was allowed to warm to room temperature and stirred for overnight. Water (1 mL) was added followed by the slow addition of 46 mg of solid sodium perborate•4H₂O. The resulting mixture was stirred overnight and then 20 mL ether was added. The organic layer was separated and washed with brine then dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (1:1 pentane/ether eluent) to provide 46 mg (47% yield) of diol as a white solid and 39 mg (40% yield) of a mixture of 16 : 17 (71:29) (total 87% yield). **Diol:** R\(_f\) 0.38 (1:1 pentane/ether); [\(\alpha\)]\(_D\)\(^{25}\) -10.6° (c 2.1, CHCl₃); FTIR (CDCl₃) 3256, 2936, 2901, 1488, 1010, 823, 734 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.39 (d, \(J = 8.3\) Hz, 2H), 6.95 (d, \(J = 8.5\) Hz, 2H), 4.19 (dd, \(J = 7.9, 3.7\) Hz, 1H), 4.04 (br, 2H), 3.92 (dd, \(J = 9.1, 8.8\) Hz, 1H), 3.77 (dd, \(J = 9.4, 4.9\) Hz, 1H), 3.42-3.36 (m, 1H), 2.56-2.50 (m, 1H), 2.05-1.98 (m, 1H), 1.91-1.85 (m, 1H), 1.78-1.73 (m, 1H), 1.20 (d, \(J = 9.8\) Hz, 1H), 1.17 (d, \(J = 7.6\) Hz, 1H), 1.04 (s, 3H), 0.89 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 141.5 (C), 131.6 (CH), 130.2 (CH), 120.0 (C), 72.4 (CH), 68.4 (CH₂), 47.4 (CH), 46.3 (CH), 45.7 (CH), 45.6 (CH), 44.5 (CH), 38.3 (C), 28.0 (CH₂), 27.7 (CH₃), 23.1 (CH₃), 20.6 (CH₃); Anal. Calcd for C\(_{18}\)H₂₅BrO₂: C, 61.19; H, 7.13. Found: C, 61.46; H, 7.36; HRMS (EI) \(m/z\) Calcd for [C\(_{18}\)H₂₅BrO₂]+: 352.1038. Found: 352.1050. Methanesulfonyl chloride was added slowly to a solution of diol (13 mg) in 2 mL pyridine at 0 °C. The resulting mixture was stirred overnight at 0 °C. The crude product was purified by flash chromatography on silica gel (10:1 pentane/ether eluent) to provide 6 mg (49% yield) product as a colorless oil. R\(_f\) 0.50 (10:1 pentane/ether); FTIR (film) 2952, 2920, 1490, 1469, 1456, 1064, 1010, 951, 817 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.43 (d, \(J = 8.2\) Hz, 2H), 7.11 (d, \(J = 8.5\) Hz, 2H), 4.22 (dd, \(J = 8.8, 7.2\) Hz, 1H), 4.10 (dd, \(J = 8.8, 2.7\) Hz, 1H), 3.59 (dd, \(J = 10.7, 8.8\) Hz, 1H), 3.04-2.97 (m, 1H), 2.63-2.57 (m, 1H), 2.26-2.20 (m, 1H), 2.17-2.10 (m, 1H), 1.92-1.87 (m, 1H), 1.87-1.82 (m, 1H), 1.30 (d, \(J = 10.1\) Hz, 1H), 1.22 (s, 3H), 1.17 (d, \(J = 7.6\) Hz, 3H), 0.89 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 140.2, 131.6, 129.5, 120.3, 83.1, 74.0, 51.2,
49.8, 47.0, 43.5, 42.9, 38.6, 28.0, 27.1, 23.2, 21.0; HRMS (EI) m/z Calcd for [C\textsubscript{18}H\textsubscript{23}BrO]\textsuperscript{+}: 334.0932. Found: 334.0935.

Matched reaction : Rh\textsubscript{3}(R-DOSP)\textsubscript{4} catalyzed decomposition of diazo (5) in the presence of (-)-\(\alpha\)-pinene :

Purified by flash chromatography on silica gel (100:1 pentane/ether eluent) to provide 180 mg (99% yield) of ent-16 as a white solid: R\textsubscript{f} 0.5 (20:1 pentane/ether); \([\alpha]_D\textsuperscript{25} -11.7^\circ\) (c 1.7, CHCl\textsubscript{3}); FTIR (CHCl\textsubscript{3}) 1736, 1657 cm\textsuperscript{-1}. \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.42 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 5.16 (s, 1H), 3.68 (s, 3H), 3.42 (d, J = 11.3 Hz, 1H), 2.92-2.87 (m, 1H), 2.13-2.09 (m, 1H), 1.98-1.94 (m, 1H), 1.69 (s, 3H), 1.51-1.47 (m, 1H), 1.20 (d, J = 8.9 Hz, 1H), 1.16 (s, 3H), 0.83 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 173.8 (C), 147.1 (C), 136.6 (C), 131.7 (CH), 130.0 (CH), 121.2 (C), 117.5 (CH), 54.3 (CH), 52.0 (CH\textsubscript{3}), 47.3 (CH), 43.7 (CH), 42.1 (CH), 40.7 (C), 27.2 (CH\textsubscript{2}), 26.3 (CH\textsubscript{3}), 23.0 (CH\textsubscript{3}), 20.4 (CH\textsubscript{3}); Anal. Calcd for C\textsubscript{19}H\textsubscript{23}BrO\textsubscript{2}: C, 62.82; H, 6.38. Found: C, 62.57; H, 6.45; MS (EI) m/z: 93.1, 362.3 (M\textsuperscript{+}).
Mismatched reaction: Rh$_2$(R-DOSP)$_4$ catalyzed decomposition of diazo (5) in the presence of (+)-α-pinene (15):

Methyl (αS, 1R, 4R, 6S)-α-(3,5,5-trimethylbicyclo[3,1,1]hept-2-en-1-yl)acetate 17: To a stirring and degassed solution of (+)-α-pinene 15 (0.5 mmol) and Rh$_2$(R-DOSP)$_4$ (19 mg, 0.01 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (255 mg, 1.0 mmol) in 2,2-dimethylbutane (10 mL) by syring-pump over 2 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (100:1 pentane/ether eluent) to provide 113.3 mg (62% yield) of 16, 17 and 8% unknown product (ratio 17:16 = 76:24). 17: R$_f$ 0.5 (20:1 pentane/ether); FTIR (CHCl$_3$) 1736 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 4.60 (d, $J = 0.9$ Hz, 1H), 3.63 (s, 3H), 3.42 (d, $J = 11.3$ Hz, 1H), 3.00-2.94 (m, 1H), 2.30-2.25 (m, 1H), 2.00-1.92 (m, 2H), 1.57 (s, 3H), 1.30 (s, 3H), 1.21 (d, $J = 9.1$ Hz, 1H), 0.87 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.7, 148.6, 136.7, 131.6, 130.4, 121.2, 116.3, 54.4, 51.9, 47.5, 44.3, 42.1, 41.0, 28.0, 26.4, 23.0, 20.4. Conversion of 17 to alcohol: A solution of borane THF complex (0.4 mL, 1 M in THF) was added to a solution of 16+17 (30 mg) in THF (2 mL) at 0 °C. The ice-water bath was removed after the addition and the reaction mixture was allowed to warm to room temperature and stirred overnight. Water (1 mL) was added followed by the slow addition of 46 mg of solid sodium perborate•4H$_2$O. The resulting mixture was stirred overnight and then 20 mL ether was added. The organic layer was separated and washed with brine then dried over anhydrous Na$_2$SO$_4$. The solvent was removed at reduced pressure and crude product was purified by flash chromatography on silica gel (3:1 pentane/ether eluent) to provide 8.3 mg (29% yield) of an acetal as a colorless oil: R$_f$ 0.36 (2:1 pentane/ether); [α]$_D^{25}$ -51.2° (c 0.25, CH$_3$Cl); FTIR (film) 3386 (br), 2920,
1491, 1070, 1010, 999, 791, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 5.79 (dd, J = 3.2, 2.0 Hz, 1H), 4.47 (dd, J = 8.0, 2.0 Hz, 1H), 3.48 (dd, J = 10.0, 2.0 Hz, 1H), 3.10 (d, J = 10.0, 8.0 Hz, 1H), 2.63 (d, J = 3.2 Hz, 1H), 2.17 (qt, J = 7.7, 2.4 Hz, 1H), 1.80-1.71 (m, 1H), 1.69-1.63 (m, 1H), 1.47-1.42 (m, 1H), 1.15 (d, J = 7.7 Hz, 3H), 1.10 (s, 3H), 0.96 (d, J = 10.2 Hz, 1H), 0.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 131.0, 130.6, 120.1, 101.9, 82.0, 55.2, 45.3, 44.0, 42.2, 41.8, 38.8, 28.6, 27.2, 23.2, 20.8; HRMS (EI) m/z Calcd for [C₁₈H₂₃BrO]⁺: 352.0881. Found: 352.0882. The nOe enhancements are shown bellow:

![nOe](image)

**Kinetic Resolution:** To a stirring and degassed solution of (±)-α-pinene 15 (5 mmol) and Rh₂(S-DOSP)₄ (9.5 mg, 0.005 mmol) in 2,2-dimethylbutane (3 mL) was added a degassed solution of methyl 4-bromophenyldiazoacetate 5 (127.5 mg, 0.5 mmol) in 2,2-dimethylbutane (10 mL) by syringe-pump over 1 h at RT. The reaction mixture was stirred for another 1 h after the addition was complete. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (100:1 pentane/ether eluent) to provide 94.5 mg (52% yield) of a mixture 16+17 (ratio 16:17 = 88:12).

The ee of 16 was determined by reduced to alcohol: Dibal-H (4 equiv.) was added to a solution of 16+17 (6.6 mg) in toluene (2 mL) at 0 °C. The ice-water bath was removed after the addition and the resulting mixture was stirred for 1 h at RT and then 5 mL solution of NH₄Cl was added. Ether (30 mL) was added and the organic layer was separated and washed with brine the dried over anhydrous Na₂SO₄. The solvent was removed at reduced pressure and crude product was purified by flash chromatography on silica gel (8:1 pentane/ether eluent) to provide 1 mg pure product and 5 mg mixture (98% yield). ¹H NMR (500 MHz, CDCl₃): δ 7.44 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H),
5.35 (d, $J = 1.2$ Hz, 1H), 3.99-4.06 (m, 1H), 3.92-3.85 (m, 1H), 2.73 (ddd, $J = 10.4$, 8.2, 4.3 Hz, 1H), 2.50-2.44 (m, 1H), 2.09 (dt, $J = 8.8$, 5.6 Hz, 1H), 1.98-1.94 (m, 1H), 1.71 (s, 3H), 1.57-1.50 (m, 2H), 1.19 (d, $J = 8.8$ Hz, 1H), 1.16 (s, 3H), 1.80 (s, 3H); HPLC analysis: 99% ee (R,R-Whelk-O1, 1.5% i-PrOH in hexane, 1 mL/min, $\lambda = 254$ nm, $t_R = 15.07$ min, major; $t_R = 24.56$ min, minor).

References: