

Supporting Information for:

**The Palladium-Catalyzed Aerobic Kinetic Resolution of Secondary Alcohols: Reaction Development, Scope, and Applications**

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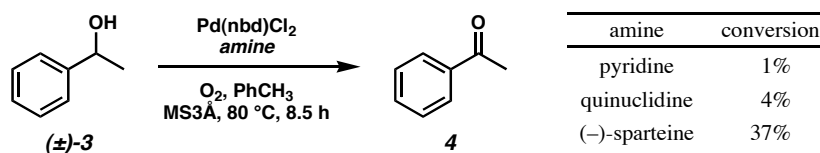
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**Materials and Methods.** Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen atmosphere using dry, deoxygenated solvents. Dichloro(sparteine)palladium(II) [Pd(sparteine)Cl<sub>2</sub>, **5**] was prepared as previously reported.<sup>1</sup> Palladium acetate [Pd(OAc)<sub>2</sub>], dichlorobis(benzonitrile)palladium(II), and dichlorobis(triphenylphosphine)palladium(II) were purchased from Strem Chemicals, Inc., Newburyport, MA. 2-Methoxy- $\alpha$ -methylbenzyl alcohol and 1-(2-furyl)ethanol were purchased from Acros Organics USA, Morris Plains, NJ. Other chemicals were purchased from the Sigma-

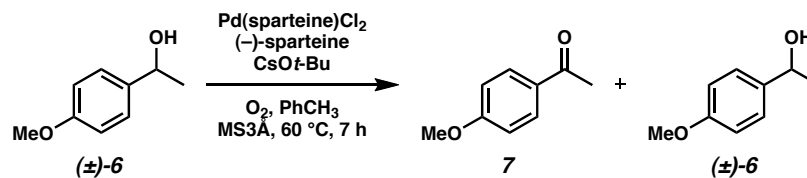
Aldrich Chemical Company, Milwaukee, WI and were used as received. Pyridine and Et<sub>3</sub>N were distilled over CaH<sub>2</sub>. Solvents were dried by passage through an activated alumina column under argon. Powdered 3 Å molecular sieves were stored in a 120 °C drying oven until immediately prior to use. Liquids and solutions were transferred via syringe. Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV at 254 nm, *p*-anisaldehyde, and potassium permanganate staining. ICN silica gel (particle size 32-63 μm) or SiliCycle SiliaFlash P60 Academic silica gel (particle size 40-63 μm; pore diameter 60 Å) was used for flash column chromatography. Bulb-to-bulb distillations were performed with a Büchi Glass Oven B-585 Kugelrohr. Analytical achiral GC was performed on an Agilent 6850 GC with FID detector using an Agilent DB-WAX (30.0 m x 0.25 mm) column at 1.0 mL/min He carrier gas flow. Chiral GC was performed on an Agilent 6850 GC with FID detector using a Chiraldex GTA column (30.0 m x 0.25 mm, purchased from Bodman Industries) at 1.0 mL/min He carrier gas flow. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak AD, Chiralcel OD-H, Chiralcel OJ, Chiralpak AS, or Chiralcel OB-H column (each is 4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm at 1.0 mL/min mobile phase, unless otherwise noted. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 instrument (at 300 MHz) and are reported relative to Me<sub>4</sub>Si (δ 0.0). Data for <sup>1</sup>H NMR spectra are reported in terms of chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 instrument (at 75 MHz) and are reported relative to Me<sub>4</sub>Si (δ 0.0). Data for <sup>13</sup>C NMR spectra are reported in terms of chemical shift (δ ppm) and coupling constant (<sup>19</sup>F, Hz). <sup>19</sup>F NMR spectra were recorded on a Varian Mercury 300

instrument (at 282 MHz) and are reported relative to external  $F_3CCO_2H$  standard ( $\delta -76.53$ ). Data for  $^{19}F$  NMR spectra are reported in terms of chemical shift ( $\delta$  ppm). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm using a 100 mm path-length cell. IR spectra were recorded on a Perkin Elmer Paragon 1000 or Spectrum BX II spectrometer and are reported in terms of frequency of absorption ( $cm^{-1}$ ). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility.

### Screening of Ligands and Additives

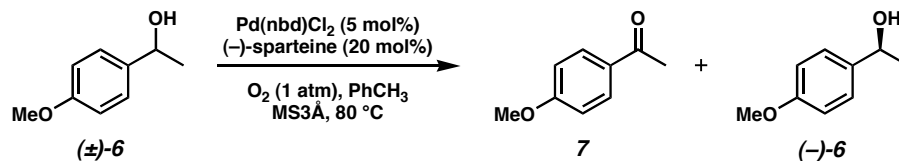


**General Ligand Screening Procedure with Pd(nbd)Cl<sub>2</sub>.** To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling, dichloro(norbornadiene)palladium(II) (Pd(nbd)Cl<sub>2</sub>, 6.7 mg, 0.025 mmol, 0.05 equiv) followed by toluene (2.5 mL) and the amine (0.10 mmol, 0.20 equiv) were added. The reaction tube was cooled to -78 °C, then vacuum evacuated and purged with O<sub>2</sub> (3x). The tube was heated to 80 °C with vigorous stirring under O<sub>2</sub> atmosphere (1 atm, balloon) for 20 min. A solution of (±)-1-phenylethanol ((±)-**3**, 60.5  $\mu$ L, 61.1 mg, 0.50 mmol, 1.0 equiv) and tridecane (36.6  $\mu$ L, 27.7 mg, 0.15 mmol, 0.30 equiv) in toluene (2.5 mL) was added, and the reaction was allowed to proceed under O<sub>2</sub> atmosphere at 80 °C. Aliquots were filtered through a small plug of silica gel (Et<sub>2</sub>O eluent), evaporated, and analyzed by GC for conversion to ketone **4**. Conversions given are the mean of two experiments.



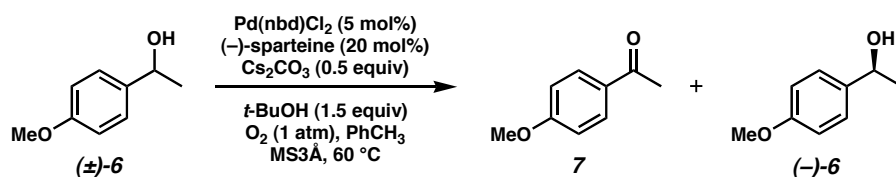
**CsOt-Bu as Additive.** To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling, complex **5** (10.3 mg, 0.025 mmol, 0.05 equiv), followed by toluene (1 mL) and then  $(-)\text{-sparteine}$  (17.2  $\mu\text{L}$ , 17.6 mg, 0.075 mmol, 0.15 equiv) were added. The reaction tube was cooled to  $-78\text{ }^\circ\text{C}$ , then vacuum evacuated and purged with  $\text{O}_2$  (3x). The tube was heated to  $60\text{ }^\circ\text{C}$  with vigorous stirring under  $\text{O}_2$  atmosphere (1 atm, balloon) for 20 min. Finely powdered  $\text{CsOt-Bu}^2$  (41.2 mg, 0.20 mmol, 0.40 equiv) was added, followed by a solution of  $(\pm)\text{-1-(4-methoxyphenyl)ethanol}$  (**(±)-6**, 76.1 mg, 0.50 mmol, 1.0 equiv) and tridecane (36.6  $\mu\text{L}$ , 27.7 mg, 0.15 mmol, 0.30 equiv) in toluene (1 mL). The reaction was allowed to proceed under  $\text{O}_2$  atmosphere at  $60\text{ }^\circ\text{C}$ . After 7 h, an aliquot was filtered through a small plug of silica gel ( $\text{Et}_2\text{O}$  eluent), evaporated, and analyzed by GC for conversion (48.3%, average of two runs) and chiral HPLC for alcohol ee (0.5% ee, average of two runs,  $s = 1.0$ ).

### General Oxidative Kinetic Resolution Conditions

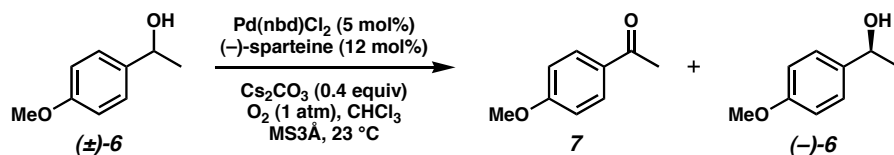


**Kinetic Resolution Conditions A.**<sup>3</sup> To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling,  $\text{Pd(nbd)Cl}_2$  (6.7 mg, 0.025 mmol, 0.05 equiv) followed by toluene (2.5 mL) and then  $(-)\text{-sparteine}$  (23.0  $\mu\text{L}$ , 23.4 mg, 0.10 mmol, 0.20 equiv) were added.<sup>4</sup> The reaction tube was then cooled to  $-78\text{ }^\circ\text{C}$ , then vacuum evacuated and purged

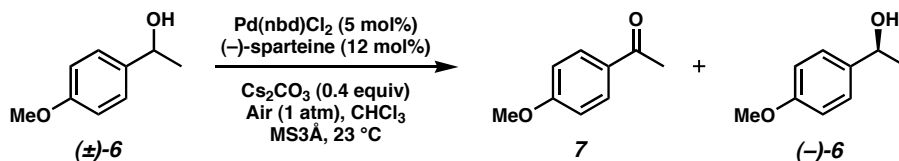
with O<sub>2</sub> (3x). Then, the tube was heated to 80 °C with vigorous stirring under O<sub>2</sub> atmosphere (1 atm, balloon) for 20 min. A solution of (±)-**6** (70.5 μL, 76.1 mg, 0.50 mmol, 1.0 equiv) and tridecane (36.6 μL, 27.7 mg, 0.15 mmol, 0.30 equiv) in toluene (2.5 mL) was added, and the reaction was allowed to proceed under O<sub>2</sub> atmosphere at 80 °C. Aliquots were filtered through a small plug of silica gel (Et<sub>2</sub>O eluent), evaporated, and analyzed by GC for conversion and chiral HPLC for alcohol ee. Purification of 4-methoxyacetophenone (**7**) and (–)-**6** was accomplished by direct chromatography of the crude reaction mixture.



**Kinetic Resolution Conditions B.**<sup>5</sup> To an oven dried reaction tube with stir bar was added 3 Å molecular sieves (500 mg). After cooling, Pd(nbd)Cl<sub>2</sub> (13.5 mg, 0.050 mmol, 0.05 equiv), followed by toluene (2 mL) and then (–)-sparteine (46.0 μL, 46.9 mg, 0.20 mmol, 0.20 equiv) were added.<sup>4</sup> The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O<sub>2</sub> (3x). The tube was heated to 60 °C with vigorous stirring under O<sub>2</sub> atmosphere (1 atm, balloon) for 20 min. Finely powdered Cs<sub>2</sub>CO<sub>3</sub> (163 mg, 0.50 mmol, 0.50 equiv) was added, followed by a solution of (±)-**6** (141 μL, 152 mg, 1.0 mmol, 1.0 equiv), anhydrous *t*-BuOH (143 μL, 111 mg, 1.5 mmol, 1.5 equiv), and tridecane (73.2 μL, 55.3 mg, 0.30 mmol, 0.30 equiv) in toluene (2 mL). The reaction was allowed to proceed under O<sub>2</sub> atmosphere at 60 °C. Aliquots were filtered through a small plug of silica gel (Et<sub>2</sub>O eluent), evaporated, and analyzed by GC for conversion and chiral HPLC for alcohol ee. Purification of **7** and (–)-**6** was accomplished by direct chromatography of the crude reaction mixture.



**Kinetic Resolution Conditions C.**<sup>6</sup> To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, Pd(nbd)Cl<sub>2</sub> (13.5 mg, 0.050 mmol, 0.05 equiv), followed by chloroform (2 mL, ACS reagent grade, stabilized with amylenes) and then (–)-sparteine (27.6 μL, 28.1 mg, 0.12 mmol, 0.12 equiv) were added.<sup>7</sup> The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O<sub>2</sub> (3x). The reaction was allowed to warm to 23 °C and stirred vigorously under O<sub>2</sub> atmosphere (1 atm, balloon) for 15 min. Finely powdered Cs<sub>2</sub>CO<sub>3</sub> (130 mg, 0.40 mmol, 0.40 equiv) was added, followed by a solution of (±)-**6** (141 μL, 152 mg, 1.0 mmol, 1.0 equiv) and tridecane (73.2 μL, 55.3 mg, 0.30 mmol, 0.30 equiv) in chloroform (2 mL). The reaction was allowed to proceed under O<sub>2</sub> atmosphere at 23 °C. Aliquots were filtered through a small plug of silica gel (Et<sub>2</sub>O eluent), evaporated, and analyzed by GC for conversion and chiral HPLC for alcohol ee. Purification of **7** and (–)-**6** was accomplished by direct chromatography of the crude reaction mixture.



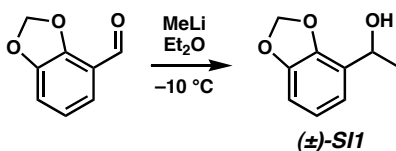
**Kinetic Resolution Conditions D.**<sup>6</sup> To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, Pd(nbd)Cl<sub>2</sub> (13.5 mg, 0.050 mmol, 0.05 equiv), followed by chloroform (2 mL, ACS reagent grade, stabilized with amylenes) and then (–)-sparteine (27.6 μL, 28.1 mg, 0.12 mmol, 0.12 equiv) were added.<sup>7</sup> A short tube containing Drierite was attached to the reaction tube. The reaction was stirred vigorously at 23 °C for 15

min. Finely powdered Cs<sub>2</sub>CO<sub>3</sub> (130 mg, 0.40 mmol, 0.40 equiv) was added, followed by a solution of (±)-**6** (141 μL, 152 mg, 1.0 mmol, 1.0 equiv) and tridecane (73.2 μL, 55.3 mg, 0.30 mmol, 0.30 equiv) in chloroform (2 mL). The reaction was allowed to proceed under an ambient air atmosphere at 23 °C. Aliquots were filtered through a small plug of silica gel (Et<sub>2</sub>O eluent), evaporated, and analyzed by GC for conversion and chiral HPLC for alcohol ee. Purification of **7** and (–)-**6** was accomplished by direct chromatography of the crude reaction mixture.

### **Data for the Synthesis of Alcohols and Ketones**

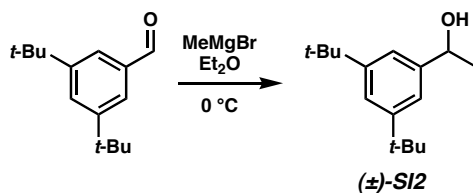
(±)-*N*-Acetyl-3-amino-1-phenylpropan-1-ol (Table 11, entry 9), (±)-*N*-(*tert*-butoxycarbonyl)-3-amino-1-phenylpropan-1-ol ((±)-**32**, Table 11, entry 10), (±)-1-(3-bromophenyl)-3-(2-(2-hydroxypropan-2-yl)phenyl)-1-propanol ((±)-**34**, Table 11, entry 11), (±)-methyl 2-(3-(3-bromophenyl)-3-hydroxypropyl)benzoate (Table 11, entry 12), and (±)-methyl 2-(4-fluorophenyl)-3-hydroxycyclopent-1-enecarboxylate ((±)-**36**, Table 14, entries 4-6) were prepared as previously described.<sup>8</sup> (±)-1-(3-Furyl)ethanol (Table 10, entry 18) was prepared by the method of Zamojski.<sup>9</sup> (±)-1-(2-Furyl)heptan-1-ol (Table 11, entry 13) was prepared by the method of D'Auria.<sup>10</sup> (±)-2-Bromocyclohex-2-enol (Table 12, entries 1-2) and (±)-2-bromocyclopent-2-enol (Table 12, entry 5) were prepared by the method of Murphy.<sup>11</sup> (±)-(*E*)-3-Methyl-4-phenyl-3-buten-2-ol (Table 12, entries 11-13) was prepared by the method of West.<sup>12</sup> (±)-2-Methylcyclopent-2-enol was prepared by the method of Bunnelle.<sup>13</sup> (±)-2-Methylcyclohex-2-enol ((±)-**26**) was prepared by the method of Minehan.<sup>14</sup> The absolute configurations of resolved alcohols were assigned based on comparisons of optical rotations to

literature values or by analogy. Authentic samples of ketones not commercially available were prepared as for **SI3** from the corresponding alcohol, unless otherwise noted.

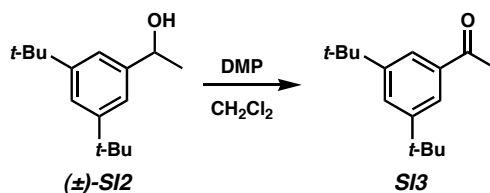


**(±)-1-(Benzo[1,3]dioxol-4-yl)ethanol ((±)-SI1, Table 10, entries 10-11).** A solution of 2,3-(methylenedioxy)benzaldehyde (500 mg, 3.05 mmol, 1.0 equiv) in Et<sub>2</sub>O (30 mL) was cooled to -10 °C. A solution of methyllithium (1.6 M in Et<sub>2</sub>O, 2.48 mL, 3.96 mmol, 1.3 equiv) was added dropwise and the reaction was allowed to warm to 23 °C. The reaction was quenched by addition of crushed ice (10 g) and then sat. NH<sub>4</sub>Cl (aq, 20 mL). The phases were separated, and the aqueous phase was extracted with Et<sub>2</sub>O (2 x 30 mL). The combined organic extracts were washed with H<sub>2</sub>O (20 mL) and brine (20 mL), dried over MgSO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (9:1→4:1 hexanes:EtOAc) to afford (±)-**SI1** as an off-white solid: *R<sub>f</sub>* 0.39 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.76 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.97 (d, *J* = 1.6 Hz, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.00 (q, *J* = 6.5 Hz, 1H), 2.11 (br. s, 1H), 1.53 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.4, 143.9, 127.3, 121.8, 118.7, 107.7, 100.9, 66.2, 23.3; IR (thin film/NaCl): 3369, 1460, 1250, 1044 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>]<sup>+</sup>, 166.0630; found, 166.0630; [α]<sub>D</sub><sup>24</sup> -26.8° (c 1.0, CDCl<sub>3</sub>; for *S* enantiomer at 99% ee).



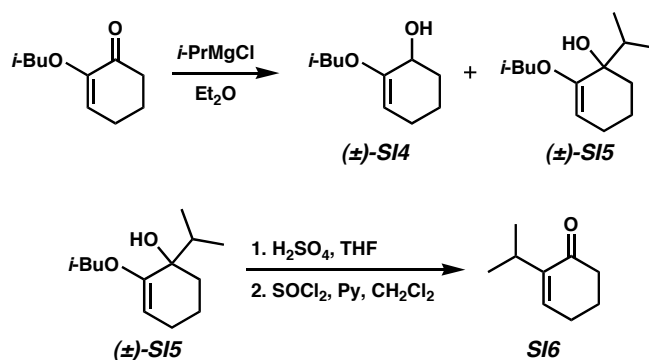


**(±)-1-(3,5-Di-*tert*-butylphenyl)ethanol ((±)-SI2, Table 10, entries 12-14).** A solution of 3,5-di-*tert*-butylbenzaldehyde (1.09 g, 5.0 mmol, 1.0 equiv) in Et<sub>2</sub>O (20 mL) was cooled to 0 °C. A solution of methylmagnesium bromide (3.0 M in Et<sub>2</sub>O, 2.5 mL, 7.5 mmol, 1.5 equiv) was added dropwise. The reaction was then quenched by slow addition of sat. NH<sub>4</sub>Cl (aq, 20 mL) and H<sub>2</sub>O (10 mL). After warming to 23 °C, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and purified by passage through a short plug of silica gel (2:1 hexanes:EtOAc) to afford (±)-SI2 (1.05 g, 90% yield) as a white solid: *R<sub>f</sub>* 0.45 (4:1 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 1.9 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 4.90 (dq, *J* = 6.4, 3.2 Hz, 1H), 1.81 (d, *J* = 3.3 Hz, 1H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.34 (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.0, 145.0, 121.7, 119.6, 71.2, 34.9, 31.5, 25.1; IR (thin film/NaCl): 3335, 2965, 1600, 1363 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>26</sub>O]<sup>+</sup>, 234.1984; found, 234.1989; [α]<sub>D</sub><sup>24</sup> -30.6° (*c* 0.85, CHCl<sub>3</sub>; for *S* enantiomer at 98% ee).



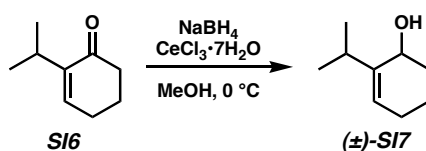
**General Procedure for the Non-Asymmetric Oxidation of Alcohols to Ketones: 3',5'-Di-*tert*-butylacetophenone (SI3).** To a solution of alcohol (±)-SI2 (23.4 mg, 0.10 mmol, 1.0 equiv)

in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) at 23 °C was added Dess-Martin periodinane<sup>15</sup> (84.8 mg, 0.20 mmol, 2.0 equiv). After 1 h, the reaction was complete by TLC. The reaction mixture was diluted with 4:1 hexanes:EtOAc (2 mL) and allowed to stir vigorously 20 min to precipitate white solid. Filtration through a short plug of silica gel (4:1 hexanes:EtOAc) afforded ketone **SI3** (22.9 mg, 99% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>16</sup>



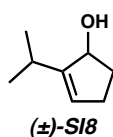
**(±)-2-Isobutoxycyclohex-2-enol ((±)-SI4, Table 12, entry 4) and 2-Isopropylcyclohex-2-enone (SI6).** To a solution of isopropylmagnesium chloride (2.0 M in Et<sub>2</sub>O, 35.7 mL, 71.3 mmol, 2.0 equiv) in Et<sub>2</sub>O (95 mL) was added a solution of 2-isobutoxycyclohex-2-enone<sup>17</sup> (6.0 g, 35.7 mmol, 1.0 equiv) in Et<sub>2</sub>O (29 mL) over 5-10 min, such that a gentle reflux was maintained. The reaction was allowed to stir for 45 min, after which it was poured slowly into a mixture of sat. NH<sub>4</sub>Cl (aq, 50 mL), H<sub>2</sub>O (50 mL), and crushed ice (50 g). After the ice melted, the phases were separated. The aqueous phase was extracted with Et<sub>2</sub>O (3 x 100 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered, and the filtrate was concentrated under reduced pressure. Purification by flash chromatography (194:5:1 hexanes:EtOAc:Et<sub>3</sub>N) afforded 2-isobutoxy-1-isopropylcyclohex-2-enol ((±)-**SI5**, 1.72 g, 23% yield) as a colorless oil, which was carried on to the next step, and 2-isobutoxycyclohex-2-enol ((±)-**SI4**, 2.45 g, 40% yield) as a colorless oil. The characterization data for (±)-**SI4** matched the data in the literature.<sup>18</sup> To a

solution of ( $\pm$ )-**SI5** (1.13 g, 5.33 mmol, 1.0 equiv) in THF (53 mL) was added conc. H<sub>2</sub>SO<sub>4</sub> (400  $\mu$ L). After 30 min, the reaction was quenched by slow addition of sat. NaHCO<sub>3</sub> (aq, 40 mL). The mixture was allowed to stir 20 min (until bubbling ceased) and then was extracted with Et<sub>2</sub>O (3 x 40 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure. To this crude  $\alpha$ -hydroxyketone in CH<sub>2</sub>Cl<sub>2</sub> (53 mL) was added pyridine (2.15 mL, 2.11 g, 26.6 mmol, 5.0 equiv) and SOCl<sub>2</sub> (777  $\mu$ L, 1.27 g, 10.7 mmol, 2.0 equiv). The reaction was allowed to stir at 23 °C for 7 h, after which it was quenched by addition of 1 N HCl (aq, 40 mL) and allowed to stir a further 10 min. The phases were separated, and the aqueous phase was extracted with Et<sub>2</sub>O (3 x 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered. Concentration of the filtrate under reduced pressure followed by flash chromatography (49:1 hexanes:EtOAc) and bulb-to-bulb distillation (25 torr, 160-164 °C) afforded 2-isopropylcyclohex-2-enone (**SI6**, 412 mg, 56% yield from ( $\pm$ )-**SI5**) as a slightly yellow oil. The characterization data for **SI6** matched the data in the literature.<sup>19</sup>

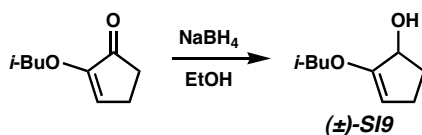


**General Procedure for the Reduction of Enones: ( $\pm$ )-2-Isopropylcyclohex-2-enol (( $\pm$ )-**SI7**, Table 12, entry 3).<sup>20</sup>** To a solution of enone **SI6** (783 mg, 5.66 mmol, 1.0 equiv) in MeOH (57 mL) at 0 °C was added CeCl<sub>3</sub>•7H<sub>2</sub>O (2.32 g, 6.23 mmol, 1.1 equiv). After allowing the solid to dissolve, NaBH<sub>4</sub> (643 mg, 17.0 mmol, 3.0 equiv) was added in small portions over 5 min. After allowing the reaction mixture to warm to room temperature, the solvent was removed under reduced pressure. H<sub>2</sub>O (50 mL) was added, and the slurry was stirred vigorously for 20 min.

The mixture was then extracted with EtOAc (4 x 60 mL). The combined organic layers were dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated and purified by flash chromatography (37:3 hexanes:EtOAc) to afford (±)-**SI7** (356 mg, 45% yield) as a colorless oil: *R<sub>f</sub>* 0.40 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.56 (t, *J* = 3.9 Hz, 1H), 4.15 (t, *J* = 3.6 Hz, 1H), 2.52-2.35 (m, 1H), 2.14-1.88 (comp. m, 2H), 1.85-1.50 (comp. m, 4H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.3, 122.7, 66.0, 32.5, 31.4, 25.5, 23.0, 21.7, 17.8; IR (thin film/NaCl): 3340, 2936, 1461, 1382, 982 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>9</sub>H<sub>16</sub>O]<sup>+</sup>, 140.1201; found, 140.1198; [α]<sub>D</sub><sup>25</sup> -24.6° (*c* 1.8, CHCl<sub>3</sub>; for *S* enantiomer at 96% ee).

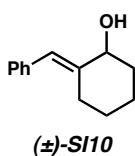


**(±)-2-Isopropylcyclopent-2-enol ((±)-SI8, Table 12, entry 6).** Prepared as for (±)-**SI7** from 2-isopropylcyclopent-2-enone<sup>21</sup> (2.48 g, 20.0 mmol) to afford, after flash chromatography (94:5:1 hexanes:EtOAc:Et<sub>3</sub>N), (±)-**SI8** (1.08 g, 43% yield) as a slightly yellow oil. The characterization data matched the data in the literature.<sup>22</sup> [α]<sub>D</sub><sup>24</sup> -27.5° (*c* 0.48, CHCl<sub>3</sub>; for *S* enantiomer at 92% ee).

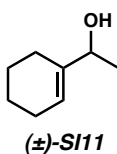


**(±)-2-Isobutoxycyclopent-2-enol ((±)-SI9, Table 12, entries 7-8).** To a solution of 2-isobutoxycyclopent-2-enone<sup>21</sup> (1.54 g, 10.0 mmol, 1.0 equiv) in EtOH (absolute, 100 mL) was added NaBH<sub>4</sub> (1.14 g, 30.0 mmol, 3.0 equiv). After 2.5 h at 23 °C, the solvent was removed

under reduced pressure and H<sub>2</sub>O (100 mL) was added. After stirring for 30 min, this mixture was extracted with EtOAc (3 x 100 mL). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (96:3:1 hexanes:EtOAc:Et<sub>3</sub>N) to afford (±)-**SI9** (688 mg, 44% yield) as a colorless oil: *R<sub>f</sub>* 0.46 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.70-4.62 (m, 1H), 4.59 (t, *J* = 2.4 Hz, 1H), 3.57-3.47 (comp. m, 2H), 2.45-2.14 (comp. m, 3H), 2.08-1.93 (m, 1H), 1.79-1.68 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.9, 96.9, 76.2, 74.8, 31.2, 28.2, 26.0, 19.5, 19.4; IR (thin film/NaCl): 3392, 2958, 2909, 2871, 1648, 1055 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>]<sup>+</sup>, 156.1150; found, 156.1152.

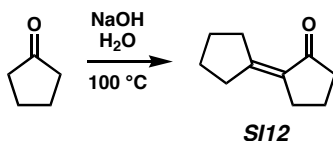


(±)-(*E*)-2-Benzylidenecyclohexanol ((±)-**SI10**, Table 12, entries 9-10). Prepared as for (±)-**SI7** from (*E*)-2-benzylidenecyclohexanone<sup>23</sup> (5.03 g, 27.0 mmol) to afford, after flash chromatography (9:1→17:3→4:1 hexanes:EtOAc), (±)-**SI10** (4.13 g, 81% yield) as a white solid. The characterization data matched the data in the literature.<sup>24</sup> [α]<sub>D</sub><sup>25</sup> -36.0° (*c* 1.2, CHCl<sub>3</sub>; for *S* enantiomer at 96% ee) [lit.<sup>25</sup> [α]<sub>D</sub><sup>20</sup> -35.2° (*c* 1.2, CHCl<sub>3</sub>; *S* enantiomer)].

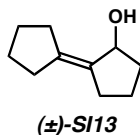


(±)-1-Cyclohexenyl-1-ethanol ((±)-**SI11**, Table 12, entries 14-15). Prepared as for (±)-**SI7** from 1-acetyl-1-cyclohexene (3.45 g, 27.8 mmol) to afford, after distillation (22 torr, 86-88 °C)

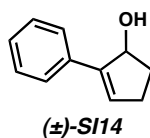
(±)-**SI11** (2.69 g, 77% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>26</sup>  $[\alpha]_D^{25} -12.1^\circ$  (*c* 0.75, CHCl<sub>3</sub>; for *S* enantiomer at 91% ee) [lit.<sup>27</sup>  $[\alpha]_D -11.2^\circ$  (*c* 0.36, CHCl<sub>3</sub>; *S* enantiomer)].



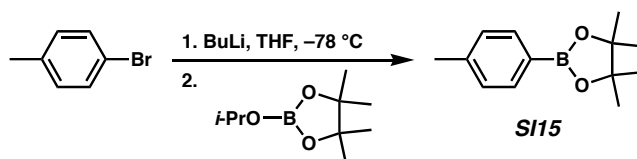
**2-Cyclopentylidenecyclopentanone (SI12).** Cyclopentanone (10.0 mL, 9.51 g, 113 mmol, 2.0 equiv) was added to 1 N NaOH (aq, 113 mL). The mixture was heated to reflux for 7 h, then cooled to 23 °C and saturated with NaCl (s). After the NaCl dissolved, the mixture was extracted with Et<sub>2</sub>O (3 x 100 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure. Distillation (30 torr, 140-142 °C) afforded **SI12** (5.92 g, 70% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>28</sup>



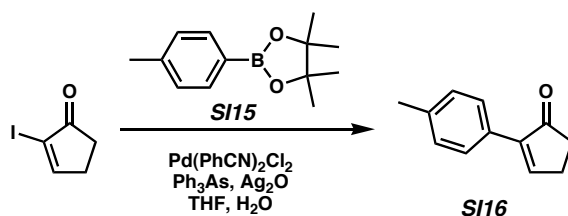
**(±)-2-Cyclopentylidenecyclopentanol ((±)-SI13, Table 12, entry 16).** Prepared as for (±)-**SI7** from **SI12** (1.10 g, 7.32 mmol) to afford, after flash chromatography (9:1 hexanes:EtOAc), (±)-**SI13** (881 mg, 79% yield) as a white solid. The characterization data matched the data in the literature.<sup>29</sup>  $[\alpha]_D^{26} +85.3^\circ$  (*c* 0.99, CHCl<sub>3</sub>; for *S* enantiomer at 94% ee).



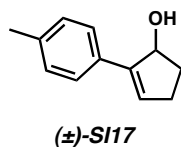
**(±)-2-Phenylcyclopent-2-enol ((±)-SI14, Table 13, entries 1-3).** Prepared as for (±)-SI7 from 2-phenylcyclopent-2-enone<sup>30,31</sup> (218 mg, 1.38 mmol) to afford, after flash chromatography (9:1→4:1→7:3 hexanes:EtOAc), **SI14** (196 mg, 89% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>



**General Procedure for the Preparation of Boronate Esters: 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (SI15).**<sup>33</sup> A solution of 4-bromotoluene (1.23 mL, 1.71 g, 10.0 mmol, 1 equiv) in THF (67 mL) was cooled to  $-78\text{ }^{\circ}\text{C}$ . A solution of *n*-butyllithium (2.5 M in hexanes, 4.40 mL, 11.0 mmol, 1.1 equiv) was added dropwise. After stirring 10 min at  $-78\text{ }^{\circ}\text{C}$ , 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.65 mL, 2.42 g, 13.0 mmol, 1.3 equiv) was added dropwise. After 10 min, the reaction was quenched at  $-78\text{ }^{\circ}\text{C}$  with sat.  $\text{NH}_4\text{Cl}$  (aq, 35 mL) and  $\text{H}_2\text{O}$  (10 mL). After warming to  $23\text{ }^{\circ}\text{C}$ , the biphasic mixture was extracted with  $\text{Et}_2\text{O}$  (3 x 60 mL). The combined organic extracts were washed with brine (30 mL), dried over  $\text{MgSO}_4$ , and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3:1 hexanes:EtOAc: $\text{Et}_3\text{N}$ ) to afford **SI15** (2.17 g, 99% yield) as a slightly yellow oil, which solidified on standing. The characterization data matched the data in the literature.<sup>34</sup>

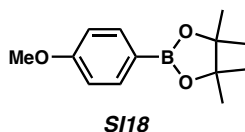


**General Procedure for the Arylation of 2-Iodoenones: 2-(4-Tolyl)cyclopent-2-enone (SI16).**<sup>30</sup> 2-Iodocyclopent-2-enone<sup>35</sup> (1.46 g, 7.0 mmol, 1.0 equiv), boronic ester **SI15** (1.83 g, 8.4 mmol, 1.2 equiv), Ag<sub>2</sub>O (2.60 g, 11.2 mmol, 1.6 equiv), Ph<sub>3</sub>As (129 mg, 0.42 mmol, 0.06 equiv), and dichlorobis(benzonitrile)palladium(II) (81 mg, 0.21 mmol, 0.03 equiv) were added to a solution of THF (18 mL) and H<sub>2</sub>O (2.3 mL). A vigorous exothermic reaction occurred. Once the reaction was complete as determined by TLC, it was filtered through Celite (140 mL EtOAc eluent). The filtrate was concentrated under reduced pressure and purified by flash chromatography (9:1 hexanes:EtOAc) to afford enone **SI16** (1.12 g, 93% yield) as a white solid. The characterization data matched the data in the literature.<sup>36</sup>

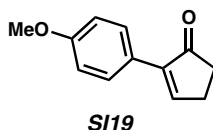


**(±)-2-(4-Tolyl)cyclopent-2-enol ((±)-SI17, Table 13, entries 4-6).** Prepared as for (±)-**SI7** from **SI16** (1.07 g, 6.18 mmol) to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), (±)-**SI17** (827 mg, 77% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>

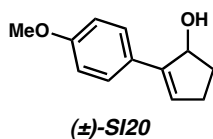




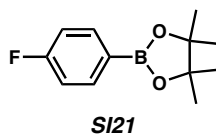
**4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (SI18).** Prepared as for **SI15** to afford, after flash chromatography (79:20:1 hexanes:EtOAc:Et<sub>3</sub>N), **SI18** (2.25 g, 80% yield) as a slightly yellow oil. The characterization data matched the data in the literature.<sup>34</sup>



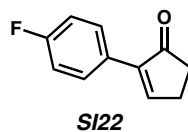
**2-(4-Methoxyphenyl)cyclopent-2-enone (SI19).** Prepared as for **SI16** from **SI18** to afford, after flash chromatography (4:1 hexanes:EtOAc), **SI19** (1.05 g, 93%) as a white solid. The characterization data matched the data in the literature.<sup>36</sup>



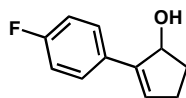
**(±)-2-(4-Methoxyphenyl)cyclopent-2-enol ((±)-SI20, Table 13, entries 7-9).** Prepared as for **(±)-SI7** from **SI19** (840 mg, 4.46 mmol) to afford, after flash chromatography (9:1→4:1→3:1 hexanes:EtOAc), **(±)-SI20** (685 mg, 81% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>



**4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)fluorobenzene (SI21).** Prepared as for **SI15** to afford, after flash chromatography (17:3:1 hexanes:EtOAc:Et<sub>3</sub>N), **SI21** (2.24 g, 84% yield) as a colorless oil: *R<sub>f</sub>* 0.49 (4:1 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93 (m, 2H), 6.78 (m, 2H), 1.05 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.6 (d, *J* = 250.2 Hz), 137.6 (d, *J* = 8.2 Hz), 115.2 (d, *J* = 20.2 Hz), 83.8, 24.9; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -108.4; IR (thin film/NaCl): 2979, 1603, 1400, 1362, 1144, 1088 cm<sup>-1</sup>; HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>16</sub>BFO<sub>2</sub>]<sup>+</sup>, 222.1227; found, 222.1236.

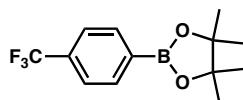


**2-(4-Fluorophenyl)cyclopent-2-enone (SI22).** Prepared as for **SI16** from **SI21** to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), **SI22** (1.03 g, 90% yield) as a white solid: *R<sub>f</sub>* 0.30 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (t, *J* = 2.9 Hz, 1H), 7.73-7.65 (m, 2H), 7.11-7.02 (m, 2H), 2.75-2.66 (m, 2H), 2.63-2.55 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.0 (d, *J* = 247.8 Hz), 158.8 (d, *J* = 1.4 Hz), 142.6, 129.1 (d, *J* = 8.0 Hz), 128.0 (d, *J* = 3.2 Hz), 115.6 (d, *J* = 21.4 Hz), 35.9, 26.4; <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -114.1; IR (thin film/NaCl): 1701, 1507, 1224, 834 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>9</sub>FO]<sup>+</sup>, 176.0637; found, 176.0631.



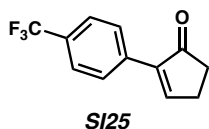
**(±)-SI23**

**(±)-2-(4-Fluorophenyl)cyclopent-2-enol ((±)-SI23, Table 13, entries 10-12).** Prepared as for (±)-SI7 from SI22 (933 mg, 5.29 mmol) to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), (±)-SI23 (792 mg, 84% yield) as a white solid:  $R_f$  0.31 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.50 (m, 2H), 7.07-6.98 (m, 2H), 6.24 (t,  $J = 2.5$  Hz, 1H), 5.20 (m, 1H), 2.73-2.59 (m, 1H), 2.50-2.34 (comp. m, 2H), 2.01-1.88 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4 (d,  $J = 246.6$  Hz), 143.7, 131.3 (d,  $J = 3.1$  Hz), 129.9 (d,  $J = 1.8$  Hz), 128.0 (d,  $J = 8.0$  Hz), 115.6 (d,  $J = 21.5$  Hz), 77.6, 34.4, 30.6;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.8; IR (thin film/NaCl): 3218, 1510, 1237, 1050, 834  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_{11}\text{H}_{11}\text{FO}]^+$ , 178.0794; found, 178.0786;  $[\alpha]_D^{25} +12.8^\circ$  (c 2.2,  $\text{CHCl}_3$ ; for *S* enantiomer at >99% ee).

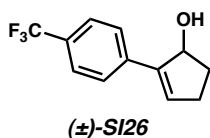


**SI24**

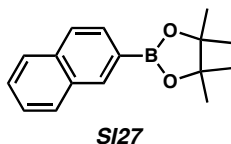
**4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride (SI24).** Prepared as for SI15 to afford, after flash chromatography (17:3:1 hexanes:EtOAc:Et<sub>3</sub>N), SI24 (3.13 g, 96% yield) as an off-white solid. The characterization data matched the data in the literature.<sup>37</sup>



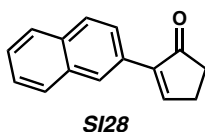
**2-(4-Trifluoromethylphenyl)cyclopent-2-enone (SI25).** Prepared as for **SI16** from **SI24** to afford, after flash chromatography (9:1 hexanes:EtOAc), **SI25** (1.14 g, 84% yield) as a white solid:  $R_f$  0.37 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (t,  $J = 2.9$  Hz, 1H), 7.81 (d,  $J = 8.0$  Hz, 2H), 7.62 (d,  $J = 7.9$  Hz, 2H), 2.79-2.72 (m, 2H), 2.66-2.60 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  207.0, 160.5, 142.4, 135.1, 130.2 (q,  $J = 32.5$  Hz), 127.3, 125.3 (q,  $J = 3.8$  Hz), 124.1 (q,  $J = 272.1$  Hz), 35.7, 26.4;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.7; IR (thin film/NaCl): 3066, 1692, 1332, 1112, 847  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_{12}\text{H}_9\text{F}_3\text{O}]^+$ , 226.0606; found, 226.0608.



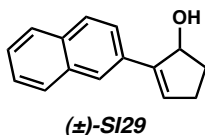
**(±)-2-(4-Trifluoromethylphenyl)cyclopent-2-enol ((±)-SI26, Table 13, entries 13-15).** Prepared as for **(±)-SI7** from **SI25** (1.14 g, 5.00 mmol) to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), **(±)-SI26** (887 mg, 77% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>



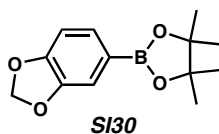
**2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (SI27).** Prepared as for **SI15** to afford, after flash chromatography (17:3:1 hexanes:EtOAc:Et<sub>3</sub>N), **SI27** (2.87 g, 94% yield) as an off-white solid. The characterization data matched the data in the literature.<sup>34</sup>



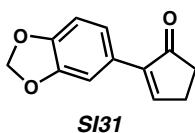
**2-(2-Naphthyl)cyclopent-2-enone (SI28).** Prepared as for **SI16** from **SI27** to afford, after flash chromatography (9:1 hexanes:EtOAc), **SI28** (180 mg, 86% yield) as an off-white solid: *R<sub>f</sub>* 0.33 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.96 (t, *J* = 3.0 Hz, 1H), 7.93-7.78 (comp. m, 3H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.52-7.44 (comp. m, 2H), 2.80-2.73 (m, 2H), 2.69-2.63 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 208.0, 159.4, 143.3, 133.5, 133.4, 129.2, 128.8, 128.3, 127.8, 126.6, 126.5, 126.4, 125.0, 36.2, 26.5; IR (thin film/NaCl): 1690, 1311, 748, 475 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>12</sub>O]<sup>+</sup>, 208.0888; found, 208.0889.



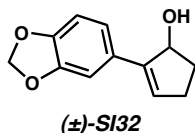
**(±)-2-(2-Naphthyl)cyclopent-2-enol ((±)-SI29, Table 13, entries 16-18).** Prepared as for (±)-**SI7** from **SI28** (1.90 g, 9.14 mmol) to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), (±)-**SI29** (1.67 g, 87% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>



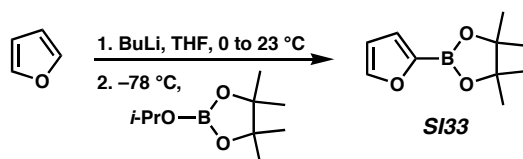
**5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzodioxole (SI30).** Prepared as for **SI15** to afford, after flash chromatography (17:3:1 hexanes:EtOAc:Et<sub>3</sub>N), **SI30** (2.43 g, 99% yield) as an off-white solid. The characterization data matched the data in the literature.<sup>38</sup>



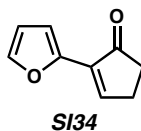
**2-(Benzo[1,3]dioxol-5-yl)cyclopent-2-enone (SI31).** Prepared as for **SI16** from **SI30** to afford, after flash chromatography (17:3→4:1→7:3 hexanes:EtOAc), **SI31** (1.37 g, 90% yield) as a white solid: *R<sub>f</sub>* 0.30 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.71 (t, *J* = 2.9 Hz, 1H), 7.27-7.19 (comp. m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 2H), 2.71-2.65 (m, 2H), 2.61-2.55 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 207.8, 157.8, 147.8, 143.0, 125.8, 121.1, 108.5, 107.6, 101.2, 36.0, 26.2; IR (thin film/NaCl): 1695, 1488, 1240, 1035, 806 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>]<sup>+</sup>, 202.0630; found, 202.0623.



**(±)-2-(Benzo[1,3]dioxol-5-yl)cyclopent-2-enol ((±)-SI32, Table 13, entries 19-21).** Prepared as for (±)-**SI17** from **SI31** (1.21 g, 6.00 mmol) to afford, after flash chromatography (9:1→17:3→4:1 hexanes:EtOAc), (±)-**SI32** (1.03 g, 84% yield) as a white solid. Characterization data have been previously reported.<sup>32</sup>

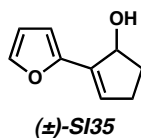


**2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)furan (SI33).** A solution of furan (1.75 mL, 1.63 g, 24.0 mmol, 1.2 equiv) in THF (120 mL) was cooled to 0 °C. A solution of *n*-butyllithium (2.26 M in hexanes, 8.84 mL, 20.0 mmol, 1.0 equiv) was added dropwise. The reaction was allowed to stir 30 min at 0 °C and 30 min at 23 °C, after which it was cooled to –78 °C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.36 mL, 5.81 g, 31.2 mmol, 1.3 equiv) was added dropwise. After stirring 10 min, the reaction was allowed to warm to 23 °C and was quenched by addition of sat. NH<sub>4</sub>Cl (aq, 50 mL) and H<sub>2</sub>O (10 mL). The mixture was extracted with Et<sub>2</sub>O (3 x 100 mL). The combined organic layers were dried over MgSO<sub>4</sub> and filtered, and the filtrate was concentrated under reduced pressure. Bulb-to-bulb distillation (0.1 torr, 90-95 °C) afforded **SI33** (3.17 g, 82% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>39</sup>

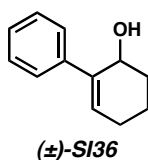


**2-(2-Furyl)cyclopent-2-en-1-one (SI34).** Prepared as for **SI16** from **SI33** to afford, after flash chromatography (19:1→17:3 hexanes:EtOAc), **SI34** (1.09 g, 55% yield) as an off-white solid: *R<sub>f</sub>* 0.51 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.79 (t, *J* = 3.1 Hz, 1H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.04 (d, *J* = 3.5 Hz, 1H), 6.44 (dd, *J* = 3.5, 1.7 Hz, 1H), 2.77-2.71 (m, 2H), 2.56-2.51 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 205.8, 154.2, 147.1, 142.5, 134.9, 111.6, 109.4,

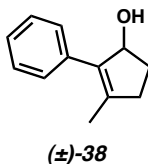
35.5, 26.9; IR (thin film/NaCl): 1706, 1326, 1132, 747  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_9\text{H}_8\text{O}_2]^+$ , 148.0524; found, 148.0521.



**(±)-2-(2-Furyl)cyclopent-2-enol ((±)-SI35, Table 13, entries 22-24).** Prepared as for (±)-SI7 from SI34 (961 mg, 6.49 mmol) to afford, after flash chromatography (19:1→9:1→4:1 hexanes:EtOAc), (±)-SI35 (793 mg, 81% yield) as an off-white solid. Characterization data have been previously reported.<sup>32</sup>



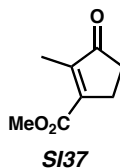
**(±)-2-Phenylcyclohex-2-enol ((±)-SI36, Table 13, entries 25-27).** Prepared as for (±)-SI7 from 2-phenylcyclohex-2-enone<sup>30</sup> (2.70 g, 15.7 mmol) to afford, after filtration through a short plug of silica gel (1:1 hexanes:EtOAc), (±)-SI36 (2.22 g, 81% yield) as an off-white solid. The characterization data matched the data in the literature.<sup>32,40</sup>



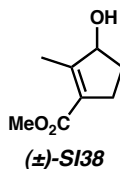
**(±)-2-Phenyl-3-methylcyclopent-2-enol ((±)-38, Table 14, entries 1-3).** Prepared as for (±)-SI7 from 2-phenyl-3-methylcyclopent-2-enone<sup>41</sup> (3.82 g, 22.2 mmol) to afford, after flash chromatography (9:1→4:1 hexanes:EtOAc), (±)-38 (3.25 g, 84% yield) as a slightly yellow oil,



which solidified to a white solid on standing. Characterization data have been previously reported.<sup>32</sup>

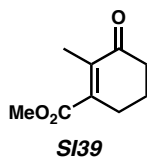


**Methyl 2-methyl-3-oxocyclopent-1-enecarboxylate (SI37).** Prepared according to the procedure of Kuethe:<sup>42</sup>  $R_f$  0.26 (4:1 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.90 (s, 3H), 2.84-2.76 (m, 2H), 2.55-2.48 (m, 2H), 2.09 (t,  $J = 2.2$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  209.9, 166.1, 154.4, 147.7, 52.3, 34.1, 26.6, 10.0; IR (thin film/ $\text{NaCl}$ ): 1713, 1438, 1226, 1076  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_8\text{H}_{10}\text{O}_3]^+$ , 154.0630; found, 154.0626.

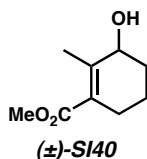


**(±)-Methyl 3-hydroxy-2-methylcyclopent-1-enecarboxylate ((±)-SI38, Table 14, entries 7-9).**

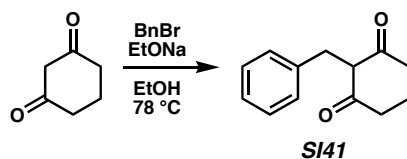
Prepared as for (±)-**SI7** from **SI37** (2.35 g, 15.2 mmol) to afford, after flash chromatography (7:3 hexanes:EtOAc), (±)-**SI38** (2.06 g, 87% yield) as a colorless oil:  $R_f$  0.10 (4:1 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.66 (t,  $J = 6.9$  Hz, 1H), 3.75 (s, 3H), 2.75-2.62 (m, 1H), 2.53-2.25 (comp. m, 2H), 2.13 (s, 3H), 1.71-1.59 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 155.2, 128.9, 81.2, 51.4, 32.2, 30.4, 36.9, 13.5; IR (thin film/ $\text{NaCl}$ ): 3419, 2951, 1715, 1436, 1220, 1054  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_8\text{H}_{12}\text{O}_3]^+$ , 156.0787; found, 156.0780;  $[\alpha]_D^{25}$   $-57.0^\circ$  ( $c$  0.82,  $\text{CHCl}_3$ ; for *S* enantiomer at >99% ee).



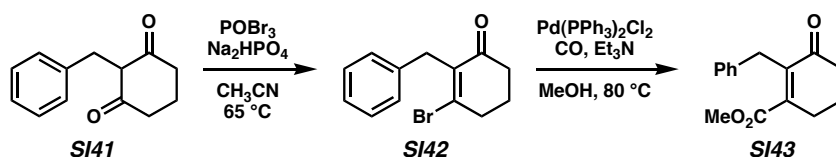
**Methyl 2-methyl-3-oxocyclohex-1-enecarboxylate (SI39).** Prepared according to the procedure of Kuethe:<sup>42</sup>  $R_f$  0.24 (4:1 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (s, 3H), 2.61-2.53 (m, 2H), 2.51-2.44 (m, 2H), 2.07-1.97 (m, 2H), 1.94 (t,  $J = 2.1$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.6, 169.0, 144.4, 137.4, 52.2, 38.0, 27.5, 22.4, 12.8; IR (thin film/NaCl): 2954, 1727, 1682, 1435, 1232, 1052  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_9\text{H}_{12}\text{O}_3]^+$ , 168.0787; found, 168.0786.



**(±)-Methyl 3-hydroxy-2-methylcyclohex-1-enecarboxylate ((±)-SI40, Table 14, entries 10-12).** Prepared as for (±)-SI7 from SI39 (4.66 g, 27.7 mmol) to afford, after filtration through a short plug of silica gel (1:1 hexanes:EtOAc), (±)-SI40 (4.71 g, 99% yield) as a colorless oil:  $R_f$  0.12 (4:1 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  4.06 (t,  $J = 4.5$  Hz, 1H), 3.74 (s, 3H), 2.41-2.12 (comp. m, 2H), 2.07 (t,  $J = 2.1$  Hz, 3H), 1.82-1.60 (comp. m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 144.0, 127.8, 69.8, 51.6, 31.6, 27.0, 18.7, 18.1; IR (thin film/NaCl): 3424, 2945, 1718, 1435, 1215, 1061  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_9\text{H}_{14}\text{O}_3]^+$ , 170.0943; found, 170.0938;  $[\alpha]_D^{25} -72.3^\circ$  ( $c$  0.95,  $\text{CHCl}_3$ ; for  $S$  enantiomer at 97% ee).

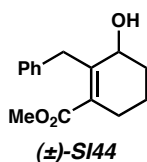


**2-Benzylcyclohexane-1,3-dione (SI41).** Prepared by modification of a procedure from Hewett.<sup>43</sup> Na (3.45 g, 150 mmol, 1.5 equiv) was added to EtOH (absolute, 200 mL). After all of the metal dissolved, cyclohexane-1,3-dione (11.2 g, 100 mmol, 1.0 equiv) was added, followed by benzyl bromide (23.8 mL, 34.2 g, 200 mmol, 2.0 equiv). The reaction was heated to reflux for 13 h. After cooling to 23 °C, the volatiles were removed under reduced pressure. Et<sub>2</sub>O (100 mL) was added, and the mixture was extracted with 1 N NaOH (2 x 100 mL). The combined aqueous extracts were cooled to 0 °C and acidified to pH 1.5 by dropwise addition of conc. H<sub>2</sub>SO<sub>4</sub>. After addition of brine (50 mL), the mixture was allowed to stand at 0 °C for 5 min. The solid was filtered to afford **SI41** (6.51 g, 32% yield) as a tan solid. The characterization data matched the data in the literature.<sup>44</sup>



**Methyl 2-benzyl-3-oxocyclohex-1-enecarboxylate (SI43).** Prepared according to the procedure of Kueth.<sup>42</sup> To a mixture of **SI41** (2.02 g, 10.0 mmol, 1.0 equiv) and Na<sub>2</sub>HPO<sub>4</sub> (710 mg, 5.0 mmol, 0.5 equiv) in CH<sub>3</sub>CN (15 mL) was added a solution of POBr<sub>3</sub> (2.15 g, 7.5 mmol, 0.75 equiv) in CH<sub>3</sub>CN (5 mL). The reaction was heated to 65 °C for 24 h. After cooling to 23 °C, H<sub>2</sub>O (6 mL) was added slowly to quench the reaction. After evaporation of CH<sub>3</sub>CN under reduced pressure, H<sub>2</sub>O (40 mL) and brine (20 mL) were added. The mixture was extracted with EtOAc (4 x 50 mL). The combined organic extracts were dried over MgSO<sub>4</sub> and filtered. The

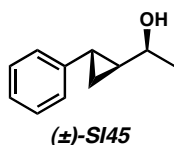
filtrate was concentrated under reduced pressure and purified by flash chromatography (9:1→17:3 hexanes:Et<sub>2</sub>O) to afford 2-benzyl-3-bromocyclohex-2-enone (**SI42**). To a solution of this bromide in MeOH (12.5 mL) was added dichlorobis(triphenylphosphine)palladium(II) (132 mg, 0.19 mmol, 0.03 equiv) followed by Et<sub>3</sub>N (1.75 mL, 1.27 g, 12.5 mmol, 2.0 equiv) in a steel bomb. The reaction was pressurized with carbon monoxide (100 psi) and heated to 80 °C behind a blast shield for 21 h. After cooling to 23 °C and venting the carbon monoxide, the reaction was diluted with Et<sub>2</sub>O (70 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:Et<sub>2</sub>O) to afford **SI43** (1.42 g, 58% yield from **SI41**) of an off-white solid: *R*<sub>f</sub> 0.45 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.25-7.10 (comp. m, 5H), 3.81 (br. s, 2H), 3.78 (s, 3H), 2.63 (t, *J* = 6.0 Hz, 2H), 2.47 (app. t, *J* = 6.7 Hz, 2H), 2.04 (tt, *J* = 6.7, 6.1 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 198.7, 168.7, 145.6, 139.4, 129.6, 128.7, 128.2, 126.0, 52.2, 38.0, 31.9, 27.7, 22.0; IR (thin film/NaCl): 2951, 1726, 1681, 1255, 1238 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [*M*]<sup>+</sup> calcd for [C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>]<sup>+</sup>, 244.1100; found, 244.1100.



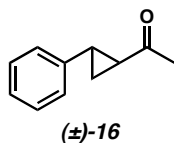
**(±)-Methyl 3-hydroxy-2-benzylcyclohex-1-enecarboxylate ((±)-SI44, Table 14, entry 13).**

Prepared as for (±)-**SI7** from **SI43** (2.02 g, 8.3 mmol) to afford, after flash chromatography (3:2 hexanes:Et<sub>2</sub>O), (±)-**SI44** (1.42 g, 70% yield) as a colorless oil: *R*<sub>f</sub> 0.29 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33-7.17 (comp. m, 5H), 4.03 (br. s, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.75 (s, 3H), 3.69 (dt, *J* = 14.4, 2.0 Hz, 1H), 2.50-2.38 (m, 1H), 2.34-2.20 (m, 1H), 1.81-1.57 (comp. m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 169.8, 143.9, 139.4, 129.7, 128.9, 128.5, 126.2,

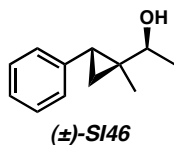
66.2, 51.7, 36.9, 31.2, 27.1, 17.5; IR (thin film/NaCl): 3412, 2943, 1715, 1234  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}]^+$  calcd for  $[\text{C}_{15}\text{H}_{18}\text{O}_3]^+$ , 246.1256; found, 246.1251;  $[\alpha]_D^{24}$   $-226.3^\circ$  ( $c$  1.83,  $\text{CHCl}_3$ ; for  $S$  enantiomer at 96% ee).



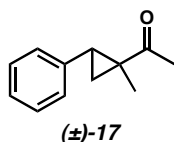
**(±)-*syn,trans*-1-(2-Phenylcyclopropyl)ethanol ((±)-SI45, Table 15, entries 4-6).** Prepared by the method of Charette.<sup>45</sup> The characterization data matched the data in the literature.<sup>46</sup>  $[\alpha]_D^{24}$   $+44.1^\circ$  ( $c$  1.1,  $\text{CHCl}_3$ ; for (1*S*, 1'*S*, 2'*S*) enantiomer at 90% ee).



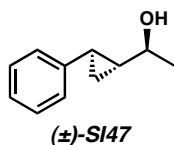
**(±)-*trans*-1-(2-Phenylcyclopropyl)ethanone ((±)-16).** Prepared as for **SI3** from (±)-**SI45** (16.5 mg, 0.10 mmol) to afford (±)-**16** (15.9 mg, 97% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>47</sup>  $[\alpha]_D^{24}$   $-275.5^\circ$  ( $c$  0.59,  $\text{CHCl}_3$ ; for (1'*R*, 2'*R*) enantiomer at 57% ee) [lit.<sup>47</sup>  $[\alpha]_D^{20}$   $+116.2^\circ$  ( $c$  0.785,  $\text{CHCl}_3$ ; for (1'*S*, 2'*S*) enantiomer)].



**(±)-*syn,trans*-1-(1-Methyl-2-phenylcyclopropyl)ethanol ((±)-SI46, Table 15, entries 7-8).** Prepared by the method of Charette.<sup>45</sup> The characterization data matched the data in the literature.  $[\alpha]_D^{24}$   $+2.1^\circ$  ( $c$  1.5,  $\text{CHCl}_3$ ; for (1*S*, 1'*S*, 2'*R*) enantiomer at 89% ee).

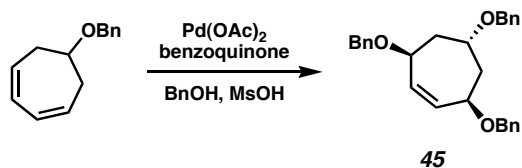


**(±)-*trans*-1-(1-Methyl-2-phenylcyclopropyl)ethanone ((±)-17).** Prepared as for **SI3** from (±)-**SI46** (17.6 mg, 0.10 mmol) to afford (±)-**17** (6.2 mg, 36% yield) as a colorless oil. The characterization data matched the data in the literature.<sup>48</sup>  $[\alpha]_D^{25} -152.1^\circ$  (*c* 1.59, abs. EtOH; for (1'*R*, 2'*S*) enantiomer at 74% ee) [lit.<sup>48</sup>  $[\alpha]_D^{25} +173.3^\circ$  (*c* 2, abs. EtOH; for (1'*S*, 2'*R*) enantiomer)].



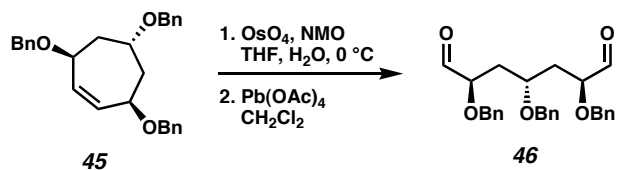
**(±)-*anti,trans*-1-(2-Phenylcyclopropyl)ethanol ((±)-SI47, Table 15, entries 9-11).** Prepared by the method of Charette.<sup>49</sup> The characterization data matched the data in the literature.<sup>50</sup>  $[\alpha]_D^{24} -60.1^\circ$  (*c* 1.0, CHCl<sub>3</sub>; for (1*S*, 1'*R*, 2'*R*) enantiomer at 94% ee) [lit.<sup>50</sup>  $[\alpha]_D +64.2^\circ$  (*c* 1.0, CHCl<sub>3</sub>; for (1*R*, 1'*S*, 2'*S*) enantiomer)].

### *meso*-Diol Syntheses, Resolutions, and Data



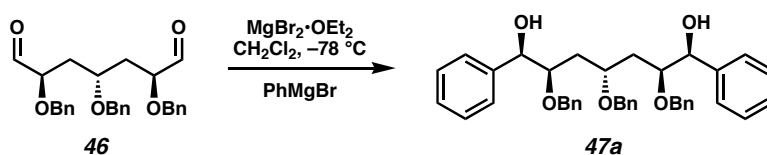
**Cycloheptene 45.** To a stirred slurry of Pd(OAc)<sub>2</sub> (35.2 mg, 0.16 mmol, 0.08 equiv) in benzyl alcohol (11 mL) was added methanesulfonic acid (20  $\mu$ L, 29.6 mg, 0.32 mmol, 0.16 equiv) and benzoquinone (432 mg, 4.0 mmol, 2.0 equiv). To the stirred solution was added a solution of the

6-benzyloxycyclohepta-1,3-diene<sup>51</sup> (400 mg, 2.0 mmol, 1.0 equiv) in benzyl alcohol (3 mL) by syringe pump over 4 h. Once the addition was complete, stirring was continued for 3 h more before the addition of more benzoquinone (216 mg, 2.0 mmol, 2.0 equiv). The reaction was warmed to 40 °C for 5 h, then cooled to room temperature. The reaction mixture was diluted with H<sub>2</sub>O (100 mL) and extracted with 2:1 Et<sub>2</sub>O:pentane (4 x 100 mL). The combined organic extracts were washed with 10% NaOH (aq, 3 x 100 mL). During the final wash, portions of NaBH<sub>4</sub> were added to the biphasic mixture to remove color. The organic extracts were dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated under reduced pressure. Excess benzyl alcohol was removed by bulb-to-bulb distillation (2 torr, 95 °C). The crude oil was purified by flash chromatography (9:1 pentane:Et<sub>2</sub>O) to provide **45** (547 mg, 66% yield) as a colorless oil: *R<sub>f</sub>* 0.84 (1:1 Et<sub>2</sub>O:pentane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.51-7.32 (comp. m, 15H), 6.06 (d, *J* = 1.2 Hz, 2H), 4.75-4.53 (comp. m, 8H), 4.08-3.99 (m, 1H), 2.37 (ddd, *J* = 13.5, 5.3, 2.1 Hz, 2H), 1.90 (ddd, *J* = 13.5, 11.0, 2.4 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.2, 138.9, 138.5, 135.4, 134.5, 128.8, 128.7, 128.7, 128.5, 128.0, 128.0, 127.9, 127.8, 127.7, 73.7, 73.0, 71.0, 71.0, 70.5, 39.5, 37.4; IR (thin film/NaCl): 2860, 1453, 1069 cm<sup>-1</sup>; HRMS-EI (*m/z*): [M+H]<sup>+</sup> calcd for [C<sub>28</sub>H<sub>31</sub>O<sub>3</sub>]<sup>+</sup>, 415.2273; found, 415.2280.



**Dialdehyde 46.** To a solution of cycloheptene **45** (698 mg, 1.59 mmol, 1.0 equiv) in THF (18 mL) and water (6 mL) was added OsO<sub>4</sub> (28 mg, 0.13 mmol, 0.08 equiv) and 4-methylmorpholine-*N*-oxide (410 mg, 3.5 mmol, 2.2 equiv). After 8 h, sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq, 10 mL) was added to the reaction, and the biphasic mixture was stirred vigorously for 15 min. The

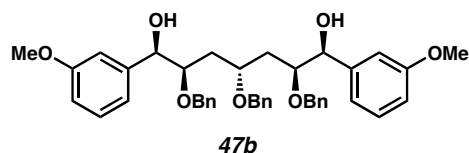
mixture was extracted with Et<sub>2</sub>O (4 x 10 mL). The combined organic extracts were washed with brine, dried over MgSO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:EtOAc) to afford a diol intermediate (635 mg, 85% yield) as a waxy white solid, which was used directly in the next step. To a solution of the diol (400 mg, 0.89 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added Pb(OAc)<sub>4</sub> (435 mg, 0.98 mmol, 1.1 equiv). After 15 min, the cloudy mixture was diluted with heptane (10 mL) and filtered over a pad of Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography (4:1 hexanes:EtOAc) to provide **46** (385 mg, 97% yield) as a clear oil: *R*<sub>f</sub> 0.31 (1:1 Et<sub>2</sub>O:pentane); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.63 (d, *J* = 1.8 Hz, 2H), 7.48-7.16 (comp. m, 15H), 4.65 (d, *J* = 11.4 Hz, 2H), 4.40 (d, *J* = 11.7 Hz, 2H), 4.29 (s, 2H), 3.96 (dq, *J* = 8.9, 1.5 Hz, 2H), 3.89 (ddd, *J* = 11.6, 7.7, 4.2 Hz, 1H), 2.14-1.82 (comp. m, 4H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 203.1, 138.2, 137.4, 128.8, 128.7, 128.4, 128.4, 128.1, 128.0, 81.2, 72.8, 72.4, 71.7, 36.0; IR (thin film/NaCl) 2866, 1732, 1117 cm<sup>-1</sup>; HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for [C<sub>20</sub>H<sub>30</sub>O<sub>5</sub>]<sup>+</sup>, 446.2093; found, 446.2093.



**General Procedure for the Addition of Aryl Grignards to Dialdehydes: *meso*-Diol **47a**.** To a solution of dialdehyde **46** (310 mg, 0.69 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0 °C was added anhydrous MgBr•OEt<sub>2</sub> (427 mg, 1.66 mmol, 2.4 equiv). The milky solution was stirred at 0 °C for 30 min, then cooled to -78 °C before addition of a solution of phenylmagnesium bromide (1.0 M in Et<sub>2</sub>O, 1.74 mL, 1.74 mmol, 2.5 equiv). The reaction was stirred for 3 h at -78 °C, then for 30 min at 23 °C before quenching with sat. NH<sub>4</sub>Cl (aq, 5 mL) and H<sub>2</sub>O (5 mL). The phases

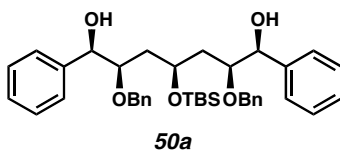


were separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL). The combined organic phases were washed with H<sub>2</sub>O (2 x 10 mL) and brine (10 mL), dried over MgSO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:EtOAc) to afford *meso*-diol **47a** (321 mg, 88% yield) as a clear oil: *R<sub>f</sub>* 0.37 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.49-7.20 (comp. m, 25H), 4.64 (dd, *J* = 4.2, 3.9 Hz, 2H), 4.46 (s, 4H), 4.25 (s, 2H), 3.90-3.71 (comp. m, 3H), 3.09 (s, 2H), 1.93-1.77 (m, 2H), 1.76-1.60 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 141.8, 138.9, 138.5, 128.8, 128.7, 128.7, 128.2, 128.1, 128.0, 128.0, 127.9, 127.1, 80.8, 76.5, 73.6, 73.2, 69.3, 37.1; IR (thin film/NaCl) 3430, 1454, 1057 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M+H]<sup>+</sup> calcd for [C<sub>40</sub>H<sub>43</sub>O<sub>5</sub>]<sup>+</sup>, 603.3110; found, 603.3124.

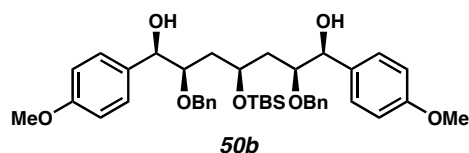


***meso*-Diol 47b.** Prepared as for **47a** from **46** (310 mg, 0.69 mmol, 1.0 equiv) and a freshly prepared solution of 3-methoxyphenylmagnesium bromide (1.0 M in Et<sub>2</sub>O, 1.74 mL, 1.74 mmol, 2.5 equiv) to afford, after flash chromatography (3:1 hexanes:EtOAc), *meso*-diol **47b** (281 mg, 61% yield) as a yellow oil: *R<sub>f</sub>* 0.10 (7:3 hexanes:EtOAc); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.40-7.16 (comp. m, 17H), 6.96-6.79 (comp. m, 6H), 4.58 (dd, *J* = 5.1, 5.0 Hz, 2H), 4.45 (d, *J* = 11.1 Hz, 2H), 4.38 (d, *J* = 11.4 Hz, 2H), 4.21 (s, 2H), 3.83-3.68 (comp. m, 7H), 2.87 (d, *J* = 4.5 Hz, 2H), 1.80 (ddd, *J* = 14.6, 8.1, 4.5 Hz, 2H), 1.68 (ddd, *J* = 14.2, 8.4, 4.5 Hz, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.7, 143.2, 138.5, 138.2, 129.4, 128.4, 128.1, 127.9, 127.8, 127.6, 127.6, 119.1, 113.4, 112.1, 80.6, 76.3, 72.9, 69.0, 55.2, 36.9; IR (thin film/NaCl) 3436, 2920, 1047 cm<sup>-1</sup>; HRMS-FAB (*m/z*): [M+H]<sup>+</sup> calcd for [C<sub>42</sub>H<sub>47</sub>O<sub>7</sub>]<sup>+</sup>, 663.3322; found, 663.3342.



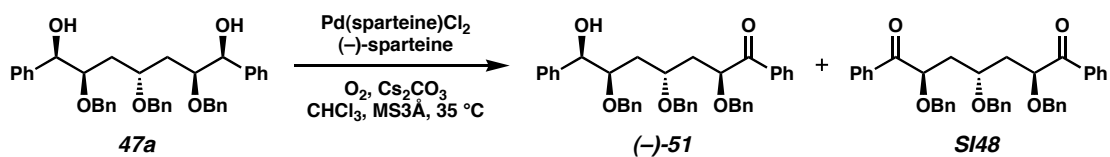


**meso-Diol 50a.** Prepared as for **47a** from **49** (393 mg, 0.84 mmol, 1.0 equiv) to afford, after flash chromatography (17:3 hexanes:EtOAc), *meso*-diol **50a** (435 mg, 98% yield) as a clear oil:  $R_f$  0.32 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54-7.06 (comp. m, 20H), 4.57 (dd,  $J = 5.2, 4.8$  Hz, 2H), 4.43 (d,  $J = 11.4$  Hz, 2H), 4.32 (d,  $J = 11.1$  Hz, 2H), 3.76-3.60 (comp. m, 3H), 2.98 (d,  $J = 4.8$  Hz, 2H), 1.92-1.59 (comp. m, 4H), 0.89 (s, 9H), 0.01 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  141.6, 138.4, 128.7, 128.6, 128.0, 128.0, 127.0, 80.8, 79.9, 76.2, 72.9, 67.5, 38.9, 26.2, 18.3, -4.1; IR (thin film/NaCl) 3445, 2928, 1454, 1048  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{39}\text{H}_{51}\text{O}_5\text{Si}]^+$ , 627.3506; found, 627.3503.



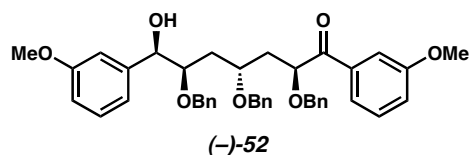
**meso-Diol 50b.** Prepared as for **47a** from **49** (393 mg, 0.84 mmol, 1.0 equiv) and a freshly prepared solution of 4-methoxyphenylmagnesium bromide (1.0 M in  $\text{CH}_2\text{Cl}_2$ , 2.1 mL, 2.10 mmol, 2.5 equiv) to afford, after flash chromatography (17:3 hexanes:EtOAc), *meso*-diol **50b** (302 mg, 52% yield) as a clear oil:  $R_f$  0.10 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.17 (comp. m, 14H), 6.90 (d,  $J = 8.1$  Hz, 4H), 4.52 (d,  $J = 5.7$  Hz, 2H), 4.47 (d,  $J = 11.4$  Hz, 2H), 4.39 (d,  $J = 11.7$  Hz, 2H), 3.78 (s, 6H), 3.71-3.54 (comp. m, 3H), 2.99 (br. s, 2H), 1.85-1.57 (comp. m, 4H), 0.92 (s, 9H), 0.02 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 138.5, 133.6, 128.7, 128.4, 128.0, 128.0, 114.0, 81.0, 75.9, 72.8, 67.6, 55.5, 38.9, 26.3, 18.3, -4.0; IR

(thin film/NaCl) 3453, 2931, 1102  $\text{cm}^{-1}$ ; HRMS-ES ( $m/z$ ):  $[M+Na]^+$  calcd for  $[C_{41}H_{54}O_7NaSi]^+$ , 709.3537; found, 709.3522.

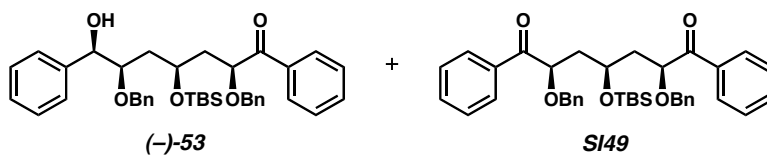


**General Procedure for the Desymmetrization of *meso*-Diols: Hydroxyketone **(-)-51**.** To an oven dried reaction tube with stir bar was added 3 Å molecular sieves (500 mg). After cooling,  $\text{Pd(sparteine)Cl}_2$  (41.2 mg, 0.10 mmol, 0.10 equiv), followed by chloroform (2 mL, ACS reagent grade, stabilized with amylenes) and then  $(-)\text{-sparteine}$  (32.2  $\mu\text{L}$ , 32.8 mg, 0.14 mmol, 0.14 equiv) were added. The reaction tube was cooled to  $-78\text{ }^\circ\text{C}$ , then vacuum evacuated and purged with  $\text{O}_2$  (3x). The reaction was warmed to  $35\text{ }^\circ\text{C}$ . Finely powdered  $\text{Cs}_2\text{CO}_3$  (130 mg, 0.40 mmol, 0.40 equiv) was added, followed by a solution of *meso*-diol **47a** (301 mg, 0.50 mmol, 0.50 equiv) in chloroform (2 mL). The reaction was allowed to proceed under  $\text{O}_2$  atmosphere at  $35\text{ }^\circ\text{C}$  until **47a** was completely consumed as determined by TLC. The reaction was filtered through Celite, and the filtrate was concentrated under reduced pressure and purified by flash chromatography to afford hydroxyketone **(-)-51** (252 mg, 84% yield, 95% ee) as a colorless oil:  $R_f$  0.49 (7:3 hexanes:EtOAc);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.57 (dd,  $J = 6.9, 6.9\text{ Hz}$ , 1H), 7.42 (dd,  $J = 7.1, 6.9\text{ Hz}$ , 2H), 7.38-7.14 (comp. m, 20H), 4.92 (d,  $J = 7.8\text{ Hz}$ , 1H), 4.69-4.57 (comp. m, 2H), 4.53-4.34 (comp. m, 3H), 4.26-4.13 (comp. m, 2H), 3.91-3.68 (comp. m, 2H), 2.90 (br. s, 1H), 2.05-1.62 (comp. m, 4H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.3, 141.4, 138.8, 138.3, 137.8, 135.1, 133.7, 129.0, 128.7, 128.7, 128.6, 128.2, 128.1, 128.0, 128.0, 127.9, 127.0, 80.9, 78.9, 76.6, 73.6, 73.0, 72.1, 71.3, 39.5, 37.1; IR (thin film/NaCl) 3467, 2874, 1692, 1454, 1095  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[M+H]^+$  calcd for  $[C_{40}H_{41}O_5]^+$ , 601.2954; found,

601.2953;  $[\alpha]_D^{20}$   $-78.1^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ ; for (2*S*, 4*R*, 6*R*, 7*R*) enantiomer at 95% ee). Also recovered was diketone **SI48** (21 mg, 7% yield) as a clear oil:  $R_f$  0.62 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 7.2$  Hz, 4H), 7.56 (dd,  $J = 7.5, 7.2$  Hz, 2H), 7.41 (dd,  $J = 7.5, 7.5$  Hz, 4H), 7.38-7.14 (comp. m, 15H), 4.88 (dd,  $J = 8.3, 4.2$  Hz, 2H), 4.62 (d,  $J = 11.1$  Hz, 2H), 4.34 (s, 2H), 4.22 (d,  $J = 11.4$  Hz, 2H), 4.15-4.02 (m, 1H), 2.06-1.74 (comp. m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 138.5, 137.5, 134.8, 133.4, 128.7, 128.7, 128.4, 128.3, 127.9, 127.7, 127.6, 78.9, 77.2, 73.6, 72.6, 71.1, 39.5; IR (thin film/NaCl) 2924, 1692, 1451  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{40}\text{H}_{39}\text{O}_5]^+$ , 599.2797; found, 599.2826.



**Hydroxyketone (-)-52.** Prepared as for (-)-**51** from **47b** (331 mg, 0.50 mmol) to afford hydroxyketone (-)-**52** (291 mg, 88% yield, 99% ee) as a slightly yellow oil:  $R_f$  0.18 (3:2 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 6.3$  Hz, 1H), 7.51 (dd,  $J = 2.9, 2.0$  Hz, 1H), 7.38-7.06 (comp. m, 18H), 6.97-6.87 (comp. m, 2H), 6.86-6.78 (m, 1H), 4.91 (dd,  $J = 9.5, 2.4$  Hz, 1H), 4.68-4.55 (comp. m, 2H), 4.47 (d,  $J = 11.4$  Hz, 1H), 4.38 (d,  $J = 11.4$  Hz, 1H), 4.21 (m, 1H), 4.14 (d,  $J = 11.1$  Hz, 1H), 3.86-3.66 (comp. m, 8H), 2.83 (d,  $J = 4.5$  Hz, 1H), 2.09-1.59 (comp. m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 160.1, 160.0, 143.0, 138.7, 138.2, 137.8, 136.4, 129.9, 129.7, 128.7, 128.6, 128.6, 128.6, 128.2, 128.1, 128.0, 128.0, 127.9, 121.5, 120.6, 119.3, 113.8, 112.7, 112.3, 80.6, 78.6, 76.5, 73.6, 73.0, 72.1, 71.3, 55.6, 55.4, 39.6, 37.0; IR (thin film/NaCl) 3473, 2934, 1692, 1597, 1095  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{42}\text{H}_{45}\text{O}_7]^+$ , 661.3165; found, 661.3157;  $[\alpha]_D^{20}$   $-56.8^\circ$  ( $c$  1.0,  $\text{CDCl}_3$ ; for (2*S*, 4*R*, 6*R*, 7*R*) enantiomer at 99% ee).



**Hydroxyketone (-)-53.** Prepared as for (-)-51 from **50a** (313 mg, 0.50 mmol) to afford hydroxyketone (-)-53 (259 mg, 83% yield, 95% ee) as an oil:  $R_f$  0.34 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.1$  Hz, 2H), 7.57 (dd,  $J = 7.8, 7.5$  Hz, 1H), 7.43 (dd,  $J = 7.4, 6.6$  Hz, 2H), 7.39-7.10 (comp. m, 20H), 4.93 (dd,  $J = 7.7, 4.5$  Hz, 1H), 4.63-4.52 (comp. m, 2H), 4.40-4.20 (comp. m, 4H), 2.84 (br. s, 1H), 2.07-1.79 (comp. m, 4H), 0.89 (s, 9H), 0.14 (s, 3H), -0.17 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.3, 142.0, 138.4, 137.7, 135.2, 133.7, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 127.8, 127.8, 81.0, 78.5, 76.1, 73.2, 72.1, 67.3, 39.3, 38.8, 26.2, 18.3, -4.3; IR (thin film/NaCl) 3478, 2929, 1692, 1094  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{39}\text{H}_{49}\text{O}_5\text{Si}]$ , 625.3349; found, 625.3345;  $[\alpha]_{\text{D}}^{20}$   $-64.1^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ ; for (2*S*, 4*S*, 6*R*, 7*R*) enantiomer at 95% ee). Also recovered was diketone **SI49** (16 mg, 5% yield) as an oil:  $R_f$  0.39 (7:3 hexanes:EtOAc);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 7.5$  Hz, 4H), 7.56 (dd,  $J = 7.5, 7.2$  Hz, 2H), 7.40 (d,  $J = 7.8$  Hz, 4H), 7.33-7.12 (comp. m, 10H), 5.03 (dd,  $J = 9.0, 3.6$  Hz, 2H), 4.59 (d,  $J = 11.7$  Hz, 2H), 4.34 (d,  $J = 11.7$  Hz, 2H), 4.24 (m, 1H), 2.20-1.90 (comp. m, 4H), 0.83 (s, 9H), -0.18 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  200.5, 137.6, 135.4, 133.6, 129.0, 128.8, 128.6, 128.5, 128.1, 100.2, 77.9, 71.6, 66.9, 38.4, 26.1, 18.2, -4.5; IR (thin film/NaCl) 2930, 1692, 1256  $\text{cm}^{-1}$ ; HRMS-FAB ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{39}\text{H}_{47}\text{O}_5\text{Si}]^+$ , 623.3193; found, 623.3210.



**Methods for Determination of Conversion**

Conversion values for *N*-acetyl-3-amino-1-phenylpropan-1-ol (Table 11, entry 9), **32** (Table 11, entry 10), **34** (Table 11, entry 11), and methyl 2-(3-(3-bromophenyl)-3-hydroxypropyl)benzoate (Table 11, entry 12) were determined by isolated yield. Conversion values for **6** (Tables 3 and 5), **8** (Table 4), **SI10** (Table 12, entries 9-10), **SI20** (Table 13, entries 7-9), **SI23** (Table 13, entries 10-12), and **SI44** (Table 14, entry 13) were determined by <sup>1</sup>H NMR of a reaction aliquot after filtration through a short plug of silica gel. All other conversions were determined by GC (Table S1) relative to internal standard (tridecane).

**Table S1.** Methods for the Determination of % Conversion

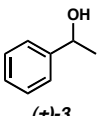
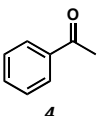
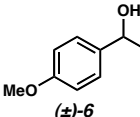
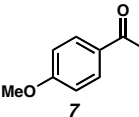
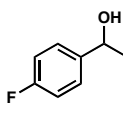
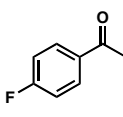


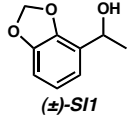
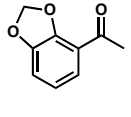
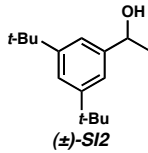
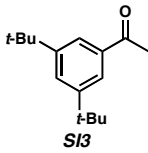
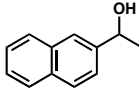
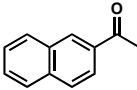








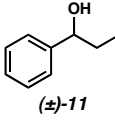
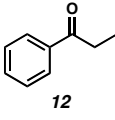
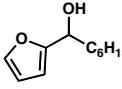
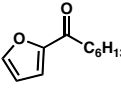


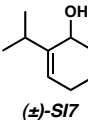
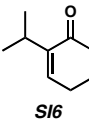
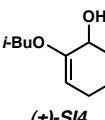
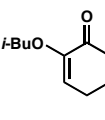
entry	alcohol	ketone	GC conditions	alcohol retention time (min)	ketone retention time (min)
1	 (±)-3	 4	100 °C, 5 min; Ramp 13 °C/min	10.6	8.9
2	 (±)-6	 7	100 °C, 5 min; Ramp 13 °C/min	14.4	13.9
3	 (±)-3	 4	70 °C, 15 min; Ramp 7 °C/min	29.4	25.5
4	 (±)-SI1	 5	100 °C, 5 min; Ramp 13 °C/min	13.4	12.6
5	 (±)-SI1	 6	70 °C, 15 min; Ramp 7 °C/min	36.3	35.0



Table S1 (continued).

6	 (±)-SI2	 SI3	100 °C, 5 min; Ramp 13 °C/min	13.5	12.6
7			70 °C, 15 min; Ramp 13 °C/min to 240 °C 240 °C, 20 min	42.0	38.9
8			50 °C Ramp 3 °C/min	23.9	– <sup>a</sup>
9			50 °C Ramp 3 °C/min	22.5	– <sup>a</sup>
10			100 °C, 5 min; Ramp 13 °C/min	13.0	12.5
11			100 °C, 5 min; Ramp 13 °C/min	14.5	13.6
12	 (±)-11	 12	100 °C, 5 min; Ramp 13 °C/min	11.5	10.0
13			50 °C Ramp 3 °C/min	38.2	35.2
14			70 °C, 15 min; Ramp 7 °C/min	28.7	31.2
15	 (±)-SI7	 SI6	100 °C, 5 min; Ramp 13 °C/min	9.0	7.8
16	 (±)-SI4		100 °C, 5 min; Ramp 13 °C/min	10.6	12.2

<sup>a</sup> Ketone is volatile and evaporates on concentration of resolution aliquots.

Table S1 (continued).





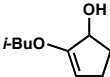
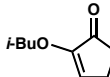
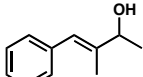
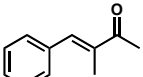


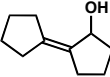
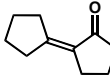
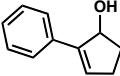
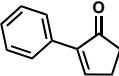
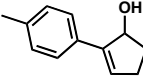
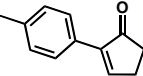
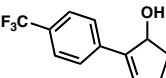
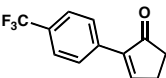
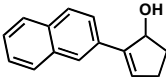
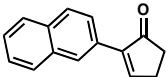
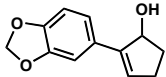
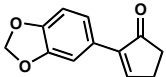
17			70 °C, 15 min; Ramp 7 °C/min	28.6	30.6
18	 (±)-SI8		100 °C, 5 min; Ramp 13 °C/min	8.0	7.4
19	 (±)-SI9		100 °C, 5 min; Ramp 13 °C/min	10.3	11.8
20			100 °C, 5 min; Ramp 13 °C/min	14.1	13.1
21	 (±)-SI11		100 °C, 5 min; Ramp 13 °C/min	9.3	8.7
22	 (±)-SI13	 SI12	70 °C, 15 min; Ramp 7 °C/min	29.5	29.7
23	 (±)-SI14		100 °C, 5 min; Ramp 13 °C/min to 240 °C 240 °C, 5 min	15.8	16.1
24	 (±)-SI17	 SI16	70 °C, 15 min; Ramp 7 °C/min	37.2	37.7
25	 (±)-SI26	 SI25	70 °C, 15 min; Ramp 7 °C/min	35.8	35.3
26	 (±)-SI29	 SI28	70 °C, 15 min; Ramp 13 °C/min to 240 °C 240 °C, 20 min	53.3	55.4
27	 (±)-SI32	 SI31	70 °C, 15 min; Ramp 13 °C/min to 240 °C 240 °C, 20 min	46.9	48.6

Table S1 (continued).

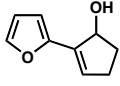
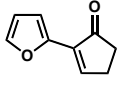
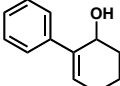
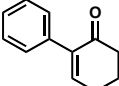
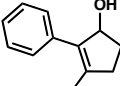
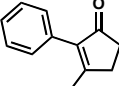
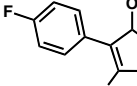
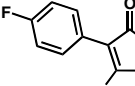
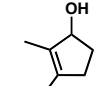
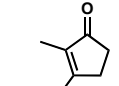
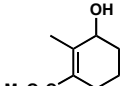
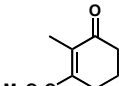






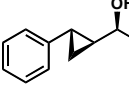
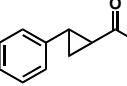
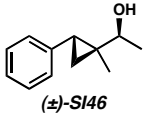
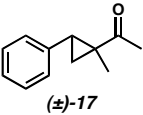
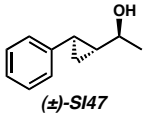
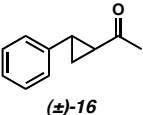
28	 (±)-SI35	 SI34	70 °C, 15 min; Ramp 7 °C/min	33.4	32.8
29	 (±)-SI36		100 °C, 5 min; Ramp 13 °C/min to 240 °C 240 °C, 5 min	15.8	16.1
30	 (±)-38		100 °C, 5 min; Ramp 13 °C/min to 240 °C 240 °C, 5 min	15.1	16.6
31	 (±)-36		70 °C, 15 min; Ramp 13 °C/min to 240 °C 240 °C, 20 min	42.3	40.3
32	 (±)-SI38	 SI37	100 °C, 5 min; Ramp 13 °C/min	14.0	12.0
33	 (±)-SI40	 SI39	100 °C, 5 min; Ramp 13 °C/min	15.1	13.2
34			70 °C, 15 min Ramp 7 °C/min	19.8	17.8
35	 (±)-26		70 °C, 15 min; Ramp 7 °C/min	23.4	20.5
36			50 °C Ramp 3 °C/min	7.4	5.0
37	 (±)-SI45	 (±)-16	100 °C, 5 min; Ramp 13 °C/min	14.2	13.1

Table S1 (continued).

38	 (±)-SI46	 (±)-17	70 °C, 15 min; Ramp 7 °C/min	33.2	31.3
39	 (±)-SI47	 (±)-16	100 °C, 5 min; Ramp 13 °C/min	14.1	13.1

## Methods for Determination of Enantiomeric Excess

Table S2. Methods for Determination of Enantiomeric Excess

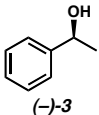
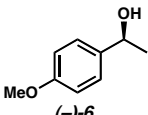
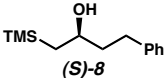
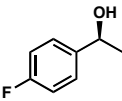

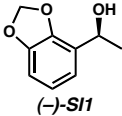
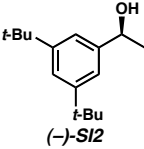
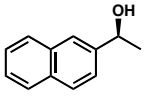
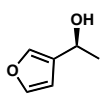
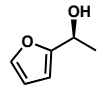
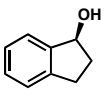
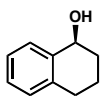
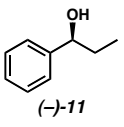
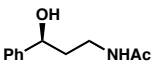
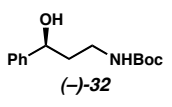
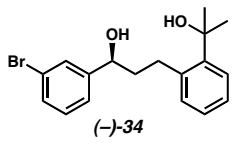
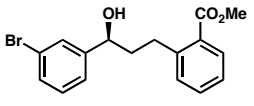
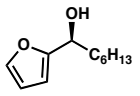

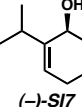
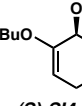

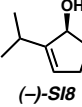
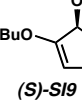

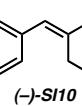
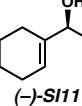
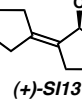
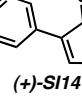
entry	alcohol (major enantiomer)	ee assay and column	assay conditions	major ( <i>S</i> ) enantiomer retention time (min)	minor ( <i>R</i> ) enantiomer retention time (min)
1	 (-)-3	HPLC OJ	4% <i>i</i> PrOH/hexanes	17.8	20.8
2	 (-)-6	HPLC OD-H	3% EtOH/hexanes	15.7	16.7
3	 ( <i>S</i> )-8	HPLC OD-H	2% <i>i</i> PrOH/hexanes	15.6	12.3
4	 F	HPLC AS	2% EtOH/hexanes	17.4	15.1
5	 OMe	HPLC OB-H	3% EtOH/hexanes	11.5	21.4
6	 (-)-SI1	HPLC OB-H	2% <i>i</i> PrOH/hexanes	32.2	18.7

Table S2 (continued).

7	 <i>(-)-512</i>	HPLC AD	0.25% <i>i</i> PrOH/hexanes	16.8	15.1
8		HPLC OJ	4% <i>i</i> PrOH/hexanes	31.3	38.7
9 <sup>a</sup>		HPLC OJ	4% EtOH/hexanes	16.0	19.0
10 <sup>a</sup>		HPLC OJ	4% EtOH/hexanes	17.0	20.0
11		HPLC OB-H	4% <i>i</i> PrOH/hexanes	19.2	11.8
12		HPLC OB-H	3% <i>i</i> PrOH/hexanes	21.3	12.2
13	 <i>(-)-11</i>	HPLC OD-H	3% EtOH/hexanes	17.6	12.0
14 <sup>b</sup>		HPLC AD	6% <i>i</i> PrOH/hexanes	23.8	27.9
15 <sup>b</sup>	 <i>(-)-32</i>	HPLC OJ	8% <i>i</i> PrOH/hexanes	20.1	10.5
16 <sup>b</sup>	 <i>(-)-34</i>	HPLC OJ	5% EtOH/hexanes	15.0	17.8
17		HPLC AD	5% EtOH/hexanes	17.1	15.8
18 <sup>c</sup>		HPLC AD	2% EtOH/hexanes	12.3	15.8

<sup>a</sup> UV detection at 220 nm. <sup>b</sup> UV detection at 210 nm. <sup>c</sup> Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH<sub>2</sub>Cl<sub>2</sub>.

Table S2 (continued).

19 <sup>c</sup>		HPLC AD	1% EtOH/hexanes	16.7	15.3
20	 (-)-SI7	GC GTA	50 °C Ramp 1 °C/min	34.6	37.0
21	 (S)-SI4	GC GTA	80 °C isothermal	53.4	52.5
22 <sup>c</sup>		HPLC OJ	1% EtOH/hexanes	26.2	28.8
23	 (-)-SI8	GC GTA	70 °C Ramp 1 °C/min	15.8	17.8
24	 (S)-SI9	GC GTA	80 °C isothermal	27.6	25.7
25		HPLC OD-H	3% <i>i</i> PrOH/hexanes	17.9	15.6
26	 (-)-SI10	HPLC OD-H	4% EtOH/hexanes	12.4	10.3
27	 (-)-SI11	GC GTA	50 °C Ramp 3 °C/min	18.7	19.0
28	 (+)-SI13	GC GTA	70 °C Ramp 1 °C/min	36.3	35.7
29	 (+)-SI14	HPLC OD-H	3% EtOH/hexanes	23.3	18.5

<sup>c</sup> Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH<sub>2</sub>Cl<sub>2</sub>.

Table S2 (continued).

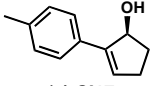
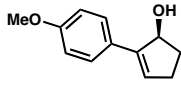
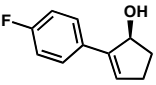
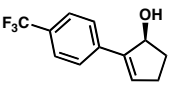
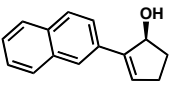
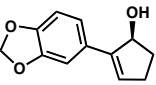
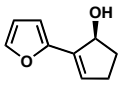
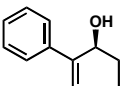
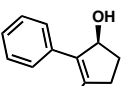
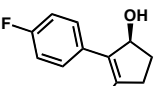
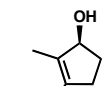
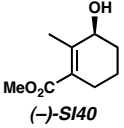
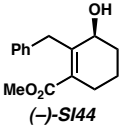

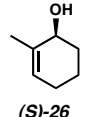

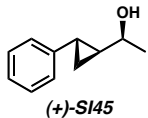
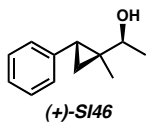
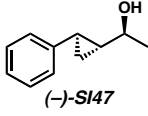
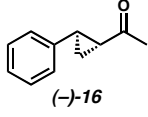
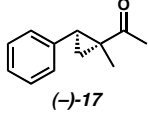
30	 (+)-SI17	HPLC OB-H	8% EtOH/hexanes	14.4	7.5
31	 (+)-SI20	HPLC AS	4% EtOH/hexanes	11.5	15.9
32	 (+)-SI23	HPLC OB-H	4% EtOH/hexanes	11.0	9.1
33	 (+)-SI26	HPLC OD-H	2% EtOH/hexanes	15.3	14.0
34	 (+)-SI29	HPLC AS	3% EtOH/hexanes	11.4	13.2
35	 (+)-SI32	HPLC OB-H	10% EtOH/hexanes	26.8	11.0
36	 (+)-SI35	HPLC AD	4% EtOH/hexanes	21.3	17.7
37	 (-)-SI36	HPLC AD	3% EtOH/hexanes	21.9	16.4
38	 (-)-38	HPLC OB-H	3% EtOH/hexanes	9.6	7.9
39	 (-)-36	HPLC OB-H	5% EtOH/hexanes	18.2	22.3
40	 (-)-SI38	HPLC AD	3% EtOH/hexanes	23.0	26.0

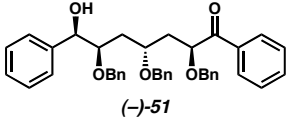
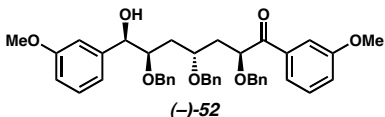
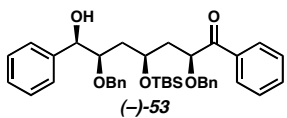
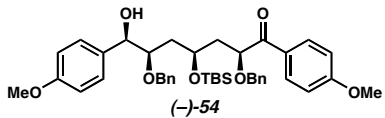
Table S2 (continued).

41	 (-)-SI40	HPLC OB-H	2% <i>i</i> PrOH/hexanes	20.8	22.9
42	 (-)-SI44	HPLC OD-H	4% EtOH/hexanes	10.2	11.5
43 <sup>c</sup>		HPLC OJ	1% EtOH/hexanes	12.0	13.2
44 <sup>c</sup>	 (S)-26	HPLC AD	1% EtOH/hexanes	9.7	8.9
45		GC GTA	40 °C isothermal	10.8	11.3
46	 (+)-SI45	HPLC OD-H	2% EtOH/hexanes	15.1 <sup>d</sup>	17.8
47	 (+)-SI46	HPLC OD-H	3% EtOH/hexanes	8.8 <sup>e</sup>	10.1
48	 (-)-SI47	HPLC OD-H	2% EtOH/hexanes	20.7 <sup>f</sup>	14.6
49	 (-)-16	HPLC OD-H	2% EtOH/hexanes	8.5 <sup>g</sup>	7.9
50	 (-)-17	HPLC OD-H	3% EtOH/hexanes	7.5 <sup>h</sup>	6.9

<sup>c</sup> Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup> Retention time for the (1*S*, 1'*S*, 2'*S*) enantiomer (shown). <sup>e</sup> Retention time for the (1*S*, 1'*S*, 2'*R*) enantiomer (shown). <sup>f</sup> Retention time for the (1*S*, 1'*R*, 2'*R*) enantiomer (shown). <sup>g</sup> Retention time for the (1'*R*, 2'*R*) enantiomer (shown). <sup>h</sup> Retention time for the (1'*R*, 2'*S*) enantiomer (shown).



Table S2 (continued).

51	 (-)-51	HPLC OJ	6% <i>i</i> PrOH/hexanes	39.3 <sup>i</sup>	29.9
52	 (-)-52	HPLC OB-H	4% <i>i</i> PrOH/hexanes	22.7 <sup>i</sup>	20.1
53	 (-)-53	HPLC OJ	2% <i>i</i> PrOH/hexanes	22.7 <sup>i</sup>	20.1
54	 (-)-54	HPLC OB-H	6% EtOH/hexanes	29.9 <sup>j</sup>	24.5

<sup>i</sup> Retention time for the (2*S*, 4*R*, 6*R*, 7*R*) enantiomer (shown). <sup>j</sup> Retention time for the (2*S*, 4*S*, 6*R*, 7*R*) enantiomer (shown).

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