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Supporting Information

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

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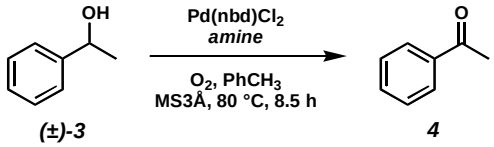
Table of Contents:

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_2, **5**] was prepared as previously reported.[i] Palladium acetate [$Pd(OAc)_2$], dichlorobis(benzonitrile)palladium(II), and dichlorobis(triphenylphosphine)palladium(II) were purchased from Strem Chemicals, Inc., Newburyport, MA. 2-Methoxy-α-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_3N were distilled over CaH_2. Solvents were dried by passage through an activated alumina column under argon. Powdered 3Å 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

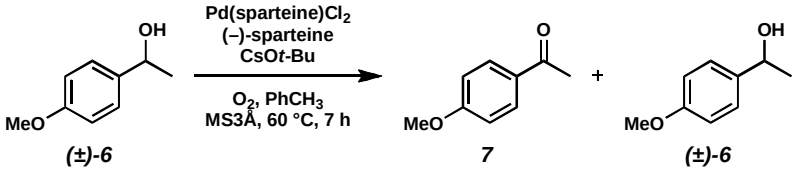
combination of UV at 254 nm, *p*-anisaldehyde, and potassium permanganate staining. ICN silica gel (particle size 32-63 μm) or SiliCycle Silia*Flash* P60 Academic silica gel (particle size 40-63 μm; pore diameter 60 Å) was used for flash column chromatography. Bulb-to-bulb distillations were performed 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. ^{1}H NMR spectra were recorded on a Varian Mercury 300 instrument (at 300 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported in terms of chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 instrument (at 75 MHz) and are reported relative to Me_4Si (δ 0.0). Data for ^{13}C NMR spectra are reported in terms of chemical shift (*d* ppm) and coupling constant (^{19}F, Hz). ^{19}F NMR spectra were recorded on a Varian Mercury 300 instrument (at 282 MHz) and are reported relative to external F_3CCO_2H standard (*d* –76.53). Data for ^{19}F NMR spectra are reported in terms of chemical shift (*d* 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



amine	conversion
pyridine	1%
quinuclidine	4%
(–)-sparteine	37%

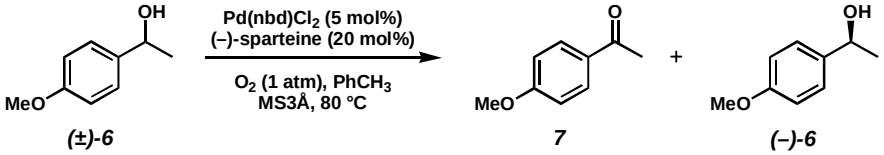
General Ligand Screening Procedure with Pd(nbd)Cl_2. To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling, dichloro(norbornadiene)palladium(II) (Pd(nbd)Cl_2, 6.7 mg, 0.025 mmol, 0.05 equiv) followed by toluene (2.5 mL) and the amine (0.10 mmol, 0.20 equiv) were added. The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). The tube was heated to 80 °C with vigorous stirring under O_2 atmosphere (1 atm, balloon) for 20 min. A solution of (±)-1-phenylethanol ((±)-**3**, 60.5 μL, 61.1 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_2 atmosphere at 80 °C. Aliquots were filtered through a small plug of silica gel (Et_2O eluent), evaporated, and analyzed by GC for conversion to ketone **4**. Conversions given are the mean of two experiments.



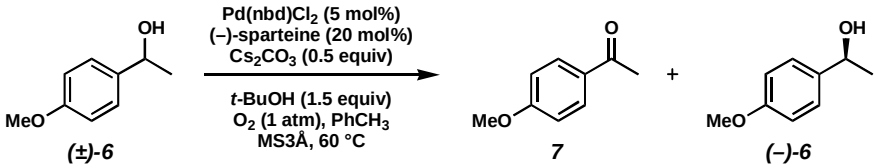
CsO*t*-Bu as Additive. To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling, complex **5** (10.3 mg, 0.025 mmol, 0.05 equiv), followed by toluene (1 mL) and then (–)-sparteine (17.2 μL, 17.6 mg, 0.075 mmol, 0.15 equiv) were added. The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). The tube was heated to 60 °C with vigorous stirring under O_2 atmosphere (1 atm, balloon) for 20 min.

Finely powdered CsO*t*-Bu[ii] (41.2 mg, 0.20 mmol, 0.40 equiv) was added, followed by a solution of (±)-1-(4-methoxyphenyl)ethanol ((±)-**6**, 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 (1 mL). The reaction was allowed to proceed under O_2 atmosphere at 60 °C. After 7 h, an aliquot was filtered through a small plug of silica gel (Et_2O 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).

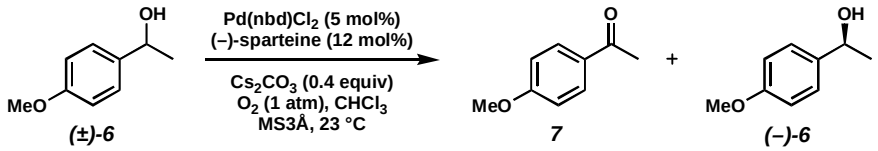
General Oxidative Kinetic Resolution Conditions



Kinetic Resolution Conditions A.[iii] To an oven dried reaction tube with stir bar was added 3Å molecular sieves (250 mg). After cooling, Pd(nbd)Cl_2 (6.7 mg, 0.025 mmol, 0.05 equiv) followed by toluene (2.5 mL) and then (–)-sparteine (23.0 μL, 23.4 mg, 0.10 mmol, 0.20 equiv) were added.[iv] The reaction tube was then cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). Then, the tube was heated to 80 °C with vigorous stirring under O_2 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_2 atmosphere at 80 °C. Aliquots were filtered through a small plug of silica gel (Et_2O 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.

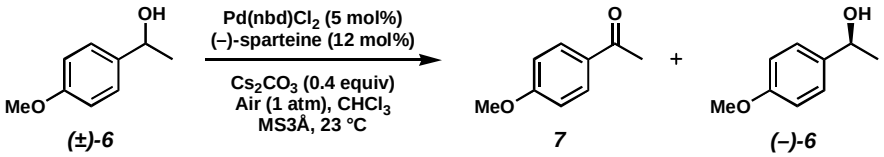


Kinetic Resolution Conditions B.[v] To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, $Pd(nbd)Cl_2$ (13.5 mg, 0.050 mmol, 0.05 equiv), followed by toluene (2 mL) and then (–)-sparteine (46.0 μL, 46.9 mg, 0.20 mmol, 0.20 equiv) were added.[iv] The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). The tube was heated to 60 °C with vigorous stirring under O_2 atmosphere (1 atm, balloon) for 20 min. Finely powdered Cs_2CO_3 (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_2 atmosphere at 60 °C. Aliquots were filtered through a small plug of silica gel (Et_2O 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.[vi] To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, $Pd(nbd)Cl_2$ (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.[vii] The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). The reaction was allowed to

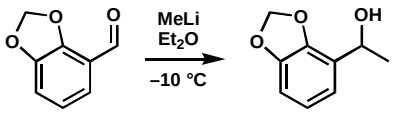
warm to 23 °C and stirred vigorously under O_2 atmosphere (1 atm, balloon) for 15 min. Finely powdered Cs_2CO_3 (130 mg, 0.40 mmol, 0.40 equiv) was added, followed by a solution of (±)-**6** (141 μL, 152 mg, 1.0 mmol, 1.0 equiv) and tridecane (73.2 μL, 55.3 mg, 0.30 mmol, 0.30 equiv) in chloroform (2 mL). The reaction was allowed to proceed under O_2 atmosphere at 23 °C. Aliquots were filtered through a small plug of silica gel (Et_2O 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.[vi] To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, $Pd(nbd)Cl_2$ (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.[vii] 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_2CO_3 (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_2O 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

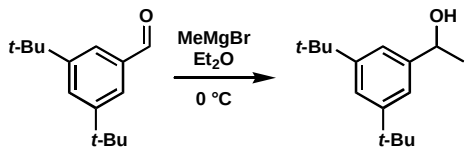
(±)-*N*-Acetyl-3-amino-1-phenylpropan-1-ol (Table 11, entry 9), (±)-*N*-(*tert*-butoxycarbonyl)-3-amino-1-phenylpropan-1-ol ((±)-**32**, Table 11, entry 10), (±)-1-(3-bromophenyl)-3-(2-(2-hydroxypropan-2-yl)phenyl)-1-propanol ((±)-**34**, Table 11, entry 11), (±)-methyl 2-(3-(3-bromophenyl)-3-hydroxypropyl)benzoate (Table 11, entry 12), and (±)-methyl 2-(4-fluorophenyl)-3-hydroxycyclopent-1-enecarboxylate ((±)-**36**, Table 14, entries 4-6) were prepared as previously described.[viii] (±)-1-(3-Furyl)ethanol (Table 10, entry 18) was prepared by the method of Zamojski.[ix] (±)-1-(2-Furyl)heptan-1-ol (Table 11, entry 13) was prepared by the method of D'Auria.[x] (±)-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.[xi] (±)-(*E*)-3-Methyl-4-phenyl-3-buten-2-ol (Table 12, entries 11-13) was prepared by the method of West.[xii] (±)-2-Methylcyclopent-2-enol was prepared by the method of Bunnelle.[xiii] (±)-2-Methylcyclohex-2-enol ((±)-**26**) was prepared by the method of Minehan.[xiv] 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.



(±)-SI1

(±)-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_2O (30 mL) was cooled to –10 °C. A solution of methyllithium (1.6 M in Et_2O, 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

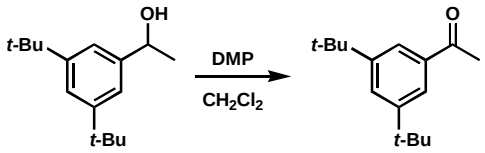
addition of crushed ice (10 g) and then sat. NH_4Cl (aq, 20 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (2 x 30 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (9:1→4:1 hexanes:EtOAc) to afford (±)-**SI1** as an off-white solid: R_f 0.39 (7:3 hexanes:EtOAc); $[\alpha]^{24}_D$ – 26.8° (*c* 1.0, $CDCl_3$; for *S* enantiomer at 99% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_9H_{10}O_3]^+$, 166.0630; found, 166.0630.



(±)-SI2

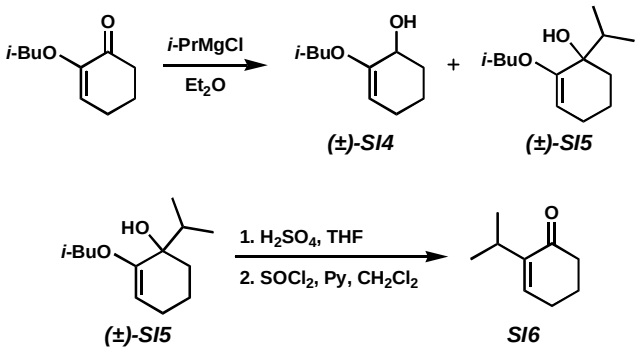
(±)-1-(3,5-Di-*tert*-butylphenyl)ethanol ((±)-SI2, Table 10, entries 12-14). A solution of 3,5-di-*tert*-butylbenzaldehyde (1.09 g, 5.0 mmol, 1.0 equiv) in Et_2O (20 mL) was cooled to 0 °C. A solution of methylmagnesium bromide (3.0 M in Et_2O, 2.5 mL, 7.5 mmol, 1.5 equiv) was added dropwise. The reaction was then quenched by slow addition of sat. NH_4Cl (aq, 20 mL) and H_2O (10 mL). After warming to 23 °C, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$ 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_f 0.45 (4:1

hexanes:EtOAc); $[\alpha]^{24}_{D}$ –30.6° (*c* 0.85, $CHCl_3$; for *S* enantiomer at 98% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{16}H_{26}O]^+$, 234.1984; found, 234.1989.



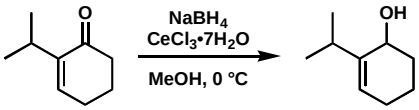
(±)-SI2 *SI3*

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_2Cl_2 (1 mL) at 23 °C was added Dess-Martin periodinane[xv] (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.[xvi]



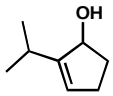
(±)-2-Isobutoxycyclohex-2-enol ((±)-SI4, Table 12, entry 4) and 2-Isopropylcyclohex-2-enone (SI6). To a solution of isopropylmagnesium chloride (2.0 M in Et_2O, 35.7 mL, 71.3 mmol, 2.0 equiv) in Et_2O (95 mL) was added a solution of 2-isobutoxycyclohex-2-enone[xvii] (6.0 g, 35.7 mmol, 1.0 equiv) in Et_2O (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_4Cl (aq, 50 mL), H_2O (50 mL), and crushed ice (50 g). After the ice melted, the phases were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic extracts were dried over $MgSO_4$ and filtered, and the filtrate was concentrated under reduced pressure. Purification by flash chromatography (194:5:1 hexanes:EtOAc:Et_3N) 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.[xviii] To a solution of (±)-**SI5** (1.13 g, 5.33 mmol, 1.0 equiv) in THF (53 mL) was added conc. H_2SO_4 (400 μL). After 30 min, the reaction was quenched by slow addition of sat. $NaHCO_3$ (aq, 40 mL). The mixture was allowed to stir 20 min (until bubbling ceased) and then was extracted with Et_2O (3 x 40 mL). The combined organic extracts were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. To this crude α-hydroxyketone in CH_2Cl_2 (53 mL) was added pyridine (2.15 mL, 2.11 g, 26.6 mmol, 5.0 equiv)

and $SOCl_2$ (777 μL, 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_2O (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$ 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 (±)-**SI5**) as a slightly yellow oil. The characterization data for **SI6** matched the data in the literature.[xix]



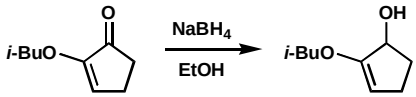
General Procedure for the Reduction of Enones: (±)-2-Isopropylcyclohex-2-enol ((±)-SI7, Table 12, entry 3).[xx] To a solution of enone **SI6** (783 mg, 5.66 mmol, 1.0 equiv) in MeOH (57 mL) at 0 °C was added $CeCl_3•7H_2O$ (2.32 g, 6.23 mmol, 1.1 equiv). After allowing the solid to dissolve, $NaBH_4$ (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_2O (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 $MgSO_4$ 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_f 0.40 (7:3 hexanes:EtOAc); $[\alpha]^{25}_D$ –24.6° (*c* 1.8, $CHCl_3$; for *S* enantiomer at 96% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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);

^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_9H_{16}O]^+$, 140.1201; found, 140.1198.



(±)-SI8

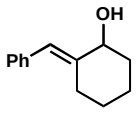
(±)-2-Isopropylcyclopent-2-enol ((±)-SI8, Table 12, entry 6). Prepared as for (±)-**SI7** from 2-isopropylcyclopent-2-enone[xxi] (2.48 g, 20.0 mmol) to afford, after flash chromatography (94:5:1 hexanes:EtOAc:Et_3N), (±)-**SI8** (1.08 g, 43% yield) as a slightly yellow oil. The characterization data matched the data in the literature.[xxii] $[\alpha]^{24}_D$ –27.5° (*c* 0.48, $CHCl_3$; for *S* enantiomer at 92% ee).



(±)-SI9

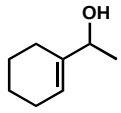
(±)-2-Isobutoxycyclopent-2-enol ((±)-SI9, Table 12, entries 7-8). To a solution of 2-isobutoxycyclopent-2-enone[xxi] (1.54 g, 10.0 mmol, 1.0 equiv) in EtOH (absolute, 100 mL) was added $NaBH_4$ (1.14 g, 30.0 mmol, 3.0 equiv). After 2.5 h at 23 °C, the solvent was removed under reduced pressure and H_2O (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_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (96:3:1 hexanes:EtOAc:Et_3N) to afford (±)-**SI9** (688 mg, 44% yield) as a colorless oil: R_f 0.46 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) d 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^{-1}; HRMS-FAB (m/z): $[M]^+$ calcd for $[C_9H_{16}O_2]^+$, 156.1150; found, 156.1152.



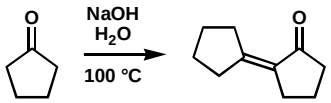
(±)-SI10

(±)-(*E*)-2-Benzylidenecyclohexanol ((±)-SI10, Table 12, entries 9-10). Prepared as for (±)-**SI7** from (*E*)-2-benzylidenecyclohexanone[xxiii] (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.[xxiv] $[\alpha]^{25}_D$ –36.0° (*c* 1.2, $CHCl_3$; for *S* enantiomer at 96% ee) [lit.[xxv] $[\alpha]^{20}_D$ –35.2° (*c* 1.2, $CHCl_3$; *S* enantiomer)].



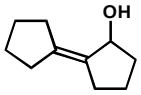
(±)-SI11

(±)-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.[xxvi] $[\alpha]^{25}_D$ –12.1° (*c* 0.75, $CHCl_3$; for *S* enantiomer at 91% ee) [lit.[xxvii] $[\alpha]_D$ –11.2° (*c* 0.36, $CHCl_3$; *S* enantiomer)].



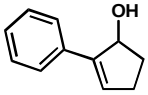
SI12

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_2O (3 x 100 mL). The combined organic extracts were dried over $MgSO_4$ 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.[xxviii]



(±)-SI13

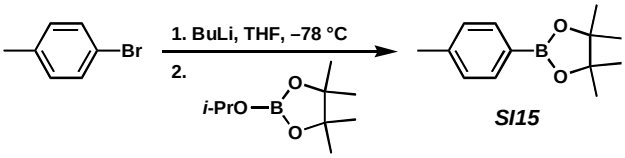
(±)-2-Cyclopentylidenecyclopentanol ((±)-SI13, Table 12, entry 16). Prepared as for (±)-**SI7** from **SI12** (1.10 g, 7.32 mmol) to afford, after flash chromatography (9:1 hexanes:EtOAc), (±)-**SI13** (881 mg, 79% yield) as a white solid. The characterization data matched the data in the literature.[xxix] $[\alpha]^{26}_{D}$ +85.3° (*c* 0.99, $CHCl_3$; for *S* enantiomer at 94% ee).



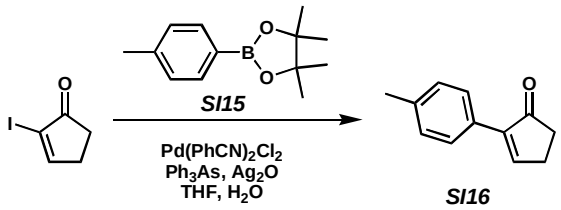
(±)-SI14

(±)-2-Phenylcyclopent-2-enol ((±)-SI14, Table 13, entries 1-3). Prepared as for (±)-**SI7** from 2-phenylcyclopent-2-enone[xxx,xxxi] (218 mg, 1.38 mmol) to afford, after flash chromatography

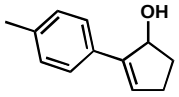
(9:1→4:1→7:3 hexanes:EtOAc), **SI14** (196 mg, 89% yield) as a white solid. Characterization data have been previously reported.[xxxii]



General Procedure for the Preparation of Boronate Esters: 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (SI15).[xxxiii] A solution of 4-bromotoluene (1.23 mL, 1.71 g, 10.0 mmol, 1 equiv) in THF (67 mL) was cooled to –78 °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 °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 °C with sat. NH_4Cl (aq, 35 mL) and H_2O (10 mL). After warming to 23 °C, the biphasic mixture was extracted with Et_2O (3 x 60 mL). The combined organic extracts were washed with brine (30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3:1 hexanes:EtOAc:Et_3N) 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.[xxxiv]

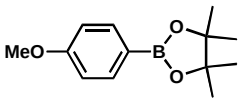


General Procedure for the Arylation of 2-Iodoenones: 2-(4-Tolyl)cyclopent-2-enone (SI16).[xxx] 2-Iodocyclopent-2-enone[xxxv] (1.46 g, 7.0 mmol, 1.0 equiv), boronic ester **SI15** (1.83 g, 8.4 mmol, 1.2 equiv), Ag_2O (2.60 g, 11.2 mmol, 1.6 equiv), Ph_3As (129 mg, 0.42 mmol, 0.06 equiv), and dichlorobis(benzonitrile)palladium(II) (81 mg, 0.21 mmol, 0.03 equiv) were added to a solution of THF (18 mL) and H_2O (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.[xxxvi]



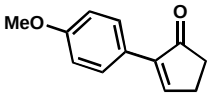
(±)-SI17

(±)-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.[xxxii]



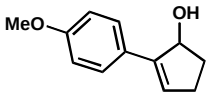
SI18

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_3N), **SI18** (2.25 g, 80% yield) as a slightly yellow oil. The characterization data matched the data in the literature.[xxxiv]



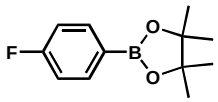
SI19

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.[xxxvi]



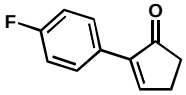
(±)-SI20

(±)-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.[xxxii]



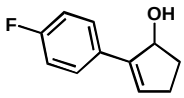
SI21

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_3N), **SI21** (2.24 g, 84% yield) as a colorless oil: R_f 0.49 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.93 (m, 2H), 6.78 (m, 2H), 1.05 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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; ^{19}F NMR (282 MHz, $CDCl_3$) *d* -108.4; IR (thin film/NaCl): 2979, 1603, 1400, 1362, 1144, 1088 cm^{-1}; HRMS-EI (*m/z*): $[M]^+$ calcd for $[C_{12}H_{16}BFO_2]^+$, 222.1227; found, 222.1236.



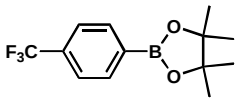
SI22

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_f 0.30 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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; ^{19}F NMR (282 MHz, $CDCl_3$) *d* -114.1; IR (thin film/NaCl): 1701, 1507, 1224, 834 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{11}H_9FO]^+$, 176.0637; found, 176.0631.



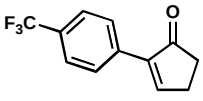
(±)-SI23

(±)-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); $[\alpha]^{25}_{D}$ +12.8° (*c* 2.2, $CHCl_3$; for *S* enantiomer at >99% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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}F NMR (282 MHz, $CDCl_3$) *d* -115.8; IR (thin film/NaCl): 3218, 1510, 1237, 1050, 834 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{11}H_{11}FO]^+$, 178.0794; found, 178.0786.



SI24

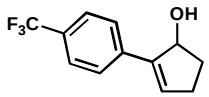
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride (SI24). Prepared as for **SI15** to afford, after flash chromatography (17:3:1 hexanes:EtOAc:Et_3N), **SI24** (3.13 g, 96% yield) as an off-white solid. The characterization data matched the data in the literature.[xxxvii]



SI25

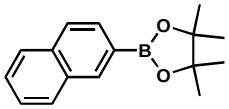
2-(4-Trifluoromethylphenyl)cyclopent-2-enone (SI25). Prepared as for **SI16** from **SI24** to afford, after flash chromatography (9:1 hexanes:EtOAc), **SI25** (1.14 g, 84% yield) as a white

solid: R_f 0.37 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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}F NMR (282 MHz, $CDCl_3$) *d* -63.7; IR (thin film/NaCl): 3066, 1692, 1332, 1112, 847 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{12}H_9F_3O]^+$, 226.0606; found, 226.0608.



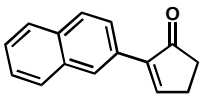
(±)-SI26

(±)-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.[xxxii]



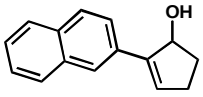
SI27

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_3N), **SI27** (2.87 g, 94% yield) as an off-white solid. The characterization data matched the data in the literature.[xxxiv]



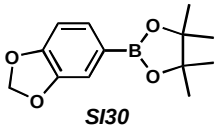
SI28

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_f 0.33 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{15}H_{12}O]^+$, 208.0888; found, 208.0889.



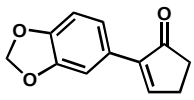
(±)-SI29

(±)-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.[xxxii]



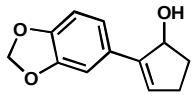
SI30

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_3N), **SI30** (2.43 g, 99% yield) as an off-white solid. The characterization data matched the data in the literature.[xxxviii]



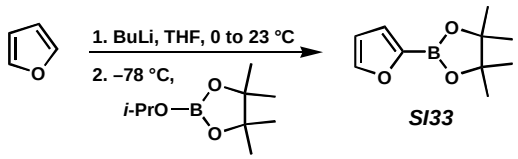
SI31

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_f 0.30 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{12}H_{10}O_3]^+$, 202.0630; found, 202.0623.



(±)-SI32

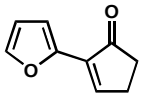
(±)-2-(Benzo[1,3]dioxol-5-yl)cyclopent-2-enol ((±)-SI32, Table 13, entries 19-21). Prepared as for (±)-**SI7** from **SI31** (1.21 g, 6.00 mmol) to afford, after flash chromatography (9:1→17:3→4:1 hexanes:EtOAc), (±)-**SI32** (1.03 g, 84% yield) as a white solid. Characterization data have been previously reported.[xxxii]



SI33

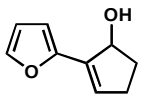
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-furan (SI33). A solution of furan (1.75 mL, 1.63 g, 24.0 mmol, 1.2 equiv) in THF (120 mL) was cooled to 0 °C. A solution of *n*-butyllithium (2.26 M in hexanes, 8.84 mL, 20.0 mmol, 1.0 equiv) was added dropwise. The reaction was allowed to stir 30 min at 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_4Cl (aq, 50 mL) and H_2O (10 mL). The mixture was extracted with Et_2O (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ 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.[xxxix]



SI34

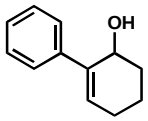
2-(2-Furyl)cyclopent-2-enone (SI34). Prepared as for **SI16** from **SI33** to afford, after flash chromatography (19:1→17:3 hexanes:EtOAc), **SI34** (1.09 g, 55% yield) as an off-white solid: R_f 0.51 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.79 (t, *J* = 3.1 Hz, 1H), 7.41 (d, *J* = 1.7 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_9H_8O_2]^+$, 148.0524; found, 148.0521.



(±)-SI35

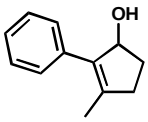
(±)-2-(2-Furyl)cyclopent-2-enol ((±)-SI35, Table 13, entries 22-24). Prepared as for (±)-**SI7** from **SI34** (961 mg, 6.49 mmol) to afford, after flash chromatography (19:1→9:1→4:1

hexanes:EtOAc), (±)-**SI35** (793 mg, 81% yield) as an off-white solid. Characterization data have been previously reported.[xxxii]



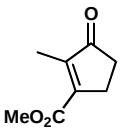
(±)-SI36

(±)-2-Phenylcyclohex-2-enol ((±)-SI36, Table 13, entries 25-27). Prepared as for (±)-**SI7** from 2-phenylcyclohex-2-enone[xxx] (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.[xxxii,xl]



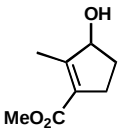
(±)-38

(±)-2-Phenyl-3-methylcyclopent-2-enol ((±)-38, Table 14, entries 1-3). Prepared as for (±)-**SI7** from 2-phenyl-3-methylcyclopent-2-enone[xli] (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.[xxxii]



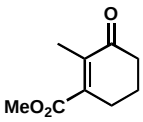
SI37

Methyl 2-methyl-3-oxocyclopent-1-enecarboxylate (SI37). Prepared according to the procedure of Kuethe:[xlii] R_f 0.26 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 209.9, 166.1, 154.4, 147.7, 52.3, 34.1, 26.6, 10.0; IR (thin film/NaCl): 1713, 1438, 1226, 1076 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_8H_{10}O_3]^+$, 154.0630; found, 154.0626.



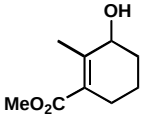
(±)-SI38

(±)-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); $[\alpha]^{25}_D$ –57.0° (*c* 0.82, $CHCl_3$; for *S* enantiomer at >99% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 167.0, 155.2, 128.9, 81.2, 51.4, 32.2, 30.4, 36.9, 13.5; IR (thin film/NaCl): 3419, 2951, 1715, 1436, 1220, 1054 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_8H_{12}O_3]^+$, 156.0787; found, 156.0780.



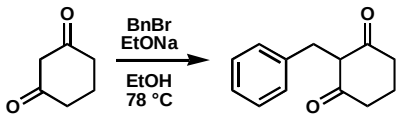
SI39

Methyl 2-methyl-3-oxocyclohex-1-enecarboxylate (SI39). Prepared according to the procedure of Kuethe:[xlii] R_f 0.24 (4:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_9H_{12}O_3]^+$, 168.0787; found, 168.0786.



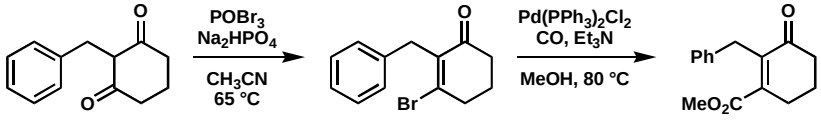
(±)-SI40

(±)-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); $[\alpha]^{25}_D$ –72.3° (*c* 0.95, $CHCl_3$; for *S* enantiomer at 97% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_9H_{14}O_3]^+$, 170.0943; found, 170.0938.



SI41

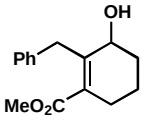
2-Benzylcyclohexane-1,3-dione (SI41). Prepared by modification of a procedure from Hewett.[xliii] Na (3.45 g, 150 mmol, 1.5 equiv) was added to EtOH (absolute, 200 mL). After all of the metal dissolved, cyclohexane-1,3-dione (11.2 g, 100 mmol, 1.0 equiv) was added, followed by benzyl bromide (23.8 mL, 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_2O (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_2SO_4. 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.[xliv]



SI41 *SI42* *SI43*

Methyl 2-benzyl-3-oxocyclohex-1-enecarboxylate (SI43). Prepared according to the procedure of Kuethe.[xlii] To a mixture of **SI41** (2.02 g, 10.0 mmol, 1.0 equiv) and Na_2HPO_4 (710 mg, 5.0 mmol, 0.5 equiv) in CH_3CN (15 mL) was added a solution of $POBr_3$ (2.15 g, 7.5 mmol, 0.75 equiv) in CH_3CN (5 mL). The reaction was heated to 65 °C for 24 h. After cooling to 23 °C, H_2O (6 mL) was added slowly to quench the reaction. After evaporation of CH_3CN under reduced pressure, H_2O (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 $MgSO_4$ and filtered. The

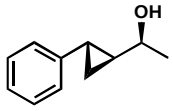
filtrate was concentrated under reduced pressure and purified by flash chromatography (9:1 ® 17:3 hexanes:Et_2O) to afford 2-benzyl-3-bromocyclohex-2-enone (**SI42**). To a solution of this bromide in MeOH (12.5 mL) was added dichlorobis(triphenylphosphine)palladium(II) (132 mg, 0.19 mmol, 0.03 equiv) followed by Et_3N (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_2O (70 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:Et_2O) to afford **SI43** (1.42 g, 58% yield from **SI41**) of an off-white solid: R_f 0.45 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{15}H_{16}O_3]^+$, 244.1100; found, 244.1100.



(±)-SI44

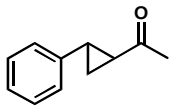
(±)-Methyl 3-hydroxy-2-benzylcyclohex-1-enecarboxylate ((±)-SI44, Table 14, entry 13). Prepared as for (±)-**SI7** from **SI43** (2.02 g, 8.3 mmol) to afford, after flash chromatography (3:2 hexanes:Et_2O), (±)-**SI44** (1.42 g, 70% yield) as a colorless oil: R_f 0.29 (7:3 hexanes:EtOAc); $[\alpha]^{24}_D$ –226.3° (*c* 1.83, $CHCl_3$; for *S* enantiomer at 96% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75

MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M]^+$ calcd for $[C_{15}H_{18}O_3]^+$, 246.1256; found, 246.1251.



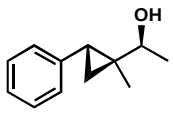
(±)-SI45

(±)-*syn,trans*-1-(2-Phenylcyclopropyl)ethanol ((±)-SI45, Table 15, entries 4-6). Prepared by the method of Charette.[xlv] The characterization data matched the data in the literature.[xlvi] $[\alpha]^{24}_D$ +44.1° (*c* 1.1, $CHCl_3$; for (1*S*, 1'*S*, 2'*S*) enantiomer at 90% ee).



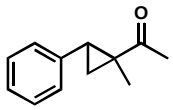
(±)-16

(±)-*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.[xlvii] $[\alpha]^{24}_D$ –275.5° (*c* 0.59, $CHCl_3$; for (1'*R*, 2'*R*) enantiomer at 57% ee) [lit.[xlvii] $[\alpha]^{20}_D$ +116.2° (*c* 0.785, $CHCl_3$; for (1'*S*, 2'*S*) enantiomer)].



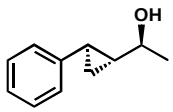
(±)-SI46

(±)-*syn,trans*-1-(1-Methyl-2-phenylcyclopropyl)ethanol ((±)-SI46, Table 15, entries 7-8). Prepared by the method of Charette.[xlv] The characterization data matched the data in the literature. $[\alpha]^{24}_D$ +2.1° (*c* 1.5, $CHCl_3$; for (1*S*, 1'*S*, 2'*R*) enantiomer at 89% ee).



(±)-17

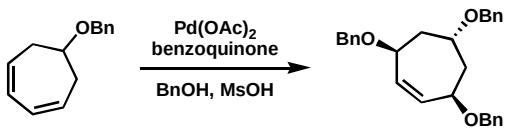
(±)-*trans*-1-(1-Methyl-2-phenylcyclopropyl)ethanone ((±)-17). Prepared as for **SI3** from (±)-**SI46** (17.6 mg, 0.10 mmol) to afford (±)-**17** (6.2 mg, 36% yield) as a colorless oil. The characterization data matched the data in the literature.[xlviii] $[\alpha]^{25}_{D}$ –152.1° (*c* 1.59, abs.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



(±)-SI47

(±)-*anti,trans*-1-(2-Phenylcyclopropyl)ethanol ((±)-SI47, Table 15, entries 9-11). Prepared by the method of Charette.[xlix] The characterization data matched the data in the literature.[l] $[\alpha]^{24}_{D}$ –60.1° (*c* 1.0, $CHCl_3$; for (1*S*, 1'*R*, 2'*R*) enantiomer at 94% ee) [lit.[l] $[\alpha]_D$ +64.2° (*c* 1.0, $CHCl_3$; for (1*R*, 1'*S*, 2'*S*) enantiomer)].

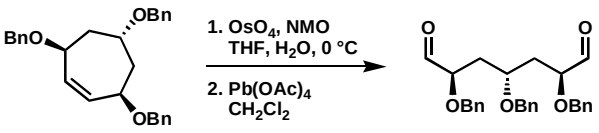
***meso*-Diol Syntheses, Resolutions, and Data**



45

Cycloheptene 45. To a stirred slurry of $Pd(OAc)_2$ (35.2 mg, 0.16 mmol, 0.08 equiv) in benzyl alcohol (11 mL) was added methanesulfonic acid (20 μL, 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

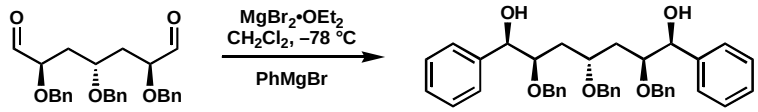
6-benzyloxycyclohepta-1,3-diene[li] (400 mg, 2.0 mmol, 1.0 equiv) in benzyl alcohol (3 mL) by syringe pump over 4 h. Once the addition was complete, stirring was continued for 3 h more before the addition of more benzoquinone (216 mg, 2.0 mmol, 2.0 equiv). The reaction was warmed to 40 °C for 5 h, then cooled to room temperature. The reaction mixture was diluted with H_2O (100 mL) and extracted with 2:1 Et_2O: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 $NaBH_4$ were added to the biphasic mixture to remove color. The organic extracts were dried over $MgSO_4$ 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_2O) to provide **45** (547 mg, 66% yield) as a colorless oil: R_f 0.84 (1:1 Et_2O:pentane); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-EI (*m/z*): $[M+H]^+$ calcd for $[C_{28}H_{31}O_3]^+$, 415.2273; found, 415.2280.



45 *46*

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_4 (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. $Na_2S_2O_3$ (aq, 10 mL) was added to the reaction, and the biphasic mixture was stirred vigorously for 15 min. The

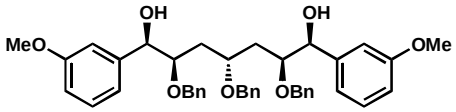
mixture was extracted with Et_2O (4 x 10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:EtOAc) to afford a diol intermediate (635 mg, 85% yield) as a 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_2Cl_2 (10 mL) was added $Pb(OAc)_4$ (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_f 0.31 (1:1 Et_2O:pentane); ^1H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-EI (*m/z*): $[M]^+$ calcd for $[C_{20}H_{30}O_5]^+$, 446.2093; found, 446.2093.



46 ***47a***

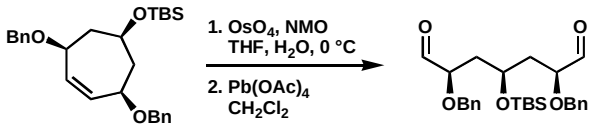
General Procedure for the Addition of Aryl Grignards to Dialdehydes: *meso*-Diol 47a. To a solution of dialdehyde **46** (310 mg, 0.69 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at 0 °C was added anhydrous MgBr•OEt_2 (427 mg, 1.66 mmol, 2.4 equiv). The milky solution was stirred at 0 °C for 30 min, then cooled to –78 °C before addition of a solution of phenylmagnesium bromide (1.0 M in Et_2O, 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_4Cl (aq, 5 mL) and H_2O (5 mL). The phases

were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were washed with H_2O (2 x 10 mL) and brine (10 mL), dried over $MgSO_4$, 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_f 0.37 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{40}H_{43}O_5]^+$, 603.3110; found, 603.3124.



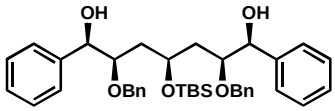
47b

***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_2O, 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_f 0.10 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 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^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{42}H_{47}O_7]^+$, 663.3322; found, 663.3342.



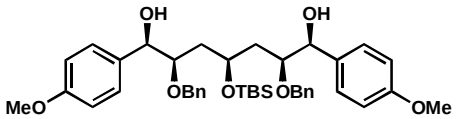
48 *49*

Dialdehyde 49. To a solution of *syn*,*syn*-3,7-bis(benzyloxy)-5-(*tert*-butyldimethylsiloxy)cyclohept-1-ene[lii] (**48**, 2.60 g, 5.92 mmol, 1.0 equiv) in THF (26 mL) and water (6 mL) was added OsO_4 (103 mg, 0.41 mmol, 0.07 equiv) and 4-methylmorpholine-*N*-oxide (1.73 g, 14.81 mmol, 2.5 equiv). After 8 h, sat. $Na_2S_2O_3$ (aq, 50 mL) was added to the reaction, and the biphasic mixture was stirred vigorously for 15 min. The mixture was extracted with Et_2O (4 x 50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (17:3 hexanes:EtOAc) to afford a diol intermediate (2.42 g, 86% yield) as a waxy white solid, which was used directly in the next step. To a solution of the diol (415 mg, 0.88 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added $Pb(OAc)_4$ (429 mg, 0.97 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 dialdehyde **49** (395 mg, 96% yield) as a clear oil: R_f 0.18 (9:1 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, J = 1.5 Hz, 2H), 7.51-7.22 (comp. m, 10H), 4.68 (d, J = 11.7 Hz, 2H), 4.51 (d, J = 11.7, 2H), 4.19 (ddd, J = 11.6, 6.0, 5.9 Hz, 1H), 3.95 (dd, J = 6.6, 2.1 Hz, 2H), 1.98-1.75 (comp. m, 4H), 0.88 (s, 9H), 0.75 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 137.4, 128.8, 128.4, 80.5, 72.8, 65.4, 37.0, 26.1, 18.2, -4.2; IR (thin film/NaCl) 2930, 1732, 1101 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{25}H_{39}O_5Si]^+$, 471.2567; found, 471.2581.



50a

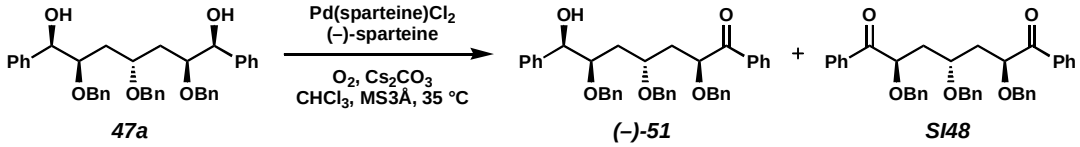
***meso*-Diol 50a.** Prepared as for **47a** from **49** (393 mg, 0.84 mmol, 1.0 equiv) to afford, after flash chromatography (17:3 hexanes:EtOAc), *meso*-diol **50a** (435 mg, 98% yield) as a clear oil: R_f 0.32 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 7.54-7.06 (comp. m, 20H), 4.57 (dd, *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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{39}H_{51}O_5Si]^+$, 627.3506; found, 627.3503.



50b

***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 CH_2Cl_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}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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

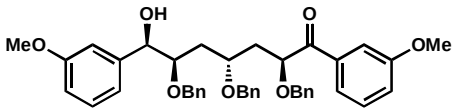
(thin film/NaCl) 3453, 2931, 1102 cm^{-1}; HRMS-ES (*m/z*): $[M+Na]^+$ calcd for $[C_{41}H_{54}O_7NaSi]^+$, 709.3537; found, 709.3522.



47a ***(–)-51*** ***SI48***

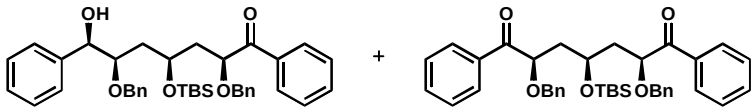
General Procedure for the Desymmetrization of *meso*-Diols: Hydroxyketone (–)-51. To an oven dried reaction tube with stir bar was added 3Å molecular sieves (500 mg). After cooling, Pd(sparteine)Cl_2 (41.2 mg, 0.10 mmol, 0.10 equiv), followed by chloroform (2 mL, ACS reagent grade, stabilized with amylenes) and then (–)-sparteine (32.2 μL, 32.8 mg, 0.14 mmol, 0.14 equiv) were added. The reaction tube was cooled to –78 °C, then vacuum evacuated and purged with O_2 (3x). The reaction was warmed to 35 °C. Finely powdered Cs_2CO_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 O_2 atmosphere at 35 °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); $[\alpha]_D^{20}$ –78.1° (*c* 1.0, $CHCl_3$; for (2*S*, 4*R*, 6*R*, 7*R*) enantiomer at 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 8.01 (d, *J* = 7.8 Hz, 2H), 7.57 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.42 (dd, *J* = 7.1, 6.9 Hz, 2H), 7.38-7.14 (comp. m, 20H), 4.92 (d, *J* = 7.8 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{40}H_{41}O_5]^+$, 601.2954; found, 601.2953. Also recovered was diketone **SI48** (21 mg, 7% yield) as a clear oil: R_f 0.62 (7:3 hexanes:EtOAc); ^1H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{40}H_{39}O_5]^+$, 599.2797; found, 599.2826.



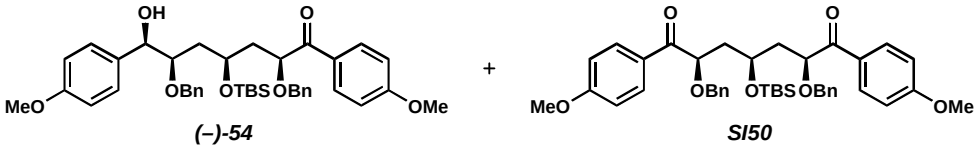
(–)-52

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); $[\alpha]_D^{20}$ –56.8° (*c* 1.0, $CDCl_3$; for (2*S*, 4*R*, 6*R*, 7*R*) enantiomer at 99% ee); ^1H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{42}H_{45}O_7]^+$, 661.3165; found, 661.3157.



(–)-53 *SI49*

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); $[\alpha]_D^{20}$ –64.1° (*c* 1.0, $CHCl_3$; for (2*S*, 4*S*, 6*R*, 7*R*) enantiomer at 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{39}H_{49}O_5SI]$, 625.3349; found, 625.3345. Also recovered was diketone **SI49** (16 mg, 5% yield) as an oil: R_f 0.39 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 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}C NMR (75 MHz, $CDCl_3$) *d* 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 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{39}H_{47}O_5Si]^+$, 623.3193; found, 623.3210.



(–)-54 *SI50*

Hydroxyketone (–)-54. Prepared as for (–)-**51** from **50b** (343 mg, 0.50 mmol) to afford hydroxyketone (–)-**54** (291 mg, 85% yield, 99% ee) as a slightly yellow oil: R_f 0.12 (7:3 hexanes:EtOAc); $[\alpha]_D^{20}$ –74.9° (*c* 1.0, $CDCl_3$; for (2*S*, 4*S*, 6*R*, 7*R*) enantiomer at 99% ee); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 8.02 (m, 2H), 7.34-7.12 (comp. m, 10H), 6.87 (d, *J* = 9.3 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.81 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.57-4.22 (comp. m, 4H), 3.98-3.61 (comp. m, 9H), 2.05-1.67 (comp. m, 4H), 0.86 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 198.7, 163.9, 159.3, 138.4, 137.8, 133.9, 131.4, 128.6, 128.6, 128.6, 128.1, 128.0, 127.9, 114.0, 113.9, 81.1, 78.6, 75.9, 73.1, 71.9, 67.3, 55.7, 55.5, 39.7, 38.7, 26.2, 18.2, -4.3; IR (thin film/NaCl) 3492, 2929, 1680, 1600, 1251 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{41}H_{53}O_7Si]^+$, 685.3561; found, 685.3556. Also recovered was diketone **SI50** (17 mg, 5% yield) as a slightly yellow oil: R_f 0.18 (7:3 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) *d* 8.02 (d, *J* = 8.4 Hz, 4H), 7.34-7.12 (comp. m, 10H), 6.87 (d, *J* = 8.4 Hz, 4H), 4.98 (dd, *J* = 9.0, 3.6 Hz, 2H), 4.57 (d, *J* = 11.7 Hz, 2H), 4.32 (d, *J* = 11.4 Hz, 2H), 4.29-4.22 (m, 1H), 3.84 (s, 6H), 2.19-1.90 (comp. m, 4H), 0.84 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) *d* 198.9, 163.9, 137.7, 131.4, 128.5, 128.4, 128.3, 128.0, 114.0, 77.8, 71.7, 67.0, 55.7, 38.7, 26.0, 18.2, -4.4; IR (thin film/NaCl) 2930, 1681, 1599, 1257 cm^{-1}; HRMS-FAB (*m/z*): $[M+H]^+$ calcd for $[C_{41}H_{51}O_7Si]^+$, 683.3404; found, 683.3433.

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 ^{1}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

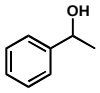
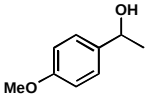
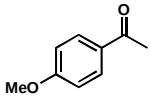
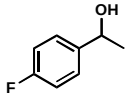
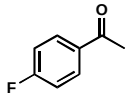
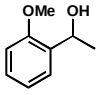
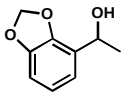
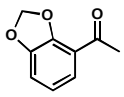
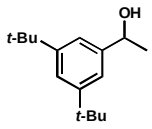
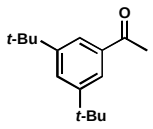
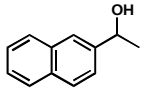
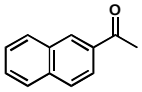
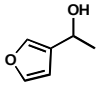
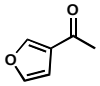
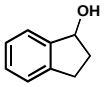
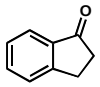
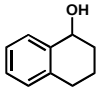
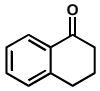
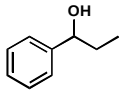
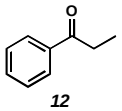
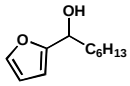
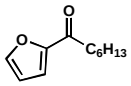
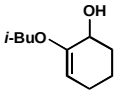
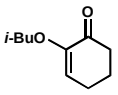
entry	alcohol	ketone	GC conditions	alcohol retention time (min)	ketone retention time (min)
1	 *(±)-3*	 *4*	100 °C, 5 min; Ramp 13 °C/min	10.6	8.9
2	 *(±)-6*	 *7*	100 °C, 5 min; Ramp 13 °C/min	14.4	13.9
3			70 °C, 15 min; Ramp 7 °C/min	29.4	25.5
4			100 °C, 5 min; Ramp 13 °C/min	13.4	12.6
5	 *(±)-SI1*		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	–[a]
9			50 °C Ramp 3 °C/min	22.5	–[a]
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

[a] Ketone is volatile and evaporates on concentration of resolution aliquots.

Table S1 (continued).

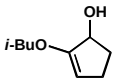
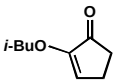
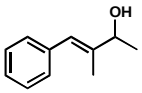
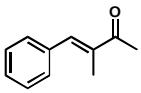
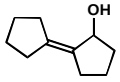
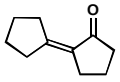
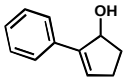
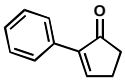
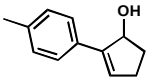
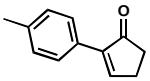
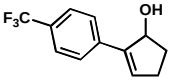
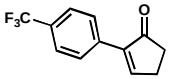
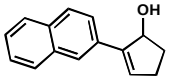
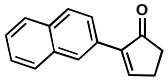
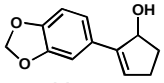
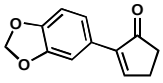
17			70 °C, 15 min; Ramp 7 °C/min	28.6	30.6
18	 *(±)-SI8*		100 °C, 5 min; Ramp 13 °C/min	8.0	7.4
19	 *(±)-SI9*		100 °C, 5 min; Ramp 13 °C/min	10.3	11.8
20			100 °C, 5 min; Ramp 13 °C/min	14.1	13.1
21	 *(±)-SI11*		100 °C, 5 min; Ramp 13 °C/min	9.3	8.7
22	 *(±)-SI13*	 *SI12*	70 °C, 15 min; Ramp 7 °C/min	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).

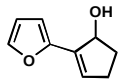
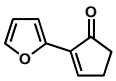
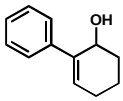
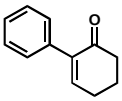
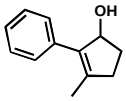
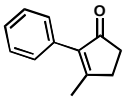
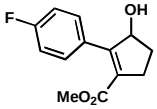
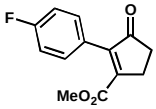
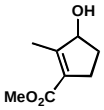
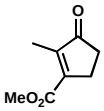
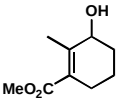
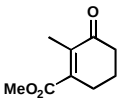
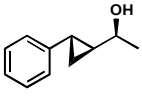
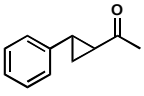
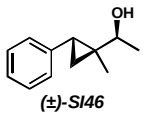
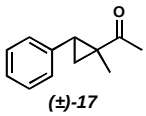
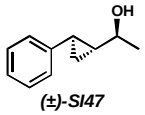
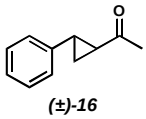
28	 ***(±)-SI35***	 ***SI34***	70 °C, 15 min; Ramp 7 °C/min	33.4	32.8
29	 ***(±)-SI36***		100 °C, 5 min; Ramp 13 °C/min to 240 °C 240 °C, 5 min	15.8	16.1
30	 ***(±)-38***		100 °C, 5 min; Ramp 13 °C/min to 240 °C 240 °C, 5 min	15.1	16.6
31	 ***(±)-36***		70 °C, 15 min; Ramp 13 °C/min to 240 °C 240 °C, 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

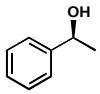
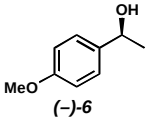
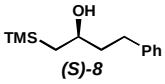
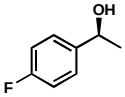
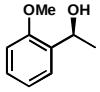
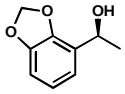
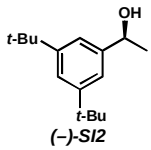
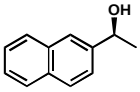
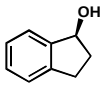
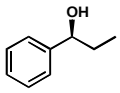
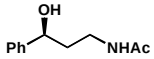
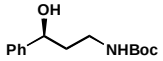
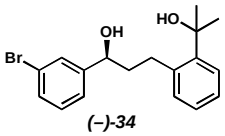
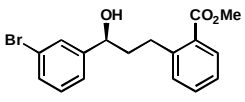
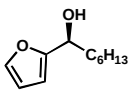
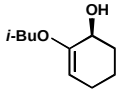
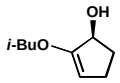
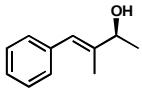
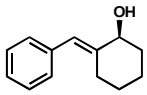
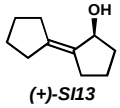
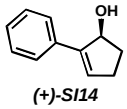
entry	alcohol (major enantiomer)	ee assay and column	assay conditions	major (*S*) enantiomer retention time (min)	minor (*R*) enantiomer retention time (min)
1	 *(–)-3*	HPLC OJ	4% *i*PrOH/hexanes	17.8	20.8
2	 *(–)-6*	HPLC OD-H	3% EtOH/hexanes	15.7	16.7
3	 *(S)-8*	HPLC OD-H	2% *i*PrOH/hexanes	15.6	12.3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

Table S2 (continued).

7	 *(–)-SI2*	HPLC AD	0.25% *i*PrOH/hexanes	16.8	15.1
8		HPLC OJ	4% *i*PrOH/hexanes	31.3	38.7
9[a]		HPLC OJ	4% EtOH/hexanes	16.0	19.0
10[a]		HPLC OJ	4% EtOH/hexanes	17.0	20.0
11		HPLC OB-H	4% *i*PrOH/hexanes	19.2	11.8
12		HPLC OB-H	3% *i*PrOH/hexanes	21.3	12.2
13	 *(–)-11*	HPLC OD-H	3% EtOH/hexanes	17.6	12.0
14[b]		HPLC AD	6% *i*PrOH/hexanes	23.8	27.9
15[b]	 *(–)-32*	HPLC OJ	8% *i*PrOH/hexanes	20.1	10.5
16[b]	 *(–)-34*	HPLC OJ	5% EtOH/hexanes	15.0	17.8
17		HPLC AD	5% EtOH/hexanes	17.1	15.8
18[c]		HPLC AD	2% EtOH/hexanes	12.3	15.8

[a] UV detection at 220 nm. [b] UV detection at 210 nm. [c] Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH_2Cl_2.

Table S2 (continued).

19[c]		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[c]		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*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

[c] Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH_2Cl_2.

Table S2 (continued).

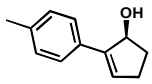
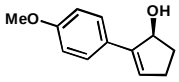
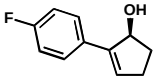
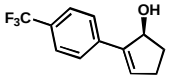
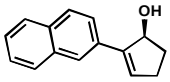
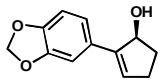
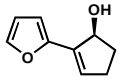
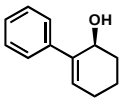
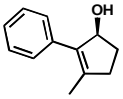
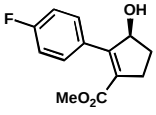
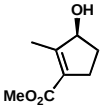
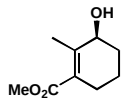
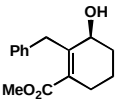
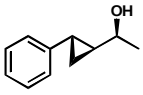
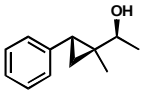
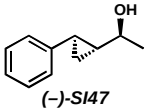
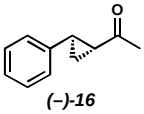
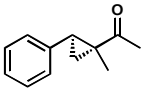
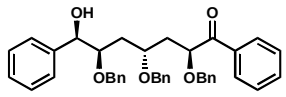
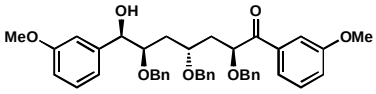
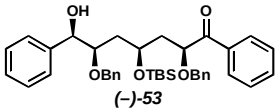
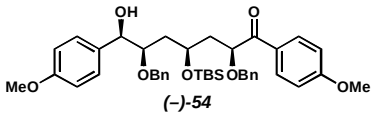
30	 *(+)-SI17*	HPLC OB-H	8% EtOH/hexanes	14.4	7.5
31	 *(+)-SI20*	HPLC AS	4% EtOH/hexanes	11.5	15.9
32	 *(+)-SI23*	HPLC OB-H	4% EtOH/hexanes	11.0	9.1
33	 *(+)-SI26*	HPLC OD-H	2% EtOH/hexanes	15.3	14.0
34	 *(+)-SI29*	HPLC AS	3% EtOH/hexanes	11.4	13.2
35	 *(+)-SI32*	HPLC OB-H	10% EtOH/hexanes	26.8	11.0
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*PrOH/hexanes	20.8	22.9
42	 *(–)-SI44*	HPLC OD-H	4% EtOH/hexanes	10.2	11.5
43[c]		HPLC OJ	1% EtOH/hexanes	12.0	13.2
44[c]	 *(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[d]	17.8
47	 *(+)-SI46*	HPLC OD-H	3% EtOH/hexanes	8.8[e]	10.1
48	 *(–)-SI47*	HPLC OD-H	2% EtOH/hexanes	20.7[f]	14.6
49	 *(–)-16*	HPLC OD-H	2% EtOH/hexanes	8.5[g]	7.9
50	 *(–)-17*	HPLC OD-H	3% EtOH/hexanes	7.5[h]	6.9

[c] Assayed as the 4-nitrobenzoate by treatment of the aliquot with 4-nitrobenzoyl chloride and 4-dimethylaminopyridine in CH_2Cl_2. [d] Retention time for the (1*S*, 1'*S*, 2'*S*) enantiomer (shown). [e] Retention time for the (1*S*, 1'*S*, 2'*R*) enantiomer (shown). [f] Retention time for the (1*S*, 1'*R*, 2'*R*) enantiomer (shown). [g] Retention time for the (1'*R*, 2'*R*) enantiomer (shown). [h] Retention time for the (1'*R*, 2'*S*) enantiomer (shown).

Table S2 (continued).

51	 *(–)-51*	HPLC OJ	6% *i*PrOH/hexanes	39.3[i]	29.9
52	 *(–)-52*	HPLC OB-H	4% *i*PrOH/hexanes	22.7[i]	20.1
53	 *(–)-53*	HPLC OJ	2% *i*PrOH/hexanes	22.7[j]	20.1
54	 *(–)-54*	HPLC OB-H	6% EtOH/hexanes	29.9[j]	24.5

[i] Retention time for the (2*S*, 4*R*, 6*R*, 7*R*) enantiomer (shown). [j] Retention time for the (2*S*, 4*S*, 6*R*, 7*R*) enantiomer (shown).

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