Supporting Information for:

Catalytic Enantioselective Decarboxylative Protonation

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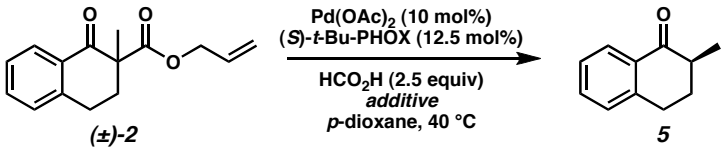
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. *p*-Dioxane was distilled over sodium prior to use unless specifically noted. Other solvents were dried by passage through an activated alumina column under argon. Brine solutions are saturated aqueous sodium chloride solutions. Palladium(II) acetate ($Pd(OAc)_2$) was purchased from Strem and used as received. (*S*)-*t*-Bu-PHOX was prepared by the method reported in our previous work.[1] Ketone starting materials, diallyl carbonate, alkyl halides, L-Selectride®, and Selectfluor™ were purchased from Aldrich and used as received. Sodium hydride (NaH) was purchased as a 60% dispersion in mineral oil from Acros and used as received. Formic acid (98%) was purchased from Fluka and used as received. Deuterated formic acid (HCO_2D and DCO_2H) were purchased from Cambridge Isotope Laboratories, Inc. and used as received. The HCO_2D (≥98% chemical purity) was from lot #PR-15324/06034FA1 and was assayed by the supplier as containing 99.6% isotopic enrichment and 4% D_2O. The DCO_2H (≥98% chemical purity) was from lot #I1-5333 and was assayed by the supplier as containing >98% isotopic enrichment and 1608 ppm H_2O. Molecular sieves were purchased from Aldrich as activated 5 μm powder and stored in a 120 °C drying oven until immediately prior to use unless otherwise noted; the 4Å molecular sieves (4ÅMS) used in this work were from batch #13128AD. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde, $KMnO_4$, or CAM staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralcel OD-H or Chiralpak AD column (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 254 nm, unless otherwise stated. Analytical chiral GC was performed with an Agilent 6850 GC utilizing a G-TA (30 m x 0.25 mm) column (1.0 mL/min carrier gas flow). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz and 75 MHz respectively), and are reported relative to Me_4Si (δ 0.0 ppm). ^{19}F NMR spectra were recorded on a Varian Mercury 300 spectrometer at 282 MHz, and are reported relative to the external standard F_3CCO_2H (δ -76.53 ppm). ^2H NMR spectra were recorded on a Varian Inova 500 spectrometer at 77 MHz, and are reported relative to Me_4Si (δ 0.0 ppm). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Data for ^{13}C, ^{19}F, and ^2H NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). Melting points were determined using a Thomas capillary melting point apparatus and the values reported are uncorrected. High resolution mass spectra were obtained from the Caltech Mass Spectral Facility.

Optimization of Reaction Conditions

Optimization reactions were carried out using the following sample procedure with variations as indicated in Tables SI 1 through SI 4.

Sample Procedure for Optimization Reactions:
In a 1 dram glass vial, a solution of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 0.10 equiv, 10 mol%) and (*S*)-*t*-Bu-PHOX (4.8 mg, 0.0125 mmol, 0.125 equiv, 12.5 mol%) in *p*-dioxane (1 mL, purchased from Aldrich and used as received) was stirred at 40 °C for 30 mins. To the solution was added oven dried powdered 3ÅMS (90 mg), followed immediately by a solution of HCO_2H (9.4 μL, 0.25 mmol, 2.5 equiv) in *p*-dioxane (1 mL) and a solution of (±)-**2** (24.4 mg, 0.10 mmol, 1.0 equiv) in *p*-dioxane (1 mL). The vial was then sealed with a teflon lined cap and stirred at 40 °C until TLC indicated complete consumption of the starting material (about 10 h). The reaction mixture was passed through a small plug of celite and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on SiO_2 using 10% Et_2O in pentane as the eluent. The ee of the product was determined to be 79% by chiral HPLC using a Chiracel OD-H column with 1% 2-propanol in hexanes as the eluent.

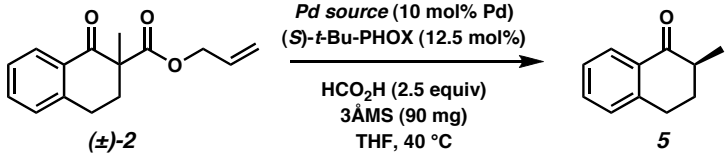
Table SI 1. Optimization of Additives.



Additive	ee of 5	Additive	ee of 5
Et_3N (1 equiv)[a]	7	Celite (90 mg)	39
None[a]	24	3ÅMS (90 mg)	79
Activated SiO_2 (90 mg)	33	4ÅMS (90 mg)	88
Activated carbon (90 mg)	8	4ÅMS (not oven dried, 90 mg)	67
$MgSO_4$ (5 equiv)	34	5ÅMS (90 mg)	85
$HC(OEt)_3$ (5 equiv)	30	13X MS (90 mg)	58

[a] Reaction performed with THF as solvent.

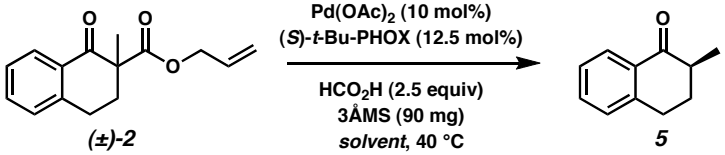
Table SI 2. Optimization of Palladium Source.



Pd source	ee of 5
$Pd(OAc)_2$	72
$[PdCl(allyl)]_2$	41
$Pd_2(dba)_3$	49
none	n/a[a]

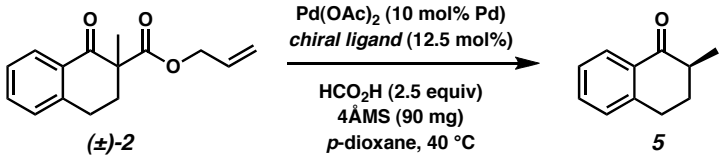
[a] No conversion observed.

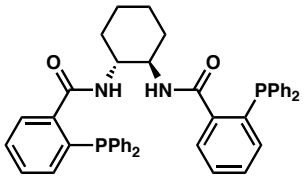
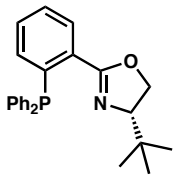
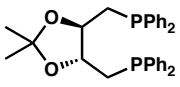
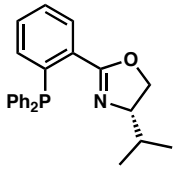
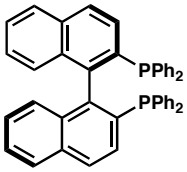
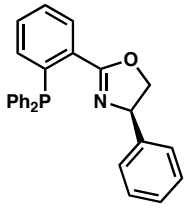
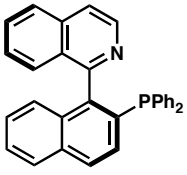
Table SI 3. Optimization of Solvent.



Solvent	ee of 5	Solvent	ee of 5
THF	72	Anisole	21
Tetrahydropyran	63	Benzene	39
p-Dioxane	79	Toluene	53
$H_3COCH_2CH_2OCH_3$	27	EtOAc	56
t-BuOMe	68	Pinacolone	4
(*i*-Pr)$_2$O	58		

Table SI 4. Optimization of Chiral Ligand.



Chiral Ligand	ee of 5	Chiral Ligand	ee of 5
 (*R,R*)-Trost Ligand	3[a]	 (*S*)-*t*-Bu-PHOX	88
 (*R,R*)-DIOP	3	 (*S*)-*i*-Pr-PHOX	87
 (*R*)-BINAP	-1	 (*R*)-Ph-PHOX	-65
 (*S*)-QUINAP	-20		

[a] The ee was measured after 72 hours at approximately 60% conversion.

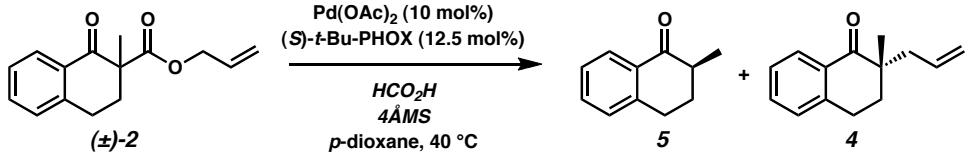
Optimization of Amount of Formic Acid and Molecular Sieves:

Optimization of amounts of HCO_2H and 4ÅMS was carried out using the following general procedure with the variations indicated in Table SI 5.

General Procedure:

Oven dried 4Å molecular sieves (4ÅMS) were placed in a 1 dram glass vial equipped with a magnetic stir bar, a screw cap, and a septum. The vial and 4ÅMS were thoroughly flame dried under vacuum and backfilled with dry argon gas. The flame drying procedure was carried out twice more, and then the vial cooled to ambient temperature (20 °C). To the cooled vial was added $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 0.10 equiv, 10 mol%), (*S*)-*t*-Bu-PHOX (4.8 mg, 0.0125 mmol, 0.125 equiv, 12.5 mol%), and freshly distilled *p*-dioxane (1.5 mL). The mixture was heated to 40 °C for 30 mins, at which point neat HCO_2H was added, followed immediately by addition of a solution of (±)-**2** (24.4 mg, 0.10 mmol, 1.0 equiv) in *p*-dioxane (1.5 mL). The reaction mixture was stirred at 40 °C until TLC indicated complete consumption of (±)-**2** (about 10 h). After cooling to ambient temperature, the reaction mixture was filtered through a pad of celite. The filtrate was concentrated by rotary evaporation and the residue purified by flash chromatography on SiO_2 using 10% Et_2O in pentane as eluent. The ee of the product was determined by chiral HPLC with a Chiracel OD-H column using 1% 2-propanol in hexanes as eluent. The ratio of **5**/**4** was determined by ^1H NMR integration.

Table SI 5. Optimization of Amount of Formic Acid and Molecular Sieves.



amount of 4ÅMS \ amount of HCO_2H (equiv)	2.5	3	3.5	4	4.5	5	5.5	6	8	10
ratio 5/4 — % ee of 5										
90 mg	n.d. 88% ee	82/18 90% ee	96/4 92% ee	100/0 90% ee	100/0 69% ee	100/0 46% ee				
135 mg	86/14 86% ee	61/39 82% ee	89/11 91% ee	90/10 92% ee	95/5 92% ee	99/1 93% ee	99/1 90% ee	100/0 86% ee		
180 mg				96/4 92% ee		95/5 91% ee		100/0 93% ee		
225 mg				83/17 92% ee		91/9 89% ee		96/4 93% ee	99/1 93% ee	100/0 69% ee
270 mg		54/46[a] 78% ee				93/7[b] 91% ee		91/9 92% ee	100/0 93% ee	100/0 92% ee

[a] Isolated **4** was found to be 86% ee; assay conditions available in ref 2. [b] Isolated **4** was found to be 87% ee; assay conditions available in ref 2.

Experimental Data:

Substrates were synthesized by the methods reported in our previous work,[2] unless otherwise stated.

Data for substrate compounds:

Substrates shown in Table 2, entries 1, 11, 12, and 14 were prepared in our previous work.[2]

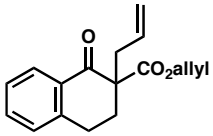
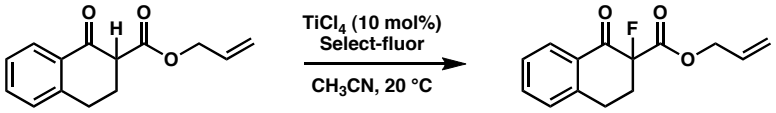


Table 2, Entry 2
Prepared using the diallyl carbonate method from 1-tetralone and allyl bromide. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 83% yield. R_f = 0.77 (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 1H), 7.47 (dd, J = 7.7, 7.4 Hz, 1H), 7.31 (dd, J = 7.7, 7.7 Hz, 1H), 7.21 (d, J = 7.4 Hz, 1H), 5.92-5.71 (comp. m, 2H), 5.21-5.06 (comp. m, 4H), 4.58 (app. d, J = 5.3 Hz, 1H), 4.58 (app. d, J = 5.6 Hz, 1H), 3.08 (ddd, J = 17.3, 10.1, 4.8 Hz, 1H), 2.93 (ddd, J = 17.3, 5.1, 4.8 Hz, 1H), 2.77 (app. ddd, J = 13.8, 7.2, 1.1 Hz, 1H), 2.70 (app. ddd, J = 13.8, 7.4, 1.1 Hz, 1H), 2.54 (ddd, J = 13.8, 5.1, 4.8 Hz, 1H), 2.16 (ddd, J = 14.1, 10.1, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 171.4, 143.3, 133.7, 133.5, 132.1, 131.7, 128.9, 128.2, 126.9, 119.2, 118.4, 65.9, 57.5, 38.7, 30.6, 25.9; IR (Neat Film NaCl) 3077, 2937, 1734, 1689, 1601, 1455, 1236, 1212, 1188, 922, 743 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{17}H_{18}O_3$ $[M]^+$: 270.1256, found 270.1249.



SI 1

Allyl 2-fluoro-1-tetralone-2-carboxylate (Table 2, Entry 3):
Neat $TiCl_4$ (45.6 µL, 0.42 mmol, 0.10 equiv, 10 mol%) was added to a 20 °C solution of **SI 1**[2] (1.00 g, 4.16 mmol, 1.0 equiv) in acetonitrile (40 mL), resulting in an immediate color change from pale yellow to dark orange-brown. After 5 min, Selectfluor™ (1.77 g, 4.99 mmol, 1.2 equiv) was added in one portion. The mixture was stirred vigorously at 20 °C for 2 h, during which time the dark orange-brown color faded to yellow. The reaction was quenched by addition of H_2O (120 mL). The aqueous phase was extracted with Et_2O (4 x 30 mL). The combined organic extracts were washed with brine (1 x 25 mL), dried over Na_2SO_4, filtered, and the filtrate concentrated *in vacuo* to a yellow oil. Purification by flash chromatography (SiO_2, 20% Et_2O in pentane) yielded the title compound as a colorless oil (879.9 mg, 85% yield). R_f = 0.41 (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 7.4, 7.4 Hz, 1H), 7.37 (dd, J = 7.7, 7.4 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 5.88 (dddd, J = 17.3, 10.4, 5.6, 5.1 Hz, 1H), 5.27 (dd, J = 17.3, 1.3 Hz, 1H), 5.24 (dd, J = 10.4, 1.1 Hz, 1H), 4.73 (app. ddd, J = 5.9, 2.1, 1.3 Hz, 1H), 4.73 (app. ddd, J = 5.9, 2.1, 1.3 Hz, 1H), 3.20 (ddd, J = 17.3, 6.4, 6.1 Hz, 1H), 3.08 (ddd, J = 17.3, 7.5, 5.1 Hz, 1H), 2.75 (dddd, $J_{H\text{-}H}$ = 7.4, 7.2, 6.4 Hz, $J_{H\text{-}F}$ = 26.3 Hz, 1H), 2.56 (dddd, $J_{H\text{-}H}$ = 7.2, 6.1, 5.3 Hz, $J_{H\text{-}F}$ = 21.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

188.6 ($J_{C\text{-}F}$ = 18.6 Hz), 167.2 ($J_{C\text{-}F}$ = 26.3 Hz), 143.2, 132.7, 130.9, 130.7, 128.9, 128.6 ($J_{C\text{-}F}$ = 0.9 Hz), 127.4, 119.4, 93.4 ($J_{C\text{-}F}$ = 194.5 Hz), 66.8, 32.0 ($J_{C\text{-}F}$ = 22.1 Hz), 25.0 ($J_{C\text{-}F}$ = 7.2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –165.2 (dd, $J_{F\text{-}H}$ = 24.5, 21.4 Hz, 1F); IR (Neat Film NaCl) 3075, 2945, 1765, 1696, 1602, 1457, 1312, 1277, 1228, 1187, 1138, 1087, 942, 913, 744 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{13}FO_3$ $[M]^+$: 248.0849, found 248.0860.

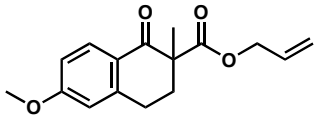


Table 2, Entry 4

Prepared using the diallyl carbonate method from 6-methoxy-1-tetralone and methyl iodide. Purified by flash chromatography (SiO_2, 5% Et_2O in pentane). 82% yield. R_f = 0.34 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.82 (dddd, *J* = 17.1, 10.4, 6.0, 5.2 Hz, 1H), 5.23-5.17 (m, 2H), 4.59 (m, 2H), 3.85 (s, 3H), 3.02 (ddd, *J* = 17.3, 9.6, 4.8 Hz, 1H), 2.89 (ddd, *J* = 17.0, 5.3, 5.3 Hz, 1H), 2.63 (ddd, *J* = 13.6, 5.1, 4.8 Hz, 1H), 2.05 (ddd, *J* = 13.8, 9.6, 5.1 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 173.0, 163.8, 145.8, 131.8, 130.7, 125.4, 118.2, 113.6, 112.6, 65.8, 55.6, 53.8, 34.1, 26.5, 20.8; IR (Neat Film NaCl) 2938, 1734, 1676, 1600, 1276, 1262, 1230, 1186, 1172, 1099, 978, 668 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{18}O_4$ $[M]^+$: 274.1205, found 274.1204.

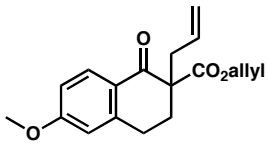


Table 2, Entry 5

Prepared using the diallyl carbonate method from 6-methoxy-1-tetralone and allyl bromide. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 83% yield. R_f = 0.45 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.91-5.72 (comp. m, 2H), 5.24-5.05 (comp. m, 4H), 4.59 (app. ddd, *J* = 5.3, 1.6, 1.3 Hz, 1H), 4.59 (app. ddd, *J* = 5.3, 1.6, 1.3 Hz, 1H), 3.85 (s, 3H), 3.05 (ddd, *J* = 17.3, 10.1, 4.8 Hz, 1H), 2.88 (ddd, *J* = 17.3, 5.3, 5.1 Hz, 1H), 2.76 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.69 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.52 (ddd, *J* = 13.8, 5.3, 4.8 Hz, 1H), 2.13 (ddd, *J* = 13.8, 10.1, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 171.5, 163.8, 145.9, 133.7, 131.8, 130.7, 125.6, 119.0, 118.3, 113.6, 112.5, 65.8, 57.2, 55.6, 38.8, 30.5, 26.3; IR (Neat Film NaCl) 3080, 2942, 1734, 1676, 1600, 1447, 1353, 1272, 1254, 1214, 925 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{18}H_{20}O_4$ $[M]^+$: 300.1362, found 300.1374.

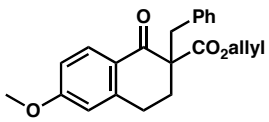


Table 2, Entry 6

Prepared using the diallyl carbonate method from 6-methoxy-1-tetralone and benzyl bromide. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 80% yield. R_f = 0.56 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.29-7.14 (comp. m, 5H),

6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 5.80 (dddd, *J* = 17.3, 10.7, 5.5, 5.5 Hz, 1H), 5.17 (app. ddd, *J* = 17.6, 3.0, 1.4 Hz, 1H), 5.15 (app. ddd, *J* = 10.5, 2.5, 1.4 Hz, 1H), 4.57 (app. ddd, *J* = 5.5, 2.5, 1.4 Hz, 1H), 4.57 (app. ddd, *J* = 5.5, 2.5, 1.4 Hz, 1H), 3.83 (s, 3H), 3.46 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 3.06 (ddd, *J* = 17.3, 11.6, 4.4 Hz, 1H), 2.79 (ddd, *J* = 17.3, 4.4, 4.4 Hz, 1H), 2.46 (ddd, *J* = 13.8, 4.4, 4.4 Hz, 1H), 1.97 (ddd, *J* = 13.5, 11.6, 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 171.4, 163.8, 145.9, 136.8, 131.6, 130.9, 130.8, 128.2, 126.8, 125.9, 118.4, 113.6, 112.4, 65.9, 58.6, 55.6, 40.2, 30.5, 26.6; IR (Neat Film NaCl) 2935, 1708, 1688, 1607, 1595, 1497, 1310, 1277, 1244, 1196, 1144, 1080, 1029, 992, 698 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{22}H_{22}O_4$ $[M]^+$: 350.1518, found 350.1503.

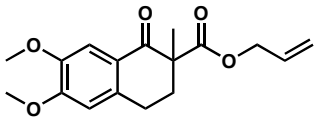


Table 2, Entry 7

Prepared using the diallyl carbonate method from 6,7-dimethoxy-1-tetralone and methyl iodide. Purified by flash chromatography (SiO_2, 20% EtOAc in hexanes). 18% yield. R_f = 0.14 (30% Et_2O in pentane); mp 78-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.23 (s, 1H), 5.83 (dddd, *J* = 17.3, 10.4, 5.6, 5.1 Hz, 1H), 5.19 (dddd, *J* = 17.3, 3.2, 1.6, 1.6 Hz, 1H), 5.16 (dddd, *J* = 10.6, 2.7, 1.3, 1.3, 1H), 4.60 (dddd, *J* = 8.2, 5.3, 2.7, 1.3 Hz, 1H), 4.60 (dddd, *J* = 8.2, 5.3, 2.7, 1.3 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 2.99 (ddd, *J* = 17.0, 9.3, 4.8 Hz, 1H), 2.86 (ddd, *J* = 17.3, 5.6, 5.3 Hz, 1H), 2.61 (ddd, *J* = 13.3, 5.8, 4.8 Hz, 1H), 2.06 (ddd, *J* = 13.3, 9.3, 4.8 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 172.9, 153.8, 148.2, 138.1, 131.8, 124.9, 118.2, 110.2, 109.3, 65.8, 56.2, 56.1, 53.5, 34.4, 25.9, 20.9; IR (Neat Film NaCl) 3079, 2938, 2836, 1732, 1672, 1600, 1513, 1454, 1368, 1269, 1239, 1183, 1105, 1018, 790 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{17}H_{20}O_5$ $[M]^+$: 304.1311, found 304.1299.

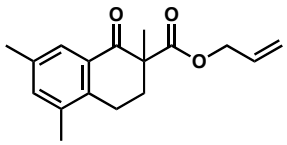


Table 2, Entry 8

Prepared using the diallyl carbonate method from 5,7-dimethyl-1-tetralone and methyl iodide. Purified by flash chromatography (SiO_2, 10 → 15% Et_2O in pentane). 40% yield. R_f = 0.67 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (br s, 1H), 7.19 (br s, 1H), 5.79 (dddd, *J* = 16.5, 10.1, 5.6, 5.6 Hz, 1H), 5.15 (dd, *J* = 16.5, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.57 (app. ddd, *J* = 5.6, 2.1, 1.3 Hz, 1H), 4.57 (app. ddd, *J* = 5.6, 2.1, 1.3 Hz, 1H), 2.93-2.73 (m, 2H), 2.64 (ddd, *J* = 13.6, 5.3, 5.3 Hz, 1H), 2.33 (s, 3H), 2.25 (s, 3H), 2.03 (ddd, *J* = 13.8, 8.5, 5.9 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 172.7, 138.6, 136.3, 136.1 (2C), 131.8 (2C), 126.1, 118.1, 65.7, 53.5, 33.3, 23.1, 21.0, 20.7, 19.3; IR (Neat Film NaCl) 2982, 2937, 1736, 1688, 1477, 1453, 1318, 1251, 1197, 1165, 1110, 1051, 984, 928, 874 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{17}H_{20}O_3$ $[M]^+$: 272.1412, found 272.1413.

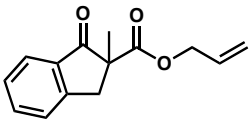


Table 2, Entry 9

Prepared using the diallyl carbonate method from 1-indanone and methyl iodide. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 30% yield. R_f = 0.55 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.3 Hz, 1H), 5.83 (dddd, *J* = 17.2, 10.6, 5.6, 5.6 Hz, 1H), 5.21 (dddd, *J* = 17.2, 2.7, 1.6, 1.1 Hz, 1H), 5.16 (dddd, *J* = 10.5, 2.4, 1.3, 1.3 Hz, 1H), 4.58 (ddd, *J* = 5.6, 2.7, 1.1 Hz, 1H), 4.58 (ddd, *J* = 5.6, 2.7, 1.1 Hz, 1H), 3.73 (d, *J* = 17.1 Hz, 1H), 3.01 (d, *J* = 17.1 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 171.8, 152.7, 135.5, 134.9, 131.7, 128.0, 126.6, 125.2, 118.3, 66.0, 56.2, 40.2, 21.2; IR (Neat Film NaCl) 3080, 2982, 2935, 1745, 1715, 1608, 1495, 1282, 1184, 967, 747 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{14}H_{14}O_3$ $[M]^+$: 230.0943, found 230.0936.

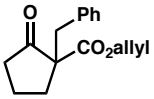


Table 2, Entry 10

Prepared using the Dieckmann cyclization method from diallyl adipate and benzyl bromide. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 36% yield. R_f = 0.17 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (comp. m, 3H), 7.17-7.09 (comp. m, 2H), 5.89 (dddd, *J* = 17.3, 10.6, 5.6, 4.8 Hz, 1H), 5.31 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.61 (app. dd, *J* = 5.6, 2.7, 1.6 Hz, 1H), 4.61 (dd, *J* = 5.6, 2.7, 1.6 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 3.14 (d, *J* = 13.8 Hz, 1H), 2.51-2.29 (m, 2H), 2.12-1.80 (comp. m, 3H), 1.70-1.51 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 170.8, 136.6, 131.7, 130.4, 128.5, 127.0, 118.8, 66.2, 61.6, 39.2, 38.5, 31.8, 19.6; IR (Neat Film NaCl) 3029, 2963, 1751, 1728, 1496, 1454, 1266, 1220, 1187, 1158, 1141, 1102, 991, 925, 703 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{18}O_3$ $[M]^+$: 258.1256, found 258.1268.

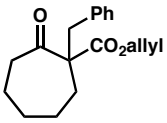
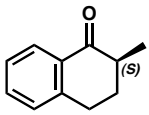


Table 2, Entry 13

Prepared using the diallyl carbonate method from cycloheptanone and benzyl bromide. Purified by flash chromatography (SiO_2, 20 → 60% CH_2Cl_2 in hexane). 44% yield. R_f = 0.35 (15% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.19 (comp. m, 3H), 7.19-7.07 (comp. m, 2H), 5.89 (dddd, *J* = 17.3, 10.4, 5.6, 5.6 Hz, 1H), 5.33 (dddd, *J* = 17.3, 2.9, 1.3, 1.3 Hz, 1H), 5.27 (dddd, *J* = 10.4, 2.7, 1.3, 1.3 Hz, 1H), 4.62 (dddd, *J* = 5.6, 5.6, 1.3, 1.3 Hz, 1H), 4.62 (dddd, *J* = 5.6, 5.6, 1.3, 1.3 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 3.03 (d, *J* = 13.8 Hz, 1H), 2.65 (ddd, *J* = 12.5, 9.0, 3.7 Hz, 1H), 2.36 (ddd, *J* = 12.8, 8.8, 2.9 Hz, 1H), 2.10 (app. dd, *J* = 13.8, 9.3 Hz, 1H), 1.94-1.62 (comp. m, 5H), 1.62-1.37 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.4, 171.7, 136.8, 131.6, 130.6, 128.3, 126.9, 119.0, 66.0, 64.4, 42.5, 40.9, 31.7, 29.9, 25.5, 24.6; IR (Neat Film NaCl) 3028, 2932, 2860, 1734, 1711, 1454, 1195, 1172, 1145, 991, 941, 702 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{18}H_{22}O_3$ $[M]^+$: 286.1569, found 286.1571.

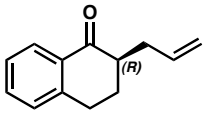
Sample Procedure for Enantioconvergent Protonation:



(*S*)-(–)-2-Methyl-1-tetralone (5, Table 2, Entry 1):[3]
A glass tube (2.5 x 10 cm with a ground glass joint) equipped with a magnetic stir bar was charged with powdered 4Å molecular sieves (540 mg) and then thoroughly flame dried under vacuum (3x, backfill with dry argon). After cooling to ambient temperature under dry argon, $Pd(OAc)_2$ (6.7 mg, 0.030 mmol, 0.10 equiv, 10 mol%), (*S*)-*t*-Bu-PHOX (14.5 mg, 0.0375 mmol, 0.125 equiv, 12.5 mol%), and freshly distilled *p*-dioxane (4.5 mL) were added, and the resulting slurry was stirred vigorously at 40 ºC for 30 min. At this point, neat HCO_2H (68 µL, 1.80 mmol, 6.0 equiv) was added to the reaction mixture, followed immediately by addition of a solution of (±)-**2** (73.3 mg, 0.30 mmol, 1.0 equiv) in *p*-dioxane (4.5 mL). When the reaction was complete by TLC, the reaction mixture was cooled to ambient temperature and then filtered through a pad of SiO_2. The filtrate was concentrated under reduced pressure and the residue purified by flash chromatography on SiO_2 using 10% Et_2O in pentane as eluent to afford (*S*)-**5** (42.1 mg, 88% yield). The material was determined to be of 94% ee, measured by chiral HPLC using a Chiracel OD-H column with 1% 2-propanol in hexanes as the eluent. $[\alpha]_D^{25}$ –44.4 (*c* 1.06, *p*-dioxane, 94% ee).

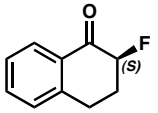
The absolute configuration was determined by comparison of the observed optical rotation to a literature value for (*S*)-2-methyl-1-tetralone: $[\alpha]_D^{22}$ –51.2 (*c* 2.5, *p*-dioxane).[4]

Data for product compounds:
Products were prepared using the above procedure, unless specifically stated otherwise.



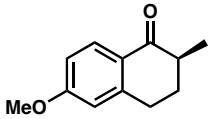
(*R*)-(–)-2-Allyl-1-tetralone (Table 2, Entry 2):[5]
Reaction performed with 5.0 equiv of HCO_2H (56.6 µL, 1.50 mmol) and 405 mg (1.35 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 88% yield, 85% ee. $[\alpha]_D^{25}$ –22.2 (*c* 0.63, MeOH, 85% ee).

The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(–)-2-allyl-1-tetralone: $[\alpha]_D^{23}$ –29.7 (*c* 1.21, MeOH, 97% ee).[5]

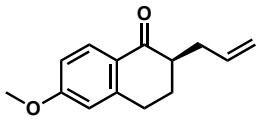


(*S*)-(–)-2-Fluoro-1-tetralone (Table 2, Entry 3):[6]
Reaction performed with 8.0 equiv of HCO_2H (90.6 μL, 2.40 mmol) and 810 mg (2.70 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 79% yield, 88% ee. $[\alpha]_D^{25}$ –56.9 (*c* 1.01, *p*-dioxane, 88% ee).

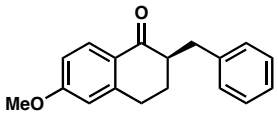
The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(+)-2-fluoro-1-tetralone: $[\alpha]_D$ +64.9 (*c* 0.43, *p*-dioxane, >95% ee).[6]



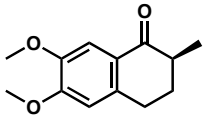
(–)-2-Methyl-6-methoxy-1-tetralone (Table 2, Entry 4):[7]
Reaction performed with 6.0 equiv of HCO_2H (67.9 μL, 1.80 mmol) and 540 mg (1.80 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 91% yield, 95% ee. $[\alpha]_D^{25}$ –62.6 (*c* 1.02, $CHCl_3$, 95% ee).



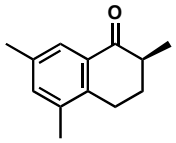
(–)-2-Allyl-6-methoxy-1-tetralone (Table 2, Entry 5):[5]
Reaction performed with 5.0 equiv of HCO_2H (56.6 μL, 1.50 mmol) and 405 mg (1.35 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 81% yield, 88% ee. $[\alpha]_D^{24.9}$ –50.28 (*c* 2.03, CH_2Cl_2, 88% ee).



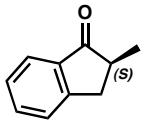
(+)-2-Benzyl-6-methoxy-1-tetralone (Table 2, Entry 6):[8]
Reaction performed with 7.0 equiv of HCO_2H (79.2 μL, 2.10 mmol) and 675 mg (2.25 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 95% yield, 78% ee. $[\alpha]_D^{25}$ +8.6 (*c* 0.79, $CHCl_3$, 78% ee).



(–)-2-Methyl-6,7-dimethoxy-1-tetralone (Table 2, Entry 7):[9]
Reaction performed with 5.0 equiv of HCO_2H (56.6 μL, 1.50 mmol) and 405 mg (1.35 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 40% Et_2O in pentane). 62% yield, 94% ee. $[\alpha]_D^{25.9}$ –86.88 (*c* 1.09, CH_2Cl_2, 94% ee).

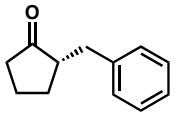


(–)-2,5,7-Trimethyl-1-tetralone (Table 2, Entry 8):[10]
Reaction performed with 5.0 equiv of HCO_2H (56.6 μL, 1.50 mmol) and 405 mg (1.35 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 75% yield, 92% ee. $[\alpha]_D^{25.8}$ –29.97 (*c* 1.00, CH_2Cl_2, 92% ee).

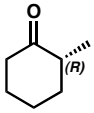


(*S*)-(+)-2-Methyl-1-indanone (Table 2, Entry 9):[3]
Reaction performed with 5 mol% $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.050 equiv), 6.25 mol% (*S*)-*t*-Bu-PHOX (7.3 mg, 0.0188 mmol, 0.0625 equiv), 5.0 equiv of HCO_2H (56.6 μL, 1.50 mmol) and 405 mg (1.35 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 83% yield, 81% ee. $[\alpha]_D^{26.3}$ +35.73 (*c* 1.50, *p*-dioxane, 81% ee).

The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-2-methyl-1-indanone: $[\alpha]_D^{22}$ –42 (*c* 1.72, *p*-dioxane).[4]

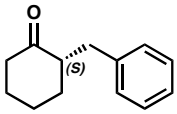


(–)-2-Benzylcyclopentanone (Table 2, Entry 10):[11]
Reaction performed with 6.0 equiv of HCO_2H (67.9 μL, 1.80 mmol) and 675 mg (2.25 g/mmol of substrate) of powdered 4Å molecular sieves. 63% yield, 60% ee. $[\alpha]_D^{27}$ –116.6 (*c* 1.11, $CHCl_3$, 60% ee).



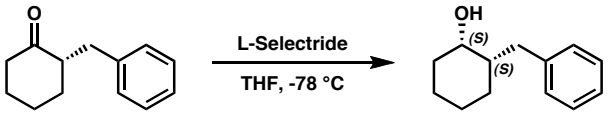
(*R*)-(–)-2-Methylcyclohexanone (Table 2, Entry 11):[3]
Reaction performed with 6.0 equiv of HCO_2H (67.9 μL, 1.80 mmol) and 675 mg (2.25 g/mmol of substrate) of powdered 4Å molecular sieves. Yield determined by GC using tridecane (30.0 μL) as an internal standard. 99% GC yield, 85% ee. Material for optical rotation was obtained by filtering the reaction mixture through a pad of SiO_2, concentrating the filtrate, dissolving the residue in 10% Et_2O in pentane, passing through a short plug of SiO_2, and concentrating the filtrate. $[\alpha]_D^{26.2}$ –6.4 (*c* 0.87, MeOH, 85% ee).

The absolute configuration was established by comparison of the optical rotation to the literature value for (*S*)-(+)-2-methylcyclohexanone: $[\alpha]_D$ +12.2 (*c* 4, MeOH, 87% ee).[12]



(*S*)-(–)-2-Benzylcyclohexanone (Table 2, Entry 12):[3]
Reaction performed with 7.0 equiv of HCO_2H (79.2 μL, 2.10 mmol) and 675 mg (2.25 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 91% yield, 92% ee. $[\alpha]_D^{25.5}$ –42.2 (*c* 1.66, MeOH, 92% ee).

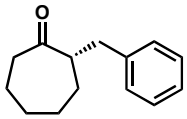
The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-(+)-2-benzylcyclohexanone: $[\alpha]_D$ +41.4 (*c* 5, MeOH, 88% ee).[12] This assignment was confirmed by reduction of the ketone to the corresponding *syn* alcohol **SI 2**.



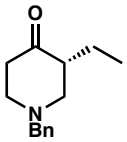
SI 2

(1*S*,2*S*)-(+)-2-benzylcyclohexanol (SI 2):[13]
To a cooled (–78 °C) solution of (–)-2-benzylcyclohexanone (43.9 mg, 0.23 mmol, 1.0 equiv) in THF (2.3 mL) was added a 1.0M solution of L-Selectride® in THF (303.1 μL, 0.30 mmol, 1.3 equiv). After 30 mins, the reaction was quenched with H_2O (500 μL) and then warmed to 25 °C. Additional H_2O (3 mL) and EtOAc (5 mL) were added and the phases separated. The aqueous phase was extracted with EtOAc (3 x 4 mL). The combined organics were then washed with brine (1 x 5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated to a colorless oil. Flash chromatography (SiO_2, 15% EtOAc in hexanes) provided the title compound as a white crystalline solid that was isolated as one diastereomer (14.1 mg, 32% yield). ^{1}H NMR data matched that previously reported for the *syn* diastereomer.[13] R_f = 0.18 (15% EtOAc in hexanes); mp 66-68 °C (lit.[13] 67-70 °C); $[\alpha]_D^{26.7}$ +30.7 (*c* 0.50, $CHCl_3$).

The absolute configuration was confirmed by comparison of the optical rotation to the literature value for (1*S*,2*S*)-(+)-2-benzylcyclohexanol: $[\alpha]_D^{20}$ +28.2 (*c* 1, $CHCl_3$).[13]



(–)-2-Benzylcycloheptanone (Table 2, Entry 13):[14]
Reaction performed with 6.0 equiv of HCO_2H (67.9 μL, 1.80 mmol) and 540 mg (1.80 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 30% CH_2Cl_2 in pentane). 69% yield, 74% ee. $[\alpha]_D^{27}$ –43.7 (*c* 1.08, MeOH, 74% ee).



(–)-1-Benzyl-3-ethyl-4-piperidone (Table 2, Entry 14):[15]
Reaction performed with 6.0 equiv of HCO_2H (67.9 μL, 1.80 mmol) and 600 mg (2.00 g/mmol of substrate) of powdered 4Å molecular sieves. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 83% yield, 84% ee. $[\alpha]_D^{25}$ –19.6 (*c* 1.03, $CHCl_3$, 84% ee).

Table SI 6. Methods for the determination of enantiomeric excess.

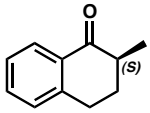
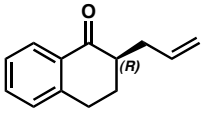
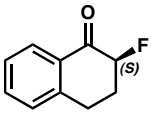
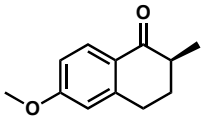
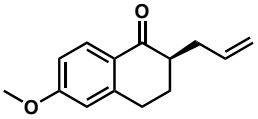
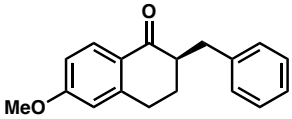
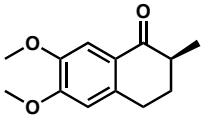
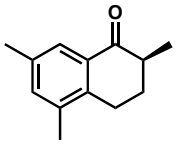
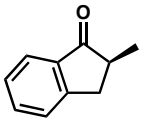
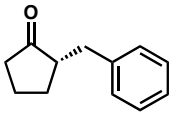
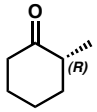
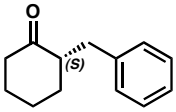
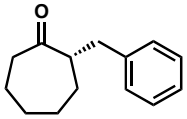
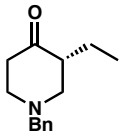
Entry	Product	Assay Conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
1		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	9.076	8.285	94
2		HPLC Chiracel OD-H 0.1% *i*-PrOH in heptane isocratic, 1.0 mL/min	21.732	19.414	85
3		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	15.860	17.707	88
4		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	16.768	15.855	95
5		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	12.796	11.807	88
6		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	25.940	23.992	78
7		HPLC Chiracel AD 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	32.596	36.115	94
8		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	7.104	7.598	92

Table SI 6. Methods for the determination of enantiomeric excess. (continued)

Entry	Product	Assay Conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
9		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	9.381	8.663	81
10		HPLC Chiralpak AD 1% EtOH in hexane isocratic, 1.0 mL/min	16.384	13.558	60
11		GC G-TA 70 ° isotherm	19.225	17.610	85
12		HPLC Chiralpak AD 1% EtOH in hexane isocratic, 1.0 mL/min	9.989	8.453	92
13		HPLC Chiralpak AD 1% EtOH in hexane isocratic, 1.0 mL/min UV detection at 210 nm	8.893	8.286	74
14		HPLC Chiracel OD-H 1% *i*-PrOH in hexane isocratic, 1.0 mL/min	11.578	10.420	84

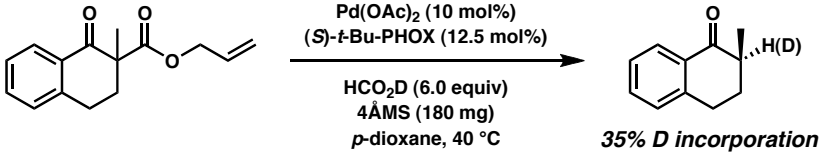
Deuterium Labeling Experiments:

General Procedure for Deuterium Labeling Experiments:

Prior to use, powdered 4ÅMS were dried under vacuum (~1 torr) for 3 days at 320 °C.[16] Subsequently, these 4ÅMS were cooled to 25 °C under dry N_2 and then immediately transferred to a glove box containing an atmosphere of dry N_2. In the labeling experiments below, the powdered 4ÅMS were weighed in the glove box, transferred to a 1 dram glass vial containing a magnetic stir bar and sealed with a screw cap and a septum. The vial was then removed from the glove box and thoroughly flame dried under vacuum, backfilling with dry N_2 (three cycles). The contents were then cooled to ambient temperature (25 °C). Once cool, $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 0.10 equiv, 10 mol%), (*S*)-*t*-Bu-PHOX (4.8 mg, 0.0125 mmol, 0.125 equiv, 12.5 mol%), and freshly distilled *p*-dioxane (1.5 mL) were added and the resulting suspension stirred at 40 °C for 30 mins. At this point, a solution of (±)-**2** (24.4 mg, 0.10 mmol, 1.0 equiv) in *p*-dioxane (1.5 mL) was added, followed immediately by addition of neat formic acid (labeled as shown below). This mixture was stirred at 40 °C until TLC indicated complete consumption of (±)-**2**. After cooling to ambient temperature, the reaction mixture was passed through a pad of SiO_2 and the filtrate concentrated by rotary evaporation. The residue was then purified by flash

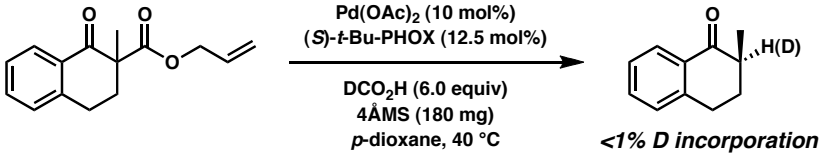
chromatography on SiO_2 using 5% Et_2O in pentane as eluent. The ee of the isolated material was determined by chiral HPLC with a Chiracel OD-H column using 1% 2-propanol in hexanes as eluent. The amount of deuterium incorporation was determined by ^1H NMR integration and deuteration was confirmed by ^2H NMR.

Deuterium Labeling Experiment 1:



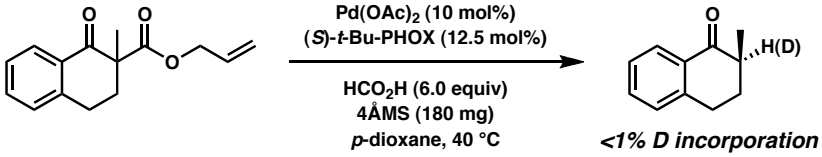
Reaction performed using HCO_2D (23.1 μL, 0.60 mmol, 6.0 equiv). Flash chromatography on SiO_2 with 5% Et_2O in pentane as eluent provided 10.2 mg of product with 89% ee. ^1H NMR integration indicates 35% deuterium incorporation at the 2-position of 2-methyl-1-tetralone (observed at δ 2.06 ppm). ^2H NMR detected deuterium incorporation at only one site. ^2H NMR (77 MHz, C_6H_6) δ 2.05.

Deuterium Labeling Experiment 2:



Reaction performed using DCO_2H (22.6 μL, 0.60 mmol, 6.0 equiv). Flash chromatography on SiO_2 with 5% Et_2O in pentane as eluent provided 13.1 mg of product with 91% ee. ^1H NMR integration indicates <1% deuterium incorporation at the 2-position of 2-methyl-1-tetralone. ^2H NMR detected no deuterium in the product material.

Deuterium Labeling Experiment 3 (control):



Reaction performed using HCO_2H (22.6 μL, 0.60 mmol, 6.0 equiv). Flash chromatography on SiO_2 with 5% Et_2O in pentane as eluent provided 12.9 mg of product (81% yield) with 93% ee. ^1H NMR integration indicates <1% deuterium incorporation at the 2-position of 2-methyl-1-tetralone. ^2H NMR detected no deuterium in the product material.

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[14] (a) Pal, S.; Mukhopadhyaya, J. K.; Ghatak, U. R. *J. Org. Chem.* **1994**, *59*, 2687-2694. (b) Kasu, H.; Ozako, S.; Kawamatsu, S.; Takatsu, S.; Ishii, M.; Tsunoda, T. *Heterocycles* **2001**, *55*, 847-850.
[15] Bonjoch, J.; Linares, A.; Bosch, J. *Heterocycles* **1987**, *26*, 2165-2174.
[16] This drying procedure was reported by Nakai for deuterium incorporation experiments, see: Sugiura, M.; Nakai, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2366-2368. If the 4ÅMS were not dried in this fashion prior to use, a lower level of deuterium incorporation was observed (15% D, 90% ee). Nakai also reported decreased levels of deuterium incorporation when less rigorous drying techniques were employed.