**Supporting Information for “Regioselective and Enantioselective
Iridium-Catalyzed Allylation of Enamines”**

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General experimental details. Elemental Analyses were performed by Robertson Microlit Laboratories, Inc. (Madison, NJ). HRMS analysis was performed by the University of Illinois Mass Spectrometry laboratory. GC/MS analysis were performed on an Agilent 6890N GC equipped with a 5973 MS and an HP-5ms column (30 m x 0.25 mm ID x 0.25 μ m film). GC analyses were obtained on an Agilent 6890 GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μ m film) and an FID detector. In both cases, the temperature program was to hold at 100 °C for 3 min, ramp from 100 – 300 °C at 40 °C/min, hold at 300 °C for 2.5 min. Optical rotations were measured on a Rudolph Instruments (Denville, NJ) Autopol IV. We thank the Zimmerman group for allowing us to use this instrument. IR spectra were obtained from thin films on NaCl plates using a Perkin-Elmer Spectrum BX FT-IR instrument. NMR spectra were acquired on 500 MHz Varian Unity or Innova instruments (University of Illinois VOICE NMR facility) and data worked up in MacNUTS software program (Acorn NMR, Inc., Livermore, CA). Chemical shifts are reported in ppm relative to residual solvent peak (CDCl_3 = 7.26 ppm for ^1H , 77.0 ppm for ^{13}C) or to external standard (CFC_3 = 0 for ^{19}F and 85% H_3PO_4 = 0 for ^{31}P). Coupling constants are given in Hertz. HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+ autosampler, 2487 dual wavelength detector). Supercritical fluid chromatography analyses were carried out on a Berger ASC-1000 instrument with a single wavelength detector (λ = 220 nm) using a chiral solid phase column.

Chromatography was conducted on Silicycle Siala-P Silica gel using hexanes/ethyl acetate, hexanes/ether, or pentane/ether mixtures. While many products were visible on TLC via UV, all products were more easily identified by strong staining with KMnO_4 (orange). NMR yields were obtained from the unpurified isolate before chromatography by adding 50 μL of dichloroethane (Aldrich, 99.8%), diluting with a small amount of CDCl_3 to be sure all material is dissolved and the solution is homogeneous and diluting a portion of this mixture in ~0.75 mL CDCl_3 for analysis (pulse delay of 10 s to ensure complete relaxation of protons).

Reaction progress was monitored by GC and GC/MS with dodecane as the internal standard (10 μL). After hydrolysis of the enamine with NaOAc/AcOH buffer and removal of the solvent, yields were determined by ^1H NMR (vide supra). Branched-to-linear ratios were determined by ^1H NMR (usually the olefin protons) and GC/MS analysis in all cases except for **3b** (NMR only), **3j** (GC only), and **3c**, **3e**, and **3f** (GC/MS only). GC/MS and NMR gave good agreement in all cases.

All starting materials were purchased from Aldrich except for crotyl alcohol, which was purchased from Alfa, and IrCl_3 , which was purchased from Pressure Chemical or obtained as a gift from Johnson-Matthey. Propyl amine was stored over KOH. THF, pentane, benzene, ether, toluene, and CH_2Cl_2 were purified by passage of the degassed solvent (Ar) through a column of activated alumina (Solvent purification system purchased from Innovative Technologies of Newburyport, MA). Enamines **2a-d** were synthesized according to the literature

procedure and either distilled (**2a-b**, **2d**) or used without further purification (**2c**).¹ Although **2d** is reported to be a single isomer, in two runs we obtained identical mixtures of regioisomers favoring the terminal enamine (68:32 ratio) that were not separable. Allylic alcohols were either purchased or synthesized by the Roush-Masamune modification of the Horner-Wadsworth-Emmons reaction.² The complex $[\text{Ir}(\text{cod})\text{Cl}]_2$ was synthesized according to the procedure of Crabtree.³ Phosphoramidite ligands were synthesized according to the published procedures.⁴ 3-Phenyl-prop-2-enyl 2-propyl carbonate (**1a**)⁵ was synthesized according to the literature procedure.

Catalyst $\text{Ir}(\text{cod})(\text{k}^2\text{-L1})(\text{L1})$.⁶ This complex was prepared by a procedure that is a condensed, single-step version of the published two-step procedure. Propyl amine (3 mL) was added to a stirred solution of 0.656 g phosphoramidite **L1** (1.21 mmol) and 0.201 g of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (0.300 mmol) in 15 mL of dry THF. The mixture was stirred at room temperature overnight (16 h), and the solvent was removed from the resulting bright yellow solution under high vacuum. The resulting solid mass, in a nitrogen filled glovebox, was dissolved in 5 mL benzene, and 5 mL of diethyl ether was added to precipitate the propylamine hydrochloride. The solution was filtered through a syringe tip filter (0.25 μm), and the solvent was again removed on high vacuum. The resulting yellow to orange powder was used without purification or it was recrystallized according to the literature procedure.⁶ ^{31}P NMR (C_6D_6 , 202 MHz) shows the catalyst is >95% $\text{Ir}(\text{cod})(\text{k}^2\text{-L1})(\text{L1})$ (two doublets at 154.2 (d, $J=47.7$ Hz, 1P) and 128.9 (d, $J=45.1$ Hz, 1P) ppm). The major contaminant in the crude material was the ligand ($^{31}\text{P}=151.5$ (s) ppm, if there was any. No noticeable difference in reactivity, b:l ratio, rate, or enantioselectivity was observed when reactions were conducted with the crude or recrystallized material.

General procedure for the synthesis of allylic carbonates. To an ice-cooled solution of the allylic alcohol (1 equiv) and pyridine (2 equiv) in dry dichloromethane (1 mL/mmol alcohol) under a nitrogen atmosphere was added the chloroformate (1.1 equiv as a 1 M solution in toluene). The solution was stirred at 0 °C and monitored by TLC (UV and KMnO_4 stain) for completion (5 min to 3 h, heavy precipitate forms as well) at which time the reaction mixture was transferred to a separatory funnel, and 10% aq HCl was added. The separatory funnel was shaken and the aqueous layer drained and discarded. The organic layer was washed once more with 10% aq HCl and then deionized water (1 x), sat. aq NaHCO_3 (1 x), and brine (1 x). The organic layer was then dried over Na_2SO_4 , filtered, and the volatile materials removed on a rotary evaporator. The residue was chromatographed on silica gel.

3-(4-anisyl)-prop-2-enyl *iso*-propyl carbonate **1b.** The general procedure was followed using *p*-methoxycinnamyl alcohol (1.83 g, 11.2 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 97:3 hexanes:EtOAc) as a white crystalline solid (2.54 g, 92% yield). mp 37-38.5 °C.

^1H NMR (CDCl_3 , 500 MHz) δ 1.31 (d, $J=6.5$ Hz, 6H), 3.80 (s, 3H), 4.74 (d, $J=6.5$ Hz, 2H), 4.90 (septet, $J=6$ Hz, 1H), 6.17 (dt, $J=16$, 6.5 Hz, 1H), 6.63 (d, $J=16$ Hz, 1H), 6.85 (d, $J=9$ Hz, 2H), 7.33 (d, $J=9$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.8, 55.2, 68.3, 71.9, 114.0, 120.3, 127.9, 128.8, 134.4, 154.5, 159.6. IR (thin film): 1739, 1513, 1250 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25; N, 0.00; found: C, 67.44; H, 7.52; N, 0.02.

3-(4-trifluoromethylphenyl)-prop-2-enyl iso-propyl carbonate 1c. The general procedure was followed using *p*-(trifluoromethyl)cinnamyl alcohol (1.01 g, 5.00 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 95:5 pentane:ether) as a clear oil (1.32 g, 91% yield). ^1H NMR (CDCl_3 , 500 MHz) δ 1.32 (d, $J=6.5$ Hz, 6H), 4.80 (dd, $J=6.5$, 1.5 Hz, 2H), 4.91 (septet, $J=6.5$ Hz, 1H), 6.39 (dt, $J=16$, 6 Hz, 1H), 6.71 (d, $J=16$ Hz, 1H), 7.48 (d, $J=8.5$ Hz, 2H), 7.58 (d, $J=8.5$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.7, 67.4, 72.2, 124.1 (q, $J=273$ Hz), 125.4, 125.6 (q, $J=3.6$ Hz), 126.8, 129.8 (q, $J=32.3$ Hz), 132.6, 139.6, 154.4. ^{19}F NMR (CDCl_3 , 470 MHz) δ -62.8. IR (thin film): 1744, 1327, 1259, 1167, 1125, 1068 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_3$: C, 58.33; H, 5.24; N, 0.00; found: C, 58.51; H, 5.14; N, 0.02.

3-(2-furyl)-prop-2-enyl iso-propyl carbonate 1d. The general procedure was followed using 3-(2-furyl)-prop-2-enol (0.660 g, 5.32 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 95:5 to 92:8 pentane:ether) as a clear oil. ^1H NMR (CDCl_3 , 500 MHz) δ 1.31 (d, $J=6.5$ Hz, 6H), 4.73 (dd, $J=6$, 1 Hz, 2H), 4.89 (septet, $J=6$ Hz, 1H), 6.22 (dt, $J=16$, 7 Hz, 1H), 6.28 (d, $J=3$ Hz, 1H), 6.37 (dd, $J=3.5$, 2 Hz, 1H), 6.49 (d, $J=16$ Hz, 1H), 7.31 (br d, $J=1.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.8, 67.5, 72.1, 109.0, 111.3, 121.1, 122.4, 142.5, 151.8, 154.5. IR (thin film): 1744, 1379, 1253, 1108 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: C, 62.85; H, 6.71; N, 0.00; found: C, 63.16; H, 6.70; N, 0.02.

3-(2-methoxyphenyl)-prop-2-enyl iso-propyl carbonate 1e. The general procedure was followed using *o*-methoxycinnamyl alcohol (1.64 g, 10.0 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 97:3 hexanes:EtOAc) as a clear oil (2.20 g, 88% yield). ^1H NMR (CDCl_3 , 500 MHz) δ 1.31 (d, $J=6$ Hz, 6H), 3.85 (s, 3H), 4.78 (dd, $J=6.5$, 1 Hz, 2H), 4.90 (septet, $J=6.5$ Hz, 1H), 6.33 (dt, $J=16$, 6.5 Hz, 1H), 6.87 (d, $J=8.5$ Hz, 1H), 6.92 (app t, $J=7.5$

Hz, 1H), 7.00 (d, $J=16$ Hz, 1H), 7.22-7.26 (m, 1H), 7.43 (dd, $J=7.5$, 1.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.8, 55.4, 68.7, 71.9, 110.8, 120.6, 123.2, 125.1, 127.2, 129.2, 129.8, 154.6, 156.9 ppm. IR (thin film): 1739, 1490, 1465, 1259, 753 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25; N, 0.00; found: C, 67.45; H, 7.51; N, 0.02.

trans-crotyl iso-propyl carbonate 1f. The general procedure was followed using crotyl alcohol (1.44 g, 20 mmol). ^1H NMR analysis showed a 95:5 *E/Z*-ratio (*Z*-carbonate, 4.68 (d, $J=7$ Hz, 2H)). The pure *E*-carbonate product was isolated by column chromatography (10% AgNO_3 on SiO_2 , 100:1 to 50:1 hexanes: Et_2O) as a clear oil (1.15 g, 36% yield). ^1H NMR (CDCl_3 , 500 MHz) δ 1.29 (d, $J=6$ Hz, 6H), 1.71-1.73 (m, 3H), 4.53 (dt, $J=7$, 1 Hz, 2H), 4.87 (septet, $J=3.5$ Hz, 1H), 5.61 (dtq, $J=15$, 8.5, 2 Hz, 1H), 5.83 (dqt, $J=15.5$, 6.5, 1 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.7, 21.8, 68.2, 71.8, 124.7, 132.1, 154.6. IR (thin film): 1742, 1262 cm^{-1} . HRMS-*El* (m/z): $[\text{M}]^+$ calcd for $\text{C}_8\text{H}_{14}\text{O}_3$, 158.09430; found, 158.09425.

2-hexenyl iso-propyl carbonate 1g. The general procedure was followed using 2-hexenol (2.00 g, 20.0 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 98:2 hexanes: EtOAc) as a clear oil (2.84 g, 90% yield). ^1H NMR (CDCl_3 , 500 MHz) δ 0.89 (t, $J=7.5$ Hz, 3H), 1.28 (d, $J=6.5$ Hz, 6H), 1.40 (sextet, $J=7$ Hz, 2H), 2.02 (q, $J=7.5$ Hz, 2H), 4.54 (dd, $J=6.5$, 1 Hz, 2H), 4.86 (septet, $J=6.5$ Hz, 1H), 5.58 (ddt, $J=15.5$, 6.5, 1.5 Hz, 1H), 5.79 (dt, $J=15.5$, 6.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.6, 21.8, 21.9, 34.2, 68.3, 71.7, 123.4, 137.1, 154.5 ppm. IR (thin film): 1743, 1261 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3$: C, 64.49; H, 9.74; N, 0.00; found: C, 64.25; H, 9.78; N, <0.02.

4-methylpentenyl iso-propyl carbonate 1h. The general procedure was followed using 4-methyl-2-pentenol (1.00 g, 10.0 mmol). The pure carbonate product was isolated by column chromatography (SiO_2 , 100:2.5 hexanes: Et_2O) as a clear oil (1.62 g, 87% yield). ^1H NMR (CDCl_3 , 500 MHz) δ 0.91 (d, $J=7$ Hz, 6H), 1.13 (d, $J=6$ Hz, 6H), 2.13 (octuplet, $J=6.8$ Hz, 1H), 4.61 (dt, $J=6$, 0.8 Hz, 2H), 4.94 (septet, $J=6.2$ Hz, 1H), 5.56 (ddt, $J=15.5$, 6, 1 Hz, 1H), 5.65 (ddt, $J=15.5$, 6.5, 1 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.8, 21.9, 30.7, 68.4, 71.8, 120.4, 143.9, 154.5 ppm. IR (thin film): 1743, 1262 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3$: C, 64.49; H, 9.74; N, 0.00; found: C, 64.58; H, 9.52; N, <0.02.

General procedure for allylation of enamines. Reactions were assembled in a nitrogen filled dry-box. The enamine **2** (1.2 equiv, 1.20 mmol) was weighed into a vial, and ZnCl₂ (68 mg, 0.50 mmol) was added. A catalyst solution containing 27.6 mg (0.0200 mmol) of Ir(cod)(κ²-**L1**)(**L1**) and 6.7 mg [Ir(cod)Cl]₂ (0.0100 mmol) in 1 mL of toluene was then added to the vial, along with a stirbar and 10 μL of dodecane as internal standard. The carbonate **1** (1.00 mmol) was then weighed into the vial. The vial was closed with a PTFE/Silicone septum lined cap, removed from the dry-box, and stirred on the benchtop in a reaction block at 25 °C. The reaction progress was monitored by GC and GC/MS. When the reaction was judged complete, the crude enamine products were hydrolyzed by diluting the reaction mixture in benzene (10-12 mL), adding AcOH/NaOAc buffer (3 mL) (a solution made from 16.45 g NaOAc·3H₂O, 24 mL AcOH, 113 mL water), and stirring for 8 h.⁷ The organic layer was then further diluted with ether (100 mL) and washed with 10% aq HCl (2x 10 mL), water (1x 10 mL), sat. aq NaHCO₃ (2x 10 mL), and brine (1x 10 mL). Finally, the organic layer was dried over Na₂SO₄, decanted into a round bottom flask, and the solvent removed under vacuum on a rotary evaporator. Branched to linear ratios and yields were then determined by NMR spectroscopy. The solvent was then removed again, and the mixture was purified on silica gel, eluting with 95:5 pentane:ether (visualized with UV and KMnO₄ stain).

(R)-(-)-1,3-diphenylpent-4-ene-1-one 3a.^{8,9} The general procedure was followed using the (*R,R,R*)-**L1**-derived catalyst, 225 mg (1.02 mmol) carbonate **1a**, 208 mg (1.2 mmol) of enamine **2a**, and a reaction time of 2 h. ¹H NMR analysis of the crude product indicated a quantitative yield of the branched isomer (vs. DCE) and a >99:1 branched:linear ratio by GC/MS. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (221 mg, 91% yield). HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99 : 1, v = 0.5 mL/min, λ = 230 nm, ~25 °C): t_R [min] = 21.5 (97.0%), 25.1 (3.0%), 94% ee. ¹H NMR (CDCl₃, 500 MHz) δ 3.37 (dd, *J*=17, 7 Hz, 1H), 3.45 (dd, *J*=16.5, 8 Hz, 1H), 4.15 (q, *J*=7.5 Hz, 1H), 5.04 (dt, *J*=17, 1.5 Hz, 1H), 5.07 (dt, *J*=10.5, 1 Hz, 1H), 6.05 (ddd, *J*=17, 10, 6.5 Hz, 1H) 7.19-7.23 (m, 1H), 7.26-7.33 (m, 4H), 7.44-7.47 (m, 2H), 7.54-7.57 (m, 1H), 7.93-7.95 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 44.0, 44.5, 114.7, 126.5, 127.7, 128.0, 128.55, 128.56,

133.0, 137.1, 140.6, 143.1, 198.2. $[\alpha]_D^{24} - 0.47^\circ$ (c 0.85, CHCl_3). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.82; N, 0.00; found: C, 86.32; H, 6.67; N, 0.02.

(R)-(+)-2-methyl-5-phenyl-hept-6-ene-3-one 3b.^{8,10} The general procedure was followed using (*R,R,R*)-**L1**-derived catalyst, 219 mg (1.00 mmol) carbonate **1a**, 167 mg (1.20 mmol) of enamine **2b**, and a reaction time of 4.5 h. ^1H NMR analysis of the crude product indicated a 99% NMR yield of the branched isomer and a >99:1 branched:linear ratio. The product was isolated by column chromatography (SiO_2 , 95:5 pentane: Et_2O) as a clear oil (173 mg, 86% yield). HPLC (Daicel Chiralcel OJ (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, $v = 1.0$ mL/min, $\lambda = 210$ nm, $\sim 25^\circ\text{C}$): t_R [min] = 9.6 (97.4%), 13.5 (2.6%), 94% ee. ^1H NMR (CDCl_3 , 500 MHz) δ 0.98 (d, $J=7$ Hz, 3H), 1.05 (d, $J=7$ Hz, 3H), 2.50 (septet, $J=7$ Hz, 1H), 2.84 (dd, $J=16.5$, 7 Hz, 1H), 2.90 (dd, $J=17$, 7 Hz, 1H), 3.96 (q, $J=7$ Hz, 1H), 5.00-5.06 (m, 2H), 5.98 (ddd, $J=17$, 10.5, 7 Hz, 1H), 7.19-7.22 (m, 3H), 7.28-7.31 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.7, 17.9, 41.3, 44.2, 45.8, 114.5, 126.5, 127.6, 128.5, 140.7, 143.1, 212.7. $[\alpha]_D^{24} + 22.9^\circ$ (c 1.98, CHCl_3). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97; N, 0.00; found: C, 82.86; H, 9.25; N, 0.02.

(S)-(+)-1-(2-Methoxyphenyl)-3-phenylpent-4-en-1-one 3c.^{8,11} The general procedure was followed using (*S,S,S*)-**L1**-derived catalyst, 222 mg (1.01 mmol) of carbonate **1a**, 244 mg (1.20 mmol) of enamine **2c**, and a reaction time of 3.5 h. ^1H NMR analysis of the crude product indicated a 96:4 branched:linear ratio. The product was isolated by column chromatography (SiO_2 , 95:5 pentane: Et_2O) as a clear oil (233 mg, 87% yield). HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.5 : 0.5, $v = 1.0$ mL/min, $\lambda = 230$ nm, $\sim 25^\circ\text{C}$): t_R [min] = 18.9 (2.0%), 20.3 (98%), 96% ee. ^1H NMR (CDCl_3 , 500 MHz) δ 3.40 (dd, $J=13$, 3 Hz, 1H), 3.44 (dd, $J=13$, 4 Hz, 1H), 3.89 (s, 3H), 4.06 (q, $J=7$ Hz, 1H), 4.99 (dt, $J=17$, 1.5 Hz), 5.01 (dt, $J=10.5$, 1.3 Hz), 6.01 (ddd, $J=17$, 10.5, 7 Hz, 1H), 6.94-6.98 (m, 2H), 7.17-7.23 (m, 3H), 7.26-7.30 (m, 2H), 7.43-7.46 (m, 1H), 7.54 (dd, $J=7.5$, 2 Hz, 1H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 44.9, 49.2, 55.5, 111.4, 114.4, 120.7, 126.3, 127.8, 128.4, 128.7, 130.3, 133.3, 141.0, 143.5, 158.2, 200.9. $[\alpha]_D^{24} + 12.5^\circ$ (c 1.78, CHCl_3). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97; N, 0.00; found: C, 82.86; H, 9.25; N, 0.02.

2-methyl-6-phenyl-oct-7-ene-4-one 3d.¹² The general procedure was followed using the (*R,R,R*)-**L1**-derived catalyst, 224 mg (1.02 mmol) carbonate **1a**, 184 mg (1.20 mmol) of enamine **2d**, and a reaction time of 5 h. ^1H NMR

analysis of the crude product indicated a 97% yield of the branched isomer and a 98:2 branched:linear ratio. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (201 mg, 91% yield). HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.95 : 0.05, ν = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 11.8 (97.9%), 14.7 (2.1%), 96% ee. ¹H NMR (CDCl₃, 500 MHz) δ 0.83 (d, J =3.5 Hz, 3H), 0.84 (d, J =3.5 Hz, 3H), 2.08 (nonuplet, J =7 Hz, 1H), 2.18 (dd, J =16, 7 Hz, 1H), 2.24 (dd, J =16, 7 Hz, 1H), 2.78 (dd, J =16.5, 7 Hz, 1H), 2.83 (dd, J =16.5, 7.5 Hz, 1H), 3.94 (q, J =7 Hz, 1H), 5.01 (dt, J =17, 1.3 Hz, 1H), 5.05 (dt, J =10.5, 1 Hz, 1H), 5.97 (ddd, J =7, 10.5, 17 Hz, 1H), 7.19-7.21 (m, 3H), 7.28-7.31 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 22.4, 22.5, 24.3, 44.3, 48.4, 52.6, 114.5, 126.5, 127.6, 128.5, 140.7, 142.9, 208.9. $[\alpha]_D^{23}$ + 17.4 ° (c 2.00, CHCl₃). Anal. Calcd for C₁₅H₂₀O: C, 83.28; H, 9.32; N, 0.00; found: C, 83.53; H, 9.60; N, 0.02. The experiment was repeated twice more with the (*R,R,R*)-**L1**-derived catalyst: (2) reaction time 2.75 h, 202 mg (92% yield, 96% ee by HPLC) (3) reaction time 4 h, 194 mg (89% yield, 96% ee by HPLC). The reaction was then run with 0.5 mol% Ir(cod)(κ^2 -**L1**)(**L1**) and 0.25 mol% [Ir(cod)Cl]₂ to afford, after 11 hours reaction time and the usual workup, 183 mg (84% yield) of product which was of 95% ee by HPLC analysis.

2-methyl-6-(4-anisyl)-oct-7-ene-4-one 3e. The general procedure was followed using the (*S,S,S*)-**L1**-derived catalyst, 251 mg (1.00 mmol) carbonate **1b**, 184 mg (1.20 mmol) of enamine **2d**, and a reaction time of 2.5 h. GC/MS analysis of the crude hydrolyzed enamine mixture showed a 97:3 branched:linear ratio. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (229 mg, 93% yield). HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, ν = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 26.6 (1.9%), 29.2 (98.1%), 96% ee. ¹H NMR (CDCl₃, 500 MHz) δ 0.83 (d, J =3.0 Hz, 3H), 0.84 (d, J =3.0 Hz, 3H), 2.08 (nonuplet, J =7 Hz, 1H), 2.17 (dd, J =16, 6.5 Hz, 1H), 2.23 (dd, J =16, 7 Hz, 1H), 2.74 (dd, J =16.5, 7.5 Hz, 1H), 2.79 (dd, J =16, 7.5 Hz, 1H), 3.78 (s, 3H), 3.88 (q, J =7 Hz, 1H), 4.98 (dt, J =17, 1.5 Hz, 1H), 5.02 (dt, J =10.5, 1.3 Hz, 1H), 5.94 (ddd, J =17, 10, 6.5 Hz, 1H), 6.82-6.85 (m, 2H), 7.10-7.13 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 22.49, 22.52, 24.3, 43.6, 48.7, 52.6, 55.2, 113.9, 114.2, 128.6, 135.0, 141.0, 158.2, 209.0. IR (thin film): 2957, 1712, 1512, 1249, 1178, 1037 cm⁻¹. $[\alpha]_D^{24}$ - 15.9 ° (c 2.68, CHCl₃). Anal. Calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00; N, 0.00; found: C, 78.29; H, 9.19; N, 0.02. The experiment was repeated with (*R,R,R*)-**L1**-derived catalyst: reaction time 4 h, 219 mg (89% yield, 96% ee by HPLC).

2-methyl-6-(4-trifluoromethylphenyl)-oct-7-ene-4-one 3f. The general procedure was followed using the (*R,R,R*)-**L1**-derived catalyst, 287 mg (0.996 mmol) carbonate **1c**, 184 mg (1.20 mmol) of enamine **2d**, and a reaction time of 10.5 h. GC/MS analysis of the crude hydrolyzed enamine mixture showed an 85:15 branched:linear ratio. The pure branched product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (223 mg, 79% yield). HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.95 : 0.05, ν = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 8.3 (2.7%), 8.8 (97.3%), 95% ee. ¹H NMR (CDCl₃, 500 MHz) δ 0.83 (d, J =2.5 Hz, 3H), 0.84 (d, J =2.5 Hz, 3H), 2.08 (nonuplet, J =6.5 Hz, 1H), 2.19 (dd, J =16, 6.5 Hz, 1H), 2.25 (dd, J =16.5, 7.5 Hz, 1H), 2.79 (dd, J =16.5, 7.5 Hz, 1H), 2.86 (dd, J =17, 7 Hz, 1H), 4.01 (q, J =7 Hz, 1H), 5.03 (br d, J =17.5 Hz, 1H), 5.09 (br d, J =10.5 Hz, 1H), 5.95 (ddd, J =17, 10.5, 6.5 Hz, 1H), 7.32 (app d, J =8 Hz, 2H), 7.55 (app d, J =8 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 22.4, 22.5, 24.4, 44.0, 48.2, 52.6, 115.3, 124.2 (q, J =145 Hz), 125.5 (q, J =3.9 Hz), 128.1, 128.8 (q, J =32.1 Hz), 139.8, 147.1, 208.2. ¹⁹F NMR (CDCl₃, 469.9 MHz) -62.7. IR (thin film): 2960, 1715, 1327, 1165, 1126, 1069 cm⁻¹. $[\alpha]_D^{23} + 6.9^\circ$ (c 1.89, CHCl₃). Anal. Calcd for C₁₆H₁₉F₃O: C, 67.59; H, 6.74; N, 0.00; found: C, 67.35; H, 7.01; N, 0.02. The experiment was repeated with the (*S,S,S*)-**L1**-derived catalyst: reaction time 11 h, 200 mg (70% yield, 93% ee by HPLC).

2-methyl-6-(2-furyl)-oct-7-ene-4-one 3g. The general procedure was followed using (*R,R,R*)-**L1**-derived catalyst, 206 mg (0.979 mmol) carbonate **1d**, 184 mg (1.20 mmol) enamine **2d**, and a reaction time of 2 h. GC/MS analysis of the crude hydrolyzed enamine mixture showed a 99:1 branched:linear ratio and ¹H NMR analysis showed a 96% yield of **3g**. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (182 mg, 90% yield). HPLC (Daicel Chiralcel AS-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, ν = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 9.1 (98.4%), 10.6 (1.6%), 97% ee. ¹H NMR (CDCl₃, 500 MHz) δ 0.88 (d, J =6.5 Hz, 6H), 2.08 (septet, J =7 Hz, 1H), 2.26 (d, J =7 Hz, 2H), 2.72 (dd, J = 16.5, 8 Hz, 1H), 2.88 (dd, J =16.5, 6.5 Hz, 1H), 4.03 (q, J =7.5 Hz, 1H), 5.05-5.11 (m, 2H), 5.88 (ddd, J =17.5, 10, 7 Hz, 1H), 6.02 (d, J =3 Hz, 1H), 6.28 (dd, J =3.5, 2 Hz, 1H), 7.31 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 22.51, 22.53, 24.4, 38.2, 46.3, 52.4, 105.3, 110.2, 116.0, 137.7, 141.3, 155.8, 208.3. IR (thin film): 2958, 1715, 1367, 1148, 1010, 921, 733 cm⁻¹. $[\alpha]_D^{24} - 47.2^\circ$ (c 2.42, CHCl₃). Anal. Calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.80; N, 0.00; found: C, 75.59; H, 9.02; N, 0.02. The experiment was repeated with (*S,S,S*)-**L1**-derived catalyst: reaction time 2.5 h, 191 mg (90% yield, 97% ee by HPLC).

2-methyl-6-(2-methoxyphenyl)-oct-7-ene-4-one 3h. The general procedure was followed using the (*S,S,S*)-**L1**-derived catalyst, 251 mg (1.00 mmol) of carbonate **1e**, 184 mg (1.20 mmol) of enamine **2d**, and a reaction time of 7.5 h. ¹H NMR analysis of the crude hydrolyzed enamine mixture showed a 98:2 branched:linear ratio and a 96% yield of **3h**. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (214 mg, 87% yield). HPLC (Daicel Chiralcel AS-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, ν = 1.0 mL/min, λ = 210 nm, ~25 °C): t_R [min] = 12.4 (88.4%), 19.0 (11.6%), 77% ee. ¹H NMR (CDCl₃, 500 MHz) δ 0.85 (d, J =1 Hz, 3H), 0.86 (d, J =0.5 Hz, 3H), 2.11 (nonuplet, J =6.5 Hz, 1H), 2.23 (dd, J =16, 6.5 Hz, 1H), 2.27 (dd, J =16, 7.5 Hz, 1H), 2.77 (dd, J =13.5, 6.5 Hz, 1H), 2.83 (dd, J =16, 8 Hz, 1H), 3.83 (s, 3H), 4.30 (q, J =7.5 Hz, 1H), 5.00 (dt, J =17, 1.3 Hz, 1H), 5.03 (dt, J =10, 1.3 Hz, 1H), 6.01 (ddd, J =17, 10, 6.5 Hz, 1H), 6.86 (app d, J =8 Hz, 1H), 6.90 (app dt, J =7.5, 1 Hz, 1H), 7.13 (dd, J =7.5, 1.5 Hz, 1H), 7.19 (app ddd, J =8, 7.5, 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 22.5, 24.38, 38.5, 47.6, 52.1, 55.4, 110.8, 114.5, 120.6, 127.5, 128.2, 131.3, 140.0, 156.8, 209.3. IR (thin film): 2957, 1713, 1493, 1465, 1244, 1030, 754 cm⁻¹. $[\alpha]_D^{24}$ – 9.8 ° (c 3.00, CHCl₃). Anal. Calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00; N, 0.00; found: C, 77.90; H, 8.72; N, 0.02. The experiment was repeated with the (*R,R,R*)-**L1**-derived catalyst: reaction time 7.5 h, 208 mg (86% yield, 76% ee by HPLC).

3-methyl-1-phenylpent-4-ene-1-one 3i.¹³ The general procedure was followed using the (*R,R,R*)-**L1**-derived catalyst, 157 mg (0.992 mmol) of carbonate **1f**, 2 equiv (347 mg, 2.00 mmol) of enamine **2a**, and a reaction time of 7.5 h. ¹H NMR analysis of the crude hydrolyzed enamine mixture showed a 95:5 branched:linear ratio and a 66% yield of **3i**. The product was isolated by column chromatography (SiO₂, 95:5 pentane:Et₂O) as a clear oil (120 mg, 69% yield). HPLC (Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.95 : 0.05, ν = 1.0 mL/min, λ = 230 nm, ~25 °C): t_R [min] = 16.0 (2.8%), 16.4 (97.2%), 94% ee. ¹H NMR (CDCl₃, 500 MHz) δ 1.10 (d, J =6.5 Hz, 3H), 2.88-2.94 (m, 2H), 3.01-3.06 (m, 1H), 4.96 (dt, J =10.5, 1 Hz, 1H), 5.03 (dt, J =17, 1.5 Hz, 1H), 5.84 (ddd, J =17, 10.5, 6.5 Hz), 7.45-7.48 (m, 2H), 7.54-7.58 (m, 1H), 7.94-7.96 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 19.8, 33.6, 45.1, 113.0, 128.1, 128.6, 133.0, 137.3, 143.1, 199.4. $[\alpha]_D^{24}$ + 0.3 ° (c 2.21, CHCl₃). $[\alpha]_{405nm}^{24}$ – 13.5 ° (c 2.21, CHCl₃). Anal. Calcd for C₁₂H₁₄O: C, 82.72; H, 8.10; N, 0.00; found: C, 82.50; H, 7.94; N, 0.02. The experiment was repeated with the (*S,S,S*)-**L1**-derived catalyst: reaction time 4.25 h, 119 mg (68% yield, 93% ee by HPLC).

2-methyl-6-vinyl-4-nonanone 3j.¹² The general procedure was followed using the (*S,S,S*)-**L1**-derived catalyst, 190 mg (1.02 mmol) of carbonate **1f**, 1.5 equiv (230 mg, 1.50 mmol) of enamine **2d**, 0.5 mL of toluene and a reaction time of 39

h at 35 °C. GC analysis of the crude hydrolyzed enamine product showed a 89:11 b:l ratio. Because the product is moderately volatile, the reaction was workup up in the normal fashion, but when the solvent was removed special care was taken to only concentrate to a volume of about 1 mL. This solution was loaded directly onto a column and chromatographed (SiO₂, 100:1 to 100:1.5 pentane:Et₂O) to yield the product as a clear oil (119 mg, 64% yield, 83% ee by HPLC (vide infra)). ¹H NMR (CDCl₃, 500 MHz) δ 0.87 (t, *J*=3.5 Hz, 3H), 0.89 (d, *J*=6.5 Hz, 6H), 1.21-1.33 (m, 4H), 2.12 (nonuplet, *J*=6.8 Hz, 1H), 2.25 (d, *J*=7 Hz, 2H), 2.37 (d, *J*=7 Hz, 2H), 2.57 (br m, 1H), 4.95-5.00 (m, 2H), 5.58 (ddd, *J*= 17.5, 10.5, 8.5 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ 14.0, 20.1, 22.6, 24.3, 36.8, 39.1, 48.7, 52.5, 114.7, 141.5, 210.1. [α]_D²⁶ + 2.1 ° (c 1.46, CHCl₃). Anal. Calcd for C₁₂H₂₂O: C, 79.06; H, 12.16; N, 0.00; found: C, 78.91; H, 11.88; N, <0.02. The enantiomers of ketone **3j** proved inseparable on chiral HPLC or chiral GC. It was derivatized by reduction to the alcohol and formation of the *O*-methoxymandelic acid ester.¹⁴

The ketone (47.4 mg, 0.261 mmol) was dissolved in 1 mL of methanol and sodium borohydride was added in one portion (48 mg, 1.27 mmol). The reaction was stirred for 30 min and the solvent removed on a rotary evaporator. The alcohols were chromatographed (dry load with CH₂Cl₂, elute with 10% ether in pentane) through a short silica column and the solvent removed to afford the product as an oil (34.4 mg, 72% yield).

The alcohol (25.5 mg, 0.138 mmol), (*R*)-*O*-methoxymandelic acid (25.3 mg, 0.152 mmol) and DMAP (4.3 mg, 0.035 mmol) were mixed in 1.3 mL of CH₂Cl₂ and DCC was added (34 mg, 0.165 mmol). The reaction was stirred for 1 hour, during which time a heavy white precipitate formed. The reaction was filtered through a silica gel plug (elute with 10% ether in pentanes) to afford the product ester as an oil (41.4 mg, 92% yield). The mixture of diastereomers was analyzed by SFC (Regis Whelk O-1 (0.46 cm x 25 cm), 125 bar, 40 °C, 0.8% MeOH in CO₂, v=2.5 mL/min): *t*_R [min] = 6.21 and 6.49 (91.5%), 7.54 and 7.73 (8.5%), 83% ee. The ratios of the peaks at 6.21 and 6.49 min to the peaks at 7.54 and 7.73 min correspond to the er of the ketone **3j**.

^1H NMR spectrum for **1f**.

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