Supporting Information for
Iridium-Catalyzed Regio- and Enantioselective Allylation of Ketone
Enolates

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Methods and Materials. Melting points (mp) were measured using a Thomas-Hoover capillary tube melting point apparatus and are uncorrected. Infrared spectra (FT-IR) were obtained from evaporated films on NaCl disks with a MIDAC M-1200 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance DPX-400 and Bruker Avance DPX-500 spectrometers at ambient probe temperature with CDCl_3 as solvent and are referenced to the residual solvent peaks CHCl_3 ($\delta = 7.26$ ppm) and CDCl_3 ($\delta = 77.0$ ppm) unless otherwise stated. Mass spectra (EI-MS) were recorded on a Micromass 70-VSE mass spectrometer. GC-MS data were obtained on an Agilent 6890-N GC system with an Alltech EC-1 capillary column (30 m x 0.25 mm x 0.25 μm) and an Agilent 5973 mass selective detector. Specific rotations ($[\alpha]$) were measured on a Perkin Elmer 341 polarimeter using a microcell with 100 mm pathlength (concentration c given as g/100 mL). HPLC analyses were carried out on a Waters chromatography system consisting of a 1525 binary pump, a 717-plus autosampler, and a 2487 dual wavelength detector. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Thin-layer chromatography was performed on Merck silica gel 60 F₂₅₄ 250 μm precoated glass plates, and components were visualized by observation under UV light or by treating the plates with phosphomolybdic acid reagent followed by heating. Flash chromatography was performed with 32-63 μm silica gel as adsorbent obtained from Sorbent Technologies.

All reactions were conducted using standard Schlenk and drybox techniques. EtOH and CHCl_3 were distilled prior to their use, and THF was dried by passing it through a column of activated alumina. $[(\text{COD})\text{IrCl}]_2$ ¹ and the phosphoramidite ligands **L1**², **L2**², **L3**³, and **L4**³ were prepared according to published procedures. All silyl enol ethers were prepared by reaction of the corresponding ketones with LDA and TMSCl under in situ quench conditions at -78 °C and were purified by vacuum distillation.⁴ All *tert*-butyloxycarbonyl substituted allylic substrates were prepared by reaction of the corresponding alcohols with (Boc)₂O under phase transfer catalysis.⁵ (*E*)-4-(Trifluoromethyl)cinnamyl alcohol was prepared by converting the corresponding cinnamic acid into its acid chloride using $(\text{COCl})_2$ and subsequent DIBAL reduction.⁶ (*E*)-4-Methoxycinnamyl alcohol, (*E*)-3-(2-furyl)prop-2-en-1-ol, and (*E*)-4-methylpent-2-en-1-ol were prepared by DIBAL reduction of the corresponding aldehydes.⁷ All other starting materials, reagents, and solvents were purchased from Aldrich Chemicals Corp. and were used as received.

General Procedure A for the Reactions of Silyl Enol Ether 1a with the Allylic Carbonate 2b. In a drybox, 40 μmol (4 mol%) of the phosphoramidite ligand **L** and 13.4 mg (20 μmol , 2 mol%) $[(\text{COD})\text{IrCl}]_2$ were dissolved in 1.0 mL THF in a screw capped vial equipped with a stirring bar. The vial was sealed with a cap containing a PTFE/silicone septum and removed from the drybox. 1.0 mL Propylamine was added by syringe, and the solution was stirred in an oil bath at 50 °C for 20 min. Then the vial was brought into to a drybox, and all volatile materials were removed in vacuo. The residual material was dissolved in a mixture of 1.0 mL THF and 0.5 mL diglyme. This solution was added to a mixture of the indicated amounts of CsF and ZnF_2 and 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**). The vial was sealed with a septum cap and removed from the drybox. The indicated amount of the acetophenone silyl enol ether **1a** was added by syringe, and the reaction was stirred in an oil bath at 50 °C. After the indicated time, the reaction mixture was allowed to cool to ambient temperature, 1.0 mL H_2O was added and the mixture was extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were dried over Na_2SO_4 and filtered through a short bed of Celite.

The solvents were removed in vacuo, and the remaining residue was analyzed by ^1H NMR spectroscopy. Then the crude material was stirred with 1.0 mL (1.0 mmol) TBAF (1M, THF) for 45 min. The mixture was diluted with 2 mL Et_2O and washed with 4 mL saturated aqueous NH_4Cl . The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 2 mL). The combined organic extracts were dried over Na_2SO_4 and filtered through a short bed of Celite. The solvents were removed in vacuo, and the remaining residue was purified by flash column chromatography.

General Procedure B for the Reactions of Silyl Enol Ethers **1 with Allylic Carbonates **2**.** In a drybox, 21.6 mg (40 μmol , 4.0 mol%) phosphoramidite ligand **L1**, 13.4 mg (20 μmol , 2.0 mol%) $[(\text{COD})\text{IrCl}]_2$, the indicated amounts of CsF and ZnF_2 , and 1.00 mmol of the respective allyl *tert*-butyl carbonate **2** were combined. This mixture was placed in a screw capped vial equipped with a stirring bar, sealed with a cap containing a PTFE/silicone septum and removed from the drybox. The indicated amount of the respective silyl enol ether **1** was added by syringe, and the reaction was stirred in an oil bath at 50 $^\circ\text{C}$ until the carbonate was fully consumed, as determined by GC. The reaction mixture was allowed to cool to ambient temperature, and 1.0 mL (1.0 mmol) TBAF (1M, THF) was added by syringe. After stirring for 45 min, the reaction mixture was diluted with 2 mL Et_2O and washed with 4 mL saturated aqueous NH_4Cl . The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 2 mL). The combined organic extracts were dried over Na_2SO_4 and filtered through a short bed of Celite. The solvents were removed in vacuo, and the remaining residue was analyzed by ^1H NMR spectroscopy to determine the ratio of branched to linear regioisomers, before the crude reaction product was purified by flash column chromatography.

^{31}P NMR Spectroscopic Studies of the Catalytic Reaction

Following the general procedure B, employing 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**) and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were stirred at ambient temperature for 15 min and were transferred to a screw capped NMR tube in a glovebox. ^{31}P NMR spectroscopy indicated the formation of the $[\text{Ir}(\text{COD})\text{Cl}(\text{L1})]$ complex. ^{31}P NMR (162 MHz, DME): δ [ppm] = 116.4 (s).⁸

In a second, otherwise identical experiment, the reaction mixture was stirred at 50 $^\circ\text{C}$ for 4 h before it was transferred to a screw capped NMR tube. GC analysis indicated approximately 40% conversion of the starting material (**2a**) and ^{31}P NMR spectroscopy revealed the disappearance of the resonance attributed to the $[\text{Ir}(\text{COD})\text{Cl}(\text{L1})]$ complex and displayed a set of two doublets due to the formation of the iridacycle **7** bearing one κ^2 , P,C-bound **L1** and one κ^1 , P-bound **L1**. ^{31}P NMR (162 MHz, DME): δ [ppm] = 128.8 (d, $^3J_{\text{P,P}}=44.6$ Hz), 154.1 (d, $^3J_{\text{P,P}}=44.6$ Hz).⁸

Spectroscopic and Analytical Data of Reaction Products

(*R*)-1,3-Diphenylpent-4-en-1-one.⁹ (Table 2, entry 3): Following the general procedure A, employing 25.3 mg (40 μmol , 4.0 mol%) of the phosphoramidite ligand **L3**, 13.4 mg (20 μmol , 2.0 mol%) $[(\text{COD})\text{IrCl}]_2$, 30 mg (0.20 mmol) CsF and 124 mg (1.20 mmol) ZnF_2 , 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**) and 230 mg (1.20 mmol) acetophenone silyl enol ether (**1a**) were reacted for 18 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 92:8, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 1 $\rightarrow$ 3% EtOAc in hexanes) afforded 215 mg (89%) of the title compound as colorless crystals. mp 47–49 $^\circ\text{C}$

(hexanes/EtOAc). R_f (SiO₂, hexanes/EtOAc = 94 : 6) 0.22. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 3.38 (dd, A of ABX, J_{AB} = 16.7 Hz, J_{AX} = 6.6 Hz, 1H), 3.44 (dd, B of ABX, J_{AB} = 16.7 Hz, J_{BX} = 7.6 Hz, 1H), 4.15 (app q, J = 6.8 Hz, 1H), 5.04 (app dt, J = 17.2, 1.3 Hz, 1H), 5.14 (app dt, J = 10.4, 1.3 Hz, 1H), 6.06 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 7.18–7.34 (m, 5H), 7.45 (m, 2H), 7.56 (m, 1H), 7.94 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ [ppm] = 44.0 (CH₂), 44.5 (CH), 114.7 (CH₂), 126.5 (CH), 127.7 (CH), 128.0 (CH), 128.5 (CH), 128.6 (CH), 133.0 (CH), 137.1, 140.6 (CH), 143.1, 198.2. 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] = 20.6 (97.7%), 23.5 (2.3%), 95% *ee*. $[\alpha]_D^{20}$ -1.6 (c = 3.14, CHCl₃).

(S)-1,3-Diphenylpentan-1-one.^{10, 11} 100 mg (423 μ mol) (+)-**4a** and 16 mg (17 μ mol, 4 mol%) [(PPh₃)₃RhCl] were dissolved in 2 mL of degassed THF under an atmosphere of N₂. The reaction vessel was flushed with H₂ and stirred for 9 h at ambient temperature under an atmosphere of H₂ (1 bar). The solvent was removed in vacuo and flash chromatography (SiO₂, 1 $\rightarrow$ 3% EtOAc in hexanes) afforded 74 mg (73%) of the title compound as colorless crystals. mp 42–44 °C (CHCl₃). R_f (SiO₂, hexanes/EtOAc = 94 : 6) 0.24. ¹H NMR (500 MHz, CDCl₃, TMS): δ [ppm] = 0.81 (t, J = 7.3 Hz, 3H), 1.65 (m, 1H), 1.79 (m, 1H), 3.20–3.32 (m, 3H), 7.15–7.31 (m, 5H), 7.43 (m, 2H), 7.53 (m, 1H), 7.90 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ [ppm] = 12.0 (CH₃), 29.2 (CH₂), 43.0 (CH), 45.6 (CH₂), 126.2 (CH), 127.6 (CH), 128.0 (CH), 128.4 (CH), 128.5, (CH) 132.9 (CH), 137.3, 144.7, 199.2. 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] = 21.3 (98.1%), 23.2 (1.9%), 96% *ee*. $[\alpha]_D^{20}$ +1.2 (c = 0.85, CHCl₃), $[\alpha]_{546}^{23}$ +9.0 (c = 2.50, EtOH). Lit [10]: $[\alpha]_{546}^{23}$ +10.5 (c = 2.5, EtOH).

(+)-3-(4-Methoxyphenyl)-1-phenylpent-4-en-1-one. (Table 3, entry 1): Following the general procedure B, employing the *R_aR_cR* enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF₂, 264 mg (1.00 mmol) *tert*-butyl allyl carbonate **2b** and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were reacted for 6 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 99:1, as determined by ¹H NMR spectroscopy. Flash chromatography (SiO₂, 6% Acetone in hexanes) afforded 253 mg (95%) of the title compound as colorless waxy crystals. R_f (SiO₂, hexanes/EtOAc = 92 : 8) 0.16. FT-IR (film): $\tilde{\nu}$ [cm⁻¹] = 3003 (m), 2956 (m), 2835 (w), 1685 (s), 1637 (w), 1611 (m), 1597 (w), 1581 (w), 1511 (s), 1448 (m), 1359 (w), 1302 (w), 1249 (s), 1205 (m), 1179 (m), 1035 (m), 990 (m), 917 (m), 830 (m), 756 (m), 691 (m), 663 (w), 538 (w). ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 3.35 (dd, A of ABX, J_{AB} = 16.6 Hz, J_{AX} = 6.8 Hz, 1H), 3.40 (dd, B of ABX, J_{AB} = 16.6 Hz, J_{BX} = 7.6 Hz, 1H), 3.79 (s, 3H), 4.09 (app q, J = 7.1 Hz, 1H), 5.01 (app dt, J = 17.2, 1.5 Hz, 1H), 5.05 (app dt, J = 10.4, 1.5 Hz, 1H), 6.03 (ddd, J = 17.2, 10.4, 6.6 Hz, 1H), 6.84 (m, 2H), 7.18 (m, 2H), 7.45 (m, 2H), 7.55 (m, 1H), 7.91–7.95 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ [ppm] = 43.8 (CH), 44.2 (CH₂), 55.2 (CH₃), 114.0 (CH), 114.3 (CH₂), 128.1 (CH), 128.6 (CH), 128.7 (CH), 133.0 (CH), 135.2, 137.2, 141.0 (CH), 158.2, 198.4. MS (DIP-EI, 70 eV): m/z (%) = 267 (6), 266 (27) [M⁺], 238 (3), 161 (5), 147 (20), 106 (9), 105 (100), 91 (8), 77 (23). Anal. calcd for C₁₈H₁₈O₂: C, 81.17; H, 6.81; found: C, 81.23; H, 6.86; HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, v = 0.6 mL/min, λ = 230 nm, ~25 °C): t_R [min] = 50.1 (2.4%), 54.6 (97.6%), 95% *ee*. $[\alpha]_D^{20}$ +3.1 (c = 2.59, CHCl₃). From a second experiment, employing (*S_aS_cS*)-**L1**, 248 mg (93%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, v =

0.6 mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 51.1 (97.9%), 57.8 (2.1%), 96% *ee*. $[\alpha]_D^{20} -3.2$ ($c = 1.17$, CHCl_3).

(-)-1-Phenyl-3-[4-(trifluoromethyl)phenyl]pent-4-en-1-one. (Table 3, entry 2): Following the general procedure B, employing the R_a,R,R enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 302 mg (1.00 mmol) *tert*-butyl allyl carbonate **2c** and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were reacted for 12 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 94:6, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 5% EtOAc in hexanes) afforded 242 mg (80%) of the title compound as colorless waxy crystals. R_f (SiO_2 , hexanes/EtOAc = 92 : 8) 0.23. FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3085 (w), 3067 (w), 2982 (w), 2901 (w), 1688 (s), 1638 (w), 1618 (w), 1581 (w), 1449 (w), 1417 (w), 1326 (s), 1165 (s), 1123 (s), 1069 (s), 1018 (m), 921 (w), 840 (m), 754 (m), 690 (m). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 3.41 (dd, A of ABX, $J_{AB} = 16.9$ Hz, $J_{AX} = 7.1$ Hz, 1H), 3.46 (dd, B of ABX, $J_{AB} = 16.9$ Hz, $J_{BX} = 7.1$ Hz, 1H), 4.22 (app q, $J = 6.8$ Hz, 1H), 5.06 (app dt, $J = 17.2$, 1.5 Hz, 1H), 5.12 (app dt, $J = 10.4$, 1.0 Hz, 1H), 6.03 (ddd, $J = 17.2$, 10.4, 6.8 Hz, 1H), 7.39 (m, 2H), 7.46 (m, 2H), 7.57 (m, 3H), 7.93 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 43.6 (CH_2), 44.2 (CH), 115.5 (CH_2), 124.2 (q, $J_{\text{C,F}} = 272$ Hz), 125.5 (CH), 128.0 (CH), 128.1 (CH), 128.6 (CH), 128.8 (q, $J_{\text{C,F}} = 32$ Hz), 133.2 (CH), 136.9, 139.9 (CH), 147.2, 197.6. MS (DIP-EI, 70 eV): m/z (%) = 304 (3) [M^+], 285 (3), 185 (5), 159 (4), 115 (5), 106 (9), 105 (100), 77 (24), 57 (13). Anal. calcd for $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}$: C, 71.04, H, 4.97, F, 18.73, O, 5.26, found: C, 70.94, H, 4.95, F, 18.84. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.5 : 0.5, $v = 0.5$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 22.3 (97.1%), 26.0 (2.9%), 94% *ee*. $[\alpha]_D^{20} -14.1$ ($c = 1.08$, CHCl_3). From a second experiment, employing (S_a,S,S)-**L1**, 252 mg (83%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.5 : 0.5, $v = 0.5$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 22.5 (2.7%), 26.0 (97.3%), 95% *ee*. $[\alpha]_D^{20} +12.6$ ($c = 1.19$, CHCl_3).

(-)-3-(2-Furyl)-1-phenylpent-4-en-1-one. (Table 3, entry 3): Following the general procedure B, employing the R_a,R,R enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 224 mg (1.00 mmol) *tert*-butyl allyl carbonate **2d** and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were reacted for 16 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 99:1, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 4% Et_2O in hexanes) afforded 170 mg (75%) of the title compound as a colorless oil. R_f (SiO_2 , hexanes/EtOAc = 92 : 8) 0.27. FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3084 (w), 3065 (w), 2982 (w), 2908 (w), 1687 (s), 1639 (w), 1597 (m), 1581 (w), 1504 (w), 1449 (m), 1409 (w), 1357 (m), 1274 (m), 1210 (m), 1011 (m), 921 (m), 740 (s), 691 (m), 599 (w). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 3.33 (dd, A of ABX, $J_{AB} = 16.8$ Hz, $J_{AX} = 7.8$ Hz, 1H), 3.48 (dd, B of ABX, $J_{AB} = 16.8$ Hz, $J_{BX} = 6.3$ Hz, 1H), 4.23 (app q, $J = 6.8$ Hz, 1H), 5.08–5.14 (m, 2H), 5.98 (m, 1H), 6.08 (dt, $J = 3.3$, 0.8 Hz, 1H), 6.29 (dd, $J = 3.3$, 1.8 Hz, 1H), 7.32 (dd, $J = 1.8$, 0.8 Hz, 1H), 7.46 (m, 2H), 7.57 (m, 1H), 7.94–7.98 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 38.5 (CH), 41.9 (CH_2), 105.4 (CH), 110.2 (CH), 116.1 (CH_2), 128.1 (CH), 128.6 (CH), 133.1 (CH), 137.0, 137.8 (CH), 141.4 (CH), 155.9, 197.7. MS (DIP-EI, 70 eV): m/z (%) = 227 (3), 226 (14) [M^+], 198 (4), 121 (3), 107 (7), 106 (9), 105 (100), 79 (6), 77 (29). Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.62; H, 6.24; found: C, 79.54; H, 6.27. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, $v = 0.4$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 39.1 (98.1%), 41.9 (1.9%), 96% *ee*. $[\alpha]_D^{20} -57.8$ ($c = 1.04$, CHCl_3). From a second

experiment, employing (*S_a,S,S*)-**L1**, 163 mg (72%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, $v = 0.4$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 39.9 (1.9%), 42.5 (98.1%), 96% *ee*. $[\alpha]_D^{20} +55.8$ ($c = 1.10$, CHCl₃).

(+)-3-Isopropyl-1-phenylpent-4-en-1-one.⁹ (Table 3, entry 4): Following the general procedure B, employing the *R_a,R,R* enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF₂, 200 mg (1.00 mmol) *tert*-butyl allyl carbonate **2e** and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were reacted for 40 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 85:15, as determined by ¹H NMR spectroscopy. Flash chromatography (SiO₂, 2% EtOAc in hexanes) afforded 140 mg (69%) of a yellowish oil consisting of a mixture of the title compound and the branched isomer in a ratio of 85:15, as determined by ¹H NMR spectroscopy. R_f (SiO₂, hexanes/EtOAc = 96 : 4) 0.18. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 0.91 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 1.74 (d septet, $J = 6.8, 5.6$ Hz, 1H), 2.63 (m, 1H), 2.98–3.03 (m, 2H), 4.94 (ddd, $J = 17.2, 1.8, 1.0$ Hz, 1H), 5.00 (dd, $J = 10.4, 1.8$ Hz, 1H), 5.69 (ddd, $J = 17.2, 10.4, 8.6$ Hz, 1H), 7.46 (m, 2H), 7.55 (m, 1H), 7.91–7.98 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ [ppm] = 18.8 (CH₃), 20.4 (CH₃), 31.5 (CH), 41.0 (CH₂), 45.9 (CH), 115.9 (CH₂), 128.1 (CH), 128.5 (CH), 132.8 (CH), 137.5, 139.1 (CH), 199.8. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes, $v = 0.3$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 61.0 (3.0%), 63.4 (97.0%), 94% *ee*. $[\alpha]_D^{20} +11.6$ ($c = 1.00$, CHCl₃). From a second experiment, employing (*S_a,S,S*)-**L1**, 162 mg (80%) of a 84:16 regioisomeric mixture were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes, $v = 0.3$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 59.0 (97.0%), 62.6 (3.0%), 94% *ee*. $[\alpha]_D^{20} -10.0$ ($c = 3.60$, CHCl₃).

(+)-1-Phenyl-3-propylpent-4-en-1-one.⁹ (Table 3, entry 5): Following the general procedure B, employing the *R_a,R,R* enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF₂, 200 mg (1.00 mmol) *tert*-butyl allyl carbonate **2e** and 288 mg (1.50 mmol) acetophenone silyl enol ether **1a** were reacted for 8 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 87:13 (¹H NMR). Flash chromatography (SiO₂, 1.5% EtOAc in hexanes) afforded 177 mg (87%) of a yellowish oil consisting of a mixture of the title compound and the branched isomer in a ratio of 87:13, as determined by ¹H NMR spectroscopy. R_f (SiO₂, hexanes/EtOAc = 96 : 4) 0.20. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 0.89 (t, $J = 6.8$ Hz, 3H), 1.22–1.51 (m, 4H), 2.76 (m, 1H), 2.97 (app d, $J = 7.1$ Hz, 2H), 4.97 (dd, $J = 10.4, 1.5$ Hz, 1H), 4.99 (app dt, $J = 17.2, 1.3$ Hz, 1H), 5.68 (ddd, $J = 17.2, 10.4, 8.3$ Hz, 1H), 7.46 (m, 2H), 7.55 (m, 1H), 7.92–7.98 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ [ppm] = 14.0 (CH₃), 20.2 (CH₂), 36.9 (CH₂), 39.5 (CH), 43.9 (CH₂), 114.6 (CH₂), 128.1 (CH), 128.5 (CH), 132.8 (CH), 137.4, 141.6 (CH), 199.5. HPLC (Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, $v = 0.5$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 22.7 (4.1%), 23.4 (95.9%), 92% *ee*. $[\alpha]_D^{20} +12.1$ ($c = 1.03$, CHCl₃). From a second experiment, employing (*S_a,S,S*)-**L1**, 196 mg (97%) of a 87:13 regioisomeric mixture were isolated: HPLC (Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.75 : 0.25, $v = 0.5$ mL/min, $\lambda = 230$ nm, ~ 25 °C): t_R [min] = 23.0 (95.4%), 24.5 (4.6%), 91% *ee*. $[\alpha]_D^{20} -10.6$ ($c = 1.03$, CHCl₃).

(+)-(E)-1-Phenyl-3-vinylhex-4-en-1-one. (Table 3, entry 6): Following the general procedure B, employing the *R_a,R,R* enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF₂, 198 mg (1.00 mmol) *tert*-butyl allyl carbonate **2f** and 288 mg (1.50 mmol) acetophenone silyl enol

ether **1a** were reacted for 18 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 95:5, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 2 $\rightarrow$ 4% EtOAc in hexanes) afforded 170 mg (85%) of the title compound as a colorless oil. R_f (SiO_2 , hexanes/EtOAc = 96 : 4) 0.19. FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 2968 (m), 2917 (m), 2856 (w), 1687 (s), 1637 (w), 1597 (w), 1580 (w), 1449 (m), 1407 (w), 1357 (w), 1260 (w), 1208 (w), 969 (s), 917 (m), 753 (s), 691 (s), 658 (w). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 1.65 (d, J = 5.3 Hz, 3H), 3.07 (app d, J = 7.1 Hz, 2H), 3.45 (app quintet, J = 6.5 Hz, 1H), 5.01 (app dt, J = 10.2, 1.2 Hz, 1H), 5.04 (app dt, J = 17.2, 1.5 Hz, 1H), 5.46 (m, AB pattern, J_{AB} = 15.4 Hz, 2H), 5.83 (ddd, J = 17.2, 10.2, 6.8 Hz, 1H), 7.46 (m, 2H), 7.56 (m, 1H), 7.94 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 17.9 (CH_3), 42.1 (CH), 43.4 (CH_2), 114.3 (CH_2), 125.8 (CH), 128.1 (CH), 128.6 (CH), 132.2 (CH), 132.9 (CH), 137.3, 140.4 (CH), 198.8. MS (DIP-EI, 70 eV): m/z (%) = 200 (3) [M^+], 185 (3), 120 (3), 106 (9), 105 (100), 79 (5), 77 (29). Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.96; H, 8.05; found: C, 83.87; H, 8.12. HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.95 : 0.05, v = 0.4 mL/min, λ = 230 nm, $\sim 25^\circ\text{C}$): t_R [min] = 28.5 (2.4%), 30.7 (97.6%), 95% *ee*. $[\alpha]_D^{20}$ +6.8 (c = 1.22, CHCl_3). From a second experiment, employing (S_a,S,S)-**L1**, 168 mg (84%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OJ-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.95 : 0.05, v = 0.4 mL/min, λ = 230 nm, $\sim 25^\circ\text{C}$): t_R [min] = 28.0 (97.5%), 30.3 (2.5%), 95% *ee*. $[\alpha]_D^{20}$ -7.8 (c = 1.16, CHCl_3).

(-)-1-(2-Methoxyphenyl)-3-phenylpent-4-en-1-one. (Table 3, entry 7): Following the general procedure B, employing the R_a,R,R enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**) and 336 mg (1.50 mmol) silyl enol ether **1b** were reacted for 18 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 98:2, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 6 $\rightarrow$ 8% EtOAc in hexanes) afforded 169 mg (63%) of the title compound as a colorless oil. R_f (SiO_2 , hexanes/EtOAc = 92 : 8) 0.17. FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3027 (m), 2942 (m), 2838 (w), 1675 (s), 1697 (s), 1485 (s), 1465 (m), 1436 (m), 1287 (s), 1245 (s), 1181 (m), 1163 (m), 1023 (m), 992 (m), 917 (w), 758 (s), 701 (s). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 3.42 (m, AB of ABX pattern, 2H), 3.89 (s, 3H), 4.06 (app q, J = 7.3 Hz, 1H), 5.00 (d, J = 17.2 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 6.01 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 6.93–6.99 (m, 2H), 7.16–7.32 (m, 5H), 7.44 (m, 1H), 7.55 (dd, J = 7.6, 1.8 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 44.9 (CH), 49.2 (CH_2), 55.5 (CH_3), 111.4 (CH), 114.4 (CH_2), 120.7 (CH), 126.3 (CH), 127.8 (CH), 128.4 (CH), 128.8, 130.3 (CH), 133.2 (CH), 141.0 (CH), 143.5, 158.2, 200.9. MS (DIP-EI, 70 eV): m/z (%) = 266 (2) [M^+], 219 (19), 203 (5), 149 (7), 136 (10), 135 (100), 117 (8), 115 (6), 91 (10), 77 (18), 57 (5). Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81; found: C, 81.05; H, 6.90. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.5 : 0.5, v = 0.5 mL/min, λ = 230 nm, $\sim 25^\circ\text{C}$): t_R [min] = 36.6 (97.7%), 39.7 (2.3%), 95% *ee*. $[\alpha]_D^{20}$ -10.8 (c = 1.00, CHCl_3). From a second experiment, employing (S_a,S,S)-**L1**, 159 mg (60%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 99.5 : 0.5, v = 0.5 mL/min, λ = 230 nm, $\sim 25^\circ\text{C}$): t_R [min] = 37.1 (2.1%), 39.1 (97.9%), 96% *ee*. $[\alpha]_D^{20}$ +11.2 (c = 1.02, CHCl_3).

(+)-2-Methyl-5-phenylhept-6-en-3-one.¹² (Table 3, entry 8): Following the general procedure B, employing the R_a,R,R enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**) and 237 mg (1.50 mmol) silyl enol ether **1c**

were reacted for 40 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 95:5, as determined by ^1H NMR spectroscopy. Flash chromatography (SiO_2 , 2.5 $\rightarrow$ 5% EtOAc in hexanes) afforded 91 mg (45%) of the title compound as a colorless oil. R_f (SiO_2 , hexanes/EtOAc = 96 : 4) 0.15. ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 0.97 (d, J = 6.8 Hz, 3H), 1.04 (d, J = 7.1 Hz, 3H), 2.50 (septet, J = 7.1 Hz, 1H), 2.85 (dd, A of ABX, J_{AB} = 16.4 Hz, J_{AX} = 7.1 Hz, 1H), 2.89 (dd, B of ABX, J_{AB} = 16.4 Hz, J_{BX} = 7.6 Hz, 1H), 3.95 (app q, J = 7.1 Hz, 1H), 5.01 (app dt, J = 17.2, 1.3 Hz, 1H), 5.05 (app dt, J = 10.4, 1.0 Hz, 1H), 5.97 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 7.16–7.35 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 17.8 (CH_3), 17.9 (CH_3), 41.3 (CH), 44.3 (CH), 45.9 (CH_2), 114.5 (CH_2), 126.5 (CH), 127.7 (CH), 128.5 (CH), 140.8 (CH), 143.1, 212.5. HPLC (Daicel Chiralcel OJ (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, v = 1.0 mL/min, λ = 210 nm, $\sim 25^\circ\text{C}$): t_R [min] = 9.1 (95.1%), 13.4 (4.9%), 90% *ee*. $[\alpha]_D^{20}$ +11.5 (c = 1.36, CHCl_3). From a second experiment, employing (S_a,S,S)-**L1**, 94 mg (46%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OJ (0.46 cm x 25 cm), hexanes/2-propanol = 99.9 : 0.1, v = 1.0 mL/min, λ = 210 nm, $\sim 25^\circ\text{C}$): t_R [min] = 9.2 (4.4%), 13.4 (95.6%), 91% *ee*. $[\alpha]_D^{20}$ -11.3 (c = 2.82, CHCl_3).

(+)-1,5-Diphenylhept-6-en-3-one. (Table 3, entry 9): Following the general procedure B, employing the R_a,R,R enantiomer of **L1**, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF_2 , 234 mg (1.00 mmol) cinnamyl *tert*-butyl carbonate (**2a**) and 331 mg (1.50 mmol) silyl enol ether **1d** were reacted for 18 h. The crude material contained a mixture of branched and linear regioisomers in a ratio of 99:1 (^1H NMR). Flash chromatography (SiO_2 , 3% EtOAc in hexanes) afforded 142 mg (54%) of the title compound as a colorless oil. R_f (SiO_2 , hexanes/EtOAc = 94 : 6) 0.20. FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3027 (m), 2927 (br, s), 1714 (s), 1638 (w), 1602 (w), 1495 (m), 1453 (m), 1407 (w), 1366 (w), 917 (w), 752 (m), 701 (s). ^1H NMR (400 MHz, CDCl_3): δ [ppm] = 2.55–2.89 (m, 6H), 3.92 (app q, J = 7.3 Hz, 1H), 4.99 (app dt, J = 17.2, 1.3 Hz, 1H), 5.04 (d, J = 10.4 Hz, 1H), 5.95 (ddd, J = 17.2, 10.4, 6.8 Hz, 1H), 7.08–7.33 (m, 10H). ^{13}C NMR (126 MHz, CDCl_3): δ [ppm] = 29.4 (CH_2), 44.6 (CH), 45.1 (CH_2), 48.3 (CH_2), 114.6 (CH_2), 126.0 (CH), 126.6 (CH), 127.6 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 140.5 (CH), 141.0, 142.8, 208.2. MS (DIP-EI, 70 eV): m/z (%) = 265 (3), 264 (13) [M^+], 159 (31), 133 (26), 132 (12), 117 (45), 115 (17), 105 (95), 92 (10), 91 (100), 77 (12), 65 (7). Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: C, 86.32; H, 7.63; found: C, 86.18; H, 7.69. HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 98 : 2, v = 0.5 mL/min, λ = 210 nm, $\sim 25^\circ\text{C}$): t_R [min] = 24.2 (96.3%), 32.4 (3.7%), 93% *ee*. $[\alpha]_D^{20}$ +8.1 (c = 1.16, CHCl_3). From a second experiment, employing (S_a,S,S)-**L1**, 140 mg (53%) of the enantiomer of the title compound were isolated: HPLC (Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexanes/2-propanol = 98 : 2, v = 0.5 mL/min, λ = 210 nm, $\sim 25^\circ\text{C}$): t_R [min] = 24.1 (2.8%), 31.2 (97.2%), 94% *ee*. $[\alpha]_D^{20}$ -9.2 (c = 1.10, CHCl_3).

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