Supporting Information for

Iridium-Catalyzed Regio- and Enantioselective Allylation of Ketone Enolates

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Methods and Materials

General Procedures for the Reactions of Silyl Enol Ethers 1 with Allylic Carbonates 2

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

Spectroscopic and Analytical Data of Reaction Products
**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 ¹³C NMR spectra were recorded on Bruker Avance DPX-400 and Bruker Avance DPX-500 spectrometers at ambient probe temperature with CDCl₃ as solvent and are referenced to the residual solvent peaks CHCl₃ (δ = 7.26 ppm) and CDCl₃ (δ = 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 ([α]) 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 CHCl₃ were distilled prior to their use, and THF was dried by passing it through a column of activated alumina. [(COD)IrCl]₂ and the phosphoramidite ligands L¹, L², L³, and L⁴ 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-butylxocarbonyl 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 (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%) [(COD)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 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 ZnF₂ and 234 mg (1.00 mmol) cinnameyl 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 H₂O was added and the mixture was extracted with CH₂Cl₂ (3 x 2 mL). The combined organic extracts were dried over Na₂SO₄ and filtered through a short bed of Celite.
The solvents were removed in vacuo, and the remaining residue was analyzed by $^1$H 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$_2$O and washed with 4 mL saturated aqueous NH$_4$Cl. The layers were separated, and the aqueous layer was extracted with Et$_2$O (2 x 2 mL). The combined organic extracts were dried over Na$_2$SO$_4$ 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%) [(COD)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 °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$_2$O and washed with 4 mL saturated aqueous NH$_4$Cl. The layers were separated, and the aqueous layer was extracted with Et$_2$O (2 x 2 mL). The combined organic extracts were dried over Na$_2$SO$_4$ and filtered through a short bed of Celite. The solvents were removed in vacuo, and the remaining residue was analyzed by $^1$H 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 [Ir(COD)Cl(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 °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 [Ir(COD)Cl(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, $^3J_{P,P}$=44.6 Hz), 154.1 (d, $^3J_{P,P}$=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%) [(COD)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 $^1$H NMR spectroscopy. Flash chromatography (SiO$_2$, 1 → 3% EtOAc in hexanes) afforded 215 mg (89%) of the title compound as colorless crystals. mp 47–49 °C
isolated: Chiralcel OD (CH)2H).

J (m), 663 (w), 538 (w).

2956 (m), 2835 (w), 1685 (s), 1637 (w), 1611 (m), 1597 (w), 1581 (w), 1511 (s), 1448 (s),


colorless waxy crystals. R chromatography (SiO2, branched and linear regioisomers in a ratio of 99:1

acetophenone (1.50 mmol) ZnF2, 264 mg (1.00 mmol) tert-butyl allyl carbonate 2b and 288 mg (1.50 mmol)

cacetophenone silyl enol ether 1a were reacted for 6 h. The crude material contained a mixture of

branch and linear regioisomers in a ratio of 99:1, as determined by 1H NMR spectroscopy. Flash

cromatography (SiO2, 6% Acetone in hexanes) afforded 253 mg (95%) of the title compound as

colorless waxy crystals. R (SiO2, hexanes/EtOAc = 92 : 8) 0.16. FT-IR (film): v [cm1] = 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, JAB = 16.6 Hz, JAX = 6.8 Hz, 1H), 3.40 (dd, B of ABX, JAB = 16.6 Hz, JBX = 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, 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 : 1, v = 0.6 mL/min, λ = 230 nm, ~25 °C): tr [min] = 30.1 (2.4%), 54.6 (97.6%), 95% ee. [α]20 D +3.1 (c = 2.59, CHCl3). From a second experiment, employing (S,S)-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, λ = 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, CHCl₃).

(−)-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) ZnF₂, 302 mg (1.00 mmol) tert-butyI allyl carbonate 2c and 288 mg (1.50 mmol) acetonaphone 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 (SiO₂, 5% EtOAc in hexanes) afforded 242 mg (80%) of the title compound as colorless waxy crystals. \( R_f \) (SiO₂, hexanes/EtOAc = 92 : 8) 0.23. FT-IR (film): \( \nu \) [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, CDCl₃): \( \delta \) [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, CDCl₃): \( \delta \) [ppm] = 43.6 (CH₂), 44.2 (CH), 115.5 (CH₂), 124.2 (q, \( J_{CF} = 272 \) Hz), 125.5 (CH), 128.0 (CH), 128.1 (CH), 128.6 (CH), 128.8 (q, \( J_{CF} = 32 \) 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 C₁₈H₁₅F₃O: 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, \( \nu = 0.5 \) 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, CHCl₃). 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, \( \nu = 0.5 \) 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, CHCl₃).

(−)-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) ZnF₂, 224 mg (1.00 mmol) tert-butyI allyl carbonate 2d and 288 mg (1.50 mmol) acetonaphone 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 (SiO₂, 4% EtOAc in hexanes) afforded 170 mg (75%) of the title compound as a colorless oil. \( R_f \) (SiO₂, hexanes/EtOAc = 92 : 8) 0.27. FT-IR (film): \( \nu \) [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, CDCl₃): \( \delta \) [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, CDCl₃): \( \delta \) [ppm] = 38.5 (CH), 41.9 (CH₂), 105.4 (CH), 110.2 (CH), 116.1 (CH₂), 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 C₁₃H₁₄O₂: 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, \( \nu = 0.4 \) 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, CHCl₃). From a second
experiment, employing (S<sub>a</sub>S,S)-L<sub>1</sub>, 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, λ = 230 nm, ~25 °C): t<sub>R</sub> [min] = 39.9 (1.9%), 42.5 (98.1%), 96% ee. [α]<sub>D</sub> <sup>20</sup> +55.8 (c = 1.10, CHCl<sub>3</sub>).

(±)-3-Isopropyl-1-phenylpent-4-en-1-one. 9 (Table 3, entry 4): Following the general procedure B, employing the R<sub>a</sub>,R,R enantiomer of L<sub>1</sub>, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF<sub>2</sub>, 200 mg (1.00 mmol) tert-butyl allyl carbonate 2e and 288 mg (1.50 mmol) acetoephone 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 <sup>1</sup>H NMR spectroscopy. Flash chromatography (SiO<sub>2</sub>, 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 <sup>1</sup>H NMR spectroscopy. R<sub>F</sub> (SiO<sub>2</sub>, hexanes/EtOAc = 96 : 4) 0.18. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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, CDCl<sub>3</sub>): δ [ppm] = 18.8 (CH<sub>3</sub>), 20.4 (CH<sub>3</sub>), 31.5 (CH), 41.0 (CH<sub>2</sub>), 45.9 (CH), 115.9 (CH<sub>2</sub>), 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, λ = 230 nm, ~25 °C): t<sub>R</sub> [min] = 61.0 (3.0%), 63.4 (97.0%), 94% ee. [α]<sub>D</sub> <sup>20</sup> +11.6 (c = 1.00, CHCl<sub>3</sub>). From a second experiment, employing (S<sub>a</sub>S,S)-L<sub>1</sub>, 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, λ = 230 nm, ~25 °C): t<sub>R</sub> [min] = 59.0 (97.0%), 62.6 (3.0%), 94% ee. [α]<sub>D</sub> <sup>20</sup> –10.0 (c = 3.60, CHCl<sub>3</sub>).

(+)-1-Phenyl-3-propylpent-4-en-1-one. 9 (Table 3, entry 5): Following the general procedure B, employing the R<sub>a</sub>,R,R enantiomer of L<sub>1</sub>, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF<sub>2</sub>, 200 mg (1.00 mmol) tert-butyl allyl carbonate 2e and 288 mg (1.50 mmol) acetoephone 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 (<sup>1</sup>H NMR). Flash chromatography (SiO<sub>2</sub>, 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 <sup>1</sup>H NMR spectroscopy. R<sub>F</sub> (SiO<sub>2</sub>, hexanes/EtOAc = 96 : 4) 0.20. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 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 (ddd, 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, CDCl<sub>3</sub>): δ [ppm] = 14.0 (CH<sub>3</sub>), 20.2 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 39.5 (CH), 43.9 (CH<sub>2</sub>), 114.6 (CH<sub>2</sub>), 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, λ = 230 nm, ~25 °C): t<sub>R</sub> [min] = 22.7 (4.1%), 23.4 (95.9%), 92% ee. [α]<sub>D</sub> <sup>20</sup> +12.1 (c = 1.03, CHCl<sub>3</sub>). From a second experiment, employing (S<sub>a</sub>S,S)-L<sub>1</sub>, 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, λ = 230 nm, ~25 °C): t<sub>R</sub> [min] = 23.0 (95.4%), 24.5 (4.6%), 91% ee. [α]<sub>D</sub> <sup>20</sup> –10.6 (c = 1.03, CHCl<sub>3</sub>).

(+)-(<em>E</em>)-1-Phenyl-3-vinylhex-4-en-1-one. (Table 3, entry 6): Following the general procedure B, employing the R<sub>a</sub>,R,R enantiomer of L<sub>1</sub>, 61 mg (0.40 mmol) CsF and 155 mg (1.50 mmol) ZnF<sub>2</sub>, 198 mg (1.00 mmol) tert-butyl allyl carbonate 2f and 288 mg (1.50 mmol) acetoephone 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 $^1$H NMR spectroscopy. Flash chromatography (SiO$_2$, 2 → 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), 1206 (w), 969 (s), 917 (m), 753 (s), 691 (s), 658 (w). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 1.65 (d, $\text{J} = 5.3$ Hz, 3H), 3.07 (app d, $\text{J} = 7.1$ Hz, 2H), 3.45 (app quintet, $\text{J} = 6.5$ Hz, 1H), 5.01 (app dt, $\text{J} = 10.2, 1.2$ Hz, 1H), 5.04 (app dt, $\text{J} = 17.2, 1.5$ Hz, 1H), 5.46 (m, AB pattern, $\text{J}_{\text{AB}} = 15.4$ Hz, 2H), 5.83 (ddd, $\text{J} = 17.2, 10.2, 6.8$ Hz, 1H), 7.46 (m, 2H), 7.56 (m, 1H), 7.94 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [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): $m/z$ (%$\text{ intensely}$) = 200 (3) [M$^+$], 185 (3), 120 (3), 106 (9), 105 (100), 79 (5), 77 (29). Anal. calcd for C$_{28}$H$_{38}$O$_2$: 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, $\lambda = 230$ nm, $\sim 25 ^\circ$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$_{\text{a,S}},$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, $\lambda = 230$ nm, $\sim 25 ^\circ$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 $R,R,R$ 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 $^1$H NMR spectroscopy. Flash chromatography (SiO$_2$, 6 → 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), 2924 (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). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 3.42 (m, AB of ABX pattern, 2H), 3.89 (s, 3H), 4.06 (app q, $\text{J} = 7.3$ Hz, 1H), 5.00 (d, $\text{J} = 17.2$ Hz, 1H), 5.04 (d, $\text{J} = 10.4$ Hz, 1H), 6.01 (ddd, $\text{J} = 17.2, 10.4, 6.8$ Hz, 1H), 6.93−6.99 (m, 2H), 7.16−7.32 (m, 5H), 7.44 (m, 1H), 7.55 (dd, $\text{J} = 7.6, 1.8$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [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 C$_{18}$H$_{18}$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, $\lambda = 230$ nm, $\sim 25 ^\circ$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$_{\text{a,S}},$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, $\lambda = 230$ nm, $\sim 25 ^\circ$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. (Table 3, entry 8): Following the general procedure B, employing the $R,R,R$ 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 $^1$H NMR spectroscopy. Flash chromatography (SiO$_2$, 2.5 → 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. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [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$_3$): $\delta$ [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, $\nu = 1.0$ mL/min, $\lambda = 210$ nm, −25 °C): $t_R$ [min] = 9.1 (95.1%), 13.4 (4.9%), 90% ee. [α]$^D_{20}$ +11.5 (c = 1.36, CHCl$_3$). From a second experiment, employing (S$_{s,s}$)-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, $\nu = 1.0$ mL/min, $\lambda = 210$ nm, −25 °C): $t_R$ [min] = 9.2 (4.4%), 13.4 (95.6%), 91% ee. [α]$^D_{20}$ −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 $R,R,R$ 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 ($^1$H 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): $\bar{\nu}$ [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). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [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$_3$): $\delta$ [ppm] = 29.4 (CH$_2$), 44.6 (CH), 45.1 (CH$_2$), 48.3 (CH$_2$), 114.6 (CH), 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), 324 (13) [M$^+$], 159 (31), 133 (26), 132 (12), 117 (45), 115 (17), 105 (95), 92 (10), 91 (100), 77 (12), 65 (7). Anal. calc'd for C$_{19}$H$_{29}$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, $\nu = 0.5$ mL/min, $\lambda = 210$ nm, −25 °C): $t_R$ [min] = 24.2 (96.3%), 32.4 (3.7%), 93% ee. [α]$^D_{20}$ +8.1 (c = 1.16, CHCl$_3$). From a second experiment, employing (S$_{s,s}$)-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, $\nu = 0.5$ mL/min, $\lambda = 210$ nm, −25 °C): $t_R$ [min] = 24.1 (2.8%), 31.2 (97.2%), 94% ee. [α]$^D_{20}$ −9.2 (c = 1.10, CHCl$_3$).

References