P-Chiral o-Phosphinophenol as a P/O Hybrid Ligand: Preparation and Use in Cu-Catalyzed Asymmetric Conjugate Addition of Diethylzinc to Acyclic Enones

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General. All manipulations were carried out under argon or nitrogen atmosphere. NMR spectra were recorded on a JEOL JMN-LA500 spectrometer (500 MHz for ^1H , 202 MHz for ^{31}P , and 125 MHz for ^{13}C) or a JEOL JMN-LA400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded in CDCl_3 at 25 °C unless otherwise noted. IR spectra were recorded on a Jasco FT/IR-200. Optical rotations were recorded on a Jasco DIP-1020 polarimeter with a sodium lamp. MS (FAB and EI) spectra were recorded on a JEOL HX-110 and a JEOL AX-500 spectrometers. HPLC analyses were performed on a Shimadzu LC-10AD pump and a SPD-10A UV detector with a chiral column. GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector and a capillary column.

Materials. All reagents were obtained from commercial sources and used without further purification. All solvents were freshly distilled. **3b**, **4** and enones are known compounds.

Conversion of 2a to 2b: determination of absolute configuration of 2a.

To a 1 mL THF solution of a phosphine-borane **2a** (0.27 mmol, 69 mg) was added tetrafluoroboric acid (4.0 mmol, 0.55 mL) in diethyl ether slowly at $-40\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. After stirring at room temperature for 13 h, degassed saturated NaHCO_3 was added to the solution at $0\text{ }^{\circ}\text{C}$, and stirred for 1 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with degassed diethyl ether five times. The combined extract was dried over Na_2SO_4 under nitrogen. The solution was passed through a column of silica gel with degassed diethyl ether elution. The eluent was concentrated under reduced pressure to give free phosphine **3a** (40 mg, 75% yield).

Borane-THF complex (1 mmol, 1 mL of 1.0 M THF solution) was added to a solution of **3a** (24 mg, 0.12 mmol) in THF (6 mL) at $0\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. After stirring at room temperature for 1 h, the reaction mixture was quenched by ice water containing HCl and diluted with diethyl ether. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined extract was washed with saturated NaHCO_3 and brine, and dried over Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 5/1) to give *tert*-butyl(2-hydroxyphenyl)methylphosphine-borane **7** (26 mg, 99% yield).

Methyl iodide (0.36 mmol, 23 μL) was added to a solution of **7** (0.12 mmol, 26.2 mg) and potassium carbonate (0.36 mmol, 50 mg) in acetone at room temperature under nitrogen atmosphere. After stirring for 30 h, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 5/1) to give **2b** (23.2 mg, 86% yield). $[\alpha]_{\text{D}}^{23} = +50.8^{\circ}$ ($c = 1.00$, CHCl_3). The absolute configuration of **2a** was determined to be S_{P} by comparison of the sign of optical rotation. The enantiomeric excess was determined to be 97% by HPLC (Chiralcel OD-H, hexane/2-propanol = 99/1, 0.5 mL/min, 254 nm). Retention time: 9.8 min [(*R*)-enantiomer], 10.2 min [(*S*)-enantiomer].

(*R*)-*tert*-Butyl((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyloxy)(2-

(methoxy)methoxyphenyl)phosphine-borane (epi-1a). ^1H NMR (500 MHz, CDCl_3) δ 7.69 (ddd, $J = 1.7, 7.7, 9.7$ Hz, 1H), 7.42 (dddd, $J = 0.9, 1.7, 7.3, 8.4$ Hz, 1H), 7.17 (ddd, $J = 0.6, 4.3, 8.4$, 1H), 7.05 (dddd, $J = 0.6, 0.8, 7.3, 7.7$ Hz, 1H), 5.19 (d, $J = 7.0$ Hz, 1H), 5.15 (d, $J = 6.8$ Hz, 1H), 4.32-4.25 (m, 1H), 3.52 (s, 3H), 2.37-2.30 (m, 1H), 1.88-1.82 (m, 1H), 1.70-1.58 (m, 2H), 1.50-1.43 (m, 1H), 1.40-1.29 (m, 1H), 1.20-0.70 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.3 (d, $J = 6.1$ Hz), 134.2 (d, $J = 6.0$ Hz), 132.9 (d, $J = 2.0$ Hz), 120.8 (d, $J = 8.0$ Hz), 120.6 (d, $J = 28.0$ Hz), 144.6 (d, $J = 6.0$ Hz), 94.8, 79.1 (d, $J = 5.0$ Hz), 56.4, 49.4 (d, $J = 7.0$ Hz), 42.9, 34.2 (d, $J = 28.0$ Hz), 33.7, 31.4 (d, $J = 33.0$ Hz), 25.3, 24.6 (d, $J = 3.0$ Hz), 22.6, 22.0, 21.1, 15.4, 14.0; ^{31}P NMR (202 MHz, CDCl_3) δ 115.4 (s); IR (NaCl plates) 2960, 2385, 1590, 1485, 1155, 1085, 985 cm^{-1} ; $[\alpha]_{\text{D}}^{22} = +13.3^{\circ}$ ($c = 1.07$, CHCl_3); HRMS Calcd for $\text{C}_{22}\text{H}_{40}\text{BKO}_3\text{P}$ $[\text{M}+\text{K}]^+$ 433.2445, Found 433.2412. Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{BO}_3\text{P}$: C, 67.01; H, 10.22. Found: C, 66.93; H, 10.21.

(*S*)-*tert*-Butyl(2-methoxyphenyl)methylphosphine (3b). ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.28 (m, 2H), 6.99-6.95 (m, 1H), 6.89-6.85 (m, 1H), 3.83 (s, 3H), 1.25 (d, $J = 5.2$ Hz, 3H), 0.99 (d, $J = 11.9$ Hz, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.4 (d, $J = 15.0$ Hz), 132.5 (d, $J = 25.0$ Hz), 130.0, 125.2 (d, $J = 20.0$ Hz), 120.3, 110.2 (d, $J = 2.0$ Hz), 55.2, 29.4 (d, $J = 12.0$ Hz), 27.2 (d, $J = 14.0$ Hz), 5.1 (d, $J = 18.1$ Hz); ^{31}P NMR (202 MHz, CDCl_3) δ -27.4 (s); HRMS Calcd for $\text{C}_{12}\text{H}_{20}\text{OP}$ $[\text{M}+\text{H}]^+$ 211.1252, Found 211.1247.

(*S*)-*tert*-Butyl(2-hydroxyphenyl)methylphosphine-borane (7). ^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 1H), 7.43-7.39 (m, 1H), 7.26-7.23 (m, 1H), 6.98-6.94 (m, 2H), 1.59 (d, $J = 9.9$ Hz, 3H), 1.40-0.54 (m, 3H), 1.15 (d, $J = 14.7$ Hz, 9H); ^{31}P NMR (202 MHz, CDCl_3) δ 17.4 (q, $J = 55.0$ Hz); IR (NaCl plates) 3405, 2965, 2360, 1595, 1435, 1340, 1290, 1200, 1080, 890, 760 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{BOP}$: C, 62.90; H, 9.60. Found: C, 62.80; H, 9.38.

1,3-Diphenylpentan-1-one. ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.87 (m, 2H), 7.55-7.50 (m, 1H), 7.45-7.40 (m, 2H), 7.31-7.15 (m, 5H), 3.31-3.22 (m, 3H), 1.85-1.74 (m, 1H), 1.70-1.57 (m, 1H), 0.80

(t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 144.6, 137.2, 132.9, 128.5, 128.4, 128.0, 127.6, 126.2, 45.6, 43.0, 29.2, 12.1; IR (NaCl plates) 1685 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 239.1439, found 239.1434; The enantiomeric excess was determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 199/1, 0.5 mL/min, 254 nm). Retention time: 23.7 min [(*S*)-enantiomer], 25.8 min [(*R*)-enantiomer].

3-(4-Methoxyphenyl)-1-phenylpentan-1-one. ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.88 (m, 2H), 7.55-7.50 (m, 1H), 7.45-7.39 (m, 2H), 7.17-7.12 (m, 2H), 6.85-6.80 (m, 2H), 3.76 (s, 3H), 3.28-3.14 (m, 3H), 1.82-1.70 (m, 1H), 1.66-1.54 (m, 1H), 0.79 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.5, 158.0, 137.3, 136.7, 132.9, 128.6, 128.5, 128.1, 113.8, 55.2, 45.9, 42.3, 29.4, 12.2; IR (NaCl plates) $1685, 1510, 1245\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$ $[\text{M}]^+$ 268.1463, found 268.1466; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 199/1, 1.0 mL/min, 254 nm). Retention times: 28.9 min [(*S*)-enantiomer], 45.8 min [(*R*)-enantiomer].

3-(4-(Dimethylamino)phenyl)-1-phenylpentan-1-one. $[\alpha]_{\text{D}}^{22} = -19.3^\circ$ ($c = 0.97$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.83 (m, 2H), 7.55-7.49 (m, 1H), 7.45-7.39 (m, 2H), 7.12-7.07 (m, 2H), 6.71-6.66 (m, 2H), 3.27-3.07 (m, 3H), 2.90 (s, 6H), 1.80-1.69 (m, 1H), 1.65-1.53 (m, 1H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 149.1, 137.3, 132.7, 132.6, 128.4, 128.1, 128.0, 112.8, 46.0, 42.1, 40.7, 29.2, 12.1; IR (NaCl plates) $1680, 1615, 1520, 1450, 1350\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{19}\text{H}_{23}\text{NO}$ $[\text{M}]^+$ 281.1780, found 281.1781; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 95/5, 0.5 mL/min, 254 nm). Retention time: 61.2 min, 72.0 min.

3-(4-Chlorophenyl)-1-phenylpentan-1-one. ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.87 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.40 (m, 2H), 7.27-7.22 (m, 2H), 7.18-7.13 (m, 2H), 3.31-3.18 (m, 3H), 1.83-1.70 (m, 1H), 1.68-1.55 (m, 1H), 0.80 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 143.1, 137.1, 133.0, 131.8, 129.0, 128.6, 128.5, 128.0, 45.4, 42.3, 29.2, 12.0; IR (NaCl plates) $1685, 1490\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{ClO}$ $[\text{M}+\text{H}]^+$ 273.1046, found 273.1042; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 199/1, 0.3 mL/min, 254 nm). Retention time: 53.6 min [(*S*)-enantiomer], 57.5 min [(*R*)-enantiomer].

3-(4-(Trifluoromethyl)phenyl)-1-phenylpentan-1-one. $[\alpha]_{\text{D}}^{22} = +5.9^\circ$ ($c = 1.39$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.92-7.87 (m, 2H), 7.57-7.50 (m, 3H), 7.46-7.40 (m, 2H), 7.37-7.32 (d, $J = 8$ Hz, 2H), 3.38-3.24 (m, 3H), 1.88-1.76 (m, 1H), 1.72-1.59 (m, 1H), 0.81 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 148.8, 137.0, 133.1, 128.6, 128.0, 127.9, 125.3 (q, $J = 38.3$ Hz), 45.1, 42.6, 29.1, 11.9; IR (NaCl plates) $1685, 1325, 1165, 1120, 1070\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{O}$ $[\text{M}+\text{H}]^+$ 307.1310, found 307.1303; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane, 0.5 mL/min, 254 nm). Retention time: 58.2 min, 74.0 min.

3-(1-Naphthyl)-1-phenylpentan-1-one. $[\alpha]_{\text{D}}^{22} = +45.6^\circ$ ($c = 1.16$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.3$ Hz, 1H), 7.94-7.88 (m, 2H), 7.87-7.82 (m, 1H), 7.71 (dd, $J = 1.7, 7.3$, 1H), 7.55-7.37 (m, 7H), 4.32-4.20 (m, 1H), 3.45-3.31 (m, 2H), 2.00-1.80 (m, 2H), 0.84 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 141.0, 137.2, 134.0, 132.9, 132.1, 128.9, 128.5, 128.0, 126.7, 125.9, 125.4, 123.4, 45.4, 28.6, 12.0; IR (NaCl plates) $1680, 775, 755, 690\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{21}\text{H}_{20}\text{O}$ $[\text{M}]^+$ 288.1514, found 288.1529; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 199/1, 0.5 mL/min, 254 nm). Retention time: 45.0 min, 60.2 min.

3-Ethyl-1-phenyloctan-1-one. $[\alpha]_{\text{D}}^{22} = -1.8^\circ$ ($c = 1.15$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.93 (m, 2H), 7.57-7.51 (m, 1H), 7.47-7.42 (m, 2H), 2.93-2.81 (m, 2H), 2.09-2.00 (m, 1H), 1.46-1.19 (m, 10H), 0.91-0.84 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.7, 137.5, 132.7, 128.5, 128.0, 43.0, 35.7, 33.5, 32.1, 26.5, 26.3, 22.6, 14.0, 10.9; IR (NaCl plates) $2925, 2860, 1685, 1450, 750, 690\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{16}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$ 233.1905, found 233.1909; The enantiomeric

excess was determined by HPLC (Chiralcel OD-H, hexane, 0.5 mL/min, 254 nm). Retention time: 40.7 min, 44.0 min.

3-Ethyl-4-methyl-1-phenylpentan-1-one. $[\alpha]_D^{22} = +4.3^\circ$ ($c = 1.06$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.93 (m, 2H), 7.57-7.51 (m, 1H), 7.49-7.42 (m, 2H), 2.91 (dd, $J = 16.1, 5.6$ Hz, H), 2.78 (dd, $J = 16.1, 7.5$ Hz, 1H), 2.02-1.94 (m, 1H), 1.85-1.74 (m, 1H), 1.46-1.21 (m, 2H), 0.93-0.85 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.0, 137.5, 132.8, 128.5, 128.1, 41.5, 40.0, 29.4, 23.9, 19.6, 18.6, 11.9; IR (NaCl plates) 2960, 1680 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}]^+$ 205.1592, found 205.1587; The enantiomeric excess was determined by GLC (Chirasil-DEX CB (30 m), 120 $^\circ\text{C}$, 35 cm/sec). Retention time: 47.8 min, 48.8 min.

3-Ethyl-4,4-dimethyl-1-phenylpentan-1-one. $[\alpha]_D^{22} = -5.3^\circ$ ($c = 0.83$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.88 (m, 2H), 7.58-7.52 (m, 1H), 7.50-7.43 (m, 2H), 3.06 (dd, $J = 17.3, 4.6$ Hz, 1H), 2.71 (dd, $J = 17.3, 6.5$ Hz, 1H), 2.05-1.95 (m, 1H), 1.71-1.59 (m, 1H), 1.15-1.02 (m, 1H), 0.90 (s, 9H), 0.83 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.7, 137.5, 132.7, 128.5, 128.0, 44.9, 40.0, 33.6, 27.6, 23.9, 13.5; IR (NaCl plates) 2960, 1690 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 219.1749, found 219.1756; The enantiomeric excess was determined by GLC (Chirasil-DEX CB (30 m), 120 $^\circ\text{C}$, 35 cm/sec). Retention time: 65.3 min, 66.8 min.

1-(4-Methoxyphenyl)-3-phenylpentan-1-one. $[\alpha]_D^{22} = +7.9^\circ$ ($c = 1.01$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.85 (m, 2H), 7.31-7.14 (m, 5H), 6.93-9.87 (m, 2H), 3.85 (s, 3H), 3.27-3.14 (m, 3H), 1.84-1.72 (m, 1H), 1.69-1.55 (m, 1H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8, 163.3, 144.8, 130.3, 128.3, 127.6, 126.2, 113.6, 55.4, 45.3, 43.2, 29.2, 12.1; IR (KBr) 1670, 1605, 1260, 1175, 700 cm^{-1} ; mp = 61-63 $^\circ\text{C}$; HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 269.1542, found 269.1548; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 9/1, 0.5 mL/min, 254 nm). Retention time: 44.9 min, 51.1 min.

1-(4-Chlorophenyl)-3-phenylpentan-1-one. $[\alpha]_D^{22} = +3.1^\circ$ ($c = 1.21$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.78 (m, 2H), 7.41-7.35 (m, 2H), 7.31-7.14 (m, 5H), 3.30-3.14 (m, 3H), 1.83-1.72 (m, 1H), 1.70-1.58 (m, 1H), 0.80 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 144.3, 139.2, 135.5, 129.4, 128.8, 128.4, 127.5, 126.3, 45.5, 43.0, 29.2, 12.0; IR (NaCl plates) 1690, 1590, 1090, 1015, 760, 700 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{ClO}$ $[\text{M}+\text{H}]^+$ 273.1046, found 273.1032; The enantiomeric excess was determined by HPLC (Chiralcel OD-H, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm). Retention time: 16.7 min, 18.5 min.

2-Methyl-6-phenyloctan-4-one. $[\alpha]_D^{22} = -34.2^\circ$ ($c = 1.20$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.23 (m, 2H), 7.20-7.12 (m, 3H), 3.10-3.00 (m, 1H), 2.73-2.60 (m, 2H), 2.21-1.97 (m, 3H), 1.72-1.49 (m, 2H), 0.82-0.74 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.7, 144.3, 128.3, 127.5, 126.1, 52.5, 50.0, 42.7, 29.2, 24.2, 22.4, 22.3, 11.9; IR (NaCl plates) 2960, 1715, 700 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 219.1749, found 219.1737; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm). Retention time: 14.3 min, 16.1 min.

1-Cyclohexyl-3-phenylpentan-1-one. $[\alpha]_D^{22} = -24.0^\circ$ ($c = 1.20$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.22 (m, 2H), 7.20-7.13 (m, 3H), 3.11-3.00 (m, 1H), 2.78-2.66 (m, 2H), 2.14-2.23 (m, 1H), 1.80-1.48 (m, 7H), 1.30-1.09 (m, 5H), 0.76 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 212.9, 144.6, 128.2, 127.5, 126.1, 51.2, 47.7, 42.5, 29.1, 28.1, 28.0, 25.7, 25.6, 25.5, 12.0; IR (NaCl plates) 2930, 1710 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$ 245.1905, found 245.1892; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm). Retention time: 15.3 min, 16.8 min.

3-Phenylundecan-5-one. $[\alpha]_D^{22} = -32.8^\circ$ ($c = 1.69$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.30-7.24 (m, 2H), 7.19-7.13 (m, 3H), 3.08-3.00 (m, 1H), 2.75-2.62 (m, 2H), 2.34-2.20 (m, 2H), 1.72-1.50

(m, 2H), 1.44 (quint, $J = 7.4$, 2H), 1.30-1.10 (m, 6H), 0.83 (t, $J = 7.1$, 3H), 0.77 (t, $J = 7.5$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 210.3, 144.4, 128.3, 127.5, 126.2, 49.6, 43.5, 42.9, 31.5, 29.2, 28.7, 23.4, 14.0, 11.9; IR (NaCl plates) 2930, 1715 cm^{-1} ; HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 247.2062, found 247.2074; The enantiomeric excess was determined by HPLC (Chiralcel OJ, hexane/2-propanol = 98/2, 0.5 mL/min, 254 nm). Retention time: 13.7 min, 15.9 min.

3-Methylundecan-5-one. $[\alpha]_{\text{D}}^{22} = -3.0^\circ$ ($c = 1.53$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 2.42-2.34 (m, 3H), 2.19 (dd, $J = 8.0$ Hz, 15.9, 1H), 1.98-1.86 (m, 1H), 1.60-1.50 (m, 2H), 1.37-1.13 (m, 8H), 0.93-0.82 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.5, 49.9, 43.4, 31.6, 30.8, 29.5, 28.9, 23.7, 22.5, 19.3, 14.0, 11.3; IR (NaCl plates) 2960, 2930, 1715 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{24}\text{O}$ $[\text{M}]^+$ 184.1827, found 184.1810; The enantiomeric excess was determined by GLC (Chiraldex G-TA (30 m), 40 $^\circ\text{C}$, 80 cm/sec). Retention time: 726 min, 773 min.

4-Methylnonan-2-one. ^1H NMR (400 MHz, CDCl_3) δ 2.83 (d, $J = 6.8$ Hz, 2H), 2.14 (s, 3H), 1.90-1.81 (m, 1H), 1.38-1.15 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H), 0.85 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.4, 48.3, 35.2, 33.4, 32.1, 30.4, 26.3, 26.2, 22.6, 14.0, 10.7; IR (NaCl plates) 2960, 2930, 1720 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 170.1671, found 170.1683; The enantiomeric excess was determined by GLC (Chiraldex G-TA (30 m), 70 $^\circ\text{C}$, 40 cm/sec). Retention time: 81.6 min [(R) -enantiomer], 83.6 min [(S) -enantiomer].

(Z)-1,3-Diphenylpropenone. ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.94 (m, 2H), 7.55-7.48 (m, 1H), 7.44-7.37 (m, 4H), 7.26-7.19 (m, 3H), 7.02 (d, $J = 12.9$ Hz, 1H), 6.62 (d, $J = 12.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.7, 139.4, 137.1, 135.1, 133.2, 129.4, 129.0, 128.8, 128.5, 128.2, 126.7; IR (KBr) 1665, 1595, 1225, 690 cm^{-1} ; mp = 43-45 $^\circ\text{C}$; HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 209.0966, found 209.0966.

1a, ^1H in CDCl_3 (400 MHz)

1a, ^{31}P in CDCl_3 (202 MHz)

epi-1a, ^1H in CDCl_3 (400 MHz)

2a, ^1H in CDCl_3 (400 MHz)

2a, ^{13}C in CDCl_3 (99 MHz)

2a, ^{31}P in CDCl_3 (202 MHz)

3a, ^{31}P in CDCl_3 (162 MHz)

3b, ¹H in CDCl₃ (500 MHz)

3b, ¹³C in CDCl₃ (126 MHz)

3b, ^{31}P in CDCl_3 (202 MHz)

7, ³¹P in CDCl₃ (162 MHz)

X-ray structure of **2b**. All hydrogen atoms were omitted for clarity.