Copper-Catalyzed Enantioselective Conjugate Addition of Diethylzinc to Acyclic Enones in the Presence of Planar-Chiral Phosphaferrocene-Oxazoline Ligands

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Supporting Information

I. General

THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. Toluene and CH₂Cl₂ were purified by passage under argon through a neutral alumina column prior to use. NEt₃ (EM Science) was distilled from KOH under argon prior to use. 3,4-Dimethyl-1-phenylphosphole¹ and 3-cyclohexyl-1-phenyl-2-propen-1-one² were prepared by literature procedures. LiCp* (Strem), ferrocenecarboxaldehyde (Strem), *t*-BuOK (Aldrich), boron trifluoride diethyl etherate (Aldrich), *n*-BuLi solution (Strem), PhMgCl solution (Aldrich), FeCl₂ (Alfa), [Cu(OTf)]₂•C₆H₆ (Aldrich), ZnEt₂ (Aldrich), trifluoroacetic anhydride (Avocado), MsCl (Aldrich), DMAP (Aldrich), (*S*)-valinol (Fluka), (*S*)-phenylglycinol (Aldrich or Acros), (*R*)-phenylglycinol (Avocado), (1*S*,2*R*)-(-)-*cis*-1-amino-2-indanol (Aldrich), acetophenone (Avocado), diisopropylamine (Aldrich), *trans*-2-octenal (Aldrich), chalcone (Avocado), *trans*-4-phenyl-3-buten-2-one (Aldrich), 4-methoxychalcone (Aldrich), and 4-chlorochalcone (Avocado) were used as

(1) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983-985.

(2) Posner, G. H.; O'Dowd, H.; Ploypradith, P.; Cumming, J. N.; Xie, S.; Shapiro, T. A. *J. Med. Chem.* **1998**, *41*, 2164-2167.

received. All the other chemicals and solvents were purchased from either Mallinckrodt or J. T. Baker and used as received.

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under argon or in a glove box under nitrogen.

II. Syntheses of Phosphaferrocene-Oxazoline Ligands

All reactions are unoptimized.

(±)-1',2',3,3',4,4',5'-Heptamethyl-2-phenylphosphaferrocene (5). A solution of 3,4-dimethyl-1-phenylphosphole (6.65 g, 35.3 mmol) and *t*-BuOK (4.76 g, 42.4 mmol) in THF (30 mL) was added to a sealed Schlenk tube and stirred for 14 h at 140 °C to give a brown solution. Separately, a suspension of LiCp* (5.0 g, 35 mmol) in THF (200 mL) was added by syringe over 70 min to a stirred solution of FeCl₂ (4.46 g, 35.2 mmol) in THF (75 mL) at 0 °C. After stirring for an additional 10 min at 0 °C, the brown solution prepared above was added to the solution of [Cp*FeCl]_n, along with additional THF (15 mL). The mixture was stirred for 70 h at r.t., and then the solvent was removed under vacuum. The residue was filtered through Celite (pentane washings), and the solvent was removed under reduced pressure. The residue was chromatographed on adsorption alumina (pentane) to give 11.11 g of an orange-red solid (29.4 mmol, 84%).

¹H NMR (CD₂Cl₂, 20 °C): δ 7.41-7.38 (m, 2H), 7.27-7.21 (m, 2H), 7.18-7.11 (m, 1H), 3.40 (d, ²J_{PH} = 36.0 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 1.72 (s, 15H). ¹³C NMR (CD₂Cl₂, 20 °C): δ 141.1 (d, ²J_{CP} = 17.6 Hz), 129.6 (d, ³J_{CP} = 9.1 Hz), 128.0, 125.4, 99.9 (d, ¹J_{CP} = 55.1 Hz), 96.7 (d, ²J_{CP} = 6.7 Hz), 88.3 (d, ²J_{CP} = 4.2 Hz), 82.9, 81.8 (d, ¹J_{CP} = 56.9 Hz), 15.1, 13.6, 10.8 (d, ³J_{CP} = 0.8 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ -56.4. M.p. 70-73 °C. FTIR (neat) 3031, 2972, 2903, 1596, 1495, 1479, 1445, 1375, 1072, 1029, 833, 756, 699, 668 cm⁻¹. HRMS (EI) calcd for C₂₂H₂₇FeP (M⁺) 378.1194, found 378.1209.

(±)-1',2',3,3',4,4',5'-Heptamethyl-5-phenyl-2-trifluoroacetylphosphaferrocene (6).

Trifluoroacetic anhydride (554 μL , 3.92 mmol) and then boron trifluoride diethyl etherate (497 μL , 3.92 mmol) were added by syringe to a stirred solution of (±)-(5) (742 mg, 1.96 mmol) in CH_2Cl_2 (12 mL) at 0 °C. The mixture was stirred for 1.5 h at r.t. to provide a purple solution, which was chromatographed (Et_2O) to give 826 mg of a red-brown solid (1.74 mmol, 89%).

^1H NMR (CD_2Cl_2 , 20 °C): δ 7.46-7.43 (m, 2H), 7.34-7.23 (m, 3H), 2.38 (s, 3H), 2.22 (s, 3H), 1.59 (s, 15H). ^{13}C NMR (CD_2Cl_2 , 20 °C): δ 189.9 (qd, $^2J_{\text{CF}} = 33.0$ Hz and $^2J_{\text{CP}} = 22.8$ Hz), 138.1 (d, $^2J_{\text{CP}} = 18.7$ Hz), 130.0 (d, $^3J_{\text{CP}} = 9.9$ Hz), 128.4, 126.8, 117.0 (q, $^1J_{\text{CF}} = 292.8$ Hz), 106.3 (dq, $^1J_{\text{CP}} = 53.6$ Hz and $^3J_{\text{CF}} = 4.4$ Hz), 99.5 (d, $^2J_{\text{CP}} = 5.1$ Hz), 96.9 (d, $^2J_{\text{CP}} = 5.7$ Hz), 85.3, 77.4 (d, $^1J_{\text{CP}} = 67.0$ Hz), 13.8, 13.8, 10.1. ^{19}F NMR (CD_2Cl_2 , 20 °C): δ -72.6 (d, $^4J_{\text{PF}} = 62.7$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C): δ -33.6 (q, $^4J_{\text{PF}} = 61.7$ Hz). M.p. 145-147 °C (dec). FTIR (neat) 2981, 2909, 1672, 1597, 1481, 1446, 1378, 1303, 1234, 1195, 1168, 1141, 1096, 1028, 927, 758, 732, 701 cm^{-1} . HRMS (EI) calcd for $\text{C}_{24}\text{H}_{26}\text{F}_3\text{FeOP}$ (M^+) 474.1017, found 474.1006.

7a and 7a'. *n*-BuLi (1.6 M solution in hexane; 1.97 mL, 3.15 mmol) was added to a stirred solution of (*S*)-valinol (163 mg, 1.58 mmol) in THF (7.0 mL) at 0 °C. The reaction mixture was stirred for 2.5 h at r.t., cooled to -70 °C, and then a solution of (±)-6 (250 mg, 0.53 mmol) in THF (7.0 mL) was added. After stirring for 20 h at 60 °C, the reaction mixture was concentrated and then passed through silica gel (washing with Et_2O) to

furnish 207 mg of an orange oil, which was used without further purification.

MsCl (63 μ L, 0.81 mmol) was added to a -70 $^{\circ}$ C mixture of 75.5 mg of this orange oil, DMAP (3.4 mg, 0.028 mmol), and NEt_3 (114 μ L, 0.82 mmol) in CH_2Cl_2 (7.0 mL). The reaction mixture was stirred for 30 min at 0 $^{\circ}$ C and then warmed to r.t. Additional NEt_3 (284 μ L, 2.04 mmol) was added, and the reaction mixture was stirred for 17 h at r.t. The solvent was removed under reduced pressure, and the residue was chromatographed (Et_2O /hexane = 1/6). The first fraction (R_f = 0.5) consisted of 68.6 mg of orange solid **7a** (0.14 mmol, 27%), and the second fraction (R_f = 0.4) consisted of 52.8 mg of orange solid **7a'** (0.11 mmol, 20%).

7a: ^1H NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ 7.42-7.38 (m, 2H), 7.29-7.23 (m, 2H), 7.19-7.14 (m, 1H), 4.24-4.15 (m, 1H), 3.91-3.84 (m, 2H), 2.42 (s, 3H), 2.18 (s, 3H), 1.63 (s, 15H), 1.76-1.60 (m, 1H), 1.01 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 3H), 0.88 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 3H). ^{13}C NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ 166.4 (d, $^2J_{\text{CP}}$ = 18.1 Hz), 140.1 (d, $^2J_{\text{CP}}$ = 18.1 Hz), 130.0 (d, $^3J_{\text{CP}}$ = 9.4 Hz), 128.3, 126.0, 101.2 (d, $^1J_{\text{CP}}$ = 52.8 Hz), 95.5 (d, $^2J_{\text{CP}}$ = 5.1 Hz), 92.7 (d, $^2J_{\text{CP}}$ = 5.2 Hz), 83.8, 79.0 (d, $^1J_{\text{CP}}$ = 54.3 Hz), 74.0 (d, $^4J_{\text{CP}}$ = 1.7 Hz), 69.1, 33.8, 19.5, 18.7, 14.1, 13.5, 10.0 (d, $^3J_{\text{CP}}$ = 0.7 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ -43.9 . M.p. 95 - 97 $^{\circ}$ C. $[\alpha]_D^{20} +92.7$ (c 0.70, THF). FTIR (neat) 2956, 2903, 1635, 1457, 1377, 1271, 1030, 758, 700 cm^{-1} . HRMS (EI) calcd for $\text{C}_{28}\text{H}_{36}\text{FeNOP}$ (M^+) 489.1878, found 489.1866.

7a': ^1H NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ 7.43-7.39 (m, 2H), 7.29-7.23 (m, 2H), 7.19-7.16 (m, 1H), 4.30-4.24 (m, 1H), 3.87-3.72 (m, 2H), 2.41 (s, 3H), 2.19 (s, 3H), 1.64 (s, 15H), 1.75-1.57 (m, 1H), 1.12 (d, $^3J_{\text{HH}}$ = 6.6 Hz, 3H), 0.92 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 3H). ^{13}C NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ 166.7 (d, $^2J_{\text{CP}}$ = 18.2 Hz), 140.2 (d, $^2J_{\text{CP}}$ = 18.0 Hz), 129.9 (d, $^3J_{\text{CP}}$ = 9.0 Hz), 128.3, 126.0, 101.0 (d, $^1J_{\text{CP}}$ = 53.1 Hz), 95.2 (d, $^2J_{\text{CP}}$ = 4.8 Hz), 92.5 (d, $^2J_{\text{CP}}$ = 5.4 Hz), 83.8, 79.4 (d, $^1J_{\text{CP}}$ = 54.6 Hz), 74.6 (d, $^4J_{\text{CP}}$ = 1.6 Hz), 70.1, 34.9, 20.4, 19.6, 14.2, 13.5, 10.1 (d, $^3J_{\text{CP}}$ = 0.7 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 $^{\circ}$ C): δ -42.4 . M.p. 106 - 109 $^{\circ}$ C. $[\alpha]_D^{20} -155.8$ (c 0.62, THF). FTIR (neat) 2956, 2904, 1631, 1597, 1447, 1377, 1295, 1120, 1030, 1009, 758, 700 cm^{-1} . HRMS (EI) calcd for $\text{C}_{28}\text{H}_{36}\text{FeNOP}$ (M^+) 489.1878, found 489.1893.

7b and 7b'. The same procedure was followed as for the synthesis of **7a** and **7a'**.

First fraction ($R_f = 0.3$ with $\text{Et}_2\text{O}/\text{hexane} = 1/7$; **7b**): orange solid, 24%. Second fraction ($R_f = 0.25$ with $\text{Et}_2\text{O}/\text{hexane} = 1/7$; **7b'**): orange solid, 22%.

7b: ^1H NMR (CD_2Cl_2 , 20 °C): δ 7.45-7.19 (m, 10H), 5.24 (dd, $^3J_{\text{HH}} = 9.9$ and 8.3 Hz, 1H), 4.59 (dd, $^3J_{\text{HH}} = 9.9$ and 8.3 Hz, 1H), 3.97 (t, $^3J_{\text{HH}} = 8.3$ Hz, 1H), 2.46 (s, 3H), 2.21 (s, 3H), 1.67 (s, 15H). ^{13}C NMR (CD_2Cl_2 , 20 °C): δ 168.5 (d, $^2J_{\text{CP}} = 18.1$ Hz), 143.8, 139.9 (d, $^2J_{\text{CP}} = 18.0$ Hz), 130.0 (d, $^3J_{\text{CP}} = 9.2$ Hz), 129.1, 128.3, 127.8, 127.2, 126.1, 101.7 (d, $^1J_{\text{CP}} = 53.0$ Hz), 95.6 (d, $^2J_{\text{CP}} = 5.0$ Hz), 93.1 (d, $^2J_{\text{CP}} = 5.4$ Hz), 84.0, 78.1 (d, $^1J_{\text{CP}} = 54.9$ Hz), 73.5, 71.2 (d, $^4J_{\text{CP}} = 1.9$ Hz), 14.1, 13.7, 10.1. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C): δ -42.7. M.p. 119-121 °C. $[\alpha]_{\text{D}}^{20} +149.8$ (c 0.88, THF). FTIR (neat) 2956, 2903, 1627, 1495, 1452, 1377, 1269, 1073, 1020, 948, 757, 699 cm^{-1} . HRMS (EI) calcd for $\text{C}_{31}\text{H}_{34}\text{FeNOP}$ (M^+) 523.1722, found 523.1732.

7b': ^1H NMR (CD_2Cl_2 , 20 °C): δ 7.45-7.18 (m, 10H), 5.22 (t, $^3J_{\text{HH}} = 9.9$ Hz, 1H), 4.67 (dd, $^3J_{\text{HH}} = 9.9$ and 8.3 Hz, 1H), 3.97 (dd, $^3J_{\text{HH}} = 9.9$ and 8.3 Hz, 1H), 2.44 (s, 3H), 2.21 (s, 3H), 1.65 (s, 15H). ^{13}C NMR (CD_2Cl_2 , 20 °C): δ 168.7 (d, $^2J_{\text{CP}} = 18.1$ Hz), 143.4, 140.0 (d, $^2J_{\text{CP}} = 17.9$ Hz), 130.0 (d, $^3J_{\text{CP}} = 9.3$ Hz), 129.0, 128.3, 127.7, 127.2, 126.1, 101.5 (d, $^1J_{\text{CP}} = 53.2$ Hz), 95.0 (d, $^2J_{\text{CP}} = 4.8$ Hz), 92.8 (d, $^2J_{\text{CP}} = 5.3$ Hz), 84.0, 79.0 (d, $^1J_{\text{CP}} = 54.7$ Hz), 73.4, 71.0, 14.2, 13.8, 10.2. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 20 °C): δ -40.9. M.p. 109-111 °C. $[\alpha]_{\text{D}}^{20} -241.3$ (c 0.76, THF). FTIR (neat) 2975, 2902, 1624, 1495, 1449, 1377, 1270, 1019, 949, 758, 700 cm^{-1} . HRMS (EI) calcd for $\text{C}_{31}\text{H}_{34}\text{FeNOP}$ (M^+) 523.1722, found 523.1705.

7c and 7c'. The same procedure was followed as for the synthesis of **7a** and **7a'**. First fraction ($R_f = 0.2$ with Et₂O/hexane = 1/4; **7c**): orange solid, 13%. Second fraction ($R_f = 0.15$ with Et₂O/hexane = 1/4; **7c'**): orange solid, 8%.

7c: ¹H NMR (CD₂Cl₂, 20 °C): δ 7.50-7.46 (m, 1H), 7.40-7.36 (m, 2H), 7.28-7.21 (m, 5H), 7.20-7.13 (m, 1H), 5.54 (d, ³J_{HH} = 8.0 Hz, 1H), 5.26 (ddd, ³J_{HH} = 8.0, 6.6, and 1.7 Hz, 1H), 3.44 (dd, ³J_{HH} = 17.9 and 6.6 Hz, 1H), 3.28 (dd, ³J_{HH} = 17.9 and 1.4 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H), 1.56 (s, 15H). ¹³C NMR (CD₂Cl₂, 20 °C): δ 167.8 (d, ²J_{CP} = 18.0 Hz), 143.4, 140.6, 140.1 (d, ²J_{CP} = 18.0 Hz), 129.9 (d, ³J_{CP} = 9.1 Hz), 128.6, 128.2, 127.6, 126.0, 126.0, 125.6, 101.4 (d, ¹J_{CP} = 53.0 Hz), 94.9 (d, ²J_{CP} = 5.0 Hz), 92.7 (d, ²J_{CP} = 5.6 Hz), 83.9, 82.1, 78.6 (d, ¹J_{CP} = 54.3 Hz), 77.7 (d, ⁴J_{CP} = 1.7 Hz), 40.2, 14.1, 13.6 (d, ³J_{CP} = 0.5 Hz), 9.9 (d, ³J_{CP} = 0.7 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ -42.6. M.p. 144-146 °C (dec). [α]_D²⁰ -2.3 (c 0.96, THF). FTIR (neat) 3025, 2952, 2907, 2854, 1684, 1622, 1496, 1479, 1459, 1427, 1377, 1286, 1264, 1197, 1167, 1073, 1026, 857, 802, 757, 746, 701 cm⁻¹. HRMS (EI) calcd for C₃₂H₃₄FeNOP (M⁺) 535.1722, found 535.1727.

7c': ¹H NMR (CD₂Cl₂, 20 °C): δ 7.50-7.47 (m, 1H), 7.42-7.39 (m, 2H), 7.28-7.15 (m, 6H), 5.56 (d, ³J_{HH} = 7.4 Hz, 1H), 5.20 (ddd, ³J_{HH} = 7.4, 5.2, and 1.9 Hz, 1H), 3.48-3.35 (m, 2H), 2.40 (s, 3H), 2.16 (s, 3H), 1.39 (s, 15H). ¹³C NMR (CD₂Cl₂, 20 °C): δ 168.1 (d, ²J_{CP} = 18.0 Hz), 143.8, 140.7, 140.2 (d, ²J_{CP} = 18.0 Hz), 129.9 (d, ³J_{CP} = 9.0 Hz), 128.6, 128.2, 127.6, 126.1, 126.0, 125.5, 101.1 (d, ¹J_{CP} = 52.8 Hz), 95.4 (d, ²J_{CP} = 5.1 Hz), 92.6 (d, ²J_{CP} = 5.5 Hz), 83.9, 82.5, 78.3 (d, ¹J_{CP} = 54.6 Hz), 77.8 (d, ⁴J_{CP} = 1.9 Hz), 39.9, 14.1, 13.6 (d, ³J_{CP} = 0.7 Hz), 9.8 (d, ³J_{CP} = 0.7 Hz). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): δ -43.0. M.p. 151-153 °C (dec). [α]_D²⁰ -183.3 (c 0.95, THF). FTIR (neat) 3052, 2961, 2935, 2903, 1623, 1496, 1478, 1463, 1425, 1377, 1310, 1270, 1239, 1196, 1164, 1120, 1095, 1053, 1023, 856, 762, 749, 725, 699 cm⁻¹. HRMS (EI) calcd for C₃₂H₃₄FeNOP (M⁺) 535.1722, found 535.1748.

III. Preparation of Enones

3-Ferrocenyl-1-phenyl-2-propen-1-one. *n*-BuLi (2.6 M solution in hexane; 635 μ L, 1.65 mmol) was added to a stirred solution of diisopropylamine (231 μ L, 1.65 mmol) in THF (4 mL) at -78 $^{\circ}$ C. The mixture was stirred for 10 min at -78 $^{\circ}$ C and then warmed to r.t. and stirred for 10 min. The mixture was cooled to -78 $^{\circ}$ C, and acetophenone (175 μ L, 1.50 mmol) was added. This mixture was stirred for 10 min at -78 $^{\circ}$ C, then warmed to r.t. and stirred for 10 min. Then, it was cooled to -78 $^{\circ}$ C, and a solution of ferrocenecarboxaldehyde (321 mg, 1.50 mmol) in THF (6 mL) was added. The reaction mixture was stirred for 30 min at -78 $^{\circ}$ C, and then warmed to r.t. and stirred for 15 h. The reaction was quenched with sat. aq. NH_4Cl , and the mixture was extracted with Et_2O . The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed under nitrogen (degassed $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2 = 1/8$), affording 151 mg of the desired product as a purple solid (0.48 mmol, 32%). The spectroscopic data of this compound were in agreement with previously reported data.³

1-Phenyl-2-octen-1-one. *trans*-2-Octenal (1.0 mL, 6.7 mmol) in THF (6.0 mL) was added to a stirred solution of PhMgCl (2.0 M solution in THF; 4.0 mL, 8.0 mmol) in THF (6.0 mL) at 0 $^{\circ}$ C. The mixture was stirred for 3 h at r.t., then quenched with sat. aq. NH_4Cl and extracted with Et_2O . The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed ($\text{Et}_2\text{O}/\text{hexane} = 1/4$) to afford 1.08 g of a colorless liquid.

This liquid was dissolved in acetone (10 mL) and cooled to 0 $^{\circ}$ C. Jones reagent (1.52 M; 4.0 mL, 6.08 mmol) was added, and the mixture was stirred for 30 min at r.t., quenched with isopropanol, and extracted with Et_2O . The organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed ($\text{Et}_2\text{O}/\text{pentane} = 1/10$) to give 697 mg of colorless liquid (3.45 mmol, 51%).

^1H NMR (CDCl_3 , 20 $^{\circ}$ C): δ 7.95-7.91 (m, 2H), 7.58-7.43 (m, 3H), 7.08 (dt, $^3J_{\text{HH}} = 15.4$

(3) Huang, J.; Huang, Y.-Z. *J. Organomet. Chem.* **1991**, 414, 49-53.

and 6.9 Hz, 1H), 6.88 (dt, $^3J_{\text{HH}} = 15.4$ and 1.1 Hz, 1H), 2.35-2.28 (m, 2H), 1.56-1.48 (m, 2H), 1.38-1.31 (m, 4H), 0.91 (t, $^3J_{\text{HH}} = 6.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20 °C): δ 191.2, 150.4, 138.2, 132.8, 128.7, 128.7, 126.0, 33.0, 31.6, 28.0, 22.6, 14.2. FTIR (neat) 3059, 2930, 2858, 1670, 1623, 1579, 1448, 1348, 1282, 1226, 1180, 1014, 988, 771, 694, 662 cm^{-1} . HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ (M^+) 202.1352, found 202.1347.

IV. Catalytic Enantioselective Conjugate Additions

General procedure (Table 1). A mixture of $[\text{Cu}(\text{OTf})_2] \cdot \text{C}_6\text{H}_6$ (1.9 mg, 3.8 μmol) and the ligand (9.0 μmol) in toluene (1.3 mL) was stirred for 1 h at r.t. Then, the reaction mixture was cooled to -70°C , and solutions of the enone (0.151 mmol) in toluene (0.6 mL) and ZnEt_2 (23.2 μL , 0.226 mmol) in toluene (0.6 mL) were added. The reaction mixture was stirred for 24 h at 0°C , and then it was quenched with 1 N HCl and extracted (Et_2O). The organic extracts were dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed on silica gel or adsorption alumina (Et_2O /pentane mixtures), thereby furnishing the desired product of conjugate addition.

(S)-(+)-1,3-Diphenyl-1-pentanone (entry 1). Ligand **7c** was used. Colorless oil; 82% yield, 86% ee. $[\alpha]_D^{20} +7.3$ (c 1.52, ethanol).

^1H NMR (CDCl_3 , 20°C): δ 7.91-7.88 (m, 2H), 7.55-7.39 (m, 3H), 7.31-7.14 (m, 5H), 3.31-3.21 (m, 3H), 1.83-1.61 (m, 2H), 0.80 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20°C): δ 199.4, 144.9, 137.4, 133.1, 128.7, 128.6, 128.3, 127.8, 126.5, 45.8, 43.2, 29.4, 12.3.

The absolute configuration of the product was determined by comparison of the optical rotation with that reported in the reported literature.⁴ The ee was determined by chiral HPLC: Daicel Chiralcel OD column with hexanes:isopropanol = 99.75:0.25, flow = 1 mL/min. Retention time: 16.6 min [(S)-enantiomer], 21.5 min [(R)-enantiomer].

(S)-(+)-3-(4-Methoxyphenyl)-1-phenyl-1-pentanone (entry 2). Ligand **7c** was used. Colorless oil; 78% yield, 90% ee. $[\alpha]_D^{20} +15.2$ (c 1.67, ethanol).

^1H NMR (CDCl_3 , 20°C): δ 7.92-7.88 (m, 2H), 7.55-7.49 (m, 1H), 7.45-7.39 (m, 2H), 7.16-7.11 (m, 2H), 6.85-6.80 (m, 2H), 3.76 (s, 3H), 3.27-3.15 (m, 3H), 1.80-1.56 (m, 2H), 0.80 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20°C): δ 199.6, 158.1, 137.4, 136.8, 133.1, 128.7, 128.7, 128.2, 113.9, 55.3, 46.0, 42.4, 29.5, 12.3.

The absolute configuration of the product was assigned by analogy with entry 1. The ee was determined by chiral HPLC: Daicel Chiralcel OD column with

(4) Brienne, M.-J.; Ouannes, C.; Jacques, J. *Bull. Soc. Chim. Fr.* **1967**, 32, 613-623.

hexanes:isopropanol = 99.4:0.6, flow = 1 mL/min. Retention time: 10.4 min [(R)-enantiomer], 11.4 min [(S)-enantiomer].

(S)-(+)-3-(4-Chlorophenyl)-1-phenyl-1-pentanone (entry 3). Ligand **7b** was used. Colorless oil; 87% yield, 80% ee. $[\alpha]_D^{20} +2.0$ (c 2.00, ethanol).

^1H NMR (CDCl_3 , 20 °C): δ 7.91-7.87 (m, 2H), 7.56-7.40 (m, 3H), 7.27-7.13 (m, 4H), 3.26-3.21 (m, 3H), 1.82-1.57 (m, 2H), 0.80 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20 °C): δ 199.0, 143.3, 137.3, 133.2, 132.0, 129.2, 128.8, 128.7, 128.2, 45.6, 42.5, 29.4, 12.2.

The absolute configuration of the product was assigned by analogy with entry 1. The ee was determined by chiral HPLC: Daicel Chiralcel OD column with hexanes:isopropanol = 99.95:0.05, flow = 1 mL/min. Retention time: 40.3 min [(S)-enantiomer], 45.1 min [(R)-enantiomer].

(-)-3-Ferrocenyl-1-phenyl-1-pentanone (entry 4). Ligand **7b** was used. Yellow oil; 88% yield, 92% ee. $[\alpha]_D^{20} -68.7$ (c 1.80, ethanol).

^1H NMR (CDCl_3 , 20 °C): δ 8.01-7.97 (m, 2H), 7.60-7.45 (m, 3H), 4.10 (s, 5H), 4.09-4.02 (m, 4H), 3.32 (dd, $^3J_{\text{HH}} = 16.5$ and 5.5 Hz, 1H), 3.24 (dd, $^3J_{\text{HH}} = 16.2$ and 7.4 Hz, 1H), 3.18-3.12 (m, 1H), 1.64-1.54 (m, 2H), 0.87 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20 °C): δ 200.0, 137.6, 133.2, 128.8, 128.3, 94.2, 68.6, 67.8, 67.3, 67.2, 66.7, 44.4, 35.7, 29.4, 11.9. FTIR (neat) 3091, 2962, 2931, 2875, 1684, 1597, 1580, 1449, 1357, 1276, 1211, 1106, 1002, 819, 753, 690 cm^{-1} . HRMS (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{FeO}$ (M^+) 346.1015, found 346.1002.

The absolute configuration of the product was not determined. The ee was determined by chiral HPLC: Daicel Chiralcel OD column with hexanes:isopropanol = 99:1, flow = 1 mL/min. Retention time: 8.4 min, 9.2 min.

(S)-(+)-3-Cyclohexyl-1-phenyl-1-pentanone (entry 5). Ligand **7c'** was used. Colorless oil; 68% yield, 84% ee. $[\alpha]_D^{20} +0.9$ (c 1.51, ethanol).

^1H NMR (CDCl_3 , 20 °C): δ 7.97-7.95 (m, 2H), 7.58-7.43 (m, 3H), 2.98 (dd, $^3J_{\text{HH}} = 16.2$ and 5.5 Hz, 1H), 2.77 (dd, $^3J_{\text{HH}} = 16.2$ and 7.4 Hz, 1H), 1.99-1.93 (m, 1H), 1.76-1.62 (m, 5H), 1.47-1.00 (m, 8H), 0.87 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 20 °C): δ 201.3, 137.7, 133.0, 128.7, 128.3, 41.3, 40.4, 40.4, 30.5, 29.5, 27.0, 27.0, 27.0, 24.2, 12.1.

The absolute configuration of the product was determined by comparison of the

optical rotation with that reported in the reported literature.⁴ The ee was determined by chiral HPLC: Regis (R,R) WHELK-O 2 column with hexanes:isopropanol = 99.75:0.25, flow = 1 mL/min. Retention time: 21.9 min [(R)-enantiomer], 24.9 min [(S)-enantiomer].

(+)-3-Ethyl-1-phenyl-1-octanone (entry 6). Ligand **7b** was used. Colorless liquid; 79% yield, 62% ee. $[\alpha]_D^{20} +1.7$ (c 1.60, ethanol).

¹H NMR (CDCl₃, 20 °C): δ 7.97-7.94 (m, 2H), 7.58-7.43 (m, 3H), 2.87 (d, ³J_{HH} = 6.9 Hz, 2H), 2.07-2.03 (m, 1H), 1.46-1.19 (m, 10H), 0.91-0.85 (m, 6H). ¹³C NMR (CDCl₃, 20 °C): δ 201.0, 137.7, 133.0, 128.7, 128.3, 43.3, 35.9, 33.7, 32.3, 26.7, 26.6, 22.9, 14.3, 11.1. FTIR (neat) 2959, 2928, 2858, 1684, 1598, 1581, 1449, 1377, 1281, 1213, 1180, 1126, 750, 691 cm⁻¹. HRMS (EI) calcd for C₁₆H₂₄O (M⁺) 232.1822, found 232.1819.

The absolute configuration of the product was not determined. The ee was determined by chiral HPLC: Daicel Chiralcel OD column with hexanes:isopropanol = 99.95:0.05, flow = 1 mL/min. Retention time: 13.1 min, 13.8 min.

(S)-(+)-4-Phenyl-2-hexanone (entry 7). Ligand **7b** was used. Pale-yellow oil; 82% yield, 81% ee. $[\alpha]_D^{20} +27.0$ (c 1.32, ethanol).

¹H NMR (CDCl₃, 20 °C): δ 7.32-7.26 (m, 2H), 7.22-7.15 (m, 3H), 3.06-2.98 (m, 1H), 2.73 (d, ³J_{HH} = 7.4 Hz, 2H), 2.02 (s, 3H), 1.73-1.51 (m, 2H), 0.78 (t, ³J_{HH} = 7.3 Hz, 3H). ¹³C NMR (CDCl₃, 20 °C): δ 208.3, 144.5, 128.6, 127.7, 126.5, 50.8, 43.2, 30.9, 29.6, 12.2.

The absolute configuration of the product was determined by comparison of the optical rotation with that reported in the reported literature.⁴ The ee was determined by chiral HPLC: Daicel Chiralcel OD column with hexanes:isopropanol = 99:1, flow = 1 mL/min. Retention time: 8.5 min [(S)-enantiomer], 9.4 min [(R)-enantiomer].