Supporting Information For:
Aminohydroxyphosphine Ligand for Copper-Catalyzed Enantioselective Conjugate
Addition of Organozinc Reagents

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Table of Contents

Experimental Details	S1
NMR Spectra	S20
Computational Details	S40
Cartesian Coordinates of Stationary Points	S43

Experimental Details

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in oven- or flame-dried reaction vessels under argon or nitrogen atmosphere. Flash chromatography was performed as described by Still et al.,¹ employing Kanto Silica gel 60 (spherical, neutral, 140-325 mesh). ¹H, ¹³C and ³¹P nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA-500 (500 MHz) or ECX-400 (400 MHz) NMR spectrometers. ¹H NMR and ¹³C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and CDCl₃ (77.0 ppm), respectively. ³¹P NMR spectra are reported in ppm and are referenced to an external standard (85% H₃PO₄: 0.0 ppm). Gas chromatographic (GC) analysis was performed on a Shimadzu GC-14B instrument equipped with an FID detector and a capillary column, γ-DEX 225 (SUPELCO, 30 m x 0.25 mm i.d., 0.25 μm film). HPLC analysis was performed on JASCO HPLC system equipped with columns Chiracel OJ-H or OB-H (Daicel, 4.6 x 250 mm) and UV/CD detectors. IR spectra were recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) and reported in cm⁻¹. Optical rotation

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2924.

was measured on a JASCO DIP-370 instrument. The absolute configurations of known compounds were determined by comparison of specific rotations with literature data.

Solvents. Dichloromethane and toluene were distilled from CaH_2 and stored over molecular sieves 4Å. Anhydrous diethyl ether and tetrahydrofuran were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and copper catalyst prior to use. Anhydrous dimethoxyethane (DME) and *t*-butyl methyl ether (TBME) were purchased from Aldrich Inc. and used as received. The water content was determined with a Karl-Fischer moisture titrator (MKC-210, Kyoto Electronics Company) to be less than 20 ppm.

Materials. Following copper complexes were purchased from commercial suppliers and used as received: $\text{Cu}(\text{OTf})_2$, ACROS Chemical; $(\text{CuOTf})_2 \cdot \text{toluene}$, Aldrich Inc.; $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, KANTO Chemical; CuI , CuBr , and CuCl , WAKO Pure Chemical; $\text{Cu}(\text{acac})_2$, Tokyo Kasei Co. $\text{CuBr} \cdot \text{SMe}_2$ was prepared according to literature.² Me_2Zn (1.0 M in hexane) and Et_2Zn (1.0 M in hexanes) were purchased from KANTO Chemical and Aldrich Inc., respectively, and used as received. Unless otherwise noted, α,β -unsaturated carbonyl compounds were purchased from Aldrich Inc., Tokyo Kasei Co., and other commercial suppliers, and were used as received. (*E*)-4-(4-Nitrophenyl)but-3-en-2-one,³ (*E*)-4-(4-methoxyphenyl)but-3-en-2-one,³ and 3-((*E*)-but-2-enoyl)oxazolidin-2-one⁴ were synthesized according to literatures. *o*-Bromodiphenylphosphinobenzene⁵ and *N,N*-dibenzylaminoaldehydes⁶ including (*S*)-2-(dibenzylamino)propanal, (*S*)-2-(dibenzylamino)-3-methylbutanal, and (*S*)-2-(dibenzylamino)-3-phenylpropanal were prepared according to literature from commercial reagents purchased from Aldrich Inc., Tokyo Kasei Co., and other suppliers.

² Lipshutz, B. In *Organometallics in Synthesis: A Manual*, 2nd Ed., Schlosser, M. Ed.; John Wiley & Sons: Chichester, U.K., 2002.

³ Kanemasa, S.; Kanai, T. *J. Am. Chem. Soc.* **2000**, 122, 10710-10711.

⁴ Corbett, R. E.; Davey, C. L. *J. Chem. Soc.* **1955**, 296.

⁵ Quintard, D.; Keller, M.; Breit, B. *Synthesis* **2004**, 905-908.

⁶ Reetz, M. T.; Drewes, M. W.; Schwickardi, R. *Org. Synth. Coll. Vol.* 10, pp. 256-262.

Synthesis of Aminohydroxyphosphine Ligands

(1R, 2S)-2-(dibenzylamino)-1-(2-(diphenylphosphino)phenyl)propan-1-ol (1) and (1S, 2S)-2-(dibenzylamino)-1-(2-(diphenylphosphino)phenyl)propan-1-ol (2): To a solution of *o*-bromodiphenylphosphinobenzene (5.22 g, 15.3 mmol) in Et₂O (60 mL) was added *n*-BuLi (1.57 M in hexane, 9.8 mL, 15.3 mmol) dropwise at room temperature over 10 min. After additional stirring for 15 min, the resulting mixture was cooled to -5 °C, followed by addition of (*S*)-2-(dibenzylamino)propanal (3.53 g, 13.9 mmol) in Et₂O (15 mL) over 15 min. The reaction mixture was stirred for 9 h and quenched by sat. NH₄Cl (10 mL). The organic layer was separated, and the aqueous layer was extracted twice with Et₂O (30 mL). The combined organic layer was washed with brine (20 mL), dried over MgSO₄, and concentrated under reduced pressure to afford the crude product. TLC analysis indicated the formation of two diastereomers **1** (*R_f* = 0.36, hexane/EtOAc = 80/20) and **2** (*R_f* = 0.40). ³¹P NMR analysis of the crude product indicated the diastereomeric ratio of **1**:**2** = 9:1. These isomers were separated by silica gel chromatography (hexane/Et₂O/CH₂Cl₂ = 15/1/1 ~ 13/1/1) to afford **1** (4.67 g, 65%) and **2** (0.61 g, 9%) both as a colorless solid. The compound **1** was recrystallized from hexane/Et₂O (10:1) to give colorless crystals, which were used for catalytic reactions.⁷

1: mp 129-130 °C; [α]_D²⁶ -121.7° (*c* = 1.24, CHCl₃); IR (powder): cm⁻¹ 3255, 1436, 999, 766, 742, 696; ¹H NMR (500 MHz, CDCl₃): δ 1.14 (d, *J* = 6.6 Hz, 3H), 3.24 (dq, *J* = 7.2, 6.6 Hz, 1H), 3.55 (d, *J* = 14.0 Hz, 2H), 3.83 (d, *J* = 14.0 Hz, 2H), 5.59 (dd, *J*_{HP} = 7.2 Hz, *J*_{HH} = 7.2 Hz, 1H), 6.82 (m, 1H), 6.93 (m, 1H), 7.07 (m, 4H), 7.20-7.39 (m, 18H); ¹³C NMR (125 MHz, CDCl₃): δ 9.5, 54.43, 54.46, 58.4 (*J*_{CP} = 3.0 Hz), 73.5 (*J*_{CP} = 24.4 Hz), 126.6 (2C), 127.5, 127.9 (*J*_{CP} = 4.8 Hz), 128.0 (4C), 128.4 (2C, *J*_{CP} = 6.6 Hz), 128.5, 128.6 (2C, *J*_{CP} = 6.6 Hz),

⁷ **Important Note:** The ligand **1** must be recrystallized to obtain reproducible results in catalytic conjugate addition. Unrecrystallized **1** gave enantioselectivities of 92-93% in the addition reaction of Et₂Zn to *trans*-2-nonen-3-one for several times. This may be due to trace amount of sulfur impurities in **1**, which originates from the Swern oxidation step in the synthesis of *N,N*-dibenzylalaninal.

128.7, 128.8 (4C), 129.0, 133.3, 133.5 (2C, $J_{\text{CP}} = 19.1$ Hz), 133.9 (2C, $J_{\text{CP}} = 19.6$ Hz), 134.7 ($J_{\text{CP}} = 13.7$ Hz), 136.3 ($J_{\text{CP}} = 10.7$ Hz), 137.1 ($J_{\text{CP}} = 10.1$ Hz), 140.0 (2C), 146.9 ($J_{\text{CP}} = 22.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ -16.3; Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{NOP}$: C, 81.53; H, 6.65; N, 2.72. Found: C, 81.71; H, 6.81; N, 2.64.

2: mp 161-163 °C; $[\alpha]_{\text{D}}^{26}$ 132.12° ($c = 0.40$, CHCl_3); IR (powder): cm^{-1} 3270, 1432, 1028, 768, 735, 692; ^1H NMR (500 MHz, CDCl_3): δ 0.70 (d, $J = 6.9$ Hz, 3H), 2.92-2.97 (m, 1H), 3.31 (d, $J = 13.2$ Hz, 2H), 3.91 (d, $J = 13.2$ Hz, 2H), 4.78 (brs, 1H), 5.50 (dd, $J_{\text{HP}} = 8.9$ Hz, $J_{\text{HH}} = 8.9$ Hz, 1H), 6.91-6.93 (m, 1H), 7.09-7.37 (m, 23H); ^{13}C NMR (125 MHz, CDCl_3): δ 7.9, 53.4 (2C), 60.8, 70.3 ($J_{\text{CP}} = 25.6$ Hz), 127.1 ($J_{\text{CP}} = 5.6$ Hz), 127.2 (2C), 127.6, 128.3 (2C, $J_{\text{CP}} = 6.0$ Hz), 128.4 (2C, $J_{\text{CP}} = 6.6$ Hz), 128.5 (5C), 128.7, 129.1 (4C), 129.4, 133.2 (2C, $J_{\text{CP}} = 19.1$ Hz), 133.9, 134.2 (2C, $J_{\text{CP}} = 20.3$ Hz), 136.1 ($J_{\text{CP}} = 14.9$ Hz), 136.7 ($J_{\text{CP}} = 10.7$ Hz), 137.5 ($J_{\text{CP}} = 10.7$ Hz), 138.9 (2C), 147.1 ($J_{\text{CP}} = 22.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ -17.2; Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{NOP}$: C, 81.53; H, 6.65; N, 2.72. Found: C, 81.55; H, 6.88; N, 2.56.

(1R, 2S)-2-(dibenzylamino)-3-methyl-1-(2-(diphenylphosphino)phenyl)butan-1-ol (3) and (1S, 2S)-2-(dibenzylamino)-3-methyl-1-(2-(diphenylphosphino)phenyl)butan-1-ol (3'):

These compounds were synthesized from (*S*)-2-(dibenzylamino)-3-methylbutanal and *o*-bromodiphenylphosphinobenzene following the procedure for the compound **1** in 63% and 13% yields, respectively.

3: mp 65-66 °C; $[\alpha]_{\text{D}}^{26}$ -144.66° ($c = 0.9$, CHCl_3); IR (powder): cm^{-1} 3244, 1434, 742, 694; ^1H NMR (400 MHz, CDCl_3): δ 1.11 (d, $J = 7.2$ Hz, 3H), 1.15 (d, $J = 6.9$ Hz, 3H), 2.36-2.47 (m, 1H), 2.97 (d, $J = 9.4$ Hz, 1H), 3.44 (d, $J = 13.4$ Hz, 2H), 3.87 (d, $J = 13.4$ Hz, 2H), 5.83 (dd, $J_{\text{HP}} = 8.9$ Hz, $J_{\text{HH}} = 8.9$ Hz, 1H), 6.76-6.79 (m, 1H), 6.82-6.86 (m, 2H), 6.92-6.95 (m, 5H), 7.12-7.55 (m, 16H); ^{13}C NMR (125 MHz, CDCl_3): δ 18.9, 24.1, 24.5, 54.89, 54.93, 64.1 ($J_{\text{CP}} = 2.4$ Hz), 71.2 ($J_{\text{CP}} = 26.8$ Hz), 126.7 (2C), 127.5, 127.8 (4C), 128.3 (2C, $J_{\text{CP}} = 7.2$ Hz), 128.5, 128.8 (2C, $J_{\text{CP}} = 7.8$ Hz), 128.9 ($J_{\text{CP}} = 4.8$ Hz), 129.1, 129.2, 129.3 (4C), 132.3, 133.9 (2C, $J_{\text{CP}} = 19.7$ Hz), 134.0 (2C, $J_{\text{CP}} = 20.3$ Hz), 135.8 ($J_{\text{CP}} = 12.5$ Hz), 135.8 ($J_{\text{CP}} = 9.5$ Hz), 137.2 ($J_{\text{CP}} = 9.5$ Hz), 139.9 (2C), 147.1 ($J_{\text{CP}} = 20.9$ Hz); ^{31}P NMR (130 MHz, CDCl_3): δ -14.2;

Anal. Calcd for C₃₇H₃₈NOP: C, 81.74; H, 7.04; N, 2.58. Found: C, 81.53; H, 7.24; N, 2.38.

3': mp 110-111 °C; $[\alpha]_D^{26}$ 42.15° (*c* = 0.62, CHCl₃); IR (powder): cm⁻¹ 3244, 1457, 1436, 740, 694; ¹H NMR (400 MHz, CDCl₃): δ 0.84 (d, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H), 1.95-2.03 (m, 1H), 3.12 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.71 (d, *J* = 13.2 Hz, 2H), 4.06 (d, *J* = 13.2 Hz, 2H), 4.51 (brs, 1H), 5.58 (dd, *J*_{HP} = 8.4 Hz, *J*_{HH} = 8.4 Hz, 1H), 6.90-6.93 (m, 1H), 6.99-7.02 (m, 1H), 7.09-7.12 (m, 1H), 7.17-7.32 (m, 21H); ¹³C NMR (125 MHz, CDCl₃): δ 21.7 (*J*_{CP} = 4.2 Hz), 22.5 (*J*_{CP} = 2.4 Hz), 27.9, 55.0 (2C), 67.4 (*J*_{CP} = 3.6 Hz), 69.4 (*J*_{CP} = 25.0 Hz), 127.1 (2C), 127.6, 128.1 (*J*_{CP} = 4.2 Hz), 128.33-128.43 (9C), 128.5, 129.3, 129.5 (4C), 133.4 (2C, *J*_{CP} = 19.7 Hz), 134.0 (2C, *J*_{CP} = 19.7 Hz), 134.2, 136.0 (*J*_{CP} = 14.3 Hz), 137.0 (*J*_{CP} = 11.3 Hz), 137.5 (*J*_{CP} = 10.1 Hz), 139.4 (2C), 148.1 (*J*_{CP} = 22.7 Hz); ³¹P NMR (130 MHz, CDCl₃): δ -16.1; Anal. Calcd for C₃₇H₃₈NOP: C, 81.74; H, 7.04; N, 2.58. Found: C, 81.53; H, 7.26; N, 2.55.

(1R, 2S)-2-(dibenzylamino)-3-phenyl-1-(2-(diphenylphosphino)phenyl)propan-1-ol (4):

This compound was synthesized from (*S*)-2-(dibenzylamino)-3-phenylpropanal and *o*-bromodiphenylphosphinobenzene following the procedure for the compound **1** in 85% yield as a mixture with a minor diastereomer **4'** (86:14).

$[\alpha]_D^{26}$ -80.68° (*c* = 0.35, CHCl₃); IR (neat): cm⁻¹ 3255, 1435, 740, 694; ¹H NMR (500 MHz, CDCl₃, major diastereomer): δ 3.03 (dd, *J* = 14.4, 4.1 Hz, 1H), 3.16 (dd, *J* = 14.4, 8.2 Hz, 1H), 3.47-3.52 (m, 1H), 3.69 (d, *J* = 14.2 Hz, 2H), 3.87 (d, *J* = 14.2 Hz, 2H), 5.82 (dd, *J*_{HP} = 6.5 Hz, *J*_{HH} = 6.5 Hz, 1H), 6.83-6.90 (m, 6H), 7.11-7.39 (m, 23H); ¹³C NMR (100 MHz, CDCl₃, major diastereomer): δ 32.8, 54.66, 54.70, 64.4, 73.2 (*J*_{CP} = 24.3 Hz), 125.7, 126.5 (2C), 127.6, 127.8 (4C), 128.1 (*J*_{CP} = 5.3 Hz), 128.2, 128.4 (2C, *J*_{CP} = 7.2 Hz), 128.5, 128.6 (2C, *J*_{CP} = 6.7 Hz), 128.8, 128.9 (4C), 129.2 (2C), 129.7 (2C), 133.5 (2C, *J*_{CP} = 19.6 Hz), 133.6, 134.0 (2C, *J*_{CP} = 19.5 Hz), 134.6 (*J*_{CP} = 14.4 Hz), 136.1 (*J*_{CP} = 11.0 Hz), 137.2 (*J*_{CP} = 10.5 Hz), 139.9 (2C), 141.5, 147.4 (*J*_{CP} = 21.9 Hz); ³¹P NMR (162 MHz, CDCl₃): δ -16.8 (major), -15.3 (minor); Anal. Calcd for C₄₁H₃₈NOP: C, 83.22; H, 6.47; N, 2.37. Found: C, 82.95; H, 6.76; N, 2.12.

Determination of Relative Configurations of Compounds 1 and 2

The compounds **1** and **2** were transformed into oxazolidinone derivatives **1c** and **2c** through three steps including oxidation of the phosphine, deprotection of the *N,N*-dibenzyl group, and oxazolidinone formation (Scheme S1). ¹H NMR analysis (coupling constants and NOE) of **1c** and **2c** confirmed their relative configurations to be *cis* and *trans*, respectively (Figure S1).

Scheme S1^a

^a (a) *m*CPBA (1.05 equiv), CH₂Cl₂, 0 °C, 30 min; (b) Pd(OH)₂ (100 w/w%), H₂, MeOH-CH₂Cl₂, rt, 24 h; (c) 1,1'-dicarbonyl diimidazole (1.5 equiv), DMF, rt, 2 h then 110 °C, 2 h.

Figure S1. Assignment of relative configurations of oxazolidinone derivatives **1c** and **2c**.

(1*R*, 2*S*)-2-(dibenzylamino)-1-(2-(diphenylphosphinyl)phenyl)propan-1-ol (1a): To a cooled (0 °C) solution of **1** (1.03 g, 2 mmol) and Na₂HPO₄ (852 mg, 6 mmol) in CH₂Cl₂ (20 mL) was added *m*CPBA (Tokyo Kasei, > 65% purity, 558 mg, 2.1 mmol) in small portions over 15 min. The resulting mixture was stirred for 30 min and then treated with sat. Na₂S₂O₃ (5 mL) and sat. NaHCO₃ (5 mL). The organic layer was separated, washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluent: EtOAc/hexane = 1:1) to afford the title compound as a colorless solid (0.86 g, 81% yield).

$[\alpha]_D^{26}$ -161.40° (*c* = 0.52, CHCl₃); IR (powder): cm⁻¹ 3344, 1437, 1165, 1025, 752, 694; ¹H

NMR (500 MHz, CDCl₃): δ 1.24 (d, J = 6.3 Hz, 3H), 3.10 (d, J = 13.5 Hz, 2H), 3.15 (d, J = 13.5 Hz, 2H), 3.43 (dq, J = 9.8, 6.3 Hz, 1H), 4.90 (d, J = 9.8 Hz, 1H), 6.88-6.96 (m, 8H), 7.18-7.54 (m, 16H); ¹³C NMR (125 MHz, CDCl₃): δ 8.7, 53.62 (2C), 63.64, 72.6 (J_{CP} = 6.0 Hz), 126.2 (J_{CP} = 13.1 Hz), 126.7 (2C), 127.8 (4C), 128.3 (J_{CP} = 11.4 Hz, 2C), 128.4 (J_{CP} = 11.9 Hz, 2C), 129.2 (4C), 130.87 (J_{CP} = 9.5 Hz), 131.25 (J_{CP} = 100.2 Hz), 131.4 (J_{CP} = 9.5 Hz, 2C), 131.5 (J_{CP} = 2.4 Hz), 131.8 (J_{CP} = 2.4 Hz), 131.9 (J_{CP} = 106.1 Hz), 131.96 (J_{CP} = 106.1 Hz), 132.0 (J_{CP} = 2.4 Hz), 132.2 (J_{CP} = 9.5 Hz, 2C), 133.0 (J_{CP} = 13.1 Hz), 139.6 (2C), 147.7 (J_{CP} = 7.2 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 35.8; Anal. Calcd for C₃₅H₃₄NO₂P: C, 79.07; H, 6.45; N, 2.63. Found: C, 79.06; H, 6.70; N, 2.43.

(1S, 2S)-2-(dibenzylamino)-1-(2-(diphenylphosphinyl)phenyl)propan-1-ol (2a): This compound was synthesized from **2** following the procedure for the synthesis of **1a**.

$[\alpha]_{\text{D}}^{26}$ 27.4° (c = 0.44, CHCl₃); IR (powder): cm⁻¹ 3412, 2354, 1437, 1187, 1117, 717, 694; ¹H NMR (500 MHz, CDCl₃): δ 0.88 (d, J = 6.9 Hz, 3H), 2.87 (dq, J = 9.2, 6.9 Hz, 1H), 3.32 (d, J = 13.5 Hz, 2H), 3.89 (d, J = 13.5 Hz, 2H), 5.33 (d, J = 9.2 Hz, 1H), 7.00-7.04 (m, 1H), 7.15-7.19 (m, 5H), 7.21-7.30 (m, 7H), 7.40-7.48 (m, 5H), 7.51-7.56 (m, 2H), 7.58-7.62 (m, 2H), 7.68-7.72 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 7.9, 53.5 (2C), 60.6, 69.8 (J_{CP} = 6.0 Hz), 126.9 (J_{CP} = 13.1 Hz), 127.0 (2C), 128.29 (4C), 128.4 (J_{CP} = 11.9 Hz, 2C), 128.5 (J_{CP} = 10.7 Hz, 2C), 128.6 (J_{CP} = 9.5 Hz), 129.1 (4C), 131.4 (J_{CP} = 9.5 Hz, 2C), 131.63 (J_{CP} = 3.6 Hz), 131.65 (J_{CP} = 101.4 Hz), 131.67 (J_{CP} = 2.4 Hz), 132.2 (J_{CP} = 9.5 Hz, 2C), 132.43 (J_{CP} = 103.7 Hz), 132.5 (J_{CP} = 2.4 Hz), 132.9 (J_{CP} = 13.1 Hz), 134.0 (J_{CP} = 102.5 Hz), 139.4 (2C), 147.4 (J_{CP} = 7.2 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 31.3; Anal. Calcd for C₃₅H₃₄NO₂P: C, 79.07; H, 6.45; N, 2.63. Found: C, 78.92; H, 6.45; N, 2.35.

(1R, 2S)-2-amino-1-(2-(diphenylphosphinyl)phenyl)propan-1-ol (1b): To a solution of **1a** (531 mg, 1 mmol) in CH₂Cl₂ (1 mL) and MeOH (4 mL) was added Pd(OH)₂/C (Aldrich, 500 mg). The resulting mixture was stirred under H₂ at room temperature for 24 h, and then filtered through a pad of Celite®. The solution was concentrated under reduced pressure to afford the title compound as a colorless solid (335 mg, 100% yield), which was used in the next step without further purification.

¹H NMR (500 MHz, CDCl₃): δ 1.20 (d, J = 6.9 Hz, 3H), 3.99 (brq, J = 6.9 Hz, 1H), 5.65 (brs, 1H), 6.91 (dd, J = 14.3, 7.5 Hz, 1H), 7.21-7.61 (m, 12H), 8.01 (dd, J = 8.0, 3.8 Hz, 1H); ³¹P NMR (162 MHz, CDCl₃): δ 35.4.

(1*R*, 2*S*)-2-amino-1-(2-(diphenylphosphinyl)phenyl)propan-1-ol (2b): This compound was prepared from **2b** following the procedure for preparation of **1b**, and used for the next step without further purification.

¹H NMR (500 MHz, CDCl₃): δ 0.88 (d, *J* = 6.9 Hz, 3H), 3.82-3.85 (m, 1H), 5.47 (brd, *J* = 8.6 Hz, 1H), 7.00 (dd, *J* = 14.3, 8.0 Hz, 1H), 7.39-7.59 (m, 12H), 7.75-7.79 (m, 1H); ³¹P NMR (162 MHz, CDCl₃): δ 35.3.

(4*S*, 5*R*)-4-methyl-5-(2-(diphenylphosphinyl)phenyl)oxazolidin-2-one (1c): To a solution of **1b** (210 mg, 0.60 mmol) in DMF (3 mL) was added 1,1'-carbonyl diimidazole (Aldrich, 146 mg, 0.90 mmol). The resulting mixture was stirred at room temperature for 2 h, and then heated at 110 °C for 2 h. The reaction mixture was concentrated under reduced pressure, and chromatographed on silica gel (eluent: EtOAc/CH₂Cl₂ = 85/15) to afford the title compound as a colorless solid (135 mg, 62%).

[α]_D²⁶ -18.01° (*c* = 0.42, CHCl₃); IR (powder): cm⁻¹ 3232, 1760, 1179, 1117, 721, 692; ¹H NMR (500 MHz, CDCl₃): δ 0.82 (d, *J* = 6.6 Hz, 3H), 4.58 (dq, *J* = 8.3, 6.6 Hz, 1H), 5.45 (brs, 1H), 6.33 (d, *J* = 8.3 Hz, 1H), 7.05 (dd, *J* = 14.3, 7.7 Hz, 1H), 7.31-7.34 (m, 1H), 7.47-7.65 (m, 11H), 7.80 (dd, *J* = 8.0, 4.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 18.3, 52.1, 78.9 (*J*_{CP} = 6.0 Hz), 127.6 (*J*_{CP} = 11.9 Hz), 128.0 (*J*_{CP} = 9.5 Hz), 128.6 (*J*_{CP} = 11.9 Hz, 2C), 128.8 (*J*_{CP} = 11.9 Hz, 2C), 129.6 (*J*_{CP} = 99.0 Hz), 131.5 (*J*_{CP} = 9.5 Hz, 2C), 131.9 (*J*_{CP} = 103.7 Hz, 2C), 132.0 (*J*_{CP} = 2.4 Hz), 132.1 (*J*_{CP} = 9.5 Hz, 2C), 132.2 (*J*_{CP} = 2.4 Hz), 132.3 (*J*_{CP} = 2.4 Hz), 133.1 (*J*_{CP} = 13.1 Hz), 140.5 (*J*_{CP} = 7.2 Hz), 158.8; ³¹P NMR (162 MHz, CDCl₃): δ 32.5; Anal. Calcd for C₂₂H₂₀NO₃P: C, 70.02; H, 5.31; N, 3.71. Found: C, 69.93; H, 5.49; N, 3.45.

(4*S*, 5*S*)-4-methyl-5-(2-(diphenylphosphinyl)phenyl)oxazolidin-2-one (2c): This compound was synthesized from **2b** following the procedure for the synthesis of **1c**.

[α]_D²⁶ -34.62° (*c* = 0.44, CHCl₃); IR (powder): cm⁻¹ 3251, 2352, 1754, 1181, 1111, 721, 694; ¹H NMR (500 MHz, CDCl₃): δ 1.33 (d, *J* = 6.3 Hz, 3H), 3.80 (dq, *J* = 6.3, 3.8 Hz, 1H), 5.64 (brs, 1H), 5.96 (d, *J* = 3.8 Hz, 1H), 7.03-7.08 (m, 1H), 7.31-7.34 (m, 1H), 7.47-7.64 (m, 10H), 7.68-7.71 (m, 1H), 8.02 (brs, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 20.9, 56.8, 80.9 (*J*_{CP} = 6.7 Hz), 127.3 (*J*_{CP} = 9.5 Hz), 127.9 (*J*_{CP} = 13.1 Hz), 128.65 (*J*_{CP} = 11.9 Hz, 2C), 128.8 (*J*_{CP} = 13.1 Hz, 2C), 129.8 (*J*_{CP} = 99.0 Hz), 131.6 (*J*_{CP} = 9.5 Hz, 2C), 132.0 (*J*_{CP} = 103.7 Hz), 132.1 (*J*_{CP} = 9.5 Hz, 2C), 132.2 (*J*_{CP} = 3.6 Hz), 132.3 (*J*_{CP} = 2.4 Hz), 132.6 (*J*_{CP} = 102.5 Hz), 132.7 (*J*_{CP} =

2.4 Hz), 133.4 ($J_{\text{CP}} = 11.9$ Hz), 144.3 ($J_{\text{CP}} = 7.2$ Hz), 159.3; ^{31}P NMR (162 MHz, CDCl_3): δ 33.2; Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{NO}_2\text{P}$: C, 70.02; H, 5.31; N, 3.71. Found: C, 70.00; H, 5.52; N, 3.71.

A Typical Procedure for Copper-Catalyzed Enantioselective Conjugate Addition in Tables 1 and 2: In a flame-dried Schlenk tube were placed a copper salt (0.03 mmol), **1** (18.6 mg, 0.036 mmol) and CH₂Cl₂ (5 mL). The resulting mixture was stirred at room temperature for 1 h, and then cooled in an ice bath followed by the addition of a substrate (1 mmol). After 15 min stirring, Et₂Zn (1.0-M in hexanes, 1.5 mL, 1.5 mmol) was added dropwise over 3 min. After stirring for the period indicated in the tables, the reaction was quenched by sat. NH₄Cl (2 mL). The resulting mixture was extracted with Et₂O (5 mL) three times, and the combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford crude product. The crude product was purified with silica gel chromatography (eluent: hexane/Et₂O = 100/0~80/20) to afford the 1,4-addition product.

Table S1. Summary of Screening of Catalysts and Reaction Conditions (Addition of Et₂Zn to *trans*-3-Nonen-2-one)^a

entry	ligand	Cu salt	solvent	time/h	yield/% ^b	ee/% ^c
1	1	Cu(OTf) ₂	CH ₂ Cl ₂	3	91	98 (<i>S</i>)
2	2	Cu(OTf) ₂	CH ₂ Cl ₂	11	80	-3
3 ^d	1 + 2	Cu(OTf) ₂	CH ₂ Cl ₂	3	90	96
4	3	Cu(OTf) ₂	CH ₂ Cl ₂	3	87	23
5 ^e	4	Cu(OTf) ₂	CH ₂ Cl ₂	3	86	30
6	1	Cu(OTf) ₂	toluene	2	90	88
7	1	Cu(OTf) ₂	Et ₂ O	2	85	87
8	1	Cu(OTf) ₂	TBME	2	87	88
9	1	Cu(OTf) ₂	THF	12	55	66
10	1	Cu(OTf) ₂	DME	12	15	3
11	1	(CuOTf) ₂ •PhMe	CH ₂ Cl ₂	3	90	95
12	1	Cu(OAc) ₂ •H ₂ O	CH ₂ Cl ₂	5	85	96
13	1	Cu(acac) ₂	CH ₂ Cl ₂	12	80	88
14	1	CuI	CH ₂ Cl ₂	12	78	93
15	1	CuBr	CH ₂ Cl ₂	12	39	71
16	1	CuBr•Me ₂ S	CH ₂ Cl ₂	12	45	56
17	1	CuCl	CH ₂ Cl ₂	12	84	91

^a Reaction was carried out on 1-mmol scale. ^b Isolated yield. ^c Determined by Chiral GC (γ-DEX 225). ^d A 9:1 mixture of **1** and **2** was used. ^e Ligand **4** was used as a diastereomeric mixture (86:14).

(R)-(-)-1, 3-Diphenyl-pentan-1-one (Table 2, entry 1):⁸ Colorless solid; $[\alpha]_D^{26} -2.56^\circ$ ($c = 1.20$, CHCl_3 for an >98% ee sample); IR (powder): cm^{-1} 2958, 2873, 1681; ^1H NMR (500 MHz, CDCl_3): δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.62-1.66 (m, 1H), 1.76-1.81 (m, 1H), 3.22-3.29 (m, 3H), 7.15-7.29 (m, 5H), 7.39-7.43 (m, 2H), 7.49-7.53 (m, 1H), 7.88-7.90 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 12.0, 29.1, 42.9, 45.5, 126.2, 127.6 (2C), 128.0 (2C), 128.3 (2C), 128.4 (2C), 132.8, 137.2, 144.6, 199.1; HPLC conditions: CHIRALCEL OJ-H, hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, 254 nm, 20 °C, t_r (minor) = 23.60 min, t_r (major) = 33.50 min.

(R)-(-)-4-Phenyl-pentan-2-one (Table 2, entry 2):⁹ Colorless oil; $[\alpha]_D^{26} -40.71^\circ$ ($c = 0.90$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2962, 2927, 1713, 1453, 1356, 1162; ^1H NMR (500 MHz, CDCl_3): δ 1.26 (d, $J = 6.9$ Hz, 3H), 2.05 (s, 3H), 2.65 (dd, $J = 8.0$ and 16.4 Hz, 1H), 2.75 (dd, $J = 6.8$ and 16.4 Hz, 1H), 3.28-3.32 (m, 1H), 7.17-7.21 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 21.9, 30.5, 35.3, 51.9, 126.2, 126.7 (2C), 128.4 (2C), 146.1, 207.8; HPLC conditions: CHIRALCEL OJ-H, hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, 268 nm, 20 °C, t_r (minor) = 16.93 min, t_r (major) = 17.97 min.

⁸ Shintani, R.; Fu, G. C. *Org. Lett.* **2002**, *4*, 369-3702.

⁹ López, F.; Harutyunyan, S. R.; Minnard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2004**, *126*, 12784-12785.

(R)-(-)-4-Phenyl-hexan-2-one (Table 2, entry 3):¹⁰ Colorless oil; $[\alpha]_D^{26} -29.9^\circ$ ($c = 2.0$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2964, 1713, 1495, 1453, 1356; ^1H NMR (500 MHz, CDCl_3): δ 0.77 (t, $J = 7.5$ Hz, 3H), 1.52-1.60 (m, 1H), 1.63-1.70 (m, 1H), 1.99 (s, 3H), 2.71 (d, $J = 6.9$ Hz, 2H), 3.00-3.05 (m, 1H), 7.15-7.18 (m, 3H), 7.25-7.28 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.8, 29.2, 30.4, 42.8, 50.3, 126.2 (2C), 127.4, 128.3 (2C), 144.1, 207.8; HPLC conditions: CHIRALCEL OJ-H, hexane/IPA = 98.0/2.0, 1.0 mL/min, 268 nm, 20 °C, t_r (minor) = 11.59 min, t_r (major) = 13.92 min.

(-)-4-(4-Nitro-phenyl)-hexan-2-one (Table 2, entry 4):¹⁰ Light yellowish oil; $[\alpha]_D^{26} -12.71^\circ$ ($c = 0.90$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2964, 2931, 1715, 1605, 1515, 1343; ^1H NMR (500 MHz, CDCl_3): δ 0.78 (t, $J = 7.5$ Hz, 3H), 1.57-1.62 (m, 1H), 1.70-1.76

(m, 1H), 2.07 (s, 3H), 2.75-2.85 (m, 2H), 3.17-3.21 (m, 1H), 7.53-7.37 (m, 2H), 8.14-8.16 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.7, 28.9, 30.4, 42.3, 49.6, 123.6 (2C), 128.4 (2C), 146.4, 152.4, 206.6; HPLC conditions: CHIRALCEL OB-H, hexane/IPA = 98.0/2.0, 1.0 mL/min, 254 nm, 20 $^\circ\text{C}$, t_r (minor) = 48.18 min, t_r (major) = 51.49 min.

(-)-4-(4-Methoxy-phenyl)-hexan-2-one (Table 2, entry 5):¹⁰ Colorless oil; $[\alpha]_D^{23}$ -33.4° (c = 0.75, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2965, 2955, 1724, 1452, 135; ^1H NMR (500 MHz, CDCl_3): δ 0.76 (t, J = 7.5 Hz, 3H), 1.49-1.53 (m, 1H), 1.60-1.67 (m, 1H), 2.00 (s, 3H), 2.68 (d, J = 6.9 Hz, 2H), 2.94-3.00 (m, 1H), 3.77 (s, 3H), 8.81-6.84 (m, 2H), 7.06-7.09 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.9, 29.4, 30.5, 42.1, 50.7, 55.1, 113.7, 128.3 (2C), 136.1 (2C), 157.9, 208.2; HPLC conditions: CHIRALCEL OJ-H, hexane/*i*PrOH = 90.0/10.0, 1.0 mL/min, 290 nm, 20 $^\circ\text{C}$, t_r (minor) = 10.34 min, t_r (major) = 11.85 min.

¹⁰ Mizutani, H.; Degrado, S. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 779-781.

(-)-4-Furan-2-yl-hexan-2-one (Table 2, entry 6):⁹ Colorless oil; $[\alpha]_D^{26} -20.75^\circ$ ($c = 1.0$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2966, 2933, 2877, 1717, 1495, 1453, 1356, 1162; ^1H NMR (500 MHz, CDCl_3): δ 0.83 (t, $J = 7.4$ Hz, 3H), 1.59 (m, 2H), 2.07 (s, 3H), 2.64 (dd, $J = 6.9$ and 16.6 Hz, 1H), 2.79 (dd, $J = 7.45$ and 16.5 Hz, 1H), 3.16-3.20 (m, 1H), 6.00 (d, $J = 3.5$ Hz, 1H), 6.25-6.26 (m, 1H), 7.29 (d, $J = 1.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.4, 26.8, 30.2, 35.9, 47.4, 105.1, 109.8, 140.9, 157.1, 207.5; GC conditions: γ -DEX 225, initial temp 60 $^\circ\text{C}$, initial time 30 min, progress rate 5 $^\circ\text{C}/\text{min}$, final temp 220 $^\circ\text{C}$, t_r (minor) = 44.67 min, t_r (major) = 44.83 min.

(-)-4-Thiophen-2-yl-hexan-2-one (Table 2, entry 7): Colorless oil; $[\alpha]_D^{26} -36.74^\circ$ ($c = 0.85$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2964, 2927, 1713, 1353, 1162; ^1H NMR (500 MHz, CDCl_3): δ 0.85 (t, $J = 7.5$, 3H), 1.55-1.61 (m, 1H), 1.67-1.74 (m, 1H), 2.06 (s, 3H), 2.70-2.80 (m, 2H), 3.37-3.40 (m, 1H), 6.79 (d, $J = 3.5$ Hz, 1H), 6.90 (dd, $J = 3.5$ and 5.2 Hz, 1H), 7.12 (d, $J = 5.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.7, 30.3, 30.6, 38.1, 51.1, 122.9, 123.9, 126.4, 148.2, 207.4; Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{OS}$: C, 65.89; H, 7.74. Found: C, 65.68; H, 7.82; GC conditions: γ -DEX 225, initial temp 100 $^\circ\text{C}$, initial time 30 min, progress rate 5 $^\circ\text{C}/\text{min}$, final temp 220 $^\circ\text{C}$, t_r (minor) = 39.64 min, t_r (major) = 39.94 min.

(S)-(-)-4-Methyl-nonan-2-one (Table 2, entry 8):¹¹ Colorless oil; $[\alpha]_D^{26} -11.4^\circ$ ($c = 0.75$, CHCl_3 for an >98% ee sample); IR (neat) cm^{-1} 2958, 2927, 2859, 1717; ^1H NMR (500 MHz, CDCl_3): δ 0.86-0.89 (m, 6H), 1.29-1.33 (m, 8H), 1.96-1.99 (m, 1H), 2.12 (s, 3H), 2.21 (dd, $J = 8.6$ and 15.7 Hz, 1H), 2.41 (dd, $J = 5.7$ and 15.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 13.9, 19.7, 22.5, 26.5, 29.2, 30.3, 31.8, 36.8, 51.2, 209.1; GC conditions: γ -DEX 225, initial temp 80°C , initial time 60 min, progress rate $5^\circ\text{C}/\text{min}$, final temp 220°C , t_r (minor) = 25.07 min, t_r (major) = 25.63 min.

(S)-(-)-4-Ethyl-nonan-2-one (Table 2, entry 9):¹⁰ Colorless oil; $[\alpha]_D^{26} -2.27^\circ$ ($c = 1.80$, CHCl_3 for an 98% ee sample obtained by a 1-mmol scale reaction); IR (neat): cm^{-1} 2957, 2915, 1717, 1459, 1355, 1165; ^1H NMR (500 MHz, CDCl_3): δ 0.83-0.89 (m, 6H), 1.17-1.36 (m, 10H), 1.83-1.87 (m, 1H), 2.13 (s, 3H), 2.33 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 10.7, 13.9, 22.5, 26.2, 26.3, 30.3, 32.0, 33.3, 35.2, 48.3, 209.3; GC conditions: γ -DEX 225, initial temp 70°C , initial time 30 min, progress rate $5^\circ\text{C}/\text{min}$, final temp 220°C , t_r (minor) = 40.50 min, t_r (major) = 40.65 min.

¹¹ Fraser, P. K.; Woodward, S. *Chem. Eur. J.* **2003**, 9, 776-783.

A Procedure for Conjugate Addition of Et₂Zn to *trans*-3-Nonen-2-one on a 10-mmol Scale (Table 2, entry 10): In an oven-dried 200 mL 2-necked flask were placed Cu(OTf)₂ (109 mg, 0.3 mmol), **1** (185.5 mg, 0.36 mmol) and CH₂Cl₂ (50 mL). The resulting mixture was stirred at room temperature for 1 h, and then cooled in an ice bath followed by the addition of *trans*-3-nonen-2-one (1.40 g, 10 mmol). After 15 min stirring, Et₂Zn (1.0-M in hexanes, 15 mL, 15 mmol) was added dropwise over 5 min. After stirring for 5 h, the reaction was quenched by sat. NH₄Cl (10 mL). The resulting mixture was extracted with Et₂O (50 mL) three times, and the combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford crude product. The crude product was purified with silica gel chromatography (eluent: hexane/Et₂O = 100/0~90/10) to afford the title compound as colorless oil (1.58 g, 93% yield). Selectivity was determined to be 97% ee as described above.

(-)-4-Ethyl-5-methyl-hexan-2-one (Table 2, entry 11):¹⁰ Colorless oil; [α]_D²⁶ -3.42° (*c* = 1.0, CHCl₃ for an >98% ee sample); IR (neat) cm⁻¹ 2954, 2859, 1714, 1350; ¹H NMR (500 MHz, CDCl₃): δ 0.81-0.87 (m, 9H), 1.18-1.33 (m, 2H), 1.69-1.78 (m, 2H), 2.14 (s, 3H), 2.24 (dd, *J* = 7.5 and 16.1 Hz, 1H), 2.37 (dd, *J* = 5.6 and 16.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 11.7, 18.4, 19.5, 23.8, 29.2, 30.2, 41.1, 45.1, 209.6; GC conditions: γ -DEX 225, initial temp 50 °C, initial time 90 min, progress rate 5 °C/min, final temp 220 °C, *t*_r (minor) = 68.15 min, *t*_r (major) = 69.34 min.

(-)-1-(2-Ethyl-cyclopentyl)-ethanone (Table 2, entry 12):¹² Colorless oil; [α]_D²⁶ -8.53° (*c* = 0.4, CHCl₃ for an >98% ee and 62:38 dr sample); IR (neat): cm⁻¹ 2961, 1710, 1493, 1163; ¹H NMR (500 MHz, CDCl₃ for syn and anti diastereo mixture 3:2): δ 0.86-0.94 (m, 6H), 1.08-1.30 (m, 4H), 1.40-2.13 (m, 14H, 2.15 (s, 3H, syn diastereomer), 2.16 (s, 3H, anti

¹² Degrado, S. J.; Mizutani, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13362-13363.

diastereomer), 2.49 (q, $J = 7.4$ Hz, 1 H for anti), 2.98 (q, $J = 7.4$ Hz, 1H for syn); ^{13}C NMR (125 MHz, CDCl_3 for anti): δ 12.7, 23.1, 24.9, 28.3, 30.3, 32.1, 45.1, 58.5, 211.7; ^{13}C NMR (125 MHz, CDCl_3 for syn): δ 13.0, 23.2, 26.4, 29.8, 29.8, 31.1, 44.3, 55.9, 211.6; GC conditions: γ -DEX 225, initial temp 55 $^\circ\text{C}$, initial time 150 min, progress rate 5 $^\circ\text{C}/\text{min}$, final temp 220 $^\circ\text{C}$, t_r (minor, syn) = 88.78 min, t_r (major, syn) = 99.33 min, t_r (major, anti) = 90.79 min, t_r (minor, anti) = 111.00 min.

(S)-(-)-3-Ethyl-cyclohexanone (Table 2, entry 13):¹³ Colorless oil; $[\alpha]_D^{26} -8.81^\circ$ ($c = 1.60$, CHCl_3 for an 82% ee sample); IR (neat): cm^{-1} 2962, 2927, 1706; ^1H NMR (500 MHz, CDCl_3): δ 0.90 (t, $J = 7.5$ Hz, 3H), 1.29-1.40 (m, 3H), 1.62-1.70 (m, 2H), 1.89-1.92 (m, 1H), 1.97-2.07 (m, 2H), 2.22-2.44 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.1, 25.2, 29.2, 30.8, 40.7, 41.4, 47.7, 212.1.

The ee was determined by ^{13}C NMR analysis of the corresponding diastereomeric ketals prepared with (*R,R*)-2,3-butanediol (cat. *p*-TsOH in toluene at reflux, yield > 95%).

(S)-(-)-3-Ethyl-cyclohexanone (*R,R*)-2,3-dimethylethylene ketal: Colorless oil; $[\alpha]_D^{26} -5.03^\circ$ ($c = 1.0$, CHCl_3 for an 82% de sample); IR (neat): cm^{-1} 2966, 2931, 2866, 1447, 1376, 1096; ^1H NMR (500 MHz, CDCl_3): δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.05-1.17 (m, 9H), 1.35-1.42 (m, 4H), 1.62-1.69 (m, 4H), 3.52-3.56 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.1, 16.8, 17.0, 23.2, 29.5, 31.2, 36.0, 37.0, 43.5, 77.9, 78.0, 108.5; ^{13}C NMR (125 MHz, CDCl_3 , minor diastereomer): δ 11.1, 16.9, 17.0, 22.8, 29.6, 31.3, 36.5, 37.1, 42.6, 77.6, 77.9, 108.5.

¹³ Degrado, S. J.; Mizutani, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 755-756.

(S)-(-)-3-Ethyl-cycloheptanone: ¹³C NMR (125 MHz, CDCl₃): δ 11.3, 24.3, 18.4, 19.9, 36.4, 37.6, 43.8, 49.5, 214.6. Colorless oil; [α]_D²⁶ -4.74° (*c* = 1.2, CHCl₃ for a 16% ee sample); IR (neat): cm⁻¹ 2962, 2925, 2859, 1698, 1457; ¹H NMR (500 MHz, CDCl₃): δ 0.83 (t, *J* = 7.5 Hz, 3H), 1.16-1.36 (m, 4H), 1.50-1.54 (m, 2H), 1.79-1.85 (m, 3H), 2.28-2.41 (m, 4H);

The ee was determined by ¹³C NMR analysis of the corresponding diastereomeric ketals prepared with (*R,R*)-2,3-butanediol.

(S)-(-)-3-Ethyl-cycloheptanone (*R,R*)-2,3-dimethylethylene ketal: Colorless oil; [α]_D²⁶ -4.76° (*c* = 1.2, CHCl₃ for a 16% ee sample); IR (neat): 2962, 2927, 1706 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.80 (t, *J* = 7.5 Hz, 3H), 1.12-1.20 (m, 8H), 1.29-1.81 (m, 11H), 3.51-3.55 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 11.3, 16.4, 16.9, 22.3, 27.5, 30.8, 34.4, 35.5, 40.4, 45.9, 77.2, 77.8, 111.7; ¹³C NMR (125 MHz, CDCl₃, minor diastereomer): δ 11.5, 16.4, 17.0, 22.7, 29.5, 31.1, 34.5, 36.3, 40.5, 46.4, 77.3, 78.2, 111.1.

(R)-(-)-3-(3-Methyl-pentanoyl)-oxazolidin-2-one (Table 2, entry 14):¹⁴ Colorless oil; $[\alpha]_D^{26} -12.18^\circ$ ($c = 1.2$, CHCl_3 for an >98% ee sample); IR (neat): cm^{-1} 2962, 2927, 2877, 1773, 1696, 1382, 1200, 1038; ^1H NMR (500 MHz, CDCl_3): δ 0.86 – 0.96 (m, 6H), 1.22 – 1.28 (m, 1H), 1.39 – 1.44 (m, 1H), 1.95 – 1.99 (m, 1H), 2.72 – 2.77 (m, 1H), 2.89 – 2.94 (m, 1H), 4.01 – 4.04 (m, 2H), 4.39 – 4.43 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 11.2, 19.1, 29.2, 31.0, 41.6, 42.4, 61.8, 153.4, 172.9.

Due to insufficient separation of this adduct on all available GLC and HPLC, the product was converted to 2,2,5-trimethyl-3-heptanone¹⁵ by treatment with $t\text{-BuLi}$ ¹⁴ and optical purity of this compound was determined by GC ($\gamma\text{-DEX}$, initial temp 60°C , initial time 30 min, progress rate $5^\circ\text{C}/\text{min}$, final temp 220°C , t_r (major) = 24.29 min, t_r (minor) = 25.27 min).

¹⁴ Hird, A. W.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, 42, 1276-1279.

¹⁵ Brown, H. C.; Joshi, N. N.; Pyun, C.; Singaram, B. *J. Am. Chem. Soc.* **1989**, 111, 1754-1758.

Figure S1. ¹H NMR Spectrum of 1.

Figure S2. ¹³C NMR Spectrum of 1.

Figure S3. ¹H NMR Spectrum of 2.

Figure S4. ¹³C NMR Spectrum of 2.

Figure S5. ¹H NMR Spectrum of **3**.

Figure S6. ^{13}C NMR Spectrum of **3**.

Figure S7. ¹H NMR Spectrum of **3'**.

Figure S8. ^{13}C NMR Spectrum of 3'.

Figure S9. ^1H NMR Spectrum of **4**.

Figure S10. ¹³C NMR Spectrum of 4.

Figure S11. ¹H NMR Spectrum of 1a.

Figure S12. ¹³C NMR Spectrum of 1a.

Figure S13. ¹H NMR Spectrum of **1b**.

Figure S14. ¹H NMR Spectrum of 1c.

Figure S15. ¹³C NMR Spectrum of 1c.

Figure S16. ¹H NMR Spectrum of **2a**.

Figure S17. ^{13}C NMR Spectrum of 2a.

Figure S18. ¹H NMR Spectrum of **2b**.

Figure S19. ¹H NMR Spectrum of 2c.

Figure S20. ¹³C NMR Spectrum of 2c.

Computational details

Methods and Models.

All calculations were performed with a Gaussian 03 package.¹⁶ The density functional theory (DFT) method was employed using the B3LYP hybrid functional.¹⁷ Structures were optimized with a basis set consisting of the Stuttgart-Dresden effective core potential (ECP) for Cu,¹⁸ the Ahlrichs SVP set for Zn,¹⁹ and 6-31G(d)²⁰ for the rest. The method and basis sets used here have been applied to related systems including copper or zinc atoms, and known to give reliable results.^{21,22} Each stationary point was adequately characterized by normal coordinate analysis.

In the present computational study, we employed **I** (R = Me or Ph) as a simplified structure of the ligand **1** (in its deprotonated form). We modeled a complex **II** that involves [MeCu] and [R'Zn]⁺ (R' = Me or Cl) moieties as reactive species, and allowed it to interact with an *S-cis* conformer of acrolein to study the C-C bond formation step.

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Results

Interaction of **II** and *S-cis* acrolein lead to β -cuprio(III)enolate intermediate **III** similarly as in the reaction of a lithium organocuprate (Figure S21).²³ The intermediate **III** undergoes C-C bond forming reductive elimination through TS **IV**. The Cu^{III} center has a square-pyramidal geometry with the apical alkoxy group, and the Zn^{II} atom takes four ligands in a tetrahedral manner. The alkoxy oxygen atom bridges both metals (Cu-O: 2.2-2.4 Å, Zn-O: ca. 2 Å; see Figure S21 and Table S2). The activation energy of reductive elimination is 9-11 kcal/mol, and much lower than the corresponding value (calculation: 15.5 kcal/mol,²³ experiment: 18.2 kcal/mol²⁴) for a lithium organocuprate (Table S2).

Figure S21. C-C bond formation step under Cu/aminohydroxyphosphine/ R_2Zn catalysis. (a) Schematic representation. (b) 3-D structures of the complex **III** and TS **IV** ($R = Ph$, $R' = Me$).

Table S2. Energy and Structural Parameters of the Complex **III** and TS **IV**

	$\Delta E^\ddagger$ (kcal/mol)	Cu-C ¹ (Å)	Cu-C ² (Å)	Cu-C ³ (Å)	Cu-C ^a (Å)	Cu-O (Å)	Zn-O (Å)	C ^a -C ³ (Å)
III (R = Me, R' = Me)	-	2.857	2.186	1.979	1.981	2.442	1.980	-
III (R = Ph, R' = Me)	-	2.835	2.182	1.986	1.983	2.425	1.982	-
III (R = Me, R' = Cl)	-	2.871	2.206	1.977	1.978	2.341	1.960	-
III (R = Ph, R' = Cl)	-	2.835	2.191	1.985	1.980	2.380	1.957	-
Me ₂ CuLi CX ^a	-	2.700	2.129	2.023	1.979	-		-
IV (R = Me, R' = Me)	10.5	2.757	2.142	2.076	2.123	2.235	2.013	2.090
IV (R = Ph, R' = Me)	10.9	2.742	2.141	2.082	2.127	2.211	2.016	2.086
IV (R = Me, R' = Cl)	9.1	2.793	2.158	2.070	2.108	2.210	1.976	2.092
IV (R = Ph, R' = Cl)	9.8	2.773	2.155	2.077	2.113	2.207	1.981	2.090
Me ₂ CuLi TS ^a	15.5	2.724	2.166	2.134	2.133	-		2.100

^a Data for conjugate addition of Me₂CuLi•LiCl•(Me₂O)₄ to 4,4-dimethylcyclohexenone (taken ref 24).

Energies and Cartesian Coordinates of Stationary Points

III (R = Me, R' = Me)

SCF Done: E(RB+HF-LYP) = -3188.40224225 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.850812	-3.135666	-1.520429
2	6	0	-1.080947	-3.282595	-0.126414
3	6	0	-1.948744	-2.421540	0.598740
4	1	0	-1.528304	-2.508877	-2.094636
5	1	0	-0.630079	-4.106061	0.422649
6	1	0	-0.381499	-3.943731	-2.074092
7	8	0	-2.633565	-1.488393	0.098520
8	1	0	-2.003229	-2.591019	1.690577
9	29	0	0.520404	-1.932551	-0.751988
10	15	0	1.899254	-0.935419	0.827219
11	6	0	2.404227	0.776696	0.302102
12	6	0	1.296670	-0.727268	2.569121
13	6	0	3.521203	-1.791607	1.155760
14	6	0	1.531873	1.642637	-0.402893
15	6	0	2.013208	2.893960	-0.811764
16	6	0	3.309964	3.315613	-0.522474
17	6	0	4.163244	2.473461	0.184347
18	30	0	-2.130720	0.409364	0.884039
19	6	0	-2.910136	0.888161	2.650356
20	6	0	3.708338	1.216953	0.581502
21	6	0	0.107684	1.201921	-0.762492
22	6	0	-0.901126	2.382228	-0.760908
23	8	0	-0.329133	0.196515	0.091383
24	7	0	-2.295843	1.880272	-0.785418
25	6	0	-3.246180	2.968648	-0.510793
26	6	0	-2.622488	1.217333	-2.060357
27	6	0	1.411027	-1.721359	-2.508362
28	1	0	1.167196	-1.715486	3.024014
29	1	0	0.336833	-0.210126	2.556714
30	1	0	2.012689	-0.152572	3.167083
31	1	0	4.122608	-1.825362	0.242090
32	1	0	3.286281	-2.823280	1.440377
33	1	0	4.115195	-1.345780	1.961200
34	1	0	1.364031	3.560090	-1.372565
35	1	0	3.647109	4.295967	-0.849050
36	1	0	5.177284	2.783631	0.421824
37	1	0	4.392989	0.571116	1.119852
38	1	0	0.161552	0.821200	-1.801594
39	1	0	-0.733645	3.064108	-1.610015
40	1	0	-0.780413	2.957496	0.164391
41	1	0	-3.198934	3.758118	-1.278219
42	1	0	-3.026963	3.408607	0.465580
43	1	0	-4.262664	2.565208	-0.486870
44	1	0	-1.976548	0.350094	-2.201400
45	1	0	-2.506331	1.904506	-2.914304
46	1	0	-3.658246	0.868645	-2.026982
47	1	0	0.705116	-1.603341	-3.336747
48	1	0	2.027886	-2.608253	-2.695304
49	1	0	2.058920	-0.838764	-2.454764
50	1	0	-2.692049	0.126146	3.409099
51	1	0	-4.002496	0.979971	2.601749
52	1	0	-2.522758	1.839759	3.035992

IV (R = Me, R' = Me)

SCF Done: E(RB+HF-LYP) = -3188.38558726 A.U. after 1 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.923342	-2.869946	-1.815793
2	6	0	-1.390991	-3.144689	-0.451279
3	6	0	-2.299499	-2.316707	0.209019
4	1	0	-1.565669	-2.187422	-2.366676
5	1	0	-1.135531	-4.089994	0.020632
6	1	0	-0.666780	-3.760745	-2.382540
7	8	0	-2.774613	-1.209996	-0.236039
8	1	0	-2.643929	-2.664327	1.200078
9	29	0	0.327439	-1.866883	-0.496178
10	15	0	1.903659	-1.033851	0.901327
11	6	0	2.519147	0.600593	0.251454
12	6	0	1.337177	-0.664535	2.626888
13	6	0	3.458988	-1.986481	1.275100
14	6	0	1.690530	1.505289	-0.460599
15	6	0	2.266834	2.672031	-0.984354
16	6	0	3.612557	2.981168	-0.799363
17	6	0	4.423161	2.105510	-0.082638
18	30	0	-2.127951	0.406141	0.841072
19	6	0	-2.784022	0.789255	2.684693
20	6	0	3.875049	0.929233	0.425094
21	6	0	0.204117	1.215290	-0.724620
22	6	0	-0.681288	2.478423	-0.553885
23	8	0	-0.269230	0.203980	0.096015
24	7	0	-2.119717	2.124051	-0.593898
25	6	0	-2.943049	3.251256	-0.130414
26	6	0	-2.548205	1.687983	-1.934334
27	6	0	0.866753	-2.069755	-2.539478
28	1	0	1.120400	-1.607297	3.140771
29	1	0	0.426466	-0.066382	2.581519
30	1	0	2.107147	-0.121388	3.185986
31	1	0	4.046675	-2.136968	0.364075
32	1	0	3.144120	-2.971449	1.636653
33	1	0	4.094559	-1.530596	2.042332
34	1	0	1.650935	3.358418	-1.558591
35	1	0	4.021006	3.898676	-1.214956
36	1	0	5.475268	2.326609	0.075692
37	1	0	4.528016	0.254653	0.967400
38	1	0	0.138839	0.917733	-1.791912
39	1	0	-0.463926	3.242562	-1.317088
40	1	0	-0.480365	2.916179	0.430403
41	1	0	-2.831369	4.135874	-0.778555
42	1	0	-2.655662	3.518715	0.889650
43	1	0	-3.995406	2.953289	-0.124192
44	1	0	-2.022856	0.774017	-2.213469
45	1	0	-2.363950	2.467310	-2.692298
46	1	0	-3.617795	1.463438	-1.911162
47	1	0	1.338933	-1.085888	-2.422723
48	1	0	0.364639	-2.079480	-3.506315
49	1	0	1.625799	-2.855355	-2.512045
50	1	0	-2.699340	-0.091153	3.334280
51	1	0	-3.841990	1.082089	2.691295
52	1	0	-2.225044	1.598272	3.173378

III (R = Ph, R' = Me)

SCF Done: E(RB+HF-LYP) = -3571.86813128 A.U. after 10 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.663047	-0.742127	3.674354
2	6	0	0.541539	-1.883156	2.842329
3	6	0	1.516201	-2.217037	1.858406
4	1	0	1.627818	-0.246545	3.744458
5	1	0	-0.295696	-2.566528	2.963758
6	1	0	0.020406	-0.640676	4.544063
7	8	0	2.589121	-1.589504	1.659723
8	1	0	1.279931	-3.081894	1.212225
9	29	0	-0.233928	0.003969	2.067407
10	15	0	-1.409271	0.002971	0.047484
11	6	0	-1.125438	1.598337	-0.873946
12	6	0	-1.067590	-1.346704	-1.164766
13	6	0	-3.261848	-0.075220	0.188603
14	6	0	0.122848	2.268228	-0.852069
15	6	0	0.233322	3.500578	-1.511051
16	6	0	-0.837043	4.064501	-2.203269
17	6	0	-2.058716	3.398067	-2.239749
18	30	0	2.718006	-0.825973	-0.325330
19	6	0	3.374876	-2.066848	-1.729689
20	6	0	-2.195559	2.181608	-1.572897
21	6	0	1.314313	1.692717	-0.077977
22	6	0	2.673803	1.995047	-0.763013
23	8	0	1.165079	0.324356	0.112709
24	7	0	3.750348	1.163328	-0.178244
25	6	0	4.972376	1.244655	-0.990792
26	6	0	4.033055	1.523624	1.221627
27	6	0	-0.561536	1.736511	2.975277
28	6	0	-0.664795	-1.106142	-2.484379
29	6	0	-0.414850	-2.169806	-3.354521
30	6	0	-0.568341	-3.486383	-2.919587
31	6	0	-0.972642	-3.736969	-1.606106
32	6	0	-1.216478	-2.675306	-0.735465
33	1	0	-0.539229	-0.085973	-2.832597
34	1	0	1.176349	4.038640	-1.482977
35	1	0	-0.713044	5.018803	-2.708729
36	1	0	-2.904817	3.820175	-2.775184
37	1	0	-3.157087	1.680603	-1.593523
38	1	0	1.319198	2.213287	0.899286
39	1	0	2.939605	3.062019	-0.688113
40	1	0	2.607427	1.737949	-1.826802
41	1	0	5.374248	2.270355	-1.028631
42	1	0	4.757815	0.908957	-2.008684
43	1	0	5.735534	0.586316	-0.565682
44	1	0	3.146167	1.355483	1.833774
45	1	0	4.348789	2.575945	1.313792
46	1	0	4.832936	0.881607	1.600724
47	1	0	0.335813	2.113628	3.478083
48	1	0	-1.352905	1.618180	3.725148
49	1	0	-0.885575	2.467207	2.224691
50	1	0	-0.096551	-1.966219	-4.373567
51	1	0	-0.370874	-4.312525	-3.597259
52	1	0	-1.094150	-4.759367	-1.257689
53	1	0	-1.524971	-2.880274	0.287005
54	6	0	-4.099316	-0.701010	-0.748667
55	6	0	-5.481321	-0.742092	-0.552947
56	6	0	-6.048671	-0.155707	0.579600
57	6	0	-5.226979	0.469666	1.519463
58	6	0	-3.845480	0.503989	1.328088
59	1	0	-3.671903	-1.161943	-1.634116
60	1	0	-6.114300	-1.233246	-1.287737
61	1	0	-7.124388	-0.189825	0.731098
62	1	0	-5.659986	0.924583	2.406611
63	1	0	-3.210921	0.981986	2.069841
64	1	0	2.714549	-2.935622	-1.834895
65	1	0	4.378269	-2.448738	-1.502850
66	1	0	3.425643	-1.587074	-2.715581

IV (R = Ph, R' = Me)

SCF Done: E(RB+HF-LYP) = -3571.85071040 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.894037	-0.715245	3.637653
2	6	0	0.886466	-1.950840	2.846279
3	6	0	1.884472	-2.242151	1.913817
4	1	0	1.869329	-0.237783	3.687415
5	1	0	0.163293	-2.729192	3.076052
6	1	0	0.416746	-0.807927	4.609378
7	8	0	2.855391	-1.472081	1.585785
8	1	0	1.824947	-3.233634	1.428592
9	29	0	-0.075427	-0.326327	1.836116
10	15	0	-1.466426	-0.035666	0.066088
11	6	0	-1.224754	1.661704	-0.669108
12	6	0	-1.178116	-1.219520	-1.317419
13	6	0	-3.305575	-0.134272	0.304587
14	6	0	0.020210	2.339361	-0.633546
15	6	0	0.079073	3.649884	-1.131083
16	6	0	-1.031053	4.282043	-1.687220
17	6	0	-2.247129	3.606781	-1.746125
18	30	0	2.742663	-0.807481	-0.356327
19	6	0	3.218782	-1.975660	-1.896840
20	6	0	-2.335769	2.314864	-1.231691
21	6	0	1.278808	1.707737	-0.016712
22	6	0	2.560599	2.033762	-0.828681
23	8	0	1.149417	0.334095	0.117181
24	7	0	3.705884	1.226296	-0.351367
25	6	0	4.832036	1.319236	-1.291757
26	6	0	4.131239	1.607345	1.005435
27	6	0	-0.175835	1.064871	3.441438
28	6	0	-1.032434	-2.579085	-1.001278
29	6	0	-0.838549	-3.525403	-2.007280
30	6	0	-0.778980	-3.124335	-3.343450
31	6	0	-0.917185	-1.773914	-3.666836
32	6	0	-1.118294	-0.826316	-2.661167
33	1	0	-1.057766	-2.894302	0.038907
34	1	0	1.016132	4.196774	-1.081154
35	1	0	-0.942446	5.295754	-2.069377
36	1	0	-3.124849	4.079777	-2.178136
37	1	0	-3.292827	1.805392	-1.262433
38	1	0	1.398271	2.186811	0.977446
39	1	0	2.814113	3.105155	-0.784663
40	1	0	2.389729	1.768881	-1.878228
41	1	0	5.204481	2.352562	-1.387449
42	1	0	4.517503	0.960820	-2.275210
43	1	0	5.650783	0.684539	-0.940949
44	1	0	3.325232	1.415055	1.714241
45	1	0	4.424172	2.669403	1.056940
46	1	0	4.985556	0.990822	1.297097
47	1	0	-0.239333	1.823904	2.650631
48	1	0	0.499247	1.447860	4.206263
49	1	0	-1.163207	0.894590	3.876985
50	1	0	-0.724047	-4.574167	-1.746268
51	1	0	-0.618180	-3.859633	-4.127234
52	1	0	-0.865581	-1.453890	-4.704340
53	1	0	-1.221048	0.222163	-2.923863
54	6	0	-3.829760	0.392040	1.497513
55	6	0	-5.196013	0.330199	1.768076
56	6	0	-6.062508	-0.276059	0.855331
57	6	0	-5.554080	-0.812839	-0.327867
58	6	0	-4.186549	-0.740442	-0.603892
59	1	0	-3.159366	0.850558	2.220794
60	1	0	-5.582717	0.745896	2.694959
61	1	0	-7.126552	-0.334401	1.068755
62	1	0	-6.221532	-1.290127	-1.040871
63	1	0	-3.805441	-1.161441	-1.529183
64	1	0	2.553708	-2.845987	-1.951425
65	1	0	4.244636	-2.359540	-1.826616
66	1	0	3.132407	-1.454447	-2.859155

III (R = Me, R' = Cl)

SCF Done: E(RB+HF-LYP) = -3608.76260335 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.500283	-3.230975	-1.557018
2	6	0	-0.866170	-3.374550	-0.187029
3	6	0	-1.828534	-2.555996	0.442203
4	1	0	-1.151734	-2.652748	-2.207645
5	1	0	-0.422377	-4.162864	0.416443
6	1	0	0.046651	-4.032508	-2.044648
7	8	0	-2.520321	-1.659141	-0.142370
8	1	0	-1.985390	-2.709447	1.522964
9	29	0	0.732883	-1.944390	-0.701072
10	15	0	1.959369	-0.836128	0.944619
11	6	0	2.435134	0.863353	0.351211
12	6	0	1.196166	-0.545383	2.609005
13	6	0	3.575751	-1.602012	1.458069
14	6	0	1.591663	1.660553	-0.462110
15	6	0	2.068646	2.898511	-0.916595
16	6	0	3.328258	3.378829	-0.565861
17	6	0	4.150471	2.608536	0.251495
18	30	0	-2.095931	0.202663	0.466052
19	17	0	-2.844450	0.834528	2.456752
20	6	0	3.703323	1.364619	0.692304
21	6	0	0.201898	1.183354	-0.902621
22	6	0	-0.851503	2.327072	-0.849391
23	8	0	-0.231988	0.110777	-0.132010
24	7	0	-2.233926	1.787567	-0.982987
25	6	0	-3.228723	2.822985	-0.639008
26	6	0	-2.485488	1.254516	-2.337378
27	6	0	1.783515	-1.821881	-2.373057
28	1	0	1.039318	-1.510457	3.103093
29	1	0	0.232949	-0.045355	2.496065
30	1	0	1.851087	0.070681	3.235128
31	1	0	4.255690	-1.666244	0.602938
32	1	0	3.353096	-2.623357	1.785979
33	1	0	4.078917	-1.083579	2.281391
34	1	0	1.443843	3.505497	-1.565907
35	1	0	3.661256	4.346881	-0.930630
36	1	0	5.135740	2.964261	0.540208
37	1	0	4.366616	0.775906	1.315844
38	1	0	0.304213	0.874613	-1.961444
39	1	0	-0.678198	3.084783	-1.627771
40	1	0	-0.793284	2.819590	0.127133
41	1	0	-3.147728	3.693523	-1.307333
42	1	0	-3.081176	3.138003	0.396083
43	1	0	-4.233500	2.401228	-0.728547
44	1	0	-1.800992	0.430420	-2.544630
45	1	0	-2.358428	2.035196	-3.103036
46	1	0	-3.508868	0.873477	-2.387981
47	1	0	1.160878	-1.770813	-3.271054
48	1	0	2.440301	-2.695965	-2.441134
49	1	0	2.391773	-0.913588	-2.295420

IV (R = Me, R' = Cl)

SCF Done: E(RB+HF-LYP) = -3608.74809965 A.U. after 1 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.594677	-3.054226	-1.777247
2	6	0	-1.121964	-3.277757	-0.422187
3	6	0	-2.115275	-2.487771	0.142825
4	1	0	-1.242328	-2.441376	-2.399131
5	1	0	-0.826129	-4.171386	0.121355
6	1	0	-0.269867	-3.964031	-2.274257
7	8	0	-2.652903	-1.442590	-0.400716
8	1	0	-2.493185	-2.796017	1.131160
9	29	0	0.543929	-1.907007	-0.484221
10	15	0	1.964301	-0.925229	0.995194
11	6	0	2.554014	0.702593	0.302858
12	6	0	1.236303	-0.493240	2.642679
13	6	0	3.522075	-1.780400	1.543748
14	6	0	1.744094	1.543070	-0.502819
15	6	0	2.312005	2.705152	-1.046016
16	6	0	3.630017	3.074883	-0.790785
17	6	0	4.421283	2.264705	0.018880
18	30	0	-2.092243	0.254467	0.424243
19	17	0	-2.755492	0.809136	2.479117
20	6	0	3.883184	1.092822	0.546305
21	6	0	0.288646	1.203970	-0.857208
22	6	0	-0.655085	2.424147	-0.671672
23	8	0	-0.191592	0.142508	-0.104855
24	7	0	-2.080985	2.024292	-0.827736
25	6	0	-2.971209	3.092647	-0.330470
26	6	0	-2.409783	1.691762	-2.228200
27	6	0	1.196088	-2.218381	-2.464659
28	1	0	1.017311	-1.417779	3.187757
29	1	0	0.305418	0.059157	2.504915
30	1	0	1.936737	0.109848	3.231070
31	1	0	4.188688	-1.952860	0.693079
32	1	0	3.220748	-2.757124	1.937535
33	1	0	4.069749	-1.250895	2.330985
34	1	0	1.710434	3.337178	-1.693889
35	1	0	4.032561	3.986561	-1.224205
36	1	0	5.452086	2.532845	0.233875
37	1	0	4.522737	0.469691	1.160893
38	1	0	0.290317	0.947673	-1.936365
39	1	0	-0.423966	3.241650	-1.370502
40	1	0	-0.537530	2.801518	0.349419
41	1	0	-2.819994	4.030327	-0.886865
42	1	0	-2.781452	3.256785	0.731999
43	1	0	-4.011637	2.777264	-0.446232
44	1	0	-1.813732	0.840954	-2.562627
45	1	0	-2.226799	2.548246	-2.895749
46	1	0	-3.464995	1.413663	-2.291421
47	1	0	1.624928	-1.211272	-2.380415
48	1	0	0.737280	-2.299386	-3.449085
49	1	0	1.979375	-2.972180	-2.358549

III (R = Ph, R' = Cl)

SCF Done: E(RB+HF-LYP) = -3992.22746189 A.U. after 11 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.473587	0.513561	3.715485
2	6	0	-0.388846	1.697756	2.935025
3	6	0	-1.386416	2.063975	1.998179
4	1	0	-1.434363	0.012236	3.798159
5	1	0	0.452832	2.375808	3.052679
6	1	0	0.194332	0.383346	4.561870
7	8	0	-2.476951	1.438057	1.824093
8	1	0	-1.183885	2.948642	1.373086
9	29	0	0.377598	-0.155190	2.051068
10	15	0	1.544870	-0.007296	0.020738
11	6	0	1.238060	-1.495668	-1.060500
12	6	0	1.160619	1.463590	-1.023010
13	6	0	3.396041	0.058487	0.140298
14	6	0	0.012359	-2.207327	-1.052047
15	6	0	-0.103340	-3.351296	-1.854369
16	6	0	0.937987	-3.786985	-2.671718
17	6	0	2.136130	-3.078746	-2.692994
18	30	0	-2.711578	0.602720	0.001964
19	17	0	-3.598538	1.848706	-1.598116
20	6	0	2.278757	-1.950670	-1.887450
21	6	0	-1.149710	-1.777292	-0.149713
22	6	0	-2.540137	-2.082232	-0.772301
23	8	0	-1.054263	-0.424680	0.169174
24	7	0	-3.618370	-1.371855	-0.034233
25	6	0	-4.886413	-1.430363	-0.786722
26	6	0	-3.799940	-1.912988	1.327298
27	6	0	0.758220	-1.903109	2.899997
28	6	0	0.508584	1.371861	-2.258470
29	6	0	0.191406	2.525793	-2.978866
30	6	0	0.529429	3.782704	-2.479154
31	6	0	1.183900	3.885055	-1.248797
32	6	0	1.490569	2.735176	-0.523203
33	1	0	0.234832	0.400050	-2.655434
34	1	0	-1.027972	-3.920529	-1.844037
35	1	0	0.809199	-4.673991	-3.286428
36	1	0	2.959245	-3.400262	-3.325165
37	1	0	3.223116	-1.417996	-1.900198
38	1	0	-1.062323	-2.385773	0.770228
39	1	0	-2.753917	-3.161769	-0.786026
40	1	0	-2.563717	-1.715581	-1.804544
41	1	0	-5.217678	-2.469913	-0.932724
42	1	0	-4.757109	-0.943505	-1.755328
43	1	0	-5.658100	-0.887532	-0.234411
44	1	0	-2.878855	-1.796070	1.900422
45	1	0	-4.077571	-2.978247	1.299415
46	1	0	-4.593603	-1.355080	1.831308
47	1	0	-0.106974	-2.304317	3.438043
48	1	0	1.588024	-1.793732	3.607556
49	1	0	1.049452	-2.602440	2.107548
50	1	0	-0.331134	2.438286	-3.926929
51	1	0	0.276838	4.678760	-3.039102
52	1	0	1.450219	4.860805	-0.850710
53	1	0	1.995797	2.826030	0.435619
54	6	0	4.220364	0.756383	-0.757072
55	6	0	5.605893	0.771396	-0.585419
56	6	0	6.189509	0.087306	0.482445
57	6	0	5.380832	-0.609016	1.382550
58	6	0	3.995684	-0.618187	1.215728
59	1	0	3.779499	1.295817	-1.589896
60	1	0	6.228836	1.318729	-1.288206
61	1	0	7.268059	0.101205	0.615240
62	1	0	5.826767	-1.139435	2.219849
63	1	0	3.371802	-1.152210	1.927405

IV (R = Ph, R' = Cl)

SCF Done: E(RB+HF-LYP) = -3992.21186615 A.U. after 8 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.661695	-0.418485	3.744256
2	6	0	-0.719125	0.990815	3.332430
3	6	0	-1.764818	1.502509	2.571501
4	1	0	-1.622858	-0.923379	3.692392
5	1	0	0.004159	1.694756	3.735746
6	1	0	-0.147656	-0.581043	4.687423
7	8	0	-2.749677	0.818157	2.092944
8	1	0	-1.758239	2.588071	2.379384
9	29	0	0.247205	-0.276794	1.882369
10	15	0	1.571830	0.034772	0.057675
11	6	0	1.356479	-1.389887	-1.129201
12	6	0	1.173482	1.548722	-0.911959
13	6	0	3.412010	0.148047	0.264066
14	6	0	0.138428	-2.103206	-1.266809
15	6	0	0.111075	-3.217174	-2.119461
16	6	0	1.224105	-3.614620	-2.856621
17	6	0	2.412284	-2.898145	-2.742964
18	30	0	-2.714324	0.573345	0.128231
19	17	0	-3.376305	2.231176	-1.194805
20	6	0	2.470663	-1.806035	-1.879996
21	6	0	-1.128055	-1.745827	-0.473659
22	6	0	-2.410486	-1.822645	-1.345890
23	8	0	-1.040203	-0.484972	0.101352
24	7	0	-3.584509	-1.280738	-0.611356
25	6	0	-4.715158	-1.066748	-1.535858
26	6	0	-3.991652	-2.157333	0.503905
27	6	0	0.445639	-2.040509	3.029789
28	6	0	0.980850	2.749538	-0.211508
29	6	0	0.699198	3.931345	-0.895319
30	6	0	0.598733	3.927181	-2.287549
31	6	0	0.785123	2.737576	-2.991863
32	6	0	1.073350	1.554153	-2.309839
33	1	0	1.036733	2.754338	0.874236
34	1	0	-0.803407	-3.796551	-2.209050
35	1	0	1.159595	-4.479185	-3.512060
36	1	0	3.292170	-3.188008	-3.310720
37	1	0	3.407347	-1.268101	-1.783284
38	1	0	-1.221677	-2.523443	0.311898
39	1	0	-2.626891	-2.849006	-1.677905
40	1	0	-2.268605	-1.197431	-2.233715
41	1	0	-5.027479	-2.009992	-2.010308
42	1	0	-4.426286	-0.343582	-2.300754
43	1	0	-5.560614	-0.652037	-0.980823
44	1	0	-3.186637	-2.232040	1.236832
45	1	0	-4.253256	-3.165750	0.146246
46	1	0	-4.862754	-1.721522	0.999878
47	1	0	0.497631	-2.547274	2.057003
48	1	0	-0.195422	-2.638726	3.676137
49	1	0	1.442818	-1.964794	3.468795
50	1	0	0.542180	4.851745	-0.339637
51	1	0	0.363612	4.844783	-2.819531
52	1	0	0.698621	2.726168	-4.075110
53	1	0	1.209574	0.632711	-2.867647
54	6	0	4.004532	-0.651346	1.255937
55	6	0	5.378041	-0.599678	1.490173
56	6	0	6.181629	0.266518	0.745095
57	6	0	5.604144	1.074496	-0.235074
58	6	0	4.229671	1.015329	-0.476473
59	1	0	3.382723	-1.315846	1.851241
60	1	0	5.819168	-1.227556	2.259927
61	1	0	7.250980	0.315407	0.932629
62	1	0	6.222770	1.754690	-0.814809
63	1	0	3.792129	1.649848	-1.241002