**The Conjugate Reduction of α,β -Unsaturated Carbonyl Compounds Catalyzed by A
Copper Carbene Complex**

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Supporting Information

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I. General Considerations

Toluene, THF, and diethyl ether were purchased from J. T. Baker in CYCLE-TAINER[®] solvent delivery kegs which were vigorously purged with argon for 2 h. Toluene was further purified by passing through two packed columns of neutral alumina and copper (II) oxide under argon pressure. THF was further purified by passing through a column of neutral alumina.¹

CuCl (99.995%) was purchased from Strem and NaO*t*-Bu was purchased from Aldrich and stored in a nitrogen-filled drybox. PMHS and anhydrous *t*-BuOH were purchased from Aldrich; CuCl₂•2H₂O (99+%), (*S*)-*p*-tol-BINAP, 1,3-bis(2,6-di-*i*-propylphenyl)imidazolium chloride, and diphenyl silane were purchased from Strem. All other reagents were available from commercial sources and were used without further purification, unless otherwise noted. All manipulations involving air-sensitive materials (except the reactions) were conducted in a Vacuum Atmospheres drybox under an atmosphere of nitrogen. All reactions, unless otherwise noted, were carried out in flasks sealed with a rubber or teflon screw septum under an atmosphere of argon.

Analytical thin layer chromatography was performed using E.M. Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with potassium permanganate. Flash chromatography was performed on E.M. Science Kieselgel 60 (230-400 mesh).

Yields refer to isolated yields of compounds of greater than 95% purity as estimated by capillary GC and ¹H NMR. Yields reported in this section refer to a single experiment, while those reported in the tables are an average of two or more runs, so the numbers may differ slightly.

All new compounds were characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy in addition to elemental analysis (Atlantic Microlabs) and/or high resolution mass spectra (Finnegan MAT System 8200 spectrometer).

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Mercury 300, a Varian Unity 300, or a Varian Inova 500. Splitting patterns are designated as follows: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; td, triplet of doublets; q, quartet; qd,

¹ (a) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15, 1518. (b) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, 78, 64.

quartet of doublets; m, multiplet. All ^1H NMR spectra are reported in δ units, parts per million (ppm) downfield from tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to deuteriochloroform (77.23 ppm), and all were obtained with ^1H decoupling.

Infrared (IR) spectra were recorded on an ASI Applied Systems ReactIR 1000 (liquids and solids were measured neat on a DiComp probe). Melting points (uncorrected) were obtained on a Mel-Temp capillary melting point apparatus.

Gas chromatography (GC) analyses were performed on a Hewlett-Packard 6890 gas chromatograph with an FID detector using 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. GC-mass spectrometry (GC-MS) analyses were performed on a Hewlett-Packard G1800B gas chromatograph with an electron ionization detector using the same GC column described above.

II. Synthesis of α,β -Unsaturated Carbonyl Compounds

Ethyl *trans*- β -methylcinnamate, ethyl 2-cyano-3-phenyl-2-butenolate, and 2-(2-*cis*-pentenyl)-3-methyl-cyclopentenone (*cis*-Jasmone) were purchased from Aldrich.

Procedures for the syntheses of 3-alkyl-cyclopent-2-enones and 2,3-dialkyl-cyclopent-2-enones.²

3-Phenethyl-cyclopent-2-enone:

Phenethylmagnesium chloride (64.0 mL, 64.0 mmol, 1.0 M in THF, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to 0 °C. 3-Ethoxycyclopentenone

² Stork, G.; Danheiser, R. L. J. *Org. Chem.* **1973**, 38, 1775.

(4.04 g, 32.0 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in THF (50 mL), then added via syringe to the phenethylmagnesium chloride solution. The resulting solution was stirred at room temperature for 12 h. At this point, the reaction was cooled to 0 °C and 1 M HCl (40 mL) was gradually added until pH=0 (as determined by ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography (4:1 hexane:ethyl acetate) afforded the product as colorless (5.56 g, 93% yield). Spectroscopic data were consistent with previously reported data for this compound.³

3-Isopropyl-cyclopent-2-enone:

Isopropylmagnesium chloride (33.7 mL, 67.4 mmol, 2.0 M in diethyl ether, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to 0 °C. 3-Ethoxycyclopentenone (4.25 g, 33.7 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in diethyl ether (34 mL), then added via syringe to the isopropylmagnesium chloride solution. The resulting solution was stirred at room temperature for 23 h. At this point, the reaction was cooled to 0 °C and 1 M HCl (40 mL) was gradually added until pH=0 (as determined by ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography (2:1 pentane:diethyl ether) afforded the product as a colorless liquid (1.61 g, 39% yield). Spectroscopic data were consistent with previously reported data for this compound.⁴

³ Matsuyama, H.; Miyazawa, Y.; Takei, Y.; Kobayashi, M. *J. Org. Chem.* **1987**, 52, 1703.

⁴ Cohen, T.; Zhang, B.; Cherkauskas, J. P. *Tetrahedron* **1994**, 50, 11569.

3-Phenyl-cyclopent-2-enone:

Phenyllithium (11.2 mL, 20.2 mmol, 1.8 M in cyclohexane:diethyl ether 7:3, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to 0 °C. 3-Ethoxycyclopentenone (1.28 g, 11.0 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in THF (16 mL), then added via syringe to the phenyllithium solution. The resulting solution was stirred at room temperature for 16 h. At this point, the reaction was cooled to 0 °C and 1 M HCl (40 mL) was gradually added until pH=0 (as determined by ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography (2:1, then 1:1 hexane:diethyl ether) afforded the product as white crystals (1.386 g, 87% yield). Melting point: 81-82 °C (literature reported:⁵ 81 °C). Spectroscopic data were consistent with previously reported data for this compound.⁵

3-Phenethyl-cyclohex-2-enone:

Phenethylmagnesium chloride (64.0 mL, 64.0 mmol, 1.0 M in THF, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to 0 °C. 3-Ethoxycyclohexenone (4.49 g, 32.0 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in THF (50 mL), then added via syringe to the phenethylmagnesium chloride solution. The resulting solution was stirred at room temperature for 16 h. At this point, the reaction was cooled to 0 °C and 1 M HCl (40 mL) was gradually added until pH=0 (as determined by

ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography (3:1 hexane:ethyl acetate) afforded the product as a colorless oil (6.34 g, 99% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.30-7.18, (5 H, m), 5.90 (1 H, s), 2.85-2.82 (2 H, m), 2.55-2.54 (2 H, m), 2.38-2.37 (2 H, m), 2.35-2.31 (2 H, m), 2.01-1.98 (2 H, m). ^{13}C NMR (125 MHz, CDCl_3): δ 200.1, 165.6, 140.9, 128.7, 128.4, 126.5, 126.2, 39.9, 37.5, 33.6, 30.1, 22.9. IR (neat): 3062, 3027, 2921, 2858, 1702, 1675, 1615, 1495, 1455, 1436, 1409, 1339, 1287, 1231, 1183, 841, 753, 700 cm^{-1} . HRMS (EI, *m/e*) calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: 200.1195 (M^+). Found: 200.1194.

2-Methyl-3-phenethyl-cyclopent-2-enone:

Phenethylmagnesium chloride (10.0 mL, 10.0 mmol, 1.0 M in THF, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to $0\text{ }^\circ\text{C}$. 2-Methyl-3-ethoxycyclopentenone (0.7 g, 5.0 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in THF (2.0 mL), then added via syringe to the phenethylmagnesium chloride solution. The resulting solution was stirred at room temperature for 12 h. At this point, the reaction was cooled to $0\text{ }^\circ\text{C}$ and 1 M HCl (10 mL) was gradually added until $\text{pH}=0$ (as determined by ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography (7:1 hexane:ethyl acetate) afforded the product as a colorless oil (0.68 g, 68% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.31-7.27 (2 H, m), 7.23-7.17 (3 H, m), 2.87-2.83 (2 H, m), 2.75-2.72 (2 H, m), 2.50-2.48 (2 H, m), 2.37-2.36 (2 H, m), 1.50 (3 H, s). ^{13}C NMR (125 MHz, CDCl_3): δ 210.4, 172.6, 141.0, 137.1, 128.8, 128.5, 126.6, 34.4,

⁵ Iwasawa, N.; Matsuo, T.; Iwamoto, M.; Ikeno, T. *J. Am. Chem. Soc.* **1998**, *120*, 3903.

33.6, 33.3, 29.7, 8.1. IR (neat): 3062, 3027, 2921, 2860, 1694, 1644, 1603, 1495, 1453, 1441, 1383, 1320, 1301, 1204, 1052, 751, 700 cm^{-1} . HRMS (EI, m/e) calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: 200.1195 (M^+). Found: 200.119.

2-Methyl-3-phenyl-cyclopent-2-enone:

Phenylmagnesium bromide (13.4 mL, 13.36 mmol, 1.0 M in THF, 2.0 equiv) was placed into an oven-dried Schlenk flask and cooled to 0 °C. 2-Methyl-3-ethoxycyclopentenone (0.936 g, 6.68 mmol, 1.0 equiv) was added to a separate dry flask, dissolved in THF (2.0 mL), then added via syringe to the phenylmagnesium bromide solution. The resulting solution was stirred at room temperature for 12 h. At this point, the reaction was cooled to 0 °C and 1 M HCl (10 mL) was gradually added until pH=0 (as determined by ColorpHfast indicator strips). The aqueous phase was separated and extracted three times with diethyl ether. The combined organic phases were dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography (7:1 hexane:ethyl acetate) afforded the product as a colorless oil (0.70 g, 61% yield). Spectroscopic data were consistent with previously reported data for this compound.⁶

Ethyl 3-phenylpent-2-enoate:

Triethylphosphonoacetate (4.49 g, 20.0 mmol) was added to an oven-dried round bottom flask and dissolved in THF (10 mL). NaH was weighed out in a nitrogen-filled dry-box, and added in one portion to the above solution (evolution of gas was observed). The resulting solution was stirred for 30 min at room temperature. Propiophenone (2.68 g, 20.0 mmol) was added to a separate oven-dried round bottom flask and dissolved in THF

(10 mL). The solution of propiophenone was then added via cannula to the reaction and the resulting solution was stirred at room temperature for 20 h. The THF was removed *in vacuo*, and diethyl ether (50 mL) and aqueous NaHCO₃ (50 mL) were added. The aqueous phase was separated and extracted (3 x 150 mL) with diethyl ether. The combined organic phases were dried over the anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (20:1 hexanes:diethyl ether) afforded the (*E*)-isomer (2.03 g, 50% yield) (*R*_f = 0.29) as a colorless oil and the (*Z*)-isomer (1.75 g, 43% yield) (*R*_f = 0.13) as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.⁷

III. Synthesis of N-Heterocyclic Carbene Copper Chloride Complex (2)

1,3-Bis(2,6-di-*i*-propylphenyl)imidazolium copper (I) chloride (2):

An oven-dried Schlenk flask was charged with 1,3-bis(2,6-di-*i*-propylphenyl)imidazolium chloride (**1**) (0.45 g, 1.06 mmol). Fresh CuCl (0.105 g, 1.06 mmol), NaOt-Bu (0.102 g, 1.06 mmol), and THF (5.3 mL) were added to this Schlenk flask. The resulting suspension was stirred at room temperature for 4 h, then filtered over celite and concentrated *in vacuo*. The title compound was obtained as a gray powder (0.387 g, 75% yield). Melting point: >300 °C. ¹H NMR (500 MHz, Acetone-*d*₆): δ 7.26 (s, 2 H), 7.57-7.54 (dd, *J* = 15.5 Hz, 8.0 Hz, 2 H), 7.43-7.41 (d, *J* = 8.0 Hz, 4 H), 2.70-2.65 (m, 4 H), 1.32-1.31 (d, *J* = 7.0 Hz, 12 H), 1.27-1.25 (d, *J* = 6.5 Hz, 12 H). ¹³C NMR (125 MHz, Acetone-*d*₆): δ 180.2, 146.0, 135.1, 130.6, 124.2, 24.4, 23.3. IR (neat): 2968, 2927, 2871,

⁶ Shindo, M.; Sato, Y.; Shishido, K. *J. Org. Chem.* **2001**, *66*, 7818.

⁷ Appella, D. H.; Moritani, Y.; Shintani, R.; Ferreira, E. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9473.

1680, 1647, 1470, 1457, 809, 764, 743 cm^{-1} . Elemental analysis: Calcd: C 66.51%, H 7.44%. Found: C 66.34, H 7.44%. HRMS (EI, m/e) calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: 389.2951 ($-\text{CuCl M}^+$). Found: 389.2962.

IV. Conjugate Reductions of α,β -Unsaturated Esters Using 2

General Procedure A: Conjugate Reduction of Trisubstituted α,β -Unsaturated Esters.

An oven-dried flask was charged with N-heterocyclic carbene copper chloride complex (**2**) (8.0 mg, 0.02 mmol, 0.3 mol %), fresh NaOt-Bu (2.0 mg, 0.02 mmol, 0.3 mol %), and toluene (1.0 mL). The mixture was stirred at room temperature for 10 min, then poly(methylhydrosiloxane) (PMHS) (0.33 mL, 5.5 mmol, 1.0 equiv) was added and the resulting yellow/orange solution was stirred at room temperature for 5 min. Additional amounts of toluene (2.0 mL) followed by PMHS (0.99 mL, 16.4 mmol, 3.0 equiv) were added to the solution of catalyst. A solution of trisubstituted α,β -unsaturated ester (5.5 mmol, 1.0 equiv) and t -BuOH (1.26 mL, 21.9 mmol 4.0 equiv) in toluene (2.5 mL) was then added via cannula to the solution of catalyst and PMHS (evolution of gas was observed). The reaction was stirred at room temperature for 1 h, then water (5 mL) was added and the biphasic mixture was stirred for 5 min. Full conversion was confirmed by gas chromatography (GC). Ethyl acetate (50 mL) and water (10 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 150 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel.

Ethyl 3-phenylbutyrate (Table 3, entry 1):

Following General Procedure A, ethyl *trans*- β -methylcinnamate (1.00 mL, 5.48 mmol mmol, 1.0 equiv) was converted in 1 h to the title compound. Purification by flash

chromatography (30:1 hexanes:ethyl acetate) afforded the pure product as a clear oil (0.947 g, 90 % yield). Spectroscopic data were consistent with previously reported data for this compound.⁷

Ethyl 3-phenylpentanoate (Table 3, entry 2):

Following General Procedure A, ethyl (*E*)-3-phenylpent-2-enoate (1.12 g, 5.48 mmol mmol, 1.0 equiv) was converted to the title compound in 1 h. Purification by flash chromatography (20:1 hexanes:ethyl acetate) afforded the pure product as a clear oil (1.08 g, 96 % yield). Spectroscopic data were consistent with previously reported data for this compound.^{7,8}

General Procedure B: Conjugate Reduction of Tetrasubstituted α,β -Unsaturated Ester.

An oven-dried flask under was charged with **2** (8.0 mg, 0.02 mmol, 3.0 mol %), fresh NaOt-Bu (2.0 mg, 0.02 mmol, 3.0 mol %), and toluene (0.5 mL). The mixture was stirred at room temperature for 10 min, then PMHS (0.395 mL, 6.58 mmol, 12.0 equiv) was added and the resulting yellow/orange solution was stirred at room temperature for 5 min. A neat tetrasubstituted α,β -unsaturated ester (0.548 mmol, 1.0 equiv) was added to the solution of catalyst in one portion at room temperature and stirred for 1 min. Then neat *t*-BuOH (0.630 mL, 6.58 mmol, 12.0 equiv) was added (evolution of gas was observed). The reaction was stirred at room temperature for 3 h, then water (1 mL) was added and the biphasic mixture was stirred for 5 min. Full conversion was confirmed by GC. Ethyl acetate (10 mL) and water (5 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 50 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel.

⁸ Katritzky, A. R.; Feng, D.; Lang, H. *J. Org. Chem.* **1997**, 62, 706.

Ethyl 2-cyano-3-phenylbutyrate (Table 3, entry 3):

Following General Procedure B, ethyl (*E/Z*)-2-cyano-3-phenylbutyrate (0.108 mL, 0.548 mmol) was converted in 3 h to the title compound (with 1.5:1 diastereomeric ratio as determined by ¹H NMR). Purification by flash chromatography (hexanes:ethyl acetate 20:1) afforded the pure as a clear oil (0.11 g, 93 % yield for the mixture of diastereomers). Spectroscopic data were consistent with previously reported data for this compound.⁹

V. Conjugate Reductions of α,β -Unsaturated Cyclic Enones Using **2**

General Procedure C: Conjugate Reduction of Trisubstituted α,β -Unsaturated Cyclic Enones.

An oven-dried flask under argon was charged with **2** (3.0 mg, 6.5×10^{-3} mmol, 0.1 mol %), fresh NaOt-Bu (1.0 mg, 6.5×10^{-3} mmol, 0.1 mol %), and toluene (1.0 mL). The mixture was stirred at room temperature for 10 min, then PMHS (0.23 mL, 3.9 mmol, 0.6 equiv) was added and the resulting yellow/orange solution was stirred at room temperature for 5 min. Additional amounts of toluene (5.5 mL) followed by PMHS (0.38 mL, 6.4 mmol, 1.0 equiv) were added to the solution of catalyst. A neat trisubstituted α,β -unsaturated cyclic enone (6.45 mmol, 1.0 equiv) was added to this solution in one portion and the reaction was stirred at room temperature for the indicated period of time. Water (5 mL) was added and the biphasic mixture was stirred for 5 min. Full conversion was confirmed by gas chromatography (GC). Ethyl acetate (50 mL) and water (10 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 150 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel.

3-Phenethylcyclopentanone (Table 3, entry 4):

Following General Procedure C, 3-phenethylcyclopentenone (1.20 g, 6.5 mmol) was converted to the title compound in 1 h. Purification by flash chromatography (hexanes:ethyl acetate 10:1) afforded the pure product as a clear oil (1.08 g, 89 % yield). Spectroscopic data were consistent with previously reported data for this compound.¹⁰

3-Phenylcyclopentanone (Table 3, entry 5):

Following General Procedure C, 3-phenylcyclopentenone (1.02 g, 6.5 mmol) was converted to the title compound in 3 h. Purification by flash chromatography (hexanes:ethyl acetate 10:1) afforded the pure product as a clear oil (0.98 g, 95 % yield). Spectroscopic data were consistent with previously reported data for this compound.^{10,11}

3-Isopropylcyclopentanone (Table 3, entry 6):

Following General Procedure C, 3-isopropylcyclopentenone (0.80 g, 6.5 mmol) was converted to the title compound in 1 h. Purification by flash chromatography (pentane:diethyl ether 10:1) afforded the pure product as a clear liquid (0.65 g, 80 %

⁹ Nanjo, K.; Suzuki, K.; Sekiya, M. *Chem. Pharm. Bull.* **1977**, 25, 2396.

¹⁰ Gadwood, R. C.; Mallick, I. M.; DeWinter, A. J. *J. Org. Chem.* **1987**, 52, 774.

¹¹ Gomez-Bengoa, E.; Heron, N. M.; Didiuk, M. T.; Luchaco, C. A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, 120, 7649.

yield). Spectroscopic data were consistent with previously reported data for this compound.¹²

3-Phenethylcyclohexanone (Table 3, entry 7):

Following General Procedure C, 3-phenethylcyclohexenone (1.29 g, 6.5 mmol) was converted in 1 h to the title compound. Purification by flash chromatography (hexanes:ethyl acetate 10:1) afforded the pure product as a clear liquid (1.21 g, 93 % yield). Spectroscopic data were consistent with previously reported data for this compound.¹⁰

General Procedure D: Conjugate Reduction of Tetrasubstituted α,β -Unsaturated Cyclic Enones.

An oven-dried flask under was charged with **2** (1.0-3.0 mol %, as indicated below), fresh NaOt-Bu (1.0-3.0 mol %, as indicated below), and toluene (0.5 mL). The mixture was stirred at room temperature for 10 min, then PMHS (0.18 mL, 3.0 mmol, 3.0 equiv) was added and the resulting yellow/orange solution was stirred at room temperature for 5 min. A neat tetrasubstituted α,β -unsaturated cyclic enone (1.0 mmol, 1.0 equiv) was added to this solution in one portion and the reaction was stirred at room temperature for the indicated period of time. Water (1 mL) was added and the biphasic mixture was stirred for 5 min. Full conversion was confirmed by GC. Ethyl acetate (20 mL) and water (10 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 100 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The product was purified by flash chromatography on silica gel.

¹² Barnhart, R. W.; Wang, X.; Noheda, P.; Bergens, S. H.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1994**, *116*, 1821.

3-Methyl-2-(2-*cis*-pentenyl)cyclopentanone (Table 3, entry 8):

Following General Procedure D, using 1.0 mol % of **2** and NaOt-Bu, *cis*-jasnone (0.175 mL, 1.00 mmol) was converted to the title compound in 1 h. GC indicated full conversion and 4:1 diastereomeric ratio. Purification by flash chromatography (pentane:diethyl ether 15:1) afforded the pure product as a clear liquid (0.141 g, 85 % yield for the mixture of diastereomers 4:1). Spectroscopic data were consistent with previously reported data for this compound.¹³

2-Methyl-3-phenethylcyclopentanone (Table 3, entry 9):

Following General Procedure D, using 1.0 mol % of **2** and NaOt-Bu, 2-methyl-3-phenethylcyclopentanone (0.20 g, 1.00 mmol) was converted to the title compound in 1 h. GC indicated full conversion and 4:1 diastereomeric ratio. Purification by flash chromatography (hexanes:ethyl acetate 20:1) afforded the pure product as a clear oil (0.182 g, 90 % yield for the mixture of diastereomers 4:1). Spectroscopic data were consistent with previously reported data for this compound.¹⁴

2-Methyl-3-phenylcyclopentanone (Table 3, entry 10):

Following General Procedure D, using 3.0 mol % of **2** and NaOt-Bu, 2-methyl-3-phenylcyclopentanone (0.172 g, 1.00 mmol) was converted to the title compound in 3 h.

¹³ Saito, S.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 2928.

¹⁴ Yun, J.; Buchwald, S. L. *Org. Lett.* **2001**, *3*, 1129.

GC indicated full conversion and 5:1 diastereomeric ratio. Purification by flash chromatography (pentane:diethyl ether 10:1) afforded the pure product as a clear oil (0.164 g, 94 % yield for the mixture of diastereomers 5:1). Spectroscopic data were consistent with previously reported data for this compound.⁹

VI. Conjugate Reductions with In Situ Generated Copper Carbene Catalyst

2-Methyl-3-phenethylcyclopentanone (Scheme 2):

An oven-dried flask was charged with 1,3-bis(2,6-di-*i*-propylphenyl) imidazolium chloride (**1**) (5.0 mg, 0.012 mmol, 1.0 mol %), CuCl₂•2H₂O (2.0 mg, 0.012 mmol, 1.0 mol %), NaO*t*-Bu (7.0 mg, 0.072 mmol, 6.0 mol %), and toluene (1.2 mL). The mixture was stirred at room temperature for 30 min, then PMHS (0.22 mL, 3.60 mmol, 3.0 equiv) was added and the resulting solution was stirred at room temperature for 15 min. A neat 2-methyl-3-phenethyl cyclopentenone (0.24 g, 1.2 mmol, 1.0 equiv) was added to this solution in one portion and the reaction was stirred at room temperature for 1 h. Water (1 mL) was added and the biphasic mixture was stirred for 5 min. GC indicated full conversion and 2:1 diastereomeric ratio for the product. Ethyl acetate (20 mL) and water (10 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 100 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Purification by flash chromatography (hexanes:ethyl acetate 20:1) afforded the pure product as a clear oil (0.21 g, 87 % yield for the mixture of diastereomers 2:1). Spectroscopic data were consistent with previously reported data for this compound.¹⁴

Ethyl 3-phenylbutyrate (Scheme 2):

An oven-dried flask was charged with **1** (5.0 mg, 0.01 mmol, 0.03 mol %), CuCl₂•2H₂O (2.0 mg, 0.01 mmol, 0.3 mol %), NaOt-Bu (7.0 mg, 0.07 mmol, 1.8 mol %), and toluene (1.0 mL). The mixture was stirred at room temperature for 30 min, then PMHS (0.23 mL, 3.8 mmol, 1.0 equiv) was added and the resulting solution was stirred at room temperature for 15 min. Additional amounts of toluene (2.8 mL) followed by PMHS (0.69 mL, 12.0 mmol, 3.0 equiv) were added to the solution of catalyst. Neat ethyl *trans*-β-methylcinnamate (0.70 mL, 3.8 mmol, 1.0 equiv) was then added in one portion and the reaction stirred for 1 min. Neat *t*-BuOH (1.47 mL, 15.3 mmol 4.0 equiv) was then added to the reaction at room temperature (evolution of gas was observed). The reaction was stirred at room temperature for 1 h, then water (5 mL) was added and the biphasic mixture was stirred for 5 min. Full conversion was confirmed by GC. Ethyl acetate (50 mL) and water (10 mL) were added and resulting phases separated. The aqueous phase was extracted with ethyl acetate (3 x 150 mL) and the combined organic extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. Purification by flash chromatography (30:1 hexanes:ethyl acetate) afforded the pure product as a clear oil (0.648 g, 88 % yield). Spectroscopic data were consistent with previously reported data for this compound.⁶