A Practical Method for Enantioselective Synthesis of All-Carbon Quaternary Stereogenic Centers through NHC-Cu-Catalyzed Conjugate Additions of Alkyl- and Arylzinc Reagents to β -Substituted Cyclic Enones

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SUPPORTING INFORMATION

General. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer, ν_{max} in cm^{-1} . Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College and at the University of Illinois Mass Spectrometry Laboratories (Urbana, Illinois). Elemental microanalyses were performed at Robertson Microlit Laboratories (Madison, NJ). Enantiomer ratios were determined by chiral GLC analysis (Alltech Associated Chiraldex GTA column (30 m x 0.25 mm) and Betadex 120 column (30 m x 0.25 mm), and by chiral HPLC analysis (Chiral Technologies Chiralpak AS column, 25 cm x 0.46 cm) in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) and flame-dried glassware with standard dry box or vacuum-line techniques. Solvents were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system: toluene and benzene were purified by being passed through a copper oxide and alumina column; CH_2Cl_2 and Et_2O were purged with Ar and purified by being passed through two alumina columns. THF was purified by distillation from sodium benzophenone ketal immediately prior to use. Chloroform and Et_3N were purified by distillation over CaH_2 . Dioxane was distilled over Na. All work-up and purification procedures were carried out with reagent solvents in air. All reagent solvents were purchased from Doe and Ingalls. Diethylzinc (neat) and $\text{Pd}(\text{OAc})_2$ (99.9+%) were purchased from Aldrich and used as received. Di-*n*-butylzinc was purchased from Fluka (1.0 M in heptane) and used as

received. Diphenylzinc was purchased from Strem Inc. (white solid) and used without purification.¹ Copper (I) triflate benzene complex (2:1) was prepared by previously reported methods.² Cu₂O (99.9%) was purchased from Strem and used without purification. Triflic anhydride was prepared by distillation of triflic acid (Aldrich) over P₂O₅ (Aldrich). 3-Methyl-2-cyclohexenone was purchased from Aldrich and distilled prior to use. Di-4-trifluoromethylphenyl zinc was prepared by previously reported methods.³ All other substrates were prepared by established methods.⁴ Chiral Ag- and Cu-based complexes were prepared according to published methods.⁵ Phenylboronic acid (Aldrich) was re-crystallized from water. Triphenylphosphine (Strem) was re-crystallized from Et₂O.

■ Representative experimental procedure for Cu-catalyzed conjugate addition of (alkyl)₂Zn reagents: An oven-dried 13x100 mm test tube charged with chiral Ag complex **4** (5.0 mg, 0.0044 mmol), (CuOTf)₂•C₆H₆ (2.1 mg, 0.0041 mmol) and 3-methyl-2-cyclohexenone (18 mg, 0.16 mmol) was weighed out under an N₂ atmosphere in a glove box. The test tube was sealed with a septum and wrapped with parafilm before removal from the glove box. Diethyl ether (1.0 mL) was added at 22 °C (syringe); the resulting solution was allowed to stir for 10 min. Diethylzinc (50 µL, 0.49 mmol) was slowly added to the mixture at –78 °C; during the addition of Et₂Zn the reaction turned dark brown. After the addition of Et₂Zn, the solution was allowed to warm to –30 °C. After 6 h at –30 °C, the reaction was quenched by the addition of a saturated aqueous solution of ammonium chloride (1 mL) and then immediately H₂O (1 mL). The mixture was washed with Et₂O (3x1 mL) and the combined organic layers were passed through a short plug (4 cm x 1 cm) of silica gel eluted with Et₂O. The volatiles were removed in vacuo and the resulting dark brown oil was purified by silica gel column chromatography (hexanes/Et₂O:10/1) to afford 21.1 mg (0.150 mmol, 92.5% yield) of **6** as a colorless oil. **Important note:** To ensure high efficiency and enantioselectivity, reactions must be set up in exactly the order described above.

■ Representative procedure for Cu-Catalyzed conjugate addition of Et₂Zn carried out on bench top and performed in undistilled diethyl ether: A 13x100 mm test tube charged with

(1) It is critical that high quality Ph₂Zn is used. For example, use of reagents purchased from Aldrich (brown solid) leads to highly inefficient transformations. Development of reliable in situ methods for preparation of alkyl- and arylzinc reagents is in progress and will be disclosed shortly.

(2) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, 95, 1889–1897.

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(4) (a) Fu, X.; Zhang, S.; Yin, J.; Schumacher, D. P. *Tetrahedron Lett.* **2002**, 43, 6673–6676. (b) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, 42, 682–685. (c) Dittami, J. P.; Nie, X. Y.; Nie, H.; Ramanathan, H.; Breining, S. *J. Org. Chem.* **1991**, 56, 5572–5578.

(5) (a) Larsen, A. O.; Leu, W.; Nieto-Oberhuber, C.; Campbell, J. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, 126, 11130–11131. (b) Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, 127, 6877–6882.

chiral Ag complex **4** (4.5 mg, 0.0036 mmol), (CuOTf)₂•toluene (1.9 mg, 0.0036 mmol), and 3-methyl-2-cyclohexenone (16 mg, 0.14 mmol) weighed out on the bench top in air, was sealed with a septum, wrapped with parafilm, and purged with N₂. Undistilled Et₂O (1.0 mL) was added at 22 °C (syringe); the resulting solution was allowed to stir for 10 min. Diethylzinc (45 μL, 0.43 mmol) was slowly added to the mixture at −78 °C; during the addition of diethylzinc the reaction turned dark brown. After the addition of Et₂Zn, the solution was allowed to warm to −30 °C. After 6 h at −30 °C, the reaction was quenched by the addition of a saturated solution of aqueous ammonium chloride (1.0 mL) and then immediately H₂O (1.0 mL). The mixture was washed with Et₂O (3x1 mL) and passed through a short plug of silica eluted with the same solvent. The volatiles were removed in vacuo to afford a light yellow oil, which was purified by silica gel column chromatography (hexanes/Et₂O: 10/1) to afford 17.0 mg (0.121 mmol, 83.3% yield) of cyclic ketone **6** as a colorless oil. **Important note:** To ensure high efficiency and enantioselectivity reactions must be set up in exactly the order described above.

(R)-(+)-3-Ethyl-3-methylcyclohexanone (6). IR (neat): 2962 (s), 2936 (s), 2879 (m), 2855 (w), 1715 (s), 1464 (m) cm^{−1}; ¹H NMR (400 MHz, CDCl₃): δ 2.27 (2H, dd, *J* = 6.8, 6.8 Hz), 2.18 (1H, d, *J* = 13.6 Hz), 2.09 (1H, d, *J* = 13.6 Hz), 1.90-1.83 (2H, m), 1.66-1.50 (2H, m), 1.35-1.29 (2H, m), 0.90 (3H, s), 0.84 (3H, t, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 212.4, 53.4, 41.0, 38.7, 35.4, 34.0, 24.4, 22.1, 7.7; Anal Calcd for C₉H₁₆O: C, 77.09; H, 11.50; Found C, 76.86; H, 11.25. HRMS Calcd for C₉H₁₆O (EI⁺): 140.1201, Found: 140.1196. Optical rotation: [α]_D²⁰ +8.0 (*c* = 1.0, CHCl₃) for an 87% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (95% ee shown below; β-dex chiral column, 80 °C, 15 psi).

(R)-3-Butyl-3-methylcyclohexanone (7). IR (neat): 2957 (s), 2931 (s), 2870 (m), 2860 (m), 1715 (s), 1467 (w), 1457 (w) cm^{−1}; ¹H NMR (400 MHz, CDCl₃): δ 2.26 (2H, dd, *J* = 7.2, 7.2 Hz), 2.17 (1H, d, *J* = 13.6 Hz), 2.09 (1H, d, *J* = 13.6 Hz), 1.88-1.81 (2H, m), 1.65-1.48 (2H, m), 1.29-1.17 (6H, m), 0.90 (6H, m); ¹³C NMR (100 MHz, CDCl₃): δ 212.7, 54.0, 41.4, 41.2, 38.7, 36.0, 25.7, 25.3, 23.5, 22.3, 14.2. HRMS Calcd for C₁₁H₂₀O (EI⁺, M+H): 169.1592, Found: 169.1593. Optical rotation: [α]_D²⁰ +1.15 (*c* = 1.00, CHCl₃) for an 86% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (86% ee sample below; β -dex column, 120 °C, 15 psi).

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.058	MM	0.1889	166.10118	14.65485	50.05075
2	26.730	MM	0.2025	165.76436	13.64158	49.94925

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.839	MM	0.1926	210.44351	18.20629	93.17922
2	26.544	MM	0.1933	15.40460	1.32817	6.82078

(R)-3-Ethyl-3-(4-pentenyl)cyclohexanone (8). IR (neat): 3087 (w), 2936 (s), 1721 (s), 1646 (w), 1463 (m), 1419 (m), 1388 (w), 1350 (w), 1318 (w), 1230 (w), 1092 (w), 1004 (m), 903 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 5.57 (1H, dddd, $J = 17.2, 10.4, 6.8, 6.8$ Hz), 5.00-4.91 (2H, m), 2.25 (2H, t, $J = 6.8$ Hz), 2.12 (2H, s), 2.02-1.96 (2H, m), 1.84-1.78 (2H, m), 1.57-1.54 (2H, m), 1.31-1.18 (6H, m), 0.76 (3H, t, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 212.8, 138.8, 114.9, 52.1, 41.3, 41.1, 36.1, 34.5, 33.6, 29.7, 22.4, 21.9, 7.6. HRMS calcd for $\text{C}_{13}\text{H}_{22}\text{O}$: 194.1671, Found: 194.1675. Optical rotation: $[\alpha]_D^{20} +4.87$ ($c = 1.29$, CHCl_3) for an 82% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (84% ee sample below; conditions: β -dex column, 130 °C, 15 psi).

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.235	MF	0.3189	483.44894	25.26414	50.17489
2	47.010	FM	0.3335	480.07880	23.99061	49.82511

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.271	MF	0.3316	57.47711	2.88916	8.04633
2	46.980	FM	0.3302	656.85004	33.15128	91.95367

(S)-3-Ethyl-3-(2-phenyl ethynyl)cyclohexanone (9). IR (neat): 2965 (m), 2926 (m), 2874 (w), 2853 (w), 2359 (w), 2338 (w), 1716 (s), 1597 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.33 (2H, m), 7.27-7.23 (3H, m), 2.59 (1H, ddd, $J = 14.0, 2.0, 2.0$ Hz), 2.44-2.38 (1H, m), 2.30-2.10 (3H, m), 2.06-1.96 (2H, m), 1.69-1.58 (3H, m), 1.07 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 209.6, 131.9, 128.3, 128.1, 123.5, 92.1, 85.1, 52.6, 41.5, 41.2, 35.9, 35.0, 23.0, 9.1; HRMS Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ (EI^+): 226.1358, Found: 226.1363. Optical rotation: $[\alpha]_D^{20} +39.87$ ($c = 1.000$, CHCl_3) for a 74% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material. (74% ee sample below; conditions: β -dex column, 140 °C, 15 psi).

(S)-3-Ethyl-3-phenylcyclohexanone (10): IR (neat): 3089 (w), 3058 (w), 3031 (w), 3024 (w) 2962 (s), 2934 (s), 2877 (m), 2355 (w), 2332 (w), 1715 (s), 1601 (w), 1498 (m), 1460 (m), 1445 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.27 (2H, m), 7.25-7.22 (2H, m), 7.20-7.15 (1H, m), 2.90 (1H, d, $J = 14.4$ Hz), 2.40 (1H, d, $J = 14.4$ Hz), 2.30-2.26 (2H, m), 2.19-2.13 (1H, m), 2.00-1.93 (1H, m), 1.84-1.54 (4H, m), 0.58 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 211.6, 145.0, 128.6, 126.7, 126.2, 50.7, 46.6, 41.2, 36.4, 35.8, 21.7, 8.1; HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ (EI^+): 202.1358, Found: 202.1362. Optical rotation: $[\alpha]_{\text{D}}^{20} +63.77$ ($c = 1.000$, CHCl_3) for a 94% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material. (90% ee sample below; conditions: β -dex column, 140 °C, 15 psi).

(R)-3-Ethyl-3-methylcycloheptanone (11): IR (neat): 2964 (m), 2929 (s), 2882 (w), 2861 (w), 1697 (s), 1464 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.51 (1H, d, $J = 12.0$ Hz), 2.41-2.37 (2H, m), 2.35 (1H, d, $J = 12.0$ Hz), 1.78-1.47 (6H, m), 1.34-1.23 (2H, m), 0.86 (3H, s), 0.83 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 214.4, 54.2, 44.1, 42.2, 35.4, 35.0, 25.5, 24.8, 24.3, 8.0; HRMS Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$ (EI^+): 154.1358, Found: 154.1356. Optical rotation: $[\alpha]_{\text{D}}^{20} +17.06$ ($c = 1.000$, CHCl_3) for an 85% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (85% ee sample below; conditions: β -dex column, 80 °C, 15 psi).

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	156.154	MM	2.5541	4.47848e5	2922.39160	50.17758
2	162.554	MM	3.1335	4.44678e5	2365.15771	49.82242

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	157.197	MM	2.6336	4.07949e5	2581.69385	92.31784
2	166.440	MM	1.8549	3.39472e4	305.02258	7.68216

(R)-3-Butyl-3-methylcycloheptanone (12). IR (neat): 2958 (s), 2934 (s), 2871 (m), 2859 (m), 1701 (s), 1461 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.51 (1H, d, $J = 12.4$ Hz), 2.41-2.35 (3H, m), 1.77-1.57 (5H, m), 1.52-1.47 (1H, m), 1.23-1.17 (6H, m), 0.90-0.86 (6H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 214.5, 55.0, 44.1, 42.7, 42.4, 35.3, 26.2, 25.8, 24.8, 24.3, 23.5, 14.2; Anal Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.06; H, 12.16; Found C, 78.89; H, 12.14; HRMS Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$ (EI^+): 182.1671, Found: 182.1668. Optical rotation: $[\alpha]_D^{20} +10.0$ ($c = 1.00$, CHCl_3) for a 77% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (77% ee sample below; conditions: β -dex column, 90 °C, 15 psi).

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	227.577	MM	1.7676	7.94163e4	748.79749	50.12005
2	233.912	MM	1.9260	7.90359e4	683.92627	49.87995

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	229.120	MM	1.7526	4.34012e4	412.74313	88.63362
2	236.015	MM	1.6311	5565.77881	56.87172	11.36638

(S)-3-Butyl-3-ethylcycloheptanone (13). IR (neat): 2958 (s), 2927 (s), 2871 (m), 2861 (m), 1697 (m), 1458 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.43 (2H, s), 2.39 (2H, t, $J = 6.2$ Hz), 1.77-1.72 (2H, m), 1.64-1.60 (2H, m), 1.57-1.53 (2H, m), 1.34-1.13 (8H, m), 0.88 (3H, t, $J = 7.0$ Hz), 0.79 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 214.8, 53.5, 44.1, 40.1, 37.7, 37.4, 30.7, 25.2, 24.4, 24.4, 23.6, 14.2, 7.6; HRMS Calcd for $\text{C}_{13}\text{H}_{24}\text{O}$ (EI^+): 196.1827, Found: 196.1827. Optical rotation: $[\alpha]_D^{20} +5.98$ ($c = 1.00$, CHCl_3) for a 76% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (76% ee sample below; conditions: β -dex column, 90 °C (300 min), 20 °C/min to 140 °C (10 min), 15 psi).

(R)-3-Ethyl-3-methylcyclooctanone (14). IR (neat): 2955 (m), 2924 (s), 2875 (w), 2852 (w), 1695 (s), 1470 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.39 (1H, d, $J = 10.8$ Hz), 2.29 (2H, ddd, $J = 8.0, 4.0, 4.0$ Hz), 2.17 (1H, d, $J = 10.8$ Hz), 1.95-1.87 (2H, m), 1.53-1.47 (2H, m), 1.42-1.25 (6H, m), 0.91 (3H, s), 0.84 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 215.5, 48.8, 45.5, 39.0, 37.0, 34.7, 29.1, 25.6, 22.0, 20.3, 8.3; HRMS Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$ (EI^+): 168.1514, Found: 168.1511. Optical rotation: $[\alpha]_D^{20} +9.28$ ($c = 0.500$, CHCl_3) for a 54% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (54% ee sample below; conditions: β -dex column, 90 °C (300 min), 20 °C/min to 140 °C (10 min), 15 psi).

■ **Representative experimental procedure for Cu-catalyzed conjugate addition of (aryl) $_2\text{Zn}$ reagents.** An oven-dried 13x100 mm test tube was charged with chiral Ag complex **4** (5.6 mg, 0.0045 mmol), $(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$ (2.7 mg, 0.0045 mmol), 3-methyl-2-cyclohexenone (20 mg, 0.18 mmol), and Ph_2Zn (120 mg, 0.55 mmol), which were weighed out under a N_2 atmosphere in a glove box (in the precise order mentioned above). The test tube was sealed with a septum and wrapped with parafilm. The reaction vessel was removed from the glove box. Diethyl ether (1.0

mL) was slowly added to the mixture in a dropwise manner (syringe) at -78°C . After the addition of Et_2O , the solution was allowed to warm to -30°C . After 48 h at -30°C , the reaction was quenched by the addition of a saturated aqueous solution of ammonium chloride (1.0 mL) and then immediately H_2O (1.0 mL). The mixture was washed with Et_2O (3 x 1 mL) and the combined organic layers were passed through a short plug of silica eluted with Et_2O . The volatiles were removed in vacuo and the resulting mixture was purified by silica gel column chromatography (hexanes/ Et_2O : 10/1) to afford 32.5 mg (0.173 mmol, 95.0% yield) of cyclic ketone **15** as colorless oil.

Important note: To ensure high efficiency and enantioselectivity, reactions must be set up in exactly the order described above.

(S)-3-Methyl-3-phenylcyclohexanone (15). IR (neat): 3087 (w), 3058 (w), 3024 (w), 3022 (w), 2962 (s), 2937 (s), 2870 (m), 2357 (w), 2332 (w), 1715 (s), 1602 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.30 (4H, m), 7.26-7.18 (1H, m), 2.89 (1H, d, $J = 14.4$ Hz), 2.44 (1H, d, $J = 14.4$ Hz), 2.31 (2H, t, $J = 6.8$ Hz), 2.22-2.16 (1H, m), 1.96-1.83 (2H, m), 1.72-1.61 (1H, m), 1.33 (3H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 211.6, 147.5, 128.6, 126.3, 125.7, 53.2, 42.9, 40.9, 38.0, 29.9, 22.1; Anal Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57; Found C, 82.67; H, 8.28; HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ (EI^+): 188.1201, Found: 188.1199. Optical rotation: $[\alpha]_{\text{D}}^{20} +70.18$ ($c = 1.000$, CHCl_3) for a 97% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (97% ee sample below; conditions: CDGTA column, 95°C (70 min), $0.5^{\circ}\text{C}/\text{min}$ to 110°C (30 min), $20^{\circ}\text{C}/\text{min}$ to 140°C (20 min), 15 psi).

(S)-3-Ethyl-3-phenylcyclohexanone (10). IR (neat): 3089 (w), 3058 (w), 3031 (w), 3024 (w), 2962 (s), 2934 (s), 2877 (m), 2355 (w), 2332 (w), 1715 (s), 1601 (w), 1498 (m), 1460 (m), 1445 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.27 (2H, m), 7.25-7.22 (2H, m), 7.20-7.15 (1H, m), 2.90 (1H, d, $J = 14.4$ Hz), 2.40 (1H, d, $J = 14.4$ Hz), 2.30-2.26 (2H, m), 2.19-2.13 (1H, m), 2.00-1.93 (1H, m), 1.84-1.54 (4H, m), 0.58 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 211.6, 145.0, 128.6, 126.7, 126.2, 50.7, 46.6, 41.2, 36.4, 35.8, 21.7, 8.1; HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$

(EI⁺): 202.1358, Found: 202.1362. Optical rotation: $[\alpha]_D^{20} +63.77$ ($c = 1.000$, CHCl_3) for a 94% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (94% ee sample below; conditions: β -dex column, 140 °C, 15 psi).

(S)-3-(4-pentenyl)-3-phenylcyclohexanone (16). IR (neat): 2936 (s), 2873 (m), 1709 (s), 1645 (m), 1438 (m), 1332 (m), 1242 (m), 996 (w), 918 (m), 762 (m), 711 (s), 667 (s) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.32-7.26 (2H, m), 7.25-7.22 (2H, m), 7.20-7.15 (1H, m), 5.63 (1H, dddd, $J = 17.2, 10.4, 6.8, 6.8$ Hz), 4.91-4.85 (2H, m), 2.91 (1H, d, $J = 14.0$ Hz), 2.42 (1H, d, $J = 14.0$ Hz), 2.26-2.26 (2H, m), 2.19-2.00 (1H, m), 2.00-1.51 (7H, m), 1.20-1.09 (1H, m), 0.99-0.88 (1H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.7, 145.3, 138.6, 128.7, 126.6, 126.3, 114.9, 51.3, 46.3, 42.8, 41.2, 36.8, 34.1, 22.9, 21.7. HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}$: 242.1671, Found: 242.1676. Optical rotation: $[\alpha]_D^{20} +45.17$ ($c = 1.970$, CHCl_3) for an 89% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (89% ee sample below; conditions: β -dex column, 120 °C, 15 psi).

(S)-3-(4-methoxyphenyl)-3-methylcyclohexanone (17). The general procedure described on page 7 was followed, except that toluene was used as the solvent. IR (neat): 2964 (s), 2880 (m), 1712 (s), 1611 (m), 1516 (s), 1455 (m), 1309 (m), 1259 (s), 1186 (m), 1041 (m), 840 (m) cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ 7.21 (2H, dt, $J = 5.6, 3.6$ Hz), 6.84 (2H, dt, $J = 5.6, 3.6$ Hz), 3.37 (3H, s), 2.83 (1H, d, $J = 14.4$ Hz), 2.40 (1H, d, $J = 14.4$ Hz), 2.85 (2H, t, $J = 6.8$ Hz), 2.17-2.11

(1H, m), 1.91-1.80 (2H, m), 1.69-1.59 (1H, m), 1.28 (3H, s). ^{13}C NMR (CDCl_3 , 100 MHz): δ 200.7, 158.0, 139.7, 126.9, 114.0, 55.4, 53.5, 42.5, 41.5, 38.3, 30.3, 22.2. HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: 218.1307, Found: 218.1298. Optical Rotation: $[\alpha]_{\text{D}}^{20} +51.71$ ($c = 0.960$, CHCl_3) for a 90% ee sample.

Optical purity was determined by chiral HPLC analysis in comparison with authentic racemic material (90% sample below; conditions: chiralpak AS column (25 cm x 0.46 cm), 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 254 nm).

(S)-3-Methyl-3-phenylcycloheptanone (18). IR (neat): 3088 (w), 3056 (m), 3032 (m), 3022 (m) 2931 (s), 2862 (s), 1949 (w), 1877 (w), 1805 (w), 1696 (s), 1599 (m), 1497 (s), 1460 (s), 1444 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.30 (4H, m), 7.22-7.17 (1H, m), 3.21 (1H, d, $J = 14.4$, 1.2 Hz), 2.71 (1H, d, $J = 14.4$ Hz), 2.46-2.36 (2H, m), 2.23-2.15 (1H, m), 1.84-1.70 (5H, m), 1.27 (3H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 213.9, 148.0, 128.7, 126.1, 125.7, 55.8, 44.3, 43.6, 39.9, 32.0, 25.9, 24.0. Anal Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97; Found C, 82.92; H, 9.11; HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ (EI^+): 202.1358, Found: 202.1359. Optical rotation: $[\alpha]_{\text{D}}^{20} +74.78$ ($c = 1.000$, CHCl_3) for a 96% ee sample.

Optical purity was determined by chiral GLC analysis in comparison with authentic racemic material (96% ee sample below; conditions: α -dex column, 140 $^\circ\text{C}$, 15 psi).

■ Representative experimental procedure for *direct* synthesis of enolsilanes

((S)-3-Methyl-3-phenylcyclohex-1-enyloxy)trimethylsilane (19). An oven-dried 13x100 mm test tube charged with Ag complex **4** (5.6 mg, 0.0045 mmol), (CuOTf)₂·C₆H₆ (2.7 mg, 0.0045 mmol), 3-methyl-2-cyclohexenone (20 mg, 0.18 mmol), and Ph₂Zn (120 mg, 0.546 mmol), which were weighed out under N₂ atmosphere in a glove box. The reaction vessel was sealed with a septum and wrapped with parafilm before being removed from the glove box. Diethyl ether (1.0 mL) was slowly added at –78 °C (syringe). After the addition of Et₂O, the solution was allowed to warm to –30 °C. After 48 h at –30 °C, the reaction was cooled to –78 °C and TMSOTf (99 μL, 0.55 mmol) was added (syringe). After the addition of TMSOTf, the mixture was allowed to warm to 22 °C and stir for 1 h. The reaction was quenched through addition of a saturated solution of aqueous NaHCO₃ (1.0 mL), and the mixture was washed with Et₂O (3x1 mL). The volatiles were removed in vacuo and the resulting dark brown oil was purified by silica gel column chromatography (hexanes/Et₂O: 20/1) to afford 46.8 mg (0.180 mmol, >98% yield) of **19** as a colorless oil. (**Note:** Before the mixture was added, the silica gel column was eluted with 0.5 mL of Et₃N.) IR (neat): 3081 (w), 3057 (w), 3029 (w), 3020 (w), 2959 (s), 2934 (s), 2867 (w), 2853 (w), 2836 (w), 1665 (s), 1251 (s), 1195 (s), 895 (s), 865 (s), 847 (s), 760 (s), 697 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.31 (4H, m), 7.22-7.18 (1H, m), 4.99-4.98 (1H, m), 2.09-2.05 (2H, m), 1.87-1.82 (1H, m), 1.68-1.60 (2H, m), 1.52-1.44 (1H, m), 1.43 (3H, s), 0.28 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 150.7, 141.4, 128.0, 126.8, 125.7, 113.5, 40.1, 39.0, 30.3, 30.0, 19.7, 0.6. HRMS Calcd for C₁₆H₂₄OSi (EI⁺): 260.1596, Found: 260.1600.

((R)-3-Ethyl-3-methylcyclohex-1-enyloxy)trimethylsilane. **Note:** This is additional data; this compound does *not* appear in the body of the text. >98% conv, >98% yield, 93% ee. IR (neat): 2962 (s), 2933 (s), 2878 (w), 2871 (w), 2851 (w), 1665 (m), 1262 (m), 1250 (s), 1203 (s), 1138 (s), 900 (s), 867 (s), 842 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 4.64 (1H, s), 1.95-1.92 (2H, m), 1.69-1.63 (2H, m), 1.41-1.21 (4H, m), 0.92 (3H, s), 0.82 (3H, t, *J* = 7.6 Hz), 0.17 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 114.7, 35.8, 34.8, 34.3, 30.1, 27.6, 19.8, 8.7, 0.5. HRMS Calcd for C₁₂H₂₄OSi (EI⁺, M-H): 211.1518, Found: 211.1512.

■ Representative experimental procedure for synthesis of enolsilanes through deprotonation/trap of ACA products

((S)-5-Methyl-5-phenylcyclohex-1-enyloxy)trimethylsilane (20). A solution of *n*-BuLi (345 μL, 0.517 mmol, 1.5 M in hexanes) was added to a cold (–78 °C) THF (2.0 mL) solution of 2,2,6,6-tetramethyl piperidine (99 μL, 0.59 mmol). The mixture was allowed to warm to 22 °C, stirred for 5 min, and cooled again to –78 °C. Optically enriched ketone **15** (65 mg, 0.34 mmol), dissolved in THF (1 mL), was added to the mixture, which was allowed to stir for 30 min at –78 °C. Trimethylsilyltriflate (187 μL, 1.03 mmol) was added and the mixture was allowed to stir for an additional 15 min at –78 °C. A saturated solution of NaHCO₃ (1.0 mL) was added and the mixture was allowed to warm slowly to 22 °C, at which time the solution was diluted through addition of H₂O (1 mL). The mixture was washed with Et₂O (3x1.0 mL) and the combined

organic layers were concentrated in vacuo. The resulting light yellow oil purified by silica gel column chromatography (hexanes/Et₂O: 20/1) to afford 86 mg (0.33 mmol, 96% yield) of enolsilane **20** as a colorless oil. (**Note:** Before the mixture was added, the silica gel column was eluted with 0.5 mL of Et₃N.) IR (neat): 3087 (w), 3056 (w), 3030 (w), 3024 (w), 2962 (s), 2924 (s), 2848 (m), 1671 (s), 1496 (m), 1443 (m), 1357 (m), 1251 (s), 1211 (s), 1186 (s), 1172 (s), 912 (s), 884 (s), 847 (s), 761 (s), 698 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.30 (4H, m), 7.24-7.19 (1H, m), 4.88-4.86 (1H, m), 2.51 (1H, d, *J* = 16.4 Hz), 2.15 (1H, d, *J* = 16.8 Hz), 2.11-2.05 (1H, m), 1.93-1.81 (2H, m), 1.75-1.68 (1H, m), 1.32 (3H, s), 0.25 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 127.3, 128.1, 125.9, 125.8, 103.3, 42.4, 37.9, 34.7, 28.3, 21.7, 0.7. HRMS Calcd for C₁₆H₂₄OSi (EI⁺): 260.1596, Found: 260.1594.

((R)-6-Methyl-6-phenylcyclohept-1-enyloxy)trimethylsilane. **Note:** This is additional data; this compound does *not* appear in the body of the text. IR (neat): 31091 (m), 3090 (m), 3057 (w), 3026 (w), 3010 (w), 2958 (s), 2929 (s), 2878 (m), 2860 (m), 1660 (m), 1458 (m), 1455 (m), 1444 (m), 1382 (m), 1296 (m), 1250 (s), 1228 (s), 1193 (m), 886 (s), 840 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.42 (2H, m), 7.33-7.28 (2H, m), 7.19-7.15 (1H, m), 4.94 (1H, t, *J* = 6.8 Hz), 2.85 (1H, d, *J* = 14.8 Hz), 2.41 (1H, d, *J* = 14.8 Hz), 2.26-2.19 (1H, m), 2.05-1.99 (2H, m), 1.78-1.47 (3H, m), 1.30 (3H, s), 0.13 (9H, s); ¹³C NMR (100 MHz, CDCl₃): δ 153.1, 149.9, 128.2, 126.2, 125.5, 107.1, 47.2, 45.2, 38.3, 29.4, 26.0, 23.8, 0.4; HRMS Calcd for C₁₇H₂₆OSi (EI⁺): 274.1753, Found: 274.1755.

■ **Representative procedure for direct synthesis of enoltriflate **21**:** An oven-dried 13x100 mm test tube charged with chiral Ag complex **4** (3.1 mg, 0.0050 mmol), (CuOTf)₂•C₆H₆ (1.3 mg, 0.0025 mmol), and 3-methyl-2-cyclohexenone (10.0 mg, 0.100 mmol). All the above were weighed out under an N₂ atmosphere in a glove box. The test tube was sealed with a septum and wrapped with parafilm before the tube was removed from the glove box. Diethyl ether (750 μL) was added at 22 °C; the resulting solution was allowed to stir for 10 min. Diethylzinc (30 μL, 0.30 mmol) was added dropwise to the mixture after it was cooled to -78 °C; during the addition of Et₂Zn the mixture turned dark brown. After addition of diethylzinc, the mixture was allowed to warm to -30 °C. After 6 h at -30 °C, Tf₂O (168 mL, 1.0 mmol) was added to the mixture by a syringe. The mixture was immediately allowed to warm to 22 °C and stir for 1 h. The reaction was quenched by the addition of a saturated solution of aqueous sodium bicarbonate (1 mL) and H₂O (1 mL). The mixture was washed with petroleum ether (3x1 mL), and the combined organic layers were passed through a short plug (4 cm x 1 cm) of silica gel eluted with petroleum ether to afford 27.0 mg (0.0992 mmol, 99.2% yield) of **22** as a colorless oil. **Important note:** To ensure high efficiency and enantioselectivity, reactions must be set up in exactly the order described above. The optical purity of the sample was obtained by treatment of the enoltriflate with MeLi to afford enantiomerically enriched cyclic ketone **6**.

(R)-3-Ethyl-3-methylcyclohex-1-enyl trifluoromethanesulfonate (21). IR (neat): 2966 (m), 2933 (m), 2856 (w), 1416 (s), 1257 (m), 1213 (s), 1153 (s), 1026 (w), 960 (w), 894 (w), 845 (w), 801 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.49 (1H, s), 2.32-2.19 (2H, m), 1.84-1.70 (2H, m), 1.50-1.30 (4H, m), 1.00 (3H, s), 0.83 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 148.7, 127.2, 118.7 (q, $J = 318.8$ Hz), 36.2, 34.8, 33.8, 27.8, 26.4, 19.7, 8.4.

(R)-(3-Ethyl-3-methylcyclohex-1-enyl)benzene (22). An oven-dried vial was charged with $\text{Pd}(\text{OAc})_2$ (1.0 mg, 0.0044 mmol), PPh_3 (2.5 mg, 0.0097 mmol), and $\text{PhB}(\text{OH})_2$ (6.7 mg, 0.055 mmol) was weighed out under an N_2 atmosphere in a glovebox. The vial was sealed with a septum prior to removal from the glovebox. In a separate vial, enol triflate **21** (12.2 mg, 0.0448 mmol) dissolved in anhydrous THF (1.0 mL) was added to the vial containing $\text{Pd}(\text{OAc})_2$, PPh_3 , and $\text{PhB}(\text{OH})_2$ through a syringe. The mixture was stirred for 10 min at 22 $^\circ\text{C}$ after which time aqueous KOH (0.5 M, 88 μL , 0.044 mmol) was added via syringe. After 45 min at 22 $^\circ\text{C}$ the reaction was quenched with H_2O (1 mL) and extracted with EtOAc (4 x 1 mL). The combined organic extracts were dried with MgSO_4 , filtered and concentrated to yield a dark brown oil, which was purified by silica gel column chromatography to afford 6.8 mg (0.033, 77%) of **22** as a colorless oil. IR (neat): 3029 (w), 2963 (s), 2936 (s), 2864 (m), 1607 (w), 1496 (w), 1447 (m), 1375 (m), 1006 (w), 879 (w), 768 (s), 697 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.37 (2H, m), 7.32-7.27 (2H, m), 7.21 (1H, tt, $J = 7.2, 1.6$ Hz), 5.81 (1H, s), 2.41-2.82 (2H, m), 1.83-1.70 (2H, m), 1.57-1.50 (1H, m), 1.44-1.35 (3H, m), 1.01 (3H, s), 0.87 (3H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 142.9, 135.2, 134.5, 128.3, 126.7, 125.3, 35.4, 35.2, 33.9, 27.8, 27.0, 20.0, 8.6. Optical Rotation: $[\alpha]_D^{20} -20.4$ ($c = 0.453$, CHCl_3) for an 87% ee sample.

■ **Proof of absolute stereochemistry.** The following sequence was carried out in order to obtain optically enriched material (**c**).

An oven-dried 13x100 mm test tube was charged with Ag complex **4** (4.9 mg, 0.0081 mmol), $(\text{CuOTf})_2 \cdot \text{C}_6\text{H}_6$ (2.0 mg, 0.0045 mmol), 3-ethyl-2-cyclohexenone (19.9 mg, 0.161 mmol) and diphenylzinc (106 mg, 0.483 mmol), weighed out under N_2 atmosphere (in the above specific order). The tube was sealed with a septum, wrapped with parafilm. Diethyl ether (1.0 mL) was added in a dropwise manner (syringe) at -78 $^\circ\text{C}$. After the addition of diethyl ether the mixture was allowed to warm to -30 $^\circ\text{C}$. After 48 h at -30 $^\circ\text{C}$, Tf_2O (142 μL , 0.850 mmol) was added at -30 $^\circ\text{C}$ through the septum by a syringe and the mixture was kept at -30 $^\circ\text{C}$ for 24 h. The reaction was quenched through addition of a saturated solution of aqueous NaHCO_3 (1.0 mL), followed by H_2O (1.0 mL). The resulting mixture was washed with Et_2O (3x1.0 mL) and passed

through a short plug of silica gel eluted with Et₂O. The volatiles were removed in vacuo and the resulting colorless oil was purified by silica gel chromatography (100% hexanes) to afford 25.5 mg (0.08 mmol, 42% yield) of enoltriflate **b** as colorless oil. **Important note:** To ensure high efficiency and enantioselectivity the reaction must be set up in exactly the order described above. IR (neat): 2973 (w), 2938 (w), 1688 (w), 1422 (s), 1252 (m), 1222 (s), 1146 (s), 1016 (w), 906 (m), 876 (w), 845 (w), 765 (w), 710 (w), 620 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.29 (2H, m), 7.25-7.18 (3H, m), 5.96 (1H, s), 2.42-2.25 (2H, m), 1.95-1.85 (2H, m), 1.80-1.65 (3H, m), 1.54-1.43 (1H, m), 0.75 (3H, t, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 146.1, 128.6, 127.0, 126.4, 124.3, 118.8 (q, *J* = 318.1 Hz), 45.0, 35.9, 34.7, 28.0, 19.3, 8.7. HRMS Calcd for C₁₅H₁₇O₃F₃S (EI⁺): 334.0851, Found: 334.0848.

1-((S)-1-Methylcyclohex-2-enyl)benzene (c). An oven-dried vial was charged with Pd(OAc)₂ (0.98 mg, 0.0044 mmol) and PPh₃ (2.3 mg, 0.0088 mmol), was weighed out under N₂ atmosphere. The vial was sealed with a septum before it was removed from the glovebox. In a separate flask, enol triflate **22** (21 mg, 0.089 mmol) dissolved in anhydrous DMF (1.0 mL) was added through a syringe to the vial containing Pd(OAc)₂ and PPh₃. The mixture was charged with Et₃N (37.0 μL, 0.267 mmol), followed by formic acid (6.8 μL, 0.18 mmol), and was heated to 60 °C for 30 min, during which time the solution turned black. The mixture was cooled to 22 °C and diluted by the addition of H₂O (1.0 mL), followed by washing with petroleum ether (5x1.0 mL). The combined organic layers were passed through a short plug of silica gel eluted with petroleum ether. The filtrate was concentrated under reduced pressure to yield **23** as a colorless oil (11.5 mg, 0.0167 mmol, 69.5% yield). IR (neat): 3065 (w), 3029 (w), 2981 (m), 2934 (s), 2874 (m), 2832 (w), 1499 (m), 1451 (m), 1374 (w), 1047 (w), 939 (w), 916 (w), 773 (s), 737 (m), 713 (s), 582 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.32-7.25 (4H, m), 7.17-7.12 (1H, m), 5.91-5.82 (2H, m), 2.01-1.97 (2H, m), 1.90-1.64 (4H, m), 1.58-1.50 (1H, m), 1.38-1.27 (1H, m), 0.73 (3H, t, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 133.0, 128.0, 127.9, 127.3, 125.5, 43.1, 36.8, 35.1, 25.7, 19.1, 8.8. HRMS Calcd for C₁₄H₁₈ (EI⁺): 186.1409, Found: 186.1404; Optical Rotation: [α]_D²⁰ -27.17 (*c* = 0.780, CHCl₃) for a 40% ee sample.

The optical rotation of cyclic alkene **c** was compared to a value reported previously by Breit, who assigned (+) rotation to the *R* enantiomer, but did not provide an exact value.⁶

■ **Preparation of *di*-4-methoxyphenyl zinc.** Mg turnings (1.8 g, 75 mmol) were weighed out into a two-neck 50 mL round bottomed flask equipped with a reflux condenser. The apparatus was then flame-dried and allowed to cool under N₂. Tetrahydrofuran (16 mL) was added, followed by the dropwise addition of 4-bromoanisole (6.2 mL, 50 mmol), such that gentle reflux could be maintained. The mixture was allowed to stir for 12 h. Titration indicated a 2.27 M

solution of the Grignard reagent. (Note: Grignard reagent solution and syringe/needle must be kept warm during titration and addition because of the arylmetal low solubility in THF.)

An oven- and flame-dried 100 mL round bottomed flask (equipped with a stir bar) was charged with ZnCl_2 (1.4 g, 10 mmol) weighed out under an N_2 atmosphere; the flask was sealed with a septum and removed from the glovebox. Diethyl ether (20 mL) was added and the solution was allowed to cool to 0 °C. A solution of the above-mentioned Grignard reagent (8.8 mL, 20 mmol) was added dropwise through a syringe (within approximately 10 min). During addition, a significant amount of white precipitate is generated. The mixture was allowed to warm to 22 °C and stir for 2 h. At this time, the solution was charged with dioxane (10 mL) and allowed to stir for an additional 30 min. (Note: 10 mL of THF can be added at this point if the solution containing Zn reagent appears too viscous for proper filtration.) At this point, an oven-dried Schlenk tube (medium porosity filter) containing approximately 5 g of oven-dried celite and a 100 mL round bottomed flask on the receiving end was quickly exchanged with the septum on the flask containing the Zn reagent. This was performed such that the round-bottomed flask containing the Zn reagent remained in a horizontal position; this ensured that celite does not fall into the flask that contains the zinc reagent. Filtration was then performed under an atmosphere of N_2 . The filtrate was then concentrated in vacuo (~0.4 mm Hg), followed by gentle heating (still under vacuum; to assist in removal of dioxane) to afford a white solid. The white solid was transferred to a sublimation apparatus under an atmosphere of N_2 , and the white solid was sublimed under stronger vacuum (0.01 mmHg) at 150 °C to afford a white powder. **Note:** The ^1H NMR of this material is identical to the ^1H NMR of the diarylzinc reagent prior to sublimation. We find that Cu-catalyzed ACA with sublimed arylmetal samples deliver slightly higher levels of enantioselectivity. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (4H, d, J = 8.4 Hz), 6.94 (4H, d, J = 8.8 Hz), 3.83 (6H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 160.1, 139.2, 138.5, 114.0, 55.1.