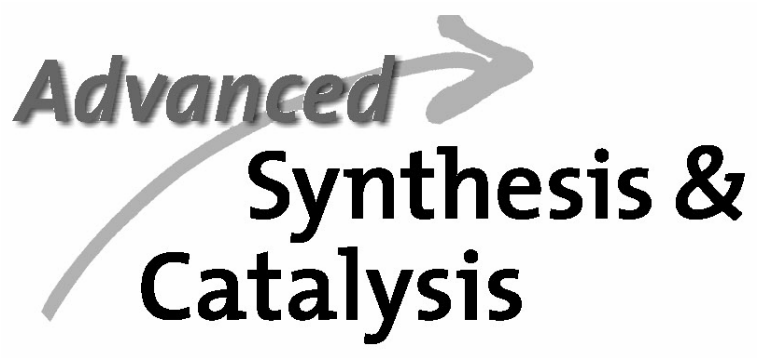

Supporting Information

<u>Supporting Information</u>: Direct Copper-Free Domino Conjugate Addition-Cycloallylation using Diorganozinc Reagents: Intramolecular Allylic Substitution of Ketone Enolates

Venukrishnan Komanduri, Fernando Pedraza and Michael J. Krische*

University of Texas at Austin, Department of Chemistry and Biochemistry
1 University Station – A5300, Austin, TX 78712-1167 (USA)

Experimental Section

General: Commercial reagents were used without further purification unless otherwise stated. Anhydrous zinc iodide (99.99+% pure) was purchased from *Aldrich* and used directly without any further purification. Diethyl and diisopropylzinc solutions were purchased from *Aldrich.* All reactions were conducted in oven-dried containers under inert atmosphere or argon. Dichloromethane was distilled over calcium hydride prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Krieselgel 60 F254). Preparative column chromatography employing silica gel was performed according to the method of Still.[1] Solvents for chromatography were listed as volume/volume ratios. Melting points were determined on a Thomas-Hoover melting point apparatus in open capillary and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer. High resolution mass spectra (HRMS, EI) were obtained on a Karatos MS9 and are reported as m/e (relative intensity). Accurate masses were reported for the molecular ion (M) or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Mercury (400 MHz) spectrometer. Chemical Shifts were reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane. Coupling constants were reported in Hertz (Hz). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Mercury 400 (100 MHz) spectrometer. Chemical shifts were reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

Carbonic acid methyl ester-8-oxo-8[1-(toluene-4-sulfonyl)-1*H*-indol-3-yl]-octa-2,6-dienyl ester (4a): To a solution of carbonic acid 8-(1*H*-indol-3-yl)-8-oxo-octa-2,6-dienyl ester methyl

[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

ester[16b] (240 mg, 0.76 mmol, 100 mol%) at 0 °C in dichloromethane (4.0 mL) were added tosyl chloride (220 mg, 1.15 mmol, 150 mol%), triethylamine (0.16 mL, 1.15 mmol, 150 mol%) and a catalytic amount of DMAP (9 mg, 0.07 mmol, 10 mol%). The reaction mixture was stirred at ambient temperature for 2 h and quenched with aqueous ammonium chloride solution and extracted with dichloromethane (2 x 20 mL). The organic layer was washed with brine solution (20 mL), dried (Na_2SO_4), filtered and the resulting liquor was concentrated *in vacuo.* Purification of the oily residue by flash column chromatography (SiO_2: 20% ethyl acetate:hexanes, R_f = 0.25) provides the title compound as an yellow solid (330 mg, 0.70 mmol) in 92% yield as a mixture of *E:Z* (8:1) isomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 7.2 Hz, 1H), 8.23 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H) 7.82 (d, *J* = 8.0 Hz, 2H), 7.37-7.30 (m, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.07-7.00 (m, 1H), 6.76 (d, *J* = 15.5 Hz, 1H) 5.88-5.81 (m, 1H), 5.70-5.63 (m, 1H), 4.58 (d, *J* = 6.0 Hz, 2H), 3.78 (s, 3H), 2.45-2.39 (m, 2H), 2.34 (s, 3H), 2.34-2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 155.5, 146.4, 145.8, 135.0, 134.8, 134.4, 131.6, 130.2, 130.1, 128.0, 127.1, 125.7, 124.7, 124.5, 123.2, 112.6, 112.9, 68.1, 56.5, 31.7, 30.7, 21.5; HRMS Calcd. for $C_{25}H_{25}NO_6S$ (M): 467.1403, Found: 467.1407; FTIR (NaCl Film): 3128, 2955, 1746, 1664, 1615, 1536, 1478, 1445, 1328, 1268, 1175, 1139, 1088, 975, 751 cm^{-1}. M.P.: 155-158 °C (obtained for mixture of *E:Z* isomers).

General Procedure for Tandem Conjugate Addition – Cycloallylation Reaction With Diorganozinc Reagents, Preparation of (2-Ethyl-5-vinyl-cyclopentyl)-phenyl-methanone (1b): To a suspension of the substrate **1a**[21] (50 mg, 0.18 mmol, 100 mol%) and zinc iodide (58 mg, 0.18 mmol, 100 mol%) in dichloromethane at 0 °C in a 15 mL sealed tube under argon atmosphere was added a 1.0 M diethylzinc solution in hexanes (0.54 mL, 0.54 mmol, 300 mol%) over a period of 5 min. Once the addition was complete, the reaction vessel was flushed with argon, sealed tightly and the reaction mixture was stirred at 35 °C for 10.5 h. The reaction mixture was cooled to room temperature, quenched with four drops of water and stirred for 30-40 min. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated *in vacuo*. Purification of the oily residue by flash column chromatography (SiO_2: 3% diethyl ether:hexanes, R_f = 0.30) provides the title compound as a colorless oil (30 mg, 0.13 mmol) in 74% yield as a 5.2:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 6.4, 1.2 Hz, 2H), 7.50 (dd, *J* = 7.2, 1.2 Hz,

1H), 7.44-7.39 (m, 2H), 5.54 (ddd, *J* = 15.6, 8.4, 7.6 Hz, 1H), 4.71 (ddd, *J* = 15.6, 1.6, 0.8 Hz, 1H), 4.67 (ddd, *J* = 8.8, 1.6, 0.8 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 1H), 3.04-2.78 (m, 1H), 2.45 (dt, *J* = 15.6, 8.0 Hz, 1H), 2.09-2.02 (m, 1H), 1.98-1.92 (m, 1H), 1.69-1.62 (m, 1H), 1.48-1.40 (m, 1H), 1.31-1.22 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 139.1, 138.2, 132.5, 128.4, 128.2, 114.5, 56.8, 48.3, 43.3, 32.7, 31.1, 28.4, 12.8; HRMS Calcd. for $C_{16}H_{20}O$ (M): 228.1514, Found: 228.1511; FTIR (NaCl Film): 2955, 2928, 2867, 1677, 1594, 1450, 1372, 1268, 1215, 1180, 914, 690 cm^{-1}.

(2-Isopropyl-5-vinyl-cyclopentyl)-phenyl-methanone (1c): In accordance with the general procedure, substrate **1a** (50 mg, 0.18 mmol, 100 mol%) was exposed to diisopropylzinc (0.54 mL, 0.54 mmol, 300 mol%) and zinc iodide (58 mg, 0.18 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 2% diethyl ether:hexanes, R_f = 0.3) provides the title compound as a colorless oil (43 mg, 0.18 mmol) in 97% yield as a 3.8:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 6.6, 1.2 Hz, 2H), 7.50 (dd, *J* = 9.6, 1.2 Hz, 1H), 7.45-7.38 (m, 2H), 5.52 (ddd, *J* = 16.8, 10.0, 9.8 Hz, 1H), 4.78 (ddd, *J* = 16.4, 1.6, 0.8 Hz, 1H), 4.69 (ddd, *J* = 10.0, 1.6, 0.4 Hz, 1H), 3.69 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.94 (td, *J* = 15.6, 9.2 Hz, 1H), 2.52-2.34 (m, 1H). 2.23-1.92 (m, 1H), 1.91-1.83 (m, 1H), 1.78-1.61 (m, 1H), 1.54-1.45 (m, 1H), 1.41-1.31 (m, 1H), 0.85 (d, *J* = 7.2 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 138.9, 138.2, 132.5, 128.4, 128.2, 114.8, 54.1, 49.2, 49.1, 33.3, 32.9, 29.7, 21.8, 20.4; HRMS Calcd. for $C_{17}H_{22}O$ (M): 242.1671, Found: 242.1662; FTIR (NaCl Film): 2968, 2930, 2876, 1679, 1591, 1452, 1378, 1264, 1215, 1000, 914, 690 cm^{-1}.

(2-Ethyl-6-vinyl-cyclohexyl)-phenyl-methanone (2b): In accordance with the general procedure, substrate **2a** (100 mg, 0.36 mmol, 100 mol%) was exposed to diethylzinc (1.04 mL, 1.10 mmol, 300 mol%) and zinc iodide (110 mg, 0.36 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 2% diethyl ether:hexanes, R_f = 0.24) provides the title compound as a colorless oil (50 mg, 0.21 mmol) in 60% yield as a 2.5:1 ratio mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.85 (m, 2H), 7.52 (t, *J* = 6.4 Hz, 1H), 7.46-7.41 (m, 2H), 5.54-5.44 (m, 1H), 4.87 (appears as a broad d, *J* = 17.2 Hz, 1H), 4.69 (d, *J* = 10.4 Hz, 1H), 3.05 (t, *J* = 10.8 Hz, 1H), 2.85 (d, *J* = 6.8 Hz, 1H), 2.45-

2.37 (m, 1H). 1.97-1.20 (m, 6H), 0.89-0.84 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,): δ 206.0, 141.0, 132.6, 128.4, 128.1, 127.9, 114.6, 55.0, 46.4, 42.3, 32.2, 30.2, 27.6, 25.0, 11.2; HRMS Calcd. for $C_{17}H_{22}O$ (M): 242.1671, Found: 242.1670; FTIR (NaCl Film): 2952, 2930, 2860, 1677, 1450, 1362, 1258, 1205, 1172, 1001, 915, 696, 660 cm^{-1}.

(2-Isopropyl-6-vinyl-cyclohexyl)-phenyl-methanone (2c): In accordance with the general procedure, substrate **2a** (50 mg, 0.17 mmol, 100 mol%) was exposed to diisopropylzinc (0.52 mL, 0.52 mmol, 300 mol%) and zinc iodide (55 mg, 0.17 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 2% diethyl ether:hexanes, R_f = 0.26) provides the title compound as a colorless oil (33 mg, 0.13 mmol) in 78% yield as a 1.4:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.89 (m, 2H), 7.53 (t, *J* = 6.4 Hz, 1H), 7.47-7.42 (m, 2H), 5.53 (ddd, *J* = 17.4, 10.4, 8.4 Hz, 1H), 4.88 (ddd, *J* = 17.2, 2.8, 2.0 Hz, 1H), 4.69 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.23 (t, *J* = 10.4 Hz, 1H), 2.47-2.39 (m, 1H), 1.89-1.71 (m, 4H), 1.43-1.17 (m, 4H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *reported for both the isomers*): δ 202.0, 201.7, 141.1, 139.3, 132.7, 132.6, 128.6, 128.5, 128.1, 128.0, 127.9, 115.3, 114.6, 109.7, 51.2, 47.0, 46.5, 41.5, 38.4, 32.3, 32.2, 29.0, 27.7, 25.1, 23.9, 23.6, 22.2, 21.5, 21.3, 20.6, 16.3, 16.1; HRMS Calcd. for $C_{18}H_{24}O$ (M): 256.1827, Found: 256.1830; FTIR (NaCl Film): 2957, 2929, 2864, 1677, 1449, 1367, 1337, 1258, 1205, 1178, 1000, 916, 695, 660 cm^{-1}.

(2-Ethyl-5-vinyl-cyclopentyl)-furan-2-yl-methanone (3b): In accordance with the general procedure, substrate **3a** (66 mg, 0.27 mmol, 100 mol%) was exposed to diethylzinc (0.80 mL, 0.80 mmol, 300 mol%) and zinc iodide (85 mg, 0.27 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% ethyl acetate:hexanes, R_f = 0.30) provides the title compound as an yellow oil (41 mg, 0.19 mmol) in 71% yield as a 3.1:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.10 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.46 (dd, *J* = 3.6, 2.0 Hz, 1H), 5.58 (ddd, *J* = 17.2, 10.4, 9.6 Hz, 1H), 4.80 (ddd, *J* = 16.8, 2.0, 0.8 Hz, 1H), 4.73 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.34 (t, *J* = 8.8 Hz, 1H), 2.99 (quintet, *J* = 8.4 Hz, 1H), 2.44 (sextet, *J* = 8.4 Hz, 1H). 2.06-1.98 (m, 1H), 1.93-1.85 (m, 1H), 1.68-1.59 (m, 1H), 1.45-1.37 (m, 1H), 1.30-1.22 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 153.7, 146.0, 138.9, 116.7, 114.6, 112.0, 56.9, 48.2, 42.9,

32.6, 31.3, 28.5, 12.7; HRMS Calcd. for $C_{14}H_{18}O_2$ (M): 218.1307, Found: 218.1302; FTIR (NaCl Film): 2957, 2929, 2864, 1677, 1449, 1367, 1337, 1258, 1205, 1178, 1000, 695, 660 cm^{-1}.

(2-Isopropyl-5-vinyl-cyclopentyl)-furan-2-yl-methanone (3c): In accordance with the general procedure, substrate **3a** (76 mg, 0.31 mmol, 100 mol%) was exposed to diisopropylzinc (0.92 mL, 0.92 mmol, 300 mol%) and zinc iodide (98 mg, 0.31 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% ethyl acetate:hexanes, R_f = 0.30) provides the title compound as an yellow oil (57 mg, 0.24 mmol) in 80% yield as a 2.6:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 2.0, 0.4 Hz, 1H), 7.13 (dd, *J* = 3.6, 0.4 Hz, 1H), 6.50 (dd, *J* = 3.6, 0.8 Hz, 1H), 5.58 (ddd, *J* = 17.2, 10.4, 8.8 Hz, 1H), 4.83 (ddd, *J* = 17.2, 9.2, 1.2 Hz, 1H), 4.76 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.53 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.94 (ddd, *J* = 16.4, 9.6, 6.8 Hz, 1H), 2.44 (ddd, *J* = 16.0, 9.6, 7.6 Hz, 1H). 2.0-1.95 (m, 1H), 1.88-1.81 (m, 1H), 1.72-1.63 (m, 1H), 1.56-1.48 (m, 1H), 1.39-1.33 (m, 1H), 0.88 (d, *J* = 7.4 Hz, 3H), 0.80 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5, 153.6, 146.1, 138.6, 116.8, 114.8, 112.1, 54.3, 49.1, 48.6, 33.1, 32.9, 29.9, 21.6, 20.4; HRMS Calcd. for $C_{15}H_{20}O_2$ (M): 232.1463, Found: 232.1457; FTIR (NaCl Film): 2957, 2929, 2864, 1677, 1449, 1367, 1337, 1258, 1205, 1178, 1000, 695, 660 cm^{-1}.

(2-Ethyl-5-vinyl-cyclopentyl)-[1-(toluene-4-sulfonyl)-1-*H*-indol-3-yl]-methanone (4b): In accordance with the general procedure, substrate **4a** (50 mg, 0.11 mmol, 100 mol%) was exposed to diethylzinc (0.32 mL, 0.32 mmol, 300 mol%) and zinc iodide (34 mg, 0.11 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% ethyl acetate:hexanes, R_f = 0.23) provides the title compound as an yellow oil (23 mg, 0.05 mmol) in 51% yield as a 2.6:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 7.2, 2.4 Hz, 1H), 8.16 (s, 1H), 7.90 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H) 7.37-7.31 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.56 (td, *J* = 17.8, 9.2 Hz, 1H), 4.81 (ddd, *J* = 17.8, 2.0, 0.8 Hz, 1H), 4.66 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.33 (dd, *J* = 9.2, 8.0 Hz, 1H), 3.05-2.96 (m, 1H), 2.59-2.49 (m, 1H), 2.36 (s, 3H), 2.13-2.06 (m, 1H), 1.99-1.91 (m, 1H), 1.75-1.65 (m, 1H), 1.52-1.43 (m, 1H), 1.38-1.19 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 145.8, 139.2, 134.8, 134.5, 132.0, 130.1, 127.8, 127.0, 125.6, 124.7, 123.2, 122.7, 114.7, 112.9, 58.6, 49.0, 43.4, 32.9, 31.5, 28.6, 21.5, 12.8; HRMS Calcd. for $C_{25}H_{27}NO_3S$

(M): 421.1712, Found: 421.1708; FTIR (NaCl Film): 3500, 2955, 2869, 1660, 1536, 1445, 1380, 1172, 1138, 1089, 992, 913, 736, 660, 576 cm^{-1}.

(2-Isopropyl-5-vinyl-cyclopentyl)-[1-(toluene-4-sulfonyl)-1-*H*-indol-3-yl]-methanone (4c): In accordance with the general procedure, substrate **4a** (67 mg, 0.14 mmol, 100 mol%) was exposed to diisopropylzinc (0.43 mL, 0.43 mmol, 300 mol%) and zinc iodide (46 mg, 0.14 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% ethyl acetate:hexanes, R_f = 0.26) provides the title compound as an yellow oil (32 mg, 0.07 mmol) in 54% yield as a 2.9:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 7.2, 2.4 Hz, 1H), 8.17 (s, 1H), 7.90 (dd, *J* = 6.5, 1.2 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H) 7.35-7.26 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.52 (td, *J* = 16.8, 10.4 Hz, 1H), 4.87 (ddd, *J* = 16.8, 2.0, 0.4 Hz, 1H), 4.65 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.47 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.98-2.89 (m, 1H), 2.53-2.45 (m, 1H), 2.35 (s, 3H), 2.06-1.93 (m, 1H), 1.90-1.83 (m, 1H), 1.74-1.64 (m, 1H), 1.59-1.50 (m, 1H), 1.43-1.33 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 145.8, 139.1, 134.9, 134.4, 132.0, 130.1, 127.8, 127.0, 125.6, 124.7, 123.2, 122.6, 114.9, 112.9, 56.3, 49.8, 49.2, 33.5, 33.1, 30.2, 21.8, 21.6, 20.5; HRMS Calcd. for $C_{26}H_{29}NO_3S$ (M): 435.1868, Found: 435.1871; FTIR (NaCl Film): 3495, 2955, 2869, 1662, 1536, 1445, 1380, 1172, 1138, 1089, 995, 913, 736, 660, 576 cm^{-1}.

(2-Ethyl-5-vinyl-cyclopentyl)-ethanone (5b): In accordance with the general procedure, substrate **5a** (80 mg, 0.38 mmol, 100 mol%) was exposed to diethylzinc (1.1 mL, 1.13 mmol, 300 mol%) and zinc iodide (120 mg, 0.38 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% diethyl ether:hexanes, R_f = 0.30) provides the title compound as a colorless oil (41 mg, 0.24 mmol) in 66% yield as a 4:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60 (ddd, *J* = 17.2, 10.0, 8.6 Hz, 1H), 5.91 (ddd, *J* = 17.0, 2.0, 0.8 Hz, 1H), 4.85 (dd, *J* = 10.4, 1.6 Hz, 1H), 2.94-2.74 (m, 1H), 2.68 (t, *J* = 8.8 Hz, 1H), 2.31-2.22 (m, 1H), 2.10 (s, 3H), 2.02-1.78 (m, 2H), 1.58-1.49 (m, 1H), 1.40-1.32 (m, 1H), 1.22-1.14 (m, 2H), 0.82 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.2, 139.0, 114.9, 62.6, 47.3, 42.0, 32.2, 31.6, 30.9, 28.4, 12.6; HRMS Calcd. for $C_{11}H_{18}O$ (M): 166.1358, Found: 166.1352; FTIR (NaCl Film): 2954, 2868, 1701, 1465, 1421, 1360, 1161, 999, 916, 731 cm^{-1}.

(2-Isopropyl-5-vinyl-cyclopentyl)-ethanone (5c): In accordance with the general procedure, substrate **5a** (52 mg, 0.24 mmol, 100 mol%) was exposed to diisopropylzinc (0.73 mL, 0.73 mmol, 300 mol%) and zinc iodide (78 mg, 0.24 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 3% diethyl ether:hexanes, R_f = 0.30) provides the title compound as an yellow oil (34 mg, 0.18 mmol) in 75% yield as a 4.0:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.62 (ddd, *J* = 17.5, 10.0, 8.4 Hz, 1H), 5.10 (ddd, *J* = 17.2, 2.0, 0.8 Hz, 1H), 4.90 (dd, *J* = 10.4, 1.6 Hz, 1H), 2.93-2.75 (m, 1H), 2.43 (t, *J* = 9.2 Hz, 1H), 2.27-2.19 (m, 1H), 2.08 (s, 3H), 1.93-1.73 (m, 2H), 1.60-1.39 (m, 2H), 1.32-1.22 (m, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 138.8, 115.2, 60.0, 48.2, 48.0, 32.9, 32.7, 31.9, 29.6, 21.5, 20.3; HRMS Calcd. for $C_{12}H_{20}O$ (M): 180.1514, Found: 180.1518; FTIR (NaCl Film): 2956, 2869, 1707, 1465, 1421, 1360, 1161, 999, 915, 733 cm^{-1}.

Cyclopropyl-(2-ethyl-5-vinyl-cyclopentyl)-methanone (6b): In accordance with the general procedure, substrate **6a** (100 mg, 0.42 mmol, 100 mol%) was exposed to diisopropylzinc (1.26 mL, 1.26 mmol, 300 mol%) and zinc iodide (134 mg, 0.42 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% diethyl ether: pentane, R_f = 0.25) provides the title compound as a colorless oil (52 mg, 0.27 mmol) in 61% yield as a 1.3:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (td, *J* = 17.2, 9.6 Hz, 1H), 5.01 (ddd, *J* = 17.2, 2.0, 0.4 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 3.01-2.93 (m, 1H), 2.87 (t, *J* = 8.4 Hz, 1H), 2.37-2.27 (m, 1H), 2.02-1.82 (m, 3H), 1.62-1.17 (m, 5H), 1.01 (t, *J* = 4.0 Hz, 1H), 0.96 (dd, *J* = 6.8, 4.4 Hz, 1H), 0.89-0.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.9, 139.5, 114.5, 62.9, 47.4, 42.3, 32.2, 31.1, 28.6, 21.9, 12.6, 10.8, 10.7; HRMS Calcd. for $C_{13}H_{20}O$ (M): 192.1514, Found: 192.1511; FTIR (NaCl Film): 2952, 2928, 1691, 1382, 1000, 1007, 913Cm^{-1}.

Cyclopropyl-(2-isopropyl-5-vinyl-cyclopentyl)-methanone (6c): In accordance with the general procedure, substrate **6a** (50 mg, 0.21 mmol, 100 mol%) was exposed to diisopropylzinc (0.63 mL, 0.63 mmol, 300 mol%) and zinc iodide (67 mg, 0.21 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% diethyl ether: pentane, R_f = 0.30) provides the title

compound as a colorless oil (40 mg, 0.19 mmol) in 87% yield as a 1.5:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.63 (ddd, *J* = 17.2, 10.0, 8.0 Hz, 1H), 5.0 (ddd, *J* = 17.2, 2.0, 1.2 Hz, 1H), 4.95 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.10 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.01-2.93 (m, 1H), 2.37-2.27 (m, 1H), 2.03-1.82 (m, 3H), 1.62-1.16 (m, 5H), 1.01-0.95 (m, 2H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6, 139.3, 114.6, 60.7, 49.8, 32.9, 32.3, 29.7, 22.1, 21.5, 20.4, 20.2, 11.3, 10.9; HRMS Calcd. for $C_{14}H_{22}O$ (M): 206.1671, Found: 206.1666; FTIR (NaCl Film): 2956, 2928, 1691, 1386, 1225, 1075, 913Cm^{-1}.

Deca-2,6-dienoic acid ethyl ester (7b): In accordance with the general procedure, substrate **7a** (48 mg, 0.19 mmol, 100 mol%) was exposed to diethylzinc (0.52 mL, 0.19 mmol, 300 mol%) and zinc iodide (62 mg, 0.19 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% diethyl ether:pentane, R_f = 0.28) provides the title compound as a pale yellow oil (22 mg, 0.11 mmol) in 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.81 (d, *J* = 16.0 Hz, 1H), 5.48-5.34 (m, 2H), 4.17(q, *J* = 6.8 Hz, 2H), 2.25 (q, *J* = 7.2 Hz, 2H), 2.16-2.12 (m, 2H), 1.95 (q, *J* = 6.8 Hz, 2H), 1.35 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 148.7, 131.5, 128.5, 121.4, 60.1, 34.6, 32.2, 31.0, 22.5, 14.2, 13.6; HRMS Calcd. for $C_{12}H_{20}O_2$ (M): 196.1463, Found: 196.1466; FTIR (NaCl Film): 2958, 2873, 1677, 1596, 1446, 1377, 1260, 1212, 1002 cm^{-1}.

2-Isopropyl-5-vinyl-cyclopentanecarboxylic acid ethyl ester (7c): In accordance with the general procedure, substrate **7a** (100 mg, 0.41 mmol, 100 mol%) was exposed to diisopropylzinc (1.27 mL, 1.27 mmol, 300 mol%) and zinc iodide (130 mg, 0.41 mmol, 100 mol%). Purification by flash column chromatography (SiO_2: 5% ethylacetate:hexanes, R_f = 0.24) provides the title compound as a colorless oil (71 mg, 0.33 mmol) in 77% yield as a 2.6:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81-5.69 (m, 1H), 4.95 (ddd, *J* = 14.4, 2.0, 0.8 Hz, 1H), 4.91 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.17-4.06 (m, 2H), 2.84-2.69 (m, 1H), 2.67-2.62 (m, 1H), 2.33-2.08 (m, 2H), 2.26-2.13 (m, 1H), 1.97-1.74 (m, 2H), 1.70-1.43 (m, 3H), 1.18 (t, *J* = 7.2 Hz, 1H), 0.83 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 138.6, 115.0, 59.9, 52.4, 49.8, 47.8, 32.9, 32.0, 29.9, 21.1, 20.4,

14.3; HRMS Calcd. for $C_{13}H_{22}O_2$ (M): 210.1620, Found: 210.1619; FTIR (NaCl Film): 2956, 2869, 1707, 1639, 1465, 1360, 1161, 999, 915, 733 cm^{-1}.

(2,5-Diethyl-cyclopentyl)-phenyl-methanone (1d): To a solution of compound **1b** (40 mg, 0.17 mmol, 100 mol%) in ethanol (2.0 mL) in a 10 mL round bottomed flask, was added catalytic amount of palladium catalyst on charcoal (18 mg, 0.017 mmol, 10 mol%) and stirred under hydrogen atmosphere at ambient temperature for 48 h. The reaction mixture was filtered through a celite pad with the aid of ethyl acetate (20 mL). The organic layer was concentrated *in vacuo*. Purification by flash column chromatography (SiO_2: 2% ethyl acetate:hexanes, R_f = 0.30) provides the title compound as a colorless oil (37 mg, 0.16 mmol) in 92% yield as a 5:1 mixture of diastereomers. *Spectral data is reported for the major isomer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.53-7.45 (m, 1H), 7.45-7.41 (m, 2H), 3.48 (t, *J* = 8.4 Hz, 1H), 2.46-2.36 (m, 1H), 2.31-2.17 (m, 1H), 2.02-1.87 (m, 2H), 1.50-1.34 (m, 2H). 1.28-1.18 (m, 2H), 1.13-0.99 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9, 148.7, 131.5, 128.5, 121.4, 60.1, 40.4, 39.2, 32.2, 31.0, 22.5, 21.9, 14.2, 13.5; HRMS Calcd. for $C_{16}H_{22}O$ (M): 230.1671, Found: 230.1677; FTIR (NaCl Film): 2958, 2929, 1723, 1655, 1311, 1265, 1196, 1162, 1043, 970 cm^{-1}.

General Procedure for the Allylic Substitution of Allylic Carbonates with Diorganozinc Reagents: In a 15-mL sealable test tube charged with carbonate **8a** (100 mg, 0.52 mmol, 100 mol%) was added dichloromethane (5.2 mL). The vessel was purged with argon gas and kept under a blanket of argon gas. The reaction mixture was cooled to 0 ^oC and a 1.0 M diethylzinc solution in hexanes (1.56 mL, 1.56 mmol, 300 mol%) was added over a period of 5 min. Once the addition was complete, the vessel was immediately sealed and the reaction mixture was warmed to 35 ^oC. The reaction mixture was allowed to stir for 16 hours, at which point 5 drops of water was added to the reaction mixture. The reaction mixture was filtered through a pad of silica gel with the aid of dichloromethane and the solution was concentrated *in vacuo*. Purification of the residue by flash column chromatography (SiO_2: neat hexanes) provides **8b** and **8c** (54 mg, 0.36 mmol) in 72% yield as a 1.7:1 mixture of regioisomers.

In accordance with the general procedure, substrate ***iso*-8a** (100 mg, 0.52 mmol, 100 mol%) was exposed to diethylzinc (1.56 mL, 1.56 mmol, 300 mol%). Purification by flash column chromatography (SiO_2: neat hexanes, R_f = 0.50) provides **8b** and **8c** as a colorless oil (47 mg, 0.31 mmol) in 61% yield as 1.7:1 mixture of regioisomers.

3-Phenyl-1-pentene (8b): The NMR data obtained for **8b** are identical to those previously reported.[2] δ 7.41-7.29 (m, 5H), 6.31-5.68 (m, 1H), 4.81-4.22 (m, 2H), 3.12 (q, *J* = 7.5 Hz, 1H), 1.65 (quintet, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 130.9, 129.8, 128.4, 126.7, 125.9, 51.7, 22.5, 13.7.

(*E*)-1-Phenyl-1-pentene (8c): The NMR data obtained for **8c** are identical to those previously reported.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.18 (m, 5H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.25-6.18 (m, 1H), 2.22-2.15 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.2, 128.3, 127.6, 126.0, 114.0, 31.6, 28.2, 12.1.

In accordance with the general procedure, substrate **9a** (100 mg, 0.48 mmol, 100 mol%) was exposed to diethylzinc (1.45 mL, 1.45 mmol, 300 mol%). Purification by flash column chromatography (SiO_2: neat hexanes, R_f = 0.60) provides **9b** and **9c** as a colorless oil (36 mg, 0.22 mmol) in 46% yield as a 1:1.6 mixture of regioisomers.

In accordance with the general procedure, substrate ***iso*-9a** (100 mg, 0.48 mmol, 100 mol%) was exposed to diethylzinc (1.45 mL, 1.45 mmol, 300 mol%). Purification by flash column chromatography (SiO_2: neat hexanes, R_f = 0.60) provides **9b** and **9c** as a colorless oil (41 mg, 0.25 mmol) in 52% yield as a 1.6:1 mixture of two regioisomers.

(*E*)-4-Phenyl-2-hexene (9b): The NMR data for **9b** are identical to those previously reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.27 (m, 5H), 5.59 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.52-5.40 (m,

---

[2] J. Tanaka, M. Nojima, S. Kusabayashi, *J. Chem. Soc., Perkin Trans. II* **1987**, 673-678.

[3] S. Farhat, I. Zouev, I. Marek, *Tetrahedron* **2004**, *60*, 1329-1337.

[4] G. Giacomelli, L. Bertero, L. Lardicci, R. Menicagli, *J. Org. Chem.* **1981**, *46*, 3707-3711.

1H), 3.11(q, *J* = 7.5 Hz, 1H), 1.70 (d, *J* = 7.0 Hz, 3H), 1.72-1.68 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.8, 128.4, 128.1, 126.7, 125.9, 50.8, 29.8, 20.2, 11.8.

(*E*)-1-Phenyl-3-methyl-1-pentene (9c): The NMR data obtained for **9c** are identical to those previously reported.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.16 (m, 5H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.15 (dd, *J* = 15.7, 7.8 Hz, 1H), 2.36-2.22 (m, 1H), 1.45 (quintet, *J* = 7.2 Hz, 2H), 1.11 (d, *J* = 6.9 Hz, 3H) 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 135.1, 128.3, 127.5, 125.9, 124.6, 38.9, 28.9, 18.0, 12.2.

In accordance with the general procedure, substrate **10a** (100 mg, 0.37 mmol, 100 mol%) was exposed to diethylzinc (1.19 mL, 1.19 mmol, 300 mol%). Purification by flash column chromatography (SiO_2: neat hexanes, R_f = 0.60) provides **10b** as a colorless oil (70 mg, 0.31 mmol) in 84% yield.

(*E*)-1,3-Diphenyl-1-pentene (10b): The NMR data obtained for **10b** are identical to those previously reported.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.16 (m, 10H), 6.41 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, *J* = 15.8, 7.6 Hz, 1H), 3.31 (quintet, *J* = 7.6 Hz, 1H), 1.90-1.79 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 137.6, 134.2, 129.4, 128.4, 127.7, 127.0, 126.2, 126.1, 51.0, 28.8, 12.3.

---

[5] J. Zhou, G.C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 1340-1341.

[6] Y. Uozumi, H. Danjo, T. Hayashi, *J. Org. Chem.* **1999**, *64*, 3384-3388.