Supporting Information 1

-- Spectra Data File

Ruthenium-Catalyzed Hydrative Cyclization of 1,5-Enynes

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General. Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under an argon atmosphere using anhydrous solvent (either distilled or passed through an activated alumina column). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using EM Science silica gel 60 F₂₅₄ plates and visualized using UV light, anisaldehyde or potassium permanganate. Flash chromatography was performed on EM Science silica gel 60 (40-63 μm) using the indicated solvent system. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , unless otherwise noted, on a Varian Mercury 300 MHz, a Varian Inova 400 MHz, a Varian Inova 500 MHz or a Varian Inova 600 MHz spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data for ^1H NMR are reported as follows chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift in ppm from the central peak of CDCl_3 (77.23 ppm). Infrared (IR) spectra were recorded on a Nicolet 730 FT-IR spectrometer and reported in frequency of the absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained from the Princeton University Mass Spectrometry Facility.

I. Preparation of Enyne Substrates

(E)-5,5-Dimethyl-oct-3-en-7-yn-2-one (1). A solution of 2,2-dimethyl-pent-4-ynal¹ (0.88 g, 8.0 mmol) and 1-(triphenylphosphoranylidene)-2-propanone (3.82 g, 12.0 mmol) was heated to reflux in toluene (20 mL) for 48 h. After cooling to ambient temperature, the solvent was evaporated and the resulting residue was triturated with hexanes. The suspension was filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **1** (0.89 g, 74%) as a colorless liquid: IR (film) 3296, 2967, 2117, 1698, 1676, 1625 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.82 (d, *J* = 16.0 Hz, 1H), 6.06 (d, *J* = 16.0 Hz, 1H), 2.28 (s, 3H), 2.25 (d, *J* = 3.0 Hz, 2H), 2.04 (t, *J* = 2.5 Hz, 1H), 1.18 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 199.3, 155.0, 128.2, 81.1, 71.1, 36.8, 31.9, 27.4, 26.3; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₀H₁₄O, 150.1045, found 150.1035.

2-Benzyl-pent-4-yn-1-ol. To diisopropylamine (15.4 mL, 110 mmol) was added *n*-butyllithium (2.5 M in Hexanes, 42.0 mL, 105 mmol) at -78 °C with stirring, then THF (100 mL) was added to dissolve all the solids generated. To this LDA solution was added ethyl hydrocinnamate (17.8 mL, 100 mmol) in 30 min. After 1 h, propargyl bromide (80% in toluene, 11.7 mL, 105 mmol) was added dropwise. The resulting mixture was

¹ Magnus, P.; Slater, M. J.; Principe, L. M. *J. Org. Chem.* **1989**, 54, 5148-5153.

kept at -78 °C for 2 h and warmed to 25 °C over 1 h. The reaction was quenched with saturated aqueous NH₄Cl, and extracted three times with EtOAc. The combined organic layers were separated, washed with 2 M aqueous HCl, saturated aqueous NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated *in vacuo* to afford ethyl 2-benzylpent-4-ynoate (21.2 g, 98%) as a clear orange yellow liquid. A solution of the ethyl ester (2.16 g, 10.0 mmol) in Et₂O (10 mL) was added to a stirred suspension of lithium aluminium hydride (0.40 g, 10.0 mmol) in Et₂O (10 mL) at 0 °C. After stirring for 30 min, the reaction mixture was quenched with saturated aqueous NH₄Cl, treated with 2 M aqueous HCl to dissolve the aluminum precipitate, and extracted with EtOAc. The combined organic layers were separated, washed with saturated aqueous NaHCO₃ and brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (20% EtOAc / Hexanes) afforded the titled alcohol² (1.05 g, 60% for 2 steps) as a light yellow oil: IR (film) 3364, 3296, 2115, 1030, 743, 701 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.10-7.36 (m, 5H), 3.70 (dd, *J* = 11.0 and 5.0 Hz, 1H), 3.65 (dd, *J* = 11.0 and 6.5 Hz, 1H), 2.74 (dd, *J* = 13.5 and 7.0 Hz, 1H), 2.69 (dd, *J* = 13.5 and 8.0 Hz, 1H), 2.31 (ddd, *J* = 17.0, 6.0 and 3.0 Hz, 1H), 2.23 (ddd, *J* = 17.0, 6.0 and 3.0 Hz, 1H), 2.04 (t, *J* = 3.0 Hz, 1H), 2.04 (m, 1H), 1.71 (s, br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 140.0, 129.4, 128.7, 126.4, 82.6, 70.5, 64.7, 41.9, 36.7, 20.0; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₂H₁₄O, 174.1045, found 174.1049.

² (a) Auger, J.; Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1977**, 140, 237-244. (b) Yamaguchi, M.; Nobayashi, Y.; Hirao, I. *Tetrahedron* **1984**, 40, 4261-4266.

2-Benzyl-pent-4-ynal. To a solution of oxalyl chloride (0.58 mL, 6.6 mmol) in CH_2Cl_2 (6 mL) was added a solution of dimethyl sulfoxide (0.94 mL, 13.2 mmol) in CH_2Cl_2 (6 mL) at -78°C . After stirring for 10 min, the alcohol obtained above (1.05 g, 6.0 mmol) in CH_2Cl_2 (6 mL) was added. The reaction mixture was stirred for 30 min and triethylamine (4.18 mL, 30.0 mmol) was added. After 5 min, the reaction mixture was warmed to 25°C . H_2O (25 mL) was added and the aqueous layers were acidified with 1% HCl in saturated aqueous NaCl, then extracted with additional CH_2Cl_2 . The combined organic layers were separated, washed with 1% HCl in saturated aqueous NaCl; saturated aqueous NaHCO_3 ; and brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to afford the aldehyde (0.98 g, 95%) as a light yellow oil: IR (film) 3291, 2732, 2119, 1727, 742, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.79 (d, $J = 1.2\text{ Hz}$, 1H), 7.20-7.33 (m, 5H), 3.11 (dd, $J = 14.0$ and 6.4 Hz , 1H), 2.94 (dd, $J = 14.0$ and 8.0 Hz , 1H), 2.78 (m, 1H), 2.43 (d, $J = 2.8\text{ Hz}$, 1H), 2.41 (dd, $J = 2.8$ and 1.2 Hz , 1H), 2.07 (t, $J = 2.8\text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 138.1, 129.3, 128.9, 126.9, 80.9, 71.2, 51.9, 34.0, 17.6; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_{12}\text{H}_{12}\text{O}$, 172.0888, found 172.0891.

(E)-5-Benzyl-oct-3-en-7-yn-2-one (12). A solution of the aldehyde prepared above (0.98 g, 5.7 mmol) and 1-(triphenylphosphoranylidene)-2-propanone (2.23 g, 8.6 mmol) in CH_2Cl_2 (20 mL) was heated to reflux for 24 h. After cooling to ambient temperature, the reaction mixture was concentrated and the resulting residue was triturated with hexanes.

The suspension was filtered and concentrated *in vacuo*. Purification by flash column chromatography (20% EtOAc / Hexanes) afforded **12** (0.81 g, 67%) as a yellow liquid: IR (film) 3292, 2118, 1697, 1676, 1627, 745, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.14-7.32 (m, 5H), 6.75 (dd, $J = 16.4$ and 7.6 Hz, 1H), 6.04 (d, $J = 16.4$ Hz, 1H), 2.89 (dd, $J = 13.6$ and 7.6 Hz, 1H), 2.79 (dd, $J = 13.6$ and 6.8 Hz, 1H), 2.69 (m, 1H), 2.22-2.36 (m, 2H), 2.23 (s, 3H), 2.07 (t, $J = 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 148.9, 138.7, 131.6, 129.4, 128.7, 126.8, 81.3, 71.1, 42.9, 39.5, 27.2, 22.7; HRMS-EI (m/z) $[\text{M}-\text{CH}_3]^+$ calc'd for $\text{C}_{14}\text{H}_{13}\text{O}$, 197.0966, found 197.0964.

(E)-4,4-Dimethyl-1-phenyl-hept-2-en-6-yn-1-one (14). A solution of 2,2-dimethyl-pent-4-ynal¹ (1.10g, 10.0 mmol) and 2-(triphenylphosphoranylidene)acetophenone (5.71 g, 15.0 mmol) in toluene (20 mL) was heated to reflux for 18 h. After cooling to ambient temperature, the reaction mixture was concentrated and triturated with hexanes. The suspension was filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **14** (0.88 g, 42%) as a yellow liquid: IR (film) 3300, 2966, 2117, 1670, 1651, 1620 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, $J = 7.5$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 7.5$ Hz, 2H), 7.03 (d, $J = 15.5$ Hz, 1H), 6.85 (d, $J = 15.5$ Hz, 1H), 2.32 (d, $J = 3.0$ Hz, 2H), 2.05 (t, $J = 3.0$ Hz, 1H), 1.25 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 191.5, 156.3, 138.2, 132.9, 128.8, 128.7, 123.0, 81.3, 71.1, 37.2, 31.8, 26.4; HRMS-EI (m/z) $[\text{M}-\text{CH}_3]^+$ calc'd for $\text{C}_{14}\text{H}_{13}\text{O}$, 197.0966, found 197.0977.

(E)-4-Benzyl-1-phenyl-hept-2-en-6-yn-1-one (16). A solution of 2-benzylpent-4-ynal (0.86 g, 5.0 mmol) and 2-(triphenylphosphoranylidene)acetophenone (2.66 g, 7.0 mmol) in toluene (20 mL) was heated to reflux for 48 h. After cooling to ambient temperature, the reaction mixture was concentrated and triturated with hexanes. The suspension was filtered and concentrated *in vacuo*. Flash chromatography (toluene) afforded **16** (0.91 g, 66%) as a yellow liquid: IR (film) 3297, 2117, 1671, 1652, 1622, 745, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.86 (m, 2H), 7.56 (m, 1H), 7.43-7.47 (m, 2H), 7.29-7.33 (m, 2H), 7.18-7.26 (m, 3H), 6.98 (dd, $J = 15.6$ and 7.6 Hz, 1H), 6.81 (d, $J = 15.6$ Hz, 1H), 2.96 (m, 1H), 2.76-2.88 (m, 2H), 2.41 (ddd, $J = 16.8$, 5.2 and 2.8 Hz, 1H), 2.34 (ddd, $J = 16.8$, 6.4 and 2.8 Hz, 1H), 2.10 (t, $J = 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.0, 150.0, 139.0, 138.0, 132.9, 129.5, 128.8, 128.7, 128.7, 126.9, 126.7, 81.6, 71.1, 43.5, 39.7, 22.9; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_{20}\text{H}_{18}\text{O}$, 274.1358, found 274.1375.

(E)-4,4-Dimethyl-hept-2-en-6-ynal (18). A solution of 2,2-dimethyl-pent-4-ynal¹ (1.10 g, 10.0 mmol) and (triphenylphosphoranylidene)acetaldehyde (3.04 g, 10.0 mmol) in toluene (20 mL) was heated to reflux for 48 h. After cooling to ambient temperature, the reaction mixture was concentrated and triturated with hexanes. The suspension was filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **18** (0.27 g, 20%) as a yellow liquid: IR (film) 3295, 2967, 2733, 2118, 1690,

1633 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.54 (d, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 15.5$ Hz, 1H), 6.11 (dd, $J = 16.0$ and 8.0 Hz, 1H), 2.29 (d, $J = 2.5$ Hz, 2H), 2.05 (t, $J = 2.5$ Hz, 1H), 1.22 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 194.6, 165.3, 130.1, 80.8, 71.4, 37.4, 31.7, 26.2; HRMS-EI (m/z) [M] $^+$ calc'd for $\text{C}_9\text{H}_{12}\text{O}$, 136.0888, found 136.0869.

(*E*)-4-Benzyl-hept-2-en-6-ynal (20). A solution of 2-benzylpent-4-ynal (1.72 g, 10.0 mmol) and (triphenylphosphoranylidene)acetaldehyde (3.65 g, 12.0 mmol) in toluene (20 mL) was heated to reflux for 48 h. After cooling to ambient temperature, the reaction mixture was concentrated and triturated with hexanes. The suspension was filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **20** (0.61 g, 31%) as a yellow liquid and the unreacted starting aldehyde (0.38g, 22%): IR (film) 3291, 2729, 2118, 1690, 1635, 745, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.51 (d, $J = 7.6$ Hz, 1H), 7.17-7.32 (m, 5H), 6.82 (dd, $J = 16.0$ and 7.2 Hz, 1H), 6.11 (dd, $J = 16.0$ and 7.6 Hz, 1H), 2.80-2.98 (m, 3H), 2.39 (ddd, $J = 16.8$, 5.2 and 2.8 Hz, 1H), 2.31 (ddd, $J = 16.8$, 6.0 and 2.8 Hz, 1H), 2.09 (t, $J = 2.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.0, 159.0, 138.4, 133.3, 129.3, 128.8, 126.9, 81.5, 71.4, 43.0, 39.3, 22.6; HRMS-EI (m/z) [M] $^+$ calc'd for $\text{C}_{14}\text{H}_{14}\text{O}$, 198.1045, found 198.1034.

(E)-4,4-Dimethyl-hept-2-en-6-ynenitrile (22). To a stirred suspension of sodium hydride (0.60 g, 15 mmol, 60% in mineral oil) in THF (20 mL) was added dropwise diethyl (cyanomethyl)phosphonate (2.43 mL, 15.0 mmol) at 0 °C. After the mixture was warmed to 25 °C over 10 min, 2,2-dimethyl-pent-4-ynal¹ (1.10 g, 10.0 mmol) was added dropwise. After stirring for 1.5 h, the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with Et₂O. The combined organic layers were separated, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **22** (0.72 g, 54%, *E/Z* = 5:1) as a colorless liquid. Characterization of (*E*)-**22**: IR (film) 3298, 2970, 2224, 2117, 1630 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.76 (d, *J* = 17.0 Hz, 1H), 5.33 (d, *J* = 16.5 Hz, 1H), 2.22 (d, *J* = 2.5 Hz, 2H), 2.06 (t, *J* = 2.5 Hz, 1H), 1.15 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 162.5, 117.8, 98.0, 80.3, 71.7, 38.0, 31.5, 25.8; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₉H₁₁N, 133.0891, found 133.0884.

4-Benzyl-hept-2-en-6-ynenitrile (24). To a stirred suspension of sodium hydride (0.32 g, 8.0 mmol, 60% in mineral oil) in THF (10 mL) was added dropwise diethyl (cyanomethyl)phosphonate (1.29 mL, 8.0 mmol) at 0 °C. The mixture was warmed to 25 °C over 10 min and 2-benzylpent-4-ynal (0.86 g, 5.0 mmol) was added dropwise. After stirring for 1.5 h, the reaction was quenched with saturated aqueous NH₄Cl and extracted

with Et₂O. The combined organic layers were separated, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc / Hexanes) afforded **24** (0.85 g, 87%, *E/Z* = 1:1) as a colorless liquid. Characterized as a 1:1 *E/Z* mixture: IR (film) 3293, 2223, 2119, 1632, 745, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.14-7.33 (m, 5H), 6.69 (dd, *J* = 16.4 and 8.0 Hz, 0.5H), 6.47 (t, *J* = 10.8 Hz, 0.5H), 5.36 (d, *J* = 11.2 Hz, 0.5H), 5.31 (dd, *J* = 16.4 and 1.2 Hz, 0.5H), 3.17 (m, 0.5H), 2.93 (dd, *J* = 13.6 and 8.0 Hz, 0.5H), 2.87 (dd, *J* = 14.0 and 7.2 Hz, 0.5H), 2.79 (dd, *J* = 13.6 and 7.2 Hz, 0.5H), 2.76 (dd, *J* = 13.6 and 6.8 Hz, 0.5H), 2.67 (m, 0.5H), 2.22-2.40 (m, 2H), 2.10 (t, *J* = 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.6, 156.1, 138.0, 137.9, 129.4, 129.3, 128.9, 128.8, 127.0, 127.0, 117.3, 115.8, 101.0, 100.7, 80.6, 80.5, 71.7, 71.5, 43.9, 42.5, 39.4, 39.2, 22.7, 22.5; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₄H₁₃N, 195.1048, found 195.1044.

Hept-2-en-6-ynenitrile (26). To diisopropylamine (1.54 mL, 11.0 mmol) was added *n*-butyllithium (1.6 M in Hexanes, 6.88 mL, 11.0 mmol) at -78 °C with stirring. THF (10 mL) was added to dissolve all the solids generated. To this LDA solution was added acetonitrile (0.56 mL, 11 mmol) in THF (5 mL) dropwise. After 30 min, 4-pentynal³ (1.00 g, 10.0 mL) was added dropwise. The resulting mixture was kept at -78 °C for 30 min and warmed to 25 °C for 1 h. The reaction was quenched with saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic layers were separated, washed

³ Adams, T. C.; Dupont, A. C.; Carter, J. P.; Kachur, J. F.; Guzewska, M. E.; Rzeszutarski, W. J.; Farmer, S. G.; Noronhablob, L.; Kaiser, C. *J. Med. Chem.* **1991**, 34, 1585-1593.

with 2 M aqueous HCl, saturated aqueous NaHCO₃, and brine; dried over MgSO₄, filtered, and concentrated *in vacuo* to afford a yellow oil. To a stirred solution of this yellow oil in CH₂Cl₂ was added triethylamine (5.58 mL, 40.0 mmol) and methanesulfonyl chloride (1.55 mL, 20.0 mmol) at -78 °C. The resulting mixture was stirred at -78 °C for 30 min and at 25 °C overnight, quenched with saturated aqueous NH₄Cl, and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and the solvent was evaporated *in vacuo* while cooled in an ice bath. Flash chromatography (30% Et₂O / Hexanes) afforded **26** (0.14 g, 13%, *E/Z*=1:2) as a yellow liquid. Characterized as a 1:2 *E/Z* mixture: IR (film) 3295, 2920, 2224, 2119, 1636 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.74 (dt, *J* = 16.0 and 7.0 Hz, 0.33H), 6.58 (dt, *J* = 11.0 and 7.5 Hz, 0.67H), 5.43 (dt, *J* = 16.0 and 2.0 Hz, 0.33H), 5.41 (dt, *J* = 11.0 and 1.5 Hz, 0.67H), 2.60-2.67 (m, 1.33H), 2.41-2.45 (m, 0.67H), 2.33-2.40 (m, 2H), 2.02 (t, *J* = 2.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 153.3, 152.6, 117.4, 115.9, 101.6, 101.3, 82.1, 82.0, 70.4, 70.3, 32.1, 30.7, 17.8, 17.4; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₇H₇N, 105.0578, found 105.0569.

(*E*)-4,4-Dimethyl-hept-2-en-6-ynoic acid ethyl ester (28). To a stirred suspension of sodium hydride (0.43 g, 11 mmol, 60% in mineral oil) in THF (20 mL) was added dropwise triethyl phosphonoacetate (2.50 mL, 12.6 mmol) at 0 °C. After 10 min, the mixture was warmed to 25 °C and 2,2-dimethyl-pent-4-ynal¹ (0.79 g, 7.2 mmol) was added dropwise. After 1.5 h, the reaction was quenched with saturated aqueous NH₄Cl,

and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Flash chromatography (10% EtOAc /) afforded **28**⁴ (0.97 g, 75%) as a colorless liquid: IR (film) 3303, 2967, 2119, 1718, 1652, 1174 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.97 (d, *J* = 16.0 Hz, 1H), 5.81 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 2.24 (d, *J* = 3.0 Hz, 2H), 2.03 (t, *J* = 3.0 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.17 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.2, 156.1, 118.8, 81.2, 71.0, 60.6, 36.8, 31.7, 26.3, 14.5; HRMS-EI (*m/z*) [M-CH₃]⁺ calc'd for C₁₀H₁₃O₂, 165.0915, found 165.0912.

3-Ethoxy-5-prop-2-ynyl-cyclopent-2-enone. To diisopropylamine (1.54 mL, 11.0 mmol) was added *n*-butyllithium (1.6 M in Hexanes, 6.88 mL, 11.0 mmol) at -78 °C with stirring. THF (10 mL) was then added to dissolve all the solids generated. To this LDA solution was added 3-ethoxy-2-cyclopentene (1.01 g, 8.00 mmol) dropwise. After 30 min, propargyl bromide (80% in toluene, 1.19 mL, 11.0 mmol) was added dropwise. The resulting mixture was kept at -78 °C for 30 min, warmed to 25 °C over 1 h, quenched with saturated aqueous NH₄Cl, and extracted with EtOAc. The combined organic layers were separated, washed with 2 M aqueous HCl, saturated aqueous NaHCO₃, and brine; dried over MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (40% EtOAc / Hexanes) afforded the titled compound⁵ (0.75 g, 57%) as a light yellow oil: IR (film) 3294, 2920, 2118, 1693, 1592, 1024 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.28 (t, *J*

⁴ Magnus, P.; Principe, L. M.; Slater, M. J. *J. Org. Chem.* **1987**, 52, 1483-1486.

⁵ Majetich, G.; Hull, K.; Desmond, R. *Tetrahedron Lett.* **1985**, 26, 2751-2754.

= 1.2 Hz, 1H), 4.07 (dq, J = 1.2 and 7.2 Hz, 2H), 2.81 (ddd, J = 15.2, 7.2 and 1.2 Hz, 1H), 2.55-2.70 (m, 3H), 2.45 (m, 1H), 1.93 (t, J = 2.4 Hz, 1H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.5, 189.3, 104.0, 81.1, 69.8, 67.9, 43.4, 34.2, 20.1, 14.3; HRMS-EI (m/z) [M] $^+$ calc'd for $\text{C}_{10}\text{H}_{12}\text{O}_2$, 164.0837, found 164.0844.

4-Prop-2-ynyl-cyclopent-2-enone (30). A solution of the enol ether prepared above (0.49 g, 3.0 mmol) in Et_2O (5 mL) was added to a stirred suspension of lithium aluminum hydride (0.11 g, 3.0 mmol) in Et_2O (5 mL) at 0 °C. After warmed to 25 °C over 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl , treated with 2 M aqueous HCl to dissolve the aluminum precipitate, and extracted with EtOAc. The combined organic layers were separated, washed with saturated aqueous NaHCO_3 , and brine; dried over MgSO_4 , filtered, and concentrated *in vacuo*. Flash chromatography (20% EtOAc / Hexanes) afforded **30**⁶ (0.24 g, 67%) as a light yellow oil: IR (film) 3289, 2916, 2117, 1713, 1589 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (dd, J = 5.5 and 2.5 Hz, 1H), 6.24 (ddd, J = 5.5, 2.0 and 0.5 Hz, 1H), 3.19 (m, 1H), 2.57 (ddd, J = 18.5, 6.5 and 0.5 Hz, 1H), 2.48 (ddd, J = 17.0, 6.0 and 2.5 Hz, 1H), 2.41 (ddd, J = 17.0, 7.0 and 2.5 Hz, 1H), 2.17 (ddd, J = 19.0, 7.5 and 1.0 Hz, 1H), 2.01 (dt, J = 1.0 and 2.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 209.1, 166.1, 135.2, 80.7, 70.7, 40.3, 40.1, 23.7.

⁶ Mayr, H.; Halberstadtkausch, I. K. *Chem. Ber.-Recl.* **1982**, 115, 3479-3515.

5-Benzyl-3-ethoxy-cyclopent-2-enone. To diisopropylamine (1.54 mL, 11.0 mmol) was added *n*-butyllithium (1.6 M in Hexanes, 6.88 mL, 11.0 mmol) at -78 °C with stirring. THF (10 mL) was then added to dissolve all the solids generated. To this LDA solution was added 3-ethoxy-2-cyclopentenone (1.26 g, 10.0 mmol) dropwise. After 30 min, benzyl bromide (1.31 mL, 11.0 mmol) was added dropwise. The resulting mixture was kept at -78 °C for 30 min, warmed to 25 °C over 1 h, quenched with saturated aqueous NH₄Cl, and extracted with EtOAc. The combined organic layers were separated, washed with 2 M aqueous HCl, saturated aqueous NaHCO₃, and brine; dried over MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (40% EtOAc / Hexanes) afforded the titled compound⁷ (1.08 g, 50%) as a yellow solid: IR (film) 2924, 1681, 1592, 1030, 745, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.18-7.31 (m, 5H), 5.26 (d, *J* = 0.5 Hz, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 3.25 (m, 1H), 2.79 (m, 1H), 2.55-2.62 (m, 2H), 2.34 (m, 1H), 1.38 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 207.4, 189.2, 139.7, 129.1, 128.7, 126.5, 104.0, 67.8, 46.8, 37.3, 34.4, 14.3; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₄H₁₆O₂, 216.1150, found 216.1157.

5-Benzyl-3-ethoxy-5-prop-2-ynyl-cyclopent-2-enone. To diisopropylamine (0.31 mL, 2.2 mmol) was added *n*-butyllithium (1.6 M in Hexanes, 1.38 mL, 2.2 mmol) at -78 °C with stirring. THF (5 mL) was then added to dissolve all the solid generated. To this

⁷ Tanyeli, C.; Ozdemirhan, D. *Tetrahedron Lett.* **2003**, 44, 7311-7313.

solution of lithium diisopropylamide was added the above benzylated ketone (0.43 g, 2.0 mmol) dropwise. After 30 min, propargyl bromide (80% in toluene, 0.26 mL, 2.2 mmol) was added dropwise. The resulting mixture was kept at -78 °C for 30 min, warmed to 25 °C over 1 h, quenched with saturated aqueous NH₄Cl, and extracted with EtOAc. The combined organic layers were separated, washed with 2 M aqueous HCl, saturated aqueous NaHCO₃, and brine; dried over MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (30% EtOAc / Hexanes) afforded and the titled compound (0.35 g, 69%) as a yellow oil and the unreacted starting material (0.08 g, 19%): IR (film) 3295, 2919, 2118, 1692, 1589, 1030, 745, 703 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.10-7.25 (m, 5H), 5.11 (s, 1H), 3.82-3.98 (m, 2H), 3.02 (d, *J* = 13.5 Hz, 1H), 2.78 (d, *J* = 13.5 Hz, 1H), 2.62 (d, *J* = 18.0 Hz, 1H), 2.57 (d, *J* = 17.5 Hz, 1H), 2.49 (dd, *J* = 16.5 and 2.5 Hz, 1H), 2.41 (dd, *J* = 17.0 and 2.5 Hz, 1H), 1.97 (t, *J* = 2.5 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 207.7, 188.8, 137.1, 130.5, 128.4, 126.9, 104.0, 80.8, 70.7, 67.8, 51.4, 41.8, 37.7, 27.4, 14.2; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₇H₁₈O₂, 254.1307, found 254.1307.

4-Benzyl-4-prop-2-ynyl-cyclopent-2-enone (32). A solution of diisobutylaluminum hydride (1.0 M in Hexanes, 0.19 mL, 0.19 mmol) was added to a solution of the enol ether prepared above (40.2 mg, 0.16 mmol) in CH₂Cl₂ (2 mL) at -78 °C. After stirred for 30 min, the reaction mixture was quenched with saturated aqueous NH₄Cl, treated with 2 M aqueous HCl to dissolve the aluminum precipitate, and extracted with EtOAc. The

combined organic layers were separated, washed with saturated aqueous NaHCO₃, and brine; dried over MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (5% EtOAc / Hexanes) afforded **32** (13.1 mg, 39%) as a colorless liquid: IR (film) 3290, 2920, 2117, 1716, 1590, 756, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 5.5 Hz, 1H), 7.23-7.32 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.13 (d, *J* = 5.5 Hz, 1H), 3.01 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 1H), 2.32-2.43 (m, 4H), 2.10 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 208.4, 169.1, 136.6, 134.0, 130.5, 128.7, 127.2, 80.5, 71.9, 48.9, 45.7, 44.3, 28.6; HRMS-EI (*m/z*) [*M*]⁺ calc'd for C₁₅H₁₄O, 210.1045, found 210.1037.

(*E*)-4-Hydroxy-hept-2-en-6-ynoic acid ethyl ester (36). To a mixture of ethyl *trans*-4-oxo-2-butenolate (1.20 mL, 10.0 mmol) and zinc dust (0.98 g, 15 mmol) in THF (20 mL) at 0 °C was added titanium tetrachloride (0.01 mL, 0.1 mmol). After 5 min, propargyl bromide (80% in toluene, 1.62 mL, 15.0 mmol) was added dropwise at 0 °C, and the resulting mixture was warmed to 25 °C over 1 h, at which time H₂O (1 mL) and hexanes (20 mL) were added. After stirred vigorously for 1 h, the suspension was filtered through a pad of silica gel and concentrated *in vacuo*. Purification by flash chromatography (20% EtOAc / Hexanes) afforded **36** (1.23 g, 73%) as a yellow oil: IR (film) 3445, 3297, 2122, 1716, 1660, 1178 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.95 (dd, *J* = 15.5 and 4.5 Hz, 1H), 6.12 (dd, *J* = 15.5 and 1.5 Hz, 1H), 4.49 (m, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 2.58 (ddd, *J* = 17.0, 5.5 and 2.5 Hz, 1H), 2.48 (ddd, *J* = 17.0, 6.5 and 2.5 Hz, 1H), 2.15 (d, br, *J* = 5.0 Hz, 1H), 2.11 (t, *J* = 2.5 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ

166.4, 147.4, 121.9, 79.4, 72.0, 69.2, 60.8, 27.3, 14.5; HRMS-EI (m/z) $[M-C_2H_5]^+$ calc'd for $C_7H_7O_3$, 139.0395, found 139.0401.

II. Preparation of the ruthenium catalyst

$[Ru_3Cl_5(dppm)_3]Cl$ (10**).** A solution of $[(p\text{-cymene})RuCl_2]_2$ (2.44 g, 4.00 mmol) and bis(diphenylphosphino)methane (dppm, 3.08 g, 8.00 mmol) in dioxane (20 mL) and H_2O (4 mL) was heated under reflux. After 12 h, an orange precipitate with a green supernatant was obtained. The precipitate was collected by suction filtration, washed with dioxane/ H_2O (5:1) until the eluent no longer retained a green color, and allowed to air dry under aspiration to afford $[Ru_3Cl_5(dppm)_3]Cl$ (**10**, 4.10 g, 92%) as an orange solid: 1H NMR (500 MHz, CD_3COCD_3) δ 7.79 (dd, $J = 12.0$ and 7.5 Hz, 24H), 7.45 (t, $J = 7.5$ Hz, 12H), 7.31 (t, $J = 7.5$ Hz, 24H), 5.19 (t, $J = 11.5$ Hz, 6H); ^{31}P NMR (202 MHz, CD_3COCD_3) δ 11.3 (s).

$[Ru_3Cl_5(dppm)_3]PF_6$ (11**).** To a stirred solution of $[Ru_3Cl_5(dppm)_3]Cl$ (**10**, 0.34 g, 0.20 mmol) in CH_2Cl_2 (5 mL) and MeOH (5 mL) was added $AgPF_6$ (61 mg, 0.24 mmol) at 25 °C. After 1 h, the orange precipitate was filtered off and washed with CH_2Cl_2 . The resulting brown filtrate was concentrated and then triturated with $CHCl_3$. The brown solid was collected by suction filtration, washed with $CHCl_3$ until the eluent no longer retained a green color, and allowed to air dry under aspiration to afford $[Ru_3Cl_5(dppm)_3]PF_6$ (**11**, 0.31 g, 87%) as an orange solid. The structure of **11** was determined by an X-ray analysis on a red-brown single crystal obtained from an acetone solution: mp 337.5–338.5 °C; 1H

NMR (500 MHz, CD₃COCD₃) δ 7.78 (dd, J = 12.0 and 7.5 Hz, 2H), 7.45 (t, J = 7.5 Hz, 12H), 7.30 (t, J = 7.5 Hz, 24H), 5.18 (t, J = 11.5 Hz, 6H); ¹³C NMR (125 MHz, CD₃COCD₃) δ 134.2 (t, J = 21 Hz), 132.3, 130.5, 128.7, 50.8 (t, J = 26 Hz); ³¹P NMR (202 MHz, CD₃COCD₃): δ 11.3 (s, 6P), -143.1 (septet, J = 707 Hz, 1P).

III. Ruthenium-Catalyzed Cyclization of 1,5-Enynes

(1Z,5E)-4,4-Dimethyl-7-oxoocta-1,5-dienyl benzoate (2). Following the literature procedure,⁸ enyne **1** (58.6 mg, 0.26 mmol) was reacted with benzoic acid (24.4 mg, 0.20 mmol) in refluxing toluene (1 mL) for 12 h in the presence of [(*p*-cymene)RuCl₂]₂ (6.1 mg, 0.01 mmol), (*p*-Cl-C₆H₄)₃P (7.3 mg, 0.02 mmol) and 4-(dimethylamino)pyridine (4.9 mg, 0.04 mmol) to afford enol benzoate **2** (38.1 mg, 70%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2963, 1731, 1675, 1623, 1266, 1110 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.36 (dd, J = 6.5 and 1.0 Hz, 1H), 6.80 (d, J = 16.5 Hz, 1H), 6.05 (d, J = 16.5 Hz, 1H), 4.97 (dt, J = 6.5 and 8.0 Hz, 1H), 2.37 (dd, J = 8.0 and 1.0 Hz, 1H), 2.22 (s, 3H), 1.14 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 199.2, 163.7, 156.4, 136.3, 133.9, 130.1, 129.4, 128.9, 128.0, 110.2, 37.5, 37.2, 27.4, 26.5; HRMS-EI (*m/z*): [M-C₃H₄O]⁺ calc'd for C₁₄H₁₆O₂, 216.1150, found 216.1144.

⁸ Goossen, L. J.; Paetzold, J.; Koley, D. *Chem. Commun.* **2003**, 706-707.

General procedure for catalyst screening experiments (Table 1). To a screw cap vial containing a ruthenium catalyst (4 μmol [Ru]), a ligand (4 μmol for diphosphane or 8 μmol for monophosphane) and H_2O (36 μL , 2 mmol) was added a solution of enyne **1** (0.20 M) and 2,5,8,11-tetraoxadodecane (0.10 M) in dioxane (0.20 mL). After sealing the vial with a screw cap, the resulting mixture was heated at 120 $^\circ\text{C}$. When the TLC analysis indicated complete consumption of the starting material (typically 12 to 24 h), the reaction mixture was cooled to ambient temperature, dried over Na_2SO_4 , filtered through a pad of silica gel, concentrated, and analyzed by ^1H NMR. All the ^1H NMR spectra were recorded on a Varian Inova 500 MHz with the recycling time 10 s and pulse flip angle 25 $^\circ$. Selected peaks for the determination of yields were: 2,5,8,11-tetraoxadodecane (δ 3.38, s, 6H), **5** (δ 0.77, s, 3H), **6** (δ 1.18, s, 6H), and **7+8+9** (δ 1.07, s, 6H). The ^1H NMR integration results were cross checked with GC-MS analyses (50 $^\circ\text{C}$ for 1 min, 50-220 $^\circ\text{C}$ with 10 $^\circ\text{C}$ per min, 220 $^\circ\text{C}$ for 10 min): **7** (R_t = 9.75 min, mw = 152); **8** (R_t = 8.15 min, mw = 138); **9** (R_t = 8.55 min, mw = 140).

General procedure for hydrative cyclization of 1,5-enynes (Table 2). To a vial equipped with a screw-cap were added an enyne substrate (0.20 mmol), $[\text{Ru}_3\text{Cl}_5(\text{dppm})_3]\text{PF}_6$ (**11**, 7.1 mg, 4 μmol , 2.0 mol %), H_2O (0.18 mL, 10 mmol), and dioxane (1.0 mL). After sealing the vial with a screw-cap, the resulting red-brown suspension was heated at 120 $^\circ\text{C}$. No special precautions were taken to exclude air or moisture, and the reaction was closely monitored by TLC analysis. Upon complete consumption of the starting enyne (typically 12 to 24 h), the yellow reaction mixture was cooled to ambient temperature, dried over Na_2SO_4 , filtered through a pad of silica gel,

and concentrated *in vacuo*. Purification by flash column chromatography afforded the cyclized product in an analytically pure form.

3,3-Dimethyl-2-(2-oxopropyl)cyclopentanone (5). Following the general procedure, the reaction of alkyne **1** (60.1 mg, 0.40 mmol) and **11** (14.2 mg, 8.0 μ mol) for 12 h gave **5** (44.4 mg, 66%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2957, 2871, 1739, 1720 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.61-2.69 (m, 2H), 2.36 (m, 1H), 2.26 (s, 3H), 2.12-2.26 (m, 2H), 1.79-1.84 (m, 2H), 1.14 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 218.8, 207.3, 56.3, 38.9, 38.0, 36.0, 34.9, 30.8, 28.3, 22.2; HRMS-EI (m/z) [M] $^+$ calc'd for $\text{C}_{10}\text{H}_{16}\text{O}$, 168.1150, found 168.1147.

(E)-5,5-dimethyloct-3-ene-2,7-dione (6). IR (film) 2964, 1717, 1675, 1623 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 6.92 (d, J = 16.0 Hz, 1H), 5.99 (d, J = 16.5 Hz, 1H), 2.54 (s, 2H), 2.26 (s, 3H), 2.10 (s, 3H), 1.17 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 207.0, 199.3, 166.9, 127.7, 54.8, 36.2, 32.0, 27.3, 27.0; HRMS-EI (m/z): [M] $^+$ calc'd for $\text{C}_{10}\text{H}_{16}\text{O}_2$, 168.1150, found 168.1147.

(2S*,3S*)-3-Benzyl-2-(2-oxopropyl)cyclopentanone (13). Following the general procedure, the reaction of alkyne **12** (42.5 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 12 h gave single diastereomer **13** (31.8 mg, 69%) as a colorless liquid after flash chromatography (10-20% EtOAc / Hexanes): IR (film) 2921, 1739, 1715, 750, 702 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 6.99-7.19 (m, 5H), 2.57-2.68 (m, 2H), 2.36-2.52 (m, 2H), 2.10-2.28 (m, 3H), 2.04 (m, 1H), 1.96 (m, 1H), 1.89 (s, 3H), 1.38 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 219.5, 206.6, 140.0, 129.1, 128.7, 126.5, 51.2, 43.1, 41.8, 41.4, 37.4, 30.2, 28.0; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_{15}\text{H}_{18}\text{O}_2$, 230.1307, found 230.1319.

3,3-Dimethyl-2-(2-oxo-2-phenyl-ethyl)cyclopentanone (15). Following the general procedure, the reaction of enyne **14** (42.4 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 12 h gave **15**⁹ (33.2 mg, 72%) as a colorless liquid after flash chromatography (2-20% EtOAc / Hexanes): IR (film) 2956, 2870, 1739, 1688 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.98-8.02 (m, 2H), 7.57 (m, 1H), 7.44-7.50 (m, 2H), 3.31 (dd, J = 17.4 and 6.3 Hz, 1H), 2.91 (m, 1H), 2.73 (dd, J = 17.7 and 5.4 Hz, 1H), 2.40 (m, 1H), 2.22 (dt, J = 19.2 and 9.9 Hz, 1H), 1.83-1.89 (m, 2H), 1.16 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 218.7, 198.7, 137.2, 133.3, 128.8, 128.4, 56.2, 39.2, 36.1, 35.0, 33.3, 28.5, 22.3; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_{15}\text{H}_{18}\text{O}_2$, 230.1307, found 230.1299.

⁹ Mikami, K.; Okubo, Y. *Synlett* **2000**, 491-492.

(2S*,3S*)-3-Benzyl-2-(2-oxo-2-phenyl-ethyl)cyclopentanone (17). Following the general procedure, the reaction of enyne **16** (54.9 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 12 h gave single diastereomer **17** (36.8 mg, 63%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2922, 1738, 1685, 747, 701 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, J = 7.0 Hz, 2H), 7.55 (d, J = 7.5 Hz, 1H), 7.43 (dd, J = 8.0 and 7.5 Hz, 2H), 7.23 (dd, J = 7.5 and 7.0 Hz, 2H), 7.16 (d, J = 7.5 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 3.20 (dd, J = 18.0 and 4.5 Hz, 1H), 3.15 (dd, J = 8.0 and 4.5 Hz, 1H), 2.83 (dd, J = 13.5 and 6.5 Hz, 1H), 2.72 (dd, J = 13.5 and 8.0 Hz, 1H), 2.30-2.46 (m, 4H), 2.12 (m, 1H), 1.55 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 219.6, 198.0, 140.0, 136.8, 133.4, 129.1, 128.7, 128.7, 128.2, 126.4, 51.2, 43.3, 41.4, 37.6, 37.3, 28.0; HRMS-EI (m/z) [M] $^+$ calc'd for $\text{C}_{20}\text{H}_{20}\text{O}_2$, 292.1463, found 292.1467.

(2,2-Dimethyl-5-oxocyclopentyl)acetaldehyde (19). Following the general procedure, the reaction of enyne **18** (54.5mg, 0.40 mmol) and **11** (14.2 mg, 8.0 μ mol) for 12 h gave **19**¹⁰ (29.6 mg, 48%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2957, 2871, 2728, 1740, 1724 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.88 (t, J = 1.0 Hz, 1H), 2.61-2.70 (m, 2H), 2.36 (m, 1H), 2.14-2.30 (m, 2H), 1.80-1.88 (m, 2H), 1.14 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 218.4, 201.1, 55.2,

¹⁰ Tsunoi, S.; Ryu, I.; Yamasaki, S.; Fukushima, H.; Tanaka, M.; Komatsu, M.; Sonoda, N. *J. Am. Chem. Soc.* **1996**, 118, 10670-10671.

39.0, 38.8, 36.1, 35.0, 28.4, 22.1; HRMS-EI (m/z) [M+H]⁺ calc'd for C₉H₁₅O₂, 155.1072, found 155.1064.

(2S*,3S*)-(2-Benzyl-5-oxocyclopentyl)acetaldehyde (21). Following the general procedure, the reaction of alkyne **20** (39.7 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μmol) for 12 h gave single diastereomer **21** (20.3 mg, 47%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2921, 2729, 1739, 1721, 753, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.65 (s, 1H), 7.14-7.30 (m, 5H), 2.83 (dd, *J* = 14.0 and 4.5 Hz, 1H), 2.69 (dd, *J* = 14.0 and 8.0 Hz, 1H), 2.64 (dd, *J* = 19.0 and 4.0 Hz, 1H), 2.58 (dd, *J* = 19.0 and 4.0 Hz, 1H), 2.39 (dd, *J* = 19.0 and 8.5 Hz, 1H), 2.20-2.30 (m, 3H), 2.09 (m, 1H), 1.53 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 218.8, 200.1, 139.6, 129.1, 128.7, 126.6, 50.0, 43.5, 42.4, 41.1, 37.2, 27.9; HRMS-EI (m/z) [M]⁺ calc'd for C₁₄H₁₆O₂, 216.1150, found 216.1147.

(2,2-Dimethyl-5-oxocyclopentyl)acetonitrile (23). Following the general procedure, the reaction of enyne **22** (53.3 mg, 0.40 mmol, *E/Z*=5:1) and **11** (14.2 mg, 8.0 μmol) for 12 h gave **23** (44.8 mg, 74%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2960, 2874, 2247, 1742 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.70 (dd, *J* = 17.0 and 4.5 Hz, 1H), 2.37 (dd, *J* = 19.5 and 9.0 Hz, 1H), 2.26 (dd, *J* = 20.0 and 8.5 Hz, 1H), 2.16 (dd, *J* = 17.0 and 8.5 Hz, 1H), 2.22 (m, 1H), 1.76-1.90 (m, 2H), 1.35 (s,

3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 215.8, 118.9, 56.5, 39.5, 35.9, 34.5, 28.7, 21.4, 12.7; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_9\text{H}_{13}\text{NO}$, 151.0997, found 151.1003.

(2S*,3S*)-(2-Benzyl-5-oxocyclopentyl)acetonitrile (25). Following the general procedure, the reaction of alkyne **24** (39.1 mg, 0.20 mmol, $E/Z=1:1$) and **11** (7.1 mg, 4.0 μmol) for 12 h gave single diastereomer **25** (34.6 mg, 81%) as a colorless liquid after flash chromatography (10% EtOAc / Hexanes): IR (film) 2927, 2247, 1744, 754, 703 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.22-7.37 (m, 5H), 3.01 (dd, $J = 13.5$ and 6.0 Hz, 1H), 2.83 (dd, $J = 13.5$ and 8.0 Hz, 1H), 2.65 (dd, $J = 17.0$ and 5.0 Hz, 1H), 2.32-2.48 (m, 2H), 2.33 (dd, $J = 17.0$ and 5.5 Hz, 1H), 2.04-2.22 (m, 3H), 1.60 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 215.9, 138.8, 129.2, 129.0, 127.0, 117.8, 50.8, 43.3, 40.7, 37.2, 27.2, 16.4; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_{14}\text{H}_{15}\text{NO}$, 213.1154, found 213.1164.

(2-Oxocyclopentyl)acetonitrile (27). Following the general procedure, the reaction of alkyne **26** (42.1 mg, 0.40 mmol, $E/Z=1:2$) and **11** (14.2 mg, 8.0 μmol) for 12 h gave **27**¹¹ (33.5 mg, 68%) as a colorless liquid after flash chromatography (20% EtOAc / Hexanes): ^1H NMR (500 MHz, CDCl_3) δ 2.72 (m, 1H), 2.36-2.50 (m, 4H), 2.08-2.22 (m, 2H), 1.86 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 216.0, 117.9, 45.4, 37.0, 28.9, 20.1, 17.2.

¹¹ Hernandez, R.; Melian, D.; Prange, T.; Suarez, E. *Heterocycles* **1995**, 41, 439-454.

(2,2-Dimethyl-5-oxocyclopentyl)acetic acid ethyl ester (29a). Following the general procedure, the reaction of alkyne **28** (36.0 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 12 h gave **29a** (8.9 mg, 23%) as a colorless liquid and **29b** (15.5 mg, 46%) as a yellow liquid after flash chromatography (10-80% EtOAc / Hexanes): IR (film) 2958, 2926, 2853, 1737, 1649, 1175 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.17 (dq, $J = 3.0$ and 7.0 Hz, 2H), 2.48-2.56 (m, 2H), 2.35 ($J = 15.6, 7.5$ and 3.5 Hz, 1H), 2.12-2.24 (m, 2H), 1.75-1.84 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.16 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 218.2, 173.1, 60.9, 57.2, 39.1, 36.0, 34.9, 29.5, 28.4, 22.0, 14.4; HRMS-EI (m/z) $[\text{M}-\text{CH}_3]^+$ calc'd for $\text{C}_{10}\text{H}_{15}\text{O}_3$, 183.1021, found 183.1015.

(2,2-Dimethyl-5-oxocyclopentyl)acetic acid (29b). IR (film) 2958, 2927, 2871, 1740, 1711, 1173 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.49-2.59 (m, 2H), 2.39 (m, 1H), 2.17-2.27 (m, 2H), 1.80-1.85 (m, 2H), 1.20 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 218.9, 177.9, 56.9, 39.2, 36.0, 34.9, 29.3, 28.3, 21.8; HRMS-EI (m/z) $[\text{M}]^+$ calc'd for $\text{C}_9\text{H}_{14}\text{O}_3$, 170.0943, found 170.0945.

cis-Hexahydro-pentalene-1,5-dione (31). Following the general procedure, the reaction of alkyne **30** (24.0 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 24 h gave single diastereomer **31**¹² (14.4 mg, 52%) as a colorless liquid after flash chromatography (20-30% EtOAc / Hexanes): IR (film) 2923, 1739 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.07 (m, 1H), 2.89 (m, 1H), 2.34-2.58 (m, 5H), 2.27 (m, 1H), 2.04 (dd, J = 19.0 and 7.5 Hz, 1H), 1.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 219.5, 216.9, 48.9, 43.2, 39.2, 37.3, 36.6, 26.1; HRMS-EI (m/z) [M]⁺ calc'd for $\text{C}_8\text{H}_{10}\text{O}_2$, 138.0681, found 138.0686.

cis-3a-Benzyl-hexahydro-pentalene-1,5-dione (33). Following the general procedure, the reaction of alkyne **32** (10.6 mg, 0.050 mmol) and **11** (1.8 mg, 1.0 μ mol) for 24 h gave single diastereomer **33** (8.6 mg, 75%) as a colorless liquid after flash chromatography (10-20% EtOAc / Hexanes): IR (film) 2919, 1741, 747, 705 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.36 (m, 3H), 7.12-7.18 (m, 2H), 2.87 (d, J = 13.6 Hz, 1H), 2.83 (d, J = 13.6 Hz, 1H), 2.62 (m, 1H), 2.29-2.55 (m, 5H), 2.04-2.18 (m, 2H), 1.98 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 219.1, 215.9, 136.9, 130.3, 128.9, 127.3, 53.8, 48.9, 47.8, 45.3, 39.4, 35.9, 30.3; HRMS-EI (m/z) [M]⁺ calc'd for $\text{C}_{15}\text{H}_{16}\text{O}_2$, 228.1150, found 228.1150.

¹² Although partial (ref 11a) and full (ref 11b) characterizations of diketone **31** have been reported, our spectral data of **31** display significant disparities. (a) Eckersley, T. J.; Parker, S. D.; Rogers, N. A. J. *Tetrahedron* **1984**, 40, 3749-3758. (b) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, 112, 3100-3109.

(5-Oxocyclopent-1-en-1-yl)acetic acid ethyl ester (35). Following the general procedure, the reaction of alkyne **34** (33.6 mg, 0.20 mmol) and **11** (7.1 mg, 4.0 μ mol) for 20 h gave **35** (17.8 mg, 53%) as a colorless liquid after flash chromatography (20% EtOAc / Hexanes)¹³: ¹H NMR (500 MHz, CDCl₃) δ 7.60 (m, 1H), 4.16 (q, J = 7.0 Hz, 2H), 3.21-3.25 (m, 2H), 2.62-2.68 (m, 2H), 2.42-2.45 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 208.7, 170.8, 160.8, 139.3, 61.2, 34.2, 30.6, 27.1, 14.4.

¹³ Bernady, K. F.; Poletto, J. F.; Nocera, J.; Mirando, P.; Schaub, R. E.; Weiss, M. J. *J. Org. Chem.* **1980**, 45, 4702-4715.