Tandem Enyne Metathesis and Claisen Rearrangement: A Versatile Approach to Conjugated Dienes of Variable Substitution Patterns

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General Information

All reactions were conducted under an argon atmosphere unless otherwise noted. Dichloromethane (CH₂Cl₂) (alumina), benzene and toluene (alumina + Q5) were drawn from a solvent purifier immediately prior to use. Dry tetrahydrofuran (THF) was obtained from a still (Na/benzophenone). Reagent

grade methanol was used for trituration and the cycloaddition reaction. Ruthenium [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (phenylmethylene)(tricyclohexylphosphine) (Grubbs' second generation catalyst) was obtained from Materia Inc. (Pasadena, CA). 1,5-Cyclooctadiene (COD) was distilled from sodium prior to use. Amines were purchased from Aldrich and distilled from CaH_2 and stored over KOH. Polymer grade ethylene gas was obtained from Matheson Tri-gas. Triethylchlorosilane was obtained from Gelest, Inc. and distilled under reduced pressure prior to use. *N,N*-dimethylaminopyridine was obtained from Acros. The remaining reagents were purchased from Aldrich and distilled when applicable. Column chromatography was carried out on Bodman industries silica gel 60 (230 – 400 mesh). Thin layer chromatography was developed on glass-backed EM science F254 silica plates and made visible with UV light, iodine, 1.7% KMnO_4 solution in water or Hanessian's stain (5 %_{w/v} cerium molybdate in 0.72 M H_2SO_4). ^1H -NMR spectra were recorded at 500 MHz and ^{13}C -NMR spectra at 125 MHz in CDCl_3 . ^1H -NMR spectra were referenced on the TMS signal for CDCl_3 . The ^{13}C -NMR spectra were referenced at 77.0 ppm for CDCl_3 . High resolution mass spectra were obtained using a ThermoFinnigan MAT95XL. Gas chromatography was performed on a Shimadzu GC-17A FID Gas chromatograph (thermal program: 40 °C, 4 min; 25 °C/min to 280 °C; 280 °C, 16.4 min) using an Agilent Technologies 19091J-433 capillary column (30m X 0.250 mm, 0.25 micron). FT-IR spectra were recorded on a Nicolet Impact series 420 IR. Optical rotations were measured on a Jasco DIP-370 polarimeter using the sodium D line at 589 nm in a 50 mm cell held at 25 °C.

Table 1 Acyclic Diene/Ireland Claisen Rearrangement

(E)-2-Methylene-1-phenyl-oct-3-enyl acetate (2B, metathesis step, entry 1). As reported in the literature:¹ To an oven-dried 50 mL Schlenk tube was added 500 mg of alkyne **2A** (2.87 mmol), 3.2 mL of 1-hexene (9 equiv, 25.86 mmol), and 3 mL of dichloromethane. The clear solution was stirred for 5 min and 122 mg Grubbs' catalyst **1** (0.14 mmol, 5 mol%) was added as a single portion. Then reaction was heated at reflux for 18 h, cooled to room temperature, concentrated *in vacuo* (rotary evaporator), and loaded directly onto a silica gel column (3 X 15 cm). Elution with 5% ethyl acetate/hexane gave 500 mg of **2B** (68%) as a clear oil. Analytical TLC (10% ethyl acetate/hexane) R_f 0.36. ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 5.95 (d, J = 16.5 Hz, 1H), 5.67 (dt, J = 16.5 Hz, 15.5 Hz, 1H), 5.19 (s, 1H), 5.15 (s, 1H), 2.07 (s, 3H), 1.99-1.95 (m, 2H), 1.27-1.15 (m, 4H), 0.81 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.76, 144.12, 138.58, 132.83, 128.47, 128.29, 128.01, 127.54, 113.95, 74.90, 32.60, 31.12, 21.96, 21.10, 13.76; FT-IR (thin flim, cm⁻¹) 3033, 2928, 1743, 1371, 1232, 1024; High resolution ESI molecular ion calcd for C₁₇H₂₂O₂ 258.1620, found 258.1614 (C₁₇H₂₂O₂), error 2.3 ppm.

(Z)-4-Benzylidenehex-5-enoic acid (2C, Claisen step, entry 1): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.23 mL LiHMDS (1M solution in THF), and 260 μ L HMPA, the yellow solution was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. Then, a solution of 300 mg (1.49 mmol) of diene **2B**, and 336 mg (2.23 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78 °C over a 5 min period. Orange solution was allowed to stir at -78 °C for 15 min then warmed to room temperature over a period of 1 h. Reaction was then heated to reflux and stirred for a further 2 h before cooled to room temperature. At this time 3 mL of 1M AcOH_(aq) was added and the reaction was stirred at room temperature for 1 h. The reaction was diluted with 15 mL of dichloromethane, washed 3 x 15 mL water, 15 mL of 1M NH₄Cl; aqueous layers were extracted with 3 x 15 mL of dichloromethane. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a silica gel column (2 x 10 cm). Gradient elution 10-50% ethyl acetate/hexane containing 1% AcOH gave 247 mg of **2C** (82%) as a slightly yellow oil. Analytical TLC (30% ethyl acetate/hexane) R_f 0.14. ¹H NMR (500 MHz, CDCl₃) δ 11.9 (bs, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.27-7.23 (m, 3H), 6.84 (dd, J = 17.5 Hz, 11 Hz, 1H), 5.68 (t, J = 7.5 Hz, 1H), 5.39 (d, J = 17.5 Hz, 1H), 5.28 (d, J = 11.0 Hz, 1H), 3.59 (d, J = 7.5 Hz, 2H), 2.65 (t, J = 6.0 Hz, 2H), 2.62 (t, J = 6.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 179.79, 140.45, 135.39, 131.94, 129.39, 128.45, 128.33, 126.00, 114.53, 33.50, 33.46, 28.24; FT-IR (thin flim, cm⁻¹)

¹ Smulik, J.A.; Diver, S.T. *J. Org. Chem.* **2000**, *65*,1788-1792.

¹) 3027, 2669, 1708, 1416, 1303, 909; High resolution ESI molecular ion calcd for C₁₄H₁₆O₂ 216.1150, found 216.1145 (C₁₄H₁₆O₂), error 3.1 ppm.

(Z)-Methyl 4-benzylidenehex-5-enoate (3C), Claisen step, entry 2): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.23 mL LiHMDS (1M solution in THF), and 260 μ L HMPA, the solution was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. A solution of 300 mg (1.49 mmol) of diene **2B**, and 336 mg (2.23 mmol) of TBSCl in 1 mL of THF was then added dropwise via syringe at -78 °C over a 5 min period. The orange solution was allowed to stir at -78 °C for 15 min, warmed to room temperature and stirred at that temperature for 3 h. Next, 25 mL of water were added and extracted with 3 x 20 mL of pentane. The organic layers were combined, concentrated *in vacuo* (rotary evaporator) to an orange oil that was dissolved in 3 mL of HMPA, to which 223 mg (2.23 mmol) of KHCO₃, and 210 mg (2.23 mmol) of KF·2H₂O were added and stirred 30 min at which time 185 μ L (2.98 mmol) of MeI were added and reaction was stirred a further 15 h at room temperature. Next, 30 mL of water was added and extracted 3 x 30 mL of pentane. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a silica gel column (2 x 10 cm). Elution 10% ethyl acetate/hexane gave 168 mg of **3C** (52%) as a slightly yellow oil. Analytical TLC (10% ethyl acetate/hexane) R_f 0.37. ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.28-7.26 (m, 3H), 6.81 (dd, J = 17.5 Hz, 11.0 Hz, 1H), 6.55 (s, 1H), 5.43 (d, J = 17.5 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H), 3.73 (s, 3H), 2.76 (t, J = 7.5 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 173.52, 137.07, 136.99, 133.43, 129.85, 129.28, 127.98, 126.73, 115.26, 51.50, 33.43, 28.92; FT-IR (thin flim, cm⁻¹) 2951, 1740, 1437, 1236, 1168, 910; High resolution ESI molecular ion calcd for C₁₄H₁₆O₂ 216.1150, found 216.1145 (C₁₇H₂₃O₂, M+H), error 1.9 ppm.

(Z)-6-Phenyl-4-vinylhex-4-enoic acid (4C), Claisen step, entry 3): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.08 mL LiHMDS (1M solution in THF), and 242 μ L HMPA, the yellow solution was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. Then a solution of 300 mg (1.39 mmol) of diene **4B**,² and 314 mg (2.08 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78 °C over a 5 min period. The orange solution was allowed to stir at -78 °C for 15 min, then warmed to room temperature over a period of 1 h. The reaction was then heated to reflux and stirred for a further 2 h before being cooled to room temperature. Then 3 mL of 1M AcOH_(aq) was added and reaction was stirred at room temperature for 1 h. The reaction was diluted with 15 mL of dichloromethane, washed 3 x 15 mL water, 15 mL of 1M NH₄Cl; aqueous layers were extracted with 3 x 15 mL of dichloromethane. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a silica gel column (2 x 10 cm). Gradient elution

10-50% ethyl acetate/hexane containing 1% AcOH gave 245 mg of **4C** (82%) as a slightly yellow oil. Analytical TLC (30% ethyl acetate in hexanes) R_f 0.23. ^1H NMR (500 MHz, CDCl_3) δ 11.9 (bs, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.33-7.31 (m, 3H), 6.86 (dd, J = 17.0 Hz, 11.0 Hz, 1H), 6.61 (s, 1H), 5.48 (d, J = 17.0 Hz, 1H), 5.29 (d, J = 11.0 Hz, 1H), 2.81 (t, J = 6.0 Hz, 2H), 2.73 (t, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 179.77, 136.99, 136.82, 133.47, 130.05, 129.35, 128.03, 126.83, 115.32, 33.47, 28.63; FT-IR (thin flim, cm^{-1}) 3022, 2667, 1708, 1417, 1301, 911; High resolution ESI molecular ion calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$ 202.0994, found 202.0988 ($\text{C}_{14}\text{H}_{14}\text{O}_2$), error 1.4 ppm.

(Z)-7-phenyl-4-vinylhept-4-enoic acid (5C, Claisen step, entry 4): To an oven-dried Schlenk tube (50 mL) equipped with a magnetic stirbar was charged with 0.75 mL of 1.0 M LiHMDS in THF (0.75 M, 1.5 equiv). This was cooled to $-78\text{ }^\circ\text{C}$ (dry ice acetone bath) for 15 min. 125 μL HMPA was added to this solution maintained at $-78\text{ }^\circ\text{C}$. In a separate round bottom flask (10 mL) was dissolved a mixture of diene **5B**¹ (0.5 mmole, 1.0 equiv) and TBSCl (0.75 mmole, 1.5 equiv) in 0.5 mL of THF. This solution was added dropwise with gas tight syringe into LiHMDS-HMPA solution maintained at $-78\text{ }^\circ\text{C}$ over 3-4 min. The flask was rinsed with additional 300 μL of THF and this solution was added to the solution of the base and HMPA. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 20 min and then slowly warmed to RT. It was stirred at RT for 24 h. The reaction was quenched by addition of 5 mL of saturated NH_4Cl solution. The reaction mixture was poured into a separatory funnel containing 20 mL of diethyl ether and 20 mL of saturated NH_4Cl solution. The organic layer was washed with distilled water (2 X 20 mL) and finally with saturated NH_4Cl solution. The organic layer was separated, dried over anhydrous Na_2SO_4 and the diethyl ether was removed *in vacuo* (rotary evaporator). The pale brown oil thus obtained was redissolved in 5 mL THF and 0.5 mL of 1.0 M HCl was added to it. This was stirred at RT for 45 min. The reaction was quenched by pouring the reaction mixture into a separatory funnel containing 20 mL distilled water and 20 mL diethyl ether. The organic layer was washed with distilled water (2 X 20 mL) and finally with saturated NH_4Cl solution (20 mL). It was dried using anhydrous Na_2SO_4 and the solvent removed *in vacuo* (rotary evaporator). The yellow oil thus obtained was purified by using silica gel flash column chromatography. Gradient elution with 10% ethyl acetate in hexanes (100 mL) followed by 20% ethyl acetate in hexanes (100 mL) afforded the desired carboxylic acid **5C** as pale yellow oil (67 mg, 58% yield). Analytical tlc: 0.33 (50% ethyl acetate in hexanes). ^1H - NMR (500 MHz, CDCl_3 , ppm) δ 7.28 – 7.25 (m, 2H), 7.19 – 7.16 (m, 3H), 6.63-6.57 (m, 1H), 5.47 (t, J = 7.5 Hz, 1H), 5.21 (d, J = 17.5 Hz, 1H), 5.09 (d, J = 12.0 Hz, 1H), 2.67 (t, J = 7.5 Hz, 2H), 2.55 – 2.44 (m, 6H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 180.0, 141.6, 135.0, 131.9,

130.3, 128.4, 128.3, 125.9, 113.8, 35.9, 33.5, 29.2, 28.0; FT-IR (thin film, cm^{-1}) 2874, 1721, 1545, 913; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$ 230.1301, found 230.1299, error 1.1 ppm.

(Z)-4-Benzylidene-5-methylhex-5-enoic acid (6C, Claisen step, entry 5): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.08 mL LiHMDS (1M solution in THF), and 242 μL HMPA, yellow solution was cooled to -78°C (dry ice/acetone) and stirred for 5 min. A solution of 300 mg (1.39 mmol) of diene **6B**,² and 313 mg (2.08 mmol) of TBSCl in 2 mL of THF were added dropwise via syringe at -78°C over a 5 min period. The orange solution was stirred at -78°C for 15 min then allowed to warm to room temperature over a period of 1 h. The reaction mixture was then heated to reflux and stirred for a further 2 h, then cooled to room temperature. Next 3 mL of 1M $\text{AcOH}_{(\text{aq})}$ was added and stirring was continued at room temperature for 1 h. The reaction was diluted with 15 mL of dichloromethane, washed 3 x 15 mL water, 15 mL of 1M NH_4Cl ; the aqueous layers were back-extracted with 3 x 15 mL of dichloromethane. The organics were combined, dried (Na_2SO_4), filtered, concentrated *in vacuo* (rotary evaporator) and loaded directly onto a silica gel column (2 X 10 cm). Gradient elution with 10-50% ethyl acetate/hexane containing 1% AcOH gave 254 mg of **6C** (85%) as an inseparable 5:1 (*Z:E*) mixture of alkene isomers as a slightly yellow oil. Analytical TLC (30% ethyl acetate/hexane) R_f 0.12. ^1H NMR (500 MHz, CDCl_3) **Major Z:** δ 7.39 (d, $J = 7.0$ Hz, 2H), 7.28 (t, $J = 7.0$ Hz, 1H), 7.21 (d, $J = 7.0$ Hz, 2H), 6.27 (s, 1H), 5.09 (s, 1H), 4.90 (s, 1H), 2.64 (t, $J = 6.5$ Hz, 2H), 2.57 (t, $J = 6.5$ Hz, 2H), 1.86 (s, 3H); **Minor E:** δ 7.39 (d, $J = 7.0$ Hz, 2H), 7.28 (t, $J = 7.0$ Hz, 1H), 7.21 (d, $J = 7.0$ Hz, 2H), 6.71 (s, 1H), 5.21 (s, 1H), 5.14 (s, 1H), 2.84 (t, $J = 8.0$ Hz, 2H), 2.64 (t, $J = 8.0$ Hz, 2H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 179.60, 143.99, 142.51, 137.29, 128.45, 127.97, 126.53, 125.63, 115.45, 33.57, 32.72, 22.15; FT-IR (thin film, cm^{-1}) 2966, 1709, 1444, 1298, 901; High resolution ESI molecular ion calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$ 216.1150, found 217.1215 ($\text{C}_{14}\text{H}_{17}\text{O}_2$ $\text{M}+\text{H}$), error 3.5 ppm. An nOe enhancement of the resonance at δ 2.05 ppm was observed when the singlet at δ 6.71 ppm was irradiated. No nOe enhancement was observed when the singlet at δ 6.27 ppm was irradiated.

(Z)-Methyl 4-benzylidene-6-ethoxyhex-5-enoate (7C, Claisen step, entry 6): To an oven-dried 100 mL Schlenk tube at room temperature was added 2.92 mL LiHMDS (1M solution in THF), and 339 μL HMPA, the solution was cooled to -78°C (dry ice/acetone) and stirred for 5 min. Then, a solution of 480 mg (1.49

² Smulik, J.A.; Diver, S. T. *Org. Lett.* **2000**, *2*, 2271-2274.

mmol) of diene **7B**³, and 441 mg (2.23 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78 °C over a 5 min period. The orange solution was allowed to stir at -78 °C for 15 min, warmed to room temperature and stirred at that temperature for 30 h. Next, 20 mL of water were added and extracted with 4 x 25 mL of pentane. Organic layers were combined, concentrated *in vacuo* (rotary evaporator) to an orange oil (808 mg) that was dissolved in 4 mL of HMPA, to which 293 mg (2.92 mmol) of KHCO₃, and 275 mg (2.92 mmol) of KF·2H₂O were added simultaneously and stirred 30 min at which time 242 μ L (3.90 mmol) of MeI were added and the reaction was stirred a further 15 h at room temperature. A 30 mL of water was added and the aqueous layer was extracted 4 x 30 mL of pentane. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a deactivated (5% triethylamine) silica gel column (2 x 10 cm). Gradient elution 5-10% ethyl acetate/hexane gave 305 mg of **7C** (60%) as an inseparable 1.3:1 (*E:Z*) mixture of alkene isomers as a slightly yellow oil. Analytical TLC (10% ethyl acetate/hexane) R_f 0.15. ¹H NMR (500 MHz, CDCl₃) **Major E**: δ 7.26-7.19 (m, 3H), 7.14-7.11 (m, 2H), 6.67 (d, J = 13.0 Hz, 1H), 6.14 (s, 1H), 5.96 (d, J = 13.0 Hz, 1H), 3.74 (q, J = 14.0 Hz, 7.0 Hz, 2H), 3.64 (s, 3H), 2.59-2.53 (m, 2H), 2.50 (t, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H); **Minor Z**: δ 7.26-7.19 (m, 3H), 7.14-7.11 (m, 2H), 6.15 (s, 1H), 5.93 (d, J = 7.0 Hz, 1H), 5.16 (d, J = 7.0 Hz, 1H), 3.80 (q, J = 14.0 Hz, 7.0 Hz, 2H), 3.62 (s, 3H), 2.80 (t, J = 7.5 Hz, 2H), 2.59-2.53 (m, 2H), 1.22 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 178.11, 173.64, 149.37, 146.54, 138.13, 137.88, 136.09, 134.84, 129.13, 129.00, 128.05, 127.89, 127.00, 126.14, 126.12, 125.00, 103.86, 102.74, 68.74, 65.67, 51.54, 51.29, 34.26, 33.72, 32.94, 29.91, 15.15, 14.77; FT-IR (thin flim, cm⁻¹) 2942, 1743, 1633, 1440, 1236, 1175; High resolution ESI molecular ion calcd for C₁₆H₂₀O₃ 260.1412, found 283.1305 (C₁₆H₂₀O₃, M+Na), error 1.6 ppm.

Scheme S1. Saponification of **8B**

(E)-3-Methylene-non-4-en-2-yl acetate (8B, metathesis step, entry 7): To an oven-dried 50 mL Schlenk tube was added 150 mg of alkyne **8A** (1.34 mmol), 1.5 mL of 1-hexene (9 equiv, 12.05 mmol), and 3 mL of dichloromethane. The clear solution was stirred for 5 min and 57 mg Grubbs' catalyst **1** (0.07 mmol, 5 mol%) was added as a single portion. The reaction was heated at reflux for 18 h, cooled to room temperature, concentrated *in vacuo* (rotary evaporator), and loaded

³ Giessert, A. J.; Snyder, L.; Markham, J.; Diver, S. T. *Org. Lett.* **2003**, *5*, 1793-1796.

directly onto a silica gel column (3 X 15 cm). Elution with 5% ethyl acetate/hexane gave 240 mg of **8B** (91%) as a clear oil. The product was determined to be greater than 90% pure by proton NMR. This product was fully characterized as the alcohol **S1**. An analytically pure sample was obtained by saponification (KOH/MeOH, rt, 1 h) and separation of the by-product by chromatography on silica gel (2 x 10 cm). (10% ethyl acetate/hexanes). **Alcohol S1**: Analytical TLC (10% ethyl acetate/hexane) R_f 0.15, ^1H NMR (500 MHz, CDCl_3) δ 6.00 (d, J = 16.0 Hz, 1H), 5.78 (dt, J = 16.0 Hz, 14 Hz, 1H), 5.09 (s, 1H), 4.96 (s, 1H), 4.53 (q, J = 6.5 Hz, 1H), 2.07 (q, J = 6.5 Hz, 2H), 1.69 (bs, 1H), 1.38-1.27 (m, 7H), 0.87 (t, J = 7.0, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.31, 131.34, 129.11, 110.56, 67.75, 32.75, 31.41, 22.79, 22.21, 13.87; FT-IR (thin flim, cm^{-1}) 3328, 2966, 2633, 2874, 1466, 1374, 985; High resolution ESI molecular ion calcd for $\text{C}_{10}\text{H}_{17}\text{O}$ (M-H) 153.1274, found 153.1273 ($\text{C}_{10}\text{H}_{17}\text{O}$; M-H), error 0.1 ppm. **By-Product S2**: Analytical TLC (10% ethyl acetate/hexane) R_f 0.17. ^1H NMR (500 MHz, CDCl_3) δ 6.19 (d, J = 16.5 Hz, 1H), 5.74 (dt, J = 16.5 Hz, 14 Hz, 1H), 5.53 (t, J = 8.0 Hz, 1H), 4.53 (q, J = 4.5 Hz, 1H), 2.15-2.09 (m, 4H), 1.46 (bs, 1H), 1.39-1.27 (m, 11H), 0.89 (t, J = 7.5, 3H), 0.87 (t, J = 7, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.13, 131.60, 126.54, 124.49, 68.83, 33.29, 31.94, 31.65, 27.04, 22.80, 22.37, 22.24, 13.94, 13.90; FT-IR (thin flim, cm^{-1}) 3368, 2960, 2874, 2854, 1466, 966; High resolution ESI molecular ion calcd for $\text{C}_{14}\text{H}_{26}\text{O}$ 210.1986, found 210.1976 ($\text{C}_{14}\text{H}_{26}\text{O}$), error 0.9 ppm.

(4Z, 5E)-4-Ethylidenedec-5-enoic acid (8C, Claisen step, entry 7): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.3 mL LiHMDS (1M solution in THF), 266 μL HMPA, yellow solution was cooled to -78°C (dry ice/acetone) and stirred for 5 min. A solution of 300 mg (1.53 mmol) of diene **8B**, and 313 mg (2.3 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78°C over a 5 min period. The orange solution was allowed to stir at -78°C for 15 min, then warmed to room temperature and stirred at that temperature for 30 h. Then 3 mL of 1M $\text{AcOH}_{(\text{aq})}$ was added and reaction was stirred at room temperature for 1 h. The reaction was diluted with 15 mL of dichloromethane, washed 3 x 15 mL water, 15 mL of 1M NH_4Cl ; aqueous layers were extracted with 3 x 15 mL of dichloromethane. The organic layers were combined, dried (Na_2SO_4), filtered, concentrated *in vacuo* (rotary evaporator) and loaded directly onto a silica gel column (2 X 10 cm). Gradient elution 10-50% ethyl acetate/hexane gave 182 mg of **8C** (61%) as a slightly yellow oil. Analytical TLC (30% ethyl acetate/hexane) R_f 0.12, ^1H NMR (500 MHz, CDCl_3) δ 6.29 (d, J = 15.5 Hz, 1H), 5.67 (dt, J = 15.5 Hz, 14.5 Hz, 1H), 5.35 (q, J = 14.5 Hz, 7 Hz, 1H), 2.48 (s, 3H), 2.14-2.09 (m, 2H), 1.69 (d, J = 7 Hz, 3H), 1.39-1.29 (m, 6H), 0.89 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 179.06, 135.08, 130.48, 125.17, 122.76, 33.50, 33.03, 31.71, 29.02, 22.28, 13.93, 13.04; FT-IR (thin flim, cm^{-1}) 2920, 1698, 1453, 958; High resolution ESI molecular ion calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$ 196.1463, found 197.1536 ($\text{C}_{12}\text{H}_{21}\text{O}_2$, M+H), error 0.1 ppm.

(4Z, 5E)-4-Benzylidenedec-5-enoic acid (9C, Claisen step, entry 8): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.33 mL LiHMDS (1M solution in THF), and 270 μ L HMPA, yellow solution was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. Subsequently a solution of 400 mg (1.55 mmol) of diene **9B**, and 351 mg (2.33 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78 °C over a 5 min period. The orange solution was allowed to stir at -78 °C for 15 min, then warmed to room temperature and stirred at that temperature for 3 h. Next, 20 mL of diethyl ether and 2 mL of brine were added. The ether layer was washed 2 x 5 mL with water. The aqueous layers were combined and extracted with 20 mL ether. The organic layers were combined, concentrated *in vacuo* (rotary evaporator) to an orange oil that was dissolved in 3 mL THF and 1 mL of 1M HCl_(aq) the orange solution was stirred at room temperature for 1 h. The reaction was poured into 20 mL of ethyl acetate, and washed with 3 mL sat. NH₄Cl. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a silica gel column (2 x 10 cm). Gradient elution 10-30% ethyl acetate/hexane gave 318 mg of **9C** (80%) as a slightly yellow oil. Analytical TLC (30% ethyl acetate/hexane) *R_f* 0.12. ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.30 (m, 2H), 7.25-7.20 (m, 3H), 6.45 (d, *J* = 15.5 Hz, 1H), 6.38 (s, 1H), 5.87 (dt, *J* = 15.5 Hz, 14.5 Hz, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.14-2.09 (m, 2H), 1.41-1.29 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 179.34, 137.51, 136.87, 132.85, 129.35, 128.02, 127.60, 126.70, 125.50, 33.67, 32.88, 31.49, 29.59, 22.23, 13.87; FT-IR (thin flim, cm⁻¹) 2926, 1708, 1444, 976; High resolution ESI molecular ion calcd for C₁₇H₂₂O₂ 258.1620, found 259.1688 (C₁₇H₂₃O₂, M+H), error 1.4 ppm.

(E)-3-Methylene-1-phenyl-non-4-en-2-yl acetate (10B, metathesis step, entry 9): To an oven-dried 50 mL Schlenk tube was added 400 mg of alkyne **4A** (2.13 mmol), 2.4 mL of 1-hexene (9 equiv, 19.15 mmol), and 6 mL of dichloromethane. The clear solution was stirred for 5 min and 90 mg Grubbs' catalyst **1** (0.11 mmol, 5 mol%) was added as a single portion. The reaction was heated at reflux for 18 h, cooled to room temperature, concentrated *in vacuo* (rotary evaporator), and loaded directly on to a silica gel column (2 X 10 cm). Elution with 5% ethyl acetate/hexane gave 539 mg of **10B** (93%) as a clear oil. Analytical TLC (10% ethyl acetate/hexane) *R_f* 0.35. ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 16.0 Hz, 1H), 5.91 (dt, *J* = 16.0 Hz, 14, 1H), 5.68 (dd, *J* = 8.0 Hz, 5 Hz, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 3.07 (dd, *J* = 5.0 Hz, 1H), 2.96 (dd, *J* = 8.0 Hz, 1H), 2.17-2.13 (m, 2H), 2.03 (s, 3H), 1.45-1.34 (m, 4H), 0.95 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.95, 144.61, 137.55, 131.87, 129.32, 128.67, 128.17, 126.46, 113.14, 74.33, 40.63, 32.81, 31.36, 22.23, 21.08, 13.93; FT-IR (thin flim, cm⁻¹)

3029, 2927, 1745, 1369, 1234, 1029; High resolution ESI molecular ion calcd for $C_{18}H_{24}O_2$ 272.1856, found 273.1849 ($C_{18}H_{25}O_2$ M+H), error 2.7 ppm.

(4Z, 5E)-4-(2-Phenyethylidene)dec-5-enoic acid (10C, Claisen step, entry 9): To an oven-dried 50 mL Schlenk tube at room temperature was added 2.76 mL LiHMDS (1M solution in THF), and 320 μ L HMPA, yellow solution was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. Then, a solution of 500 mg (1.84 mmol) of diene **10B**, and 416 mg (2.75 mmol) of TBSCl in 1 mL of THF were added dropwise via syringe at -78 °C over a 5 min period. The orange solution was allowed to stir at -78 °C for 15 min, then warmed to room temperature and stirred at that temperature for 30 h. Then 3 mL of 1M AcOH_(aq) was added and reaction was stirred at room temperature for 1 h. The reaction was diluted with 15 mL of dichloromethane, washed 3 x 15 mL water, 15 mL of 1M NH₄Cl; aqueous layers were extracted with 3 x 15 mL of dichloromethane. The organic layers were combined, dried (Na₂SO₄), filtered, concentrated *in vacuo* (rotary evaporator), loaded directly onto a silica gel column (2 x 10 cm). Gradient elution 10-30% ethyl acetate/hexane gave 425 mg of **10C** (85%) as a slightly yellow oil. Analytical TLC (30% ethyl acetate/hexane) R_f 0.15. ¹H NMR (500 MHz, CDCl₃) δ 7.27-7.23 (m, 2H), 7.17-7.13 (m, 3H), 6.39 (d, J=16.0 Hz, 1H), 5.76 (dt, J=16.0 Hz, 15 Hz, 1H), 5.49 (t, J=7.5, 1H), 3.48 (d, J=7.5, 2H), 2.56-2.50 (m, 4H), 2.15-2.11 (m, 2H), 1.43-1.23 (m, 4H), 0.89 (t, J=7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 180.05, 140.85, 135.22, 131.72, 128.38, 128.32, 126.79, 125.87, 125.17, 33.69, 33.45, 33.02, 31.59, 29.08, 22.26, 13.91; FT-IR (thin film, cm⁻¹) 3032, 2926, 1709, 1254, 837; High resolution ESI molecular ion calcd for $C_{18}H_{24}O_2$ 272.1772, found 272.1771($C_{17}H_{23}O_2$, M+H), error 0.4 ppm.

(E)-4-Methylene-1-phenyldec-5-en-3-yl acetate (11B, metathesis step, entry 9): To a dry 100 mL Schlenk tube was added a solution of 40 mL of dichloromethane and 405 mg (2.0 mmol) of racemic acetate **5A**. To this mixture was added in 2.48 mL (10 mmol) of 1-hexene. Exactly 0.9 mg (0.1 mmol) of catalyst **1** was added, followed immediately by capping the schlenk tube with a cold finger condenser. The reaction vessel was then placed in an oil bath allowing the reaction to stir at reflux for 26 h (completion determined disappearance of **5A** by GC at 13.13 min). Any remaining catalyst was inactivated by adding 0.048 mL (0.5 mmol) of ethyl vinyl ether, refluxing for 1 h and then allowing the reaction vessel to cool to room temperature. The solution was then concentrated *in vacuo* (rotary evaporator) The compound was purified by flash column chromatography on silica(15 x 2.5 cm of silica in 1:10 ethyl acetate in hexanes), resulting in 404 mg (71%) of the *E*-diene **11B**. Analytical TLC: R_f = 0.29 (1:10 ethyl acetate in hexanes). ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.30-7.28 (m, 2H), 7.22-7.17 (m, 3H), 5.99 (d, 1H, J = 16 Hz), 5.70 (dt, 1H, J = 16

Hz, 6.8 Hz), 5.48 (t, 1H, J = 6.0 Hz), 5.07 (d, 2H, J = 5.5 Hz), 2.71-2.60 (m, 2H), 2.09 (s, 3H), 2.09-2.00 (m, 4H), 1.37-1.30 (m, 4H), 0.91 (t, 3H, J = 6.8 Hz); ^{13}C NMR (125.7 MHz, CDCl_3 , ppm) δ 169.8, 144.9, 141.2, 131.6, 128.5, 128.22, 128.21, 125.8, 112.4, 73.0, 35.6, 32.6, 31.7, 31.2, 22.0, 20.9, 13.7; IR (CH_2Cl_2 , cm^{-1}) 3026, 2960, 2927, 2861, 1742, 1650, 1604, 1499, 1453, 1367, 1242, 1031, 965, 893, 748, 696; ESI-MS molecular ion calculated for $\text{C}_{19}\text{H}_{26}\text{O}_2$ 286.19, found 309.18 (M + Na), error 2.5 ppm.

(4Z,5E)-4-(3-Phenylpropylidene)dec-5-enoic acid (11C), Claisen step, entry 10): To an dry 50 mL Schlenk tube was introduced 1.5 mL LHMDs (1.0 M in THF) and 250 μL of HMPA and the contents stirred at -78°C for 15 min. In a separate 10 mL rb flask was added a solution of 286 mg (1.0 mmol) of diene **11B** in 0.7 mL of THF. To this solution was added 226 mg (1.5 mmol) of TBSCl and allowed to stir for 5 min. The solution of TBSCl and diene **11B** were then added dropwise over 10 min. via syringe into the solution of LHMDs and HMPA. The reaction was stirred at -78°C for 1 h then let warm to room temperature, stirred for a further 23 h. The solution was diluted with 20 mL of diethyl ether and 2 mL of brine were added. The ether layer was extracted and washed 2 x 5 mL of water. The organic layers were combined, concentrated to a pale yellow oil that was dissolved in 3 mL THF and 1 mL of 1.0 M HCl and stirred at room temperature, for 1 h. The reaction was diluted with 20 mL of ethyl acetate and washed with 3 mL sat. NH_4Cl . The organic layers were combined, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The compound was purified by flash column chromatography on silica (15 x 2.5 cm of silica in 1:10 then 1:1 ethyl acetate in hexanes) resulting in 162 mg (57%) carboxylic acid **11C**. Analytical TLC: R_f = 0.12 ^1H NMR (500 MHz, CDCl_3 , ppm) δ 7.26 (t, 2H, J = 7.5 Hz), 7.20-7.16 (m, 3H), 6.23 (d, 1H, J = 16.0 Hz), 5.68 (dt, 1H, J = 16.0, 7.0 Hz), 5.32 (t, 1H, J = 7.5 Hz), 2.66 (t, 2H, J = 7.5 Hz), 2.49-2.42 (m, 6H), 2.10 (q, 2H, J = 7.0 Hz), 1.38-1.25 (m, 4H), 0.90 (t, 3H, J = 7.0 Hz); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 180.1, 141.8, 134.9, 130.9, 128.4, 128.2, 127.6, 125.8, 125.3, 35.9, 33.7, 32.9, 31.6, 29.2, 29.0, 22.2, 13.9; IR (CH_2Cl_2 , cm^{-1}) 3026, 2960, 2927, 2861, 1709, 1604, 1499, 1453, 1413, 1307, 1209, 965, 748, 696; ESI-MS molecular ion calculated for $\text{C}_{19}\text{H}_{26}\text{O}_2$ 286.19, found 309.18 (M + Na), error -1.9 ppm.

Methylene-Free Synthesis of Cyclic Dienes (Table 2)

1-(Cyclohexa-1,5-dienyl)-3-phenylpropyl acetate (12B), metathesis step, entry 1): Into an oven-dried 100 mL Schlenk tube equipped with a stirbar and a cold finger condenser was added *all-cis* polybutadiene (433 mg, 8 mmol), 20 mL CH_2Cl_2 followed by Grubbs' second generation catalyst **1** (42 mg, 5 mol %). This solution was immersed in an oil bath maintained at 45 °C. The alkyne **5A** (202 mg, 1 mmol) was dissolved in *ca.* 2 mL of CH_2Cl_2 and this solution was added to the solution of *all-cis* PB and the catalyst in CH_2Cl_2 at 45 °C over a period of 4 h by means of a gas tight syringe (syringe pump). After the addition was complete, the reaction mixture was stirred at 45 °C for an additional 30 min. Ethyl vinyl ether (144 mg, 2 mmol) was added and the reaction mixture was stirred at 45 °C for an additional 30 min. The reaction mixture was then concentrated and partially purified by passing a small plug of silica gel (5.0 cm), eluted with 1 % ethyl acetate in hexanes (100 mL) to remove the catalyst and the solvent subsequently removed *in vacuo* (rotary evaporator). The viscous yellow oil thus obtained was further purified by bulb-to-bulb distillation. The distillate (204 mg) was obtained as colorless oil at 97 °C (1.7 mm of Hg). The purification of the distillate using silica gel (elution with 2% ethyl acetate in hexanes) afforded the cyclohexadiene **12B** (164 mg, 64%) as colorless oil. Analytical tlc: R_f 0.44 (12% ethyl acetate in hexanes). ^1H – NMR (500 MHz, CDCl_3 , ppm) δ 7.28 – 7.25 (m, 2H), 7.18 – 7.15 (m, 3H), 5.96 – 5.88 (m, 1H), 5.74 – 5.73 (m, 1H), 5.23 (t, J = 7.0 Hz, 1H), 2.60 – 2.56 (m, 2H), 2.19 – 2.11 (m, 4H), 2.04 – 1.99 (m, 4H), 1.93 – 1.87 (m, 1H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 170.3, 141.4, 134.2, 128.3, 128.2, 127.8, 125.8, 123.6, 122.9, 75.7, 34.8, 31.7, 22.1, 21.9, 21.2; FT-IR (thin film, cm^{-1}) 2933, 1738, 1370, 1238, 1020; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ 256.1458, found 279.1350, $[\text{M}+\text{Na}]^+$, error 1.9 ppm.

(6-Ethylcyclohexa-1,5-dienyl)methyl acetate (13B), metathesis step, entry 2): Into an oven-dried 50 mL Schlenk tube equipped with a magnetic stirbar and a cold finger condenser, was added 1,5-COD (1.1 mL, 9.0 mmol, 9.0 equiv) followed by 20 mL CH_2Cl_2 . This solution was purged with Ar for *ca.* 5 min. Subsequently, Grubbs' second generation catalyst (42 mg, 5 mol %) was added to this solution and the schlenk tube was immersed into an oil bath maintained at 45 °C. The alkyne (126 mg, 1.0 mmol, 1.0 equiv) was dissolved in 2.0 mL CH_2Cl_2 and this was taken up in a 5.0 mL gas tight syringe. This solution of the alkyne was added to the contents of the schlenk tube over 4 h (syringe pump). After the addition was complete, the reaction mixture was stirred at 45 °C for an additional

45 min. The reaction mixture was concentrated to afford a dark brown viscous oil. To this was added ice-cold methanol (10 mL) and the heterogeneous mixture was stirred at 0 °C for *ca.* 10 min. The methanol was collected by decantation and the extraction was repeated two more times. The methanol extracts were combined and the solvent removed *in vacuo* (rotary evaporator). The brown oil thus obtained was further purified by means of flash column chromatography using silica gel. Elution with 1% ethyl acetate in hexanes afforded the cyclohexadiene derivative **13B** (130 mg, 72% yield) as pale yellow oil. Analytical tlc: R_f = 0.34 (10% ethyl acetate in hexanes). ^1H – NMR (500 MHz, CDCl_3 , ppm), δ 5.92 (s, 1H), 5.62 (s, 1H), 4.61 (s, 2H), 2.14-2.10 (m, 6H), 2.07 (s, 3H), 1.04 (t, J = 7.5Hz, 3H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 170.9, 137.0, 132.6, 128.2, 121.2, 65.4, 24.6, 22.5, 22.1, 21.1, 12.9; FT-IR (thin film, cm^{-1}) 2935, 1741, 1376, 1228, 1023, 964, 829; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ 180.1145, found 180.1144, error 0.7 ppm.

1-[(1E,6Z)-Cyclohepta-1,6-dienyl]-3-phenylpropyl acetate (15B, metathesis step, entry 4): Into an oven-dried Schlenk tube (100 mL) equipped with magnetic stirbar and a cold finger condenser was added CH_2Cl_2 (50 mL) followed by Grubbs' second generation catalyst (42.4 mg, 5 mol %) and the solution was immersed into an oil bath maintained at 45 °C. Alkyne **5A** (202 mg, 1.0 mmol) and cyclopentene (272 mg, 4.0 mmol) were dissolved in *ca.* 2.0 mL CH_2Cl_2 and this solution was then added to the solution of the catalyst in CH_2Cl_2 at 45 °C over a period of 16 h by means of a gas tight syringe (syringe pump). After the reaction was complete, the reaction mixture was stirred at 45 °C for additional 45 min. Ethyl vinyl ether (144 mg, 2 mmol) was then added and the reaction mixture was stirred at 45 °C for additional 30 min. The reaction mixture was then concentrated *in vacuo* (rotary evaporator) to afford a viscous brown oil. The latter was purified by flash column chromatography using silica gel. Elution with 2% ethyl acetate in hexanes afforded the cycloheptadiene **15B** (176 mg, 65% yield) as pale yellow oil. Analytical tlc: R_f = 0.38 (10% ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm), δ 7.28 – 7.25 (m, 2H), 7.17 (t, J = 7.5 Hz, 3H), 5.95 (dt, J = 12.0, 5.0 Hz, 1H), 5.89 (t, J = 5.0 Hz, 1H), 5.82 (d, J = 12.0 Hz, 1H), 5.16 (t, J = 7.0 Hz, 1H), 2.63 – 2.56 (m, 2H), 2.31-2.27 (m, 4H), 2.07 – 2.00 (m, 4H), 1.93 – 1.81 (m, 3H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 170.1, 141.4, 134.98, 134.95, 132.0, 128.25, 128.22, 125.8, 123.9, 78.6, 35.4, 31.8, 31.4, 29.8, 26.8, 21.2; FT-IR (thin film, cm^{-1}) 2933, 1742, 1367, 1249, 1031; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$ 270.1614, found 270.1617, error 0.9 ppm.

General procedure for the Claisen rearrangement of the cycloienes to the corresponding carboxylic acids (Table 2)

An oven-dried Schlenk tube (50 mL) equipped with a magnetic stirbar was charged with 0.75 mL of 1.0 M LiHMDS in THF (0.75 M, 1.5 equiv). This was cooled to -78 °C (dry ice-acetone bath) for 15 minutes. 125 μ L HMPA was added to this solution maintained at -78 °C. In a separate round bottom flask (10 mL) was dissolved a mixture of cycloiene (0.5 mmol, 1.0 equiv) and TBSCl (0.75 mmol, 1.5 equiv) in 0.5 mL THF. This solution was added dropwise with gas tight syringe into LiHMDS-HMPA solution maintained at -78 °C over 3-4 minutes. The flask was rinsed with additional 300 μ L THF and this solution was added to the solution of the base and HMPA. The reaction mixture was stirred at -78 °C for 20 min and then slowly warmed to RT. It was stirred at RT for 24 h. The reaction was quenched by addition of 5 mL of saturated NH_4Cl solution. The reaction mixture was poured into a separatory funnel containing 20 mL of diethyl ether and 20 mL of saturated NH_4Cl solution. The organic layer was washed with distilled water (2 X 20 mL) and finally with saturated NH_4Cl solution. The organic layer was separated, dried over anhydrous Na_2SO_4 and the diethyl ether was removed *in vacuo* (rotary evaporator). The pale brown oil thus obtained was redissolved in 5 mL THF and 0.5 mL of 1.0 M HCl was added to it. This was stirred at RT for 45 min. The reaction was quenched by pouring the reaction mixture into a separatory funnel containing 20 mL distilled water and 20 mL diethyl ether. The organic layer was washed with distilled water (2 X 20 mL) and finally with saturated NH_4Cl solution (20 mL). It was dried using anhydrous Na_2SO_4 and the solvent removed *in vacuo* (rotary evaporator). The yellow oil thus obtained was purified by using silica gel flash column chromatography. Gradient elution with 10% ethyl acetate in hexanes (100 mL) followed by 20% ethyl acetate in hexanes (100 mL) afforded the desired carboxylic acid as pale yellow oil.

(Z)-2-[2-(3-Phenylpropylidene)cyclohex-3-enyl]acetic acid (12C, entry 1): As the general experimental. The carboxylic acid **12C** was obtained as pale yellow oil (87 mg, 68% yield). Analytical tlc: 0.30 (50% ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.27 – 7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 6.29 (d, J = 10.0 Hz, 1H), 5.76 – 5.74 (m, 1H), 5.27 (t, J = 7.5 Hz, 1H), 2.81 – 2.79 (m, 1H), 2.64 (t, J = 7.5 Hz, 2H), 2.46 – 2.36 (m, 4H), 2.18 – 2.09 (m, 2H), 1.79 – 1.74 (m, 1H), 1.72 – 1.67 (m, 1H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 179.6, 141.8, 135.7, 128.6, 128.4, 128.2, 125.8, 125.4, 122.9, 38.3, 37.0, 36.0, 28.8, 26.9, 22.4; FT-IR (thin film, cm^{-1}) 2933, 1716, 1460, 1295, 939; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ 256.1458, found 256.1456, error 0.8 ppm.

2-(3-Ethyl-2-methylenecyclohex-3-enyl)acetic acid (13C, entry 2): As the general experimental. The carboxylic acid **13C** was obtained as a pale yellow oil (55 mg, 61% yield). Analytical tlc: 0.28 (50% ethyl acetate in hexanes). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm) δ 5.63 (s, 1H), 4.98 (s, 1H), 4.87 (s, 1H), 2.93-2.88 (m, 1H), 2.50 (dd, $J = 15.0, 7.5$ Hz, 1H), 2.41 (dd, $J = 15.0, 7.5$ Hz, 1H), 2.24-2.14 (m, 4H), 1.83-1.77 (m, 1H), 1.71-1.66 (m, 1H), 1.04 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , ppm) δ 179.6, 145.4, 137.0, 124.7, 108.2, 38.2, 37.5, 27.2, 25.7, 22.8, 13.1; FT-IR (thin film, cm^{-1}) 2929, 1708, 1604, 1292, 1202, 888; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ 180.1145, found 180.1142, error 1.7 ppm.

2-[(2Z, 3Z)-2-(2-Phenylethylidene)cyclohept-3-enyl]acetic acid (14C, entry 3): As the general experimental. The carboxylic acid **14C** was obtained as pale yellow oil (81 mg, 63% yield). Analytical tlc: 0.28 (50% ethyl acetate in hexanes). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm) δ 7.27-7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 6.32 (dd, $J = 12.0, 1.0$ Hz, 1H), 5.84 (dt, $J = 12.0, 5.0$ Hz, 1H), 5.47 (t, $J = 7.5$ Hz, 1H), 3.41 (d, $J = 7.5$ Hz, 2H), 3.05 – 2.99 (m, 1H), 2.60 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.47 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.26 – 2.23 (m, 2H), 1.93 – 1.85 (m, 1H), 1.77 – 1.64 (m, 2H), 1.56 – 1.50 (m, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , ppm) δ 179.7, 140.9, 139.7, 132.9, 128.34, 128.30, 127.8, 125.8, 125.5, 41.6, 39.3, 34.8, 34.2, 29.5, 24.1; FT-IR (thin film, cm^{-1}) 2933, 1716, 1470, 1301, 939; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ 256.1458, found 256.1454, error 1.5 ppm.

2-[(2Z, 3Z)-2-(3-phenylpropylidene)cyclohept-3-enyl]acetic acid (15C, entry 4): As the general experimental. The carboxylic acid **15C** was obtained as pale yellow oil (91 mg, 68% yield). Analytical tlc: R_f 0.28 (50% ethyl acetate in hexanes). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , ppm) δ 7.17 – 7.14 (m, 2H), 7.07 – 7.04 (m, 3H), 6.02 (dd, $J = 12, 1.0$ Hz, 1H), 5.63 (dt, $J = 12.0, 5.0$ Hz, 1H), 5.2 (t, $J = 7.5$ Hz, 1H), 2.86 – 2.80 (m, 1H), 2.54 (t, $J = 7.5$ Hz, 2H), 2.43 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.32 (dd, $J = 15.0, 8.0$ Hz, 1H), 2.27-2.23 (m, 2H), 2.07 (dd, $J = 10.0, 5.0$

Hz, 2H), 1.76 – 1.70 (m, 1H), 1.57 – 1.52 (m, 1H), 1.50 – 1.42 (m, 1H), 1.40 – 1.34 (m, 1H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 178.8, 141.9, 139.3, 132.1, 128.4, 128.2, 127.8, 126.3, 125.7, 41.6, 39.2, 35.7, 34.8, 29.9, 29.4, 24.0; FT-IR (thin film, cm^{-1}) 2940, 1709, 1503, 1459, 1295, 709; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$ 270.1614, found 270.1612, error 1.0 ppm.

Methyl 2-[(2Z, 3Z)-2-(3-phenylpropylidene)cyclohept-3-enyl]acetate (16C):

An oven-dried Schlenk tube (50 mL) equipped with a magnetic stirbar was charged with 0.75 mL of 1.0 M LiHMDS in THF (0.75 M, 1.5 equiv). This was cooled to $-78\text{ }^{\circ}\text{C}$ (dry ice-acetone bath) for 15 minutes. 125 μL HMPA was added to this solution maintained at $-78\text{ }^{\circ}\text{C}$. In a separate round bottom flask (10 mL) was dissolved a mixture of cyclodiene **15B** (0.5 mmol, 1.0 equiv.) and TBSCl (0.75 mmol, 1.5 equiv) in 0.5 mL THF. This solution was added dropwise with gas tight syringe into LiHMDS-HMPA solution maintained at $-78\text{ }^{\circ}\text{C}$ over 3-4 minutes. The flask was rinsed with additional 300 μL THF and this solution was added to the solution of the base and HMPA. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min and then slowly warmed to RT. It was stirred at RT for 24 h. The reaction mixture was concentrated at this stage to afford a pale brown oil. To this was added HMPA (1 mL), KHCO_3 (100 mg, 2.0 equiv), KF (94.2 mg, 2.0 equiv) and MeI (156 mL, 5.0 equiv) and this reaction mixture was stirred at RT for 15 h. The reaction was quenched by pouring the reaction mixture into a separatory funnel containing 20 mL distilled water and 20 mL diethyl ether. The organic layer was washed with distilled water (2 X 20 mL) and finally with saturated NaCl solution (20 mL). It was dried using anhydrous Na_2SO_4 and the solvent removed *in vacuo* (rotary evaporator). The yellow oil thus obtained was purified by using silica gel flash column chromatography. Elution with 2% ethyl acetate in hexanes afforded the desired ester **16C** (90 mg, 63% yield) as pale yellow oil. Analytical tlc: 0.34 (10% ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.27 – 7.24 (m, 2H), 7.17 – 7.14 (m, 3H), 6.14 (dd, J = 12.0, 1.0 Hz, 1H), 5.73 (dt, J = 12.0, 5.0 Hz, 1H), 5.29 (t, J = 7.0 Hz, 1H), 3.62 (s, 3H), 2.97 – 2.91 (m, 1H), 2.64 (t, J = 7.0 Hz, 2H), 2.50 (dd, J = 15.0, 8.0 Hz, 1H), 2.41 – 2.33 (m, 3H), 2.19 – 2.15 (m, 2H), 1.84 – 1.77 (m, 1H), 1.68 – 1.53 (m, 2H), 1.49 – 1.43 (m, 1H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 173.2, 141.9, 139.5, 131.9, 128.4, 128.2, 127.7, 126.2, 125.7, 51.3, 41.9, 39.3, 35.7, 34.7, 29.8, 29.5, 23.9; FT-IR (thin film, cm^{-1}) 2920, 1749, 1433, 1249, 1143; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2$ 284.1771, found 284.1776, error 1.7 ppm. When the vinylic triplet at δ 5.29 ppm was irradiated, nOe enhancement was seen for the protons at δ 2.97-2.91 ppm, 2.64 ppm (allylic protons) and 2.50 ppm.

Mode Selective Ene Reaction / Cycloaddition Reaction

Compound 12D: The carboxylic acid **12C** (51 mg, 0.2 mmole) was dissolved in a mixture of 1.0 mL CH₂Cl₂ and 0.6 mL of CH₃OH. This solution was cooled to 0 °C using an ice bath for 15 min. To this solution was added TMSCHN₂ (120 µL, 1.2 equiv) (2.0 M solution in ether). The reaction mixture was stirred at 0 °C for 20 min and then slowly brought to RT. The reaction mixture was concentrated and purified using silica gel flash column chromatography (1 X 10 cm). Elution with 2 % ethyl acetate in hexanes afforded the desired methyl ester **12D** (49 mg, 91% yield) as colorless oil. Analytical tlc: 0.31 (10% ethyl acetate in hexanes). ¹H- NMR (500 MHz, CDCl₃, ppm) δ 7.29-7.26 (m, 2H), 7.18-7.16 (m, 3H), 6.30 (d, J = 10.0 Hz, 1H), 5.77-5.75 (m, 1H), 5.23 (t, J = 7.5 Hz, 1H), 3.64 (s, 3H), 2.82-2.79 (m, 1H), 2.68-2.63 (m, 2H), 2.44-2.32 (m, 4H), 2.17-2.13 (m, 2H), 1.78-1.72 (m, 1H), 1.67-1.63 (m, 1H); ¹³C-NMR (125 MHz, CDCl₃, ppm) δ 173.4, 141.2, 135.9, 128.6, 128.4, 128.2, 125.8, 125.2, 122.9, 51.4, 38.3, 37.3, 36.0, 28.8, 27.0, 22.5; FT-IR (thin film, cm⁻¹) 3028, 2925, 1738, 1435, 1274, 1156, 1019; High-resolution MS (EI⁺, *m/z*) molecular ion calcd for C₁₈H₂₂O₂Na₁ 293.1517, found 293.1519, error 0.7 ppm.

Tandem Cycloadduct 18: An oven-dried, argon-cooled schlenk tube equipped with a stir bar and a cold finger condenser was charged with a solution of the *s-trans* diene **12D** (27.0 mg, 0.1 mmole) and BocNHOH (61.5 mg, 0.5 mmole, 5.0 equiv) in 2 mL CH₂Cl₂. This solution was cooled in an ice bath for *ca.* 15 min. A solution of Pr₄NIO₄ (207 mg, 0.55 mmoles, 5.5 equiv) dissolved in 2.0 mL CH₂Cl₂ was taken up into a gas tight syringe (5.0 mL capacity). The solution of the oxidant was added to the solution of the diene and the hydroxamic acid maintained at 0 °C, over a period of 2 h. Analysis of the reaction mixture after *t* = 2 h (tlc) revealed complete consumption of the diene. The reaction mixture was concentrated *in vacuo* (rotary evaporator) and purified by using silica gel flash column chromatography (1 X 10 cm). Gradient elution with 10% ethyl acetate in hexanes followed by 20% ethyl acetate in hexanes afforded the major diastereomer (26 mg, 48% yield) and the minor diastereomer (15 mg, 28% yield) both as pale yellow oils.

Characterization of the major diastereomer: Analytical tlc: 0.23 (25 % ethyl acetate in hexanes). ¹H- NMR (500 MHz, CDCl₃, ppm) δ 7.30-7.26 (m, 2H), 7.22-7.17 (m, 3H), 6.48 (d, J = 6.0 Hz, 1H), 5.99 (s, 1H), 5.13 (br s, 1H), 4.74-4.72 (m, 2H), 3.72 (s, 3H), 3.32 (d, J = 17.0 Hz, 1H), 2.80 (d, J = 17.0 Hz, 1H), 2.66-2.56

(m, 2H), 2.23-2.216 (m, 1H), 2.14-2.08 (m, 1H), 1.99-1.92 (m, 2H), 1.84-1.78 (m, 1H), 1.59-1.53 (m, 1H), 1.48 (s, 9H), 1.44 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 170.6, 161.8, 155.9, 141.8, 140.7, 128.8, 128.39, 128.35, 125.9, 83.2, 81.5, 78.9, 53.9, 51.8, 37.5, 32.3, 28.8, 29.8, 28.2, 28.0, 20.0; FT-IR (thin film, cm^{-1}) 3380, 2935, 1737, 1393, 1162, 1093, 913; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_8\text{Na}_1$ 555.2682, found 555.2667, error 2.7 ppm. NOE data: Irradiation of the multiplet at δ = 4.74-4.72 (exocyclic allylic methine proton) resulted in the enhancement of the proton signals at δ = 6.48 (3.5 %) and 2.14-2.08 (2.17 %). Irradiation of the proton at δ = 3.32 (downfield proton of the AB quartet) resulted in the enhancement of the proton signals at δ = 5.99 (0.35 %), 5.13 (1.7 %) and 2.80 (17.6 %). Irradiation of the proton at δ = 2.80 (upfield proton of the AB quartet) resulted in the enhancement of the proton signals at δ = 5.99 (0.97 %), 5.13 (1.5 %) and 3.32 (15.6 %). In addition, irradiation of the methine proton at δ 4.74-4.72 ppm gave nOe enhancement with the methyl protons of the *tert*-butyl group appearing at δ 1.44 ppm (upfield Boc group).

Characterization of the minor diastereomer: Analytical tlc: 0.09 (25 % ethyl acetate in hexanes). ^1H -NMR (500 MHz, CDCl_3 , ppm) δ 7.31-7.28 (m, 2H), 7.21-7.19 (m, 3H), 6.62 (d, J = 6.0 Hz, 1H), 6.45 (br s, 1H), 4.97 (t, J = 6.0 Hz, 1H), 4.77-4.75 (m, 1H), 3.68 (s, 3H), 3.08 (d, J = 15.5 Hz, 1H), 2.82 (d, J = 15.5 Hz, 1H), 2.67-2.56 (m, 2H), 2.19-2.06 (m, 4H), 1.57-1.53 (m, 2H), 1.43 (s, 9H), 1.42 (s, 9H); ^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 169.9, 158.1, 156.5, 141.7, 141.3, 129.2, 128.43, 128.39, 126.0, 82.7, 81.6, 78.5, 56.5, 51.8, 50.5, 38.2, 32.3, 31.1, 29.7, 28.2, 28.1, 21.2; FT-IR (thin film, cm^{-1}) 3254, 2976, 1742, 1685, 1368, 1167; High-resolution MS (EI^+ , m/z) molecular ion calcd for $\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_8\text{Na}_1$ 555.2682, found 555.2682, error 0.0 ppm. NOe data: Irradiation of the multiplet at δ = 4.77-4.75 resulted in the enhancement of the proton signal at δ = 6.62 (2.2 %). Irradiation of the proton at δ = 3.08 (downfield proton of the AB quartet) resulted in the enhancement of the proton signals at δ = 4.97 (2.40 %) and 2.82 (14.2 %). Irradiation of the proton at δ = 2.82 (upfield proton of the AB quartet) resulted in the enhancement of the proton signals at δ = 4.97 (0.89 %) and 3.08 (15.8 %).

Chirality Transfer

Scheme S2. Preparation of Enantiomerically-Enriched Propionate **20**

(*R*)-5-Phenylpent-1-yn-3-yl acetate (*R*-5A): To a dry 100 mL round bottom flask was added 3.92 g (19.38 mmol) of alkyne **5A** and 40 mL of pH 7.0 phosphate buffer. To this solution was added a slurried mixture of 43 mg of ChiroCLEC-PC (dry) and 2.0 mL of storage buffer (1.0 mL of 10mM CaCl₂ and 1.0 mL of pH 6.02, 10 mM TRIS). The reaction mixture was allowed to stir for 141 h at room temperature. The solution was filtered and the products were extracted 2 x 50 mL of ether, dried (MgSO₄), and concentrated *in vacuo*. The products were separated by flash column chromatography on silica (15 x 2.5 cm of silica in 1:4 ethyl acetate/hexanes) producing 2.07 g of (*R*)-acetate ***R*-5A**⁴ (53%), 88% ee by HPLC ((*R,R*)-Whelk-O1, 1% IPA-hexanes, 1 mL/min), and 1.40 g of (*S*)-alcohol ***S*-19**. Analytical TLC: (*R*)-acetate ***R*-5A** *R*_f = 0.44 (1:4 ethyl acetate/hexanes), (*S*)-alcohol ***S*-19** *R*_f = 0.23 (1:4 ethyl acetate/hexanes). NMR data of ***R*-5A** matched that reported in literature:⁴ ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.30 (t, 2H, *J* = 7.5 Hz), 7.21 (t, 3H, *J* = 7.5 Hz), 5.36 (dt, 1H, *J* = 6.5 Hz, 1.5 Hz), 2.80 (t, 2H, *J* = 7.5 Hz), 2.52 (d, 1H, *J* = 1.5 Hz), 2.15-2.09 (m, 2H), 2.09 (s, 1H); [*α*]_D +34° (c 1.0, CHCl₃).

(*R*)-5-Phenylpent-1-yn-3-yl propionate (S3**):** To a dry 50 mL round bottom flask was added a solution of 17 mL of methanol and 678 mg (3.35 mmol) of ***R*-5A**. To this solution was added 937 mg (6.70 mmol) of K₂CO₃ and the contents were stirred for 1.3 h at room temperature. The product was extracted with 2 x 50 mL of diethyl ether and washed with 50 mL of water. The organic layer was collected and washed with 50 mL of saturated NH₄Cl, dried (Na₂SO₄), and concentrated. This gave 505 mg (94%) of crude alcohol ***R*-19**. The sample was >95% pure by ¹H NMR and was carried onto the next reaction. Analytical TLC: *R*_f = 0.24 (1:4 ethyl acetate in hexanes). Next, a solution of 4.2 mL of CH₂Cl₂ and 505 mg (3.15

⁴ Smulik, J. A.; Diver, S.T. *J. Org. Chem.* **2000**, *65*, 1788-1792.

mmol) of crude alcohol **R-19** was added to a dry 25 mL round bottom flask and stirred at 0 °C. To this solution was added dropwise 0.659 mL (4.73 mmol) of triethylamine followed by 39 mg (0.32 mmol) of DMAP, added in one portion. Exactly 1.10 mL (12.61 mmol) of propionyl chloride was added dropwise over 10 min and allowed to stir at 0 °C for another 30 min. The reaction was allowed to room temperature and stirred for 24 h. The products were extracted with 2 x 30 mL of diethyl ether and washed with 30 mL of 1 M HCl. The combined ether layers were dried (Na₂SO₄) and concentrated *in vacuo*. The crude was purified via flash column chromatography on silica (5 x 2.5 cm of silica in 1:4 ethyl acetate in hexanes) affording 652 mg (96%) of alkyne **S3**. Analytical TLC: R_f = 0.53 (1:4 ethyl acetate in hexanes). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.31 (t, 2H, J = 7.5 Hz), 7.22 (t, 3H, J = 7.5 Hz), 5.39 (dt, 1H, J = 6.5 Hz, 2.0 Hz), 2.81 (t, 2H, J = 8 Hz), 2.52 (d, 1H, J = 2 Hz), 2.37 (dq, 2H, J = 7.5 Hz, 4 Hz), 2.13 (m, 2H), 1.18 (t, 3H, J = 7.5 Hz); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 173.2, 140.6, 128.4, 128.3, 126.1, 81.0, 73.8, 63.1, 36.1, 31.1, 27.4, 8.9; IR (CH₂Cl₂, cm⁻¹) 3294, 3066, 3028, 2984, 2940, 2127, 1742, 1603, 1496, 1451, 1364, 1174, 1080, 1036, 752, 701; ESI-MS molecular ion calculated for C₁₄H₁₆O₂ 216.11, found 216.11 (M), error -2.0 ppm.

(*R*)-4-Methylene-1-phenylhex-5-en-3-yl propionate (*R*-20): To an oven-dried Fischer-Porter reaction tube was added a solution of 290 mg (1.34 mmol) of alkyne **ent-S3** and 27 mL of dichloromethane. The flask was then sealed and pressurized with ethylene while flushing argon from the system. The ethylene pressure was then released slowly and 68 mg (0.09 mmol) of catalyst **1** was added to the reaction mixture and sealed up once again. The flask was re-pressurized and flushed 6 times with ethylene, maintaining the pressure at 80 psig, and let stir for 6 h until completion by GC. The reaction was purged of ethylene concentrated and purified by flash column chromatography on silica (15 x 2.5 cm of silica in 1:8 ethyl acetate in hexanes) resulting in 308 mg (94%) of pure diene **R-20**, determined to be 94% ee by HPLC ((*R,R*)-Whelk-O1, 1% IPA in hexanes, 0.5 mL/min). GC analysis (ret. time = 14.63 min). Analytical TLC: R_f = 0.56 (1:4 ethyl acetate in hexanes). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.30 (t, 2H, J = 7.5 Hz), 7.21-7.17 (m, 3H), 6.32 (dd, 1H, J = 17.5 Hz, 11 Hz), 5.53 (t, 1H, J = 6.5 Hz), 5.28 (d, 1H, J = 17.5 Hz), 5.19 (d, 2H, J = 7.5 Hz), 5.11 (d, 1H, J = 11 Hz), 2.73-2.60 (m, 2H), 2.37 (q, 2H, J = 7.5 Hz), 2.05 (dt, 2H, J = 7.5 Hz), 1.18 (t, 3H, J = 7.5 Hz); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 173.4, 145.3, 141.2, 135.5, 128.4, 128.3, 125.9, 115.1, 114.7, 72.5, 35.7, 31.8, 27.7, 9.1; IR (CH₂Cl₂, cm⁻¹) 3095, 3033, 2980, 2940, 2861, 1743, 1598, 1493, 1453, 1361, 1209, 1085, 1025, 913, 755, 702; ESI-MS molecular ion calculated for C₁₆H₂₀O₂ 244.15, found 244.15 (M), error 0.5 ppm; [α]_D -10° (c 1.0, CHCl₃).

(*R,Z*)-2-Methyl-7-phenyl-4-vinylhept-4-enoic acid (S4**):** To a dry 100 mL Schlenk tube was added a solution of 28 mL of diethyl ether and 208 mg (0.85

mmol) of diene **R-20** and cooled to -78 °C. In a separate 50 mL Schlenk tube, a solution of 0.5 M KHMDS in toluene was made from solid KHMDS under inert atmosphere. Exactly 3.74 mL (1.87 mmol) of the KHMDS solution was added to the reaction slowly via syringe over 10 min. and allowed to stir for an additional 5 min. Chlorotrimethylsilane (0.348 mL, 2.72 mmol) was then added to the reaction. The reaction was allowed to warm to room temperature and stirred for 33 h. The products were then extracted with 2 x 50 mL diethyl ether and washed successively with 50 mL NH₄Cl and 50 mL of water. The combined organic layers were dried (MgSO₄), concentrated, and purified by flash column chromatography (15 x 2.5 cm of silica in 1:5 then 1:1 ethyl acetate in hexanes) providing 171 mg (82%) of carboxylic acid **S4**. Analytical TLC: R_f = 0.10 (1:4 ethyl acetate in hexanes). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.30 (t, 2H, J = 7.5 Hz), 7.20 (m, 3H), 6.62 (dd, 1H, J = 17.5 Hz, 11 Hz), 5.48 (t, 1H, J = 7.0 Hz), 5.25 (d, 1H, J = 17.5 Hz), 5.13 (d, 1H, J = 11 Hz), 2.76-2.68 (m, 4H), 2.50 (q, 2H, J = 8.0 Hz), 2.18 (dd, 1H, J = 13 Hz, 8.0 Hz), 1.13 (d, 3H, J = 7.0 Hz); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 183.1, 141.6, 134.0, 132.0, 131.9, 128.4, 128.3, 125.9, 114.0, 38.2, 37.3, 35.9, 29.3, 16.4; IR (CH₂Cl₂, cm⁻¹) 3079, 3026, 2907, 2670, 1709, 1597, 1499, 1453, 1426, 1295, 1249, 1117, 1077, 913, 755, 702; ESI-MS molecular ion calculated for C₁₆H₂₀O₂ 244.15, found 244.14 (M), error -3.4 ppm; [α]_D +16° (c 1.0, CHCl₃).

(S,Z)-Methyl 2-methyl-7-phenyl-4-vinylhept-4-enoate (S-21): In a dry 1 dram vial was added 0.26 mL of dichloromethane and 0.13 mL methanol to 64.7 mg (0.26 mmol) of **S4** and the solution cooled to 0 °C. A 2.0 M solution of (trimethylsilyl)diazomethane (0.265 mL, 0.53 mmol) was added dropwise via syringe, during which evolution of N₂ gas is observed. The reaction was then stirred for 20 min at room temperature. The crude solution was then concentrated *in vacuo* (rotary evaporator) and purified by flash column chromatography on silica (8.3 x 2.5 cm of silica in 1:20 ethyl acetate in hexanes) affording 58.7 mg (86%) of methyl ester **S-21**. Analytical tlc: R_f = 0.50 (1:4 ethyl acetate in hexanes). HPLC analysis of the methyl ester **S-21** showed 73% ee (CHIRALCEL OJ, 1% IPA in hexanes, 0.3 mL/min). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.30 (t, 2H, J = 7.5 Hz), 7.19-7.17 (m, 3H), 6.60 (dd, 1H, J = 17.5 Hz, 11 Hz), 5.43 (t, 1H, J = 7.0 Hz), 5.22 (d, 1H, J = 17.5 Hz), 5.10 (d, 1H, J = 11 Hz), 3.63 (s, 3H), 2.70-2.63 (m, 4H), 2.47 (dq, 2H, J = 7.5 Hz, 3.0 Hz), 2.16 (dd, 1H, J = 13 Hz, 8.0 Hz), 1.08 (d, 3H, J = 6.5 Hz); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 176.9, 141.6, 134.2, 132.1, 131.6, 128.3, 128.28, 125.8, 113.9, 51.4, 38.4, 37.6, 35.9, 29.3, 16.7; IR (CH₂Cl₂, cm⁻¹) 3085, 3027, 2944, 1735, 1607, 1498, 1466, 1364, 1261, 1204, 1172, 1121, 993, 910, 750, 705; ESI-MS molecular ion calculated for C₁₇H₂₂O₂ 258.16, found 284.15 (M + Na), error 1.9 ppm.

(S, Z)-2-Methyl-7-phenyl-4-vinylhept-4-en-1-ol (S-22). To a dry 20 mL vial was added a solution of **S-21**, 128 mg (0.50 mmol), in 5 mL of ether and stirred at 0

°C for 10 min. Lithium aluminum hydride, 74 mg (1.98 mmol), was added to the reaction mixture portionwise until gas evolution had ceased. The reaction was then allowed to warm to room temperature and stirred for an additional 0.5 h. The mixture was quenched by the addition of 5 mL of 1M HCl, diluted with 20 mL of water and subsequently extracted with 3 x 50 mL portions of ether. The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo* (rotary evaporator). The crude product was then purified by flash column chromatography on silica gel (2 g, 1:4 ethyl acetate-hexanes) affording 110 mg (96%) of alcohol (*S*-**22**) as a colorless oil. Analytical TLC: R_f = 0.29 (1:4 ethyl acetate-hexanes). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.31-7.27 (m, 2H), 7.21-7.18 (m, 3H), 6.64 (dd, J = 11.0 Hz, 17.5 Hz, 1H), 5.42 (t, J = 7.5 Hz, 1H), 5.24 (d, J = 17.5 Hz, 1H), 5.11 (dd, J = 11.0 Hz, 1H), 3.48 (dd, J = 5.5 Hz, 11.0 Hz, 1H), 3.42 (dd, J = 5.5 Hz, 11.0 Hz, 1H), 2.71 (t, J = 8.0 Hz, 2H), 2.52 (q, J = 7.5 Hz, 2H), 2.33 (dd, J = 6.5 Hz, 13.5 Hz, 1H), 1.96 (dd, J = 8.0 Hz, 13.5 Hz, 1H), 1.85 (sext., J = 6.5 Hz, 1H), 1.45 (bs, 1H), 0.88 (d, J = 6.5 Hz, 3H); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 141.7, 135.4, 132.7, 131.0, 128.4, 128.3, 125.8, 114.0, 68.1, 37.6, 36.0, 34.5, 29.2, 16.8; IR (CH₂Cl₂, cm⁻¹) 3355, 3085, 3026, 2960, 2927, 2868, 1644, 1598, 1493, 1453, 1381, 1032, 992, 907, 755, 696; ESI-MS molecular ion calculated for C₁₆H₂₂O 230.17, found 230.17 (M), error 2.6 ppm. [α]_D^{25° C} = -2.1° (c 1.0, CHCl₃).

Mosher Ester Analysis of **22**

For assignment of absolute configuration, analyses of the corresponding (*R*)- and (*S*)-MTPA esters were conducted according to Kobayashi⁵: To a dry 1 dram vial was added a solution of 15.6 mg (0.13 mmol) of 4-(dimethylamino)pyridine, 40 mg (0.19 mmol) of dicyclohexylcarbodiimide, and 14.0 mg (0.06 mmol) of alcohol **22** in 400 mL of dichloromethane. A solution of 28 mg (0.12 mmol) of (*R*)-(+)- α -methoxy- α -(trifluoromethyl)phenylacetic acid in 400 mL of dichloromethane was added dropwise to the solution of **22**. The reaction was stirred for 24 h, and concentrated *in vacuo* (rotary evaporator). The same procedure was repeated using (*S*)-(-)- α -methoxy- α -(trifluoromethyl)phenylacetic acid with 19.4 mg (0.08 mmol) of **22**. The crude MTPA esters were then analyzed separately by ¹H NMR spectroscopy without further purification, examining the AB part of the ABX systems corresponding to the diastereotopic methylene protons (adjacent to the chiral center).

Selected portion of the ¹H NMR spectrum of the (*S*)-MTPA ester of **22**: ¹H NMR (500 MHz, CDCl₃, ppm) δ 4.16 (dd, *J* = 5.5 Hz, 11.0 Hz, 1H), 4.00 (dd, *J* = 5.5 Hz, 11.0 Hz, 1H); The separation of ν_A and ν_B was found to be $\delta\Delta=0.16$ ppm.

Selected portion of the ¹H NMR spectrum of the (*R*)-MTPA ester of **22**: ¹H NMR (500 MHz, CDCl₃, ppm) δ 4.09 (AB quartet, *J*_{AB} = 10.7 Hz, *J*_{AX} = 5.3 Hz, 1H), 4.06 (AB quartet, *J*_{BA} = 10.7 Hz, *J*_{BX} = 5.1 Hz, 1H). The separation of ν_A and ν_B was found to be $\delta\Delta=0.03$ ppm.

The crude (*S*)-MTPA-derived ester resulted in a large splitting of the diastereotopic oxymethylene protons similar in magnitude ($\Delta\delta$) to that observed by Kobayashi et al.⁵ for the *S*-configuration. Also in accord with the predictive model, the (*R*)-MTPA-derived Mosher ester resulted in small chemical shift separation of ν_A and ν_B , also leading to the assignment of the *S*-configuration. These observations led to the assignment of (*S*)-configuration to the chiral center in **22**.

⁵ Tsuda, M.; Toriyabe, Y.; Endo, T.; Kobayashi, J. *Chem. Pharm. Bull.* **2003**, *51*, 448-451.

*Determination of E/Z Ratio in Model Silyl Ketene Acetal **S6***

To a dry 25 mL Schlenk tube was added a solution of 33.8 mg (0.16 mmol) propionate menthyl ester **S5**⁶ in 5 mL of diethyl ether and allowed to stir at -78 °C. To this solution was introduced 0.636 mL (0.32 mmol) of a 0.5 M solution of KHMDS in toluene via syringe over 5 min and let stir for 5 min. Then, 0.061 mL (0.48 mmol) of TMSCl was immediately added to the reaction. After stirring for 10 min the reaction vessel was concentrated. Under argon, approximately 0.6 mL of benzene-*d*₆ was added to the reaction and syringed into a dry NMR tube for analysis. Solvent suppression of any left over ether resulted in a 95:5 *E*:*Z* ratio by ¹H NMR. ¹H NMR of menthyl propionate ester **S5** matched that reported. *E* and *Z*-enolate shifts matched similar compounds reported.⁷ ¹H NMR (500 MHz, CDCl₃, ppm) *E*-enolate δ 3.78 (q, 1H, *J* = 6.5 Hz, RCOC=CHCH₃), *Z*-enolate 3.57 (q, 1H, RCOC=CHCH₃).

⁶ Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560-4567.

⁷ Ireland, R. E.; Wipf, P.; Armstrong, J. D. III. *J. Org. Chem.* **1991**, *56*, 650-657.

Chiral Cyclohexadiene Diol Synthesis

Scheme S3. Synthesis of Triene **26**

1-((4*S*,5*R*)-5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-yn-1-ol (S7): To a 200 mL, rb flask equipped with a magnetic stir bar and rubber septa, were added 1.60 g **24**⁸ (10 mmol) and 100 mL tetrahydrofuran. The solution was cooled to 0 °C and 40 mL (10 mmol, 2 equiv) of a 0.5M solution of ethynlmagnesium bromide in diethyl ether was added dropwise via syringe. The solution was allowed to warm to ambient temperature and then stirred for 12 h, at which time the starting material was consumed (GC analysis). The reaction was diluted with 40 mL of diethyl ether and quenched by the addition of 50 mL of a saturated NH₄Cl solution. The organic phase was separated and the remaining aqueous phase was extracted with diethyl ether (3 X 100 mL). The combined organic phases were washed with water then 100 mL of a saturated brine solution, dried (Na₂SO₄) and concentrated *in vacuo* (rotary evaporator) to give a crude orange oil. The crude oil was purified by flash chromatography on silica gel (4.2 X 11 cm column, 1:1 ethyl acetate/ hexanes) to give 1.77 g (95% yield) of the product **S7** as a light yellow oil. Analytical TLC R_f 0.31 (1:1 ethyl acetate/

⁸ Jeong, L. S. et al., *J. Org. Chem.* **2001**, 66, 6490-6494.

hexanes, KMnO_4 visualization); $[\alpha]_{\text{D}}^{25}$ -31.1 ($c = 0.52$, CHCl_3); GC analysis (ret time 12.70 min) ; ^1H NMR (500 MHz, CDCl_3 , ppm) δ 4.58 (dd, $J = 7.0$, 2.0 Hz, 1H), 4.33 (dt $J = 10.5$, 6.5 Hz, 1H), 4.23 (t, $J = 7.0$ Hz, 1H), 3.96 (dd, $J = 11.5$, 4.0 Hz, 1H), 3.92 (dd, $J = 12.0$, 6.0 Hz, 1H), 2.54 (d, $J = 2.0$ Hz, 1H), 1.50 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 108.84, 82.12, 78.80, 76.86, 74.33, 61.29, 60.14, 27.35, 25.04; FT-IR (thin film, cm^{-1}) 3440, 3289, 2999, 2940, 2887, 1387, 1216, 1163, 1051, 854; High-resolution ESI molecular ion calculated for $\text{C}_9\text{H}_{14}\text{O}_4 + \text{Na}$ 209.079, found 209.078, error 0.8 ppm.

S8

(4*R*,5*R*)-2,2-Dimethyl-4-((triethylsilyloxy)methyl)-5-((*R*)-1-(triethylsilyloxy)prop-2-ynyl)-1,3-dioxolane (S8): To a 200 mL, rb flask containing a magnetic stir bar were added 1.39 g **S7** (7.46 mmol) and 70 mL dichloromethane, followed by 2.18 mL triethylamine (15.67 mmol, 2.1 equiv). After 15 min, 2.63 mL triethylchlorosilane (15.67 mmol, 2.1 equiv) was added dropwise by syringe at room temperature. The reaction was stirred 19 h and was then quenched with a saturated NH_4Cl solution. The crude organic solution was transferred to a separatory funnel and washed successively with water (50 mL) and brine (50 mL) and dried (Na_2SO_4). The crude solution was concentrated *in vacuo* (rotary evaporator) to give a light orange oil which was purified by flash chromatography on silica gel (4.2 X 11 cm column, 1:4 ethyl acetate/ hexanes), providing 2.25 g (73% yield) of product **S8** as a light yellow oil. Analytical TLC R_f 0.57 (1:4 ethyl acetate/ hexanes, KMnO_4 visualization); $[\alpha]_{\text{D}}^{25}$ +10.7 ($c = 0.56$, CHCl_3); GC analysis (ret time 16.67 min) ^1H NMR (500 MHz, CDCl_3 , ppm) δ 4.57 (dd, $J = 6.0$, 2.5 Hz, 1H), 4.28 (m, 1H), 4.12 (t, $J = 6.0$ Hz, 1H), 4.04 (dd, $J = 11.0$, 3.5 Hz, 1H), 3.80 (dd, $J = 11.0$, 8.0 Hz, 1H), 2.46 (d, $J = 1.5$ Hz, 1H), 1.49 (s, 3H), 1.36 (s, 3H), 0.97 (q, $J = 8.0$ Hz, 18H), 0.66 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 123.92, 108.86, 82.99, 79.54, 78.47, 74.19, 62.13, 61.92, 27.42, 25.17, 6.78, 4.88, 4.35; FT-IR (thin film, cm^{-1}) 3309, 3276, 2954, 2882, 1485, 1420, 1374, 155, 1091, 1031, 738; High-resolution MS ESI molecular ion calcd for $\text{C}_{21}\text{H}_{42}\text{O}_4\text{Si}_2 + \text{Na}$ 437.2519, found 437.2514, error 2.7 ppm.

S9

(4*R*,5*R*)-2,2-Dimethyl-4-((*R*)-2-methylene-1-(triethylsilyloxy)but-3-enyl)-5-((triethylsilyloxy)methyl)-1,3-dioxolane (S9): A 300 mL aerosol reaction vessel was charged with 3.81 g **S8** (9.18 mmol) and 90 mL dichloromethane. The vessel was sealed and charged to 80 psig with ethylene and purged (4X) to pre-saturate the solution with ethylene. The vessel was vented and 467 mg **Ru gen-2** (6 mol%, 0.55 mmol) were added. The vessel was charged to 80 psig with ethylene and the dark red solution was stirred for 24 h, at which time the starting material was consumed (GC analysis). The crude reaction was filtered through a pad of silica gel (7 g) and 0.5 mL dimethylsulfoxide was added. After stirring for 24 h, the crude solution was concentrated *in vacuo* (rotary evaporator) and the product was isolated by flash chromatography on silica gel (3 X 18 cm column, 5% ethyl acetate/ hexanes) to give 3.11 g (92% yield) of the diene **S9** as a faint yellow oil. Analytical TLC R_f 0.33 (5% ethyl acetate/ hexanes, KMnO_4 visualization); $[\alpha]_D^{25} +17.8$ ($c = 0.56$, CHCl_3); GC analysis (ret time 17.49 min) ^1H NMR (500 MHz, CDCl_3 , ppm) δ 6.34 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.48 (dd, $J = 17.5, 0.5$ Hz, 1H), 5.28 (s, 1H), 5.20 (s, 1H), 5.12 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 6.5$ Hz, 1H), 4.18 (m, 2H), 3.99 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.77 (dd, $J = 11.5, 8.0$ Hz, 1H), 1.43 (s, 3H), 1.31 (s, 3H), 0.95 (m, 18H), 0.63 (t, $J = 8.0$ Hz, 6H), 0.58 (t, $J = 8.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 146.63, 135.48, 116.81, 115.28, 108.10, 79.25, 78.35, 72.13, 62.51, 27.83, 25.32, 6.89, 6.72, 4.96, 4.38; FT-IR (thin film, cm^{-1}) 2960, 2920, 2874, 1472, 1426, 1380, 1241, 1209, 1143, 1083, 1004, 912, 827, 741; High-resolution MS ESI molecular ion calcd for $\text{C}_{23}\text{H}_{46}\text{O}_4\text{Si}_2 + \text{Na}$ 465.2832, found 465.2827, error 1.0 ppm.

25

(*R*)-1-((4*R*,5*R*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl)-2-methylenebut-3-enyl acetate (25): To a 25 mL rb flask containing 25 mL dichloromethane, cooled to -78°C , were added 10 mL (19.9 mmol, 4.4 equiv) of 2M oxalyl chloride in dichloromethane and 2.8 mL (39.6 mmol, 8.8 equiv) dimethylsulfoxide. The solution was stirred for 15 min and a solution of 2.0 g (4.5 mmol, 1 equiv) **S7** in 20 mL dichloromethane was added slowly (ca. 5 min) by syringe. The solution

was maintained at -78 °C for 20 min and was allowed to warm to -40 °C. The solution was kept at -40 °C for 30 min, at which time the starting material was consumed (TLC). The reaction was cooled to -78 °C and 9.4 mL (67.5 mmol, 15 equiv) of triethylamine were added. The reaction was removed from the cooling bath and allowed to come to room temperature. The reaction was quenched by the addition of 40 mL of a saturated NH_4Cl solution. The organic phase was treated with water (60 mL) and brine (2 X 50 mL) and then dried (Na_2SO_4). The crude aldehyde solution was diluted with 40 mL tetrahydrofuran and the dichloromethane was removed by rotary evaporation, at reduced pressure (500 mmHg, 35 °C), leaving approximately 38 mL crude solution.

To a 100 mL, three-neck rb flask equipped with a 125 mL, pressure-equalizing addition funnel were added, 4.82 g (13.5 mmol, 3 equiv) $\text{Ph}_3\text{PCH}_3\text{Br}$ and 50 mL tetrahydrofuran. The slurry was cooled to -78 °C and 6.0 mL (12.6 mmol, 2.8 equiv) of 2.09 M *n*-butyllithium solution in hexanes was added slowly by syringe (ca. 10 min). After the addition was complete, the reaction was allowed to warm to rt and stirred for 1 h. The red phosphorane solution was returned to the -78 °C bath and the addition funnel was charged with the aldehyde solution (40 mL) from above. The aldehyde solution was added dropwise over 30 min and the reaction was stirred at -78 °C for 30 min. The reaction was removed from the cooling bath and allowed to stir at ambient temperature for 3 h. The reaction was quenched with water (50 mL) and the aqueous phase was extracted with diethyl ether (3 X 100 mL). The combined organic phases were treated with brine (200 mL) and dried (Na_2SO_4). The organics were filtered and stored at -20 °C overnight. The crude organic slurry was filtered through a 3" pad of silica gel (5 g) and the filtrate was concentrated (rotary evaporator) to give 0.60 g of a light orange oil. The presence of the desired product was verified by GC analysis (ret time 14.61 min) and the crude oil was carried through to the next reaction without further purification.

To a 200 mL rb flask containing a magnetic stir bar were placed the crude triene from above (0.60 g) and 45 mL tetrahydrofuran. The solution was cooled to 0 °C in an ice bath and 5.0 mL (4.95 mmol, 1.1 equiv) of a 1M tetrabutylammonium fluoride solution in tetrahydrofuran was added dropwise via a polyethylene syringe. After 20 min, the reaction was diluted with 50 mL ethyl acetate. The crude solution was washed successively with water (30 mL) and brine (30 mL), followed by drying (Na_2SO_4) and filtration through a 1" pad of silica (2 g). Concentration (rotary evaporator) of the crude product gave 1.26 g of a light orange oil. The presence of the crude product was verified by GC analysis (ret time 12.28 min) and the compound was used in the next reaction without further purification.

To a 200 mL, rb flask were added the crude alcohol from the previous reaction (1.26 g), 45 mL dichloromethane and 1.35 mL triethylamine (13.5 mmol, 3 equiv). After 5 min, 1.3 mL acetic anhydride (13.5 mmol, 3 equiv) and 55 mg dimethylaminopyridine (0.45 mmol, 10 mol %) were added to the flask and the reaction was stirred 12 h at ambient temperature. The reaction was quenched

with saturated NH_4Cl solution (100 mL) and the crude organic solution was washed with sodium bicarbonate solution (2 X 50 mL), water (100 mL) and brine (2 X 50 mL) and then dried (Na_2SO_4). Concentration (rotary evaporator) of the crude solution gave a light yellow oil which was purified by flash chromatography on silica gel (4.2 X 21 cm column, 1:4 ethyl acetate/ hexanes with 1% triethylamine) giving 459.2 mg (40% yield, 4 steps) of **25** as a light yellow oil. Analytical TLC R_f 0.4 (1:4 ethyl acetate/ hexanes, KMnO_4 visualization); $[\alpha]_D^{25}$ -44.6 ($c = 0.56$, CHCl_3); GC analysis (ret time 14.61 min); ^1H NMR (500 MHz, CDCl_3 , ppm) δ 6.34 (dd, $J = 17.5, 11.0$ Hz, 1H), 5.83 (ddd, $J = 17.0, 10.0, 7.5$ Hz, 1H), 5.53 (d, $J = 17.5$ Hz, 1H), 5.37 (dd, $J = 17.5, 1.0$ Hz, 1H), 5.34 (s, 1H), 5.30 (d, $J = 10.0$ Hz, 1H), 5.25 (s, 1H), 5.23 (d, $J = 11.0$ Hz, 1H), 5.15 (d, $J = 11.0$ Hz, 1H), 4.68 (t, $J = 6.5$ Hz, 1H), 4.40 (dd, $J = 9.5, 6.5$ Hz, 1H), 1.98 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 169.0, 143.3, 135.2, 132.7, 118.2, 118.1, 115.6, 109.1, 78.9, 77.8, 71.7, 27.6, 25.1, 20.9; FT-IR (thin film, cm^{-1}) 3098.4, 2999.6, 2940.4, 2887.8, 1762.3, 1597.8, 1433.3, 1374.0, 1222.7, 1163.4, 1038.4, 998.9, 919.9, 873.9; High-resolution MS ESI molecular ion calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4 + \text{Na}$ 275.1259, found 275.1259, error 0.0 ppm.

(Z)-Methyl 4-(((4S,5R)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)methylene)hex-5-enoate (26): To a 10 mL rb flask was added, 1.5 mL 1M LiHMDS solution in tetrahydrofuran (1.5 mmol, 1.5 equiv). The solution was cooled in a -78°C bath for 5 min and 0.174 mL HMPA (1.0 mmol, 1 equiv) was added via microliter syringe. After 15 min, a solution of 252 mg **25** (1.0 mmol, 1 equiv), 226 mg *t*-butyldimethylchlorosilane (1.5 mmol, 1.5 equiv) and 1.0 mL tetrahydrofuran was added by syringe. After 15 min, the reaction was removed from the cooling bath and stirred at rt for 19 h, at which time the starting material was consumed (TLC analysis). The reaction was quenched with 10 mL water and the aqueous phase was extracted with pentane (4 X 10 mL). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo* (rotary evaporator) to give an orange oil. The crude oil was diluted with 3.0 mL HMPA and 150 mg KHCO_3 (1.5 mmol, 1.5 equiv) and 141 mg $\text{KF}_2 \cdot \text{H}_2\text{O}$ (1.5 mmol, 1.5 equiv) were added. After stirring 40 min, 0.12 mL iodomethane (2.0 mmol, 2.0 equiv) was added by microliter syringe. The reaction was stirred 18 h at ambient temperature, at which time, the reaction was complete (TLC analysis). The reaction was quenched by the addition of 15 mL water. The aqueous phase was extracted with pentane (5 X 20 mL) and the combined organic phases were dried (Na_2SO_4). The crude product was concentrated to give an orange oil which was purified by flash

chromatography on silica gel (3 X 13 cm column, 1:4 ethyl acetate/ hexanes) to give 166 mg (62% yield) of the product as a faint yellow oil. The triene **26** was isolated as a 10:1 mixture of stereoisomers. Analytical TLC R_f 0.44 (1:4 ethyl acetate/ hexanes, KMnO_4 visualization); GC analysis (ret time 14.22, 14.33 min); NMR Data for the major isomer: ^1H NMR (500 MHz, CDCl_3 , ppm) δ 6.55 (dd, J = 17.5, 11.0 Hz, 1H), 5.71 (ddd, J = 17.0, 10.0, 7.0, 1H), 5.37 (d, J = 8.5 Hz, 1H), 5.30 (d, J = 17.5 Hz, 1H), 5.63 (d, J = 17.0, 1H), 5.21 (d, J = 11, 1H), 5.17 (d, J = 10.5, 1H), 5.07 (dd, J = 8.5, 6.5 Hz, 1H), 4.56 (t, J = 6.5 Hz, 1H), 3.66 (s, 3H), 2.55 (m, 2H), 2.46 (m, 2H), 1.51 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 173.37, 139.16, 134.14, 131.81, 125.63, 118.03, 116.29, 108.73, 79.95, 74.07, 51.58, 33.15, 28.44, 28.07, 25.52; FT-IR (thin film, cm^{-1}) 3098, 2986, 2953, 1748, 1439, 1360, 1248, 1215, 1169, 1057, 991, 925, 879; High-resolution MS ESI molecular ion calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4 + \text{Na}$ 289.1416, found 289.1423, error 2.4 ppm.

Major isomer of **26**: The regiochemical assignment of the major isomer was supported by nOe studies. Irradiation of the vinylic proton at δ 5.37 ppm gave nOe enhancement of the methine resonance at δ 5.07 ppm and the allylic methylene protons appearing at δ 2.55 ppm.

27

Methyl-3-((3a*S*,7a*R*)-2,2-dimethyl-3a,7a-dihydrobenzo[d][1,3]dioxol-5-yl)propanoate (27): To a 50 mL Schlenk flask, equipped with a magnetic stir bar, were added 25 mg **26** (0.094 mmol) and 1 mL dichloromethane, followed by 4.8 mg **Ru gen-2** (0.006 mmol, 6 mol %). The flask was fit with a cold finger condenser and the reaction was placed in a 40 °C oil bath. After 2 h, the reaction was complete (TLC analysis) 1 mL of ethyl vinyl ether was added to deactivate the catalyst and the crude reaction was then passed through a plug of silica and concentrated. The crude product was purified by flash chromatography on silica gel (2.8 X 10 cm column, 1:4 ethyl acetate/ hexanes) to give 11.1 mg (50% yield) of the cyclohexadiene **27** as a clear oil. Analytical TLC R_f 0.49 (1:4 ethyl acetate/ hexanes, I_2 visualization); $[\alpha]_D^{25}$ -10.5 (c = 0.40, CHCl_3); GC analysis (ret time 14.10 min); ^1H NMR (500 MHz, CDCl_3 , ppm) δ 5.88 (dd, J = 10.0, 2.5 Hz, 1H), 5.85 (d, J = 9.5 Hz, 1H), 5.62 (s, 1H), 4.62 (m, 2H), 3.67 (s, 3H), 2.45 (m, 4H), 1.40 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 , ppm) δ 173.20, 134.81,

126.44, 126.16, 119.33, 104.76, 70.55, 70.42, 51.70, 32.39, 30.57, 26.73, 24.75;
FT-IR (CHCl_3 , CaF_2 cell, cm^{-1}) 2951, 2940, 2917, 2906, 1738, 1444, 1387, 1370,
1268, 1166, 1053, 1036; High-resolution MS ESI molecular ion calcd for
 $\text{C}_{13}\text{H}_{18}\text{O}_4 + \text{Na}$ 261.1103, found 261.1101, error 0.8 ppm.

Proton and Carbon NMR Spectra for New Compounds

DAC2273

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: DAC2273

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 1.000 sec

Pulse 46.9 degrees

Acq. time 1.800 sec

Width 6000.6 Hz

16 repetitions

OBSERVE HL, 399.918918 MHz

DATA PROCESSING

Line broadening 0.9 Hz

FT size 32768

Total time 0 min, 44 sec

13C OBSERVE

Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 12761.7 Hz
SFO 125.760 MHz
OBSERVE CH1 300.136658 MHz
DECOUPLE CH1 300.1354431 MHz
Power 1023.08
Continuously on
WALTZ-16 irradiated
DATA PROCESSING
F1 size 65536
Total time 1 hr, 58 min, 57 sec

2C

dc2248_methylster

Pulse Sequence: sipul

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2248_methylster

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8983908 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

3C

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Sample #2, user 1-14-87
 File: dc2248_methylster.cl3
 INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 6.000 sec
 Pulse 81.8 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 72 repetitions
 OBSERVE C13, 125.6995629 MHz
 DECOUPLE H1, 499.9008903 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 131072
 Total time 1 hr, 2 min, 51 sec

dc2245

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2245

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8983908 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dc_2245_c13

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc_2245_c13

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

32 repetitions

OBSERVE C13, 75.4536647 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

dc_2245_c13

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc_2245_c13

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

32 repetitions

OBSERVE C13, 75.4536647 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

AAK-1V-butadiene-claisen
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 Sample #2
 File: AAK-1V-butadiene-claisen-1H
 INOVA-500 1Hnmr data.C1206.001F010.f001
 Relax. delay 2.000 sec
 Pulse 30.6 degrees
 Acc. time 1.811 sec
 Wch 10000 Hz
 32 repetitions
 OBSERVE H1 415.8984239 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 2 min, 20 sec

Compound 5C
 (1H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient Temperature
Sample #2: user 1-14-07
F1: 101.625 MHz
INDRA-500 - raw data: chn1.bur616.daw

Relax. delay 6.000 sec
Pulse 11.0 degrees
Pulse 11.0 degrees
Width 3737.8 Hz
486 repetitions
OBSERVE C13, 125.695595 MHz
DECOUPLE H1, 499.500893 MHz
Power 49 dB
continuously on
VOLT-16 modulated
DATA PROCESSING
F1: 101.625 MHz
F2: 125.131727 MHz
Total time 4 hr, 9 min, 58 sec

Compound 5C
(¹³C-NMR spectrum)

dc2260_pure

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2260_pure

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8983908 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dc2260_cl3

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2260_cl3

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

64 repetitions

OBSERVE Cl3, 75.4536621 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

dc2281_2

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2281_2

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984331 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

STANDARD PROTON PARAMETERS

Pulse Sequence: sput1
 Solvent: CDCl3
 Ambient temperature
 Sample #2
 File: dc_alc_separation_9
 INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec
 Pulse 34.6 degrees
 Acq. time 1.891 sec
 Width 10000.0 Hz
 16 repetitions

OBSERVE HL, 499.8984130 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 1 min, 18 sec

dc_alc_sep_C13

Pulse Sequence: sput

Solvent: CDCl₃

Ambient temperature

Sample #2

File: dc_alc_sep_C13

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

192 repetitions

OBSERVE C13, 75.4536601 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

dc_alc_seperation_6

Pulse Sequence: sfpul

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc_alc_seperation_6

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984133 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dcf_alc_sep_double_C13

Pulse Sequence: sfpul

Solvent: CDCl3

Ambient temperature

Sample #2

File: dcf_alc_sep_double_C13

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

4512 repetitions

OBSERVE C13, 75.4536589 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 119 hr, 22 min, 32 sec

dc2253_2

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2253_2

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984127 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dc2253_c13

Pulse Sequence: zgpg30

Solvent: CDCl₃

Ambient temperature

Sample #2, user 1-14-87

File: dc2253_c13

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 6.000 sec

Pulse 81.8 degrees

Acq. time 1.300 sec

Width 37037.0 Hz

7296 repetitions

OBSERVE C13, 125.6995503 MHz

DECOUPLE H1, 499.9008903 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

PT size 131072

Total time 129 hr, 57 min, 0 sec

dc2258

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2258

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984267 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dc2258_cl3

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2258_cl3

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

32 repetitions

OBSERVE C13, 75.4536550 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

dc2254_colmn

Pulse Sequence: sipul

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2254_colmn

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984084 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

9C

dc225a_c13

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

GENI-300 "foesy.chem.buffalo.edu"

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.206 sec

Width 18761.7 Hz

5296 repetitions

OBSERVE C13, 75.4536589 MHz

DECOUPLE W1, 300.0754431 MHz

Power 1023 dB

continuously on

Waltz-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 124 hr, 13 min, 7 sec

dc2273_6

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2273_6

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8983908 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

dc2273_cl3_6

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2, user 1-14-87

File: dc2273_cl3_6

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 6.000 sec

Pulse 81.8 degrees

Acq. time 1.300 sec

Width 37037.0 Hz

200 repetitions

OBSERVE C13, 125.6995567 MHz

DECOUPLE H1, 499.9008903 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

PT size 131072

Total time 1 hr, 2 min, 51 sec

dc2272_6

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2272_6

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984133 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

dc2276_c13

Pulse Sequence: sgpr1

Solvent: CDCl3

Ambient temperature

Sample #2

File: dc2276_c13.a

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

64 repetitions

OBSERVE C13, 75.4536664 MHz

DECOUPLE H1, 300.0754431 MHz

Power 1.023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 55 min, 2 sec

K941179

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

File: d2252

INOVA-500 "nordata1.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.5 degrees

Acq. time 1.551 sec

Width 10095.0 Hz

16 repetitions

Observed Hz: 99.893368 MHz

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

8pk1179_C13

Pulse Sequence: s2D01

Solvent: CDCl3

Ambient temperature

User: 1-14-97

File: dc2254_C13

INVO-998 "nerdata1.chem.buffalo.edu"

Relax. delay 6.000 sec

Pulse 81.5 degrees

Acq. time 1.300 sec

Width 3783.0 Hz

81 repetitions 25.445781 MHz

Observed C13, 125.754 MHz

Decouple H1, 400.146603 MHz

Power 50 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 13172

Total time 1 hr, 2 min, 51 sec

11B

kp1183

Pulse Sequence: zgpg30

Solvent: CDCl3

Acquisition temperature

File: kp1183

INOVA-500 -nordata1.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 11.3 degrees

Acq. time 1.831 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8084330 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

AAK-cyclohexadiene-substrate

Pulse Sequence: zgpg30

Solvent: CDCl3

Acquire Temperature

Sample #2

File: AAK-IV-cyclohexadiene-substrate-1M

INOVA-500 "nvardata.chm.buffalo.edu"

Relax. delay 2.000 sec

Pulse 39.6 degrees

Acq. time 1.831 sec

Gain 1011.8

32 Channels

ORFIVE H1 499.998478 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 2 min., 20 sec

Compound 12B

(¹H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient temperature
 Sample #2, user 1-14-87
 File: AAK-IV-Cyclohexadiene-substrate-13C
 INOVA-500 "harddata.chen.buffalo.edu"

Relax. delay 6.000 sec
 Pulse 81.8 degrees
 Acq. time 1.300 sec
 FID 3265100 Hz
 SFO 125.631100 MHz
 OBSERVE C13, 125.631523 MHz
 DECOUPLE H1, 499.368563 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FI size 131072
 Total time 5 hr, 7 min, 36 sec

Compound 12B
 (¹³C-NMR spectrum)

cyclohexadiene-cholesten-1H

Pulse Sequence: zgpg30

Solvent: CDCl3

Acquisition Temperature

File Name: TV-Cyclohexadiene-cholesten-1H

INOVA-500 "nmrdata.chen.buffalo.edu"

Relax. delay: 2.000 sec

Pulse: 36.5 degrees

Acq. time: 3.551 sec

Width: 10000.0 Hz

32 repetitions

OBSERVE: H1, 499.8984220 MHz

DATA PROCESSING

Line broadening: 0.7 Hz

FI size: 65536

Total time: 2 min, 20 sec

Compound 12C
(¹H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 Sample #2 user 1-14-87
 1116: add-14-cyclohexylidene-13C
 140A-500 "harddata.chk.buffalo.edu"

Relax. delay 8.000 sec
 Pulse 01.800000 sec
 Acq. time 3.500 sec
 Width 37137.0 Hz
 384 repetitions
 OBSERVE C13, 125.6185503 MHz
 DECOUPLE H1, 455.3485503 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT 162.131872
 Total time 3 hr, 7 min, 36 sec

Compound 12C
 (¹³C-NMR spectrum)

ANK-IV-237-f1-1H
 Pulse Sequence: s2pul1
 Solvent: CDCl3
 Ambient temperature
 Sample #2
 File: ANK-IV-237-f1-1H
 INOVA-500 ¹HMRdata.chem.buffalo.edu
 Relax. delay 2.000 sec
 Pulse 34.8 degrees
 Acq. time 1.091 sec
 Width 1000.0 Hz
 32
 32
 OBSERVE H1 499.8144071 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 2 min, 28 sec

Compound 12D
 (¹H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul3
 Solvent: CDCl3
 Ambient temperature
 Sample #2, user 1-19-87
 File: dmh-1v-237-f1-13C
 INOVA-500 "nmrdata.chk, buffalo.edu"

Relax. delay 8.000 sec
 Pulse 61.0 degree
 Acc. time 1.500 sec
 Wdth 3702.0 Hz
 Wdth (ppm) 100
 OBSERVE C13, 125.689555 MHz
 DECOUPLE H1, 455.5008903 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 Time 13.072 sec
 Total time 4 hr, 8 min, 58 sec

Compound 12D
 (13C-NMR spectrum)

Adk-IV-pentynylacetate-cyclohexadiene
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Sample #2
1H NMR pentynylacetate-cyclohexadiene-1H
1400A-500 "nmrdata.chea-baffa1o.edu"
Relax. delay 2.880 sec
Acq. time 1.091 sec
Acq. date 11/03/01
Width 10000.0 Hz
32 repetitions
OBSERVE H1, 499.8183843 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 2 min, 20 sec

Compound 13B
(1H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 Sample #2, user 1-14-87
 File: pentylacetate-cyclohexadiene-13C
 INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 6.000 sec
 Pulse 81.6 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 Spectrometer
 OBSERVE C13, 125.6895518 MHz
 DECOUPLE H1, 499.9089933 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 131072
 Total time 2 hr, 5 min, 13 sec

Compound 13B
 (13C-NMR spectrum)

Compound 13C
(¹H-NMR spectrum)

Add-claisen-int-yna
 Pulse Sequence: 32pul
 Solvent: CDCl3
 Ambient temperature
 Sample #2
 File: Add-IV-int-yna-claisen-1H
 INOVA-500 "ovrdm.chm.buffalo.edu"
 Relax. delay 2.000 sec
 Pulse 36.6 degrees
 Acq. time 1.833 sec
 Wdth 16000.0 Hz
 320000000
 OBSERVE H1
 499.8504825 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 2 min, 20 sec

cycloheptadiene-claisen-dan-1H

Pulse Sequence: zgpg30

Solvent: CDCl3

Acq. time: 1.00 sec

Sample #2

File: AAK-1V-cyclohep-claisen-dan-1H

INDVA-500 "nerdata.Chem.Buffalo.edu"

Relax. delay: 2.000 sec

Pulse: 34.6 degrees

Acq. time: 1.00 sec

Width: 10000.0 Hz

32 repetitions

Observed F1: 300.135 MHz

Observed F2: 300.135 MHz

FT size: 65536

Time: 2 min, 20 sec

Compound 14C
(¹H-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30
 Solvent: CDCl₃
 Acquisition temperature:
 Sample #2 user 1-14-82
 File: aak-1v-cycloheptadiene-5an-13C
 INOVA-500 "narda@chem.buffalo.edu"

Relax. delay 6.000 sec
 Pulse 81.8 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 6240 repetitions
 OBSERVE C13, 125.695555 MHz
 DECOUPLE H1, 499.9008103 MHz
 Power 46 dB
 Continous 13C on
 WALTZ-16 simulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 131072
 Total Time 20 hr, 47 min, 55 sec

AKC-IV-cycloheptadiene-substrate
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 Sample 2
 File: AKC-IV-cycloheptadiene-substrate-1H
 INOVA-500 "nar\data\chem\buffalo.edu"

Compound 15B
 (1H-NMR spectrum)

Relax. delay 2.000 sec
 Pulse 30.000 sec
 Acq. time 1.091 sec
 Width 10000.0 Hz
 32 repetitions
 OBSERVE H1, 499.8384083 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 2 min, 20 sec

Pulse sequence: s2pul

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: j-13-87
File: 04x-1y-cyclohepta-substrate-13C
INQV4-500 "cardata1.chem.buffalo.edu"

Relax. delay 6.000 sec
pulse 01.8 degrees
Acq. time 1.380 sec
Width 37037.8 Hz
352 repetitions
FREQ 125.4855658 MHz
RECEIVER 11.459-80.000 MHz
power 40 dB
Continuously on
WATERGATE regulated
DATA PROCESSING
Line broadening 8.5 Hz
F1 size 131072
Total time 2 hr, 5 min, 3 sec

Compound **15B**
(¹³C-NMR spectrum)

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Sample: 25.0% in CDCl3
 INOVA-500 "harddata.cem buffalo.edu"

Relax. delay 6.000 sec
 Acquisition time 1.300 sec
 Width 37837.0 Hz
 2300 repetitions
 OBSERVE C13, 125.699527 MHz
 DECOUPLE H1, 499.900803 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 131072
 Total time 20 hr, 47 min, 55 sec

Compound 15C
 (¹³C-NMR spectrum)

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl₃
Sample temperature
Sample #2
File: AMX-IV-cyclohepta-1,6-dien-3-yl
INDIA-560 "nmr data - chem. buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.6 degrees
Acq. time 1.833 sec
Width 10000.0 Hz
22 repetitions
OBSERVE: H1, 499.8564162 MHz
DATA PROCESSING
F1 size 65536
F1 512x65536
Total time 2 min, 28 sec

Compound 16C
(¹H-NMR spectrum)

Compound 16C
(¹³C-NMR spectrum)

STANDARD CARBON PARAMETERS
Pulse Sequence: zgpg30
Solvent: CDCl₃
Ambient temperature
Sample: 16C-14-27
File: 16C-14-27-cyclohexadien-1-yl-phenyl-ester
INOVA-500 VarData.Chem.Buffalo.edu

Relax. delay 6.000 sec
Acq. 1.6000000000000000
Acq. 1.6000000000000000
Width 37037.8 Hz
544 repetitions
OBSERVE C13, 125.699568 MHz
DECOUPLE H1, 415.9008103 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
16C-14-27
FT 16C-14-27
Total time 6 hr, 5 min, 58 sec

STANDARD CARBON PARAMETERS

Pulse Sequence: zgpg30
 Solvent: CDCl₃
 Acquisition Temperature: 25.00°C
 Sample #2: user 1-14-87
 File: AM-1V-niradoseme-13C
 INOVA-500 "merdata.chem.buffalo.edu"

Relax. delay 8.000 sec
 Pulse 81.0 degrees
 Acq. time 1.386 sec
 Width 37037.0 Hz
 582 repetitions
 DESKEV C13, 125.699544 MHz
 DECOUPLE H1, 499.966903 MHz
 Power 18.00 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 131072
 Total time 2 hr, 5 min, 13 sec

kpk117b_00ac

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

File: kpk117b_00ac

INOVA-500 "harddata1.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.431 sec

Width 18000.0 Hz

16 Spectra

DATA PROCESSING

Line broadening 0.7 Hz

FT size 55536

Total time 1 min, 18 sec

xpk1185
 Pulse sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 File: xpk1185
 300V1-510 "merdata1.chem.buffalo.edu"
 Relax. delay 2.880 sec
 Pulse 34.8 degrees
 Acq. time 1.891 sec
 Width 18000.0 Hz
 F2 100.626131 MHz
 QNP 13C 101.325400 MHz
 DATA PROCESSING
 Line broadening 8.7 Hz
 FT size 65536
 Total time 1 min, 18 sec

S2

8PK1107

Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
File: 8PK1107
INOVA-500 "narda01.chem.buffalo.edu"

Relax. delay 2.000 sec
Pulse 34.5 degrees
Acq. time 1.891 sec
Width 18880.0 Hz
IS repetitions
OBSERVED F1 100.625000 MHz
UNLOCKED F2 500.136000 MHz
F1 time broadening 0.7 Hz
F1 size 85136
Total time 3 min, 15 sec

Kp1187_C13

Pulse sequence: zgpg30

Solvent: CDCl3

Ambient temperature

File: Kp1187_C13

INOVAS-500 "nerdata".chem.buffalo.edu

Relax, delay 5.000 sec

Pulse 90.8 degrees

Acq. time 1.706 sec

Width 18741.7 Hz

334 repetitions

DECOUPLE C13, 75.458667 MHz

DECOUPLE C13, 300.1354631 MHz

Power 1023 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 65536

Total time 1 hr, 55 min, 2 sec

Pulse Sequence: s2pul
Solvent: CDCl₃
Acq solvent temperature: 25
F1: kpk215
INNOVA-500 nerdata@chem.buffalo.edu

```
relax, delay 2.038 sec  
Pulse 34.6 degrees  
Acq. time 1 min, 11 sec  
Width 10000 Hz.  
16 repetitions  
0895R040 HI 499.893577 MHz  
Data 80C5555700000000  
Line broadening 0.7 Hz  
FT size 65536  
Total time 1 min, 18 sec
```

KK1215_C13

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

File: KK1215_C13

INOVA-500 "neridol.chem.buffalo.edu"

Relax. delay 5.000 sec

Pulse 18.0 degrees

Acq. time 1.786 sec

Width 12761.7 Hz

128 repetitions

Observed F1 50.013185 MHz

Observed F2 38.073431 MHz

Power 1823 dB

Continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

F1 5128.85538

Total time 1 hr, 55 min, 2 sec

CC(C)(COC(=O)C)C/C=C/C(C)C1=CC=CC=C1

xpk121b_c13
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 File: xpk121b_c13
 INOVA-300 "nerdnet1.chen.buffalo.edu"
 Relax. delay 5.000 sec
 Pulse 11.0 degrees
 Acq. time 1.798 sec
 Width 18761.7 Hz
 Frequency 300.135 MHz
 QPCPRGVE C13, 75.453653 MHz
 DECOUPLE H1, 398.0754431 MHz
 Power 1823 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 1 hr, 55 min, 2 sec

kpk1291
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 INOVA-500 "tocsy.chem.buffalo.edu"
 Relax. delay 2.000 sec
 Pulse 34.6 degrees
 Acq. time 1.891 sec
 Width 10000.0 Hz
 Frequency 125.761 MHz
 OBSERVING 99.9984008 MHz
 DATA PROCESSING
 Line broadening 0.7 Hz
 FT size 65536
 Total time 1 min, 18 sec

kpk1291_C13

Pulse Sequence: s2pu1

Solvent: CDCl3

Ambient temperature

GEMINI-300 "roesy.chem.buffalo.edu"

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.706 sec

Width 18761.7 Hz

388 repetitions

OBSERVE C13, 75.4536612 MHz

DECOUPLE H1, 300.0754451 MHz

Power 1023.46

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr 0.59 min, 57 sec

BMS 4116

Pulse Sequence: zgpg30

Solvent: CDCl3

Ambient temperature

Sample #2

File: 4116

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984036 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

S7

STANDARD CARBON PARAMETERS

Pulse Sequence: sfpul

Solvent: CDCl₃
 Ambient temperature
 Sample #2, user 1-14-87
 File: 4107.c13
 INOVA-500 ¹nmrdata.chem.buffalo.edu*

Relax. delay 6.000 sec
 Pulse 81.8 degrees
 Acq. time 1.300 sec
 Width 37037.0 Hz
 51.2 repetitions
 OBSERVE C13, 125.6995538 MHz
 DECOUPLE H1, 499.9008903 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 2.0 Hz
 FT size 131072
 Total time 1 hr, 2 min, 51 sec

BMS 4135

Pulse Sequence: sipul

Solvent: CDCl3

Ambient temperature

Sample #2

File: 4135

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984030 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

S8

BMS 4135

Pulse Sequence: sfpul

Solvent: CDCl₃

Ambient temperature

Sample #2, user 1-14-87

File: 4135.c13

INOVA-500 ¹Hmrdata.chem.buffalo.edu*

Relax. delay 6.000 sec

Pulse 81.8 degrees

Acq. time 1.300 sec

Width 37037.0 Hz

312 repetitions

OBSERVE C13, 125.6995504 MHz

DECOUPLE H1, 499.9008903 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 131072

Total time 1 hr, 2 min, 51 sec

S8

BMS 4137

Pulse Sequence: sipul

Solvent: CDCl3

Ambient temperature

Sample #2

File: 4137

INOVA-500 'nmrdata.chem.buffalo.edu'

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE HL, 499.8984030 MHz

DATA PROCESSING

Line broadening 0.7 Hz

PT size 65536

Total time 1 min, 18 sec

S9

Pulse Sequence: s2pul

Ambient temperature

File: 4137 c13

[illegible]

Pulse 81.8 degrees

Width 37037.0 Hz

100 repetitions
OBSERVE C13 1.25

DECOUPLER HI, 499.9008903 MHz
Power 40 dB

continuously on
water is modulated

DATA PROCESSING

FT size 131072

Total time 1 hr, 2 min, 51 sec

BMS 4160 f14

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Sample #2

File: 4160 f14

INOVA-500 "nmrdata.chem.buffalo.edu"

25

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984033 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

BMS 4160 C13

Pulse Sequence: s2pul

Solvent: CDCl₃
Ambient temperature
Sample #2, user 1-14-87
File: 4160_c13
INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 6.000 sec
Pulse 81.8 degrees
Acq. time 1.300 sec
Width 37037.0 Hz
6784 repetitions
OBSERVE C13, 125.6995521 MHz
DECOUPLE H1, 499.9008903 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 20 hr, 18 min, 41 sec

BMS 4143

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Sample #2

File: 4143

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984024 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

BMS 4143 c13

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

Sample #2, user 1-14-87

File: 4143_f5_c13

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 6.000 sec

Pulse 81.8 degrees

Acq. time 1.300 sec

Width 37037.0 Hz

432 repetitions

OBSERVE C13, 125.6995538 MHz

DECOUPLE H1, 499.9008903 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 131072

Total time 1 hr, 2 min, 51 sec

BMS 4165

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Sample #2

File: 4165

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 2.000 sec

Pulse 34.6 degrees

Acq. time 1.891 sec

Width 10000.0 Hz

16 repetitions

OBSERVE H1, 499.8984027 MHz

DATA PROCESSING

Line broadening 0.7 Hz

FT size 65536

Total time 1 min, 18 sec

BMS 4165 C13

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Sample #2, user 1-14-87

File: BMS4165.c13.g

INOVA-500 "nmrdata.chem.buffalo.edu"

Relax. delay 5.000 sec

Pulse 90.0 degrees

Acq. time 1.295 sec

Width 37037.0 Hz

34448 repetitions

OBSERVE C13, 125.6759287 MHz

DECOUPLE H1, 499.8054204 MHz

Power 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 5.0 Hz

FT size 131072

Total time 350 hr, 14 min, 0 sec