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Supporting Information to Accompany:

Rhodium(I)-Catalyzed [4+2+2] Cycloadditions of 1,3-Dienes, Alkenes, and Alkynes for the Synthesis of Cyclooctadienes

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General methods and Chromatography: Unless otherwise specified, all reactions were carried out in oven-dried glassware ($> 120\text{ }^{\circ}\text{C}$) which was allowed to cool under a dry atmosphere of nitrogen. Liquids and solutions were transferred via syringe or stainless steel cannula. Stirring of reaction vessels was accomplished with TeflonTM coated magnetic stir bars. Elevated temperatures were maintained in thermostat-controlled oil baths. Organic solutions were concentrated using a Heidolf rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates (0.25 mm, silica gel 60, F₂₅₄, glass-backed, Merck) were visualized by ultraviolet light or treatment with acidic anisaldehyde stain followed by gentle heating. Chromatographic purification of products was accomplished by flash chromatography, as described by Still and co-workers.¹ Silica gel 60, 230-400 mesh was purchased from EM Science. [RhCl(CO)₂]₂ was purchased from Strem Chemicals. 1,2 dichloroethane (DCE) (99+%, ACS reagent grade) was purchased from Aldrich Chemical Co and always distilled prior to use. But-3-yn-2-one was purchased from Lancaster. All alkynes as well as 2,3-dimethylbutadiene were purchased from Aldrich Chemical Co. and distilled prior to use. AgSbF₆ was purchased from Aldrich Chemical Co. and was used as a solution in DCE (0.02 M), which was stored in a schlenk flask at $-25\text{ }^{\circ}\text{C}$ and was used for several weeks after preparation. All other starting materials were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Tetrahydrofuran (THF), diethyl ether, and dichloromethane were dried prior to use by elution through an alumina column (Solv-tek Inc).

Physical and Spectroscopic Measurements: NMR spectra were measured on a Varian, INOVA 600 MHz (¹H at 600 MHz, ¹³C at 150 MHz), Varian INOVA 500 (¹H at 500 MHz, ¹³C at 125 MHz) or Varian MERCURY 400 (¹H at 400 MHz, ¹³C at 100 MHz) magnetic resonance spectrometer. Data for ¹H NMR spectra are reported as follows: chemical shift (ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, dq = doublet of quartets, dddd = doublet of doublet of doublets of doublets, ddddd = doublet of doublet of doublet of doublet of doublets, sept = septet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts are reported as δ values in parts per million and are referenced to the residual solvent resonances (HCCl₃: $\delta = 7.26$ ppm for ¹H, $\delta = 77.0$ ppm for ¹³C). Nuclear Overhauser effect (nOe) data were measured at

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

500 MHz or 600 MHz and are reported as follows: H (irradiated)→H (observed), % enhancement. Data for ^{13}C are reported in terms of chemical shift and quantity of carbons. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX Fourier transform spectrometer. Absorption frequencies are reported in wavenumbers (cm^{-1}) for thin films of neat material on NaCl or KBr plates. High-resolution mass spectra (HRMS) were recorded at the NIH regional mass spectrometry facility at the University of California, San Francisco. Reported mass values are with error limits of ± 1 millimass unit. Low-resolution mass spectra (LRMS) were recorded at the Stanford University mass spectrometry facility.

[4+2+2] Representative Procedure and Characterization Data for Cycloadducts:

Representative Procedure: Freshly distilled 1,2-dichloroethane (DCE, 0.90 mL) was added to an oven-dried, N_2 flushed, round bottom flask equipped with a septum containing chlorodicarbonylrhodium (I) dimer (3.5 mg, 0.009 mmol) and a stir bar. Silver hexafluoroantimonate (0.02M in DCE, 0.90 mL, 0.018 mmol) was added via syringe under N_2 followed by diene-ene **1** (50 mg, 0.18 mmol) and methyl propargyl ether (19 μL , 0.22 mmol). Positive nitrogen pressure was removed and reaction vessel placed into a temperature controlled oil bath set to 40 $^\circ\text{C}$. After 3 hours no starting material could be detected via TLC. The solvent was removed *in vacuo* and the residue was purified via flash column chromatography (20% Et_2O /Pentane) yielding cycloadducts **2a** (40 mg, 0.12 mmol, 67%), and **2b** (9 mg, 0.03 mmol, 18%) as a clear oils.

Characterization for **2a**:

^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 5.46-5.50 (m, 1H), 5.08 (d, J = 8.5 Hz, 1H), 3.74 (d, 11.5 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.62 (d, 11.5 Hz, 1H), 3.25 (s, 3H), 2.93-3.00 (m, 2H), 2.61 (dd, J = 19 Hz, 6 Hz, 1H), 2.53 (dd, J = 15 Hz, 7.5 Hz, 1H), 2.40 (dd, J = 12.5 Hz, 12.5 Hz, 1H), 2.27-2.35 (m, 2H), 2.27 (dd, J = 14 Hz, 2.8 Hz, 1H), 2.17-2.24 (m, 1H), 1.79 (dd, J = 13.5 Hz, 2.7 Hz, 1H), 1.73 (dd, J = 13 Hz, 1H), 1.01 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H) ppm.

^{13}C NMR (125 Mhz, CDCl_3 , 25 $^\circ\text{C}$) δ = 173.3, 173.2, 144.3, 135.8, 126.0, 124.6, 79.8, 59.6, 57.4, 52.7 (2C), 44.8, 40.2, 40.1, 39.7, 36.9, 30.9, 28.9, 21.6, 21.3 ppm.

FT-IR (NaCl, thin film) ν = 2955, 2927, 2876, 2820, 1735, 1435, 1264, 1250, 1201, 1166, 1103, 1082 cm^{-1} .

TLC: R_f = 0.21 (20% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for C₂₀H₃₀O₅ (M^+): 320.2093. Found: 320.2093.

Characterization for **2b**:

¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 5.59-5.64 (m, 1H), 5.11 (d, J = 8.5 Hz, 1H), 3.72-3.74 (m, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 3.28 (s, 3H), 3.01 (dddd, J = 7.5 Hz, 7.5 Hz, 7.5 Hz, 3.4 Hz, 1H), 2.95 (dd, J = 18 Hz, 2.0 Hz, 1H), 2.58 (d, 18.5 Hz, 1H), 2.57 (dd, J = 14 Hz, .8 Hz, 1H), 2.27-2.49 (m, 4H), 2.24 (dd, J = 14 Hz, 4 Hz, 1H), 1.83 (ddd, J = 12 Hz, 9.5 Hz, 2.4 Hz, 1H), 1.71 (dd, J = 12 Hz, 12 Hz, 1H), 1.02 (d, J = 7 Hz, 3H), 1.01 (d, J = 7 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ = 173.2, 173.1, 143.5, 136.3, 127.6, 125.1, 80.2, 59.8, 57.3, 52.7 (2C), 45.6, 40.4, 39.9, 39.6, 36.9, 32.0, 28.0, 21.7, 21.4 ppm.

FT-IR (NaCl, thin film) ν = 2956, 2922, 2871, 2820, 1734, 1435, 1269, 1248, 1199, 1165, 1110, 1080 cm⁻¹.

TLC: R_f = 0.32 (20% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for C₂₀H₃₀O₅ (M^+): 320.2093. Found: 320.2089.

Characterization for **3a**²:

Protection of **21a**:

N,N-dimethylformamide (0.28 mL) was added via syringe to a screw capped vial containing **21a** (50 mg, 0.15 mmol). *Tert*-butyldimethylsilyl chloride (TBSCl, 111 mg, 0.74 mmol) and imidazole (101 mg, 1.49 mmol) were then added. The vial was flushed with argon and sealed with a screw cap. After stirring at r.t., for 6.5 hours, the reaction was transferred to a separatory funnel containing saturated aqueous ammonium chloride

² Compounds **3a** and **3b** could not be separated using silica gel chromatography. However, after deprotection, the corresponding alcohols could be easily separated using silica gel chromatography.

(20 mL) and Et₂O (20 mL) and extracted with Et₂O (2 x 20 mL). The organic layers were combined, washed with saturated aqueous sodium bicarbonate (20 mL), brine (20 mL) and dried over MgSO₄. The organic layers were concentrated *in vacuo* and the residue was purified via column chromatography (10% Et₂O/pentane) yielding **3a** as a clear oil (26 mg, 54%).

¹H NMR (500 MHz, CDCl₃, 25 °C) δ= 5.44 (s, 1H), 5.06 (d, *J* = 8.0 Hz, 1H), 3.86-3.93 (m, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 2.92-3.00 (m, 2H), 2.61 (dd, *J* = 19 Hz, 5.5 Hz, 1H), 2.53 (dd, *J* = 14.5 Hz, 7.5 Hz, 1H), 2.41 (dd, *J* = 12 Hz, 12 Hz, 1H), 2.24-2.33 (m, 3H), 2.16-2.24 (m, 1H), 1.73 (*J* = 13 Hz, 13 Hz, 1H), 1.64 (*J* = 13.5 Hz, 2.6 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ= 173.3, 173.2, 144.8, 137.7, 124.5, 121.9, 69.2, 59.7, 52.7 (2C), 45.0, 40.2, 40.0, 39.7, 37.0, 30.9, 28.7, 25.9 (3C), 21.6, 21.4, 18.3, -5.3 (2C) ppm.

FT-IR (NaCl, thin film) ν= 2954, 2932, 2856, 1735, 1445, 1251, 1197, 1165, 1093, 1066 cm⁻¹.

TLC: R_f = 0.42 (20% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (*m/z*) calculated for C₂₅H₄₂O₅Si (M⁺): 450.2802, calculated for C₂₁H₃₃O₅Si (M-*t*Bu)⁺: 393.2097. Found: 393.2092.

Characterization for **3b**:

Protection of **21b**:

N,N-dimethylformamide (0.2 mL) was added via syringe to a screw cap vial containing **21b** (12.5 mg, 0.037 mmol). *Tert*-butyldimethylsilyl chloride (TBSCl, 11 mg, 0.073 mmol) and imidazole (10 mg, 0.15 mmol) were then added. The vial was flushed with argon and sealed with a screw cap. After stirring at r.t., for 7 hours, the reaction was transferred to a separatory funnel containing saturated aqueous ammonium chloride (20 mL) and Et₂O (20 mL) and extracted with Et₂O (2 x 20 mL). The organic layers were combined, washed with saturated aqueous sodium bicarbonate (20 mL), brine (20 mL) and dried over MgSO₄. The organic layers were concentrated *in vacuo* and the residue was purified via column chromatography (10% Et₂O/pentane) yielding **3b** as a clear oil (16.6 mg, 99%).

^1H NMR (600 MHz, CDCl_3 , 25 °C) δ = 5.58-5.62 (m, 1H), 5.12 (d, J = 8.4 Hz, 1H), 3.94 (s, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 3.02 (dddd, J = 12 Hz, 7.8 Hz, 7.8 Hz, 4.4 Hz, 1H), 2.90 (d, J = 18 Hz, 1H), 2.57 (dd, J = 13.8 Hz, 7.8 Hz, 1H), 2.52 (d, J = 18 Hz, 1H), 2.25-2.34 (m, 4H), 2.22 (dd, J = 13.8 Hz, 4.1 Hz, 1H), 1.80-1.85 (m, 1H), 1.71 (dd, J = 12 Hz, 12 Hz, 1H), 1.01 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.91 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.3 (2C), 143.8, 138.7, 125.4, 124.1, 69.8, 60.1, 53.0, 52.9, 46.1, 40.9, 40.3, 39.8, 37.1, 31.7, 28.2, 26.2 (3C), 21.9, 21.7, 18.7, -5.0 (2C) ppm.

FT-IR (NaCl, thin film) ν = 2956, 2927, 2849, 1736, 1732, 1463, 1435, 1385, 1361, 1259, 1198, 1164, 1096, 1067.

TLC: R_f = 0.42 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{25}\text{H}_{42}\text{O}_5\text{Si}$ (M^+): 450.2802, calculated for $\text{C}_{25}\text{H}_{42}\text{O}_5\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 473.2699. Found: 473.2690.

Characterization for **21a**:

Experimental: THF (6.6 mL) was added under N_2 to a round bottom flask containing a mixture of **3a** and **3b** (2.4:1, 350 mg, 0.78 mmol) and the flask was placed into a 0 °C cooling bath. After 10 minutes, Tetra-*n*-butylammonium fluoride (TBAF, 1.0 M in THF, 1.16 mL, 1.16 mmol) was added and reaction was allowed to warm to r.t.. Additional TBAF was added after 1 hour (0.4 mL, 1.0 M in THF, 0.4 mmol) and 2 hours (0.8 mL, 1.0 M in THF, 0.8 mmol). After 30 additional minutes, water (~10 mL) was added slowly and the mixture was poured into a separatory funnel and extracted with Et_2O (3 x 20 mL). The organic layers were combined, washed with brine (50 mL), dried with MgSO_4 and concentrated *in vacuo*. The residue was purified via column chromatography (25% EtOAc /pentane) yielding **21a** (184 mg, 71%) and **21b** (77 mg, 28%) as clear oils.

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.47-5.50 (m, 1H), 5.08 (d, J = 8.5 Hz, 1H), 3.88-3.92 (m, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 2.93-3.00 (m, 2H), 2.62 (dd, J = 19 Hz, 6.0 Hz, 1H), 2.54 (dd, J = 14 Hz, 7.5 Hz, 1H), 2.46 (dd, J = 12.5 Hz, 12.5 Hz, 1H), 2.25-2.35 (m, 3H), 2.17-2.24 (m, 1H), 1.79 (dd, J = 12 Hz, 2.5 Hz, 1H), 1.75 (dd, J = 8.0 Hz, 8.0 Hz, 1H), 1.35 (bs, 1H), 1.01 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.3, 173.1, 144.4, 138.3, 124.5, 124.0, 70.0, 59.6, 52.7(2C), 45.0, 40.1, 40.0, 39.6, 36.9, 30.9, 29.0, 21.6, 21.3 ppm.

FT-IR (NaCl, thin film) ν = 3400, 2954, 2929, 2869, 1732, 1434, 1268, 1204, 1165, 1118, 1063 cm^{-1} .

TLC: R_f = 0.32 (40% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{19}\text{H}_{28}\text{O}_5$ (M^+): 336.1937, calculated for $\text{C}_{19}\text{H}_{27}\text{O}_5$ (M-H) $^+$: 335.1859. Found: 335.2034.

Characterization for **21b**:

^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 5.61-5.65 (m, 1H), 5.13 (J = 8 Hz, 1H), 3.90-3.98 (m, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 2.97-3.05 (m, 2H), 2.60 (d, J = 17.5 Hz, 1H), 2.57 (dd, J = 14 Hz, 7.5 Hz, 1H), 2.26-2.37 (m, 4H), 2.22 (dd, J = 14 Hz, 4.0 Hz, 1H), 1.84 (ddd, J = 13.5 Hz, 10 Hz, 2.3 Hz, 1H), 1.72 (dd, J = 11.5 Hz, 11.5 Hz, 1H), 1.29 (bs, 1H), 1.02 (d, J = 7.0 Hz, 3H), 1.01 (d, J = 7.0 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ = 173.1, 173.0, 143.3, 139.1, 125.7, 125.2, 70.3, 59.8, 52.7 (2C), 45.6, 40.5, 40.0, 39.5, 36.8, 31.8, 28.0, 21.7, 21.4 ppm.

FT-IR (NaCl, thin film) ν = 3400, 2958, 2918, 2871, 1729, 1436, 1260, 1199, 1163, 1109, 1064 cm^{-1} .

TLC: R_f = 0.39 (50% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{19}\text{H}_{28}\text{O}_5$ (M^+): 336.1937, calculated for $\text{C}_{19}\text{H}_{28}\text{O}_5\text{Na}$ (M+Na) $^+$: 359.1834. Found: 359.1833.

Characterization for **4a**³:

³ Due to the high level of regioselectivity when cyclopropylacetylene is used, **4b** was not generated in sufficient quantity to be characterized.

¹H NMR (500 MHz, CDCl₃, 25 °C) δ= 5.23 (dd, *J* = 4.4 Hz, 4.4 Hz, 1H), 5.02 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.95 (ddd, *J* = 7.5 Hz, 7.5 Hz, 2.8 Hz, 1H), 2.88 (dd, *J* = 18.5 Hz, 2.3 Hz, 1H), 2.56 (dd, *J* = 18.5 Hz, 5.5 Hz, 1H), 2.48 (dd, *J* = 14 Hz, 7.5 Hz, 1H), 2.39 (dd, *J* = 12.5 Hz, 12.5 Hz, 1H), 2.22-2.33 (m, 3H), 2.11-2.20 (m, 1H), 1.60 (dd, *J* = 13 Hz, 13 Hz, 1H), 1.49 (dd, *J* = 13.5 Hz, 2.9 Hz, 1H), 1.26 (dddd, *J* = 9 Hz, 9 Hz, 6 Hz, 6 Hz, 1H), 0.99 (d, *J* = 6.0 Hz, 3H), 0.98 (d, *J* = 6.0 Hz, 3H), 0.45-0.54 (m, 2H), 0.27-0.35 (m, 2H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ= 177.4, 173.2, 145.2, 139.3, 123.9, 120.8, 59.6, 52.7 (2C), 45.1, 40.2, 40.0, 39.7, 37.0, 31.1, 30.0, 21.7, 21.5, 20.1, 4.5, 3.9 ppm.

FT-IR (NaCl, thin film) ν= 3080, 3005, 2956, 1733, 1458, 1435, 1249, 1197, 1164, 1117, 1067, 1017 cm⁻¹.

TLC: *R_f* = 0.50 (20% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (*m/z*) calculated for C₂₁H₃₀O₄ (M⁺): 346.2144. Found: 346.2142.

Characterization for **5a**:

¹H NMR (500 MHz, CDCl₃, 25 °C) δ= 6.89 (ddd, *C* 5.5 Hz, 3.6 Hz, 1.3 Hz, 1H), 5.10-5.13 (m, 1H), 4.12-4.20 (m, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 3.11 (dddd, *J* = 20.5 Hz, 4.3 Hz, 2.1 Hz, 2.1 Hz, 1H), 2.88 (dddd *J* = 7.5 Hz, 7.5 Hz, 7.5 Hz, 2.2 Hz, 1H), 2.80 (dd, *J* = 20 Hz, 5.5 Hz 1H), 2.58 (dd, *J* = 14 Hz, 3.1 Hz, 1H), 2.53 (dd, *J* = 14.5 Hz, 7.5 Hz, 1H), 2.30-2.40 (m, 3H), 2.27 (dd, *J* = 14.5 Hz, 2.5 Hz, 1H), 2.18 (dddd, *J* = 12.5 Hz, 12.5 Hz, 7.0 Hz, 7.0 Hz, 2.8 Hz, 1H), 2.17 (dd, *J* = 15 Hz, 13 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ= 173.2 (2C), 168.5, 143.2, 140.4, 131.6, 125.3, 60.7, 59.6, 52.8, 52.7, 44.6, 39.9, 39.8, 39.4, 36.9, 31.8, 26.1, 21.6, 21.3, 14.3 ppm.

FT-IR (NaCl, thin film) ν= 2957, 1734 1706, 1436, 1365, 1267, 1237, 1189, 1010, 1077 cm⁻¹.

TLC: *R_f* = 0.28 (20% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (*m/z*) calculated for C₂₁H₃₀O₆ (M⁺): 378.2042. Found: 378.2047.

Characterization for **5b**:

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 6.94-6.99 (m, 1H), 5.17 (dd, J = 7.2 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.73 (s, 3H), 3.73 (s, 3H), 3.10-3.13 (m, 1H), 2.95-3.02 (m, 1H), 2.57 (dd, J = 14 Hz, 7.6 Hz, 1H), 2.35-2.48 (m, 4H), 2.30 (sept, J = 7.2 Hz, 1H) 2.20 (dd, J = 14 Hz, 5.6 Hz, 1H), 2.05 (dd, J = 13.6 Hz, 10 Hz, 1H), 1.75 (dd, J = 11.2 Hz, 11.2 Hz, 1H), 1.29 (t, J = 7.2 Hz, , 3H), 1.01 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 172.8, 172.7, 168.3, 143.2, 140.9, 131.5, 125.2, 60.7, 59.6, 52.8, 52.7, 43.8, 41.1, 40.3, 39.4, 36.4, 29.4, 29.4, 21.7, 21.5, 14.3 ppm.

FT-IR (NaCl, thin film) ν = 2954, 2928, 2869, 1735, 1706, 1457, 1436, 1374, 1246, 1163, 1011, 1069 cm^{-1} .

TLC: R_f = 0.35 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{21}\text{H}_{30}\text{O}_6$ (M^+): 378.2042, calculated for $\text{C}_{21}\text{H}_{30}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 401.1940. Found: 401.1950.

nOe:

Characterization for **6a**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 6.77 (dd, J = 5 Hz, 5Hz, 1H), 5.14 (d, J = 8.5 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.18 (ddd, J = 20.5 Hz, 4.1 Hz, 1.8 Hz, 1H), 2.82-2.89 (m, 2H), 2.74 (dd, J = 13.5 Hz, 2.9 Hz, 1H), 2.54 (dd, J = 14 Hz, 7.5 Hz, 1H), 2.30-2.39 (m, 2H), 2.28 (s, 3H), 2.24 (dd, J = 14 Hz, 2.7 Hz, 1H), 2.19 (dd, J = 13 Hz, 13 Hz, 1H), 2.02-2.11 (m, 1H), 1.79 (dd, J = 14 Hz, 14 Hz, 1H), 1.02 (d, J = 6.5 Hz, 3H), 1.01 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 199.7, 172.9 (2C), 142.9, 141.9, 141.5, 125.7, 59.6, 52.8 (2C), 44.4, 41.7, 39.9, 39.5, 36.9, 32.2, 25.5, 24.2, 21.7, 21.3 ppm.

FT-IR (NaCl, thin film) ν = 2956, 2932, 2876, 1732, 1665, 1435, 1378, 1354, 1267, 1195, 1164, 1118, 1166 cm^{-1} .

TLC: R_f = 0.38 (50% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{20}\text{H}_{28}\text{O}_5$ (M^+): 348.1937, calculated for $\text{C}_{20}\text{H}_{28}\text{O}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 371.1834. Found: 371.1835.

nOe:

Characterization for **6b**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 6.83-6.89 (m, 1H), 5.18 (d, J = 7.0 Hz, 1H), 3.73 (s, 6H), 3.24 (d, J = 17 Hz, 1H), 2.92-3.01 (m, 2H), 2.37-2.60 (m, 4H), 2.29 (s, 3H), 2.15-2.27 (m, 2H), 2.08 (ddd, J = 14.5 Hz, 9.5 Hz, 2.1 Hz, 1H), 1.76 (dd, J = 12 Hz, 12 Hz, 1H), 0.98 (d, J = 7 Hz, 3H), 0.96 (d, J = 7 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 199.8, 172.7, 172.6, 143.6, 142.8, 141.1, 125.0, 59.5, 52.8 (2C), 43.7, 41.4, 40.4, 39.3, 36.3, 30.1, 27.5, 25.7, 21.7, 21.5 ppm.

FT-IR (NaCl, thin film) ν = 2956, 2932, 2866, 1731, 1666, 1435, 1382, 1349, 1256, 1207, 1163, 1099, 1027 cm^{-1} .

TLC: R_f = 0.42 (50% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{20}\text{H}_{28}\text{O}_5$ (M^+): 348.1937. Found: 348.1938.

nOe:

Characterization for **7**:

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 5.48-5.45 (m, 1H), 5.41-5.46 (m, 1H), 5.08 (d, J = 8.5 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.04 (dddd, J = 8.0 Hz, 8.0 Hz, 8.0 Hz, 3.6 Hz, 1H), 2.92-2.99 (m, 1H), 2.52-2.59 (m, 2H), 2.21-2.40 (m, 5H), 1.8 (ddd, J = 13.5 Hz, 9.0 Hz, 2.8 Hz, 1H), 1.72 (dd, J = 12 Hz, 12 Hz, 1H), 1.01 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.3, 173.1, 144.6, 129.2, 128.6, 124.9, 59.8, 52.7 (2C), 45.7, 40.3, 39.8, 39.7, 36.9, 31.2, 28.1, 21.6, 21.4 ppm.

FT-IR (NaCl, thin film) ν = 3006, 2955, 2929, 2870, 1733, 1436, 1267, 1247, 1197, 1162, 1117, 1066 cm^{-1} .

TLC: R_f = 0.52 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{18}\text{H}_{26}\text{O}_4$ (M^+): 306.1831. Found: 306.1844.

Characterization for **14a**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.47 (s, 1H, C7), 5.07 (d, J = 8.5 Hz, 1H, C10), 3.76 (d, J = 12.5 Hz, 1H, C13), 3.73 (s, 3H, C1), 3.72 (s, 3H, C1), 3.65 (d, J = 12.5 Hz, 1H, C13), 3.27 (s, 3H, C14), 3.03 (d, J = 19 Hz, 1H, C8), 2.97 (d, J = 7.5 Hz, 1H, C11), 2.56 (dd, J = 19 Hz, 4.0 Hz, 1H, C8), 2.46 (dd, J = 15 Hz, 8 Hz, 1H, C12), 2.39 (dd, J = 13 Hz, 13 Hz, 1H, C5), 2.34 (dd, J = 15 Hz, 5.5 Hz, 1H, C3), 2.27 (d, J = 14.5 Hz, 1H, C12), 2.17-2.21 (m, 1H, C4), 1.85 (d, J = 13.5 Hz, 1H, C5), 1.77 (s, 3H, C15), 1.72 (dd, J = 13 Hz, 13 Hz, 1H, C3) ppm. **COSY** ($\text{H}_7 \leftrightarrow \text{H}_{8a}$, $\text{H}_7 \leftrightarrow \text{H}_{8b}$).

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.3, 173.1, 136.5, 135.1, 126.7, 124.9, 79.2, 59.7, 57.6, 52.7, 52.7, 44.2, 40.4, 40.1, 39.6, 34.3, 29.5, 25.8 ppm.

FT-IR (NaCl, thin film) ν = 2951, 2925, 2817, 1734, 1435, 1376, 1268, 1249, 1202, 1167, 1102 cm^{-1} .

TLC: R_f = 0.18 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{18}\text{H}_{26}\text{O}_5$ (M^+): 322.1780. Found: 322.1775.

Characterization for **14b**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.62 (t, J = 6.5 Hz, 1H, C6), 5.11 (dt, J = 7.0 Hz, 1.5 Hz, 1H, C10), 3.73-3.74 (m, 2H, C13), 3.73 (s, 3H, C1), 3.72 (s, 3H, C1), 3.28, (s, 3H, C14), 2.99-3.04 (m, 2H, C8, C11), 2.53 (d, J = 18 Hz, 1H, C8), 2.49 (dd, J = 14 Hz, 7.5 Hz, 1H, C12), 2.37 (dd, J = 13 Hz, 7.5 Hz, 1H, C3), 2.25-2.33 (m, 2H, C4, C5), 2.21 (dd, J = 14 Hz, 5.0 Hz, 1H, C12), 1.89 (dd, J = 11.5 Hz, 8.0 Hz, 1H, C5), 1.77 (s, 3H, C15), 1.70 (dd, J = 13 Hz, 11.5 Hz, 1H, C3) ppm. **COSY** ($\text{H}_6 \leftrightarrow \text{H}_{5a}$, $\text{H}_6 \leftrightarrow \text{H}_{5b}$).

^{13}C NMR (125 MHz, CDCl_3 , 25°C) δ = 173.1, 173.0, 135.3, 134.4, 128.0, 126.9, 79.7, 59.7, 57.4, 52.7 (2C), 44.8, 40.6, 40.0, 39.8, 35.1, 29.0, 25.4.

FT-IR (NaCl, thin film) ν = 2957, 2924, 2876, 2819, 1733, 1435, 1269, 1248, 1200, 1166, 1109, 1028 cm^{-1} .

TLC: R_f = 0.24 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{18}\text{H}_{26}\text{O}_5$ (M^+): 322.1780. Found: 322.1785.

Characterization for **15a**:

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ = 5.69 (dddd, J = 11.2 Hz, 6.4 Hz, 4.8 Hz, 1.8 Hz, 1H), 5.51 (dd, J = 5.2 Hz, 5.2 Hz, 1H), 5.27 (ddd, J = 10.4 Hz, 7.6 Hz, 2.3 Hz, 1H), 3.80 (ddd, J = 14.5 Hz, 1.8 Hz, 1.8 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.66 (ddd, J = 14.5 Hz,

$J = 1.5$ Hz, 1.5 Hz, 1 H), 3.28 (s, 3 H), 3.03 (dd, $J = 14.8$ Hz, 10.5 Hz, 1 H), 2.82 - 2.89 (m, 2 H), 2.32 - 2.50 (m, 3 H), 2.46 (dd, $J = 15.5$ Hz, 15.5 Hz, 1 H), 2.14 - 2.25 (m, 1 H), 1.93 (dd, $J = 13.2$ Hz, 3.2 Hz, 1 H), 1.71 (dd, $J = 12.8$ Hz, 12.8 Hz, 1 H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25°C) $\delta = 173.4$, 173.2 , 136.7 , 132.0 , 128.2 , 125.8 , 78.6 , 58.7 , 57.6 , 52.8 (2C), 43.2 , 40.2 , 39.7 , 39.4 , 29.4 , 29.2 ppm.

FT-IR (NaCl, thin film) $\nu = 2952$, 2922 , 2817 , 1733 , 1546 , 1436 , 1269 , 1249 , 1197 , 1165 , 1105 , 1084 cm^{-1} .

TLC: $R_f = 0.27$ (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{17}\text{H}_{24}\text{O}_5$ (M^+): 308.1624. Found: 308.1618.

nOe:

Characterization for **15b**:

^1H NMR (400 MHz, CDCl_3 , 25°C) $\delta = 5.67$ (dddd, $J = 8.5$ Hz, 1.0 Hz, 5.0 Hz, 2.1 Hz, 1 H), 5.62 (dd, $J = 8$ Hz, 8 Hz, 1 H), 5.28 (ddd, $J = 10$ Hz, 7.0 Hz, 2.1 Hz, 1 H), 3.73 - 3.75 (m, 2 H), 3.73 (s, 3 H), 3.72 (s, 3 H), 3.27 (s, 3 H), 3.05 - 3.11 (m, 1 H), 2.76 - 2.90 (m, 2 H), 2.30 - 2.45 (m, 4 H), 2.19 - 2.28 (m, 1 H), 1.96 (ddd, $J = 13$ Hz, 8.5 Hz, 3.4 Hz, 1 H), 1.70 (dd, $J = 12.5$ Hz, 12.5 Hz, 1 H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25°C) $\delta = 173.3$, 173.1 , 136.0 , 132.0 , 128.1 , 127.7 , 79.2 , 59.7 , 57.4 , 52.8 (2C), 44.2 , 39.9 , 39.7 (2C), 30.5 , 28.7 ppm.

FT-IR (NaCl, thin film) $\nu = 2953$, 2925 , 2819 , 1733 , 1449 , 1435 , 1269 , 1248 , 1197 , 1165 , 1119 , 1106 cm^{-1} .

TLC: $R_f = 0.30$ (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{17}\text{H}_{24}\text{O}_5$ (M^+): 308.1624. Found: 308.1624.

nOe:

Characterization for **16a**:

^1H NMR (600 MHz, CDCl_3 , 25 °C) δ = 5.53-5.56 (m, 1H), 5.19 (d, J = 7.8 Hz, 1H), 3.96 (dd, J = 8.4 Hz, 5.5 Hz, 1H), 3.91 (dd, J = 7.8 Hz, 7.8 Hz, 1H), 3.74-3.77 (m, 2H), 3.68 (d, J = 11.4 Hz, 1H), 3.27 (s, 3H), 3.23 (dd, J = 9.6 Hz, 8.4 Hz, 1H), 3.03-3.08 (m, 2H), 2.64 (dd, J = 18.6 Hz, 6.0 Hz, 1H), 2.41-2.51 (m, 2H), 2.33 (sept, J = 6.6 Hz, 1H), 1.78 (dd, J = 13.2 Hz, 2.1 Hz, 1H), 1.04 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 144.9, 135.9, 126.1, 122.9, 80.1, 74.0, 72.4, 57.4, 44.9, 41.3, 36.8, 31.1, 26.5, 21.7, 21.3 ppm.

FT-IR (NaCl, thin film) ν = 2959, 2927, 2866, 1462, 1378, 1360, 1186, 1101, 1049 cm^{-1} .

TLC: R_f = 0.17 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{15}\text{H}_{24}\text{O}_2$ (M^+): 236.1778. Found: 236.1768.

Characterization for **16b**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.67 (ddd, J = 8.5 Hz, 5.5 Hz, 1.8 Hz, 1H), 5.21 (d, J = 8 Hz, 1H), 3.97 (dd, J = 8.5 Hz, 5.5 Hz, 1H), 3.90 (J = 8.0 Hz, 8.0 Hz, 1H), 3.76-3.77 (m, 2H), 3.75 (dd, J = 8.5 Hz, 3.1 Hz, 1H), 3.30 (s, 3H), 3.19 (dd, J = 10 Hz, 8.0 Hz, 1H), 3.10 (dddd, J = 8.0 Hz, 8.0 Hz, 5.5 Hz, 2.6 Hz, 1H), 3.04 (dd, J = 18 Hz, 2.1 Hz, 1H), 2.61 (d, J = 18 Hz, 1H), 2.49-2.57 (m, 1H), 2.36-2.41 (m, 1H), 2.33 (sept, J = 6.5 Hz, 1H), 1.80 (ddd, J = 12 Hz, 9.5 Hz, 2.8 Hz, 1H), 1.04 (d, J = 6.5 Hz, 3H), 1.04 (d, J = 6.5 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 144.2, 136.3, 127.3, 123.21, 80.2, 74.1, 72.5, 57.4, 45.8, 41.1, 36.8, 32.2, 25.4, 21.7, 21.4 ppm.

FT-IR (NaCl, thin film) ν = 2960, 2925, 2868, 1462, 1382, 1358, 11889, 1098, 1039 cm^{-1} .

TLC: R_f = 0.23 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{15}\text{H}_{24}\text{O}_2$ (M^+): 236.1778. Found: 236.1775.

Characterization for **17a** and **17b**⁴:

17a + 17b: **^1H NMR** (500 MHz, CDCl_3 , 25 °C) δ = 7.74 (dd, J = 8.5 Hz, 2.0 Hz), 7.34 (dd, J = 18.5 Hz, 0.7 Hz), 5.52-5.56 (m, **17b**), 5.46-5.49 (m, **17a**), 4.49-4.43 (m, **17a**, **17b**), 3.66-3.70 (m, 1H), 3.60 (dd, J = 11.5 Hz, 1.3 Hz), 3.31-3.39 (m), 3.25 (s, **17b**), 3.22 (s, **17a**), 2.88-3.00 (m), 2.65 (dd, J = 10.5 Hz, 10.5 Hz), 2.56-2.62 (m), 2.43 (s), 2.34 (dd, J = 12.5 Hz, 12.5 Hz), 2.20-2.29 (m), 2.13 (sept, J = 7.0 Hz), 1.71-1.79 (m), 0.91 (d, J = 7 Hz, **17b**), 0.90 (d, J = 7 Hz, **17a**), 0.87 (d, J = 7.0 Hz, **17b**), 0.87 (d, J = 7.0 Hz, **17a**) ppm.

17a: **^{13}C NMR** (125 MHz, CDCl_3 , 25 °C) δ = 145.8, 143.4, 134.4, 133.9, 129.6 (2C), 127.5 (2C), 126.7, 120.9, 79.8, 57.5, 53.3, 51.4, 42.9, 39.8, 36.8, 32.1, 26.7, 21.5 (2C), 21.0 ppm.

17b: **^{13}C NMR** (125 MHz, CDCl_3 , 25 °C) δ = 145.2, 143.4, 137.1, 133.8, 129.7 (2C), 127.5 (2C), 125.8, 121.1, 79.8, 57.4, 53.3, 51.5, 43.6, 39.5, 36.9, 33.1, 25.5, 21.5 (2C), 21.0 ppm.

17a + 17b: **FT-IR** (NaCl, thin film) ν = 2958, 2927, 2874, 2820, 1597, 1462, 1449, 1345, 1159, 1091, 1040 cm^{-1} .

TLC: R_f = 0.18 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{22}\text{H}_{31}\text{NO}_3\text{S}$ (M^+): 389.2025. Found: 389.2015.

Characterization for **18a**:

⁴ Compounds 15a and 15b could not be separated via silica gel column chromatography. As a result, the ^1H spectrum is reported as a mixture with resonances assigned to the particular isomer whenever possible.

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.52 (d, J = 6.5 Hz, 1H), 5.26 (d, 9.0 Hz, 1H), 3.77-3.81 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 3.56 (d, J = 12 Hz, 1H), 3.23 (s, 3H), 2.98 (d, J = 18.5 Hz, 1H), 2.79 (dd, J = 14.5 Hz, 7.5 Hz, 1H), 2.52-2.62 (m, 3H), 2.31 (sept, J = 6.5 Hz, 1H), 2.26 (d, J = 14.5, 1H), 2.12 (s, 2H), 1.61 (d, J = 14 Hz, 1H), 1.00 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 0.95 (s, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.7, 173.6, 142.8, 135.0, 127.0, 125.5, 81.0, 59.2, 57.3, 53.0, 52.8, 51.2, 47.2, 46.4, 38.3, 36.8, 35.7, 30.8, 24.5, 21.4, 21.0 ppm.

FT-IR (NaCl, thin film) ν = 2955, 2872, 1735, 1450, 1434, 1253, 1198, 1147, 1115 cm^{-1} .

TLC: R_f = 0.30 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{21}\text{H}_{32}\text{O}_5$ (M^+): 364.2250. Found: 364.2242.

nOe:

Characterization for **18b**:

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.57-5.62 (m, 1H), 5.24 (d, J = 9.0 Hz, 1H), 3.75 (d, J = 5.5 Hz, 2H), 3.74 (s, 6H), 3.27 (s, 3H), 2.92 (d, J = 18 Hz, 1H), 2.77 (dd, J = 14.5 Hz, 7.0 Hz, 1H), 2.52-2.36 (m, 3H), 2.33 (sept, J = 7.0 Hz, 1H), 2.27 (d, J = 14.5 Hz, 1H), 2.07-2.13 (m, 2H), 1.64 (dd, J = 13.5 Hz, 9.5 Hz, 1H), 1.00 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H), 0.98 (s, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.8, 173.6, 142.3, 136.0, 127.0, 126.7, 80.4, 59.4, 57.1, 52.9, 52.8, 51.6, 47.0, 46.3, 38.0, 37.2, 34.9, 32.0, 25.0, 21.5, 20.9 ppm.

FT-IR (NaCl, thin film) ν = 2956, 2917, 2871, 1733, 1462, 1435, 1253, 1198, 1147, 1109 cm^{-1} .

TLC: R_f = 0.33 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{21}\text{H}_{32}\text{O}_5$ (M^+): 364.2250. Found: 364.2238.

nOe:

Characterization for **19a**:

Experimental Note: In addition to isolating cycloadduct **19a** (37%) from the reaction mixture, unreacted starting diene-ene **13** (24%) was also recovered.

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 5.42 (J = 10.5 Hz, 5.0 Hz, 1.7 Hz, 1H), 5.36 (J = 3.6 Hz, 1H), 3.75 (d, J = 12 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.64 (J = 12 Hz, 1H), 3.27 (s, 3H), 3.08-3.16 (m, 1H), 3.01-3.08 (m, 1H), 2.48 (dd, J = 14 Hz, 8.0 Hz, 1H), 2.37-2.47 (m, 3H), 2.27 (dd, J = 14 Hz, 3.9 Hz, 1H), 2.21-2.30 (m, 1H), 1.86 (dd J = 14 Hz, 2.8 Hz, 1H), 1.70 (dd, J = 12 Hz, 12 Hz, 1H), 1.15 (d, J = 7.5 Hz, 3H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 173.1, 173.0, 135.1, 134.3, 132.1, 130.6, 79.4, 59.7, 57.5, 52.8 (2C), 43.3, 40.5, 40.3, 39.6, 33.4, 29.9, 22.5 ppm.

FT-IR (NaCl, thin film) ν = 2954, 2927, 2819, 1733, 1434, 1268, 1252, 1199, 1167, 1113, 1096 cm^{-1} .

TLC: R_f = 0.27 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{18}\text{H}_{26}\text{O}_5$ (M^+): 322.1780. Found: 322.1782.

ROESY CORRELATIONS:

Experimental for **20**:

Silver hexafluoroantimonate (6.0 mL of a 0.01 M solution in DCE, 0.06 mmol) was added under N₂ to a round bottom flask equipped with a septum containing chlorodicarbonylrhodium (I) dimer (11.5 mg, .03 mmol), bicyclo[2.2.1]hept-2-ene (334 mg, 3.55 mmol). Methyl propargyl ether (50 μ L, 0.60 mmol), followed by 2,3-dimethyl-1,3-butadiene (333 μ L, 3.55 mmol) were added via syringe. Positive nitrogen pressure was removed and reaction vessel placed into a temperature controlled oil bath set to 40 $^{\circ}$ C. After 24 hours no starting material could be detected via TLC. The solvent was removed *in vacuo* and the residue was purified via flash column chromatography (3% Et₂O/Pentane) yielding cycloadduct **20** as a clear oil (82 mg, 0.34 mmol).

Characterization for **20**:

¹H NMR (500 MHz, CDCl₃, 25 $^{\circ}$ C) δ = 5.46 (d, J = 4.7 Hz, 1H), 3.81 (d, J = 12 Hz, 1H), 3.70 (d, J = 12 Hz, 1H), 3.25 (s, 3H), 3.21 (d, J = 14.5 Hz, 1H), 2.53 (dd, J = 8.5 Hz, 5.0 Hz, 1H), 2.38 (dd, J = 13.5 Hz, 13.5 Hz, 1H), 2.26 (d, J = 15 Hz, 1H), 2.08 (s, 1H), 1.90 (dd, J = 10 Hz, 10 Hz, 1H), 1.86 (s, 1H), 1.72 (s, 3H), 1.66-1.68 (m, 1H), 1.63 (s, 3H), 1.47 (ddd, J = 11 Hz, 3.8 Hz, 3.8 Hz, 2H), 1.36-1.39 (m, 1H), 1.21-1.26 (m, 2H), 1.00 (ddd, J = 10 Hz, 1.5 Hz, 1.5 Hz, 1H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 $^{\circ}$ C) δ = 133.3, 132.6, 130.7, 123.8, 75.8, 57.5, 52.1, 46.8, 46.3, 42.8, 39.7, 35.2, 34.1, 29.3 (2C), 24.0, 23.7 ppm.

FT-IR (NaCl, thin film) ν = 2946, 2920, 2870, 2815, 1447, 1373, 1298, 1191, 1140, 1094 cm⁻¹.

TLC: R_f = 0.65 (10% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for C₁₇H₂₆O (M⁺): 246.1984 Found: 246.1987.

nOe:

nOe: ($H_b \rightarrow H_a$, 4%), ($H_d \rightarrow H_c$, 4%), ($H_d \rightarrow H_f$, 7%), ($H_e \rightarrow H_g$, 3%), ($H_e \rightarrow H_h$, 6%).

Synthesis of Starting Materials:

Experimental: Triphenyl phosphine (5.71 g, 21.8 mmol) in dichloromethane (20 mL) was added dropwise under N_2 to a round bottom flask, cooled to 0 °C, containing carbon tetrabromide (7.89 g, 23.8 mmol), alcohol **22** (2.50 g, 19.8 mmol), dichloromethane (60 mL) and a stir bar. After addition of triphenyl phosphine was complete (~5 min), the reaction was allowed to warm to room temperature. Solvent was removed *in vacuo* and residue was suspended in pentane, cooled to -78 °C, and gravity filtered cold to remove the triphenyl phosphine oxide. This process was repeated two additional times. The combined organic filtrates were dried with $NaSO_4$ and concentrated *in vacuo* yielding a yellow oil. In a separate flask, THF (40 mL) was added under N_2 to a round bottom flask containing NaH (60% dispersion in mineral oil, 752 mg, 18.8 mmol). Dimethyl allylmalonate (2.70 mL, 16.8 mmol) was then added dropwise. After 20 minutes, crude bromide was added in one portion. After 5 hours, H_2O (5 mL) was added dropwise. The reaction was then poured into a separatory funnel containing saturated aqueous NH_4Cl (60 mL) and Et_2O (50 mL) and extracted with Et_2O (3 x 50 mL). Organic layers were combined and washed with saturated aqueous $NaHCO_3$ (50 mL), H_2O (50 mL), and brine (50 mL) then dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified via flash column chromatography (20% Et_2O /Pentane) yielding **1** as a clear oil (2.21 g, 9.07 mmol, 54%).

1H NMR (400 MHz, $CDCl_3$, 25°C) δ = 6.05 (d, J = 16 Hz, 1H), 5.66 (dddd, J = 17.2 Hz, 9.6 Hz, 7.2 Hz, 7.2 Hz, 1H), 5.54 (ddd, J = 15.6 Hz, 7.6 Hz, 7.6 Hz, 1H), 5.12 (d, J = 2.8 Hz, 1H), 5.09 (s, 1H), 4.88 (d, J = 2.8 Hz, 2H), 3.71 (s, 6H), 2.66 (d, J = 13.2 Hz, 2H), 2.65 (d, J = 13.2 Hz, 2H), 2.51 (sept, J = 6.8 Hz, 1H), 1.05 (d, J = 6.8 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ = 171.2 (2C), 152.2, 136.1, 132.3, 122.3, 119.2, 111.4, 58.0, 52.3 (2C), 37.2, 36.3, 29.3, 22.1 (2C) ppm.

FT-IR (NaCl, thin film) ν = 3080, 2960, 2874, 1738, 1436, 1327, 1280, 1244, 1213, 1142, 1111, 1033 cm^{-1} .

TLC: R_f = 0.74 (20% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{16}\text{H}_{24}\text{O}_4$ (M^+): 280.1675. Found: 280.1682.

Experimental: Et_2O (30.8 mL) was added under N_2 to a 200 mL 3-necked round bottom flask equipped with an internal thermometer. Ester **23** was added and the flask was placed into a -78 °C cooling bath. DIBAL-H (1.0 M in hexane, 20.2 mL) was then added via syringe pump over 1 hour. The reaction was allowed to stir for an additional 30 minutes at -78 °C upon completion of addition and then allowed to slowly warm to room temperature at which time all starting material had been consumed as judged via TLC. The reaction flask was then cooled to 0 °C and $\text{NaSO}_4 \cdot 10 \text{H}_2\text{O}$ (~40 g) was added slowly and reaction was warmed to room temperature and stirred for 1 hour. The resulting suspension was filtered through celite, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography (30% Et_2O , Pentane) yielding **22** as a clear oil (917 mg, 7.27 mmol, 90%).

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 6.23 (d, J = 16 Hz, 1H), 5.91 (dt, J = 16 Hz, 6 Hz, 1H), 4.98 (d, J = 13 Hz, 2H), 4.21 (dd, J = 5.0 Hz, 5.0 Hz, 2H), 2.58 (sept, J = 7.0 Hz, 0.9 Hz, 1H), 1.09 (d, J = 7.0 Hz, 6H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 151.9, 133.3, 127.2, 112.5, 63.9, 29.3, 22.1 (2C) ppm.

FT-IR (NaCl, thin film) ν = 3339, 2963, 2931, 2873, 1606, 1460, 1381, 1097, 1020 cm^{-1} .

TLC: R_f = 0.23 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_8\text{H}_{14}\text{O}$: 126.1045 (M^+). Found: 126.1044.

Experimental: NaH (60% dispersion in mineral oil, 3.36 g, 78.0 mmol) was added to a 500 mL 3-necked flask containing THF (200 mL) and equipped with an overhead mechanical stirrer, an internal thermometer, and a 50 mL addition funnel. The flask was placed in a 0 °C cooling bath and triethyl phosphonoacetate (14.47 mL, 83.96 mmol) in THF (22.2 mL) was added slowly via addition funnel (over ~15 min). After an additional

15 minutes α -isopropylacrolein **24**⁵ (7.63 g, 77.74 mmol) was added slowly via the addition funnel (over ~10 min) causing solution to turn yellow. The reaction was allowed to stir for 4 hours at 0 °C after which time saturated aqueous ammonium chloride (100 mL) was added and slowly and reaction was warmed to room temperature. The reaction was poured into a separatory funnel and extracted with Et₂O (3 x 150 mL). The organic layers were then combined, washed with H₂O (25 mL), brine (50 mL), dried over NaSO₄, and concentrated *in vacuo*. The residue was purified via short-path distillation (0.25 torr, bp=72°C) yielding **23** as a clear oil (8.53 g, 50.7 mmol, 65%).

¹H NMR (300MHz, CDCl₃, 25 °C) δ = 7.10 (d, *J* = 15.9 Hz, 1H), 5.77 (d, *J* = 15.9 Hz, 1H), 5.15 (s, 1H), 5.12 (s, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.39 (sept, *J* = 6.6 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 6H) ppm.

¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 167.0, 150.9, 146.4, 119.6, 117.5, 60.1, 28.8, 21.8 (2C), 14.1 ppm.

FT-IR (NaCl, thin film) ν = 3094, 2996, 1716, 1630, 1602, 1461, 1366, 1279, 1180, 1039 cm⁻¹

TLC: *R_f* = 0.59 (10% Et₂O/pentane), one spot, anisaldehyde stain.

LRMS (*m/z*) calculated for C₁₀H₁₆O (M⁺); 168 Found: 168.

Experimental: Dimethyl allylmalonate (803 μ L, 5.18 mmol) was added dropwise under N₂ to a stirring solution of sodium hydride (60% dispersion in mineral oil, 248 mg, 6.21 mmol) in THF (10 mL). After 15 minutes 5-Bromo-2-methyl-penta-1,3-diene⁶ (1.0 g, 6.21 mmol), was added and the reaction was stirred at room temperature for 20 hours after which time saturated aqueous ammonium chloride (20 mL) was added. The mixture was poured into a separatory funnel and extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with saturated sodium bicarbonate (30 mL), brine (30 mL) and dried over MgSO₄. After concentration *in vacuo*, the residue was purified via flash column chromatography (10% Et₂O/Pentane) yielding a clear oil (472 mg, 1.91 mmol, 37%).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 6.16 (d, *J* = 15.6 Hz, 1H), 5.60-5.70 (m, 1H), 5.43 (ddd, *J* = 15.2 Hz, 7.6 Hz, 7.6 Hz, 1H), 5.07-5.13 (m, 2H), 4.89 (d, *J* = 7.6 Hz, 2H), 3.71 (s, 6H), 2.68 (dd, *J* = 7.6 Hz, 1.1 Hz, 2H), 2.63 (ddd, *J* = 7.6 Hz, 1.1 Hz, 1.1 Hz, 2H), 1.79 (s, 3H) ppm.

⁵ Urban, E.; Riehs, G. *Tetrahedron* **1996**, 52, 1121-1230.

⁶ Laird, T.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans I*, **1980**, 2033-2048.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 171.2 (2C), 141.6, 137.0, 132.3, 123.4, 119.2, 115.9, 58.0, 52.4 (2C), 37.1, 36.0, 18.5 ppm.

FT-IR (NaCl, thin film) ν = 3081, 2953, 2844, 1737, 1642, 1610, 1437, 1328, 1290, 1276, 1245, 1213, 1143, 1034 cm^{-1} .

TLC: R_f = 0.61 (15% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{14}\text{H}_{20}\text{O}_4$ (M^+): 252.1362. Found: 252.1362.

Experimental: Dimethyl allylmalonate (860 μL , 7.53 mmol) was added dropwise under N_2 to a stirring solution of NaH (60% dispersion in mineral oil, 361 mg, 15.06 mmol) in THF (20 mL). After 20 minutes 1-bromo-penta-2,4-diene⁷ was added and the reaction was allowed to stir for 20 minutes after which time, the reaction was cooled to 0 °C. Water was slowly added until H_2 evolution was complete. Saturated aqueous ammonium chloride (20 mL) was added and extracted with Et_2O (3 x 30 mL). The organic layers were combined and washed with saturated ammonium chloride (2 x 20 mL), water (20 mL), brine (40 mL), and dried over magnesium sulfate. After concentration *in vacuo*, purification via flash column chromatography (30% Et_2O /Pentane) yielding a clear oil (663 mg, 3.91 mmol, 54%).

^1H NMR (500 MHz, CDCl_3 , 25 °C) δ = 6.29 (dt, J = 17.0 Hz, 10.5, 1H), 6.10 (dd, J = 15.0, 10.5 Hz, 1H), 5.65 (m, 1H), 5.51 (dt, J = 15.5 Hz, 8.0 Hz, 1H), 5.09-5.15 (m, 3H), 5.02 (dd, J = 10.0, 0.8 Hz, 1H), 3.72 (s, 6H), 2.67 (d, J = 7.5 Hz, 2H), 2.64 (d, J = 7.5 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl_3 , 25 °C) δ = 171.1 (2C), 136.5, 135.1, 132.2, 127.7, 119.3, 116.5, 57.8, 52.4 (2C), 37.1, 35.8 ppm.

FT-IR (NaCl, thin film) ν = 3083, 3009, 2954, 2844, 1737, 1642, 1603, 1437, 1328, 1287, 1245, 1215, 1164, 1006 cm^{-1} .

TLC: R_f = 0.63 (10% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{13}\text{H}_{18}\text{O}_4$ (M^+): 238.1205. Found: 238.1201.

⁷ Prévost, C.; Miginiac, P.; Miginiac-Groizeleau, L. *Bull. Soc. Chira. Fr.* **1964**, 2485.

Experimental: THF (20 mL) was added under N₂ to an oven-dried 50 mL round bottom flask containing sodium hydride (60% dispersion in mineral oil, 80 mg, 2.0 mmol) and a stir bar. Alcohol **22** (230 mg, 1.82 mmol) was slowly added at room temperature and stirred for 1 hour. Allyl bromide was then added and the reaction was stirred for 21 hours, followed by heating to 60 °C for 2 hours. Saturated aqueous ammonium chloride (10 mL) was added, and the solution was extracted with diethyl ether (3 X 5 mL). The organic layers were combined, washed with brine (20 mL) and dried over sodium sulfate. The solution was concentrated under *in vacuo* and purified via flash chromatography to yield 181 mg (59% yield) of a clear colorless oil.

¹H NMR (500 MHz, CDCl₃, 25 °C) δ = 6.23 (d, *J* = 16.0 Hz, 1H), 5.93 (ddt, *J* = 10.5, 17.0 Hz, *J* = 5.5 Hz, 1H), 5.84 (dt, *J* = 16.0 Hz, 6.0 Hz, 1H), 5.29 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.99 (s, 1H), 4.97 (s, 1H), 4.06 (d, *J* = 6.0 Hz, 2H), 3.99 (d, *J* = 5.5 Hz, 2H), 2.59 (sept, *J* = 6.8 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 6H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ = 152.0, 134.7, 134.6, 124.7, 117.1, 112.4, 70.9 (2C), 29.2, 22.2 (2C) ppm.

FT-IR (NaCl, thin film) ν = 3090, 2962, 2930, 2872, 2848, 1647, 1606, 1461, 1420, 1382, 1356, 1255, 1109, 1069 cm⁻¹.

TLC: R_f = 0.80 (10% EtOAc/pentane), one spot, anisaldehyde stain.

HRMS (*m/z*) calculated for C₁₁H₁₈O: 166.1358 g/mol (M⁺), for C₈H₁₃ (M-Oallyl)⁺: 109.1028 g/mol. Found: 109.1017 g/mol.

Experimental: THF (16 mL) was added under N₂ to a round bottom flask containing alcohol **22** (100 mg, 0.79 mmol) and a stir bar. N-Allyl-4-methyl-benzenesulfonamide⁸ (116 mg, 0.79 mmol) and triphenyl phosphine (400 mg, 0.95 mmol) were then added and the reaction vessel was cooled to 0 °C. Diisopropyl azodicarboxylate (DIAD, 186 μ L,

⁸ Brummond, K. M.; Chen, H.; Mitasev, B.; Casarez, A. D. *Org. Lett.* **2004**, *16*, 2161-2163.

0.95 mmol) was then added dropwise and reaction was slowly warmed to room temperature. After 24 hours additional DIAD (100 μ l, 0.51 mmol) was added. After 12 hours the solvent was removed *in vacuo* and the residue was purified via flash column chromatography (15% Et₂O/Pentane) yielding a clear oil (193 mg, 0.60 mmol, 76%).

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.02 (d, *J* = 16 Hz, 1H), 5.63 (dddd, *J* = 16.4 Hz, 12.8 Hz, 6.4 Hz, 6.4 Hz, 1H), 5.43 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 5.17 (dd, *J* = 2.7 Hz, 1.4 Hz, 1H), 5.13 (dd, *J* = 4.8 Hz, 1.2 Hz, 1H), 4.91 (d, *J* = 14 Hz, 2H), 3.86 (d, *J* = 6.8 Hz, 2H), 3.80 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.39 (sept, *J* = 6.8 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 6H) ppm.

¹³C NMR (125 MHz, CDCl₃, 25 °C) δ = 151.5, 143.1, 137.4, 136.1, 132.7, 129.6 (2C), 127.1 (2C), 122.2, 118.8, 112.8, 49.3, 48.9, 29.1, 22.0 (2C), 21.4 ppm.

FT-IR (NaCl, thin film) ν = 2962, 2927, 2872, 1599, 1445, 1347, 1305, 1160, 1092, 972, 907 cm⁻¹.

TLC: *R_f* = 0.43 (10% Et₂O/pentane), one spot, anisaldehyde stain.

HRMS (*m/z*) calculated for C₁₈H₂₅NO₂S (M⁺): 319.1606. Found: 319.1593.

Experimental: Triphenyl phosphine (1.37 g, 5.23 mmol) in dichloromethane (10 mL) was added dropwise under N₂ to a round bottom flask cooled to 0°C containing carbon tetrabromide (1.88 g, 5.70 mmol), alcohol **22** (600 mg, 4.75 mmol), dichloromethane (20 mL) and a stir bar. After addition of triphenylphosphine was complete (~5 min), reaction was allowed to warm to room temperature. Solvent was removed *in vacuo* and residue was suspended in pentane and cooled to -78°C and gravity filtered cold to remove triphenyl phosphine-oxide. This process was repeated two additional times. The combined organic filtrates were dried with NaSO₄ and concentrated *in vacuo* yielding a yellow oil. In a separate flask, THF (10 mL) was added under N₂ to a round bottom flask containing NaH (60% dispersion in mineral oil, 113 mg, 2.81 mmol). Dimethyl 2-methylallylmalonate⁹ (437 μ l, 2.51 mmol) was then added dropwise. After 20 minutes, crude bromide was added in one portion. After 5 hours, H₂O (5 mL) was added dropwise. The reaction was then poured into a separatory funnel and containing saturated aqueous ammonium chloride (50 mL) and Et₂O (50 mL) and extracted with Et₂O (3 x 50 mL). The organic layers were combined and washed with NaHCO₃ (sat, 50 mL), H₂O (50 mL), and brine (50 mL) then dried over MgSO₄. The solvent was removed *in vacuo*

⁹ Laidig, G. J.; Hegedus, L. S. *Synthesis* **1995**, 5, 527-532.

and the residue was purified via flash column chromatography (15% Et₂O/Pentane) yielding a clear oil (207 mg, 0.70 mmol, 28%).

¹H NMR (500 MHz, CDCl₃, 25 °C) δ= 6.03 (d, *J* = 16 Hz, 1H), 5.58 (ddd, *J* = 15.2 Hz, 7.6 Hz, 7.6 Hz, 1H), 4.85-4.89 (m, 3H), 4.73-4.75 (m, 1H), 3.70 (s, 6H), 2.69-2.71 (m, 3H), 2.68 (d, *J* = 1.2 Hz, 1H), 2.51 (sept, *J* = 6.8 Hz, 1H), 1.66 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 171.6 (2C), 152.3, 140.4, 135.9, 122.7, 115.8, 111.3, 57.6, 52.3 (2C), 40.6, 36.3, 29.3, 23.1, 22.1 (2C) ppm.

FT-IR (NaCl, thin film) ν = 3078, 3029, 2960, 2873, 1738, 1645, 1605, 1436, 1378, 1331, 1269, 1239, 1204, 1178, 1088, 1074, 1061 cm⁻¹.

TLC: R_f = 0.26 (10% EtOAc/pentane), one spot, anisaldehyde stain stain.

HRMS (*m/z*) calculated for C₁₇H₂₆O₄ (M⁺): 294.1831. Found: 294.1837.

Experimental: THF (20 mL) was added under N₂ to an oven-dried flask containing hexa-2,4-dien-1-ol (1.08m, 11.0 mmol) and a stir bar. The flask was then placed into a dry ice/acetone bath (-78 °C). *n*-BuLi (2.5 M in Et₂O, 4.60 mL, 11.5 mmol) was added dropwise over 5 minutes and the yellow solution was stirred for 15 minutes. Methanesulfonyl chloride (0.89 mL, 11.5 mmol) was then added dropwise causing the solution to become colorless. After 15 minutes a solution of LiBr (4.34 g in 10 mL of THF, 50 mmol), which was prepared in an oven-dried flask containing 4 Å molecular sieves, was added and the reaction was then allowed to warm to room temperature. In a separate oven-dried flask THF (15 mL) was added under N₂ to dimethyl allylmalonate (1.61 mL, 10 mmol) followed by the slow addition of NaH (60% in mineral oil, 0.44 g, 11 mmol). The flask was stirred for 20 minutes at room temperature then placed into a dryice/acetone bath (-78 °C). The solution containing the diene was then transferred via cannula to the flask containing the malonate and the reaction was allowed to warm to room temperature and was stirred for 12 hours. Saturated aqueous ammonium chloride (20 mL) was added and mixture was poured into a separatory funnel and extracted with Et₂O (3 x 25 mL). The organic layer were combined and washed with brine (3 x 25 mL) and dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified via flash column chromatography (6% to 8% Et₂O/pentane gradient) yielding a colorless oil (1.71 g, 68%).

¹H NMR (500 MHz, CDCl₃, 25 °C) δ= 5.93-6.05 (m, 2H), 5.54-5.68 (m, 2H), 5.26-5.35 (m, 1H), 5.08 (m, 1H), 5.05-5.07 (m, 1H), 3.68 (s, 6H), 2.59-2.63 (m, 4H), 1.70 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ = 171.2 (2C), 134.6, 132.3, 131.1, 128.7, 124.0, 119.1, 57.9, 52.3 (2C), 36.9, 35.8, 17.9 ppm.

FT-IR (NaCl, thin film) ν = 3080, 3020, 2954, 2855, 1732, 1661, 1642, 1436, 1378, 1286, 1212, 1157, 1076 cm^{-1} .

TLC: R_f = 0.53 (20% Et_2O /pentane), one spot, anisaldehyde stain.

HRMS (m/z) calculated for $\text{C}_{14}\text{H}_{20}\text{O}_4$ (M^+): 252.1362. Found: 252.1371.

JPC-I-259-major

Data Collected on:

nmr1-inova500

Archive directory:

/export/home/jpchrist/vnmrsys/data

Sample directory:

File: JC-I-259-major

Pulse Sequence: s2pul

Solvent: CDCl3

Pulse 60.0 degrees

Acq. time 4.000 sec

Width 8000.0 Hz

32 repetitions

OBSERVE H1, 499.7485737 MHz

DATA PROCESSING

FT size 131072

Total time 2 min

JPC-I-259-minor

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JC-I-259-minor

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
38 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 4 min

JPC-II-188

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-188-pure

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
56 repetitions
OBSERVE H1, 499.7485733 MHz
DATA PROCESSING
FT size 131072
Total time 8 min

JPC-II-190

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-II-190-pure

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
68 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 17 min

JPC-II-74

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-II-47-1H

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 4 min

STANDARD PROTON PARAMETERS

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-90-major-pure

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
128 repetitions
OBSERVE H1, 499.7485734 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 8 min

STANDARD 1H OBSERVE

Data Collected on:

nmr1-inova500

Archive directory:

/export/home/jpchrist/vnmrSYS/data

Sample directory:

File: JPC-II-90-minor-pure

Pulse Sequence: s2pul

Solvent: CDCl3

Relax. delay 0.500 sec

Pulse 57.1 degrees

Acq. time 4.002 sec

Width 4997.5 Hz

64 repetitions

OBSERVE H1, 400.115372 MHz

DATA PROCESSING

line broadening 0.5 Hz

FT size 65536

Total time 4 min

STANDARD PROTON PARAMETERS

Data Collected on:

nmr1-inova500

Archive directory:

/export/home/jpchrist/vnmr/sys/data

Sample directory:

File: JC-I-148-2-1H

Pulse Sequence: s2pul

Solvent: CDCl3

Pulse 60.0 degrees

Acq. time 4.000 sec

Width 8000.0 Hz

16 repetitions

OBSERVE H1, 499.7485740 MHz

DATA PROCESSING

FT size 131072

Total time 1 min

STANDARD PROTON PARAMETERS

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-55-top-pure

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
36 repetitions
OBSERVE H1, 499.7485733 MHz
DATA PROCESSING
FT size 131072
Total time 8 min

JPC-II-178-pure

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-II-178-pure

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
92 repetitions
OBSERVE H1, 400.115372 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 9 min

STANDARD PROTON PARAMETERS

Data Collected on:

nmr1-inova500

Archive directory:

/export/home/jpchrist/vnmrsys/data

Sample directory:

File: JC-I-262-major

Pulse Sequence: s2pul

Solvent: CDCl3

Pulse 60.0 degrees

Acq. time 4.000 sec

Width 8000.0 Hz

32 repetitions

OBSERVE H1, 499.7485729 MHz

DATA PROCESSING

FT size 131072

Total time 2 min

JPC-I-262-minor

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JC-I-261-minor

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 2 min

JPC-I-257-major

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JC-I-257-major

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
84 repetitions
OBSERVE H1, 400.115368 MHz
DATA PROCESSING
FT size 65536
Total time 9 min

15a

JPC-I-257-minor

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JC-I-257-minor

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 8 min

```
Data Collected on:
nmrl-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-93-major
Pulse Sequence: s2pul
Solvent: CDCl3
```

JPC-I-262-minor

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jjchrist/vnmrSYS/data
Sample directory:

File: JC-I-261-minor

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 2 min

JPC-I-243-mix

Data Collected on:

nmr1-inova500

Archive directory:

/export/home/jpchrist/vnmrsys/data

Sample directory:

File: JC-I-243-pure

Pulse Sequence: s2pul

Solvent: CDCl3

Pulse 60.0 degrees

Acq. time 4.000 sec

Width 8000.0 Hz

32 repetitions

OBSERVE H1, 499.748580 MHz

DATA PROCESSING

FT size 131072

Total time 2 min

JPC-I-265-major

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-I-265-major-1H

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
24 repetitions
OBSERVE H1, 499.7485737 MHz
DATA PROCESSING
FT size 131072
Total time 17 min

STANDARD PROTON PARAMETERS

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-I-265-MINOR-1H

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
24 repetitions
OBSERVE H1, 499.7485739 MHz
DATA PROCESSING
FT size 131072
Total time 17 min

STANDARD 1H OBSERVE

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-94-pure-better

Pulse Sequence: s2pul
Solvent: CDCl3

Relax. delay 0.500 sec
Pulse 57.1 degrees
Acq. time 4.002 sec
Width 4997.5 Hz
32 repetitions
OBSERVE H1, 400.115374 MHz
DATA PROCESSING
FT size 65536
Total time 2 min

STANDARD PROTON PARAMETERS

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JC-11-33

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.7485738 MHz
DATA PROCESSING
FT size 131072
Total time 1 min

JPC-II-175

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrsys/data
Sample directory:

File: JPC-II-187-major

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
32 repetitions
OBSERVE H1, 499.7485733 MHz
DATA PROCESSING
FT size 131072
Total time 4 min

JPC-II-187-minor

Data Collected on:
nmr1-inova500
Archive directory:
/export/home/jpchrist/vnmrSYS/data
Sample directory:

File: JPC-II-187-minor

Pulse Sequence: s2pul
Solvent: CDCl3

Pulse 60.0 degrees
Acq. time 4.000 sec
Width 8000.0 Hz
40 repetitions
OBSERVE H1, 499.7485735 MHz
DATA PROCESSING
FT size 131072
Total time 4 min