Studies of the Generation and Pericyclic Behavior of Cyclic Pentadienyl Carbanions. Alkylation Reactions As An Efficient Route to Functionalized *cis*-Bicyclo[3.3.0] octenes.

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General

Infrared spectra were obtained on a Nicolet Avatar 360 spectrometer and are reported in wavenumbers (cm^{-1}). All samples were prepared as thin films on sodium chloride plates from a solution in CH_2Cl_2 . ^1H NMR and ^{13}C NMR were reported for samples in CDCl_3 , and are reported in parts per million (ppm) downfield (δ) using residual CHCl_3 as an internal standard set to δ 7.26 and δ 77.16 respectively. NMR data are reported in the form: δ (multiplicity, number of protons, coupling constants). The NMR data was reprocessed using line broadening, gaussian, and sine bell functions as necessary to enhance resolution. All mass spectral (HRMS) data was obtained on Thermo Mat95XP Magnetic Sector mass spectrometer equipped with a Trace GC by use of a chemical ionization (CI) with methane as the reagent gas. Mass spectra were internally calibrated using perfluorokerosene. Analytical thin layer chromatography (TLC) was performed using glass-backed silica gel 60 (F_{254}) plates (0.25mm thickness) (EM Science). All compounds were visualized using UV light and/or staining with ethanolic *p*-anisaldehyde or potassium permanganate. Column chromatography was performed using 230–450 mesh silica gel (Sorbent Technologies) and aluminum oxide (activated basic, Brockmann I, standard grade, ~ 150 mesh, 58 Å; purchased from Aldrich, 199443). All reagents and solvents were used as received unless otherwise noted. Ethyl acetate (EtOAc) and hexanes for flash chromatography were distilled over marble chips prior to use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled, prior to use, under N_2 from sodium/benzophenone ketyl. All other solvents were distilled from calcium hydride (CaH_2) under dry air. Trimethylsilyl chloride (TMSCl), benzaldehyde, isobutyraldehyde were distilled in a U-tube, under argon, immediately before use. All reactions were conducted in flame dried glassware under an atmosphere of argon unless otherwise noted. All non-volatile compounds were pumped to constant weight at ambient temperature (0.2–0.05 mmHg) following removal of solvents by rotary evaporation. Experimental procedures and analytical data for the compounds **5**, **8-12**, **14-16**, **19** and **20** were reported in our earlier communication.¹

¹ Williams, D. R.; Reeves, J. T. *J. Am. Chem. Soc.* **2004**, *126*, 3434–3435.

[2-(2,2-Dimethylpropyl)-1,3a,4,5,6,6a-hexahydropentalen-1-yl]phenyl methanol (6). A solution of **1** (51 mg, 0.43 mmol) in Et₂O (5.0 mL) was treated dropwise at -78°C with *t*-BuLi (0.27 mL, 0.46 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at -78°C for 15 min, then at rt for 1.5 h. The reaction mixture was recooled to -78°C and treated dropwise with a solution of benzaldehyde (66 μL , 0.64 mmol, 1.5 equiv). After stirring at -78°C for 10 min, the reaction mixture was warmed to rt, quenched with saturated aqueous NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr = 1.6:1. Column chromatography on SiO₂ (pentane/Et₂O, 95:5→90:10) provided two diastereomers of **6** [nonpolar diastereomer (**6a**): 47 mg, polar diastereomer (**6b**): 30 mg; 64% combined yield] as colorless oils. Nonpolar diastereomer (**6a**): IR (neat) 3410, 2948, 1450, 1361 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 4 H), 7.26-7.22 (m, 1 H), 5.49 (s, 1 H), 4.98 (s, 1 H), 3.08 (br s, 1 H), 2.77 (s, 1 H), 2.51-2.48 (m, 1 H), 2.03 (dt, 2 H, J = 8.8, 13.6 Hz), 1.84 (d, 1 H, J = 1.6 Hz), 1.63-1.54 (m, 2 H), 1.44-1.32 (m, 4 H), 0.98 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 140.8, 136.9, 128.2, 126.7, 125.8, 72.0, 64.8, 49.1, 42.0, 41.0, 35.3, 32.5, 32.1, 30.3, 25.3; MS (ESI) m/z (rel. intensity) 307 ([M+Na]⁺, 100), 267 (85); HRMS (ESI) calcd for C₂₀H₂₈ONa (M+Na): 307.2038, found: 307.2030. Polar diastereomer (**6b**): IR (neat) 3387, 2944, 1450, 1361 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.20 (m, 5 H), 5.21 (s, 1 H), 4.85 (b, 1 H), 2.93 (s, 1 H), 2.64-2.58 (m, 1 H), 2.50-2.45 (m, 1 H), 1.99-1.96 (m, 1 H), 1.91 (d, 1 H, J = 13.6 Hz), 1.81 (d, 1 H, J = 13.6 Hz), 1.78-1.72 (m, 1 H), 1.59-1.32 (m, 5 H), 0.84 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 143.2, 140.3, 136.7, 127.8, 127.0, 126.3, 76.3, 64.1, 49.0, 44.7, 43.1, 35.0, 32.2, 31.9, 30.1, 25.6; MS (ESI) m/z (rel. intensity) 307 ([M+Na]⁺, 65), 267 (100); HRMS (ESI) calcd for C₂₀H₂₈ONa (M+Na): 307.2038, found: 307.2039.

1-[2-(2,2-Dimethylpropyl)-1,3a,4,5,6,6a-hexahydropentalen-1-yl]cyclohex-2-enol (7). A solution of **1** (30 mg, 0.25 mmol) in Et₂O (1.5 mL) was treated dropwise at -78°C with *t*-BuLi (0.16 mL, 0.28 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at -78°C for 10 min, then at rt for 1 h. The reaction mixture was recooled to -78°C and treated dropwise with a solution of cyclohexenone (36 μL , 0.38 mmol, 1.5 equiv). After stirring at -78°C for 10 min, the reaction mixture was warmed to rt, quenched with saturated aqueous NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr = 2.5:1. Column chromatography on SiO₂ (hexanes/EtOAc, 95:5) provided two diastereomers of **7** [nonpolar diastereomer (**7a**): 12 mg, polar diastereomer (**7b**): 30 mg; 61% combined yield] as colorless oils. Nonpolar diastereomer (**7a**): IR (neat) 3476, 2944, 1473, 1363, 957 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.82 (ddd, 1 H, *J* = 9.6, 5.2, 2.0 Hz), 5.62-5.59 (m, 1 H), 5.29 (s, 1 H), 3.01 (br s, 1 H), 2.54 (s, 1 H), 2.46 (d, 1 H, *J* = 13.2 Hz), 2.18-2.12 (m, 1 H), 2.09-2.00 (m, 1 H), 1.96 (d, 1 H, *J* = 13.2 Hz), 1.96-1.85 (m, 1 H), 1.75-1.31 (m, 11 H), 0.91 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 142.0, 135.6, 133.9, 129.6, 73.8, 66.6, 49.0, 45.7, 43.8, 36.0, 32.6, 32.2, 31.3, 30.4, 25.5, 25.4, 18.6; MS (ESI) *m/z* (rel. intensity) 257 ([M-OH]⁺, 100), 218 (90); HRMS (ESI) calcd for C₁₉H₂₉ (M-OH): 257.2269, found: 257.2266. Polar diastereomer (**7b**): IR (neat) 3456, 2946, 1476, 1361, 1260, 1080 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.85 (ddd, 1 H, *J* = 9.6, 5.2, 2.0 Hz), 5.71-5.67 (m, 1 H), 5.31 (s, 1 H), 3.00 (b, 1 H), 2.55 (s, 1 H), 2.52-2.46 (m, 1 H), 2.27 (d, 1 H, *J* = 13.6 Hz), 2.08-1.99 (m, 1 H), 1.94-1.84 (m, 1 H), 1.89 (d, 1 H, *J* = 13.6 Hz), 1.83-1.76 (m, 1 H), 1.71-1.31 (m, 10 H), 0.89 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 141.2, 136.5, 132.9, 130.7, 67.8, 66.6, 48.7, 44.7, 43.4, 35.8, 32.9, 32.8, 32.3, 30.4, 25.6, 25.5,

18.6; MS (ESI) m/z (rel. intensity) 257 ($[M-OH]^+$, 100), 201 (62); HRMS (ESI) calcd for $C_{19}H_{29}(M-OH)$: 257.2269, found: 257.2276.

3-(2-pentyl-1,3a,4,5,6,6a-hexahydropentalen-1-yl)pentan-3-ol (13). A solution of (–)-sparteine (74 μ L, 0.321 mmol, 1.1 equiv) in hexanes (2.0 mL) was treated dropwise at -78°C with $n\text{-BuLi}$ (0.13 mL, 0.321 mmol, 1.1 equiv). A solution of **1** (35 mg, 0.292 mmol) in hexanes (1.0 mL) was added dropwise and the reaction mixture was stirred at -78°C for 10 min, then at rt for 1.5 h. The reaction mixture was recooled to -78°C and treated dropwise with 3-pentanone (0.2 mL). The reaction mixture was stirred at -78°C for 10 min, warmed to rt and quenched with saturated aqueous NaHCO_3 solution and extracted with Et_2O . The combined organic layers were dried (MgSO_4), filtered and concentrated. ^1H NMR of the crude product showed a dr > 20:1. Column chromatography on SiO_2 (hexanes/ Et_2O , 85:15) provided **13** (59 mg, 77%) as a colorless oil. IR (neat) 3620, 3493, 3028, 2946, 2860, 1646, 1458, 1377, 1254, 1127 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.28 (s, 1 H), 3.00 (br, 1 H), 2.49 (s, 1 H), 2.37-2.31 (m, 1 H), 2.22-2.14 (m, 1 H), 2.08-2.01 (m, 1 H), 1.84-1.75 (m, 1 H), 1.67-1.60 (m, 1H), 1.58-1.21 (m, 14 H), 1.16 (s, 1 H), 0.95-0.86 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.3, 132.2, 62.7, 48.9, 45.0, 35.9, 32.3, 32.1, 31.9, 30.3, 28.7, 28.2, 25.6, 22.8, 14.2, 7.9; MS (EI) m/z (rel. intensity) 263 ($[M-H]^+$, 2), 247 (76), 178 (100); HRMS (EI) calcd for $C_{18}H_{31}O$ (M-H): 263.2375, found: 263.2367.

3-(2-Isobutyl-1,3a,4,5,6,6a-hexahydropentalen-1-yl)propionic acid ethyl ester (17). A solution of **1** (30 mg, 0.25 mmol) in Et₂O (1.2 mL) was treated dropwise at -78°C with *i*-PrLi (0.39 mL, 0.28 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at -78°C for 10 min, then at rt for 1 h. The reaction mixture was recooled to -78°C and treated with a solution of CuCN (23 mg, 1 equiv) and LiCl (21 mg, 2 equiv) in THF (1 mL). After 10 min a solution of ethyl acrylate (32 μL , 0.30 mmol, 1.2 equiv) and TMSCl (50 μL , 0.39 mmol) in THF (0.7 mL) was added dropwise. The reaction mixture was stirred at -78°C for 2 h, warmed to rt and quenched with saturated aqueous NaHCO₃ solution and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr = 7.2:1. Column chromatography on SiO₂ (hexanes/Et₂O, 95:5) provided **17** (45 mg, 68%, major diastereomer) as a colorless oil. IR (neat) 3028, 2951, 2867, 1737, 1469, 1447, 1374, 1238, 1165, 1095, 1037 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.13 (s, 1 H), 4.12 (q, 2 H, J = 6.8 Hz), 3.08-3.04 (m, 1 H), 2.37-2.22 (m, 3 H), 2.20-2.15 (m, 1 H), 1.95-1.86 (m, 2 H), 1.80-1.64 (m, 3 H), 1.59-1.52 (m, 1H), 1.50-1.28 (m, 5 H), 1.25 (t, 3 H, J = 7.2 Hz), 0.90 (d, 3 H, J = 6.4 Hz), 0.80 (d, 3 H, J = 6.0 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 174.2, 144.5, 129.9, 60.3, 54.3, 48.9, 47.0, 38.4, 35.5, 32.4, 31.8, 29.0, 26.2, 25.3, 23.5, 22.0, 14.3; MS (EI) m/z (rel. intensity) 265 (60), 264 (M⁺, 81), 219 (100), 120 (59); HRMS (EI) calcd for C₁₇H₂₈O₂: 264.2089, found: 264.2093.

(2-neopentyl-1,3a,4,5,6,6a-hexahydropentalen-1-yl)(phenyl)methanone (18). A solution of **1** (150 mg, 1.25 mmol) in Et₂O (6.0 mL) was treated dropwise at –78 °C with *t*-BuLi (0.81 mL, 1.38 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at –78 °C for 10 min, then at rt for 1.25 h. The reaction mixture was recooled to –78 °C and treated with a solution of CuCN (112 mg, 1 equiv) and LiCl (105 mg, 2 equiv) in THF (5.0 mL). After 15 min benzoyl chloride (0.16 mL, 1.38 mmol, 1.1 equiv) was added dropwise. The reaction mixture was allowed to warm gradually to rt over 15 h, quenched with saturated aqueous NaHCO₃ solution and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr > 20:1. Column chromatography on SiO₂ (hexanes/Et₂O, 95:5) provided **18** (254 mg, 72%) as a colorless oil. IR (neat) 2949, 1714, 1678, 1447, 1276, 1200 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.00-7.98 (m, 2 H), 7.57-7.52 (m, 1 H), 7.48-7.40 (m, 2 H), 5.49 (s, 1 H), 4.21 (s, 1 H), 3.28 (br s, 1 H), 2.70-2.64 (m, 1 H), 2.11 (d, 1 H, *J* = 14.0 Hz), 1.91-1.82 (m, 1 H), 1.75 (d, 1 H, *J* = 13.6 Hz), 1.70-1.54 (m, 5 H), 0.90 (s, 9 H); ¹³C NMR (101 MHz, CDCl₃) δ 202.3, 139.7, 137.2, 136.0, 132.9, 129.6, 128.7, 128.4, 65.5, 50.0, 47.2, 43.4, 35.4, 32.3, 31.7, 30.1, 25.4; MS (CI) *m/z* (rel. intensity) 151 (35), 105 (100); HRMS (CI) calcd for C₂₀H₂₆O: 282.1984, found: 282.1989.

2-pentyl-3a,4,5,6,7,7a-hexahydro-1H-indene (33). A solution of TMEDA (0.65 mL) and triene **30** (265 mg, 1.98 mmol) in hexanes (3.0 mL) was treated dropwise at –78 °C with *n*-BuLi (0.87 mL, 2.18 mmol, 2.5M/hexanes, 1.1 equiv). The reaction mixture was stirred at –78 °C for 10 min, at rt for 1.5 h,

and finally at 120 °C for 1 h. The reaction mixture was cooled to –78 °C and quenched with water (1 mL). The reaction mixture was extracted with Et₂O, and the combined organic layers were washed with 10% aqueous HCl solution, saturated NaHCO₃, dried (MgSO₄), filtered and concentrated. Column chromatography on 10 wt% AgNO₃/SiO₂ (pentane/benzene, 98:2) provided **33** (118 mg, 31%) as a colorless oil. IR (neat) 2922, 2852, 1642, 1451, 1377 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.26 (s, 1 H), 2.55-2.47 (m, 1 H), 2.20-2.12 (m, 2 H), 2.05-2.01 (m, 2 H), 1.95-1.88 (m, 1 H), 1.60-1.22 (m, 14 H), 0.89 (t, 3 H, *J* = 6.8 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 144.6, 128.9, 43.8, 40.4, 38.1, 31.9, 31.8, 29.0, 28.4, 27.6, 23.5, 23.2, 22.7, 14.3; MS (CI) *m/z* (rel. intensity) 192 (M⁺, 35), 191 (50), 121 (100); HRMS (CI) calcd for C₁₄H₂₄: 192.1878, found: 192.1874.

(1Z,4Z)-3-methylenecyclohepta-1,4-diene (36). A suspension of methyltriphenyl phosphonium bromide (3.97 g, 11.11 mmol, 1.2 equiv) in Et₂O (100 mL) was treated dropwise at –78 °C with *n*-BuLi (4.44 mL, 11.11 mmol, 2.5 M/hexanes, 1.2 equiv). The reaction mixture was stirred at 0 °C for 1.5 h, recooled to –78 °C and treated dropwise with a solution of 2,6-cycloheptadienone (1.00 g, 9.26 mmol, 1.0 equiv) in Et₂O (5 mL). The reaction mixture was stirred at –78 °C and monitored by TLC, quenched with saturated aqueous NaHCO₃ solution, and extracted with Et₂O. The combined organic extracts were dried (Na₂SO₄), filtered and concentrated (bath temperature = 0 °C). The resultant crude product was diluted with pentane and filtered through a short pad of basic activated Al₂O₃, rinsing with pentane, and the combined pentane filtrate was concentrated (bath temperature = 0 °C) to provide pure **36** (592 mg, 60%) as a colorless liquid. Compound **36** slowly decomposes by polymerization and is best stored at –20 °C as a solution (~0.2 M) in pentane and filtered through basic activated Al₂O₃ immediately prior to use. IR (neat) 3079, 3020, 2929, 2838, 1763, 1571, 1445, 1264 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.10 (d, 2 H, *J* = 11.6 Hz), 5.86-5.84 (m, 2 H), 5.07 (s, 2 H), 2.36-2.35 (m, 4 H); ¹³C NMR (101 MHz,

CDCl₃) δ 144.4, 131.8, 131.1, 120.9, 28.4; MS (EI) m/z (rel. intensity) 106 (M^+ , 100), 43(100); HRMS (EI) calcd for C₈H₁₀: 106.0777, found: 106.0774.

(2Z,4Z)-3-pentylcyclohepta-2,4-dienecarboxylic acid (40). A solution of (–)-sparteine (0.19 mL, 0.8 mmol, 1.2 equiv) in hexanes (3.0 mL) was treated dropwise at –78 °C with *n*-BuLi (0.32 mL, 0.8 mmol, 2.5 M/hexane, 1.2 equiv). A solution of **36** (73.8 mg, 0.7 mmol, 1.0 equiv) in hexanes (2.0 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 10 min, then at rt for 1 h. The reaction mixture was cannulated into a slurry of CO₂ in THF (3 mL) at –78 °C. The reaction mixture was allowed to warm to rt gradually over 3 h, acidified with 10% aqueous HCl solution, and extracted with Et₂O. The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/Et₂O, 80:20) provided **40** (120 mg, 82%) as a colorless oil. IR (neat) 3019, 2959, 2927, 2852, 2677, 1706, 1453, 1418, 1294, 1233 cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 5.97–5.93 (m, 1 H), 5.81 (d, 1 H, J = 4.4 Hz), 5.77 (d, 1 H, J = 11.2 Hz), 3.28–3.26 (m, 1 H), 2.32–2.04 (m, 5 H), 1.43–1.26 (m, 7 H), 0.88 (t, 3 H, J = 6.4 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 181.3, 139.3, 134.0, 129.5, 124.5, 45.3, 39.0, 33.2, 31.5, 29.0, 28.9, 22.7, 14.2; MS (CI) m/z (rel. intensity) 208 (M^+ , 100), 163 (91); HRMS (CI) calcd for C₁₃H₂₀O₂: 208.1458, found: 208.1461.

3-((2Z,4Z)-3-neopentylcyclohepta-2,4-dienyl)pentan-3-ol (41). A solution of **36** (50 mg, 0.472 mmol) in Et₂O (2.2 mL) was treated dropwise at –78 °C with *t*-BuLi (0.29 mL, 0.493 mmol, 1.7 M/pentane, 1.05 equiv). The reaction mixture was stirred at –78 °C for 10 min, then at rt for 1 h. The reaction mixture was recooled to –78 °C and treated dropwise with 3-pentanone (0.10 mL, ~2.0 equiv). The reaction mixture was stirred at –78 °C for 10 min, warmed to rt and quenched with saturated aqueous NaHCO₃ solution and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (hexanes/EtOAc, 90:10) provided **41** (79 mg, 67%) as a colorless oil. IR (neat) 3475, 2946, 2882, 1649, 1463, 1363, 1236, 1160 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.86-5.76 (m, 2 H), 5.68 (d, 1 H, *J* = 4.8 Hz), 2.36-2.16 (m, 3 H), 2.06-1.99 (m, 1 H), 1.95 (s, 2 H), 1.74-1.43 (m, 5 H), 0.89-0.85 (m, 15 H); ¹³C NMR (101 MHz, CDCl₃) δ 135.7, 132.6, 132.4, 132.1, 76.3, 52.8, 46.2, 31.9, 30.7, 30.0, 29.1, 28.4, 7.8; MS (ESI) *m/z* (rel. intensity) 273 ([M+Na]⁺, 100), 261 (33); HRMS (ESI) calcd for C₁₇H₃₀ONa (M+Na): 273.2194, found: 273.2187.

((2Z,4Z)-3-pentylcyclohepta-2,4-dienyl)(phenyl)methanol (42). A solution of (–)-sparteine (0.25 mL, 1.1 mmol, 1.1 equiv) in hexanes (7.2 mL) was treated dropwise at –78 °C with *n*-BuLi (0.44 mL, 1.1 mmol, 1.1 equiv). A solution of **36** (100 mg, 1.0 mmol) in hexanes (4.0 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 10 min, then at rt for 1 h. The reaction mixture was recooled to –78 °C and treated dropwise with benzaldehyde (0.12 mL, 1.2 equiv). The reaction mixture was allowed to warm to rt and quenched with saturated aqueous NaHCO₃ solution and extracted with

Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr = 1:1.2. Column chromatography on SiO₂ (pentane/Et₂O, 4:1) provided mixture of diastereomers of **42** (211 mg, 78%) as colorless oil. IR (neat) 3545, 3389, 3085, 3066, 3031, 3008, 2918, 2852, 1949, 1883, 1813, 1653, 1606, 1494, 1459, 1424, 1373, 1019 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.16 (m, 10 H), 5.83-5.78 (m, 2 H), 5.69-5.60 (m, 3 H), 5.30 (d, 1 H, *J* = 4.8 Hz), 4.62 (dd, 1 H, *J* = 6.8, 2.0 Hz), 4.55 (dd, 1 H, *J* = 6.8, 3.6 Hz), 2.61 (br, 2 H), 2.34-2.05 (m, 4 H), 1.97-1.83 (m, 6 H), 1.80-1.56 (m, 4 H), 1.36-1.08 (m, 12 H), 0.83-0.79 (m, 6 H); ¹³C NMR (101 MHz, CDCl₃) δ 143.6, 143.4, 138.8, 137.9, 134.3, 133.9, 129.4, 129.1, 128.8, 128.5, 128.4, 128.1, 127.7, 127.5, 126.7, 126.66, 77.9, 76.7, 47.2, 47.0, 39.7, 39.4, 32.6, 31.6, 31.5, 29.5, 29.4, 29.1, 28.7, 22.7, 14.2; MS (CI) *m/z* (rel. intensity) 271 ([M+H]⁺, 4), 253 (16), 164 (82), 163 (19), 108 (64), 107 (100), 93 (21); HRMS (CI) calcd for C₁₉H₂₇O (M+H): 271.2062, found: 271.2071.

((2Z,4Z)-3-isobutylcyclohepta-2,4-dienyl)(phenyl)sulfane (43). A solution of **36** (50.0 mg, 0.47 mmol) in Et₂O (2.5 mL) was treated dropwise at -78 °C with *i*-PrLi (0.78 mL, 0.52 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at -78 °C for 10 min, then at rt for 1 h. The reaction mixture was recooled to -78 °C and treated dropwise with a solution of PhSSPh (110.0 mg, 0.49 mmol, 1.05 equiv) in Et₂O (2.5 mL). The reaction mixture was allowed to warm to rt, quenched with saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane) provided **43** (78 mg, 65%) as a colorless oil. IR (neat) 2953, 2919, 2850, 1650, 1583, 1463, 1437, 1377, 1257, 1088, 1025 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.20 (m, 5H), 5.95-5.89 (m, 1H), 5.72-5.69 (m, 2H), 4.07 (br s, 1H), 2.67-2.60 (m, 1H), 2.31-2.27 (m, 1H), 2.06-1.86 (m, 4H), 1.70 (sept, 1H, *J* = 6.8 Hz), 0.86 (d, 6H, *J* = 6.4 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 137.3, 135.8, 134.4, 131.6, 129.0, 128.7, 128.5, 126.8,

49.8, 49.3, 31.4, 27.7, 27.5, 22.5, 22.3; MS (EI) m/z (rel. intensity) 258 (M^+ , 15), 220 (32), 206 (16), 205 (88), 150 (16), 149 (100), 109 (30), 105 (27), 93 (81), 91 (49), 83 (33), 79 (40); HRMS (EI) calcd for $C_{17}H_{22}S$: 258.1442, found: 258.1449.

((2Z,4Z)-3-isobutylcyclohepta-2,4-dienyl)trimethylsilane (44). A solution of **36** (50 mg, 0.472 mmol) in Et_2O (4.0 mL) was treated dropwise at $-78\text{ }^{\circ}C$ with $i\text{-PrLi}$ (0.74 mL, 0.519 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at $-78\text{ }^{\circ}C$ for 10 min, then at rt for 1 h. The reaction mixture was recooled to $-78\text{ }^{\circ}C$ and treated dropwise with $TMSCl$ (0.11 g, 0.13 mL, 1.0 mmol). The reaction mixture was allowed to warm to rt, recooled to $-78\text{ }^{\circ}C$, quenched with saturated $NaHCO_3$ solution, and extracted with Et_2O . The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Column chromatography on SiO_2 (pentane) provided **44** (72 mg, 65%) as a colorless oil. IR (neat) 3395, 2954, 2923, 2867, 1645, 1464, 1362, 1245 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 5.77-5.66 (m, 2 H), 5.60 (d, 1 H, $J = 5.6$ Hz), 2.43-2.20 (m, 2 H), 2.00-1.79 (m, 5 H), 1.68 (sept, 1 H, $J = 6.4$ Hz), 0.87 (d, 6 H, $J = 6.8$ Hz), 0.02 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.5, 132.4, 131.9, 129.6, 50.3, 33.9, 31.8, 29.1, 28.1, 22.5, -2.3; MS (CI) m/z (rel. intensity) 237 (35), 222 (M^+ , 24), 193 (37), 181 (100), 165 (31), 147 (27), 107 (33); HRMS (CI) calcd for $C_{14}H_{26}Si$: 222.1804, found: 222.1801.

(2Z,4Z)-3-isobutylcyclohepta-2,4-dienol (45). A solution of **36** (50 mg, 0.472 mmol) in Et₂O (4.0 mL) was treated dropwise at –78 °C with *i*-PrLi (0.74 mL, 0.519 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at –78 °C for 1.5 h, then treated rapidly with a solution of Davis' oxaziridine (148 mg, 0.566 mmol, 1.2 equiv) in THF (3 mL). The reaction mixture was quenched after 1 min with saturated aqueous NaHCO₃ solution and allowed to warm to rt. The mixture was extracted with Et₂O, and the combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (hexanes/Et₂O, 90:10) provided **45** (29 mg, 37%) as a colorless oil. IR (neat) 3334, 2953, 1464, 1365, 1026 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.94 (dt, 1 H, *J* = 11.2, 5.2 Hz), 5.70-5.64 (m, 2 H), 4.37 (br s, 1 H), 2.30-2.25 (m, 2 H), 2.09-2.01 (m, 1 H), 1.98-1.93 (m, 1 H), 1.89-1.81 (m, 2 H), 1.74-1.64 (m, 1 H), 1.61 (br s, 1 H), 0.87 (d, 3 H, *J* = 6.4 Hz), 0.86 (d, 3 H, *J* = 6.4 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 135.7, 134.8, 132.1, 128.7, 69.9, 49.4, 35.6, 27.6, 25.3, 22.6, 22.2; MS (CI) *m/z* (rel. intensity) 166 (M⁺, 17), 149 (100); HRMS (CI) calcd for C₁₁H₁₈O: 166.1358, found: 166.1356.

(3-Isobutyl-6,6-dimethyl-cyclohexa-2,4-dienylsulfanyl)-benzene (51). A solution of **46** (100.0 mg, 0.8 mmol) in Et₂O (12 mL) was treated dropwise at –78 °C with *i*-PrLi (1.29 mL, 0.9 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at –78 °C for 10 min, then at rt for 1 h. The reaction mixture was recooled to –78 °C and treated dropwise with a solution of PhSSPh (170.0 mg, 0.8 mmol) in Et₂O (5 mL). The reaction mixture was allowed to warm to rt over 1 h, quenched with

saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane) provided **51** (110 mg, 50%) as a colorless oil. IR (neat) 3074, 3058, 3028, 2952, 2918, 2861, 1656, 1580, 1481, 1466, 1436, 1379, 1352 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.41 (m, 2H), 7.28-7.16 (m, 3H), 5.74 (dd, 1H, *J* = 9.6, 1.2 Hz), 5.55 (d, 1H, *J* = 9.9 Hz), 5.49 (app d, 1H, *J* = 5.1 Hz), 3.80 (d, 1H, *J* = 5.1 Hz), 1.94-1.83 (m, 2H), 1.74-1.65 (m, 1H), 1.20 (s, 3H), 1.15 (s, 3H), 0.88 (d, 3H, *J* = 6.6 Hz), 0.84 (d, 3H, *J* = 6.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 138.0, 136.8, 134.7, 131.8, 128.8, 126.5, 125.1, 123.0, 56.2, 44.8, 36.4, 27.5, 27.4, 25.1, 22.7, 22.4; MS (EI) *m/z* (rel. intensity) 271 ([M-H]⁺, 2), 164 (11), 163 (100), 107 (9); HRMS (EI) calcd for C₁₈H₂₃S (M-H): 271.1520, found: 271.1532.

3-(2,2-Dimethyl-propyl)-6,6-dimethyl-cyclohexa-2,4-dienecarboxylic acid (52). A solution of **46** (100.0 mg, 0.8 mmol) in Et₂O (8 mL) was treated dropwise at -78 °C with *t*-BuLi (0.53 mL, 0.9 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at -78 °C for 10 min, then at rt for 1 h. The reaction mixture was cannulated into a slurry of CO₂ in THF (12 mL) at -78 °C. The reaction mixture was allowed to warm to rt gradually over 3 h, acidified with 10% aqueous HCl solution and extracted with EtOAc. The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether, 95:5) provided **52** (79 mg, 45%) as a colorless oil. IR (neat) 3032, 2958, 2864, 1702, 1363 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.72 (d, 1H, *J* = 9.9 Hz), 5.45-5.39 (m, 2H), 3.25 (d, 1H, *J* = 3.3 Hz), 1.96 (s, 2H), 1.24(s, 3H), 1.02 (s, 3H), 0.90 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 180.0, 136.8, 134.3, 126.8, 120.4, 52.3, 49.4, 33.9, 32.0, 29.9, 28.7, 21.9; MS (EI) *m/z* (rel. intensity) 223 (60), 222 (M⁺, 100), 177 (36), 167 (93), 166 (32), 153 (36), 121 (77); HRMS (EI) calcd for C₁₄H₂₂O₂: 222.1619, found: 222.1612.

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(1-Isobutyl-4,4-dimethyl-cyclohexa-2,5-dienyl)-trimethyl-silane (53). A solution of **46** (100.0 mg, 0.8 mmol) in Et₂O (12 mL) was treated dropwise at $-78\text{ }^{\circ}\text{C}$ with *i*-PrLi (1.29 mL, 0.9 mmol, 0.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min, then at rt for 1 h. The reaction mixture was recooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with TMSCl (0.22g, 0.26 ml, 2.0 mmol). The reaction mixture was allowed to warm to rt gradually overnight, recooled to $-78\text{ }^{\circ}\text{C}$, quenched with saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane) provided **53** (59 mg, 31%) as a colorless oil. IR (neat) 3003, 2952, 2901, 2868, 1467, 1245, 903, 834, 740 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.39-5.29 (m, 4 H), 2.17-1.63 (m, 3 H), 1.02 (d, 6 H, $J = 3.6\text{ Hz}$), 0.88 (s, 3 H), 0.86 (s, 3 H), -0.04 (s, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 132.5, 127.8, 35.9, 33.1, 31.9, 31.3, 29.2, 26.4, 24.8, -4.1; MS (EI) m/z (rel. intensity) 236 (M⁺, 6), 221 (12), 147 (6), 107 (6), 105 (12), 74 (7), 73 (100), 57 (6); HRMS (EI) calcd for C₁₅H₂₈Si: 236.1955, found: 236.1953.

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1-(6,6-dimethyl-3-pentylcyclohexa-2,4-dienyl)-2-methylpropan-1-ol (54). A solution of (–)-sparteine (0.16 mL, 0.70 mmol, 1.1 equiv) in hexanes (2.0 mL) was treated dropwise at $-78\text{ }^{\circ}\text{C}$ with *n*-BuLi (0.28 mL, 0.7 mmol, 1.1 equiv). A solution of **46** (75 mg, 0.60 mmol) in hexanes (2.6 mL) was added dropwise and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min, then at rt for 1 h. The reaction mixture was recooled to $-78\text{ }^{\circ}\text{C}$ and treated dropwise with isobutyraldehyde (0.07 mL). The reaction mixture was allowed to warm to rt gradually overnight, recooled to $-78\text{ }^{\circ}\text{C}$, quenched with saturated

NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. ¹H NMR of the crude product showed a dr = 3.3:1. Column chromatography on SiO₂ (pentane/Et₂O, 98:2) provided two diastereomers of **54** [nonpolar diastereomer (**54a**): 75 mg, polar diastereomer (**54b**): 25 mg; 67% combined yield] as colorless oils. Nonpolar diastereomer (**54a**): IR (neat) 3575, 3486, 3020, 2961, 2931, 2868, 1465, 1376, 1358 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.67 (dd, 1 H, *J* = 9.6, 1.6 Hz), 5.57 (d, 1 H, *J* = 9.2 Hz), 5.33 (d, 1 H, *J* = 5.2 Hz), 3.33 (ddd, 1 H, *J* = 9.2, 6.8, 2.0 Hz), 2.20-2.19 (m, 1 H), 2.07 (t, 2 H, 7.2 Hz), 1.76 (d, 1 H, *J* = 6.8 Hz), 1.74-1.66 (m, 1 H), 1.46-1.23 (m, 6 H), 1.13 (s, 3 H), 1.10 (s, 3 H), 0.98 (d, 3 H, *J* = 6.8), 0.90-0.87 (m, 6 H); ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 137.5, 124.2, 117.8, 78.8, 45.6, 35.7, 33.6, 31.5, 31.4, 28.9, 28.2, 24.1, 22.6, 20.1, 19.5, 14.2; MS (CI) *m/z* (rel. intensity) 251 (11), 250 ([M]⁺, 4), 233 (37), 179 (100), 177 (85), 163 (22); HRMS (CI) calcd for C₁₇H₃₀O: 250.2291, found: 250.2289. Polar diastereomer (**54b**): IR (neat) 3487, 2953, 2921, 2853, 1462, 1379 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.68 (dd, 1 H, *J* = 9.6, 1.2 Hz), 5.45 (d, 1 H, *J* = 9.2 Hz), 5.25 (d, 1 H, *J* = 5.2 Hz), 3.57 (ddd, 1 H, *J* = 8.0, 5.6, 2.8 Hz), 2.06-1.94 (m, 4 H), 1.43-1.24 (m, 7 H), 1.15 (s, 3 H), 1.13 (s, 3 H), 0.94 (d, 3 H, *J* = 6.8), 0.90-0.86 (m, 6 H); ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 135.1, 124.5, 121.2, 76.0, 48.3, 35.4, 34.8, 31.6, 30.5, 29.2, 28.1, 25.0, 22.6, 20.8, 15.2, 14.2; MS (CI) *m/z* (rel. intensity) 250([M]⁺, 13), 234 (16), 233 (88), 207 (19), 178 (66), 177 (100); HRMS (CI) calcd for C₁₇H₃₀O: 250.2291, found: 250.2280.

[3-(2,2-Dimethyl-propyl)-6,6-dimethyl-cyclohexa-2,4-dienyl]-methanol (55). A solution of **46** (70.0 mg, 0.6 mmol) in Et₂O (6 mL) was treated dropwise at -78 °C with *t*-BuLi (0.41 mL, 0.7 mmol, 1.7 M/pentane, 1.2 equiv). The reaction mixture was stirred at -78 °C for 10 min, then at rt for 1 h. The reaction mixture was recooled to -78 °C and treated dropwise with a solution of paraformaldehyde (40.0 mg, 1.2 mmol) in Et₂O (1 mL). The reaction mixture was allowed to warm to rt over 1h, quenched

with saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether, 90:10) provided **55** (60 mg, 46%) as a colorless oil. IR (neat) 3355, 3030, 2957, 2868, 1478, 1366, 1030 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.68 (dd, 1H, *J* = 10.8, 1.2 Hz), 5.41-5.38 (m, 2H), 3.75-3.64 (m, 2H), 2.21-2.16 (m, 1H), 1.95 (s, 2H), 1.47 (bs, 1H), 1.09 (s, 3H), 0.97 (s, 3H), 0.89 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 134.0, 127.0, 124.4, 63.2, 49.7, 47.2, 33.0, 31.8, 29.9, 28.5, 22.5; MS (EI) *m/z* (rel. intensity) 208 (M⁺, 13), 177 (35), 71 (100), 69 (92), 57 (67), 55 (38); HRMS (EI) calcd for C₁₄H₂₄O: 208.1827, found: 208.1835.

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3-(4,4-Dimethyl-1-pentyl-cyclohexa-2,5-dienyl)-pentan-3-ol (56). A solution of (–)-sparteine (0.16 mL, 0.70 mmol, 1.1 equiv) in hexanes (2.0 mL) was treated dropwise at –78 °C with *n*-BuLi (0.28 mL, 0.7 mmol, 1.1 equiv). A solution of **46** (67 mg, 0.60 mmol) in hexanes (3.5 mL) was added dropwise and the reaction mixture was stirred at –78 °C for 10 min, then at rt for 1 h. The reaction mixture was re-cooled to –78 °C and treated dropwise with 3-pentanone (0.07 mL). The reaction mixture was allowed to warm to rt gradually overnight, re-cooled to –78 °C, quenched with saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (10% ether in pentane) provided **56** (60 mg, 38%) as a colorless oil. IR (neat) 3487, 3015, 2950, 2864, 1466 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.62 (d, 2 H, *J* = 10.5 Hz), 5.40 (d, 2 H, *J* = 10.5 Hz), 1.69-1.55 (m, 5 H), 1.46-1.41 (m, 2 H), 1.30-1.16 (m, 6 H), 1.04 (s, 3 H), 1.01 (s, 3 H), 0.93-0.83 (m, 9 H); ¹³C NMR (75 MHz, CDCl₃) δ 136.8, 127.3, 77.7, 49.9, 33.6, 33.3, 32.7, 30.4, 29.7, 27.7, 25.4, 22.9, 14.3, 9.4; MS (CI) *m/z* (rel. intensity) 265 (100), 264 (M⁺, 50); HRMS (CI) calcd for C₁₈H₃₂O: 264.2448, found: 264.2455.

(2Z,6Z)-4,4-diphenylcyclohepta-2,6-dienone (57a). To a stirred mixture of 4,4-diphenylcycloheptanone (300 mg, 1.1 mmol) in DMSO (18 mL) under Ar atmosphere was added IBX (1.54 g, 5.5 mmol, 5 equiv) at rt. The reaction mixture was heated at 80 °C for 12 h, cooled to rt and diluted with Et₂O. The organic layer was washed with 5% aqueous NaHCO₃ solution and water and dried (MgSO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether, 90:10) provided **57a** (220 mg, 76%). IR (neat) 3059, 3031, 2945, 1649, 1605, 1495, 1440, 1403, 1296 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.24 (m, 10H), 7.04 (d, 1H, *J* = 12.6 Hz), 6.54 (dt, 1H, *J* = 12.0, 6 Hz), 6.36 (dd, 1H, *J* = 12.6, 2.1 Hz), 6.15-6.10 (m, 1H), 3.40 (d, 2H, *J* = 6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 192.0, 152.0, 145.9, 141.2, 133.9, 132.1, 128.6, 127.8, 126.9, 53.4, 40.1; MS (EI) *m/z* (rel. intensity) 260 (M⁺, 100); HRMS (EI) calcd for C₁₉H₁₆O: 260.1196, found: 260.1191.

(1Z,4Z)-3-methylene-6,6-diphenylcyclohepta-1,4-diene (57). A suspension of methyltriphenylphosphoniumbromide (360 mg, 1.0 mmol) in Et₂O (9 mL) was treated dropwise at –78 °C with *n*-BuLi (0.40 mL, 1.0 mmol, 2.5 M/hexanes). The mixture was stirred at 0 °C for 30 min, recooled to –78 °C and treated dropwise with a solution of **57a** (220 mg, 0.8 mmol) in Et₂O (15 mL). The mixture was stirred at –78 °C and was monitored by TLC until complete consumption of starting material was observed. The reaction was quenched with saturated aqueous NaHCO₃ solution, and extracted with Et₂O. The combined organic extracts were dried (K₂CO₃), filtered and concentrated. Column chromatography on basic activated Al₂O₃ (pentane) provided **57** (140 mg, 67%). IR (neat) 3086, 3052, 3019, 2919, 2849, 1492, 1440 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.16 (m, 10H), 6.29-6.25 (m, 1H), 6.14 (d, 1H, *J* = 11.7 Hz), 6.04 (d, 1H, *J* = 11.7 Hz), 5.63 (dt, 1H, *J* = 12.0, 6.0 Hz), 5.18 (s, 1H), 5.09 (s, 1H), 3.11 (d, 2H, *J* = 6.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 148.8, 143.3, 139.5, 131.6, 130.1, 128.8, 128.2, 128.0, 126.1, 122.5, 40.7, 29.9; MS (EI) *m/z* (rel. intensity) 278 (49), 277 (100), 258 (M⁺, 33), 167 (43); HRMS (EI) calcd for C₂₀H₁₈: 258.1403, found: 258.1411.

A solution of **57** (140.0 mg, 0.5 mmol) in Et₂O (5.4 mL) was treated dropwise at –78 °C with *t*-BuLi (0.35 mL, 0.6 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at –78 °C for 10 min, then at rt for 12 h. The reaction mixture was recooled to –78 °C and quenched with saturated NaHCO₃ solution, and extracted with Et₂O. The combined organic layers were dried (K₂CO₃), filtered and concentrated. ¹H NMR of the crude product showed a *dr* = 1:1.5. Column chromatography on SiO₂

(hexane) provided **58** (80 mg, 50%) as an inseparable 1:1.5 mixture of olefin isomers and a colorless oil. IR (neat) 3080, 3053, 3030, 2953, 2907, 2865, 2727, 1949, 1604, 1588, 1489, 1473, 1443, 1362, 1232, 1075, 1033, 964, 764, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.17 (m, 20H), 7.14 (d, 1H, J = 11.6 Hz), 6.97 (d, 1H, J = 12 Hz), 6.72 (d, 1H, J = 15.6 Hz), 6.20 (d, 1H, J = 12 Hz), 6.00 (d, 1H, J = 15.6 Hz), 5.91-5.82 (m, 2H), 5.79-5.70 (m, 1H), 2.43 (s, 2H), 2.10 (s, 2H), 1.87 (dd, 3H, J = 6.8, 1.6 Hz), 1.75 (dd, 3H, J = 6.8, 1.2 Hz), 0.99 (s, 9H), 0.86 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.1, 141.6, 140.2, 140.0, 138.3, 137.2, 130.9, 130.9, 129.3, 128.6, 128.3, 128.2, 128.1, 127.8, 127.7, 127.3, 127.2, 125.7, 125.0, 123.7, 47.1, 39.8, 33.3, 32.8, 31.1, 30.5, 19.1, 18.6; MS (EI) m/z (rel. intensity) 316 (M^+ , 32), 220 (98), 205 (100), 167 (77); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{28}$: 316.2191, found: 316.2193.

2-Hydroxymethyl-4,4-dimethyl-cyclohex-2-enone (60). To a stirred mixture of paraformaldehyde (192 mg, 6.4 mmol, 1 equiv) and imidazole (435 mg, 6.4 mmol, 1 equiv) in THF (6.4 mL) and 1 M NaHCO_3 (25.6 mL) was added 4,4-dimethylcyclohex-2-enone (1.60 g, 12.9 mmol, 2 equiv) at rt. The reaction mixture was stirred at rt for 48 h. The reaction mixture was quenched with 1 N HCl solution, and extracted with CH_2Cl_2 . The aqueous layer was washed with CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4), filtered and concentrated. Column chromatography on SiO_2 (pentane/ether 1:1) provided recovered 4,4-dimethylcyclohex-2-enone (840 mg) and **60** (600 mg, 64%, brsm) as a colorless oil. IR (neat) 3471, 2965, 2860, 1684, 1474, 1377, 1178 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.50 (s, 1H), 4.04 (d, 2H, J = 4.8 Hz), 3.32 (app s, 1H), 2.31 (t, 2H, J = 6.6 Hz), 1.70 (t, 2H, J = 6.9 Hz), 1.02 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 199.8, 155.3, 135.0, 60.6, 35.7, 34.4, 32.5, 27.5; MS (CI) m/z (rel. intensity) 155 ($[\text{M}+\text{H}]^+$, 89), 137 (100); HRMS (CI) calcd for $\text{C}_9\text{H}_{15}\text{O}_2$ ($\text{M}+\text{H}$): 155.1072, found: 155.1067.

2-Methoxymethyl-4,4-dimethyl-cyclohex-2-enone (60a). A solution of **60** (600 mg, 3.90 mmol, 1 equiv) in CH₂Cl₂ was treated in one portion with proton-sponge[®] (5.01 g, 23.4 mmol, 6 equiv, Aldrich 158496-50G) under argon atmosphere. The mixture was cooled to 0 °C and treated with trimethyloxonium tetrafluoroborate (1.73 g, 11.7 mmol, 3 equiv). The reaction mixture was allowed to warm to rt and stirred for 3 h. The reaction mixture was quenched with 1 N HCl and extracted with ether. The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether, 80:20) provided **60a** (450 mg, 69%) as a colorless oil. IR (neat) 3326, 2966, 2926, 2864, 2806, 1680, 1469, 1407 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.46 (s, 1H), 3.83 (d, 2H, *J* = 1.2 Hz), 3.16 (s, 3H), 2.26 (t, 2H, *J* = 6.3 Hz), 1.66 (t, 2H, *J* = 6.9 Hz), 0.99 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 197.7, 154.8, 132.7, 68.7, 58.2, 35.7, 34.2, 32.4, 27.6; MS (CI) *m/z* (rel. intensity) 212 (20), 169 ([M+H]⁺, 17), 153 (40), 137 (100); HRMS (CI) calcd for C₁₀H₁₇O₂ (M+H): 169.1229, found: 169.1232.

2-Methoxymethyl-4,4-dimethyl-cyclohexa-2,5-dienone (60b). A solution of diisopropylamine (0.43 mL, 3.1 mmol) in THF (4 mL) was treated dropwise at 0 °C with *n*-BuLi (1.24 mL, 3.1 mmol, 2.5 M/hexanes, 1.2 equiv). After 10 min, the reaction mixture was cooled to -78 °C and treated dropwise with a solution of **60a** (442 mg, 2.6 mmol, 1 equiv) in THF (1.74 mL). The reaction mixture was stirred at -78 °C for 30 min and was treated in one portion with a solution of PhSeBr (730 mg, 3.1 mmol, 1.2 equiv) in THF (1.74 mL). After 30 min the reaction mixture was quenched with saturated NH₄Cl solution, extracted with ether, washed with brine, dried (MgSO₄) and concentrated. The resultant residue was dissolved in CH₂Cl₂ (5.80 mL) and pyridine (1.2 mL) and the mixture was treated with 30% H₂O₂ (3.50 mL). The reaction mixture was stirred at rt for 20 min and poured into 1 N HCl solution, extracted with ether, washed with saturated NaHCO₃ solution, dried (MgSO₄) and concentrated. Column chromatography on SiO₂ (pentane/ether 80:20) provided **60b** (240 mg, 56%) as a colorless oil.

IR (neat) 3264, 2966, 2926, 2863, 2819, 1673, 1636, 1471, 1412, 1247, 1136, 1067 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.74-6.72 (m, 2H), 6.06-6.03 (m, 1H), 4.06 (d, 2H, $J = 1.6$ Hz), 3.29 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 184.9, 156.7, 151.6, 133.5, 126.9, 68.7, 58.6, 37.7, 26.6; MS (EI) m/z (rel. intensity) 169 (70), 168 (82), 167 (37), 166 (M^+ , 43), 165 (100), 151 (100); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$: 166.0994, found: 166.0996.

1-Methoxymethyl-3,3-dimethyl-6-methylene-cyclohexa-1,4-diene (61). A suspension of methyltriphenylphosphoniumbromide (572 mg, 1.6 mmol) in Et_2O (15 mL) was treated dropwise at -78 $^\circ\text{C}$ with $n\text{-BuLi}$ (0.72 mL, 1.80 mmol, 2.5 M/hexanes). The mixture was stirred at 0 $^\circ\text{C}$ for 30 min, recooled to -78 $^\circ\text{C}$ and treated dropwise with a solution of **60b** (240 mg, 1.4 mmol) in Et_2O (7 mL). The mixture was gradually warmed to rt and then refluxed for 14 h. The reaction mixture was then cooled to 0 $^\circ\text{C}$, quenched with saturated aqueous NaHCO_3 solution, and extracted with Et_2O . The combined organic extract were dried (K_2CO_3), filtered and concentrated (bath temperature = 0 $^\circ\text{C}$). Column chromatography on basic activated Al_2O_3 (pentane/ether 95:5) provided **61** (120 mg, 52%) as a colorless oil. IR (neat) 3076, 3057, 3027, 2966, 2925, 2853, 2808, 1667, 1587, 1471, 1437, 1090 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 6.06 (d, 1H, $J = 9.9$ Hz), 5.74 (s, 1H), 5.59 (d, 1H, $J = 9.9$ Hz), 4.97 (s, 1H), 4.79 (s, 1H), 4.04 (s, 2H), 3.29 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.0, 137.8, 134.0, 133.7, 128.6, 126.2, 73.4, 58.0, 36.4, 29.7; MS (EI) m/z (rel. intensity) 164 (M^+ , 100); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: 164.1201, found: 164.1200.

(2Z,6Z)-2-(Hydroxymethyl)cyclohepta-2,6-dienone (62). To a stirred mixture of 30% formaldehyde (7.4 mL, 74.0 mmol, 2 equiv) and DMAP (450.0 mg, 3.7 mmol, 0.1 equiv) in THF (20 mL) was added dropwise a solution of cyclohepta-2,6-dienone (4.0 g, 37.0 mmol, 1 equiv) in THF (5 mL) at rt. The reaction mixture was stirred at rt for 24 h. The reaction mixture was quenched with 1.5 N HCl solution, and extracted with CH₂Cl₂. The organic layer was washed with saturated aqueous NaHCO₃ solution and brine and the aqueous layer was further extracted with CH₂Cl₂. The combined organic extracts were dried (Na₂SO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether 1:1) provided recovered cyclohepta-2,6-dienone (2.30 g) and **62** (1.28 g, 59%, brsm) as a colorless oil. IR (neat) 3417, 2926, 1658, 1604, 1409, 1276, 1214 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.73 (t, 1H, *J* = 5.7 Hz), 6.65 (dt, 1H, *J* = 5.4, 11.4 Hz), 6.12-6.06 (m, 1H), 4.23 (s, 2H), 2.92 (s, 1H), 2.47-2.38 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 194.0, 145.1, 142.1, 141.6, 133.5, 65.1, 26.9, 26.8; MS (EI) *m/z* (rel. intensity) 138 (M⁺, 78), 137 (100), 123 (100), 90 (96); HRMS (EI) calcd for C₈H₁₀O₂: 138.0675, found: 138.0670.

(2Z,6Z)-2-(Methoxymethyl)cyclohepta-2,6-dienone (62a). A solution of **62** (250 mg, 1.81 mmol, 1 equiv) in CH₂Cl₂ was treated in one portion with proton-sponge[®] (2.31g, 10.8 mmol, 6 equiv, Aldrich 158496-50G) under argon atmosphere. The mixture was cooled to 0 °C and treated with trimethyloxonium tetrafluoroborate (0.8 g, 5.4 mmol, 3 equiv). The reaction mixture was allowed to warm to rt and stirred for 3 h. The reaction mixture was quenched with 1 N HCl and extracted with ether. The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Column chromatography on SiO₂ (pentane/ether, 4:1) provided **62a** (220 mg, 82%) as a colorless oil. IR (neat) 2926, 1659, 1611, 1411, 1274, 1208, 1112, 1071 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.76 (t, 1H, *J* = 6.0 Hz), 6.63 (dt, 1H, *J* = 11.7, 5.7 Hz), 6.12-6.08 (m, 1H), 4.11 (d, 2H, *J* = 1.2 Hz), 3.37 (s, 3H), 2.53-2.47 (m, 2H), 2.45-2.38 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 192.6, 144.4, 140.1, 140.0, 133.6, 72.1,

58.7, 27.2, 26.9; MS (CI) m/z (rel. intensity) 153 ($[M+H]^+$, 100); HRMS (CI) calcd for $C_9H_{13}O_2$ ($M+H$): 153.0910, found: 153.0913.

(1E,4Z)-2-(Methoxymethyl)-3-methylenecyclohepta-1,4-diene (63). A suspension of methyltriphenylphosphoniumbromide (776 mg, 2.17 mmol) in Et_2O (20 mL) was treated dropwise at $-78\text{ }^\circ\text{C}$ with $n\text{-BuLi}$ (0.84 mL, 2.1 mmol, 2.5 M/hexanes). The mixture was stirred at $0\text{ }^\circ\text{C}$ for 30 min, recooled to $-78\text{ }^\circ\text{C}$ and treated dropwise with a solution of **62a** (220 mg, 1.4 mmol) in Et_2O (5 mL). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 15 min and quenched with saturated aqueous $NaHCO_3$ solution, and extracted with Et_2O . The combined organic extracts were dried (K_2CO_3), filtered and concentrated (bath temperature = $0\text{ }^\circ\text{C}$). Column chromatography on basic activated Al_2O_3 (pentane/ether 9:1) provided **63** (46 mg, 21%) as a colorless oil. IR (neat) 3013, 2956, 2923, 2850, 2361, 1458, 1124, 1084 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.09-6.04 (m, 2H), 5.77 (dt, 1H, $J = 8.4, 3.9$ Hz), 5.33 (s, 1H), 5.19 (s, 1H), 4.05 (s, 2H), 3.33 (s, 3H), 2.38-2.34 (m, 2H), 2.29-2.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 136.4, 132.8, 131.5, 131.3, 118.9, 77.1, 57.7, 27.5, 27.3; MS (EI) m/z (rel. intensity) 150 (M^+ , 23), 137 (32), 121 (100), 117 (42), 111 (38), 109 (35), 105 (56), 97 (68), 95 (53), 91 (70); HRMS (EI) calcd for $C_{10}H_{14}O$: 150.1039, found: 150.1037.

3-(2,2-Dimethyl-propyl)-6,6-dimethyl-4-methylene-bicyclo[3.1.0]hex-2-ene (66). A solution of **61** (80.0 mg, 0.5 mmol) in Et_2O (10 mL) was treated dropwise at $-78\text{ }^\circ\text{C}$ with $t\text{-BuLi}$ (0.35 mL, 0.6 mmol, 1.7 M/pentane, 1.1 equiv). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 10 min, then at rt for 16 h. The reaction mixture was recooled to $-78\text{ }^\circ\text{C}$ and quenched with saturated $NaHCO_3$ solution, and extracted with Et_2O . The combined organic layers were dried (K_2CO_3), filtered and concentrated. Column chromatography on SiO_2 (pentane) provided **66** (50 mg, 56%) as a colorless oil. IR (neat) 3088, 3019,

2955, 2865, 1626, 1477, 1361, 862 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.74 (s, 1H), 4.94 (s, 2H), 2.10-1.91 (m, 4H), 1.10 (s, 3H), 0.91 (s, 9H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 142.9, 135.9, 104.8, 40.0, 36.8, 36.2, 31.6, 31.2, 30.2, 26.9, 14.6; MS (CI) m/z (rel. intensity) 261 (73), 260 (100), 245 (37), 205 (29), 203 (34), 191 ($[\text{M}+\text{H}]^+$, 29), 175 (65), 119 (40); HRMS (CI) calcd for $\text{C}_{14}\text{H}_{23}$ ($\text{M}+\text{H}$): 191.1800, found: 191.1796.

(Z)-5-methylene-4-neopentylhepta-1,3,6-triene (68). A solution of **63** (46 mg, 0.31 mmol) in Et_2O (3.0 mL) was treated dropwise at $-78\text{ }^\circ\text{C}$ with $t\text{-BuLi}$ (0.18 mL, 0.31 mmol, 1.7 M/pentane, 1.0 equiv). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 10 min, then at rt for 16 h. The reaction mixture was quenched with saturated aqueous NaHCO_3 solution, and extracted with Et_2O . The combined organic layers were dried (MgSO_4), filtered and concentrated. Column chromatography on SiO_2 (pentane) provided **68** (42 mg, 78%) as a colorless oil. IR (neat) 2956, 2925, 2856, 1583, 1464, 1365, 990, 894 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.48-6.32 (m, 2 H), 6.05 (d, 1 H, $J = 10.8\text{ Hz}$), 5.28 (d, 1 H, $J = 1.6\text{ Hz}$), 5.16-5.11 (m, 3 H), 5.03 (s, 1 H), 4.97 (dd, 1 H, $J = 10.4, 2.0\text{ Hz}$), 2.18 (s, 2 H), 0.91 (s, 9 H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 140.4, 137.8, 134.9, 132.2, 118.5, 116.7, 115.9, 51.4, 32.8, 30.1; MS (CI) m/z (rel. intensity) 176 (M^+ , 50), 120 (100); HRMS (CI) calcd for $\text{C}_{13}\text{H}_{20}$: 176.1565, found: 176.1569.

Table S1. Energies of species involved in this study.

	E(SCF)	E(SCF)	E(SCF)	ZPE	H	S	TS	G(GP)	G(Solv)	G(Sol)
	eV	eV	kcal/mol	kcal/mol	kcal/mol	eu	kcal/mol	kcal/mol	kcal/mol	kcal/mol
Compound	6-31G**	cc-pVTZ++	cc-pVTZ++	6-31G**	cc-pVTZ++	6-31G**		cc-pVTZ++		cc-pVTZ++
CO ₂	-5131.459	-5132.557	-118359.55	7.28	-118352.27	51.155	15.25	-118367.52	-1.94	-118369.46
Li	-198.222	-198.235	-4571.41	0.00	-4571.41	31.796	9.48	-4580.89	-105.01	-4685.90
Cyclooctadienide	-8474.095	-8470.892	-195343.36	103.12	-195240.24	84.967	25.33	-195265.58	-41.57	-195307.15
Cyclooctadienide (TS)	-8472.807	-8469.407	-195309.12	101.83	-195207.29	80.468	23.99	-195231.28	-40.98	-195272.26
1,3a,4,5,6,6a-hexahydropentalen-1-ide	-8473.802	-8470.634	-195337.41	103.25	-195234.16	81.412	24.27	-195258.44	-42.96	-195301.40
24a	-13823.359	-13816.976	-318626.96	191.97	-318434.99	121.816	36.32	-318471.31	-37.05	-318508.36
24a-TS	-13822.237	-13815.945	-318603.18	190.66	-318412.52	117.737	35.10	-318447.63	-36.56	-318484.19
26a	-13823.242	-13816.919	-318625.65	192.14	-318433.51	118.301	35.27	-318468.78	-38.15	-318506.93
34a	-18956.847	-18951.900	-437041.09	203.60	-436837.49	132.614	39.54	-436877.03	-45.84	-436922.87
31a	-14893.076	-14886.229	-343284.51	209.89	-343074.62	127.863	38.12	-343112.75	-35.22	-343147.97
31a-TS	-14891.688	-14884.879	-343253.38	208.64	-343044.74	124.123	37.01	-343081.75	-35.95	-343117.70
32a	-14893.079	-14885.971	-343278.56	210.52	-343068.04	124.805	37.21	-343105.25	-37.13	-343142.38
35a	-20026.666	-20021.049	-461696.25	221.87	-461474.38	141.542	42.20	-461516.58	-45.69	-461562.27
23	-8679.876	-8676.112	-200075.85	106.73	-199969.12	87.456	26.08	-199995.19	-8.77	-200003.96
23-TS	-8678.639	-8674.628	-200041.63	105.90	-199935.73	82.585	24.62	-199960.35	-11.65	-199972.00
25	-8679.746	-8675.813	-200068.95	106.73	-199962.22	85.714	25.56	-199987.78	-14.87	-200002.65
24	-14029.074	-14022.283	-323361.45	195.62	-323165.83	124.718	37.18	-323203.01	-8.79	-323211.80
24-TS	-14027.794	-14021.055	-323333.13	195.06	-323138.07	119.735	35.70	-323173.77	-11.73	-323185.50
26	-14029.048	-14022.304	-323361.93	195.75	-323166.18	123.329	36.77	-323202.96	-14.90	-323217.86
34	-19162.876	-19157.141	-441774.06	206.38	-441567.68	137.681	41.05	-441608.73	-25.53	-441634.26
31	-15098.492	-15091.263	-348012.71	213.56	-347799.15	130.233	38.83	-347837.98	-9.07	-347847.05
31-TS	-15097.486	-15090.011	-347983.84	212.73	-347771.11	126.572	37.74	-347808.84	-9.18	-347818.02
32	-15098.844	-15091.551	-348019.35	214.09	-347805.26	122.604	36.55	-347841.81	-15.60	-347857.41
35	-20232.694	-20226.582	-466435.95	224.68	-466211.27	143.097	42.66	-466253.93	-25.34	-466279.27

Table S2. Energy Components for Homolytic Bond Cleavages.

	E(SCF)	E(SCF)	E(SCF)
	eV	eV	kcal/mol
Compound	6-31G**	cc-pVTZ++	cc-pVTZ++
Hydrogen Atom	-13.613	-13.662	-315.05
n-pentyl Radical	-5363.190	-5360.405	-123613.85
Lithiated Cyclic Radical Anion (GS)	-8661.128	-8657.602	-199649.00
Lithiated Cyclic Radical Anion (TS)	-8658.912	-8655.395	-199598.10

Table S3. Cartesian Coordinates of Optimized Geometries

Cyclooctadienide				C	-0.837703340	-3.202354052	1.143757531
				C	0.529771892	-3.923965884	1.116522693
				C	1.457249832	-2.908865146	0.427322388
				C	0.598319829	-2.337463410	-0.738576637
				C	0.914299888	-0.925021237	-1.199573388
				H	-1.946616217	-0.304835304	0.447632089
				H	-1.604380402	-2.600490704	-0.815797051
				H	-0.921580547	-2.598884941	2.055899790
				H	-1.675912915	-3.916264627	1.146014256
				H	0.872688487	-4.239133601	2.113308162
				H	0.465242559	-4.834332191	0.500519937
				H	1.695767653	-2.089093357	1.117381816
				H	2.406242089	-3.349894781	0.089279658
				H	0.612657536	-3.100655268	-1.540475723
				H	1.932078715	-0.631904696	-1.466605827
				H	0.100830588	1.001230569	-0.544545768
				24a			
				C	0.105905555	-0.190321966	0.388829152
				C	-1.140906860	-0.830004358	0.117058531
				C	-1.667242168	-2.100192606	0.080510924
				C	-1.046284143	-3.440827081	0.342202866
				C	0.419139309	-3.653778390	-0.096897832
				C	1.451526838	-3.333612091	1.002653449
				C	1.945163148	-1.921750095	1.122227863
				C	1.350917397	-0.709321162	0.861121640
				C	0.124256320	1.307969363	0.102499013
				C	0.590917109	1.697890758	-1.321478078
				H	-1.906863432	-0.087520928	-0.141660558
				H	-2.741080740	-2.147286424	-0.112243954
				H	-1.079499481	-3.731687173	1.418907863
				H	-1.674884472	-4.196752907	-0.157317618
				H	0.539606737	-4.715317382	-0.367542456
				H	0.631334502	-3.070479837	-1.000223841
				H	0.998225700	-3.708762809	1.951315419
				H	2.333869277	-3.979969802	0.855569940
				H	2.943738194	-1.854805303	1.560556515
				H	2.050988522	0.110359415	1.070661200
				H	-0.879436758	1.741189000	0.249179610
				H	0.781742141	1.834046679	0.816769473
				C	0.598488656	3.209524797	-1.596250477
				H	1.598824267	1.288629998	-1.482403412
				H	-0.058552918	1.193885482	-2.051999171
				H	-0.412639814	3.615586844	-1.433485802
				H	1.242404116	3.711305638	-0.856563955
				C	1.068419995	3.589362123	-3.007740880
				C	1.066929692	5.100055792	-3.273746698
				H	2.080450814	3.191770213	-3.170149144
				H	0.428435460	3.088919275	-3.748361776
Cyclooctadienide ==> 5,5-cis Bicyclic Anion (TS)							
				C	-0.070855355	0.151155871	-0.072386686
				C	-0.176774171	0.135662566	2.197387785
				C	2.015238160	0.087207950	1.160782548
				C	1.364711084	0.191795206	-0.077766184
				C	-0.850542881	-1.162324672	-0.190674924
				C	-1.828482034	-1.351252881	0.971999528
				C	-0.964067527	-1.178789105	2.223951355
				C	1.252702110	0.174960049	2.334787003
				H	1.915808577	0.673265734	-0.894392857
				H	-0.549622628	0.908784990	-0.719416438
				H	-1.378786248	-1.218001377	-1.157992970
				H	-0.142682093	-2.004455627	-0.177458798
				H	-2.608101990	-0.574387691	0.940729636
				H	-2.336774625	-2.330080368	0.941286389
				H	-1.580876197	-1.247137755	3.136470238
				H	-0.258161911	-2.021655621	2.265662629
				H	-0.712961361	0.884208812	2.809169809
				H	1.726637896	0.640379692	3.207218656
				H	3.109235081	0.141776207	1.212028614
1,3a,4,5,6,6a-hexahydropentalen-1-ide							
				C	0.021141589	-0.091758622	-0.517082630
				C	-0.980297652	-0.749794844	0.203140088
				C	-0.844483337	-2.233814981	-0.093291972

H	1.408783757	5.338176070	-4.288905256
H	0.060724011	5.521734357	-3.155359042
H	1.724740758	5.626070891	-2.570445469

24a-TS

C	-0.074347705	0.153710980	-0.073277332
C	-0.181884849	0.137235286	2.197054014
C	2.022849590	0.097630415	1.163832439
C	1.358147572	0.205521997	-0.071242084
C	-0.842967815	-1.166891472	-0.191165250
C	-1.818731490	-1.366500597	0.971052511
C	-0.956516832	-1.184689173	2.222473497
C	1.244055269	0.188520878	2.332085974
C	3.534706339	0.077727810	1.235592221
C	4.118667956	-1.349798753	1.253715127
H	1.911958076	0.691665873	-0.884247834
H	-0.555610950	0.908360500	-0.720633406
H	-1.369916303	-1.224946542	-1.158562560
H	-0.127482523	-0.202475378	-0.179895163
H	-2.607937688	-0.599642915	0.939599610
H	-2.314450390	-2.351365326	0.940527153
H	-1.571742410	-1.257174607	3.135262581
H	-0.241938193	-2.019986735	2.265835937
H	-0.723636138	0.882668667	2.806072961
H	1.717466533	0.665276914	3.199612933
H	3.960952422	0.616566410	0.373030727
H	3.876754460	0.604379716	2.142065979
C	5.650384685	-1.413439339	1.325822548
H	3.684772507	-1.887369762	2.107785184
H	3.767851473	-1.875808825	0.355425556
H	6.081661131	-0.870263685	0.470717025
H	5.998631521	-0.881026281	2.224435113
C	6.207856659	-2.843753050	1.343458001
C	7.737912740	-2.910009721	1.414888508
H	5.779494858	-3.386619036	2.197536756
H	5.861708820	-3.376212436	0.446614389
H	8.101900493	-3.944659756	1.426143629
H	8.196469792	-2.406557092	0.554923422
H	8.113641957	-2.416502201	2.319639694

26a

C	0.023647439	-0.080395053	-0.516827730
C	-0.982317963	-0.749609751	0.192475047
C	-0.844138836	-2.232668671	-0.092733557
C	-0.835784092	-3.195647904	1.148137530
C	0.525602333	-3.927317363	1.112648904
C	1.457889284	-2.916047470	0.424062756
C	0.599774246	-2.336585541	-0.737313189
C	0.917409048	-0.924343203	-1.188797320
C	0.173219717	1.426681423	-0.481794655
C	0.938329178	1.909580405	0.767687328
H	-1.951642306	-0.300207539	0.417091325
H	-1.604261588	-2.602147607	-0.812356669
H	-0.908005435	-2.587350087	2.057959083
H	-1.680157410	-3.901562407	1.159340037
H	0.870566476	-4.246785842	2.106928157
H	0.452444731	-4.835463947	0.494589295
H	1.704038847	-2.100711980	1.116883013
H	2.403201882	-3.361456483	0.082195672
H	0.614216452	-3.093152914	-1.544929476
H	1.935236651	-0.628560077	-1.455419875
H	0.694889303	1.777204346	-1.384939915
H	-0.818480956	1.907404336	-0.485495493
C	1.054152404	3.434216377	0.896831936
H	0.430208833	1.491852210	1.647294487
H	1.942621122	1.462382074	0.755316602

H	1.560968842	3.844139062	0.007943584
H	0.046136724	3.879600350	0.896604145
C	1.803609352	3.891592470	2.156516785
C	1.915905492	5.414986440	2.291863756
H	1.298362379	3.481903132	3.043187412
H	2.811149688	3.450237029	2.156545783
H	2.454444755	5.705786922	3.203053956
H	2.449959994	5.850409618	1.437332865
H	0.923733078	5.883270364	2.328858022

34a

C	0.339629950	0.030390224	0.339252049
C	-0.981540607	-0.687363044	0.524582547
C	-0.626223340	-2.175913108	0.325860251
C	-0.503805687	-3.025688747	1.608472071
C	0.545583415	-4.093115373	1.256846874
C	1.615433504	-3.294103320	0.485476510
C	0.811964453	-2.213537955	-0.303511659
C	1.291137714	-0.790567666	-0.139287231
C	0.455192915	1.500441356	0.634431326
C	1.764101930	2.166491045	0.198117312
C	-2.107370120	-0.139517363	-0.480476155
H	-1.369951524	-2.603521621	-0.352270044
H	-0.127022964	-2.406393321	2.435653182
H	-1.461903669	-3.450449330	1.931950842
H	0.948080744	-4.624713123	2.129470311
H	0.095150045	-4.847386756	0.596494090
H	2.293751528	-2.805358081	1.197312807
H	2.233567189	-3.929142866	-0.161722540
H	0.770914407	-2.494424997	-1.366184200
H	2.301321219	-0.486079592	-0.407192698
H	-0.421561310	1.968515290	0.165206611
H	0.311095862	1.652767274	1.717860831
C	1.814430012	3.669493217	0.502732474
H	2.618508854	1.672783345	0.685252148
H	1.903133337	2.013024279	-0.881040520
H	-1.386787295	-0.490935547	1.530130396
O	-2.359586484	1.085899360	-0.352348288
O	-2.616640896	-0.982571459	-1.252754934
H	0.966297964	4.167059039	0.011048229
H	1.671998941	3.830311807	1.582233775
C	3.122742353	4.341159422	0.062733264
C	3.171594002	5.844206143	0.360405409
H	3.969667562	3.843721545	0.557067815
H	3.266877983	4.178412197	-1.014689223
H	4.118366511	6.292881387	0.035912171
H	2.359676803	6.374940953	-0.151200124
H	3.062600053	6.038887462	1.434389230

31a

C	-0.037847150	-0.248416984	0.269479051
C	-1.180949263	-0.969124499	-0.187824381
C	-1.731921986	-2.206247428	0.054311514
C	-1.165822936	-3.289280668	0.926052538
C	1.985561054	-3.163882785	0.677936316
C	1.901095805	-1.769131337	1.254305971
C	1.117221618	-0.663186087	1.023542145
C	-0.028335373	1.243851440	-0.048148499
C	0.950147657	1.664913554	-1.170085994
H	-1.805411374	-0.362097395	-0.855670982
H	-2.633862367	-2.465165818	-0.503481161
H	-0.580728179	-2.852808622	1.743040373
H	-1.979302433	-3.861923283	1.403361192
H	1.946251332	-3.919946810	1.489734294
H	3.008279179	-3.279856205	0.270707438
H	2.725972189	-1.588676014	1.949724009

H	1.546656469	0.203897577	1.551053032
H	-1.035638174	1.585174803	-0.332610278
H	0.241232047	1.834993577	0.849699052
C	0.990951717	3.174286775	-1.452897772
H	1.956272913	1.315654922	-0.900225182
H	0.682472814	1.124860217	-2.089492313
C	-0.267986450	-4.282978993	0.152904398
C	0.995223214	-3.622486391	-0.411875235
H	0.033406164	-5.121148844	0.807632783
H	-0.853487226	-4.720505595	-0.670537027
H	0.706543219	-2.774993813	-1.042072138
H	1.507693371	-4.346678253	-1.064112644
H	-0.012526041	3.521085513	-1.744264744
H	1.234051843	3.713209346	-0.524311162
C	1.995189994	3.576554953	-2.541983503
C	2.026801204	5.082503477	-2.829081913
H	2.998969066	3.241595092	-2.246767698
H	1.759662298	3.034720189	-3.468307141
H	2.756203832	5.336109820	-3.607926231
H	1.046335813	5.442050323	-3.163917967
H	2.291799014	5.650894942	-1.929406055

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C	-0.047183729	1.351392276	0.304462483
C	0.196606703	1.140695321	2.653585144
C	1.881399263	0.123979668	1.202116440
C	1.183388291	0.646721564	0.097873251
C	-1.422646173	0.708278524	0.171917109
C	-1.059741417	0.318068726	2.893822951
C	1.463299255	0.497685594	2.491965308
C	3.182968615	-0.622682214	1.002047817
C	2.998257826	-2.150794952	0.904289576
H	1.809918821	0.874452116	-0.776803661
H	-0.094697698	2.317579848	-0.236980118
H	-1.374050762	-0.364175124	0.396559973
H	-1.753291450	0.756648109	-0.883995068
H	-0.973478359	-0.636708193	2.362774976
H	-1.123104722	0.034809832	3.963636619
H	0.202660593	1.986119261	3.367858064
H	2.263805873	0.636441654	3.230435126
H	3.679003569	-0.274912294	0.080355951
H	3.871237074	-0.409349867	1.836677734
C	4.301000965	-2.937277944	0.704597471
H	2.493197533	-2.496308013	1.816630856
H	2.307356340	-2.362266027	0.076792636
C	-2.496799011	1.390917534	1.036338943
C	-2.391278240	0.997808676	2.530908685
H	-2.375274399	2.475985545	0.919717222
H	-3.506139341	1.158081717	0.660898188
H	-3.215612921	0.316081848	2.794501886
H	-2.528285022	1.884692517	3.166791810
H	4.809706085	-2.580231353	-0.204187712
H	4.990208869	-2.723558968	1.536197020
C	4.096511997	-4.455152109	0.600530613
C	5.397866929	-5.241500630	0.403644853
H	3.587913144	-4.813130430	1.506533724
H	3.411699600	-4.670017932	-0.231659708
H	5.216058609	-6.320805878	0.332264401
H	5.913278455	-4.930695892	-0.513444957
H	6.090187327	-5.076335799	1.238314210

32a

C	0.025355544	-0.028781130	-0.501054691
C	-0.922168469	-0.699105003	0.289518777
C	-0.858703986	-2.166676200	-0.100508995
C	-1.076031772	-3.188752323	1.048618593

C	1.574763753	-2.815339977	0.283888083
C	0.566253801	-2.295082130	-0.772143346
C	0.848347316	-0.877135538	-1.246820674
C	0.193906844	1.476586777	-0.468145824
C	0.889389163	1.961564473	0.818655748
H	-1.870658354	-0.240022932	0.580765347
H	-1.600562150	-2.420848822	-0.892620061
H	-0.736082155	-2.734093223	1.989680434
H	-2.148175787	-3.398600231	1.179916228
H	1.558353354	-2.102567219	1.117170156
H	2.595488863	-2.802895775	-0.122789188
H	0.539383709	-3.043889284	-1.585337072
H	1.845897344	-0.587917386	-1.588950474
H	0.769892179	1.813812467	-1.342582610
H	-0.789609177	1.971191259	-0.533749273
C	1.022045800	3.486168855	0.933175354
H	0.328593063	1.565901810	1.674014544
H	1.884583155	1.499260003	0.870730166
C	-0.304374003	-4.492090505	0.796992255
C	1.224172829	-4.235195037	0.794928467
H	1.719036743	-4.998783756	0.176620374
H	1.618311730	-4.371069641	1.813402558
H	-0.556662905	-5.266263205	1.537479201
H	-0.610824243	-4.893954396	-0.179449069
H	1.583714782	3.875521350	0.070224495
H	0.023851963	3.946152913	0.871465431
C	1.707029375	3.951711020	2.225789387
C	1.818173825	5.475493418	2.349852038
H	1.154283380	3.555055396	3.088146414
H	2.710241272	3.507541603	2.283234044
H	2.312961048	5.775438996	3.281415541
H	0.827782035	5.946003603	2.334418605
H	2.392955663	5.900043510	1.517953473

35a

C	0.414612364	0.118818534	0.274305127
C	-0.884004634	-0.603657358	0.564540087
C	-0.534526898	-2.105437986	0.408452146
C	-0.667108414	-2.910267194	1.709275435
C	1.846486399	-3.113122247	0.649092027
C	0.930041860	-2.167294836	-0.156865743
C	1.372819877	-0.724112572	-0.144847773
C	0.514050056	1.610909075	0.435086942
C	1.800110424	2.254259999	-0.092513309
C	-2.092018123	-0.111803143	-0.371228615
H	-1.243522141	-2.501821726	-0.326332257
H	-0.080442673	-2.428955286	2.505686206
H	-1.710602526	-2.888475054	2.048073050
H	2.069519844	-2.663939778	1.626149309
H	2.813982141	-3.230308861	0.140457385
H	0.908486358	-2.557191431	-1.188879089
H	2.374814445	-0.428724084	-0.451730012
H	-0.382803723	2.029155454	-0.041921827
H	0.396559760	1.854042128	1.504962382
C	1.828476063	3.779132292	0.077338869
H	2.674781935	1.820265733	0.414452587
H	1.916272946	2.007848506	-1.156963697
H	-1.220938786	-0.366186621	1.586833215
O	-2.348503536	1.116002715	-0.277982246
O	-2.654934313	-0.993309755	-1.058881135
C	1.182214904	-4.485237120	0.843291592
C	-0.205839406	-4.370793394	1.544045036
H	-0.176081473	-4.862382656	2.525989582
H	-0.956637223	-4.913711712	0.956006469
H	1.059885933	-4.950014971	-0.144349863
H	1.845825329	-5.152220013	1.409781685
H	0.960294844	4.216502993	-0.434818530

H	1.708004898	4.032180266	1.141091952
C	3.111739719	4.433551084	-0.452310299
C	3.132817552	5.957375549	-0.290914882
H	4.060423493	6.395494631	-0.677322996
H	2.297370852	6.422659285	-0.826651598
H	3.044022667	6.244607419	0.763470924
H	3.979684055	4.000350043	0.064232437
H	3.235452610	4.178071981	-1.513654607

23

C	0.195999143	-0.166503334	0.209500799
C	-0.989225599	-0.792341592	-0.270395166
C	-1.335392372	-2.124962906	-0.488481815
C	-1.071977246	-3.342804533	0.378725374
C	0.293448867	-4.042882926	0.337166528
C	1.398938052	-3.249029027	1.047627633
C	1.989006661	-2.012590259	0.395316445
C	1.502513868	-0.707408639	0.382520294
H	-1.684567724	-0.070680827	-0.707227484
H	-2.229163507	-2.232314391	-1.101253387
H	-1.260996085	-3.079774586	1.433473218
H	-1.835543371	-4.081718600	0.110729945
H	0.192767318	-5.014645626	0.841933647
H	0.583380485	-4.251042896	-0.703765549
H	1.005913820	-2.977755898	2.042129448
H	2.237415936	-3.930684020	1.229831295
H	3.072646557	-2.061715184	0.299843044
H	2.277071056	0.061743970	0.324068946
Li	0.662163553	-1.509905338	-1.398372948
H	0.160107326	0.918550054	0.211980081

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C	-0.068664978	0.120361246	-0.045318454
C	-0.168486425	0.113547463	2.158420528
C	2.054373169	0.094058128	1.156440955
C	1.387339134	0.208737413	-0.080050429
C	-0.803838245	-1.216525745	-0.179297535
C	-1.765061776	-1.445892057	0.979802108
C	-0.898062857	-1.230996608	2.213066833
C	1.276512790	0.215291805	2.326789268
H	1.925625784	0.515128594	-0.975361040
H	-0.566799041	0.852977345	-0.704987072
H	-1.318468713	-1.246161198	-1.146906071
H	-0.065211752	-2.026886325	-0.189160511
H	-2.585600282	-0.716221701	0.952379031
H	-2.210368384	-2.447339392	0.956282039
H	-1.485185579	-1.281245095	3.137770384
H	-0.154793720	-2.035501209	2.265862696
H	-0.734941189	0.837966517	2.769566582
H	1.728456718	0.523586216	3.267981555
Li	0.739682888	1.737759613	1.093857137
H	3.141794171	0.138123222	1.206256460

25

C	-0.005871320	-0.073913886	-0.501342772
C	-1.141615975	-0.825452461	-0.178961438
C	-0.773068199	-2.314059600	-0.250605670
C	-0.792372403	-3.092101178	1.103741596
C	0.562554366	-3.819854217	1.170385800
C	1.533915396	-2.832738596	0.506497857
C	0.749380343	-2.302515027	-0.724929861
C	1.010624676	-0.840712283	-1.116615977
H	-2.012399741	-0.457151267	0.350243390
H	-1.405604802	-2.880556354	-0.963814616
H	-0.866802948	-2.371175418	1.925752579

H	-1.648115132	-3.770306044	1.187723789
H	0.848338740	-4.085548964	2.193877466
H	0.522383942	-4.751807842	0.590609718
H	1.743820487	-1.998180968	1.186994333
H	2.493237536	-3.282754844	0.229388904
H	0.908631261	-3.015695430	-1.546927440
H	2.014266782	-0.467977595	-1.289010458
Li	-0.736544305	-0.983741880	-2.200687528
H	0.030102860	1.013874703	-0.426361532

24

C	0.191285291	-0.136732495	0.220500911
C	-0.972428175	-0.796498111	-0.281040587
C	-1.300030417	-2.134552864	-0.503307916
C	-1.070201555	-3.343009430	0.386401510
C	0.287073037	-4.056614142	0.379039226
C	1.388766082	-3.236273326	1.061696691
C	1.965818768	-2.019294442	0.363208020
C	1.494921313	-0.708055852	0.356555169
C	0.084071618	1.367675766	0.419765539
C	-0.330380154	1.771192875	1.849207533
H	-1.675875144	-0.087536416	-0.730486923
H	-2.171889146	-2.250008688	-1.146221323
H	-1.275006219	-3.060391773	1.433176096
H	-1.838394159	-4.076652519	0.116069660
H	0.177592438	-5.006946916	0.921872280
H	0.581285138	-4.305283646	-0.651293146
H	0.996357542	-2.931575288	2.046563469
H	2.232238256	-3.906053159	1.265712843
H	3.043754364	-2.083635198	0.220488956
H	2.281687454	0.049617664	0.277477205
H	1.047344050	1.846363277	0.189689774
H	-0.650289767	1.787354334	-0.283596387
C	-0.443352563	3.287868005	2.052230270
H	-1.291818665	1.296163921	2.086502536
H	0.395907717	1.356683431	2.561125075
Li	0.662914049	-1.498398217	-1.422416651
H	-1.158884267	3.701422558	1.326855221
H	0.522989181	3.760615600	1.824671417
C	-0.878482049	3.685272680	3.469482273
C	-0.981885537	5.200794210	3.669434553
H	-1.848019754	3.220429425	3.692907717
H	-0.168939418	3.267602826	4.196226979
H	-1.299579021	5.451219532	4.686890033
H	-0.017795007	5.690887208	3.492723061
H	-1.707401076	5.643506101	2.977297158

24-TS

C	-0.067940335	0.118130788	-0.042370398
C	-0.170099659	0.111888117	2.154985739
C	2.072044271	0.112483527	1.158787122
C	1.385215230	0.222740244	-0.071663332
C	-0.793818689	-1.223621558	-0.178210773
C	-1.757826933	-1.457923660	0.977527717
C	-0.895958011	-1.234903239	2.213239743
C	1.272823830	0.224063826	2.319328222
C	3.579144710	0.093315899	1.232720708
C	4.156822272	-1.333343948	1.244465219
H	1.921370917	0.540901193	-0.965633144
H	-0.572597484	0.846476528	-0.702051020
H	-1.304396572	-1.258236111	-1.147951944
H	-0.049731662	-2.029202697	-0.185037867
H	-2.583489701	-0.734142327	0.946084068
H	-2.196438740	-2.462314259	0.953846264
H	-1.486011885	-1.284200613	3.136212304
H	-0.150375619	-2.037005531	2.272662010

H	-0.739107483	0.832879066	2.768327861
H	1.722464773	0.538277153	3.261064433
H	3.999697198	0.638906933	0.376772587
H	3.910281789	0.617203329	2.139918200
C	5.685057530	-1.368987088	1.341350669
H	3.719858360	-1.885210195	2.086640947
H	3.830536058	-1.854926827	0.335540705
Li	0.702345099	1.740425164	1.095818523
H	6.118050958	-0.800016296	0.505915379
H	6.004746322	-0.848662281	2.255814205
C	6.263701761	-2.787923137	1.339031495
C	7.790087164	-2.819918727	1.447902399
H	5.825137365	-3.358130287	2.168830454
H	5.950807119	-3.303456182	0.421258847
H	8.172126320	-3.846101635	1.438650812
H	8.258535478	-2.283658991	0.614487391
H	8.131458992	-2.346791126	2.375892727

26

C	0.007036421	-0.057150276	-0.510020452
C	-1.123086283	-0.815942329	-0.171533575
C	-0.774201176	-2.305581614	-0.246767224
C	-0.798636398	-3.097053466	1.099781660
C	0.562615238	-3.813166252	1.176229910
C	1.529279388	-2.820599485	0.513349426
C	0.746849169	-2.304329786	-0.724810288
C	1.003760442	-0.850313680	-1.138424904
C	0.129213738	1.436072315	-0.310541306
C	0.816374012	1.779696641	1.026227461
H	-1.992096711	-0.436711665	0.354908573
H	-1.412566613	-2.864994214	-0.963659979
H	-0.889651163	-2.383924055	1.926942504
H	-1.648781434	-3.784055442	1.169060212
H	0.844461707	-4.072413262	2.202512594
H	0.534108903	-4.747951638	0.600220207
H	1.727996540	-1.980597492	1.190733101
H	2.494249366	-3.263359496	0.243718416
H	0.904033500	-3.032198094	-1.534772285
H	2.008897839	-0.485635171	-1.326693646
H	0.712590579	1.873585915	-1.131865532
H	-0.861718513	1.908701702	-0.336834388
C	1.017509413	3.284626170	1.244945993
H	0.219910346	1.363393903	1.848474728
H	1.788233309	1.270889817	1.065266915
Li	-0.750193753	-1.031162097	-2.199130035
H	1.631090173	3.693649067	0.429209433
H	0.047698601	3.798915284	1.180590475
C	1.677999430	3.617055792	2.590011279
C	1.898398020	5.117764773	2.804937605
H	1.057663073	3.217879615	3.403811757
H	2.640420760	3.092124972	2.658828946
H	2.364441163	5.320551960	3.774918559
H	2.549614724	5.537589695	2.029734095
H	0.950478671	5.667129894	2.771102522

34

C	0.325069153	0.077308219	0.265014492
C	-1.004598344	-0.645687796	0.510030508
C	-0.672605927	-2.141021570	0.283178858
C	-0.544053316	-2.977006574	1.574979111
C	0.506395014	-4.043454733	1.226973106
C	1.568743301	-3.251986774	0.439927060
C	0.757081961	-2.188002269	-0.361274112
C	1.243085183	-0.768243967	-0.222535871
C	0.469066140	1.546493161	0.555775608
C	1.821503847	2.164747428	0.184465039

C	-2.074862564	-0.073244337	-0.421552891
H	-1.411628729	-2.592654607	-0.382518316
H	-0.165591853	-2.346434131	2.391137637
H	-1.499703311	-3.398028974	1.906007370
H	0.914672657	-4.553775326	2.106185030
H	0.056523538	-4.811910409	0.584514813
H	2.250115714	-2.752283925	1.139455093
H	2.181991187	-3.889619875	-0.205317160
H	0.708036774	-2.478622677	-1.418962286
H	2.258785560	-0.482341654	-0.483282733
H	-0.341672679	2.083512601	0.044891953
H	0.271270121	1.712209615	1.626663321
C	1.888163702	3.673405538	0.455071892
H	2.621826674	1.659715039	0.741398675
H	2.026564163	1.978939771	-0.878224436
H	-1.362054841	-0.446459418	1.529588415
O	-2.642263878	1.025716154	-0.088116126
O	-2.362221476	-0.653288823	-1.520846031
Li	-3.462538397	0.821882612	-1.734878920
H	1.094514280	4.179566323	-0.113021279
H	1.668817745	3.866199272	1.514889111
C	3.243160307	4.298726130	0.097480228
C	3.298061941	5.809366767	0.346483696
H	4.033660850	3.803130723	0.677020304
H	3.468896695	4.093284383	-0.957785649
H	4.277336872	6.225033350	0.087004544
H	2.544870856	6.336306879	-0.250467857
H	3.105751163	6.044626958	1.399514429

31

C	0.075957103	-0.211293638	0.385571934
C	-1.128644828	-0.964296434	0.245319476
C	-1.691245087	-2.154120610	0.751314410
C	-1.243576751	-3.608904443	0.916577321
C	1.700087785	-3.019549044	0.949879316
C	1.752488806	-1.696388802	1.664263610
C	1.219357124	-0.509744627	1.214084836
C	0.093960389	1.168212833	-0.259959085
C	0.840548674	1.213689851	-1.607089672
H	-1.905956416	-0.324341870	-0.181525628
H	-2.773768500	-2.119854349	0.637224081
H	2.527272661	-1.610218020	2.426308116
H	1.693593860	0.393077110	1.616572072
H	-0.933040208	1.528436302	-0.414799504
H	0.576310709	1.888590303	0.419642663
C	0.894306725	2.609647103	-2.240601833
H	1.862952980	0.841556753	-1.455971477
H	0.362898847	0.510251946	-2.302516435
C	-0.348307787	-4.056200411	2.103376432
C	1.128373739	-4.213241517	1.732697546
Li	-0.574682574	-0.999748613	2.256797387
H	-2.176991622	-4.176273324	0.989502702
H	-0.773073202	-3.963236017	-0.013454277
H	-0.459132427	-3.346331982	2.937074381
H	-0.711069858	-5.016526587	2.491052669
H	1.238039616	-5.110593501	1.108451889
H	1.726559661	-4.391210587	2.635858917
H	1.146014151	-2.898496736	0.013126089
H	2.731600705	-3.274875492	0.661868856
H	-0.128415322	2.973533486	-2.416153436
H	1.347312236	3.316079101	-1.529772200
C	1.679570515	2.649469819	-3.558840860
C	1.742742339	4.044799861	-4.187836098
H	2.699479034	2.283127480	-3.380368714
H	1.227020812	1.946334852	-4.270830436
H	2.313337168	4.039487246	-5.122313830
H	0.739462886	4.423515370	-4.413673632

H 2.220555798 4.762973533 -3.511684953

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C -0.404047142 0.487278617 0.156684115
C -0.300939923 0.103747953 2.417199222
C 1.829658926 0.251876284 1.170568759
C 1.041730674 0.602854234 0.047841854
C -1.118660312 -0.800630587 -0.235150094
C -1.094458673 -1.199990320 2.462266322
C 1.156441000 0.144754050 2.410340659
C 3.340057145 0.235104644 1.089400730
C 3.901887850 -1.167189139 0.780936313
H 1.510299682 1.119385245 -0.790671060
H -0.950748922 1.321839933 -0.322340691
H -0.486138081 -1.661952502 -0.001378358
H -1.199081005 -0.797069099 -1.332650937
H -0.539756116 -2.005301301 1.971559181
H -1.154562731 -1.498268099 3.519232806
H -0.745124319 0.755725860 3.196996026
H 1.719046052 0.333139314 3.326310609
H 3.676234621 0.929709194 0.306722248
H 3.769150095 0.587340556 2.037888280
C 5.430965024 -1.198932688 0.664649304
H 3.575445381 -1.860019252 1.567629521
H 3.453251780 -1.530374775 -0.153001980
C -2.523664081 -0.981061170 0.352109936
C -2.516020306 -1.084445565 1.898331683
H -3.160259325 -0.149053174 0.025063303
H -2.967832181 -1.884799870 -0.083050261
H -3.113228608 -1.945403749 2.221802785
H -2.994261370 -0.203930483 2.346060188
Li 0.467415308 1.856036120 1.536359185
H 5.750976309 -0.508001768 -0.129188861
H 5.877585046 -0.817274965 1.594518395
C 5.991193944 -2.597522800 0.372701291
C 7.517692867 -2.625110724 0.242999640
H 5.679237319 -3.284776759 1.170909593
H 5.538412551 -2.982508234 -0.551217547
H 7.885201642 -3.636778764 0.040404761
H 7.858165156 -1.978402202 -0.574090192
H 8.000455294 -2.274627960 1.162744902

32

C -0.128694353 -0.050864488 -0.624063061
C -1.218644922 -0.777234539 -0.132798760
C -0.949180597 -2.274740975 -0.320990908
C -1.200384828 -3.160541135 0.920509993
C 1.480590728 -2.687287572 0.345444447
C 0.547383019 -2.315997633 -0.826441975
C 0.753094722 -0.889553932 -1.362653981
C 0.057501708 1.438818906 -0.455311458
C 0.993194779 1.769458245 0.724502497
H -1.997679665 -0.387149162 0.512781908
H -1.584031280 -2.724706897 -1.131380811
H -0.947411357 -2.590012692 1.822361637
H -2.265601686 -3.407576412 1.000580229
H 1.359539720 -1.930428969 1.130310121
H 2.526516877 -2.628361736 0.022197430
H 0.663487859 -3.089424320 -1.597614535
H 1.740855383 -0.551658941 -1.665143006
H 0.480961284 1.867753304 -1.372672288
H -0.911316549 1.927387573 -0.292102426
C 1.223594326 3.273294734 0.916403356
H 0.569960363 1.343391943 1.642420785
H 1.955053116 1.266204235 0.567919473
C -0.343545588 -4.431760137 0.854307157

C 1.169177465 -4.093126950 0.908257797
H 1.729843992 -4.854212080 0.351820708
H 1.523964907 -4.151569293 1.944650849
H -0.607455803 -5.121109549 1.664702227
H -0.575192964 -4.960185930 -0.080545083
Li -1.157863438 -0.954025991 -2.197893730
H 1.662045488 3.695962737 0.001737144
H 0.256481823 3.778128982 1.049746873
C 2.130810586 3.600726246 2.109538881
C 2.366652894 5.102571981 2.295232786
H 1.688291211 3.184964238 3.024006529
H 3.094960157 3.091692918 1.981515708
H 3.011847403 5.304294325 3.155961405
H 2.844231100 5.541209747 1.412270574
H 1.422514902 5.634663007 2.456649965

35

C 0.289221466 0.168205965 0.313375204
C -1.020898458 -0.588579713 0.552951369
C -0.620125540 -2.086359075 0.467929473
C -0.544384513 -2.745018148 1.854095609
C 1.765773832 -3.119770137 0.405044276
C 0.786488547 -2.104004498 -0.226418536
C 1.237826054 -0.668160143 -0.126232515
C 0.384926466 1.649474738 0.556500839
C 1.737278999 2.285957730 0.215441706
C -2.059263032 -0.146667298 -0.482080991
H -1.348177967 -2.624162881 -0.145747055
H 0.150528165 -2.168742383 2.479730257
H -1.519776028 -2.687784057 2.352735062
H 2.198571040 -2.703518343 1.324527547
H 2.607086164 -3.298146161 -0.275781524
H 0.659617517 -2.383948011 -1.283124368
H 2.250316921 -0.367518379 -0.382927159
H -0.418986433 2.148571371 -0.001883320
H 0.144531995 1.844390206 1.613781589
C 1.775534821 3.798798007 0.468352929
H 2.528834286 1.800330585 0.801973846
H 1.975419604 2.089243584 -0.838283615
H -1.441837795 -0.323483061 1.532548705
O -2.683537515 0.953972052 -0.286205350
O -2.269935004 -0.841676144 -1.531270496
C 1.037705014 -4.432436741 0.723456939
C -0.078842731 -4.215181535 1.779118806
H 0.274827667 -4.525714433 2.769700278
H -0.933651702 -4.861283508 1.545156886
H 0.601288484 -4.819504805 -0.206762294
H 1.745022108 -5.195589733 1.067809371
Li -3.454440258 0.532426842 -1.912190337
H 0.985067330 4.286649659 -0.119656099
H 1.534985342 4.000572071 1.521884721
C 3.127692374 4.439393161 0.126825608
C 3.161426567 5.951973518 0.368562869
H 3.916138111 3.956436422 0.719720008
H 3.370511624 4.231454399 -0.924098568
H 4.138153237 6.378118711 0.116447624
H 2.407899295 6.466985872 -0.238222679
H 2.956375644 6.190049918 1.418501392

Table S4. Vibrational Frequencies (cm⁻¹)

Cyclooctadienide

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=====
96.44  98.71  232.05  301.45  366.03  438.53
451.58  527.78  624.39  625.77  679.22  707.97
709.37  828.35  859.59  863.47  908.92  938.22
951.89  1016.38  1059.39  1068.04  1074.38  1162.53
1216.75  1253.91  1266.01  1318.04  1341.64  1354.46
1364.36  1380.33  1429.72  1459.93  1483.28  1493.84
1498.83  1525.33  1619.38  1646.84  2795.22  2795.46
2945.58  2965.42  2986.12  3018.36  3024.11  3078.02
3082.98  3096.11  3103.95
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Cyclooctadienide ==> 5,5-cis Bicyclic Anion (TS)

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-412.89  110.57  247.56  355.78  393.92  441.55
452.40  510.41  572.95  645.52  666.06  735.80
829.89  835.00  869.95  900.85  915.17  917.96
943.92  981.64  1016.32  1078.16  1091.64  1118.91
1127.57  1163.21  1198.67  1205.62  1276.06  1314.89
1327.15  1344.62  1362.50  1407.18  1423.13  1484.81
1490.28  1493.95  1507.12  1536.63  2921.49  2924.59
2954.24  2961.75  2980.89  3005.85  3016.01  3028.85
3033.91  3037.34  3073.33
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1,3a,4,5,6,6a-hexahydropentalen-1-ide

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80.97  209.71  287.27  372.74  450.69  516.45
546.04  583.43  607.14  690.22  781.62  788.40
847.92  896.32  901.85  913.90  919.29  978.68
993.22  1016.20  1038.24  1074.74  1097.15  1100.42
1127.74  1163.66  1211.86  1255.11  1270.80  1287.27
1305.48  1309.89  1315.38  1332.81  1342.51  1436.42
1486.93  1492.43  1512.27  1539.36  2835.59  2900.43
2982.94  2997.68  3011.77  3021.56  3056.84  3058.38
3067.94  3098.51  3111.18
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24a

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33.08  39.73  68.18  83.12  97.18  114.37
152.03  160.59  205.59  258.46  298.43  306.82
339.28  371.77  389.95  439.80  453.49  462.45
549.73  640.65  670.19  687.68  726.97  734.38
756.47  764.39  828.52  837.17  888.53  896.73
902.84  929.14  950.43  971.89  993.17  1000.75
1020.16  1056.35  1058.05  1068.31  1074.13  1116.35
1127.10  1152.55  1160.19  1231.27  1252.11  1256.28
1264.20  1275.37  1302.82  1321.67  1331.58  1332.40
1339.79  1359.26  1367.90  1368.91  1390.49  1395.71
1419.11  1419.50  1470.53  1479.79  1483.63  1491.71
1495.36  1498.39  1501.84  1502.95  1511.62  1514.18
1525.02  1616.25  1655.34  2805.46  2811.10  2944.01
2945.60  2957.53  2981.79  2988.03  2989.12  3009.04
3014.03  3017.18  3020.53  3020.64  3028.58  3044.53
3058.71  3076.02  3084.53  3089.73  3090.55  3096.58
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24a-TS

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=====
-412.37  40.49  50.11  54.35  100.88  125.06
134.72  140.71  222.05  253.33  298.12  301.87
325.21  408.55  416.29  442.04  459.23  462.37
=====

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509.67	611.65	664.86	693.79	706.38	736.47
762.49	793.02	834.38	851.90	856.38	897.32
905.93	915.07	918.19	967.29	980.09	989.90
1007.38	1027.35	1037.08	1061.35	1091.24	1093.38
1129.76	1130.80	1165.36	1197.19	1201.02	1206.95
1229.43	1252.98	1277.01	1286.05	1313.01	1316.74
1327.05	1328.44	1330.53	1335.88	1351.58	1372.89
1398.21	1411.80	1417.34	1419.19	1483.67	1489.96
1491.68	1497.18	1503.15	1507.33	1511.61	1514.49
1515.06	1517.88	1526.01	2932.42	2934.85	2959.53
2963.89	2967.19	2985.01	2995.12	3001.12	3008.25
3017.50	3017.81	3021.00	3024.53	3025.84	3030.51
3035.41	3036.06	3051.34	3070.25	3089.12	3094.45

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26a

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38.33	47.68	69.33	81.02	116.04	133.10
144.02	203.70	253.62	263.75	285.57	316.20
387.03	411.21	442.91	478.64	515.09	581.68
592.46	657.60	686.05	712.52	741.70	768.14
786.48	841.66	849.82	889.99	900.98	903.52
915.64	959.81	967.60	987.39	997.39	1004.79
1026.14	1036.76	1042.52	1060.94	1083.77	1093.55
1121.28	1129.83	1161.01	1171.55	1219.69	1227.02
1246.20	1259.91	1263.92	1278.31	1291.86	1294.90
1307.88	1312.90	1317.42	1327.58	1330.54	1333.87
1344.10	1369.53	1398.92	1419.90	1487.87	1491.54
1493.68	1498.30	1499.55	1506.29	1511.70	1512.01
1518.63	1527.10	1527.59	2846.82	2906.36	2978.69
2985.68	2986.98	3001.56	3009.41	3010.25	3013.62
3017.42	3018.68	3022.53	3026.07	3043.75	3058.47
3067.95	3068.13	3081.58	3086.80	3091.91	3101.25

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34a

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26.08	41.60	47.68	62.19	71.63	108.84
134.30	144.65	159.75	187.81	199.14	236.13
255.44	265.39	326.04	363.88	404.28	431.98
474.57	495.54	545.68	613.34	637.86	689.17
705.81	737.48	751.25	783.89	805.40	819.10
859.69	862.31	878.99	899.60	911.99	920.32
935.63	956.58	980.26	999.96	1014.20	1023.67
1038.80	1050.61	1064.84	1065.74	1110.48	1123.52
1136.12	1148.62	1160.57	1185.06	1198.22	1226.09
1236.10	1254.71	1264.18	1278.52	1285.53	1293.79
1299.97	1308.35	1323.50	1331.77	1337.43	1341.89
1343.87	1349.06	1368.39	1372.96	1402.92	1413.63
1422.23	1495.97	1498.72	1499.12	1499.70	1504.82
1511.95	1517.39	1519.12	1526.70	1697.44	1755.18
2974.56	2988.96	3000.22	3001.84	3005.08	3012.58
3015.06	3015.58	3024.32	3026.42	3032.90	3039.04
3049.22	3054.03	3065.20	3065.37	3072.31	3091.14
3095.99	3097.14	3158.77			

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31a

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31.66	38.64	50.43	60.85	98.27	110.02
145.98	161.40	198.85	218.05	244.93	249.89
302.51	338.91	343.84	382.08	411.48	433.14
452.03	490.17	541.87	620.91	642.66	699.07
715.28	730.59	751.74	762.91	802.74	823.66
846.99	871.45	896.64	922.99	939.69	954.64
963.01	967.94	997.27	1012.78	1022.19	1042.16
1058.47	1082.59	1100.35	1115.30	1126.47	1136.94
1162.81	1196.34	1230.05	1249.94	1256.39	1272.30

1296.41	1298.13	1319.41	1327.08	1330.23	1334.17
1342.56	1367.69	1371.99	1381.41	1384.18	1394.39
1410.70	1418.03	1467.29	1472.52	1479.04	1486.87
1494.77	1496.58	1500.27	1500.99	1506.55	1511.11
1513.59	1524.46	1614.76	1650.15	2881.51	2903.97
2907.97	2941.68	2965.18	2969.22	2991.40	2995.01
3000.67	3010.80	3014.18	3020.86	3023.60	3025.93
3034.35	3051.18	3065.16	3073.34	3078.39	3089.76
3096.59	3096.62	3106.96			

31a-TS

-385.11	36.82	45.10	54.53	65.21	112.28
128.75	140.71	188.76	202.99	252.99	257.57
294.64	327.02	356.43	403.34	413.04	431.50
443.85	459.52	549.50	605.56	688.02	696.91
723.06	736.56	762.35	769.09	796.19	827.86
843.32	852.62	890.33	898.69	938.48	955.57
968.01	972.54	1005.74	1011.35	1031.51	1037.00
1061.59	1075.91	1095.56	1102.39	1129.89	1155.01
1196.84	1200.99	1215.55	1223.09	1229.93	1237.40
1253.61	1280.13	1287.72	1314.83	1326.87	1330.07
1331.10	1340.83	1347.65	1371.55	1373.45	1377.35
1398.68	1419.51	1427.73	1433.21	1482.78	1488.36
1494.52	1497.36	1503.27	1511.68	1512.91	1516.19
1517.27	1521.57	1526.17	1530.02	2885.61	2890.87
2910.54	2922.05	2962.41	2971.00	2994.48	2995.35
2998.09	3004.39	3012.06	3017.26	3021.30	3024.68
3025.10	3025.76	3041.04	3049.86	3051.19	3069.67
3072.04	3089.50	3094.55			

32a

25.75	41.74	44.52	90.85	106.33	129.61
134.51	186.55	207.40	245.88	249.36	284.83
313.13	375.66	387.31	422.92	440.40	465.30
515.08	554.50	611.23	652.14	691.34	721.63
735.03	759.75	763.36	798.01	845.20	846.91
885.89	897.28	926.08	959.05	962.93	971.30
1005.05	1006.23	1031.28	1036.46	1042.73	1061.47
1064.75	1079.12	1084.33	1104.22	1126.63	1129.09
1166.35	1183.35	1224.89	1244.28	1246.94	1256.93
1267.61	1271.26	1289.87	1295.08	1311.20	1317.49
1323.77	1329.06	1336.26	1344.39	1362.91	1368.37
1370.00	1370.86	1397.11	1418.51	1485.90	1492.63
1495.66	1496.97	1499.03	1504.73	1507.49	1511.25
1516.98	1519.49	1525.69	1527.46	2797.71	2911.69
2973.53	2982.63	2993.99	2996.20	3004.68	3011.39
3020.32	3020.51	3021.48	3022.24	3026.95	3031.00
3032.66	3043.93	3055.96	3072.69	3080.17	3084.04
3086.36	3091.26	3097.34			

35a

11.90	24.84	40.33	47.94	63.88	93.87
117.07	133.62	142.31	172.35	192.97	202.32
225.96	248.23	272.91	317.87	359.32	396.32
421.06	437.01	474.55	485.93	534.42	589.54
602.93	692.56	728.15	735.94	750.82	773.14
778.10	792.71	807.67	845.77	858.52	889.55
899.19	903.85	946.16	955.97	970.86	979.37
1012.46	1035.64	1043.85	1049.58	1065.91	1069.16
1081.33	1094.88	1123.71	1133.76	1134.79	1138.86
1161.21	1184.59	1223.09	1234.19	1247.64	1250.39
1261.20	1280.21	1285.53	1289.82	1303.26	1317.27

1322.92	1331.18	1336.01	1347.46	1355.75	1366.10
1370.33	1377.49	1378.61	1401.21	1405.16	1414.94
1421.80	1493.86	1494.21	1498.47	1500.85	1504.10
1511.56	1514.78	1516.96	1526.21	1526.70	1704.23
1754.73	2959.41	2976.15	2982.73	3002.77	3004.40
3008.89	3010.28	3014.78	3020.33	3026.96	3031.09
3036.91	3038.29	3042.89	3051.84	3053.98	3055.41
3066.56	3069.26	3075.87	3096.18	3101.90	3156.03

23

72.18	154.37	260.73	274.33	309.94	334.79
403.55	460.83	479.36	494.31	581.91	618.63
728.71	751.70	775.80	782.44	836.43	863.61
898.38	899.67	982.98	985.50	1003.77	1067.83
1079.62	1080.52	1176.48	1206.71	1261.36	1305.45
1320.84	1324.83	1358.40	1375.51	1382.43	1422.44
1451.53	1479.78	1487.00	1494.71	1514.52	1546.80
1586.93	2974.05	2975.85	2998.65	3043.72	3064.31
3067.23	3093.86	3095.93	3142.46	3143.16	3184.04

23-TS

-446.26	99.84	237.40	339.77	392.93	417.80
456.76	509.06	520.40	550.02	591.29	636.06
680.25	691.53	784.89	849.15	867.34	894.93
918.20	950.81	956.71	967.39	1031.45	1034.82
1077.83	1101.69	1113.03	1146.20	1185.47	1192.03
1202.57	1283.76	1334.54	1348.34	1358.80	1363.25
1402.54	1409.50	1451.77	1494.59	1501.33	1502.32
1514.87	2944.82	2951.45	3029.21	3036.67	3039.15
3075.87	3076.78	3088.59	3146.92	3154.87	3173.05

25

50.75	184.88	253.19	287.50	330.61	412.73
526.63	565.59	576.75	599.20	621.98	698.33
725.93	770.33	796.52	868.17	898.51	916.92
921.25	974.47	982.45	995.34	1025.13	1042.15
1075.76	1082.08	1104.94	1154.06	1181.26	1208.87
1266.00	1274.39	1296.08	1311.33	1327.59	1339.95
1346.40	1360.84	1419.19	1493.86	1499.55	1502.42
1519.47	2875.87	2995.90	3032.58	3045.10	3051.48
3088.37	3095.50	3103.11	3147.36	3208.16	3223.37

24

34.95	47.25	48.80	72.08	111.20	123.19
140.63	170.01	243.05	248.36	264.10	284.40
314.93	342.20	364.23	391.10	424.99	436.05
482.95	486.65	499.81	603.08	621.74	696.59
734.78	757.88	758.98	770.17	783.43	837.67
860.39	868.16	901.43	905.97	961.34	972.74
977.90	990.04	1011.12	1037.51	1056.61	1066.29
1075.80	1081.89	1127.42	1131.81	1180.77	1182.43
1230.76	1257.53	1264.29	1275.65	1303.65	1307.83
1330.43	1331.32	1336.63	1342.08	1358.95	1375.20
1382.90	1387.88	1403.39	1408.76	1426.39	1454.84
1471.83	1486.50	1487.39	1488.82	1495.60	1498.32
1503.47	1513.36	1515.42	1525.35	1530.09	1593.42
2973.01	2977.15	2995.99	3000.45	3010.77	3024.14
3031.31	3033.57	3037.73	3038.52	3045.54	3060.56
3061.22	3064.12	3070.10	3072.68	3077.62	3106.48
3110.77	3136.02	3138.62			

24-TS

-445.11	41.89	49.36	50.12	94.30	122.34
134.77	140.04	223.95	251.53	275.73	314.84
320.34	370.40	422.50	425.17	464.06	484.10
507.52	519.16	572.55	591.08	673.19	687.43
693.98	737.59	754.49	765.92	819.02	848.57
874.80	884.36	907.43	918.18	928.19	952.97
977.71	998.29	1015.28	1044.40	1044.82	1046.98
1071.34	1101.31	1104.78	1135.98	1148.11	1185.59
1189.13	1200.85	1211.93	1230.84	1267.89	1286.31
1288.44	1321.14	1334.38	1336.53	1341.67	1343.29
1348.73	1362.41	1390.75	1405.68	1412.20	1413.74
1428.02	1480.41	1492.79	1499.30	1499.47	1499.78
1503.09	1506.65	1513.90	1514.95	1518.16	1527.50
2942.62	2947.48	3009.17	3014.77	3025.79	3028.71
3035.38	3036.07	3036.28	3037.55	3037.94	3048.91
3061.41	3074.74	3075.13	3082.77	3087.38	3104.63
3109.16	3140.09	3143.29			

26

34.69	46.88	47.58	61.70	113.72	128.28
135.59	202.20	228.91	250.47	267.41	286.39
303.07	325.68	396.67	436.59	451.15	523.99
575.26	581.88	603.63	664.39	701.85	728.17
737.35	755.57	765.39	773.26	851.13	855.13
899.37	907.67	912.10	921.87	966.82	974.24
992.93	998.10	1011.05	1030.83	1042.34	1045.71
1066.94	1091.38	1095.09	1130.13	1151.03	1166.38
1182.35	1224.05	1226.26	1258.06	1260.53	1271.20
1277.16	1297.88	1311.48	1329.05	1330.11	1335.78
1337.27	1341.76	1350.00	1363.74	1385.16	1408.98
1426.49	1457.26	1495.31	1498.68	1499.42	1500.74
1503.72	1508.85	1513.33	1517.90	1520.43	1526.50
2850.30	2990.89	3010.35	3020.11	3024.74	3031.94
3035.27	3037.56	3037.66	3043.33	3050.61	3052.62
3062.57	3083.68	3087.21	3093.99	3101.79	3105.60
3109.43	3190.84	3209.02			

34

30.52	39.31	52.26	59.81	66.60	98.19
108.29	133.83	137.59	159.88	179.44	192.00
238.24	249.80	254.19	317.46	364.56	373.71
425.96	471.69	476.49	494.88	547.31	616.55
641.92	666.63	704.31	730.96	735.75	754.55
805.93	823.43	840.42	862.86	879.76	902.09
911.74	916.93	932.79	952.38	975.32	982.42
1005.35	1019.69	1028.88	1041.65	1052.88	1068.32
1069.58	1117.66	1127.86	1136.83	1154.44	1170.84
1197.93	1225.36	1234.79	1252.57	1262.36	1269.65
1289.25	1296.83	1300.42	1308.05	1327.93	1330.00
1336.14	1341.72	1350.17	1351.64	1357.93	1369.38
1406.17	1419.06	1427.27	1449.88	1489.06	1499.49
1501.95	1504.02	1504.11	1513.24	1516.72	1521.72
1526.25	1579.79	1718.12	3002.83	3013.03	3022.72
3027.62	3030.26	3030.28	3034.29	3036.34	3038.01
3038.46	3043.36	3044.58	3059.48	3077.29	3084.29
3088.36	3097.48	3106.03	3109.98	3110.06	3188.79

31

33.28	43.09	47.29	82.79	110.34	112.29
140.43	142.18	183.99	224.94	247.18	249.05
264.78	301.82	308.70	355.11	383.83	392.56
435.96	438.94	485.06	497.78	519.40	562.03
640.65	682.50	734.38	737.12	758.26	761.50
785.46	807.84	827.28	850.06	857.31	904.49
941.57	965.16	972.69	975.36	989.49	1010.69
1012.10	1035.91	1042.07	1066.40	1095.43	1109.11
1116.61	1132.05	1159.96	1185.12	1208.54	1232.11
1263.45	1270.00	1276.30	1301.69	1304.07	1330.93
1335.01	1341.61	1352.54	1354.06	1361.70	1385.08
1388.74	1394.74	1408.65	1415.68	1426.10	1460.79
1468.84	1485.99	1491.31	1494.86	1498.29	1503.15
1505.38	1506.83	1513.05	1515.29	1525.30	1529.93
1614.03	2986.67	2992.83	2996.16	3001.48	3009.68
3022.39	3023.86	3029.52	3031.94	3036.57	3038.51
3049.22	3058.39	3059.84	3061.30	3071.25	3075.13
3081.50	3088.18	3106.46	3110.61	3132.15	3137.15

31-TS

-426.25	35.00	43.30	51.28	55.40	113.08
128.25	138.87	191.72	205.03	252.31	267.86
274.57	321.53	372.34	377.01	402.03	419.70
441.30	468.22	484.37	546.94	564.64	600.81
665.50	689.38	699.91	737.62	742.71	764.89
784.56	797.38	843.46	857.12	861.57	906.27
938.46	952.61	960.23	979.80	992.90	1011.59
1033.00	1040.88	1042.58	1067.34	1085.45	1102.15
1104.90	1132.46	1155.36	1190.66	1202.11	1215.23
1229.33	1233.80	1242.31	1264.07	1285.96	1287.57
1320.67	1332.37	1337.91	1338.97	1346.31	1361.83
1378.42	1382.58	1386.46	1409.96	1416.67	1426.56
1429.57	1477.20	1488.78	1492.46	1495.73	1499.47
1499.62	1505.22	1513.52	1517.36	1521.01	1526.49
1535.47	2889.78	2923.08	3004.04	3006.50	3008.71
3011.04	3023.37	3026.35	3033.58	3034.89	3035.95
3041.04	3046.73	3052.64	3060.15	3075.63	3081.48
3082.07	3103.75	3103.81	3107.75	3121.75	3131.81

32

-14.08*	37.75	41.60	85.04	108.46	123.43
130.65	181.59	205.25	237.11	243.25	250.17
289.87	295.97	326.74	379.12	403.98	423.76
446.95	494.53	562.76	566.58	602.24	662.19
702.49	734.21	738.78	761.62	765.54	771.31
795.85	847.86	849.29	896.21	904.86	930.30
960.96	973.61	974.93	1009.79	1014.61	1030.00
1043.53	1049.16	1067.39	1068.33	1090.59	1094.87
1115.35	1130.49	1136.60	1176.76	1199.94	1225.81
1254.99	1258.54	1263.08	1267.95	1278.50	1293.13
1300.66	1328.05	1330.79	1334.30	1335.75	1352.41
1371.45	1378.75	1381.41	1383.71	1388.21	1408.38
1425.70	1451.16	1494.87	1495.77	1498.61	1503.44
1503.89	1510.48	1512.86	1514.80	1519.84	1524.13
1526.07	2709.90	3013.87	3016.00	3024.50	3026.96
3030.90	3032.76	3039.32	3041.71	3043.05	3044.18
3044.77	3060.42	3061.49	3069.11	3075.70	3078.59
3089.84	3091.78	3110.15	3114.91	3175.74	3211.14

* corresponds to a physically meaningless twisting mode of the *n*-pentyl group and is considered “numerical noise”.

29.78	39.22	48.96	53.84	61.67	92.64
98.60	126.22	134.00	151.21	173.77	182.66
201.39	226.13	248.39	264.73	303.67	354.30
361.90	414.42	436.12	467.80	479.05	486.46
525.35	586.70	630.59	672.31	720.40	731.20
735.27	753.96	776.21	794.74	809.73	844.95
853.64	878.34	903.27	914.87	927.99	947.93
972.48	978.75	983.11	1014.65	1038.62	1040.88
1051.89	1067.97	1069.29	1087.51	1098.67	1125.68
1134.05	1135.74	1142.92	1159.93	1212.80	1235.16
1246.42	1252.47	1265.02	1275.02	1291.00	1295.83
1299.16	1305.27	1330.36	1334.77	1335.44	1336.27
1349.82	1363.20	1372.71	1379.12	1383.59	1394.42
1405.82	1418.74	1427.03	1449.19	1489.49	1498.03
1499.49	1503.96	1505.25	1513.24	1516.07	1516.66
1526.22	1527.54	1579.20	1722.52	3001.01	3001.47
3013.38	3022.22	3022.53	3027.85	3029.64	3031.38
3034.19	3038.26	3038.69	3040.69	3043.56	3059.17
3059.37	3069.77	3071.71	3076.87	3084.93	3094.90
3106.50	3109.87	3188.30			

Additional Comments on Computational Methods.

In our experience, double- ζ basis set is reliable only for computing geometries, whereas a triple- ζ quality basis set, such as cc-pVTZ, is needed for a robust and consistent evaluation of energies. These calculations are, however, about one order of magnitude more expensive. Thus, using a double- ζ basis set for geometry optimizations and a triple- ζ basis set for evaluating the energies constitutes a reasonable compromise between accuracy and computational cost. In this case, additional complications arise from the fact that treating anionic species requires diffuse functions. Exploratory calculations show clearly that they are important for obtaining reliable energies. Thus, we used Dunning's correlation-consistent triple- ζ basis set cc-pVTZ++ including a double set of polarization and diffuse functions for evaluating the energies.² While this provides accurate electronic energies, it can still be argued that the 6-31G**/B3LYP geometries may not be sufficiently accurate. To address this issue, a test geometry optimization on compound **24** was conducted at the 6-31++G**/B3LYP. The computed bond lengths are shown in Figure S1. As can be seen, the structures are in good agreement, with a root mean square deviation (RMSD) of 0.041 Å for the bond lengths.

Figure S1. Structure comparison for geometry optimizations conducted at 6-31G**/B3LYP and 6-31++G**/B3LYP [Hydrogens omitted for clarity]. Bond lengths are given in Å.

² Dunning, T. H. *J. Chem. Phys.* **1989**, 90, 1007-1023.

Low Temperature ^1H NMR Study of Tandem Carbolithiation/Electrocyclization of **1**

^1H NMR at -65°C

¹H NMR at -35 °C

^1H NMR at +5 °C

^1H NMR at +15 °C

^1H NMR & ^{13}C NMR Spectra of Compounds

77.467
77.149
76.830

69.914

49.364

35.623

27.600
25.340
22.595
22.231

135.691
134.811
132.126
128.699

ppm

53

53

58

63