

SUPPORTING INFORMATION

Triquinanes: A ‘One Pot’ IMDA-Tandem Metathesis Cascade Strategy: Ring Closing Metathesis Dominates Norbornene ROM!

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Capnellene References¹

Experimental Procedures

General Methods. All non-aqueous reactions were performed under argon in flame-dried glassware using dry solvents. Tetrahydrofuran was distilled from sodium/benzophenone. Dichloromethane, toluene and triethylamine were distilled from calcium hydride. *n*-Butyllithium solutions in hexanes from Aldrich Chemical Company were titrated prior to use against diphenylacetic acid and used directly. Starting materials were purchased from Aldrich Chemical Company and used without further purification unless otherwise stated. DIBAL-D was prepared from LiD (Strem Chemicals, 99.5% D)

(1) Selected total syntheses of (±)-Δ⁹⁽¹²⁾-capnellene: (a) Lemièrre, G.; Gandon, V.; Cariou, K.; Hours, A.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2009**, *131*, 2993. (b) Samajdar, S.; Patra, D.; Ghosh, S. *Tetrahedron* **1998**, *54*, 1789. (c) Singh, V.; Prathap, S.; Porinchu, M. *J. Org. Chem.* **1998**, *63*, 4011. (d) Singh, V.; Prathap, S.; Porinchu, M. *Tetrahedron Lett.* **1997**, *38*, 2911. (e) Tanaka, K.; Ogasawara, K. *J. Chem. Soc. Chem. Commun.* **1996**, 1839. (f) Ohshima, T.; Kagechika, K.; Adachi, M.; Sodeoka, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7108. (g) Balme, G.; Bouyssi, D. *Tetrahedron* **1994**, *50*, 403. (h) Gambacorta, A.; Fabrizi, G.; Bovicelli, P. *Tetrahedron Lett.* **1992**, *48*, 4459. (i) Shono, T.; Kise, N.; Fujimoto, T.; Tominaga, N.; Morita, H. *Tetrahedron Lett.* **1992**, *57*, 7175. (j) Ihara, M.; Suzuki, T.; Katogi, M.; Taniguchi, N.; Fukumoto, K. *J. Chem. Soc., Chem. Commun.* **1991**, 646. (k) Wang, Y.; Mukherjee, D.; Birney, D.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 4504. (l) Uyehara, T.; Furuta, M.; Akamatsu, M.; Kato, T.; Yamamoto, Y. *J. Org. Chem.* **1989**, *54*, 5411. (m) Iyoda, M.; Kushida, T.; Kitami, S.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1607. (n) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855. (m) Mehta, G.; Murthy, A. N.; Reddy, D. S. K.; Reddy, M. V. *J. Am. Chem. Soc.* **1986**, *108*, 3443. (n) Curran, D. P.; Chen, M. H. *Tetrahedron Lett.* **1985**, *26*, 4991. (o) Liu, H. J.; Kulkarni, G. *Tetrahedron Lett.* **1985**, *26*, 4847. (p) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500. (q) Piers, E.; Karunaratne, V. *Can. J. Chem.* **1984**, *62*, 629. (r) Mehta, G.; Reddy, D. S.; Murty, A. N. *J. Chem. Soc., Chem. Commun.* **1983**, 824. (s) Huguet, J.; Karpf, M.; Dreiding, A. S. *Helv. Chem. Acta* **1982**, *65*, 2413. (t) Birch, A. M.; Pattenden, G. *Tetrahedron Lett.* **1982**, *23*, 991. (u) Fujita, T.; Ohtsuka, T.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1982**, *23*, 4091. (v) Oppolzer, W.; Battig, K. *Tetrahedron Lett.* **1982**, *23*, 4669. (w) Little, R. D.; Carroll, G. L. *Tetrahedron Lett.* **1981**, *22*, 4389. (x) Stevens, K. E.; Paquette, L. A. *Tetrahedron Lett.* **1981**, *22*, 4393. Enantioselective: (y) Sonawane, H. R.; Nanjundian, B. S.; Shah, V. G.; Kulkarni, D. G.; Ahuja, J. R. *Tetrahedron Lett.* **1991**, *32*, 1107. (z) Ohshima, T.; Kagechika, K.; Adachi, M.; Sodeoka, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1996**, *118*, 7108. (zz) Unnatural (+) isomer: Meyers, A. I.; Bienz, S. *J. Org. Chem.* **1990**, *55*, 791.

and used according to Kavin *et al.*² Low temperature baths were ice/water (0 °C) and solid CO₂/acetone (-78 °C). Reaction temperatures are those of the bath. Microwave reaction were conducted in a CEM MAR SX oven using 100 mL sealed quartz vessels at 600 or 1200 watts. The temperature was monitored with a CEM EST-300+ probe immersed in the reaction mixture and the pressure was monitored with a CEM XP 1500 probe.

Reactions were monitored by thin layer chromatography (TLC) using commercial aluminum-backed silica gel sheets coated with silica gel 60 F₂₅₄ (E. Merck). TLC spots were developed by heating the plate after treatment with a phosphomolybdic acid (5%) or a solution of KMnO₄ in aqueous potassium hydroxide. Room temperature corresponds to 22 °C. Anhydrous sodium sulfate (Na₂SO₄) was used to dry solutions in organic solvents. Excess solvents were removed (concentrated) *in vacuo* at pressures obtained by a water or air aspirator connected to a Büchi rotary evaporator. Trace solvents were removed on a vacuum pump. Product purification by flash chromatography was performed with E. Merck Silica Gel 60 (230-400 mesh) according to Still *et al.*³

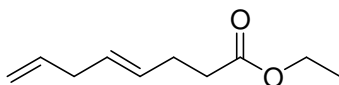
¹H NMR (500 or 300 MHz) and ¹³C NMR (125 or 75MHz) spectra were recorded on a Bruker AVANCE 500 / 300 spectrometers or a Varian Inova 500 spectrometer. Chemical shifts are reported downfield from tetramethylsilane (δ scale) in ppm and calibrated on the residual proton signal of the solvent (7.24 ppm for CHCl₃). ¹H NMR data are reported as follows: Chemical shift (multiplicity, coupling constants (Hz), and integration). Low resolution mass spectroscopy (MS) using electron impact (EI), were recorded on a V.G. Micromass 7070 HS mass spectrometer with an electron beam energy of 70 eV. High resolution mass spectroscopy (HRMS) were recorded on a Kratos Concept-11A mass spectrometer with an electron beam energy of 70 eV. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrometer. The purity of all title compounds was judged to be >95% as determined by a combination of ¹H NMR and ¹³C NMR analyses. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), ap (apparent); the list of couplings

(2) Kalvin D. M.; Woodard R. W. *Tetrahedron* **1984**, *40*, 3387.

(3) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

constants (J) corresponds to the order of the multiplicity assignment. Couplings constants (J) are reported to the nearest 0.5 Hz..

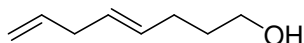
Ethyl-(4*E*)-octa-4,7-dienoate (9a)



A solution of 1,5-hexadien-3-ol (2 mL, 17.9 mmol) and propionic acid (80 μ L, 1.07 mmol) in triethyl orthoacetate (22.9 mL, 125 mmol) was heated to 145 $^{\circ}$ C. These conditions ensured the distillation of ethanol. Upon completion was (~3 h), the reaction was cooled to (22 $^{\circ}$ C) and diluted with Et₂O. The organic phase was washed with HCl (10% aq, 3x), NaHCO₃ (sat. aq, 3x), brine, dried, concentrated and chromatographed (petroleum ether/ Et₂O, 19:1) to afford **9a** as a colorless oil (2.38 g, 79%).

¹H NMR (300 MHz, CDCl₃) δ 5.78 (ddt, J = 17.1, 10.2, 6.3 Hz, 1H), 5.52-5.39 (m, 2H), 5.03-4.93 (m, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.73-2.69 (m, 2H), 2.36-2.28 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.6, 137.4, 129.7, 129.3, 115.4, 60.6, 37.0, 34.6, 28.3, 14.6; IR (neat) 2980, 1737 cm⁻¹; HRMS (EI) m/z calcd for C₁₀H₁₆O₂ (M⁺) 168.1150, found 168.1171.

(4*E*)-Octa-4,7-dien-1-ol (10a)

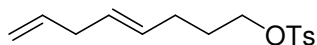


A solution of ester **9a** (1 g, 5.94 mmol) in dry THF (10 mL) was added dropwise to a suspension of LiAlH₄ (450 mg, 11.9 mmol) in dry THF (20 mL) at 22 $^{\circ}$ C. After 30 min, H₂O was added dropwise until mixture turned white. HCl (10% aq) was added until the solution turned clear. Et₂O extracts (3x) were combined and washed with H₂O and brine, dried concentrated, and chromatographed (petroleum ether/ Et₂O, 3:1) to afford **10a** as a colorless oil (690 mg, 92%).

¹H NMR (300 MHz, CDCl₃) δ 5.79 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 5.46-5.42 (m, 2H), 5.03-4.92 (m, 2H), 3.62 (t, J = 6.6 Hz, 2H), 2.73-2.70 (m, 2H), 2.11-2.05 (m, 2H), 1.62

(quintet, $J = 6.9$ Hz, 2H), 1.50 (bs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.6, 131.2, 128.8, 115.3, 62.9, 37.1, 32.7, 29.2; IR (neat) 3352, 2929, 912 cm^{-1} ; too unstable for MS.

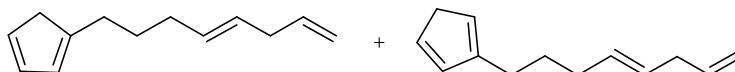
(4E)-Octa-4,7-dien-1-yl-4-methylbenzenesulfonate (4a)



Triethylamine (1.78 mL, 12.78 mmol), *p*-toluenesulfonyl chloride (1.63 g, 8.53 mmol) and DMAP (26 mg, 0.213 mmol) were added to a solution of alcohol **10a** (538 mg, 4.26 mmol) in CH_2Cl_2 (20 mL). The mixture stirred at 22 °C for 24 h. The reaction was washed with HCl (10% aq, 3x), H_2O , brine, dried, concentrated, and chromatographed (petroleum ether/ Et_2O , 19:1 or pure CH_2Cl_2) to afford **4a** as a colorless oil (948 mg, 79%).

^1H NMR (300 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 5.73 (ddt, $J = 16.7, 10.4, 6.4$ Hz, 1H), 5.38-5.22 (m, 2H), 4.99-4.92 (m, 2H), 3.99 (t, $J = 6.4$ Hz, 2H), 2.67-2.63 (m, 2H), 2.42 (s, 3H), 2.04-1.98 (m, 2H), 1.68 (quintet, $J = 6.5$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.0, 137.3, 133.5, 130.2, 129.7, 129.6, 128.3, 115.4, 70.2, 36.9, 28.8, 28.5, 22.1; IR (neat) 3076, 2925, 1362, 1177 cm^{-1} ; too unstable for MS.

1-((4E)-Octa-4,7-dien-1-yl)cyclopenta-1,3-diene/2-((4E)-Octa-4,7-dien-1-yl)cyclopenta-1,3-diene (5a)



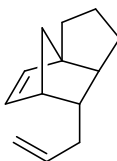
Procedure A: Freshly distilled cyclopentadiene (1.5 mL) was treated with NaH (1.5 mmol, THF 1M) and the solution of added to a cool (0 °C) solution of tosylate **4a** (300 mg, 1.07 mmol) in THF (5 mL). The reaction warmed slowly to 22 °C and stirred for 6 h. Diluted with HCl (10% aq) and the aqueous phase was extracted with petroleum ether (3x). The combined petroleum ether extracts (3x) were washed with H_2O , brine, dried

concentrated, and chromatographed (petroleum ether) to afford **5a** as a colorless oil (186 mg, 61%).

Procedure B: Ethylmagnesium bromide (5.25 mL, 1 M in THF, 5.25 mmol) was added to a solution of freshly distilled cyclopentadiene (0.432 mL, 5.25 mmol) in THF (5 mL) at 0 °C. The solution was heated at reflux for 4 h. The solution was cooled to 0 °C and to this was added a solution of tosylate **4a** (500 mg, 1.75 mmol) in THF (5 mL). The reaction stirred at 22 °C for 16 h. Diluted with HCl (10% aq) and the aqueous phase was extracted with petroleum ether (3x). Combined petroleum ether extracts (3x) were washed with H₂O, brine, dried and concentrated.. Chromatography (petroleum ether) to afforded **5a** as a colorless oil (186 mg, 61%). Note: this compound slowly degrades on prolonged storage (1 month) and should be used shortly after its preparation.

¹H NMR (300 MHz, CDCl₃) δ 6.43-5.98 (m, 3H), 5.87-5.74 (m, 1H), 5.50-5.36 (m, 2H), 5.03-4.94 (m, 2H), 2.92 (bs, 1H), 2.85 (bs, 1H), 2.72-2.70 (m, 2H), 2.41-2.31 (m, 2H), 2.03-2.01 (m, 2H), 1.65-1.52 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 150.2, 147.4, 137.8, 135.1, 134.0, 132.8, 131.8, 131.7, 130.8, 128.34, 128.29, 126.7, 126.3, 115.1, 43.6, 41.6, 37.1, 32.7, 32.6, 30.5, 29.8, 29.7, 28.9; IR (neat) 2929, 1432, 972 cm⁻¹; HRMS calcd for C₁₃H₁₈ (M⁺) 174.1408, found 174.1400.

6-*endo*-Tricyclo[5.2.1.0^{1,5}]dec-8-ene (**6a**)

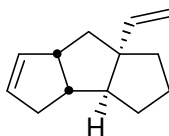


A microwave quartz vessel was charged with substituted cyclopentadiene (**5a**) (100 mg, 0.572 mmol), chlorobenzene (5 mL) and a carboflonTM. The solution was degassed with argon for 15 min. The microwave apparatus was assembled rapidly and the reaction was heated at 210 °C and 310 psi for 2 h. The solution was directly loaded onto the chromatographic column. Purification with petroleum ether to afforded **6a** as a clear oil (80 mg, 80%).

¹H NMR (500 MHz, CDCl₃) δ 6.16 (d, *J* = 5.6 Hz, 1H), 5.92 (dd, *J* = 5.6, 2.9 Hz, 1H), 5.77 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 4.96-4.89 (m, 2H), 2.77 (bs, 1H), 1.97-1.77 (m,

7H), 1.66-1.61 (m, 1H), 1.38 (d, $J = 8.1$ Hz, 1H), 1.30-1.22 (m, 1H), 1.21 (d, $J = 8.1$ Hz, 1H), 1.12-1.07 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.7, 138.5, 132.6, 114.4, 63.5, 53.0, 52.0, 49.0, 47.2, 39.2, 31.5, 27.1, 27.0; IR (neat) 2951, 2906, 2864 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{18}$ (M^+) 174.1408, found 174.1411.

1-Vinyl-*cis-anti-cis*-[6.3.0.0^{2,6}]undec-8-ene (7a)



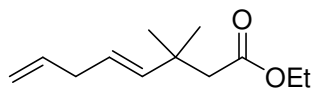
Procedure A: A microwave quartz vessel was charged with substituted cyclopentadiene (**5a**) (100 mg, 0.572 mmol), chlorobenzene (5 mL) and a Carboflon.[®] The solution was degassed with argon for 15 min. The microwave apparatus was assembled rapidly and the reaction was heated at 210 °C and 310 psi for 2 h. The quartz vessel was removed from the apparatus, resealed with a septum and the solution was degassed with argon for 10 min. The solution was then purged with ethylene for another 10 min. Under the ethylene atmosphere, Grubbs 1st generation catalyst (24.3 mg, 0.0286 mmol) was added. After being stirred at 22 °C for 2 h under ethylene the reaction was quenched with DMSO (0.100 mL). The mixture was concentrated *in vacuo* and chromatographed (petroleum ether) to afford **7a** as a clear oil (65 mg, 65%).

Procedure B: A solution of Diels-Alder adduct **6a** (50.0 mg, 0.287 mmol) in benzene (5 mL) was degassed with argon for 15 min. The solution was purged with ethylene for another 10 min. Under an ethylene atmosphere, Grubbs 1st generation catalyst was added (12.2 mg, 0.0144 mmol) and after being stirred at 22 °C for 2 h under ethylene the reaction was quenched with DMSO (0.050 mL). The mixture was concentrated *in vacuo* and chromatographed (petroleum ether) to afford **7a** as a clear oil (49.5 mg, 98%).

^1H NMR (500 MHz, CDCl_3) δ 5.87 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.61-5.49 (m, 2H), 4.87 (dd, $J = 17.4, 1.4$ Hz, 1H), 4.80 (dd, $J = 10.6, 1.4$ Hz, 1H), 3.19-3.14 (m, 1H), 2.55-2.49 (m, 1H), 2.33-2.29 (m, 1H), 2.16-2.11 (m, 1H), 1.90 (dd, $J = 13.0, 8.5$ Hz, 1H), 1.82-1.59 (m, 6H), 1.58-1.48 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.3, 135.5, 128.0, 109.0,

58.6, 58.2, 50.8, 49.8, 43.4, 39.4, 36.4, 31.4, 23.9; IR (neat) 2953, 2927, 2856 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{18}(\text{M}^+)$ 174.1408, found 174.1393.

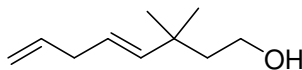
Ethyl-(4E)-3,3-dimethylocta-4,7-dienoate (9b)



A solution of 6-Methylhepta-1,5-dien-4-ol (**8b**) (3.00 g, 23.8 mmol) and phenol (111 mg, 1.18 mmol) in triethyl orthoacetate (30.5 ml, 166 mmol) was heated to 145 °C. These conditions ensured the distillation of ethanol. Upon completion (~24 h), the reaction was cooled to 22 °C and diluted with Et_2O . The organic phase was washed with HCl (10% aq, 3x), NaOH (10% aq, 3x), brine, dried concentrated, and chromatographed (petroleum ether/ Et_2O , 19:1 (200 mL) to 9:1 (200 mL) to 3:1) to afford **9b** as a colorless oil (3.03 g, 65%).

^1H NMR (300 MHz, CDCl_3) δ 5.80 (ddt, $J = 17.1, 10.1, 6.3$ Hz, 1H), 5.50 (dt, $J = 14.3, 1.2$ Hz, 1H), 5.34 (dt, $J = 15.6, 6.3$ Hz, 1H), 5.02-4.93 (m, 2H), 4.06 (q, $J = 7.1$ Hz, 2H), 2.72 (tq, $J = 6.3, 1.4$ Hz, 2H), 2.24 (s, 2H), 1.21 (t, $J = 7.1$ Hz, 3H), 1.10 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.2, 140.2, 137.6, 129.6, 124.4, 116.3, 115.2, 60.3, 47.6, 37.0, 35.8, 27.9, 14.7; IR (neat) $\nu = 2962, 2930, 1735$ cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2(\text{M}^+)$ 196.1463, found 196.1492.

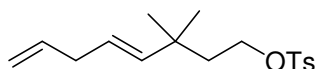
(4E)-3,3-Dimethylocta-4,7-dien-1-ol (8b)



A solution of ester **9b** (500 mg, 2.55 mmol) in THF (10 mL) was added dropwise to a suspension of LiAlH_4 (193 mg, 5.09 mmol) in THF (10 mL) at 22 °C. After 30 min, H_2O was added dropwise until mixture turned white. HCl (10% aq) was added until the solution turned colorless. Et_2O extracts (3x) were combined and washed with H_2O and brine, dried concentrated, and chromatographed (petroleum ether/ Et_2O , 3:1) to afford **8b** as a colorless oil (340 mg, 87%).

^1H NMR (300 MHz, CDCl_3) δ 5.79 (ddt, $J = 17.1, 10.3, 6.4$ Hz, 1H), 5.45 (d, $J = 15.8$ Hz, 1H), 5.34 (dt, $J = 9.6, 6.0$ Hz, 1H), 5.02-4.95 (m, 2H), 3.62 (t, $J = 7.1$ Hz, 2H), 2.73 (bt, $J = 5.9$ Hz, 2H), 1.57 (t, $J = 7.1$ Hz, 2H), 1.37 (bs, 1H), 0.99 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.5, 137.6, 124.5, 115.3, 68.3, 60.6, 45.8, 37.1, 35.3, 28.0; IR (neat) $\nu = 3345, 2959, 2936, 2899\text{ cm}^{-1}$; too unstable for MS.

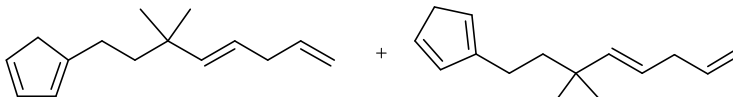
(4E)-3,3-Dimethylocta-4,7-dien-1-yl 4-methylbenzenesulfonate (4b)



Triethylamine (5.96 mL, 42.8 mmol), *p*-toluenesulfonyl chloride (5.44 g, 28.5 mmol) and DMAP (86 mg, 0.710 mmol) were added to a solution of alcohol **10b** (2.20 g, 14.2 mmol) in CH_2Cl_2 (30 mL). The mixture stirred at 22 °C for 24 h. The reaction was washed with HCl (10% aq, 3x), H_2O , brine, dried concentrated, and chromatographed (petroleum ether/ Et_2O , 19:1 or 100% CH_2Cl_2) to afford **4b** as a colorless oil (4.07 g, 93%).

^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 5.72 (m, 1H), 5.24 (m, 2H), 4.95 (m, 2H), 3.98 (t, $J = 7.4$ Hz, 2H), 2.66 (m, 2H), 2.42 (s, 3H), 1.63 (t, $J = 7.4$ Hz, 2H), 0.93 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.0, 139.8, 137.5, 133.5, 130.1, 128.2, 125.3, 115.4, 68.7, 41.2, 37.0, 35.2, 27.9, 22.0; IR (neat) 2962, 1363 cm^{-1} ; too unstable for MS

1-((4E)-3,3-Dimethylocta-4,7-dien-1-yl)cyclopenta-1,3-diene/2-((4E)-3,3-Dimethylocta-4,7-dien-1-yl)cyclopenta-1,3-diene (5b)



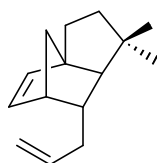
Procedure A: Freshly distilled cyclopentadiene (2.1 mL) was treated with NaH (1.5 mmol, THF 1M) and the solution of added to a 0 °C solution of tosylate **4b** (318 mg, 1.07

mmol) in THF (5 mL) was added via cannula. The reaction was slowly warmed to 22 °C and stirred for 1.5 h. The mixture was extracted with petroleum ether (3x). The petroleum ether extracts (3x) were combined and washed with H₂O, brine, dried and concentrated. Chromatography (petroleum ether) afforded **5b** as a colorless oil (186 mg, 86%).

Procedure B: Ethylmagnesium bromide (4.86 mL, 1 M in THF, 4.86 mmol) was added to a solution of freshly distilled cyclopentadiene (0.400 mL, 4.86 mmol) in THF (5 mL) at 0 °C. The solution was heated at reflux for 4 h. The solution was cooled to 0 °C and a solution of tosylate **4b** (500 mg, 1.62 mmol) in THF (5 mL) added. The reaction stirred at 22 °C for 16 h. Diluted with HCl (10% aq) and the aqueous phase was extracted with petroleum ether (3x). Combined petroleum ether extracts (3x) were washed with H₂O, brine, dried concentrated, and chromatographed (petroleum ether) to afford **5b** as a colorless oil (194 mg, 60%).

¹H NMR (300 MHz, CDCl₃) δ 6.42-5.92 (m, 3H), 5.84 (ddt, *J* = 17.1, 10.3, 6.3 Hz, 1H), 5.47-5.27 (m, 2H), 5.04-4.95 (m, 2H), 2.92 (s, 1H) 2.85 (s, 1H), 2.77 (bt, 2H), 2.33-2.22 (m, 2H), 1.53-1.42 (m, 2H), 1.00 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 151.0, 148.1, 141.6, 141.5, 138.1, 135.3, 134.0, 132.8, 130.7, 126.0, 125.5, 124.1, 115.1, 43.8, 43.1, 42.3, 41.6, 37.2, 36.1, 36.1, 27.7, 26.3, 25.5; IR (neat) 2959, 2917 cm⁻¹; HRMS calcd for C₁₅H₂₂ (M⁺) 202.1721, found 202.1730.

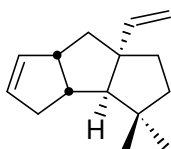
4,4-Dimethyl-6-*endo*-allyltricyclo[5.2.1.0^{1,5}]dec-8-ene (**6b**)



A microwave quartz vessel was charged with substituted cyclopentadiene **5b** (100 mg, 0.495 mmol), chlorobenzene (5 mL) and a Carboflon[®]. The solution was degassed with argon for 15 min. The microwave apparatus was quickly assembled and the reaction was heated at 210 °C and 310 psi for 1.5 h. The solution was directly loaded onto the chromatographic column. Purification using pure petroleum ether to afford **6b** as a clear oil (54 mg, 45%).

^1H NMR (500 MHz, CDCl_3) δ 6.18 (d, $J = 5.7$ Hz, 1H), 5.90 (dd, $J = 5.7, 2.8$ Hz, 1H), 5.76 (ddt, $J = 17.0, 10.0, 7.2$ Hz, 1H), 4.96-4.89 (m, 2H), 2.75 (bs, 1H), 2.04-1.99 (m, 1H), 1.93-1.87 (m, 1H), 1.81-1.52 (m, 5H), 1.38 (broad dd, 1H), 1.12 (dt, $J = 7.9, 1.9$ Hz, 1H), 0.97 (s, 6H), 0.82 (dd, $J = 5.1, 2.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.2, 138.7, 132.3, 114.7, 65.2, 62.6, 50.8, 47.8, 44.3, 42.3, 40.6, 36.5, 32.9, 28.1, 26.8; IR (neat) 2957, 2864, 908 cm^{-1} ; HRMS calcd for $\text{C}_{15}\text{H}_{22}(\text{M}^+)$ 202.1721, found 202.1712.

1-Vinyl-4,4-dimethyl-*cis-anti-cis*-tricyclo[6.3.0.0^{2,6}]undec-8-ene (7b)



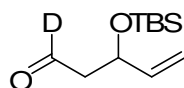
Procedure A: The substituted cyclopentadiene **5b** (100 mg, 0.495 mmol) in benzene (5 mL) was added to a microwave quartz vessel containing with a Carboflon.[®] The solution was degassed with argon for 15 min. The microwave apparatus was quickly assembled and the reaction was heated at 210 $^{\circ}\text{C}$ and 310 psi for 4 h. The quartz vessel was removed, sealed with a septum and the solution was degassed with argon for 10 min. The solution was purged with ethylene for another 10 min. Grubbs 1st generation catalyst (21.0 mg, 0.0248 mmol) was quickly added and the reaction was stirred at 22 $^{\circ}\text{C}$ for 2 h under and quenched with DMSO (0.10 mL). The mixture was concentrated *in vacuo* and chromatographed (petroleum ether) to afford **7b** as a clear oil (42.1 mg, 15%).

Procedure B: A solution of Diels-Alder adduct **6b** (50.0 mg, 0.247 mmol) in benzene (5 mL) was degassed with argon for 15 min. The solution was purged with ethylene for another 10 min. Under ethylene, Grubbs 1st generation catalyst was added (10.5 mg, 0.0124 mmol). The reaction was stirred at 22 $^{\circ}\text{C}$ for 2 h under ethylene and quenched with DMSO (0.050 mL). The mixture was concentrated *in vacuo* and chromatographed (petroleum ether) to afford **7b** as a clear oil (49.2 mg, 98%).

^1H NMR (500 MHz, CDCl_3) δ 6.00 (dd, $J = 17.5, 10.5$ Hz, 1H), 5.61-5.52 (m, 1H), 4.90 (dd, $J = 17.5, 1.0$ Hz, 1H), 4.75 (dd, $J = 10.5, 1.5$ Hz, 1H), 3.11-3.09 (m, 1H), 2.56-2.53 (m, 2H), 2.14-2.10 (m, 1H), 1.88-1.84 (m, 2H), 1.77 (dd, $J = 13.5, 8.0$ Hz, 1H), 1.57 (bd, $J = 3.3$ Hz, 1.53-1.46 (m, 3H), 1.43-1.40 (m, 1H), 1.01 (s, 3H), 0.95 (s, 3H); ^{13}C NMR

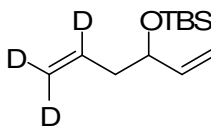
(125 MHz, CDCl₃) δ 150.0, 136.0, 128.7, 107.8, 69.7, 58.5, 52.3, 45.6, 45.1, 41.7, 41.1, 40.0, 36.4, 30.3, 25.8; IR (neat) 2943, 2863, 1467, 900 cm⁻¹; HRMS calcd for C₁₅H₂₂ (M⁺) 202.1721, found 202.1726.

3-tert-Butyldimethylsilyloxy-1-deuterio-penten-4-enal



3-Tert-butyldimethylsilyloxy-pent-4-enoic acid ethyl ester (**11**) (5g, 19.4 mmol) in toluene (150 mL) was cooled to -78 °C and DIBAL-D (1.6 M in hexanes/Et₂O) was added dropwise. The reaction was monitored by TLC (petroleum ether/ Et₂O 20/1) and the addition was stopped when formation of di-deuterio-alcohol was detected (*ca.* 11 mL, 17.6 mmol, 0.9 equiv.). Dry MeOH (20 mL) was added followed by a saturated solution of Rochelle salt (40 mL) at -78 °C. The reaction mixture was then allowed to warm to 22 °C and diluted with Et₂O. The entire reaction mixture was then filtered through Celite®. The aqueous layer was extracted with ether and the combined organic layers were dried, concentrated and chromatographed (petroleum ether/Et₂O 20/1) to afford 2.7 g of the desired aldehyde (12.6 mmol, 65%, ~99% D). HRMS (EI) *m/z* calcd for C₇H₁₂D₂O₂Si [M-tBu]⁺ 158.0748, found 158.0748. ¹H NMR (300 MHz, CDCl₃) δ 5.90 (ddt, *J* = 16.3, 10.2, 6.3 Hz, 1H), 5.29 (d, *J* = 16.3 Hz, 1H), 5.14 (d, *J* = 10.7 Hz, 1H) 4.67 (m, 1H), 2.63 (dd, *J* = 15.6, 6.9 Hz, 1H), 2.53 (dd, *J* = 15.6, 5.1 Hz, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 201.3 (t, *J*_{C,D} = 26 Hz), 139.9, 114.8, 51.0, 25.7, 18.1, -4.4, -5.1; IR (neat) ν = 2956, 2929, 2858, 1712, 831, 775 cm⁻¹.

tert-Butyl(5,6,6 trideuteriohexa-1,5-dien-3-yloxy)dimethylsilane (**12**)

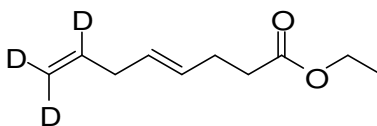


n-BuLi (2.5M hexanes, 12.0 mmol, 4.8 mL) was added dropwise to a 0 °C suspension of trideuteiomethyltriphenylphosphonium iodide (5.28 g, 13.0 mmol) in THF (100 mL).

The reaction was stirred for a further 15 min after addition was complete. The deuterio-aldehyde (2.15 g, 10 mmol) in THF (10 mL) was added to the reaction flask and allowed to warm to 22 °C. Stirring was continued for 3 h, the mixture was concentrated to ~50 mL, and petroleum ether (200 mL) added to precipitate the phosphine oxide and excess of phosphonium iodide. The supernatant was filtered through a short pad of silica and eluted with additional petroleum ether (200 mL). Evaporation of the solvent gave **12** as a colorless oil (2.14 g, 95%, > 99% D).

^1H NMR (300 MHz, CDCl_3) δ 5.80 (ddt, J = 16.3, 10.4, 5.8 Hz, 1H), 5.15 (dt, J = 16.3, 1.5 Hz, 1H), 5.03 (dt, J = 10.4, 1.45 Hz, 1H), 4.14 (m, 1H), 2.26 (m, 2H), 0.88 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.0, 134.2 (t, $J_{\text{C,D}}$ = 24 Hz), 116.0 (quintet, $J_{\text{C,D}}$ = 24 Hz), 113.6, 77.3, 42.5, 25.7, 18.1, -4.6, -5.0; IR (neat) ν = 2956, 2929, 2858, 1251, 1080, 771, 713 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_8\text{H}_{12}\text{D}_3\text{OSi} [\text{M-tBu}]^+$ 158.1080, found 158.1074.

Ethyl-(4E)-(7,8,8-trideuterio)-octa-4,7-dienoate (9a-D₃)

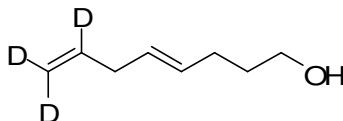


TBAF (10 mL, 1M in THF) was added to silyl ether **12** (2.1 g, 9.8 mmol) in (20 mL). The reaction was stirred overnight (~15 h), diluted with Et_2O (150 mL), and the ether layer washed with water (4x100 mL). The organic layer was dried and concentrated. This crude material was dissolved in triethyl orthoacetate (23 mL, 125 mmol) and propionic acid (80 μL , 1.07 mmol) added and heated to 145 °C. These conditions ensured the distillation of ethanol. Upon completion (~3 h), the reaction was cooled to 22 °C and diluted with Et_2O . The organic phase was washed with HCl (10% aq, 3x), NaHCO_3 (sat. aq, 3x), brine, dried, concentrated and chromatographed (petroleum ether/ Et_2O , 19:1) to afford **9a-D₃** as a colorless volatile liquid (1.3 g, 79%).

^1H NMR (300 MHz, CDCl_3) δ 5.45 (m, 2H), 4.10 (q, J = 7.2 Hz, 2H), 2.73-2.69 (m, 2H), 2.38-2.27 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 173.2, 136.5 (t, $J_{\text{C,D}}$ = 24 Hz), 129.4, 129.0, 114.3 (quintet, $J_{\text{C,D}}$ = 24 Hz), 60.3, 36.4, 34.3, 27.9, 14.3; IR

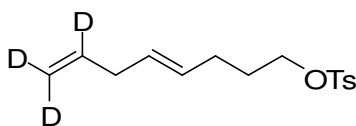
(neat) $\nu = 2980, 1737 \text{ cm}^{-1}$; HRMS (EI) m/z calcd for $\text{C}_8\text{H}_{11}\text{D}_3\text{O}$ (M^+) 129.1233 found 129.1225.

7,8,8-Trideuterio-(4E)-octa-4,7-dien-1-ol (10a-D₃)



A solution of ester **9a-D₃** (1.1 g, 6.43 mmol) in dry THF (20 mL) was added dropwise to a suspension of LiAlH_4 (488 mg, 12.9 mmol) in dry THF (20 mL) at 22°C . After 30 min, the mixture was cooled to 0°C and H_2O was carefully added dropwise until mixture turned white. HCl (10% aq) was added until the solution became clear. The organic layer was extracted with Et_2O (3x 100 mL), washed with H_2O , brine, dried, concentrated, and chromatographed (pentane/ Et_2O , 3:1) to afford **10a-D₃** as a colorless volatile oil (760 mg, 92%). ^1H NMR (300 MHz, CDCl_3) δ 5.45 (m, 2H), 3.63 (t, $J = 6.6$ Hz, 2H), 2.71 (m, 2H), 2.08 (m, 2H), 1.62 (quintet, $J = 6.8$ Hz, 2H), 1.40-1.26 (bs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.7 (t, $J_{\text{C,D}} = 23$ Hz), 130.8, 128.4, 114.2 (quintet $J = 24$ Hz), 62.5, 36.4, 32.3, 28.9 IR (neat) 3338, 2932, 1053 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_8\text{H}_{11}\text{D}_3\text{O}$ (M^+) 129.1233 found 129.1225

7,8,8-Trideuterio-(4E)-octa-4,7-dien-1-yl-4-methylbenzenesulfonate (4a-D₃)

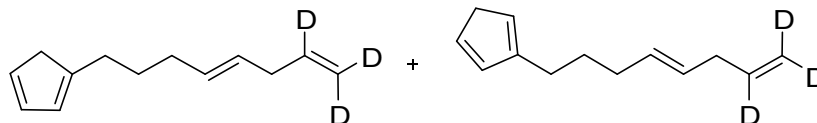


The tosylate **4a-D₃** was prepared by procedure described for **4a** with **4a-D₃** (600 mg, 4.65 mmol), Et_3N (1.93 mL, 13.9 mmol), *p*-toluenesulfonyl chloride (1.77 g, 9.30 mmol) and DMAP (28 mg, 0.232 mmol) in CH_2Cl_2 (20 mL) to afford **4a-D₃** as a colorless oil (948 mg, 79%). (1.31 g, 97%).

^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 5.44-5.25 (m, 2H), 4.04 (t, $J = 6.4$ Hz, 2H), 2.65 (d, $J = 5.9$ Hz, 2H), 2.43 (s, 3H), 2.01 (q, $J = 7.1$ Hz, 2H), 1.68 (quintet, $J = 6.6$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.0, 136.8 (t, $J_{\text{C,D}} = 23$ Hz), 133.6, 130.2, 129.8, 129.6, 128.3, 114.7 (quintet, $J_{\text{C,D}} = 23$ Hz), 70.2,

36.9, 28.8, 28.5, 22.1; IR (neat) 3076, 2925, 1362, 1177 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{D}_3\text{O}_3\text{S} (\text{M}^+)$ 283.1321 found 283.1618

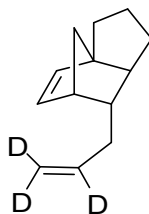
1-(4*E*)-7,8,8-Trideuterio-octa-4,7-dien-1-yl)cyclopenta-1,3-diene/2-(4*E*)-7,8,8-trideuterio-octa-4,7-dien-1-yl)cyclopenta-1,3-diene (5a-D₃**)**



The cyclopentadienes **5a-D₃** were prepared as above for **5a** with 2.8 mL solution of cyclopentadienylsodium (2.8 mmol, 1M in THF) and tosylate **4a-D₃** (500 mg, 1.77 mmol) in THF (7 mL) to afford **5a-D₃** as a colorless oil (310 mg, 99%).

^1H NMR (300 MHz, CDCl_3) δ 6.44-5.99 (m, 3H), 5.50-5.36 (m, 2H), 2.95 (bs, 1H), 2.88 (bs, 1H), 2.72-2.70 (m, 2H), 2.41-2.31 (m, 2H), 2.03-2.01 (m, 2H), 1.65-1.52 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.7, 147.0, 137.0 (t, $J_{\text{C,D}} = 23$ Hz), 134.7, 133.6, 132.4, 131.3, 131.2, 130.4, 128.34, 128.29, 126.7, 126.3, 125.8, 114.1 (quintet, $J_{\text{C,D}} = 23$ Hz), 43.2, 41.2, 36.5, 32.3, 32.2, 30.1, 29.4, 29.3, 28.6; IR (neat) 2927, 1429, 970, 711 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{D}_3 (\text{M}^+)$ 177.1597, found 177.1575

6-endo-Allyl-2',2',3'-trideuterotricyclo[5.2.1.0^{1,5}]dec-8-ene (6a-D₃**)**

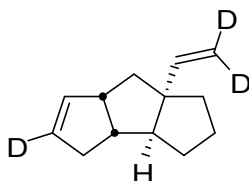


The adduct **6a-D₃** was prepared with procedure above for **6a** with 100 mg of cyclopentadiene **5a-D₃** (0.57 mmol) in chlorobenzene (5 mL) to afford **6a-D₃** (80 mg, 80%).

^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, $J = 5.6$ Hz, 1H), 5.91 (dd, $J = 5.6, 2.9$ Hz, 1H), 2.77 (bs, 1H), 1.99-1.73 (m, 7H), 1.69-1.60 (m, 1H), 1.38 (d, $J = 8.1$ Hz, 1H), 1.30-1.22 (m, 1H), 1.21 (d, $J = 8.2$ Hz, 1H), 1.12-1.07 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.6, 137.8 (t, $J_{\text{C,D}} = 23$ Hz), 132.5, 113.6 (quintet, $J_{\text{C,D}} = 23$ Hz), 63.4, 52.9, 52.0, 48.9,

47.0, 38.9, 31.4, 27.0, 22.9; IR (neat) 2951, 2906, 2864 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{D}_3$ (M^+) 177.1597, found 177.1589.

1-Vinyl-2',2'-didetero-*cis-anti-cis*-tricyclo[6.3.0.0^{2,6}]undec-8-deuteroene (7a-D₃)



A solution of **6a-D₃** (50.0 mg, 0.282 mmol) in degassed benzene (5 mL) was added Grubbs 1st generation catalyst (10.5 mg, 0.0124 mmol) was added. After 2h of stirring at rt under an argon atmosphere, DMSO (50 μL) was added and the solvent removed under reduced pressure. Flash chromatography on silica gel (pure petroleum ether) afford **7a-D₃** as a clear oil (49 mg, 90% purity). Despite intensive effort, ^1H and ^{13}C NMR showed the presence of an unknown contaminant possessing the same R_f as **7a-D₃** that could not be removed.

^1H NMR (500 MHz, CDCl_3) δ 5.87 (dd, $J = 17.5, 10.7$ Hz, 1H), 5.61-5.49 (m, 1H), 3.16 (m, 1H), 2.55-2.49 (m, 1H), 2.33-2.29 (m, 1H) 2.16-2.11 (m, 1H), 1.90 (dd, $J = 13.0, 8.5$ Hz, 1H), 1.82-1.59 (m, 6H), 1.58-1.48 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.3, 135.5, 128.0, 109.0, 58.6, 58.2, 50.8, 49.8, 43.4, 39.4, 36.4, 31.4, 23.9; IR (neat) 2953, 2927, 2856 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{D}_3(\text{M}^+)$ 177.1597, found 177.1590.

General procedure for low temperature NMR studies.

A solution of **6a** or **6a-D₃** (5 mg, 29 μmol) in degassed (Ar) CD_2Cl_2 (3 mL) was cooled to -78°C . A solution of benzyldiene-bis(tricyclohexylphosphine) dichlororuthenium (24 mg, 29 μmol , 0.4 mL, degassed CD_2Cl_2) was slowly added stirred vigorously for 5 min. The suspension was quickly transferred into an NMR tube and rapidly inserted into the pre-cooled (-18°C) NMR probe (Varian 5 mm indirect HCN probe, 500 MHz). Spectra were recorded using 45 deg. (3.4 μs) pulse and 128 transients were acquired. The FID was then Fourier transformed without line broadening and phased.