Supplementary Material (ESI) for Chemical Communications

Indium Tribromide-promoted Arene Terminated Epoxy Olefin Cyclization

Jun-Feng Zhao, Yu-Jun Zhao and Teck-Peng Loh *

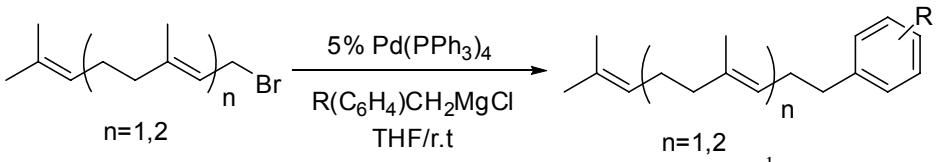
Division of Chemistry and Biological Chemistry
School of Physical and Mathematical Sciences
Nanyang Technological Universit
Singapore 637616

Supplementary Material

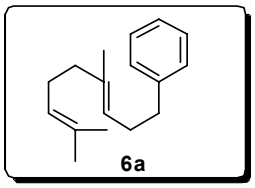
General Methods

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification with the following exceptions: Hexane, dichloromethane, ethyl acetate and diethyl ether were fractionally distilled. Aldehydes were distilled before used. Analytical thin layer chromatography (TLC) was performed using Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating on a hot plate. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300 and Bruker AMX 400 spectrophotometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); qu(quintet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); td (triplets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). High Resolution Mass (**HRMS**) spectra were obtained using Finnigan MAT95XP GC/HRMS (Thermo Electron Corporation).Mass spectral data were reported in units of mass to charge (m/z) and relative intensity (**RI**). X-Ray crystallography analysis was performed on Bruker X8 APEX X-Ray diffractometer.

General procedure for preparation of polyene



The procedure was following the method developed by Martin Demuth.[1] To an oven-dried 100mL round-bottom flask with a magnetic stirring bar was added [$(Ph_3P)_4$-Pd] (0.25 mmol, 5 mol%) and dry THF (20 mL). The solution was cooled to 0^oC prior to addition of allylic bromide (5.0 mmol, 1.0 eq.). The solution was stirred for 5 minutes and was treated with the Grignard reagent (7.5 mmol in 1.0M THF solution, 1.5 eq.). The reaction mixture was allowed to proceed at room temperature for another 24 hours before quenching with ice water 30 mL. The aqueous layer was extracted with diethyl ether (2 × 30 mL), and the combined organic extracts were washed with water (30 mL) and brine (30 mL) and dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The residual crude product was purified by column chromatography to afford the desired product.



(*E*)-(4,8-Dimethylnona-3,7-dienyl)benzene (**6a**): colorless oil, 86% yield.

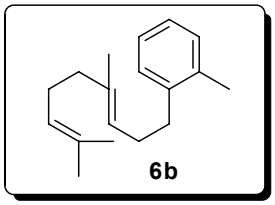
R_f: 0.91 (Hexane : Et_2O = 9:1)

^1H NMR(400 MHz, $CDCl_3$): 7.30–7.20 (m, 5H), 5.21 (tq, *J* = 7.1, 1.2 Hz, 1H), 5.11 (tt *J* = 6.8, 1.4 Hz, 1H), 2.66 (t, *J* = 6.7 Hz, 2H), 2.34 (dt, *J* = 7.7, 7.6 Hz, 2H), 2.08 (t, *J* = 7.1, 6.6 Hz, 2H), 2.01 (t, *J* = 7.1 Hz, 2H), 1.71(s, 3H), 1.58 (s, 3H), 1.63 (s, 3H)

^{13}C NMR(100 MHz, $CDCl_3$): 142.5, 135.8, 131.4, 128.5, 128.2, 125.7. 124.4, 123.6, 39.8, 36.2, 30.0, 26.7, 25.7, 17.7, 16.0

HRMS (EI): *m*/*z* calculated for $C_{17}H_{24}$ $[M]^+$: 228.1878 Found: 228.1877

FTIR (KBr): ν 3085, 2923, 1653, 1604, 1496, 1453, 1376, 1108, 1030, 836, 746, 698 cm^{-1}



(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-2-methylbenzene (**6b**): colorless oil, 68% yield.

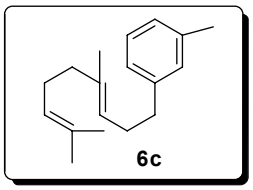
R_f: 0.91 (Hexane : Et_2O = 9:1)

^1H NMR (400 MHz, $CDCl_3$): 7.20–7.10 (m, 4H), 5.27 (t, *J* = 6.1, 1H), 5.15 (m, 1H), 2.66 (m, 2H), 2.37 (s, 3H), 2.27–2.31 (m, 2H), 2.15–2.09 (m, 2H), 2.06–2.01 (m, 2H), 1.74 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 140.6, 135.9, 135.8, 131.4, 130.1, 128.9, 125.9, 125.8, 124.4, 123.8, 39.7, 33.4, 28.7, 26.7, 25.7, 19.3, 17.7, 15.9

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}$ $[M]^+$: 242.2035, Found: 242.2022

FTIR (KBr): ν 2924, 1491, 1449, 1437, 1383, 1320, 741, 698 cm^{-1}



(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-3-methylbenzene (**6c**): colorless oil, 63% yield.

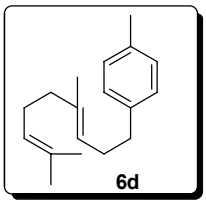
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.23–7.19 (m, 1H), 7.05–7.03 (m, 3H), 5.24 (tq, *J* = 6.8,1.2 Hz, 1H), 5.14 (tt, *J* = 7.9, 1.5 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 2.37–2.31 (m, 2H), 2.14–2.09 (m, 2H), 2.05–2.01 (m, 2H), 1.74 (s, 3H), 1.65 (s, 3H), 1.62 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 137.7, 135.7, 131.4, 129.3, 128.2, 126.4, 125.5, 124.4, 123.8, 39.8, 36.1, 30.1, 26.8, 25.8, 21.5, 17.7, 16.0

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}$ $[M]^+$: 242.2035, Found: 242.2028

FTIR (KBr): ν 2922, 1608, 1489, 1448, 1375, 1107, 1093, 781, 698 cm^{-1}



(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-4-methylbenzene (**6d**): colorless oil, 61% yield.

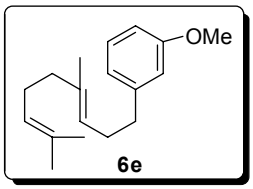
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.13–7.11 (m, 4H), 5.24 (tq, *J* = 6.1, 1.0 Hz, 1H), 5.16 (tt, *J* = 6.3,1.3 Hz, 1H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 2.34–2.31 (m, 2H), 2.14–2.07 (m, 2H), 2.05–2.02 (m, 2H), 1.66 (s, 3H), 1.64 (s, 3H), 1.52 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 139.4, 135.7, 135.1, 131.3, 128.9, 128.4, 124.4, 123.8, 39.8, 35.8, 30.2, 26.8, 25.8, 21.1, 17.7, 16.0

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}$ $[M]^+$: 242.2035, Found: 242.2031

FTIR (KBr): ν 2965, 2920, 2854, 1514, 1448, 1375, 808 cm^{-1}.



(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-3-methoxybenzene (**6e**): colorless oil , 63% yield.

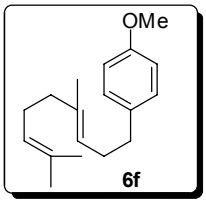
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.25–7.15 (m, 1H), 6.84–6.77 (m, 3H), 5.23 (tq, *J* = 7.1, 1.2 Hz, 1H), 5.13 (tt, *J* = 6.7, 1.2 Hz, 1H), 3.83 (s, 3H), 2.66(t, *J* = 7.4 Hz, 2H), 2.37–2.35 (m, 2H), 2.13–2.08 (m, 2H), 2.04–2.00 (m, 2H), 1.72 (s, 3H), 1.64 (s, 3H), 1.60 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 159.6, 144.1, 135.8, 131.4, 129.2, 124.4, 123.6, 120.9, 114.3, 110.9, 55.1, 39.8, 36.2, 29.9, 26.8, 25.7, 17.7, 16.0

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1980

FTIR (KBr): ν 2916, 2835, 1602, 1583, 1489, 1452, 1437, 1261, 1151, 1045, 777, 694 cm^{-1}



6f

(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-4-methoxybenzene (**6f**):colorless oil, 65% yield.

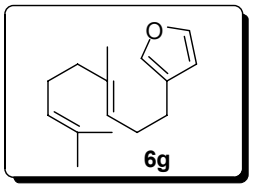
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.14–7.11 (m, 2H), 6.85–6.33 (m, 2H), 5.19 (tq, *J* = 6.9, 0.8 Hz, 1H), 5.11 (tt, *J* = 6.8, 1.3 Hz, 1H), 3.80 (s, 3H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.32-2.26 (m, 2H), 2.11–2.26 (m, 2H), 2.02–2.06 (m, 2H), 1.71 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 135.7, 134.6, 131.3, 129.4, 124.4, 123.7, 113.6, 55.3, 39.8, 35.2, 30.2, 26.7, 25.7, 17.7, 16.0

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1975

FTIR (KBr): ν 2962, 2922, 2833, 1612, 1512, 1454, 1440, 1300, 1246, 1176, 1039, 821 cm^{-1}



6g

(E)-3-(4,8-dimethylnona-3,7-dienyl)furan (**6g**): colorless oil, 65% yield.

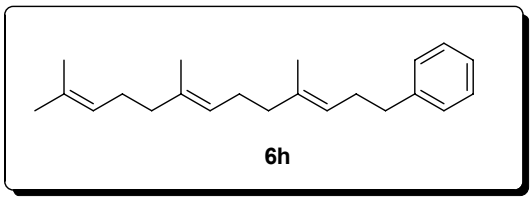
R_f: 0.95 (Hexane : Et_2O = 9:1)

^{1}H NMR (300 MHz, $CDCl_3$): 7.34 (t, *J* = 1.60 Hz, 1H), 7.22 (m, 1H), 6.29 (d, *J* = 0.9 Hz, 1H), 5.17 (td, *J* =7.0, 1.1 Hz, 1H), 5.09 (m, 1H), 2.46(t, *J* = 7.6 Hz, 2H), 2.25 (q, *J* = 7.3 Hz, 2H), 1.97 -2.11 (m, 4H), 1.69 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): 142.5, 138.8, 135.8, 131.4, 125.0, 124.3, 123.8, 111.1, 39.7, 28.5, 26.7, 25.7, 25.0, 17.7, 16.0.

HRMS (EI): *m*/*z* calculated for $C_{15}H_{22}O$ $[M]^+$: 218.1671, Found: 218.0437

FTIR (KBr): ν 2964, 2916, 2852, 1500, 1438, 1382, 1163, 1026, 873, 777 cm^{-1}



6h

(3*E*,7*E*)-4,8,12-trimethyltrideca-3,7,11-trienyl)benzene (6h), colorless oil, 87% yield.

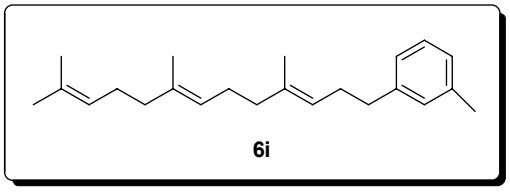
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.32–7.25 (m, 2H), 7.22–7.16 (m, 3H), 5.25–5.18 (m, 1H), 5.17–5.08 (m, 2H), 2.66 (t, *J* =7.9 Hz, 2H), 2.32 (q, *J* = 8.4 Hz, 2H), 2.09 (q, *J* = 6.6 Hz, 4H), 2.01 (q, *J* = 3.7 Hz, 4H), 1.71 (s, 3H), 1.62 (s, 6H), 1.64 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 135.8, 135.0, 131.3, 128.5, 128.2, 125.7, 124.4, 124.2, 123.6, 39.8, 39.7, 36.2, 30.0, 26.8, 26.6, 25.7, 17.7, 16.0, 16.0

HRMS (EI): *m*/*z* calculated for $C_{22}H_{32}$ $[M]^+$: 296.2504, Found: 296.2494

FTIR (KBr): ν 2965, 2920, 2855, 1495, 1452, 1381, 1029, 746, 698 cm^{-1}



6i

1-methyl-3-((3*E*,7*E*)-4,8,12-trimethyltrideca-3,7,11-trienyl)benzene (6i), colorless oil, 66% yield.

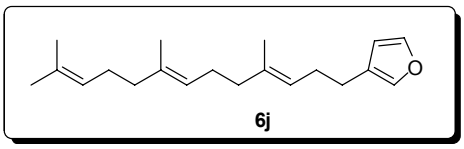
R_f: 0.91 (Hexane : Et_2O = 9:1)

^{1}H NMR (400 MHz, $CDCl_3$): 7.20–7.10 (m, 1H), 7.04–6.90 (m, 3H), 5.19 (td, *J* = 7.1, 1.3 Hz, 1H), 5.15–5.05 (m, 2H), 2.59 (dd, *J* = 9.7, 7.5 Hz, 2H), 2.32 (s, 3H), 2.33–2.23 (m, 2H), 2.13–2.02 (m, 4H), 2.02–1.93 (m, 4H), 1.68 (s, 3H), 1.56 (s, 6H), 1.51 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.4, 137.7, 135.7, 135.0, 131.3, 129.3, 128.1, 126.4, 125.5, 124.4, 124.2, 123.7, 39.8, 39.7, 36.1, 30.1, 26.8, 26.7, 25.7, 21.4, 17.7, 16.0, 16.0

HRMS (EI): *m*/*z* calculated for $C_{23}H_{34}$ $[M]^+$: 310.2661, Found: 310.2645

FTIR (KBr): ν 2965, 2918, 2853, 1608, 1443, 1383, 1094, 1041, 781, 698 cm^{-1}



6j

3-((3E,7E)-4,8,12-trimethyltrideca-3,7,11-trienyl)furan (6j): colorless oil, 70% yield.

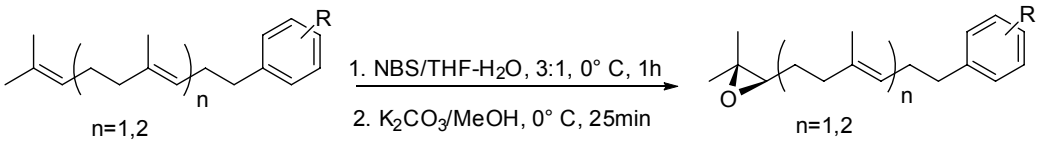
^{1}H NMR (300 MHz, $CDCl_3$): 7.24 (t, *J* = 1.6 Hz, 1 H), 7.21 (br. s, 1 H), 6.28 (d, *J* = 0.8 Hz, 1H), 5.18 (td, *J* = 7.0, 1.2 Hz, 1 H), 5.11 (m, 2 H), 2.46 (t, *J* = 6.9 Hz, 2 H), 2.25 (q, *J* = 7.3 Hz, 2 H), 1.96 – 2.07 (m, 8 H), 1.69 (s, 3H), 1.61 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): 142.5, 138.8, 135.8, 135.0, 131.3, 125.0, 124.4, 124.2, 123.7, 111.1, 39.7, 39.6, 28.5, 26.8, 26.6, 25.7, 25.1, 17.7, 16.1, 16.0.

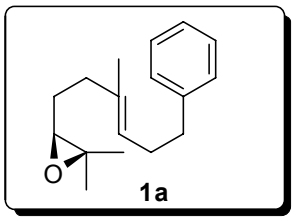
HRMS (EI): *m*/*z* calculated for $C_{20}H_{30}O$ $[M]^+$: 286.2297, Found: 286.2291

FTIR (KBr): ν 2965, 2918, 2853, 1500, 1440, 1383, 1165, 1064, 1026, 873, 777 cm^{-1}

General procedure for preparation of polyene 1a~1j



According to the procedure developed by van Tamelen[2, 3], epoxy olefins were easily prepared from polyenes. A total amount of NBS (3.35 mmol) in a THF-H_2O solution (68:32, 20 mL) in freshly prepared 4 mL portions was added dropwise to polyene (2.58 mmol) in a THF-H_2O solution (68:32, 25 mL) over 0.5 h at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then diluted with $CHCl_3$ (30 mL). The organic solution was washed with brine, dried (Na_2SO_4), and concentrated in vacuo to afford an oil. Chromatography on silica gel eluting with ethyl acetate-hexanes gave bromohydrin of about 30% yield**.** K_2CO_3 (2.65 mmol) was added to bromohydrin (2.65 mmol) in absolute MeOH (10 mL). the reaction mixture was stirred at room temperature for 30 min, diluted with H_2O, and extracted with CH_2Cl_2. The organic solution was washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give an oil. Chromatography on silica gel eluting with ethyl acetate-hexanes gave epoxide olefin of about 95% yield**.**



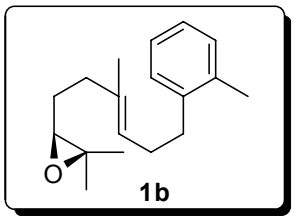
2,2-dimethyl-3-(3-methyl-6-phenylhex-3-enyl)oxirane (1a): colorless oil, 28% yield.

^{1}H NMR (300 MHz, $CDCl_3$): 7.17 -7.26 (m, 5 H), 5.29 (t, *J* = 7.2 Hz, 1 H), 2.67 (m, 3 H), 2.31 (m, 2 H), 2.02 – 2.20 (m, 2 H), 1.62-1.73 (m, 2H), 1.57 (s, 3 H), 1.30 (s, 3 H), 1.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): 142.3, 134.9, 128.5, 128.3, 125.7, 124.2, 64.1, 58.3, 36.3, 36.1, 29.9, 27.5, 24.9, 18.8, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{17}H_{24}O$ $[M]^+$: 244.1827, Found: 244.1830

FTIR (KBr): 3370, 2959, 2924, 1495, 1452, 1377, 1122, 876, 748, 698 cm^{-1}



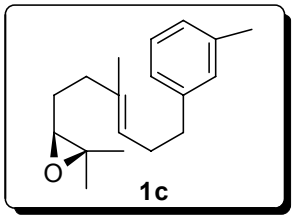
2,2-dimethyl-3-(3-methyl-6-o-tolylhex-3-enyl)oxirane (1b): colorless oil, 27% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.14 (m, 4 H), 5.30 (t, *J* = 6.4 Hz, 1 H), 2.73 (t, *J* = 6.3 Hz, 1 H), 2.65 (dd, *J* = 7.7, 8.2 Hz, 2 H), 2.35 (s, 3 H), 2.28 (m, 2 H), 2.08 – 2.22 (m, 2 H), 1.62-1.77 (m, 2H), 1.61 (s, 3 H), 1.33 (s, 3 H), 1.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 140.3, 135.7, 134.7, 130.0, 128.8, 125.8, 125.7, 124.3, 64.1, 58.2, 36.3, 33.3, 28.6, 27.4, 24.8, 19.3, 18.7, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1981

FTIR (KBr): 3370, 2960, 2926, 1491, 1456, 1377, 1122, 876, 740 cm^{-1}



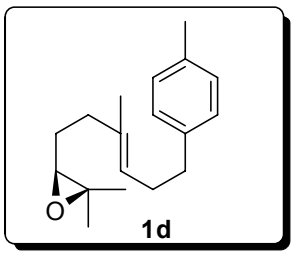
(E)-2,2-dimethyl-3-(3-methyl-6-m-tolylhex-3-enyl)oxirane (1c): colorless oil, 29% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.17 (t, *J* = 7.4 Hz, 1 H), 7.00 (m, 3 H), 5.24 (t, *J* = 6.9 Hz, 1 H), 2.70 (t, *J* = 6.2 Hz, 1 H), 2.61 (dd, *J* = 7.7, 8.2 Hz, 2 H), 2.34 (s, 3 H), 2.29 (m, 2 H), 2.05 – 2.22 (m, 2 H), 1.62-1.72 (m, 2H), 1.59 (s, 3 H), 1.30 (s, 3 H), 1.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 142.2, 137.7, 134.7, 129.2, 128.1, 126.4, 125.4, 124.3, 64.2, 58.3, 36.0, 30.0, 27.5, 24.9, 21.4, 18.7, 16.0.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1981

FTIR (KBr): 3406, 2960, 2922, 1608, 1485, 1450, 1377,1248, 1122, 876, 783, 700 cm^{-1}



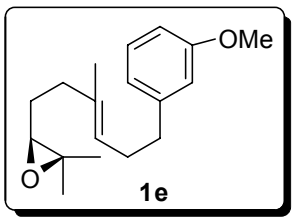
2,2-dimethyl-3-(3-methyl-6-p-tolylhex-3-enyl)oxirane (1d): colorless oil, 28% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.09 (m, 4 H), 5.24 (t, *J* = 7.1 Hz, 1 H), 2.69 (t, *J* = 6.1 Hz, 1 H), 2.61 (dd, *J* = 7.3, 8.3 Hz, 2 H), 2.32 (s, 3 H), 2.28 (m, 2 H), 2.04 – 2.20 (m, 2 H), 1.62-1.73 (m, 2H), 1.59 (s, 3 H), 1.30 (s, 3 H), 1.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 139.1, 135.1, 134.7, 128.8, 128.3, 124.3, 64.1, 58.3, 36.3, 35.6, 30.0, 27.4, 24.8, 20.9, 18.7, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1977

FTIR (KBr): 3368, 2958, 2956, 1514, 1449, 1437, 1377, 1120, 876, 806 cm^{-1}



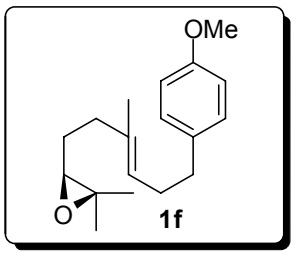
3-(6-(3-methoxyphenyl)-3-methylhex-3-enyl)-2,2-dimethyloxirane (1e): colorless oil, 28% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.19 (td, *J* = 7.4, 0.9 Hz, 1 H), 6.76 (m, 3 H), 5.23 (td, *J* = 7.0, 1.0 Hz, 1 H), 3.79 (s, 3 H), 2.69 (t, *J* = 6.3 Hz, 1 H), 2.62 (dd, *J* = 7.3, 8.1 Hz, 2 H), 2.30 (m, 2 H), 2.04 – 2.20 (m, 2 H), 1.60-1.73 (m, 2H), 1.59 (s, 3 H), 1.29 (s, 3 H), 1.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.6, 143.9, 134.9, 129.2, 124.2, 120.9, 114.2, 110.9, 64.1, 58.3, 55.1, 36.3, 36.1, 29.8, 27.4, 24.9, 18.7, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O_2$ $[M]^+$: 274.1933, Found: 274.1919

FTIR (KBr): 3387, 2958, 2922, 1600, 1584, 1487, 1454, 1437, 1377, 1261, 1151, 874, 779, 696 cm^{-1}



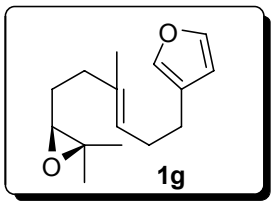
(E)-3-(6-(4-methoxyphenyl)-3-methylhex-3-enyl)-2,2-dimethyloxirane (1f): colorless oil, 28% yield.

^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, *J* = 8.6Hz, 2 H), 6.82 (d, *J* = 8.6Hz, 2 H), 5.22 (t, *J* = 6.9 Hz, 1 H), 3.78 (s, 3 H), 2.69 (t, *J* = 6.3 Hz, 1 H), 2.62 (dd, *J* = 7.3, 7.9 Hz, 2 H), 2.28 (q, *J* = 7.6Hz, 2 H), 2.04 – 2.20 (m, 2 H), 1.60-1.73 (m, 2H), 1.57 (s, 3 H), 1.29 (s, 3 H), 1.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): 157.7, 134.8, 134.4, 131.6, 129.3, 124.3, 113.7, 113.0, 64.2, 58.3, 55.2, 36.3, 35.1, 30.2, 27.4, 24.9, 18.7, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O_2$ $[M]^+$: 274.1933, Found: 274.1870

FTIR (KBr): 3340, 2959, 2924, 1612, 1512, 1454, 1443, 1377, 1246, 1176, 1037, 823 cm^{-1}



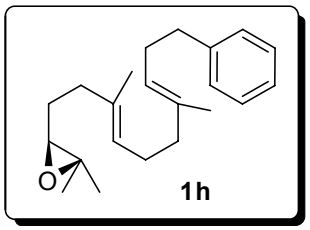
3-(6-(3,3-dimethyloxiran-2-yl)-4-methylhex-3-enyl)furan (1g): colorless oil, 29% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.32 (s, 1 H), 7.19 (s, 1 H), 6.26 (s, 1 H), 5.20 (dd, *J* = 6.9, 5.9 Hz, 1 H), 2.68 (t, *J* = 6.1 Hz, 1 H), 2.45 (dd, *J* = 7.1, 8.1 Hz, 2 H), 2.26 (m, 2 H), 2.04 – 2.20 (m, 2 H), 1.58-1.73 (m, 2H), 1.59 (s, 3 H), 1.28 (s, 3 H), 1.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 142.5, 138.8, 134.8, 124.8, 124.3, 110.9, 64.0, 58.3, 36.3, 28.4, 27.3, 24.9, 24.8, 18.7, 16.0.

HRMS (EI): *m*/*z* calculated for $C_{15}H_{22}O_2$ $[M]^+$: 234.1620, Found: 234.1613

FTIR (KBr): 3404, 2960, 2920, 1500, 1444, 1379, 1163, 1122, 1024, 874, 779 cm^{-1}



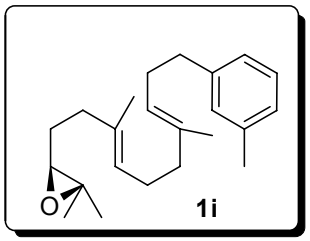
3-((3E,7E)-3,7-dimethyl-10-phenyldeca-3,7-dienyl)-2,2-dimethyloxirane (1h): colorless oil, 37% yield.

^{1}H NMR (300 MHz, $CDCl_3$): 7.14 -7.29 (m, 5 H), 7.00 (m, 3 H), 5.18 (m, 2 H), 2.70 (t, *J* = 6.2 Hz, 1 H), 2.64 (dd, *J* = 7.4, 8.2 Hz, 2 H), 2.29 (q, *J* = 7.6 Hz, 2 H), 1.96 – 2.20 (m, 6 H), 1.59-1.70 (m, 5 H), 1.55 (s, 3 H), 1.30 (s, 3 H), 1.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): 142.3, 135.6, 134.0, 128.5, 128.2, 125.6, 124.8, 123.7, 64.2, 58.3, 39.6, 36.3, 36.1, 30.0, 27.5, 26.6, 24.9, 18.8, 16.0, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{22}H_{32}O$ $[M]^+$: 312.2453, Found: 312.1124

FTIR (KBr): 3404, 2959, 2922, 2855, 1495, 1452, 1377, 1122, 1030, 876, 748, 698 cm^{-1}



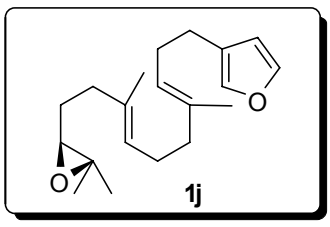
(3,7-dimethyl-10-*m*-tolydeca-3,7-dienyl)-2,2-dimethyloxirane (1i): colorless oil, 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.17 (t, *J* = 7.23 Hz, 1 H), 7.00 (m, 3 H), 5.18 (m, 2 H), 2.69 (t, *J* = 6.4 Hz, 1 H), 2.60 (dd, *J* = 7.7, 8.2 Hz, 2 H), 2.34 (s, 3 H), 2.29 (q, *J* = 7.6 Hz, 2 H), 1.96 – 2.20 (m, 6 H), 1.59-1.70 (m, 5 H), 1.58 (s, 3 H), 1.31 (s, 3 H), 1.27 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 142.3, 137.7, 135.5, 134.0, 129.3, 128.1, 126.4, 125.4, 124.8, 123.8, 64.2, 58.3, 39.6, 36.3, 36.1, 30.0, 27.5, 26.6, 24.9, 21.4, 18.8, 16.0, 15.9.

HRMS (EI): *m*/*z* calculated for $C_{23}H_{34}O$ $[M]^+$: 326.2610, Found: 326.1262

FTIR (KBr): 2958, 2922, 2855, 1608, 1487, 1449, 1377, 1248, 1122, 876, 781, 700 cm^{-1}



3-((3E,7E)-10-(3,3-dimethyloxiran-2-yl)-4,8-dimethyldeca-3,7-dienyl)furan (1j): colorless oil, 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$): 7.33 (br. s, 1 H), 7.20 (s, 1 H), 6.27 (s, 1 H), 5.15 (m, 2H), 2.70 (t, *J* = 6.3 Hz, 1 H), 2.44 (dd, *J* = 7.1, 8.2 Hz, 2 H), 2.23 (q, *J* = 7.4Hz, 2 H), 1.97 – 2.16 (m, 6 H), 1.54 – 1.69 (m, 8 H), 1.29 (s, 3 H), 1.26 (s, 3 H).

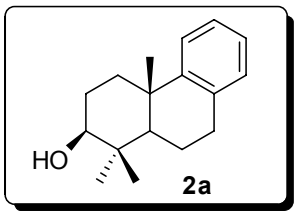
^{13}C NMR (100 MHz, $CDCl_3$): 142.6, 138.8, 135.6, 134.1, 124.9, 124.8, 123.8, 111.1, 64.2, 58.3, 39.6, 36.3, 28.4, 27.5, 26.5, 25.0, 24.9, 18.7, 16.0, 16.0.

HRMS (EI): *m/z* calculated for $C_{20}H_{30}O_2$ $[M]^+$: 302.2246, Found: 302.2235

FTIR (KBr): 3421, 2961, 2920, 2855, 1500, 1447, 1377, 1248, 1122, 874, 777 cm^{-1}

General procedure for preparation of polyene 2a~2i

To a solution of epoxy olefin (0.1 mmol, 1.0 eq.) in DCM (1 mL) was added indium bromide (71.0 mg, 0.2 mmol, 2.0 eq.) at room temperature. The reaction was allowed to stir at room temperature for 1 hour before quenching with saturated $NaHCO_3$ aqueous solution (5 mL). The aqueous layer was extracted with DCM (3 × 20 mL), and the combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residual crude product was purified by flash column chromatography.



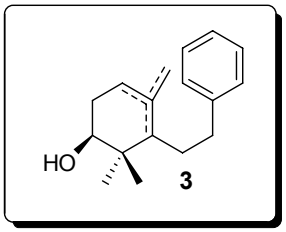
1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2a): White solid, yield: 57%.

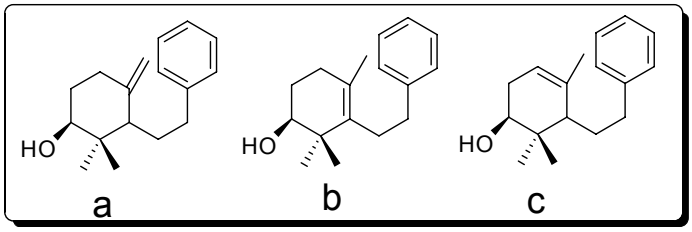
^{1}H NMR (400 MHz, $CDCl_3$): 7.24 (d, *J* =7.3 Hz, 1 H), 7.04–7.12 (m, 3H), 3.30 (dd, *J* = 11.0, 5.0 Hz, 1 H), 2.97 (dd, *J* = 16.9, 6.4 Hz, 1 H), 2.86 (ddd, *J* = 16.9, 11.5, 7.3 Hz, 1 H), 2.32 (dt, *J* = 13.0, 3.5 Hz, 1 H), 1.71-1.89 (m, 4 H), 1.57 (br. s, OH), 1.55 (td, *J* = 12.8, 4.6 Hz, 1 H), 1.33 (dd, *J* = 12.3, 2.2 Hz, 1H), 1.20 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.3, 135.0, 129.0, 125.7, 125.4, 124.5, 126.4, 125.5, 124.4, 78.7, 49.7, 39.0, 37.6, 36.9, 30.7, 28.1, 28.0, 24.9, 18.8, 15.4.

HRMS (EI): *m/z* calculated for $C_{17}H_{24}O$ $[M]^+$: 244.1827, Found: 244.1819

FTIR (KBr): 3306, 2970, 2933, 2876, 1487, 1435, 1217, 1092, 1026, 762 cm^{-1}





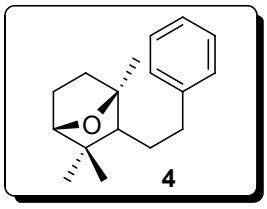
Monocyclic products, yield: mixture of isomers, isomer ratio: 1 : 1 : 2 based on ^{13}C NMR

^{1}H NMR (400 MHz, $CDCl_3$): 7.32–7.17 (m, 20H), 5.27 (bs, 2H), 4.95 (s, 1H), 4.72 (s, 1H), 3.54 (dd, *J* = 8.61, 2.48 Hz, 1H), 3.47 (dd, *J* = 8.08, 5.56 Hz, 2H), 3.41 (dd, *J* = 9.61, 4.04 Hz, 1H), 2.88–2.73 (m, 3H), 2.68–2.56 (m, 5H) 2.39 (m, 2H), 2.27 (m, 5H), 2.08 (t, *J* = 6.41Hz, 3H), 1.96 (m, 5H), 1.79 (m, 13H), 1.70 (m, 5H), 1.60 (m, 7H), 1.37 (m, 4H), 1.70 (m, 5H), 1.26 (s, 1H), 1.14 (s, 3H), 1.06 (s, 3H), 1.00 (s, 3H), 0.95 (s, 6H), 0.84 (s, 6H), 0.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.2, 143.0, 142.9, 142.7, 136.7, 135.2, 128.5, 128.4, 128.4, 128.3, 128.1,126.9, 125.8, 125.7, 118.7, 108.6, 77.2, 76.0, 74.9, 51.2, 48.9, 40.6, 40.2, 38.1, 38.0, 36.5, 34.9, 32.9, 32.2, 31.8, 31.4, 30.8, 29.7, 27.6, 26.7, 26.4, 25.9, 25.3, 22.6, 21.8, 19.7, 16.1, 15.7.

MS (EI): *m*/*z* calculated for $C_{17}H_{24}O$ $[M]^+$: 244.18, Found: 244.03, 244.05, 244.11.

FTIR (KBr): ν 3442 (br. s, OH), 2964, 2935, 1709, 1645, 1602, 1454, 1379, 1363, 1028, 750, 698 cm^{-1}



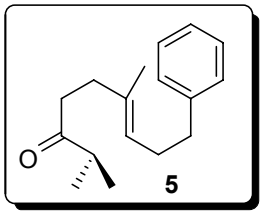
1,3,3-trimethyl-2-phenethyl-7-oxabicyclo[2.2.1]heptane (4): Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 7.17 – 7.30 (m, 5 H), 3.74 (d, *J* = 5.4 Hz, 1 H), 2.66 (ddd, *J* = 5.9, 10.6, 13.2 Hz, 1 H), 2.55 (ddd, *J* = 6.4, 10.0, 13.6 Hz, 1 H), 1.95 (ddd, *J* = 4.8, 8.8, 12.6 Hz, 1 H), 1.44-1.75 (m, 5 H), 1.38 (s, 3H), 1.30 (dd, *J* = 6.0, 8.5 Hz, 1 H), 1.13 (s, 3H), 1.11 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 142.8, 128.4, 128.3, 125.8, 86.7, 86.1, 55.5, 45.3, 39.0, 36.2, 30.0, 26.2, 25.8, 23.4, 18.9.

MS (EI): *m*/*z* calculated for $C_{17}H_{24}O$ $[M]^+$: 244.18, Found: $[M]^+$ + 1 245.10

FTIR (KBr): ν 2960, 1728, 1602, 1497, 1454, 1381, 1364, 1192, 999, 872, 698 cm^{-1}



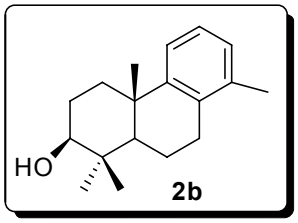
(E)-2,6-dimethyl-9-phenylnon-6-en-3-one (5): Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): 7.17 – 7.30 (m, 5 H), 5.18 (td, *J* = 6.9, 1.2 Hz, 1 H), 2.65 -2.49 (m, 5 H), 2.35 -2.19 (m, 4 H), 1.55 (s, 3H), 1.10 (s, 3H), 1.08 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): 214.5, 142.2, 134.7, 128.5, 128.2, 125.7, 124.1, 40.9, 39.1, 36.0, 33.5, 30.0, 18.3, 16.1.

MS (EI): *m*/*z* calculated for $C_{17}H_{24}O$ $[M]^+$: 244.18, Found: 244.13

FTIR (KBr): ν 2968, 2931, 1709, 1613, 1504, 1452, 1383, 1217, 756 cm^{-1}



1,1,4a,8-Tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2b): White solid, yield: 54%.

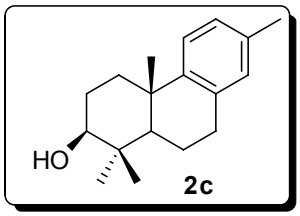
^{1}H NMR (400 MHz, $CDCl_3$): 7.14 (d, *J* =7.4 Hz, 1 H), 7.06 (dd, *J* =7.4, 6.9 Hz, 1 H), 6.97 (d, *J* = 6.9 Hz, 1 H), 3.30 (dd, *J* = 11.0, 4.7 Hz, 1 H), 2.83 (dd, *J* = 16.9, 6.6 Hz, 1 H), 2.63 (ddd, *J* = 16.9, 11.5, 7.7 Hz, 1 H), 2.33 (dt,

J = 13.2, 3.4 Hz, 1 H), 2.20 (s, 3H), 1.97 (dd, *J* = 13.3, 7.7 Hz, 1 H), 1.73-1.83 (m, 3 H), 1.53 (m, 1 H), 1.40 (br. s, OH), 1.32 (dd, *J* = 12.5, 1.9 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H), 0.90 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.4, 136.3, 133.6, 127.0, 125.6, 122.2, 78.7, 49.2, 38.9, 37.7, 37.3, 28.5, 28.1, 28.0, 25.0, 19.9, 18.7, 15.4.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1979

FTIR (KBr): 3426, 3007, 2966, 2943, 2868, 1471, 1454, 1375, 1215, 1088, 1034, 756 cm^{-1}



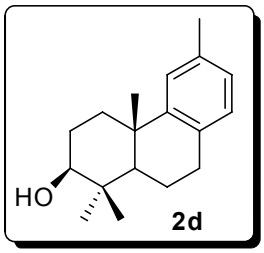
1,1,4a,7-Tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2c): White solid, yield: 51%.

^{1}H NMR (300 MHz, $CDCl_3$): 7.13 (d, *J* =8.1 Hz, 1 H), 6.95 (dd, *J* =8.1 Hz, 1 H), 6.87 (s, 1 H), 3.30 (dd, *J* = 11.0, 4.9 Hz, 1 H), 2.76 - 2.97 (m, *2* H), 2.31 (dt, *J* = 13.2, 3.2 Hz, 1 H), 2.27 (s, 3H), 1.72-1.69 (m, 4 H), 1.53 (m, 1 H), 1.40 (br. s, OH), 1.32 (dd, *J* = 12.1, 2.3 Hz, 1H), 1.21 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H)

^{13}C NMR (75 MHz, $CDCl_3$): 146.5, 134.9, 134.8, 129.5, 126.6, 124.4, 78.8, 49.9, 39.0, 37.3, 37.0, 30.6, 28.2, 28.0, 24.9, 20.8, 18.8, 15.4.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1974

FTIR (KBr): 3342, 2944, 2924, 2862, 1496, 1454, 1375, 1217, 1085, 1030, 813, 756 cm^{-1}



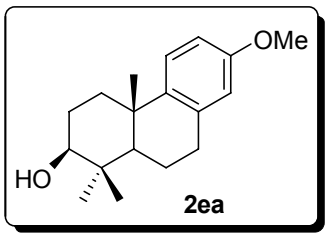
1,1,4a,6-Tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2d): White solid, yield: 51%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.04 (s, 1 H), 6.94 (d, *J* =8.0 Hz, 1 H), 6.90 (dd, *J* =8.0 Hz, 1 H), 3.30 (dd, *J* = 11.0, 4.9 Hz, 1 H), 2.77 - 2.96 (m, *2* H), 2.32 (dt, *J* = 13.0, 3.6 Hz, 1 H), 2.29 (s, 3H), 1.71-1.91 (m, 4 H), 1.54 (m, 1 H), 1.40 (br. s, OH), 1.32 (dd, *J* = 12.4, 2.4 Hz, 1H), 1.20 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 149.2, 135.0, 131.9, 128.9, 126.3, 125.0, 78.8, 49.9, 39.0, 37.6, 36.9, 30.3, 28.2, 28.0, 24.9, 21.3, 18.9, 15.4.

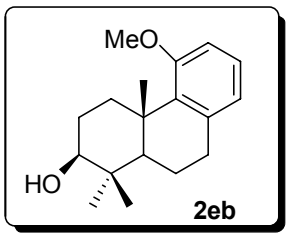
HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O$ $[M]^+$: 258.1984, Found: 258.1978

FTIR (KBr): 3400, 2944, 2964, 2943, 2868, 1502, 1454, 1375, 1217, 1089, 1030, 806 cm^{-1}



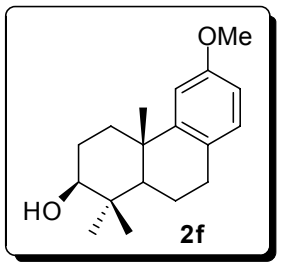
2ea

7-methoxy-1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2ea): White solid, yield: 37%.
^{1}H NMR (400 MHz, $CDCl_3$): 7.14 (d, *J* =8.7, 1 H), 6.69 (dd, *J* =8.7, 2.9 Hz, 1 H), 6.57 (d, *J* = 2.9 Hz, 1 H), 3.75 (s, 3H), 3.30 (dd, *J* = 10.6, 4.0 Hz, 1 H), 2.79 - 2.92 (m, 2 H), 2.28 (dt, *J* = 13.1, 3.3 Hz, 1 H), 1.68 - 1.90 (m, 4 H), 1.51 (td, *J* = 13.2, 4.6 Hz, 1 H), 1.40 (br. s, OH), 1.30 (dd, *J* = 12.2, 2.3 Hz, 1H), 1.17 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): 157.2, 141.9, 136.4, 125.6, 113.2, 112.0, 78.8, 55.1, 50.0, 38.9, 37.1, 30.9, 28.2, 28.0, 24.8, 24.9, 18.8, 15.4.
HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O_2$ $[M]^+$: 274.1933, Found: 274.1913
FTIR (KBr): ν 3396, 2964, 2941, 2835, 1606, 1573, 1499, 1473, 1242, 1033, 756 cm^{-1}



2eb

5-methoxy-1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2eb): White solid, yield: 40%.
^{1}H NMR (400 MHz, $CDCl_3$): 7.04 (dd, *J* =7.8, 6.6 Hz, 1 H), 6.67 (d, *J* =6.6, 1 H), 6.66 (d, *J* = 7.8 Hz, 1 H), 3.77 (s, 3H), 3.30 (m, 1 H), 3.16 (dt, *J* = 13.7, 3.5 Hz, 1 H), 2.86 (m, 2 H), 1.79 – 1.83 (m, 1 H), 1.79 – 1.83 (m, 1 H), 1.55 – 1.62 (m, 1 H), 1.40 (br. s, OH), 1.30 (dd, *J* = 12.2, 2.3 Hz, 1H), 1.20 – 1.30 (m, 2 H), 1.26 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 138.0, 136.7, 126.2, 122.2, 109.1, 78.8, 55.0, 52.7, 39.4, 39.3, 34.6, 33.1, 28.6, 28.3, 19.7, 18.7, 15.9, 15.4.
HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O_2$ $[M]^+$: 274.1933, Found: 274.1924
FTIR (KBr): ν 3426, 2966, 2934, 2868, 1608, 1573, 1454, 1242, 1215, 1032, 756 cm^{-1}



2f

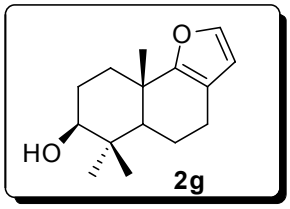
6-methoxy-1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2β-ol (2f): White solid, yield: 58%.
^{1}H NMR (400 MHz, $CDCl_3$): 6.96 (d, *J* =8.2, 1 H), 6.77 (d, *J* = 2.6 Hz, 1 H), 6.66 (dd, *J* = 8.2, 2.6 Hz, 1 H), 3.76 (s, 3H), 3.30 (dd, *J* = 10.8, 4.6 Hz, 1 H), 2.73 - 2.93 (m, 2 H), 2.26 (dt, *J* = 13.2, 3.4 Hz, 1 H), 1.67 - 1.90 (m, 4 H),

1.55 (td, *J* = 13.1, 4.7 Hz, 1 H), 1.41 (br. s, OH), 1.30 (dd, *J* = 12.1, 2.1 Hz, 1 H), 1.19 (s, 3 H), 1.06 (s, 3 H), 0.90 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 150.6, 129.8, 127.3, 110.9, 110.2, 78.7, 55.3, 49.7, 39.0, 37.8, 36.9, 29.8, 28.2, 28.0, 24.8, 18.9, 15.4.

HRMS (EI): *m*/*z* calculated for $C_{18}H_{26}O_2$ $[M]^+$: 274.1933, Found: 274.1893

FTIR (KBr): ν 3439, 2964, 2941, 2835, 1610, 1573, 1505, 1454, 1258, 1039, 806 cm^{-1}



2g

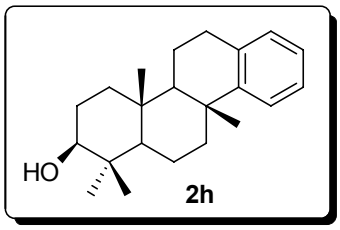
6,6,9a-trimethyl-4,5,5a,6,7,8,9,9a-octahydronaphtho[1,2-b]furan-2β-ol (2g): White solid, yield: 58%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.18 (d, *J* =1.8 Hz, 1 H), 6.12 (d, *J* = 1.8 Hz, 1 H), 3.30 (dd, *J* = 10.8, 4.6 Hz, 1 H), 2.51 (m, 1 H), 2.36 (m, 1 H), 2.14 (dt, *J* = 13.2, 3.5 Hz, 1 H), 1.59 - 1.86 (m, 4 H), 1.51 (td, *J* = 12.9, 3.5 Hz, 1 H), 1.36 (br. s, OH), 1.33 (dd, *J* = 12.1, 1.3 Hz, 1H), 1.19 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 140.3, 113.9, 110.0, 78.9, 51.5, 38.7, 36.2, 33.7, 28.2, 27.5, 22.8, 21.3, 19.4, 15.4.

HRMS (EI): *m*/*z* calculated for $C_{15}H_{22}O_2$ $[M]^+$: 234.1620, Found: 234.1605

FTIR (KBr): ν 3326, 2968, 2940, 1505, 1215, 1080, 1016, 756 cm^{-1}



2h

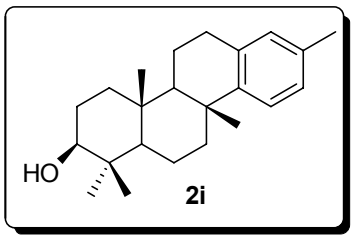
1,1,4a,10b-Tetramethyl-1,2,3,4,4a,5,6,6b,11,12,12a,12b-dodecahydrochrysen-2β-ol (2h): White solid, yield: 35%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.24 (d, *J* =8.2 Hz, 1 H), 7.12 (td, *J* =8.2, 1.35 Hz, 1 H), 7.06 (td, *J* =7.6, 1.35 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 3.20 (dd, *J* = 11.0, 5.0 Hz, 1 H), 2.92 (dd, *J* = 17.1, 5.2 Hz, 1 H), 2.82 (ddd, *J* = 17.1, 11.3, 7.1, Hz, 1 H), 2.41 (dt, *J* = 12.4, 2.8 Hz, 1 H), 1.84 (m, 2 H), 1.65 - 1.74 (m, 4 H), 1.45 - 1.62 (m, 2 H), 1.35 (br. s, OH), 1.25 (dd, *J* = 12.0, 2.0 Hz, 1H), 1.19 (s, 3H), 1.01 (td, *J* = 12.6, 4.8 Hz, 1 H), 0.99 (s, 3H), 0.94 (s, 3H), 0.84 (dd, *J* = 12.1, 2.1 Hz, 1 H), 0.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 150.0, 135.0, 128.8, 125.7, 125.2, 124.6, 78.9, 55.12, 55.08, 40.6, 38.8, 38.3, 38.0, 37.4, 30.8, 28.0, 27.3, 26.1, 18.8, 18.1, 16.3, 15.3.

HRMS (EI): *m*/*z* calculated for $C_{22}H_{32}O$ $[M]^+$: 312.2453, Found: 312.1132

FTIR (KBr): ν 3446, 2992, 2964, 2934, 2868, 1479, 1449, 1028, 669 cm^{-1}



2i

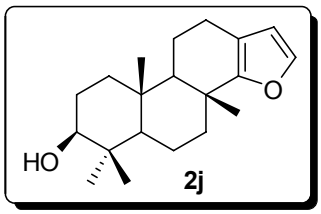
1,1,4a,8,10b-Pentamethyl-1,2,3,4,4a,5,6,6b,11,12,12a,12b-dodecahydrochrysen-2β-ol (2i): White solid, yield: 31%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.13 (d, *J* =8.1 Hz, 1 H), 6.93 (d, *J* =8.1Hz, 1 H), 6.84 (s, 1 H), 3.20 (dd, *J* = 10.8, 5.2 Hz, 1 H), 2.89 (dd, *J* = 16.3, 5.8 Hz, 1 H), 2.78 (ddd, *J* = 17.0, 11.4, 7.3, Hz, 1 H), 2.39 (dt, *J* = 9.3, 2.9 Hz, 1 H), 2.26 (s, 3H), 1.82 (m, 2 H), 1.57 - 1.76 (m, 4 H), 1.42 - 1.60 (m, 2 H), 1.33 (br. s, OH), 1.24 (m, 1H), 1.18 (s, 3H), 1.04 (td, *J* = 11.6, 5.0 Hz, 1 H), 0.99 (s, 3H), 0.93 (s, 3H), 0.84 (dd, *J* = 9.6, 2.5 Hz, 1 H), 0.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 147.2, 134.9, 134.6, 129.4, 126.6, 124.6, 78.9, 55.3, 55.2, 40.7, 38.9, 38.3, 37.7, 37.3, 30.7, 28.0, 27.3, 26.1, 20.8, 18.8, 18.1, 16.3, 15.3.

HRMS (EI): *m*/*z* calculated for $C_{23}H_{34}O$ $[M]^+$: 326.2610, Found: 326.1228

FTIR (KBr): ν 3452, 2988, 2962, 2930, 2868, 1496 1435, 1359, 1215, 756, 669 cm^{-1}



2j

3b,6,6,9a-tetramethyl-3b,4,5,5a,6,7,8,9,9a,9b,10,11-dodecahydrophenanthro[1,2-b]furan-2β-ol (2j): White solid, yield: 37%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.20 (d, *J* =1.8 Hz, 1 H), 6.12 (d, *J* = 1.8 Hz, 1 H), 3.30 (dd, *J* = 11.1, 4.9 Hz, 1 H), 2.21 - 2.53 (m, 3 H), 1.81 (dd, *J* = 13.1, 4.0 Hz, 2H), 1.21 - 1.73 (m, 8 H), 1.13 (m, 1 H), 1.35 (br. s, OH), 1.21 (s, 3H), 0.99 (s, 3H), 0.90 (s, 3H), 0.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 159.6, 140.1, 113.6, 110.0, 78.8, 56.7, 55.6, 39.0, 38.3, 37.0, 37.0, 36.7, 28.0, 27.2, 25.5, 22.9, 22.4, 18.6, 18.0, 16.5, 15.2.

HRMS (EI): *m*/*z* calculated for $C_{20}H_{30}O_2$ $[M]^+$: 302.2246, Found: 302.2221

FTIR (KBr): ν 3479, 2957, 2928, 2866, 2849, 1504, 1454, 1382, 1215, 1024, 756, 667 cm^{-1}

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3. Zoretic, P. A.; Fang, H. Q., *J. Org. Chem.*, **1998**, *63*, 7213-7217.