Highly Efficient Kinetic Resolution of
Bishomoallylic Alcohols: Synthesis of *R*-Sulcatol

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Supplementary Material

Supporting Information

General

Experiments involving moisture and/or air sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification with following exceptions: Hexane, dichloromethane, ethyl acetate were fractionally distilled. Aldehydes were distilled before used.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F₂₅₄ pre-coated 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 packed as a slurry using hexane and were equilibrated with the appropriate solvent system prior to loading. The analyte was loaded as a concentrated solution with the appropriate solvent system or in minimum dichloromethane.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. Liquid samples were examined as film between NaCl salt plates.

Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Bruker Avance DPX 300 spectrophotometer (CDCl₃ as solvent). Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from tetramethylsilane (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), tt (triplet of triplet), 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).

Chiral high performance liquid chromatography (HPLC) was performed on a JASCO HPLC system comprising of DG-980-50 3-Line Degasser, LG-980-02 Ternary Gradient Unit, PU-980 Intelligent HPLC Pump, UV 975 Intelligent UV/VIS Detector and AS-950 Intelligent Sampler, and employing a Daicel Chiralcel OD or Daicel Chiralpak AD column.

Mass spectrometries were performed by the staff from the Chemical and Molecular Analysis Center of the National University of Singapore. Mass spectral data were reported in units of mass to charge (m/z) and % intensity.

Optical rotation was measured using a JASCO DIP-1000 Digital Polarimeter equipped with a sodium vapour lamp at 589nm.

Systematic nomenclature for the compounds follows the numbering system as defined by IUPAC. Compounds were named using the CS ChemOffice 8.0 ChemDraw Ultra program.

General Reaction Procedure:

To a solution of bishomoallylic alcohol **1** (0.3 mmol, 1 equiv.) and steroidal aldehyde **2** (0.3 mmol, 1 equiv.) in CH₂Cl₂ under nitrogen was added In(OTf)₃ (0.03 mmol, 0.1 equiv.) at room temperature with stirring. The mixture was stirred for 4 h. The resolved bishomoallylic alcohol **1** was converted to its corresponding 3,5-dinitrobenzoic ester directly after the reaction.

Purification by silica gel flash column chromatography afforded the desired product.

Data

1-(Benzyloxy)-7-methyloct-6-en-3-ol, 1a

R_f: 0.40 (n-hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: [M]⁺ = 248.1776; found: [M]⁺: 248.1766

FTIR (NaCl, neat): 3415, 2926, 2865, 1717, 1452, 1096, 1075, 739, 699 cm⁻¹

¹H NMR (300 MHz, CDCl₃): δ 7.35–7.26 (m, 5H), 5.13 (tt, *J* = 6.97, 1.39 Hz, 1H), 4.53 (s, 2H), 3.85–3.78 (m, 1H), 3.73–3.62 (m, 2H), 2.14–2.05 (m, 2H), 1.78–1.74 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.57–1.44 (m, 2H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 137.9 (C), 131.6 (C), 128.3 (2C, CH), 127.6 (CH), 127.5 (2C, CH), 124.1 (CH), 73.1 (CH₂), 70.6 (CH), 68.9 (CH₂), 37.3 (CH₂), 36.3 (CH₂), 25.6 (CH₃), 24.1 (CH₂), 17.5 (CH₃) ppm

1-(Benzyloxy)-7-methyloct-6-en-3-yl 3,5-dinitrobenzoate

R_f: 0.55 (n-hexane:ethyl acetate = 4:1)

Selectivity: >99% ee (*R_t* = 24.31, 26.73 min; chiralcel OD column; n-hexane:isopropanol = 99:1; Flow rate: 0.5 mL/min)

FTIR (NaCl, neat): 2961, 2864, 1729, 1546, 1345, 1279, 731, 721 cm⁻¹

[α]²⁵: -4.31° (c = 0.0260 g/mL, CH₂Cl₂, >99% ee)

¹H NMR (300 MHz, CDCl₃): δ 9.10 (t, *J* = 2.09 Hz, 1H), 9.00 (d, *J* = 2.09 Hz, 2H), 7.17–7.11 (m, 5H, **Ph**), 5.47–5.39 (m, 1H), 5.10 (tt, *J* = 6.97, 1.39 Hz, 1H), 4.37 (s, 2H), 3.60 (t, *J* = 5.23 Hz, 2H), 2.10–2.00 (m, 2H), 1.91–1.67 (m, 4H), 1.64 (s, 3H), 1.55 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 162.3 (C), 148.2 (2C,C), 137.9 (C), 134.5 (C), 132.7 (C), 129.3 (2C, **CH**), 128.1 (2C, **CH**), 127.7 (2C, **CH**), 127.5 (**CH**), 123.0 (**CH**), 122.0 (**CH**), 75.4 (**CH**), 73.2 (**CH₂**), 67.2 (**CH₂**), 34.5 (**CH₂**), 34.4 (**CH₂**), 25.7 (**CH₃**), 24.0 (**CH₂**), 17.7 (**CH₃**) ppm

(10R,13S,17R)-17-((S)-1-((2R,3R,6R)-6-(2-(benzyloxy)ethyl)-tetrahydro-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-1,7,8,10,11,12,13,15,16,17-decahydro-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one, 3a

R_f: 0.48 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): cald: $[M]^+$ = 558.4073; found: $[M]^+$: 558.4080

FTIR (NaCl, neat): 2940, 1670, 1451, 1377, 1102, 737, 699 cm^{-1}

$[\alpha]^{25}$: +30.44° (c = 0.0497 g/mL, CH_2Cl_2)

1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.32 (m, 5H), 5.73 (br s, 1H), 4.72 (s, 2H), 4.52–4.49 (m, 2H), 3.63–3.53 (m, 2H), 3.42–3.35 (m, 1H), 3.25 (dd, J = 10.11, 1.05 Hz, 1H), 1.18 (s, 3H), 0.88 (d, J = 6.27 Hz, 3H), 0.66 (s, 3H) ppm

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 199.7 (C), 171.7 (C), 146.9 (C), 138.7 (C), 128.3 (2C, CH), 127.5 (2C, CH), 127.5 (CH), 123.7 (CH), 111.8 (CH₂), 80.9 (CH), 74.5 (CH), 73.1 (CH₂), 67.2 (CH₂), 55.9 (CH), 53.8 (CH), 52.3 (CH), 45.7, 42.0 (C), 39.7 (CH₂), 38.6 (C), 36.7 (CH), 36.4 (CH₂), 35.7 (CH), 35.7 (CH₂), 34.0 (CH₂), 32.9 (CH₂), 32.0 (2C, CH₂), 30.5 (CH₂), 27.6 (CH₂), 24.0 (CH₂), 21.1 (CH₂), 19.7 (CH₃), 17.4 (CH₃), 12.4 (CH₃), 11.8 (CH₃) ppm

2,7-Dimethyloct-6-en-3-ol, 1b

R_f: 0.45 (n-hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): cald: $[\text{M}]^+ = 156.1514$; found: $[\text{M}]^+ : 156.1514$

FTIR (NaCl, neat): 3379, 2962, 2931, 1466, 1377, 1057 cm^{-1}

^1H NMR (300 MHz, CDCl_3): δ 5.13 (t, $J = 6.97$ Hz, 1H), 3.38–3.32 (m, 1H), 2.22–2.00 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.54–1.33 (m, 3H), 0.90 (d, $J = 2.09$ Hz, 3H), 0.88 (d, $J = 2.09$ Hz, 3H) ppm

^{13}C NMR (75.4 MHz, CDCl_3): δ 131.9 (C), 124.3 (CH), 76.4 (CH), 34.0 (CH_2), 33.5 (CH), 25.7 (CH_3), 24.7 (CH_2), 18.8 (CH_3), 17.6 (CH_3), 17.1 (CH_3) ppm

2,7-Dimethyloct-6-en-3-yl 3,5-dinitrobenzoate

R_f: 0.70 (n-hexane:ethyl acetate = 4:1)

Selectivity: >99% ee ($R_t = 7.52, 8.38$ min; chiralcel OD column; n-hexane:isopropanol = 99:1; Flow rate: 1 mL/min)

FTIR (NaCl, neat): 2967, 2932, 1729, 1548, 1345, 1279, 731, 722 cm^{-1}

$[\alpha]^{25}$: -23.08° (c = 0.0208 g/mL, CH_2Cl_2 , >99% ee)

¹H NMR (300 MHz, CDCl₃): δ 9.22 (t, *J* = 2.10 Hz, 1H), 9.15 (d, *J* = 2.10 Hz, 2H), 5.14–5.07 (m, 2H), 2.08–2.00 (m, 2H), 1.86–1.66 (m, 3H), 1.62 (s, 3H), 1.54 (s, 3H), 1.00 (d, *J* = 2.79 Hz, 3H), 0.98 (d, *J* = 2.79 Hz, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 162.3 (C), 148.7 (2C,C), 134.4 (C), 132.5 (C), 129.3 (2C,CH), 123.2 (CH), 122.2 (CH), 81.8 (CH), 31.6 (CH), 31.0 (CH₂), 25.6 (CH₃), 24.3 (CH₂), 18.5 (CH₃), 17.7 (CH₃), 17.6 (CH₃) ppm

(10R,13S,17R)-1,7,8,10,11,12,13,15,16,17-decahydro-17-((S)-1-((2R,3R,6R)-tetrahydro-6-isopropyl-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one, 3b

C₃₂H₅₀O₂
Exact Mass: 466.3811
Mol. Wt.: 466.7382

R_f: 0.53 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: [M]⁺ = 466.3811; found: [M]⁺: 466.3813

FTIR (KBr, pellet): 2942, 1665, 1266, 1069, 739 cm⁻¹

[α]²⁵: +42.29° (c = 0.0647 g/mL, CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃): δ 5.72 (br s, 1H), 4.75–4.72 (m, 2H), 3.21 (dd, *J* = 10.08, 1.74 Hz, 1H), 1.17 (s, 3H), 0.92 (d, *J* = 6.96 Hz, 3H), 0.89 (d, *J* = 6.24 Hz, 3H), 0.86 (d, *J* = 6.96 Hz, 3H), 0.66 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 199.7 (C), 171.8 (C), 147.1 (C), 123.7 (CH), 111.6 (CH₂), 82.9 (CH), 80.8 (CH), 55.8 (CH), 53.8 (CH), 52.2 (CH), 45.7 (CH), 42.0 (C), 39.7 (CH₂), 38.6 (C), 36.9 (CH), 35.7 (CH), 35.6 (CH₂), 33.9 (CH₂), 33.3 (CH), 32.9 (CH₂), 32.0 (CH₂), 30.6 (CH₂), 28.7 (CH₂), 27.6 (CH₂), 24.0 (CH₂), 21.1 (CH₂), 19.7 (CH₃), 18.8 (CH₃), 18.6 (CH₃), 17.4 (CH₃), 12.4 (CH₃), 11.8 (CH₃) ppm

1-Cyclohexyl-5-methylhex-4-en-1-ol, 1c

R_f: 0.55 (n-hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: $[M]^+$ = 196.1827; found: $[M]^+$: 196.1826

FTIR (NaCl, neat): 3322, 2926, 2851, 1447, 1347, 1088, 1062, 966 cm^{-1}

1H NMR (300 MHz, $CDCl_3$): δ 5.14 (tt, J = 6.97, 1.39 Hz, 1H), 3.39–3.33 (m, 1H), 2.21–1.98 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 1.57–0.97 (m, 12H) ppm

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 131.7 (C), 124.3 (CH), 75.8 (CH), 43.6 (CH), 34.0 (CH₂), 29.2 (CH₂), 27.7 (CH₂), 26.5 (CH₂), 26.3 (CH₂), 26.2 (CH₂), 25.6 (CH₃), 24.6 (CH₂), 17.6 (CH₃) ppm

1-Cyclohexyl-5-methylhex-4-enyl 3,5-dinitrobenzoate

R_f: 0.70 (n-hexane:ethyl acetate = 4:1)

Selectivity: >99% ee (R_t = 63.09, 69.87 min; chiralpak AD column; n-hexane:isopropanol = 99:1; Flow rate: 0.1 mL/min)

FTIR (NaCl, neat): 2930, 2855, 1729, 1548, 1345, 1279, 731, 722 cm^{-1}

$[\alpha]^{25}$: -11.59° (c = 0.0270 g/mL, CH_2Cl_2 , >99% ee)

1H NMR (300 MHz, $CDCl_3$): δ 9.23 (t, J = 2.09 Hz, 1H), 9.15 (d, J = 2.09 Hz, 2H), 5.14–5.06 (m, 2H), 2.07–2.00 (m, 2H), 1.79–1.74 (m, 13H), 1.62 (s, 3H), 1.54 (s, 3H) ppm

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 162.3 (C), 148.7 (2C,C), 134.5 (C), 132.5 (C), 129.4 (2C, CH), 123.2 (CH), 122.2 (CH), 81.4 (CH), 41.5 (CH), 31.2 (CH₂), 29.1

(CH₂), 28.3 (CH₂), 26.3 (CH₂), 26.0 (CH₂), 26.0 (CH₂), 25.7 (CH₃), 24.7 (CH₂), 17.7 (CH₃) ppm

(10R,13S,17R)-17-((S)-1-((2R,3R,6R)-6-cyclohexyl-tetrahydro-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-1,7,8,10,11,12,13,15,16,17-decahydro-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one, 3c

C₃₅H₅₄O₂
Exact Mass: 506.4124
Mol. Wt.: 506.8021

R_f: 0.53 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: [M]⁺ = 506.4142; found: [M]⁺: 506.4128

FTIR (KBr, pellet): 2928, 1673, 1447, 1378 cm⁻¹

[α]²⁵: +36.02° (c = 0.0804 g/mL, CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃): δ 5.71 (br s, 1H), 4.73–4.70 (m, 2H), 3.19 (dd, *J* = 10.11, 1.41 Hz, 1H), 1.17 (s, 3H), 0.88 (d, *J* = 6.24 Hz, 3H), 0.65 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 199.7 (C), 171.9 (C), 147.2 (C), 123.7 (CH), 111.6 (CH₂), 82.2 (CH), 80.9 (CH), 55.7 (CH), 53.7 (CH), 52.2 (CH), 45.9 (CH), 43.1 (CH), 42.1 (C), 39.7 (CH₂), 38.6 (C), 36.9 (CH), 35.7 (CH), 35.7 (CH₂), 34.0 (CH₂), 33.0 (CH₂), 32.0 (CH₂), 30.7 (CH₂), 29.1 (CH₂), 28.9 (CH₂), 28.8 (CH₂), 27.6 (CH₂), 26.7 (CH₂), 26.3 (CH₂), 26.2 (CH₂), 24.1 (CH₂), 21.1 (CH₂), 19.7 (CH₃), 17.4 (CH₃), 12.5 (CH₃), 11.8 (CH₃) ppm

Single crystal x-ray diffraction analysis of 3c:

Empirical formula	C ₃₅ H ₅₄ O ₂
Formula weight	506.78
Temperature	223(2)K
Wavelength	0.71073Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 6.2915(10)Å α = 90° b = 16.082(3) Å β = 90° c = 30.679(5) Å γ = 90°
Volume	3104.1(9)Å ³
Z	4
Density (calculated)	1.084 Mg/m ³
Absorption coefficient	0.065 mm ⁻¹
F(000)	1120
Crystal size	0.38 × 0.28 × 0.16 mm ³
Theta range for data collection	1.83 to 27.50°
Index ranges	-8 ≤ h ≤ 8, -20 ≤ k ≤ 20, -39 ≤ l ≤ 39
Reflections collected	30138
Independent reflections	7123 [R(int) = 0.0569]
Completeness to theta = 27.50°	99.9%
Absorption correction	Sadabs, (Sheldrick 2001)
Max. and min. transmission	0.9897 and 0.9759
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7123 / 15 / 358
Goodness-of-fit on F ²	1.102
Final R indices [I>2sigma(I)]	R1 = 0.0830, wR2 = 0.1702
R indices (all data)	R1 = 0.1117, wR2 = 0.1836
Absolute structure parameter	-3(2)
Largest diff. Peak and hole	0.284 and -0.197 e.Å ⁻³

5-Methyl-1-phenylhex-4-en-1-ol, 1d

R_f: 0.55 (n-hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: $[M]^+$ = 190.1358; found: $[M]^+$: 190.1354

FTIR (NaCl, neat): 3360, 2922, 2856, 1451, 1061, 760, 701 cm^{-1}

1H NMR (300 MHz, $CDCl_3$): δ 7.36–7.27 (m, 5H), 5.15 (tt, J = 6.97, 1.39 Hz, 1H), 4.71–3.67 (m, 1H), 2.12–2.03 (m, 2H), 1.91–1.72 (m, 2H), 1.70 (s, 3H), 1.59 (s, 3H) ppm

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 144.7 (C), 132.2 (C), 128.3 (2C, CH), 127.4 (CH), 125.9 (2C, CH), 123.8 (CH), 74.1 (CH), 38.9 (CH₂), 25.7 (CH₃), 24.4 (CH₂), 17.7 (CH₃) ppm

5-Methyl-1-phenylhex-4-enyl 3,5-dinitrobenzoate

R_f: 0.70 (n-hexane:ethyl acetate = 4:1)

Selectivity: >99% ee (R_t = 12.03, 15.43 min; chiralcel OD column; n-hexane:isopropanol = 98:2; Flow rate: 1 mL/min)

FTIR (NaCl, neat): 2926, 2861, 1728, 1545, 1345, 1279, 1170, 721 cm^{-1}

$[\alpha]^{25}$: +20.06° (c = 0.0164 g/mL, CH_2Cl_2 , >99% ee)

1H NMR (300 MHz, $CDCl_3$): δ 9.22 (t, J = 2.09 Hz, 1H), 9.16 (d, J = 2.09 Hz, 2H), 7.45–7.27 (m, 5H), 6.06–6.02 (m, 1H), 5.14 (tt, J = 6.62, 1.39 Hz, 1H), 2.27–1.96 (m, 4H), 1.67 (s, 3H), 1.52 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 161.9 (C), 148.7 (2C,C), 139.2 (C), 134.2 (C), 133.1 (C), 129.4 (2C, CH), 128.8 (2C, CH), 128.6 (CH), 126.8 (2C, CH), 122.6 (CH), 122.3 (CH), 79.0 (CH), 35.9 (CH₂), 25.7 (CH₃), 24.2 (CH₂), 17.7 (CH₃) ppm

(10R,13S,17R)-1,7,8,10,11,12,13,15,16,17-decahydro-17-((S)-1-((2R,3R,6R)-tetrahydro-6-phenyl-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one, 3d

R_f: 0.40 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: [M]⁺ = 500.3654; found: [M]⁺: 500.3653

FTIR (NaCl, neat): 2940, 1669, 1450, 1266, 1063, 739, 700 cm⁻¹

[α]²⁵: +47.54° (c = 0.071 g/mL, CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃): δ 7.35–7.33 (m, 5H), 5.71 (br s, 1H), 4.82–4.79 (m, 2H), 4.33 (d, *J* = 10.8 Hz, 1H), 3.48 (d, *J* = 9.75 Hz, 1H), 1.17 (s, 3H), 1.02 (d, *J* = 5.94 Hz, 3H), 0.69 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 199.6 (C), 171.7 (C), 146.8 (C), 144.2 (C), 128.0 (2C, CH), 126.8 (CH), 125.4 (2C, CH), 123.7 (CH), 112.0 (CH₂), 81.2 (CH), 79.1 (CH), 55.7 (CH), 53.8 (CH), 51.9 (CH), 45.4 (CH), 42.1 (C), 39.6 (CH₂), 38.5 (C), 37.0 (CH₂), 35.7 (CH₂), 35.6 (CH₂), 34.5 (CH₂), 33.9 (CH₂), 32.9 (CH₂), 31.9 (CH₂), 30.7 (CH₂), 27.7 (CH₂), 24.0 (CH₂), 21.0 (CH₂), 19.8 (CH₃), 17.4 (CH₃), 12.5 (CH₃), 11.8 (CH₃) ppm

7-Methyl-1-phenyloct-6-en-3-ol, 1e

R_f: 0.43 (n-hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: $[M]^+$ = 218.1671; found: $[M]^+$: 218.1670

FTIR (NaCl, neat): 3361, 2926, 2858, 1452, 1080, 747, 699 cm^{-1}

1H NMR (300 MHz, $CDCl_3$): δ 7.31–7.16 (m, 5H), 5.13 (tt, J = 7.32, 1.38 Hz, 1H), 3.65–3.64 (m, 1H), 2.85–2.62 (m, 2H), 2.14–2.00 (m, 2H), 1.81–1.72 (m, 2H), 1.62 (s, 3H), 1.60 (s, 3H), 1.56–1.48 (m, 2H) ppm

^{13}C NMR (75.4 MHz, $CDCl_3$): δ 142.2 (C), 132.0 (C), 128.4 (2C, CH), 128.3 (2C, CH), 125.7 (CH), 124.0 (CH), 71.1 (CH), 39.1 (CH₂), 37.4 (CH₂), 32.0 (CH₂), 25.7 (CH₃), 24.3 (CH₂), 17.6 (CH₃) ppm

7-Methyl-1-phenyloct-6-en-3-yl 3,5-dinitrobenzoate

R_f: 0.55 (n-hexane:ethyl acetate = 4:1)

Selectivity: 92% ee (R_t = 11.85, 15.13 min; chiralcel OD column; n-hexane:isopropanol = 98:2; Flow rate: 1 mL/min)

FTIR (NaCl, neat): 2925, 2859, 1728, 1545, 1344, 1277, 1169, 721 cm^{-1} ;

$[\alpha]^{25}$: +11.33° (c = 0.0331 g/mL, CH_2Cl_2 , 92% ee);

1H NMR (300 MHz, $CDCl_3$): δ 9.20 (t, J = 2.09 Hz, 1H), 9.03 (d, J = 2.09 Hz, 2H), 7.23–7.04 (m, 5H), 5.32–5.26 (m, 1H), 5.09 (tt, J = 6.97, 1.39 Hz, 1H), 2.16–1.73 (m, 6H), 1.64 (s, 3H), 1.55 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 162.2 (C), 148.6 (2C,C), 141.1 (C), 134.2 (C), 132.7 (C), 129.3 (2C, CH), 128.5 (2C, CH), 128.3 (2C, CH), 125.9 (CH), 122.9 (CH), 122.2 (CH), 77.3 (CH), 35.3 (CH₂), 34.1 (CH₂), 31.9 (CH₂), 25.7 (CH₃), 24.0 (CH₂), 17.7 (CH₃) ppm

(10R,13S,17R)-1,7,8,10,11,12,13,15,16,17-decahydro-17-((S)-1-((2R,3R,6R)-tetrahydro-6-phenethyl-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one, 3e

C₃₇H₅₂O₂
Exact Mass: 528.3967
Mol. Wt.: 528.8076

R_f: 0.40 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: [M]⁺ = 528.3967; found: [M]⁺: 528.3966

FTIR (NaCl, neat): 2944, 1679, 1452, 1379, 880, 862, 759, 702 cm⁻¹

[α]²⁵: +18.16° (c = 0.0861 g/mL, CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃): δ 7.30–7.15 (m, 5H), 5.73 (br s, 1H), 4.77–4.73 (m, 2H), 3.22 (dd, *J* = 10.08, 1.41 Hz, 1H), 3.18–3.14 (m, 1H), 2.85–2.62 (m, 2H), 1.18 (s, 3H), 0.93 (d, *J* = 6.96 Hz, 3H), 0.69 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 199.6 (C), 171.7 (C), 147.0 (C), 142.5 (C), 128.5 (2C, CH), 128.2 (2C, CH), 125.6 (CH), 123.7 (CH), 111.7 (CH₂), 80.8 (CH), 76.4 (CH), 55.9 (CH), 53.7 (CH), 52.1 (CH), 45.8 (CH), 42.1 (C), 39.7 (CH₂), 38.6 (C), 37.8 (CH₂), 37.0 (CH), 35.7 (CH), 35.6 (CH₂), 33.9 (CH₂), 32.9 (CH₂), 32.0 (CH₂), 32.0 (CH₂), 31.8 (CH₂), 30.4 (CH₂), 27.8 (CH₂), 24.0 (CH₂), 21.0 (CH₂), 19.7 (CH₃), 17.4 (CH₃), 12.4 (CH₃), 11.7 (CH₃) ppm

6-methylhept-5-en-2-yl 3,5-dinitrobenzoate

R_f: 0.60 (n-hexane:ethyl acetate = 4:1)

Selectivity: 96% ee (R_t = 13.01, 14.58 min; chiralcel OD column; n-hexane:isopropanol = 99:1; Flow rate: 1 mL/min)

FTIR (NaCl, neat): 2976, 2926, 1728, 1546, 1345, 1280, 1171, 722 cm^{-1}

[α]²⁵: -34.47° (c = 0.0257 g/mL, CH_2Cl_2 , 98% ee)

¹H NMR (300 MHz, $CDCl_3$): δ 9.21 (t, J = 2.09 Hz, 1H), 9.14 (d, J = 2.09 Hz, 2H), 5.30–5.20 (m, 1H), 5.11 (tt, J = 6.97, 1.39 Hz, 1H), 2.13–2.06 (m, 2H), 1.93–1.67 (m, 2H), 1.65 (s, 3H), 1.56 (s, 3H), 1.41 (d, J = 6.27 Hz, 3H) ppm

¹³C NMR (75.4 MHz, $CDCl_3$): δ 162.0 (C), 148.6 (2C,C), 134.5 (C), 132.6 (C), 129.3 (2C, CH), 122.9 (CH), 122.1 (CH), 74.1 (CH), 35.7 (CH₂), 25.6 (CH₃), 24.0 (CH₂), 19.9 (CH₃), 17.6 (CH₃) ppm

(10R,13S,17R)-1,7,8,10,11,12,13,15,16,17-decahydro-17-((S)-1-((2R,3R,6S)-tetrahydro-6-methyl-3-(prop-1-en-2-yl)-2H-pyran-2-yl)ethyl)-10,13-dimethyl-2H-cyclopenta[a]phenanthren-3(6H,9H,14H)-one

R_f: 0.45 (hexane:ethyl acetate = 4:1)

HRMS (m/z, EI): calcd: $[M]^+$ = 438.3498; found: $[M]^+$: 438.3495

FTIR (NaCl, neat): 2933, 1679, 1445, 1381, 1074, 888 cm^{-1}

[α]²⁵: +49.33° (c = 0.1339 g/mL, CH_2Cl_2)

¹H NMR (300 MHz, CDCl₃): δ 5.70 (br s, 1H), 4.74–4.71 (m, 2H), 3.32–3.28 (m, 1H), 3.24 (d, *J* = 10.08 Hz, 1H), 1.16 (s, 3H), 1.11 (d, *J* = 6.27 Hz, 3H), 0.87 (d, *J* = 6.27 Hz, 3H), 0.65 (s, 3H) ppm

¹³C NMR (75.4 MHz, CDCl₃): δ 199.6 (C), 171.7 (C), 147.1 (C), 123.7 (CH), 111.7 (CH₂), 80.9 (CH), 73.9 (CH), 55.7 (CH), 53.8 (CH), 51.9 (CH), 45.5 (CH), 42.1 (C), 39.5 (CH₂), 38.6 (C), 36.6 (CH), 35.7 (CH), 35.6 (CH₂), 33.9 (CH₂), 33.7 (CH₂), 32.9 (CH₂), 32.0 (CH₂), 30.5 (CH₂), 27.6 (CH₂), 24.0 (CH₂), 22.1 (CH₃), 21.0 (CH₂), 19.7 (CH₃), 17.4 (CH₃), 12.4 (CH₃), 11.8 (CH₃) ppm