Supporting Information

Bismuth(III) Triflate-catalysed Tandem Cyclisations Towards Complex Polycyclic Ethers

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1 General Experimental
All reactions with air or moisture sensitive reagents were conducted in dried glassware under an atmosphere of nitrogen using anhydrous solvents. Unless otherwise stated, all reagents and catalysts were purchased with the classification reagent-grade and used as received from their suppliers without further purification. Solvents for flash and thin layer chromatography [petroleum ether (PE), ethyl acetate (EtOAC), diethyl ether (Et$_2$O), pentane (P)] were used as received without further purification.
All solvents for the use in reactions were freshly distilled. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were distilled from sodium/benzophenone ketyl, dichloromethane (CH$_2$Cl$_2$) and dimethylsulfoxide (DMSO) were dried by distillation over CaH$_2$. Methylolithium and tert-butyllithium were purchased as a 1.6 M solution in diethyl ether and a 1.9 M solution in pentane respectively and titrate before use.\[^{1}\]
Reactions were monitored by analytical Thin Layer Chromatography (TLC), which was performed on 0.20 mm precoated silica plates (Silica gel 60, F254, Macherey-Nagel). UV-active substances were detected by fluorescence detection with UV-light at wavelengths of 254 nm and 366 nm respectively. Detection of non UV-active substances was carried out by staining with p-anisaldehyde (0.7 mL p-anisaldehyde, 1.7 mL acetic acid and 9.5 mL conc. sulfuric acid in 250 mL ethanol), and subsequent heating. Separations via column chromatography were carried out on a CombiFlash® Rf+ (Teledyne Isco, USA), using CHROMABOND® Flash columns (Macherey-Nagel GmbH & Co. KG, Germany). UV-active substances were detected by fluorescence detection with UV-light at wavelengths of 254 nm and 366 nm respectively. Detection of non UV-active substances was carried out by staining with p-anisaldehyde (0.7 mL p-anisaldehyde, 1.7 mL acetic acid and 9.5 mL conc. sulfuric acid in 250 mL ethanol), and subsequent heating. Separations via column chromatography were carried out on a CombiFlash® Rf+ (Teledyne Isco, USA), using CHROMABOND® Flash columns (Macherey-Nagel GmbH & Co. KG, Germany). NMR spectra (\(^1\)H, \(^{13}\)C, COSY, DEPT135, HSQC, HMBC, NOESY) were recorded on a Bruker AV-200 or AV-500 spectrometer at a temperature of 300 K. Chemical shifts (\(\delta\)) are given in parts per million (ppm) and refer to the residual proton signal of the used solvent. In \(^1\)H-spectra the CDCl\(_3\) residual peak was applied as an internal standard with a chemical shift of 7.26 ppm. \(^{13}\)C-spectra were calibrated according to the deuterium-coupled signals of the used solvent (CDCl\(_3\) = 77.16 ppm).\(^1\) Coupling constants \(^1\)J are given in Hertz (Hz) and result from averaging of the experimentally found values. Spectral splitting patterns are designated as: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), sept. (septet), m (multiplet), m, (centered multiplet), br (broad), virt. (virtual). COSY, HSQC, HMBC, and NOESY correlations were established to identify the structures of some cyclic molecules. Infrared spectra were recorded on a Jasco FT/IR-4600 spectrometer. Samples were analyzed directly in substance with the attenuated total reflexion method (ATR). Absorption maxima are reported in wavenumbers (cm\(^{-1}\)) and characterised with the following symbols, according to their form and intensity: s (strong), m (medium), w (weak), b (broad). Analytical GC analyses were performed on a Shimadzu GC-2025 capillary gas chromatograph. Analytical GC/MS analyses were performed on a Shimadzu QP2010S-MS chromatograph (EI, 70 eV) equipped with a SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm). High resolution mass spectrometry (HRMS) was performed on a mass spectrometer LTQ-Orbitrap hybrid.
2 Experimental Procedures

2.1 Synthesis of the starting materials

2.1.1 Synthesis of dihydropyranyl and dihydrofuranyl derivatives 1a, 1b, 1c, 1l, 3a and 3b.

The starting dienols were generally synthesised in one step from the corresponding ketones, 2,3-dihydrofuran or 3,4-dihydro-1H-pyran using tert-butyllithium in THF at -78 °C. In the cases where the ketone was not directly available, different procedures were necessary.

General procedure 1: tert-BuLi mediated addition of enol ethers to aldehydes and ketones

To a 2 M solution of the enol ether (1.2–1.3 eq.) in anhydrous THF, tert-BuLi (1.9 M in pentane, 1.0 – 1.2 eq.) was added dropwise at -78 °C. The mixture was allowed to warm to -5 °C and stirred at this temperature for 3 hours, before being recooled to -78 °C, followed by addition of the adequate ketone or aldehyde (1.0 eq.). The solution was slowly warmed to room temperature and stirred for an additional 2 – 3 hours. Then 5 mL of a saturated aqueous NH₄Cl solution were added, the forming precipitate was dissolved in water and the aqueous phase was extracted with ether (3 × 50 mL). The organic extracts were washed with brine, dried over MgSO₄ and the solvent was removed in vacuo.

The residue was purified via flash column chromatography on NEt₃ basified silica gel to afford the alcohols in good yields.

2-(3,4-dihydro-2H-pyran-6-yl)-6-methylhept-5-en-2-ol (1a)

Compound 1a was synthesised according to general procedure 1 starting from 3,4-dihydropyran (2.52 g, 30.0 mmol, 2.71 mL) and 6-methylhept-5-en-2-one (3.16 g, 25.0 mmol, 3.69 mL). The crude product was purified by flash chromatography (PE + 3% NEt₃/EtOAc = 95/5) and isolated as a yellow oil (3.53 g, 16.8 mmol, 67%). TLC: Rf = 0.32 (PE/EtOAc = 95/5), [p-anisaldehyde]. 

$^{1}$H-NMR (200 MHz, CDCl₃): δ [ppm] = 1.28 (s, 3H), 1.55 (bs, 3H), 1.68 (bs, 3H), 1.55-2.09 (m, 8H), 2.13 (bs, 1H, OH), 4.00 (t, $^{3}J = 5.1$ Hz, 2H), 4.79 (t, $^{3}J = 3.8$ Hz, 1H), 5.09-5.16 (m, 1H). $^{13}$C-NMR (50 MHz, CDCl₃): δ [ppm] = 17.6, 20.0, 22.4, 23.1, 25.7, 25.8, 40.2, 46.3, 73.6, 94.1, 124.5, 131.7, 157.2. IR (neat): ν (cm⁻¹) = 3464 (b, OH), 2967 (m), 2927 (m), 2850 (m), 1670 (m), 1985 (s), 918 (s). ESI-HRMS: m/z calcd. for C₁₃H₂₃O₂ [MH]⁺: 211.1693, found: 211.1693.
2-(4,5-dihydrofuran-2-yl)-6-methylhept-5-en-2-ol (1b)

Compound 1b was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (3.33 g, 47.5 mmol, 3.60 mL) and 6-methylhept-5-en-2-one (5.00 g, 39.6 mmol). Purification by flash chromatography (PE+3% NEt/EtOAc = 95/5) afforded the title compound 1b as a yellow oil (5.24 g, 26.7 mmol, 67%). TLC: \( R_f = 0.30 \) (PE/EtOAc = 95/5), [\( p \)-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 1.31 (s, 3H), 1.56 (s, 3H), 1.63 (s, 3H), 1.50-1.72 (m, 2H), 1.90-2.04 (m, 2H), 2.25 (s, 1H, OH), 2.60 (td, \( \delta J = 9.3 \) Hz, 2.4 Hz, 2H), 4.31 (t, \( \delta J = 9.3 \) Hz, 2H), 4.76 (t, \( \delta J = 2.4 \) Hz, 1H), 5.05-5.12 (m, 1H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 17.6, 22.9, 25.6, 25.9, 30.0, 40.2, 70.3, 71.4, 93.7, 124.2, 131.7, 162.3. IR (neat): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3402 (OH), 2967 (s), 2924 (s), 2857 (s), 1644 (w), 1447 (m), 1376 (m), 1175 (m). APGC-HRMS: \( m/z \) calcd. for C\(_{12}\)H\(_{20}\)O\(_2\)[M-H\(^-\)]\(^+\): 195.1385, found: 195.1378.

2-ethoxy-3,7-dimethylocta-1,6-dien-3-ol (1c)

Compound 1c was synthesised according to general procedure 1 starting from ethyl vinyl ether (3.23 g, 44.4 mmol, 4.30 mL) and 6-methylhept-5-en-2-one (2.36 g, 18.5 mmol). Purification by flash chromatography (PE+3% NEt/ EtOAc = 95/5) afforded the title compound 1c as a yellow oil (2.17 g, 10.93 mmol, 59%). TLC: \( R_f = 0.34 \) (PE/EtOAc = 95/5), [\( p \)-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 1.24-1.39 (m, 6H), 1.49-1.78 (m, 8H), 1.85-2.08 (m, 2H), 2.21 (s, 1H, OH), 3.74 (q, \( \delta J = 7.0 \) Hz, 2H), 3.95 (d, \( \delta J = 2.5 \) Hz, 1H), 4.19 (d, \( \delta J = 2.5 \) Hz, 1H), 5.01-5.22 (m, 1H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 14.42, 17.58, 22.89, 25.67, 26.54, 40.49, 62.99, 74.15, 79.37, 124.42, 131.69, 166.27. IR (neat): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3472 (OH), 2977 (m), 2914 (m), 1656 (w), 1615 (m), 1445 (m), 1186 (s), 1120 (s), 1060 (s), 809 (s). ESI-HRMS: \( m/z \) calcd. for C\(_{12}\)H\(_{20}\)O\(_2\)[MH\(^+\)]: 199.1694, found: 199.1693.

2-(4,5-dihydrofuran-2-yl)-5-methylhex-5-en-2-ol (3a)

Compound 3a was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (2.01 g, 28.7 mmol, 2.17 mL) and 5-methylhex-5-en-2-one (2.50 g, 22.1 mmol, 2.89 mL). Purification by flash chromatography (PE+3% NEt/EtOAc = 95/5) afforded the title compound 3a as a yellow oil (3.96 g, 21.7 mmol, 98%). TLC: \( R_f = 0.47 \) (PE/EtOAc = 9:1), [\( p \)-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 4.78 (t, \( \delta J = 2.4 \) Hz, 1H), 4.67 (m, 2H), 4.33 (t, \( \delta J = 9.3 \) Hz, 2H), 2.62 (td, \( \delta J = 9.3, 2.5 \) Hz, 2H), 2.22 (s, 1H, OH), 2.07-1.94 (m, 2H), 1.80-1.66 (m, 5H), 1.34 (s, 3H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 162.16, 146.01, 109.70, 93.79, 71.30, 70.35, 38.25, 32.29, 29.98, 25.90, 22.59. IR (neat): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3452 (OH), 2933 (m), 2860 (m), 1650 (m), 1449 (m), 1366 (m), 1175 (m), 1082 (s), 934 (s), 883 (s). ESI-HRMS: \( m/z \) calcd. for C\(_{11}\)H\(_{19}\)O\(_2\)[MH\(^+\)]: 183.1380, found: 183.1380.
Compound 3b was synthesised according to general procedure 1 starting from 3,4-dihydropyran (2.49 g, 28.7 mmol, 2.70 mL) and 5-methylhex-5-ene-2-one (2.50 g, 22.1 mmol, 2.89 mL). Purification by flash chromatography (PE+3% NEt₃/EtOAc = 95/5) afforded the title compound 3b as a yellow oil (4.04 g, 20.6 mmol, 93%). TLC: R_f = 0.27 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 4.79 (t, 3_J = 3.8 Hz, 1H), 4.72 – 4.66 (m, 2H), 3.98 (t, 3_J = 5.0 Hz, 2H), 2.17 (s, 1H, OH), 2.12 – 1.88 (m, 4H), 1.86 – 1.63 (m, 7H), 1.29 (s, 3H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 157.05, 146.35, 109.57, 94.18, 73.45, 66.27, 38.27, 32.50, 25.77, 22.62, 22.34, 19.94. IR (neat): ν (~ cm⁻¹) = 3446 (b, OH), 2930 (m), 2849 (m), 1670 (m), 1447 (m), 1372 (w), 1285 (w), 1095 (s), 1067 (m), 917 (s), 883 (s). ESI-HRMS: m/z calcd. for C₁₂H₂₁O₂ [MH]^+: 197.1536, found: 197.1536.

2.1.2 Synthesis of dienols 1d, 1e, 1f, 1g, 1j, 1k, 1l, 3c and 3d

Alcohols 1d, 1e, 1f, 1g, 1j, (E)-1l, (Z)-1l, 3c and 3d were synthesised in three steps starting from the corresponding β-keto ester S1. Deprotonation of S1 and subsequent alkylation afforded S2. Decarboxylation in the presence of potassium hydroxide afforded the ketones S3, which were then subjected to the conditions described in general procedure 1.

![Diagram](https://via.placeholder.com/150)

General procedure 2: Synthesis of S2 from the corresponding β-keto esters

To a 0.5 M solution of β-keto ester S1 and potassium carbonate in acetone was added the halide derivative. The mixture was stirred at room temperature for 20 h. After completion (monitored by TLC or GC-MS) the solution was quenched with a hydrochloric acid solution 1 N. The organic layer
was extracted with diethyl ether. The organic extracts were washed with brine, dried over MgSO₄ and the solvent was removed under reduced pressure to give the desired product as a yellow oil. The residue was purified via flash column chromatography on silica gel to afford the corresponding β-keto esters S2.

**Ethyl 2-benzyol-4-methylpent-4-enoate (S2c-d')**

Compound S2c-d' was synthesised according to general procedure 2 starting from ethyl benzoylacetate (1.35 g, 70.0 mmol, 12.22 mL) and methallyl chloride (7.24 g, 80.0 mmol, 7.89 mL). Crude product was used in the next step without further purification. The title compound was obtained as a yellow oil (6.87 g, 27.9 mmol, 40%). TLC: \( R_f = 0.76 \) (PE/EtOAc = 98:2), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 8.06 – 7.96 (m, 2H), 7.60 – 7.42 (m, 3H), 4.83 – 4.69 (m, 2H), 4.55 (dd, \( ^1J = 7.8, 6.8 \) Hz, 1H), 4.14 (q, \( ^1J = 7.1 \) Hz, 2H), 2.73 (m, 2H), 1.77 (s, 3H), 1.17 (t, \( ^1J = 7.2 \) Hz, 3H). CAS number: 118067-01-9. The experimental data are in accordance with those reported in the literature.[¹]

**Ethyl 5-methyl-2-propionylhex-4-enoate (S2d-e)**

Compound S2d-e was synthesised according to general procedure 2 starting from ethyl 3-oxopentanoate (7.00 g, 47.1 mmol, 6.92 mL) and prenyl bromide (7.16 g, 47.1 mmol, 5.55 mL). Crude product was used in the next step without further purification. The title compound was obtained as a yellow oil (10.0 g, 47.1 mmol, 90%). TLC: \( R_f = 0.61 \) (PE/EtOAc = 95:5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 5.00 (m, 1H), 4.16 (q, \( ^1J = 7.1 \) Hz, 2H), 3.50 – 3.37 (m, 1H), 2.62 – 2.41 (m, 4H), 1.69 – 1.58 (m, 6H), 1.24 (t, \( ^1J = 7.1 \) Hz, 2H), 1.04 (t, \( ^1J = 7.2 \) Hz, 2H). ¹³C-NMR (50 MHz, CDCl₃): \( \delta \) [ppm] = 205.79, 169.68, 134.60, 119.89, 61.18, 58.77, 35.42, 27.03, 25.69, 17.70, 14.06, 7.57. CAS number: 105519-89-9. The experimental data are in accordance with those reported in the literature.[¹]

**Ethyl 2-benzyol-5-methylhex-4-enoate (S2f-g)**

Compound S2f-g was synthesised according to general procedure 2 starting from ethyl benzoylecetate (12.50 g, 58.5 mmol, 11.26 mL) and prenyl bromide (9.69 g, 58.5 mmol, 7.51 mL). Crude product was used in the next step without further purification. The title compound was obtained as a yellow oil (10.0 g, 47.1 mmol, 90%). TLC: \( R_f = 0.53 \) (PE/EtOAc = 95:5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 7.98 (m, 2H), 7.50 (m, 3H), 5.15-5.06 (m, 1H), 4.29 (t, \( ^1J = 7.3 \) Hz, 1H), 4.13 (q, \( ^1J = 7.1 \) Hz, 2H), 2.64-2.73 (m, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 1.16 (t, \( ^1J = 7.1 \) Hz, 3H). CAS number: 4535-59-5. The experimental data are in accordance with those reported in the literature.[¹]
Methyl (E)-2-acetyl-5-phenylpent-4-enoate (S2j-k)

Compound S2j-k was synthesised according to slightly modified general procedure 2. Methyl acetoacetate (2.32 g, 20.0 mmol, 2.15 mL) was added dropwise to a 0 °C suspension of NaH (0.96 g, 24.0 mmol, 1.2 eq.) in 35 mL THF. After 15 minutes a solution of cinnamyl bromide (3.94 g, 20.0 mmol, 2.96 mL, 1.0 eq.) in 35 mL THF was added carefully at 0 °C. The ice bath was removed and the mixture was stirred overnight (17 h) at room temperature until TLC showed full conversion of the starting material. The reaction was quenched with H2O, and the aqueous phase was extracted with EtOAc (3 × 40mL). The organic extracts were washed with water and brine, dried over MgSO4 and the solvent was evaporated under reduced pressure to afford the crude product as a 2:1 mixture of the title compound S2j-k and the double alkylated product. Purification by flash chromatography afforded the mono alkylated compound (1.89 g, 8.12 mmol, 41%). TLC: Rf = 0.45 (PE/EtOAc = 9:1), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 2.26 (s, 3H), 2.76 (ddd, δJ = 7.3 Hz, 1.2 Hz, 2H), 3.61 (t, δJ = 7.4 Hz, 1H), 3.75 (s, 3H), 6.11 (dt, δJ = 15.8 Hz, 7.1 Hz, 1H), 6.46 (br d, δJ = 15.8 Hz, 1H), 7.19-7.36 (m, 5H). CAS number: 85217-77-2. The experimental data are in accordance with those reported in the literature.[1]

Methyl (E)-2-acetyl-5,9-dimethyldeca-4,8-dienoate ((E)-S21)

Compound (E)-S21 was synthesised according to general procedure 2 starting from methyl acetoacetate (1.0 g, 3.97 mmol, 0.98 mL) and geranyl bromide (862 mg, 3.97 mmol, 0.78 mL). Purification by flash chromatography afforded the title compound as a yellow oil (652 g, 2.58 mmol, 65%). TLC: Rf = 0.62 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 5.09 – 4.95 (m, 2H), 3.72 (s, 3H), 3.46 (t, δJ = 7.5 Hz, 1H), 2.55 (t, δJ = 7.6 Hz, 2H), 2.22 (s, 3H), 2.11 – 1.86 (m, 4H), 1.70 – 1.55 (m, 9H). CAS number: 51933-45-0. The experimental data are in accordance with those reported in the literature.[1]

Ethyl (Z)-2-acetyl-5,9-dimethyldeca-4,8-dienoate ((Z)-S21)

Compound (Z)-S21 was synthesised according to general procedure 2 starting from ethyl acetoacetate (900 mg, 6.8 mmol, 0.88 mL) and freshly prepared neryl bromide (1.21 g, 5.5 mmol, 0.94 mL) from nerol (To a solution of nerol in THF was added PBr3 at 0 °C. The solution was stirred at 0 °C for 15 min, and was then diluted with ether/water and washed with saturated NaHCO3, water and brine and dried over Na2SO4. The solvent was removed in vacuo and neryl bromide was obtained as a brown oil which was used in the next step without further purification). Purification by flash chromatography afforded the title compound as a yellow oil (691 mg, 2.59 mmol, 47%). TLC: Rf = 0.62 (PE/EtOAc = 95/5), [p-anisaldehyde]. CAS
number: 72444-96-3.

**General procedure 3: Synthesis of ketones S3 from decarboxylation of S2**

To a solution of potassium hydroxide in Ethanol:Water (1:1) stirred at room temperature was added S2. The mixture was stirred at reflux (100°C) for 3h. After completion (monitored by TLC) the mixture was cooled to room temperature and extracted with diethyl ether. The organic extracts were washed with water and brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was purified via flash column chromatography on silica gel to afford the corresponding ketones S3.

4-methyl-1-phenylpent-4-en-1-one (S3c'-d')

Compound S3c'-d' was synthesised according to general procedure 3 starting from S2c'-d' (6.0 g, 24.4 mmol) and KOH (1.7 g, 30.4 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (3.8 g, 21.9 mmol, 90%). **TLC:** \( R_f = 0.79 \) (PE/EtOAc = 95/5), [p-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 8.02 – 7.90 (m, 2H), 7.63 – 7.40 (m, 3H), 4.80 – 4.67 (m, 2H), 3.18 – 3.05 (m, 2H), 2.51 – 2.39 (m, 2H), 1.79 (s, 3H). \(^{13}\)C-NMR (50 MHz, CDCl₃): \( \delta \) [ppm] = 199.86, 144.83, 133.13, 128.73, 128.44, 128.17, 110.33, 36.98, 32.03, 22.91. **CAS number:** 1078-36-0. The experimental data are in accordance with those reported in the literature.\(^{[1]}\)

7-methyloct-6-en-3-one (S3d-e)

Compound S3d-e was synthesised according to general procedure 3 starting from S2d-e (10.0 g, 47.1 mmol) and KOH (3.3 g, 58.9 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (6.1 g, 43.4 mmol, 92%). **TLC:** \( R_f = 0.78 \) (PE/EtOAc = 95/5), [p-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 5.11 – 4.96 (m, 1H), 2.47 – 2.33 (m, 4H), 2.25 (t, \( ^2J = 7.4 \) Hz, 2H), 1.65 (s, 3H), 1.60 (s, 3H), 1.03 (t, \( ^3J = 7.3 \) Hz, 3H). **CAS number:** 762-47-0. The experimental data are in accordance with those reported in the literature.\(^{[1]}\)

5-methyl-1-phenylhex-4-en-1-one (S3f-g)

Compound S3f-g was synthesised according to general procedure 3 starting from S2f-g (15.0 g, 57.6 mmol) and KOH (4.0 g, 72.0 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (10.0 g, 53.3 mmol, 93%). **TLC:** \( R_f = 0.76 \) (PE/EtOAc = 95/5), [p-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl₃): \( \delta \) [ppm] = 7.99 – 7.94 (m, 2H), 7.56 – 7.41 (m, 3H), 5.21 – 5.13 (m, 1H), 3.00 (dd, \( ^3J = 8.0, 6.8 \) Hz, 2H), 2.42 (q, \( ^3J = 7.4 \) Hz, 2H), 1.74 – 1.51 (m, 6H). \(^{13}\)C-NMR
(50 MHz, CDCl₃): δ [ppm] = 200.20, 137.17, 133.03, 128.68, 128.44, 128.18, 123.07, 38.90, 25.84, 23.07, 17.83. CAS number: 4535-64-2. The experimental data are in accordance with those reported in the literature.[1]

(E)-6-phenylhex-5-en-2-one (S3j-k)

Compound S3j-k was synthesised according to general procedure 3 starting from S2j-k (1.87 g, 8.06 mmol) and KOH (0.57 g, 10.1 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound S3j-k as a pale yellow oil (1.28 g, 7.36 mmol, 91%). TLC: Rf = 0.40 (PE/EtOAc = 9:1), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 2.06 (s, 3H), 2.32-2.43 (m, 2H), 2.47-2.55 (m, 2H), 6.10 (dt, 3J = 15.8 Hz, 6.4 Hz, 1H), 6.31 (d, 3J = 15.8 Hz, 1H), 7.06-7.27 (m, 5H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 27.14, 30.1, 43.2, 126.1, 127.1, 128.6, 128.9, 130.8, 137.4, 208.03. CAS number: 33599-88-1. The experimental data are in accordance with those reported in the literature.[1]

(E)-6,10-dimethylundeca-5,9-dien-2-one ((E)-S31)

Compound (E)-S31 was synthesised according to general procedure 3 starting from (E)-S21 (1.00 g, 3.96 mmol) and KOH (278 mg, 4.95 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound (E)-S31 as a pale yellow oil (703 mg, 3.61 mmol, 91%). TLC: Rf = 0.76 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (500 MHz, CDCl₃): δ [ppm] = 5.10 – 5.04 (m, 2H), 2.45 (t, 3J = 7.4 Hz, 2H), 2.30 – 2.22 (m, 2H), 2.13 (s, 3H), 2.09 – 2.02 (m, 2H), 1.99 – 1.93 (m, 2H), 1.68 – 1.66 (m, 3H), 1.61 – 1.60 (m, 3H), 1.60 – 1.59 (m, 3H). ¹³C-NMR 125 MHz, CDCl₃): δ [ppm] = 209.02, 136.52, 131.55, 124.32, 122.66, 43.91, 39.78, 30.09, 26.76, 25.83, 22.62, 17.82, 16.12. CAS number: 3796-70-1. The experimental data are in accordance with those reported in the literature.[1]

(Z)-6,10-dimethylundeca-5,9-dien-2-one ((Z)-S31)

Compound (Z)-S31 was synthesised according to general procedure 3 starting from (Z)-S21 (690 mg, 2.59 mmol) and KOH (182 mg, 3.24 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound (Z)-S31 as a pale yellow oil (467 mg, 2.40 mmol, 93%). TLC: Rf = 0.79 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 5.16 – 4.98 (m, 2H), 2.51 – 2.38 (m, 2H), 2.32 – 2.17 (m, 2H), 2.13 (s, 3H), 2.07 – 1.91 (m, 4H), 1.71 – 1.65 (m, 6H), 1.60 (s, 3H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 208.95, 136.63, 131.82, 124.29, 123.45, 44.15, 32.01, 30.07, 26.64, 25.86, 23.50, 22.41, 17.79. CAS number: 3879-26-3. The experimental data are in accordance with those reported in the literature.[1]
3-(3,4-dihydro-2H-pyran-6-yl)-7-methyloct-6-en-3-ol (1d)

Compound 1d was synthesised according to general procedure 1 starting from 3,4-dihydropyran (2.29 g, 26.4 mmol, 2.49 mL) and S3d-e (3.00 g, 20.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/EtOAc = 95/5) and isolated as a yellow oil (2.42 g, 10.8 mmol, 53%). TLC: Rf = 0.72 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 5.24 – 5.06 (m, 1H), 4.79 (t, 3J = 3.7 Hz, 1H), 4.02 – 3.88 (m, 2H), 2.13 – 1.93 (m, 4H), 1.85 – 1.38 (m, 12H), 0.82 (t, 3J = 7.4 Hz, 2H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 155.58, 131.68, 124.74, 95.25, 76.22, 66.14, 38.46, 31.69, 25.71, 22.58, 22.47, 20.07, 17.63, 7.74. IR (neat): ν (cm⁻¹) = 3417 (b, OH), 2966 (m), 2858 (m), 2355 (w), 1659 (m), 1453 (m), 1375 (m), 1160 (m), 1094 (m), 1001 (m), 773 (w), 746 (m), 556 (m), 473 (m). ESI-HRMS: m/z calcd. for C14H24O2 [MH]+: 225.1848, found: 225.1849.

3-(4,5-dihydrofuran-2-yl)-7-methyloct-6-en-3-ol (1e)

Compound 1e was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (1.85 g, 26.4 mmol, 2.00 mL) and S3d-e (3.00 g, 20.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/EtOAc = 95/5) and isolated as a yellow oil (3.22 g, 15.3 mmol, 75%). TLC: Rf = 0.64 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 5.20 – 5.09 (m, 1H), 4.81 (t, 3J = 2.4 Hz, 1H), 4.34 (t, 3J = 9.3 Hz, 2H), 2.64 (td, 3J = 9.3, 2.4 Hz, 2H), 2.12 – 1.90 (m, 3H), 1.77 – 1.47 (m, 10H), 0.86 (t, 3J = 7.4 Hz, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 161.21, 132.07, 124.60, 95.18, 74.79, 70.53, 38.49, 31.82, 30.17, 25.88, 22.70, 17.82, 7.95. IR (neat): ν (cm⁻¹) = 3487 (b, OH), 2966 (m), 2924 (m), 2858 (m), 2355 (w), 1659 (m), 1453 (m), 1375 (m), 1160 (m), 1094 (m), 1001 (m), 936 (s). ESI-HRMS: m/z calcd. for C13H22O2 [MH]+: 211.1693, found: 211.1693.

1-(3,4-dihydro-2H-pyran-6-yl)-5-methyl-1-phenylhex-4-en-1-ol (1f)

Compound 1f was synthesised according to general procedure 1 starting from 3,4-dihydropyran (2.03 g, 23.4 mmol, 2.20 mL) and S3f-g (3.50 g, 18.0 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/EtOAc = 95/5) and isolated as a yellow oil (2.60 g, 9.54 mmol, 53%). TLC: Rf = 0.56 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 7.55 – 7.46 (m, 2H), 7.38 – 7.21 (m, 3H), 5.16 – 5.05 (m, 1H), 4.95 (t, 3J = 3.8 Hz, 1H), 3.96 (t, 3J = 5.1 Hz, 2H), 2.74 (s, 1H, OH), 2.19 – 1.72 (m, 8H), 1.65 (s, 3H), 1.53 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 156.31, 145.06, 131.83, 127.83, 126.75, 125.55, 124.39, 96.33, 77.37, 66.45, 39.24, 25.68, 22.43, 22.22, 20.06, 17.58. IR (neat): ν (cm⁻¹) = 3568 (b, OH), 2967 (m), 2926 (m), 2850 (m), 1668 (m), 1446 (m), 1062 (s), 916 (s), 764 (m), 700 (s). ESI-HRMS: m/z calcd. for C15H25O2 [MH]+: 273.1848, found: 273.1849.
1-(4,5-dihydrofuran-2-yl)-5-methyl-1-phenylhex-4-en-1-ol (1g)

Compound 1g was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (2.03 g, 23.4 mmol, 2.20 mL) and S3f-g (3.50 g, 18.0 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/ EtOAc = 95/5) and isolated as a yellow oil (2.60 g, 9.54 mmol, 53%). TLC: Rf = 0.56 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 7.65 – 7.41 (m, 2H), 7.42 – 7.08 (m, 3H), 5.19 – 5.07 (m, 1H), 4.93 (t, 2J = 2.5 Hz, 1H), 4.34 (t, 2J = 9.3 Hz, 2H), 2.67 (td, 2J = 9.5, 2.7 Hz, 2H), 2.59 (s, 1H), 2.19 – 1.81 (m, 4H), 1.65 (s, 3H), 1.53 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 161.39, 144.19, 132.25, 128.13, 127.21, 125.51, 124.26, 95.72, 75.41, 70.58, 40.20, 30.19, 25.83, 22.51, 17.76. IR (neat): ν (cm⁻¹) = 3481 (b, OH), 2965 (m), 2921 (m), 2858 (m), 1655 (w), 1446 (m), 1067 (m), 1005 (m), 935 (m). ESI-HRMS: m/z calcd. for C17H22O2 [MH]+: 259.1693, found: 259.1693.

1-(4,5-dihydrofuran-2-yl)-4-methyl-1-phenylpent-4-en-1-ol (3c)

Compound 3c was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (1.05 g, 14.9 mmol, 1.13 mL) and S3c'-d' (2.00 g, 11.5 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/ EtOAc = 95/5) and isolated as a yellow oil (1.93 g, 7.9 mmol, 69%). TLC: Rf = 0.44 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 7.56 – 7.46 (m, 2H), 7.41 – 7.25 (m, 3H), 4.94 (t, 2J = 2.5 Hz, 1H), 4.71 – 4.63 (m, 2H), 4.44 – 4.28 (m, 2H), 2.69 (td, 2J = 9.4, 2.5 Hz, 2H), 2.59 (s, 1H), 2.27 – 2.01 (m, 3H), 1.99 – 1.79 (m, 1H), 1.70 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 161.20, 146.22, 144.09, 128.19, 127.28, 125.49, 109.76, 95.83, 75.22, 70.58, 38.35, 31.74, 30.20, 22.87. IR (neat): ν (cm⁻¹) = 3484 (b, OH), 2961 (m), 2631 (m), 2360 (m), 1649 (m), 1446 (m), 1006 (m), 935 (s), 884 (m), 700 (s). ESI-HRMS: m/z calcd. for C16H20O2 [MH]+: 245.1536, found: 245.1536.

1-(3,4-dihydro-2H-pyran-6-yl)-4-methyl-1-phenylpent-4-en-1-ol (3d)

Compound 3d was synthesised according to general procedure 1 starting from 3,4-dihydropyran (1.25 g, 14.5 mmol, 1.36 mL) and S3e'-d' (1.80 g, 10.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/ EtOAc = 95/5) and isolated as a yellow oil (1.86 g, 7.2 mmol, 70%). TLC: Rf = 0.47 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 7.56 – 7.47 (m, 2H), 7.40 – 7.23 (m, 3H), 4.95 (t, 2J = 3.8 Hz, 1H), 4.72 – 4.61 (m, 2H), 4.05 – 3.89 (m, 2H), 2.78 (s, 1H), 2.23 – 1.75 (m, 8H), 1.70 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 156.30, 146.50, 145.14, 128.04, 126.98, 125.71, 109.56, 69.63, 77.38, 66.64, 37.56, 31.84, 22.91, 22.35, 20.19. IR (neat): ν (cm⁻¹) = 3564 (b, OH), 2931 (m), 2848 (w), 2358 (w), 1668 (m), 1446 (m), 1286 (m), 1233 (m), 1063 (s), 916 (m), 883 (m), 765 (m), 700 (s). ESI-HRMS: m/z calcd. for C17H20O2 [MH]+: 259.1693, found: 259.1693.
**{(E)-2-(3,4-dihydro-2H-pyran-6-yl)-6-phenylhex-5-en-2-ol (1j)}**

Compound 1j was synthesised according to general procedure 1 starting from 3,4-dihydropyran (348 mg, 4.13 mmol, 0.37 mL, 1.2 eq.) and ketone S3j-k (600 mg, 3.44 mmol). The crude product was purified by flash chromatography (PE+3% NEt\textsubscript{3}/EtOAc = 95/5) and isolated as a yellow oil (783 mg, 3.03 mmol, 73%). TLC: \( R_f = 0.27 \) (PE/EtOAc = 9/1), [\(-\)anisaldehyde]. \(^1\text{H}-\text{NMR} \) (200 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 1.26 (s, 3H), 1.64-1.81 (m, 4H), 1.98 (s, 1H), 1.95-2.20 (m, 4H), 3.94 (t, \( \text{J} = 4.4 \text{ Hz}, 2 \text{H} \)), 4.25 (t, \( \text{J} = 3.8 \text{ Hz}, 1 \text{H} \)), 7.29 (m, 5H). \(^1\text{C}-\text{NMR} \) (50 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 20.1, 22.5, 26.0, 28.2, 40.0, 66.5, 73.5, 94.4, 126.0, 126.9, 128.6, 129.8, 131.1, 138.0, 157.2. \(^\text{IR} \) (neat): \( \nu \) (cm\textsuperscript{-1}) = 3443 (b, OH), 2926 (m), 2858 (w), 1659 (w), 1447 (w), 1364 (w), 1175 (w), 1072 (m), 961 (s), 739 (s), 691 (s). \(^{\text{ESI-HRMS}}: m/z \) calcd. for C\textsubscript{17}H\textsubscript{23}O\textsubscript{2} [MH\textsuperscript{+}]\textsuperscript{+}: 259.1693, found: 259.1693.

**{(E)-2-(4,5-dihydropyran-2-yl)-6-phenylhex-5-en-2-ol (1k)}**

Compound 1k was synthesized according to general procedure 1 starting from 2,3-dihydropyran (290 mg, 4.13 mmol, 0.31 mL, 1.2 eq.) and ketone S3j-k (600 mg, 3.44 mmol). Purification by flash chromatography (PE+3% NEt\textsubscript{3}/EtOAc = 95/5) afforded the title compound 1k as a yellow oil (742 mg, 3.04 mmol, 74%). TLC: \( R_f = 0.26 \) (PE/EtOAc = 9/1), [\(-\)anisaldehyde]. \(^1\text{H}-\text{NMR} \) (200 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 1.32 (s, 3H), 1.69-1.78 (m, 2H), 1.97 (s, 1H), 2.12-2.24 (m, 2H), 2.58 (d, \( \text{J} = 9.4 \text{ Hz}, 2 \text{H} \)), 4.30 (t, \( \text{J} = 9.3 \text{ Hz}, 2 \text{H} \)), 4.76 (t, \( \text{J} = 2.4 \text{ Hz}, 1 \text{H} \)), 6.16 (dt, \( \text{J} = 15.8 \text{ Hz}, 6.4 \text{ Hz}, 1 \text{H} \)), 6.34 (d, \( \text{J} = 15.8 \text{ Hz}, 1 \text{H} \)), 7.07-7.29 (m, 5H). \(^1\text{C}-\text{NMR} \) (50 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 26.2, 28.0, 30.2, 40.0, 70.6, 71.4, 94.1, 126.0, 127.0, 128.6, 130.0, 130.8, 137.9, 162.2. \(^\text{IR} \) (neat): \( \nu \) (cm\textsuperscript{-1}) = 3443 (b, OH), 2926 (m), 2858 (w), 1659 (w), 1447 (w), 1364 (w), 1175 (w), 1072 (m), 961 (s), 739 (s), 691 (s). \(^{\text{ESI-HRMS}}: m/z \) calcd. for C\textsubscript{16}H\textsubscript{22}O\textsubscript{2} [MH\textsuperscript{+}]\textsuperscript{+}: 245.15363, found: 245.1536.

**{2-(3,4-dihydro-2H-pyran-6-yl)-6,10-dimethylundeca-5,9-dien-2-ol (1l)}**

Compound 11 was synthesised according to general procedure 1 starting from 3,4-dihydropyran (2.01 g, 23.2 mmol, 2.18 mL) and geranyl acetone (3.5 g, 17.8 mmol). The crude product was purified by flash chromatography (PE+3% NEt\textsubscript{3}/EtOAc = 95/5) and isolated as a yellow oil (3.35 g, 12.0 mmol, 68%). TLC: \( R_f = 0.30 \) (PE/EtOAc = 95/5), [\(-\)anisaldehyde]. \(^1\text{H}-\text{NMR} \) (200 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 3.44 (s), 4.06 (m, 1H), 4.30 (t, \( \text{J} = 3.8 \text{ Hz}, 1 \text{H} \)), 4.76 (t, \( \text{J} = 3.8 \text{ Hz}, 2 \text{H} \)), 7.29 (m, 5H).
Compound (E)-11 was synthesised according to general procedure 1 starting from 3,4-dihydropyran (402 mg, 4.64 mmol, 0.44 mL) and (E)-S3I (700 mg, 3.57 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/EtOAc = 95/5) and isolated as a yellow oil (804 mg, 2.89 mmol, 81%). TLC: Rf = 0.31 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 5.21 – 5.01 (m, 2H), 4.79 (t, J = 3.8 Hz, 1H), 3.99 (dd, J = 5.7, 4.5 Hz, 2H), 2.15 (s, 1H), 2.10 – 1.91 (m, 8H), 1.86 – 1.74 (m, 2H), 1.72 – 1.54 (m, 11H), 1.28 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 157.40, 135.46, 131.54, 124.55, 124.43, 94.27, 73.80, 66.42, 40.36, 39.87, 26.82, 25.95, 25.85, 23.22, 22.55, 20.16, 17.83, 16.10. IR (neat): ν (cm⁻¹) = 3456 (b, OH), 2927 (m), 2851 (m), 1670 (m), 1447 (m), 1375 (m), 1285 (m), 1086 (s), 1066 (s), 919 (s).

(Z)-2-(3,4-dihydro-2H-pyran-6-yl)-6,10-dimethylundeca-5,9-dien-2-ol ((Z)-11)

Compound (Z)-11 was synthesised according to general procedure 1 starting from 3,4-dihydropyran (268 mg, 3.09 mmol, 0.29 mL) and (Z)-S3I (467 mg, 2.38 mmol). The crude product was purified by flash chromatography (PE+3% NEt3/EtOAc = 95/5) and isolated as a yellow oil (623 mg, 2.24 mmol, 94%). TLC: Rf = 0.31 (PE/EtOAc = 95/5), [p-anisaldehyde]. 1H-NMR (200 MHz, CDCl3): δ [ppm] = 5.22 – 5.06 (m, 2H), 4.79 (t, J = 3.8 Hz, 1H), 3.99 (dd, J = 5.6, 4.6 Hz, 2H), 2.16 – 1.89 (m, 9H), 1.86 – 1.75 (m, 2H), 1.73 – 1.56 (m, 11H), 1.28 (s, 3H). 13C-NMR (50 MHz, CDCl3): δ [ppm] = 157.34, 135.54, 131.65, 125.33, 124.51, 94.29, 73.71, 66.42, 40.73, 32.07, 26.76, 25.87, 23.57, 23.06, 22.53, 20.15, 17.79. IR (neat): ν (cm⁻¹) = 3439 (b, OH), 2929 (m), 2854 (m), 2360 (m), 1670 (m), 1448 (m), 1286 (m), 1086 (s), 1067 (s), 919 (s).

2.1.3 Synthesis of dienols 1h and 1i

Alcohols 1h and 1i were synthesised in three steps from iso-butynitrile and prenyl bromide. Nitriles S4h-i were reduced using MeLi and subsequent acid hydrolysis afforded the corresponding ketone SSh-i. Introduction of the enol ether moiety following the conditions described in general procedure 1 afforded the tertiary alcohol.
2,2,5-trimethylhex-4-enenitrile (S4h-i)\[^{[1]}\]

A solution of \(n\)-butyllithium (2.5 M in cyclohexane, 1 eq.) was added dropwise to an ice cold solution of diisopropylamine (1 eq.) in dry THF. After stirring for 10 minutes at this temperature, isobutyronitrile (5 eq., 11.2 g, 160 mmol, 14.7 mL) was added to the mixture. Premyl bromide (1 eq., 5.30 g, 32.0 mmol, 4.11 mL) was added after another mixing of 10 minutes at 0° C. Reaction conversion was followed by GC-MS and seen as complete after 15 minutes stirring at 0° C. The reaction was quenched by addition of saturated NH\(_4\)Cl aqueous solution and extracted with Et\(_2\)O. The combined organic layers were dried over MgSO\(_4\) and concentrated under reduced pressure. The resulting oil was purified using a quick filtration over silica by elution with a PE-Et\(_2\)O mixture (9:1). Concentration of the eluent under reduced pressure resulted in the compound S4h-i as a pale yellow oil (4.20 g, 30.6 mmol, 96%). \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 5.29 – 5.19 (m, 1H), 2.22 (d, \(^3J = 7.6\) Hz, 2H), 1.78 – 1.74 (m, 3H), 1.64 (s, 3H), 1.31 (s, 6H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 136.41, 125.22, 118.14, 39.13, 32.81, 26.21, 25.92, 18.05. **CAS number:** 13899-89-3.

3,3,6-trimethylhept-5-en-2-one (S5h-i)\[^{[1]}\]

A methylithium solution (1.2 eq., 1.6M in pentane, 21.9 mmol, 13.7 mL) was added dropwise to a solution of the nitrile S4h-i (1 eq., 2.50 g, 18.2 mmol) in dry THF (0.5M) at -20° C. After stirring for 15 minutes at -10/-20° C., full conversion was observed by GC-MS. The reaction was quenched with a H\(_2\)SO\(_4\) solution (2 eq., 2 M, 36.4 mmol, 18.2 mL) and stirred at ambient temperature till full hydrolysis of the in situ formed imine was observed. The mixture was then extracted with Et\(_2\)O and washed with a saturated NaHCO\(_3\) aqueous solution. The combined organic phases were dried over MgSO\(_4\) and concentrated under reduced pressure. The resulting oil was purified with column chromatography by eluting with a PE-Et\(_2\)O mixture (95:5). Concentration of the desired fractions under reduced pressure resulted in the compound S5h-i as a colorless oil. (2.20 g, 14.3 mmol, 78%). \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 4.99 (m, 1H), 2.20 (d, \(^3J = 7.3\) Hz, 2H), 2.11 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.10 (s, 6H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 214.01, 134.20, 119.58, 48.25, 37.98, 25.91, 25.23, 24.04, 17.88. **CAS number:** 2550-19-8.

2-(3,4-dihydro-2H-pyran-6-yl)-3,3,6-trimethylhept-5-en-2-ol (1h)

Compound 1h was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (0.95 g, 11.0 mmol, 1.03 mL) and ketone S5h-i (1.30 g, 8.43 mmol). The crude product was purified by flash chromatography (PE+3% NEt\(_3\)/EtOAc = 95/5) and isolated as a yellow oil (1.40 g, 5.86 mmol, 69%). TLC: \(R_f = 0.61\) (PE/EtOAc = 95/5), \(\rho\)-anisaldehyde. \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 5.29 – 5.16 (m, 1H), 4.74 (t, \(^3J = 3.8\) Hz, 1H), 4.06 – 3.89 (m, 2H), 2.52 (s, 1H), 2.17 – 1.96 (m, 4H), 1.87 – 1.67 (m, 5H), 1.60 (bs, 3H), 1.28 (s, 3H), 0.87 (m, 6H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \(\delta\) [ppm] =
156.76, 132.78, 121.89, 96.68, 78.12, 65.82, 41.61, 35.31, 26.12, 22.39, 22.26, 22.06, 20.13, 17.87. IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 3511 (OH, b), 2966 (m), 2927 (m), 2875 (m), 2359 (w), 2342 (w), 1662 (m), 1449 (m), 1375 (m), 1329 (m), 1266 (m), 1074 (s), 920 (s). ESI-HRMS: m/z calcd. for C$_{13}$H$_2$O$_2$ [MH$^+$]: 239.05, found: 239.06.

2-(4,5-dihydrofuran-2-yl)-3,3,6-trimethylhept-5-en-2-ol (1i)

Compound 1i was synthesised according to general procedure 1 starting from 2,3-dihydrofuran (1.13 g, 16.0 mmol, 1.22 mL) and ketone S$^{5h}$-i (1.90 g, 12.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt$_3$/EtOAc = 95/5) and isolated as a yellow oil (1.74 g, 7.77 mmol, 63%). TLC: $R_f$ = 0.57 (PE/EtOAc = 95/5), [p-anisaldehyde]. $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ [ppm] = 5.29 – 5.15 (m, 1H), 4.76 (t, $^3J$ = 2.5 Hz, 1H), 4.32 (t, $^3J$ = 9.3 Hz, 2H), 2.63 (td, $^3J$ = 9.3, 2.5 Hz, 2H), 2.26 (s, 1H), 2.01 – 2.10 (m, 2H), 1.71 (s, 3H), 1.60 (s, 3H), 1.32 (s, 3H), 0.90 (d, $^3J$ = 2.1 Hz, 6H). $^{13}$C-NMR (50 MHz, CDCl$_3$): $\delta$ [ppm] = 162.23, 133.08, 121.57, 95.46, 76.78, 70.00, 41.20, 35.29, 30.04, 26.11, 22.41, 22.30, 21.88, 17.89. IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 3498 (b, OH), 2966 (m), 2920 (m), 1650 (m), 1452 (m), 1365 (m), 1083 (m), 1060 (s), 936 (s). ESI-HRMS: m/z calcd. for C$_{14}$H$_{22}$O$_2$ [MH$^+$]: 225.1849, found: 225.1849.

2.2 Cyclisation products 2a-l, 4a-d, 7a-c

General procedure 4: Bi(OTf)$_3$ catalysed cyclisation reactions

Bi(OTf)$_3$ was added to a 0.1 M solution of the cyclisation precursor in the corresponding solvent (CH$_2$Cl$_2$ or CH$_3$NO$_2$) at room temperature and the reaction was followed by TLC and/or GC. Upon completion, the reaction was quenched by addition of a saturated aqueous NaHCO$_3$ solution. The aqueous phase was extracted with CH$_2$Cl$_2$ and the combined organic extracts were washed with brine, dried over MgSO$_4$ and concentrated in vacuo. Purification by column chromatography afforded the corresponding cyclisation products.

Polycyclic ether (2a)

Compound 2a was synthesised according to general procedure 4 starting from dienol 1a (1.50 g, 7.13 mmol) in CH$_2$Cl$_2$ at room temperature, Bi(OTf)$_3$ (1 mol%, 47 mg, 0.07 mmol) were added and the mixture was stirred for 1.5 h. Purification by flash chromatography (P/Et$_2$O = 95/5) afforded 2a (936 mg, 4.45 mmol, 62%) as a pale yellow oil. TLC: $R_f$ = 0.34 (P/Et$_2$O = 95/5), [p-anisaldehyde]. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 1.03 (s, 3H), 1.20 (s, 3H), 1.21 (s, 3H), 1.46-1.49 (m, 1H), 1.51-1.64 (m, 6H), 1.69-1.74 (m, 1H), 1.78-1.81 (m, 1H), 2.09-2.11 (m, 1H), 2.33 (bs, 1H), 3.38-3.43 (m, 1H), 3.74-3.77 (m, 1H). $^{13}$C-NMR (125 MHz,
Compounds 2b were synthesised according to **general procedure 4** starting from dienol 1b (1.00 g, 6.0 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (1 mol%, 33 mg, 0.05 mmol) was added and the mixture was stirred for 30 minutes. Purification by flash chromatography (P/Et₂O = 95/5) afforded *trans-2b* (275 mg, 1.40 mmol, 28%) as a pale yellow oil and *cis-2b* (580 mg, 3.00 mmol, 58%) as a pale yellow oil. The overall yield of cycloisomerisation products was 86%.

**Polycyclic ethers (trans-2b) and (cis-2b)**

Compounds 2b were synthesised according to **general procedure 4** starting from dienol 1b (1.00 g, 6.0 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (1 mol%, 33 mg, 0.05 mmol) was added and the mixture was stirred for 30 minutes. Purification by flash chromatography (P/Et₂O = 95/5) afforded *trans-2b* (275 mg, 1.40 mmol, 28%) as a pale yellow oil and *cis-2b* (580 mg, 3.00 mmol, 58%) as a pale yellow oil. The overall yield of cycloisomerisation products was 86%.

**Polycyclic ethers (trans-2c) and (cis-2c)**

Compounds 2c were synthesised according to **general procedure 4** starting from dienol 1c (100 mg, 0.5 mmol) in CH₃NO₂ and 4Å molecular sieves at room temperature, Bi(OTf)₃ (1 mol%, 33 mg, 0.005 mmol) was added and the mixture was stirred for 5 minutes. Purification by flash chromatography (P/Et₂O = 95/5) afforded *trans-2c* (53 mg, 0.267 mmol, 53%) as a pale yellow oil and *cis-2c* (29 mg, 0.146 mmol, 29%) as a pale yellow oil. The overall isolated yield of cycloisomerisation products was 82%.
Polycyclic ethers (trans-2d) and (cis-2d)

Compounds 2d were synthesised according to general procedure 4 starting from dienol 1d (100 mg, 0.45 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (0.1 mol%, 0.3 mg, 0.0004 mmol) was added and the mixture was stirred for 1.5 h. Purification by flash chromatography (P/EtOAc = 95/5) afforded trans-2d (69 mg, 0.308 mmol, 69%) as a pale yellow oil and cis-2d (12 mg, 0.053 mmol, 12%) as white crystals. The overall isolated yield of cycloisomerisation products was 81%.

**trans-2d:** TLC: Rₛ = 0.78 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 3.96 – 3.81 (m, 1H), 3.63 – 3.43 (m, 1H), 2.48 (s, 1H), 2.31 – 2.15 (m, 1H), 1.99 – 1.49 (m, 11H), 1.35 (s, 3H), 1.33 (s, 3H), 1.01 (t, ³J = 7.5 Hz, 3H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 88.1, 87.43, 77.36, 64.75, 47.19, 30.59, 29.29, 29.26, 27.35, 26.62, 23.02, 21.14, 21.09, 8.69. IR (neat): ν(C=O) (cm⁻¹) = 2962 (m), 2934 (m), 2361 (w), 1456 (m), 1377 (m), 1273 (m), 1195 (m), 1175 (m), 1100 (s), 1076 (s), 1042 (s), 973 (s), 910 (s), 884 (s), 856 (s).

**cis-2d:** TLC: Rₛ = 0.44 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 3.92 – 3.76 (m, 1H), 3.53 (td, ³J = 11.4, 3.4 Hz, 1H), 2.32 (d, ³J = 3.0 Hz, 1H), 1.90 – 1.34 (m, 12H), 1.38 (s, 3H), 1.26 (s, 3H), 0.93 (t, ³J = 7.5 Hz, 3H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 88.91, 88.04, 78.75, 64.91, 44.94, 29.95, 28.79, 27.99, 26.50, 22.50, 21.72, 20.95, 8.84. IR (neat): ν(C=O) (cm⁻¹) = 2955 (s), 2929 (s), 2849 (m), 2362 (m), 1438 (w), 1354 (w), 1239 (m), 1104 (s), 1078 (s), 1051 (s), 972 (s), 917 (s). APGC-HRMS: m/z calcd. for C₁₄H₁₄O₂[M]⁺: 224.1776, found: 224.1779.

Polycyclic ethers (trans-2e) and (cis-2e)

Compounds 2e were synthesised according to general procedure 4 starting from dienol 1e (100 mg, 0.475 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (0.1 mol%, 0.3 mg, 0.0005 mmol) was added and the mixture was stirred for 5 min. Purification by flash chromatography (P/EtOAc = 95/5) afforded trans-2e (22 mg, 0.105 mmol, 22%) as a pale yellow oil and cis-2e (61 mg, 0.290 mmol, 61%) as a pale yellow oil. The overall isolated yield of cycloisomerisation products was 83%.

**trans-2e:** TLC: Rₛ = 0.59 (PE/EtOAc = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 3.97 – 3.81 (m, 1H), 3.72 – 3.56 (m, 1H), 2.30 – 2.17 (m, 1H), 2.11 – 1.81 (m, 4H), 1.80 – 1.35 (m, 6H), 1.24 (s, 3H), 1.20 1155 (s), 1113 (s), 1100 (s), 1062 (m). **ESI-HRMS:** m/z calcd. for C₁₂H₂₃O₂ [M]⁺: 199.1693, found: 199.1694.
Polycyclic ethers (trans-2g) and (cis-2g)

Compounds 2g were synthesised according to general procedure 4 starting from dienol 1g (100 mg, 0.387 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (0.1 mol%, 0.3 mg, 0.0004 mmol) was added and the mixture was stirred for 10 min. Purification by flash chromatography (P/Et₂O = 95/5) afforded trans-2g (22 mg, 0.085 mmol, 22%) as a pale yellow oil and cis-2g (75 mg, 0.290 mmol, 75%) as white crystals. The overall isolated yield of cycloisomerisation products was 99%.

trans-2g: TLC: R₇ = 0.59 (PE/EtOAc = 95/5), [p-anisaldehyde].

trans-2g: Chemical Formula: C₁₉H₂₄O₂
Molecular Weight: 272.39

(1H-NMR (200 MHz, CDCl₃): δ [ppm] = 7.57 – 7.48 (8H), 7.36 – 7.23 (8H), 3.84 – 3.73 (8H), 3.66 – 3.48 (8H), 2.56 – 2.39 (8H), 2.28 – 1.71 (8H), 1.65 – 1.45 (8H), 1.38 (8H), 1.35 (8H), 0.82 – 0.50 (8H).

cis-2g: Chemical Formula: C₁₉H₂₂O₂
Molecular Weight: 258.36

(1H-NMR (200 MHz, CDCl₃): δ [ppm] = 7.62 – 7.52 (8H), 7.36 – 7.20 (8H), 3.67 (dt), 1.38 – 1.33 (8H), 1.26 – 1.10 (8H).

13C-NMR (50 MHz, CDCl₃): δ [ppm] = 2968 (m), 2941 (m), 1446 (w), 1271 (w), 1079 (s), 1032 (m), 984 (m), 849 (m), 758 (s), 699 (s).

cis-2g: TLC: R₇ = 0.47 (PE/EtOAc = 95/5), [p-anisaldehyde].

Polycyclic ether (2f)

Compound 2f was synthesised according to general procedure 4 starting from dienol 1f (100 mg, 0.37 mmol) in CH₂Cl₂ at room temperature, Bi(OTf)₃ (1 mol%, 2.4 mg, 0.004 mmol) was added and the mixture was stirred for 6 h. Purification by flash chromatography (P/Et₂O = 95/5) afforded trans-2f (67 mg, 0.246 mmol, 67%) as a white solid. TLC: R₇ = 0.65 (PE/EtOAc = 95/5), [p-anisaldehyde].

1H-NMR (200 MHz, CDCl₃): δ [ppm] = 7.34 – 7.25 (8H), 7.20 – 7.10 (8H), 3.85 – 3.70 (8H), 3.55 – 3.31 (8H), 2.55 – 2.49 (8H), 2.40 – 2.19 (8H), 2.10 – 1.66 (8H), 1.66 – 1.36 (8H), 1.30 (8H), 1.13 – 0.92 (8H).

13C-NMR (50 MHz, CDCl₃): δ [ppm] = 139.15, 127.72, 126.89, 125.72, 96.58, 87.50, 77.94, 67.58, 54.31, 34.71, 30.07, 28.49, 28.41, 26.24, 23.67

IR (neat): ν [cm⁻¹] = 2965 (m), 2938 (m), 2859 (w), 1444 (w), 1276 (w), 1092 (m), 1075 (m), 1034 (s), 759 (s), 699 (s). ESI-HRMS: m/z calcd. for C19H23O2[M+H]⁺: 273.1855, found: 273.1841.
Polycyclic ether (trans-2h)

Compound 2h was synthesised according to general procedure 4 starting from dienol 1h (100 mg, 0.42 mmol) in CH\textsubscript{2}Cl\textsubscript{2} at room temperature, Bi(OTf)\textsubscript{3} (1 mol%, 2.8 mg, 0.004 mmol) was added and the mixture was stirred for 7 h. Purification by flash chromatography (P/Et\textsubscript{2}O = 95/5) afforded trans-2h (50 mg, 0.210 mmol, 50%) as a pale yellow oil. TLC: \(R_f = 0.78\) (PE/EtOAc = 95/5), \([p\text{-anisaldehyde}]\). \textsuperscript{1}H-NMR (200 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] = 3.89 – 3.72 (m, 1H), 3.78 – 3.62 (m, 1H), 2.43 – 2.23 (m, 1H), 2.14 – 1.62 (m, 6H), 1.30 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H). \textsuperscript{13}C-NMR (50 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] = 89.52, 88.77, 77.54, 64.25, 47.60, 40.99, 36.57, 34.02, 31.80, 29.69, 26.75, 26.30, 24.12, 11.77. IR (neat): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2964 (m), 2865 (w), 1451 (m), 1379 (m), 1159 (w), 978 (m), 926 (m), 896 (m).

Polycyclic ethers (trans-2i) and (cis-2i)

Compounds 2i were synthesised according to general procedure 4 starting from dienol 1i (100 mg, 0.45 mmol) in CH\textsubscript{3}NO\textsubscript{2} at room temperature, Bi(OTf)\textsubscript{3} (1 mol%, 2.95 mg, 0.002 mmol) was added and the mixture was stirred for 10 minutes. Purification by flash chromatography (P/Et\textsubscript{2}O = 95/5) afforded trans-2i (21 mg, 0.094 mmol, 21%) as a pale yellow oil and cis-2i (61 mg, 0.272 mmol, 61%) as a pale yellow oil. The overall yield of cycloisomerisation products was 82%.

trans-2i: TLC: \(R_f = 0.71\) (PE/EtOAc = 95/5), \([p\text{-anisaldehyde}]\). \textsuperscript{1}H-NMR (200 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] = 3.97 – 3.78 (m, 1H), 3.78 – 3.62 (m, 1H), 2.43 – 2.23 (m, 1H), 2.14 – 1.62 (m, 6H), 1.30 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H). \textsuperscript{13}C-NMR (50 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] = 96.29, 87.81, 77.62, 65.84, 52.92, 41.02, 38.24, 31.80, 29.36, 28.69, 26.75, 26.30, 24.12, 11.77. IR (neat): \(\tilde{\nu}\) (cm\textsuperscript{-1}) = 2964 (m), 2865 (w), 1451 (w), 1379 (m), 1159 (w), 1077 (s), 978 (w), 926 (m), 896 (m).
cis-2i: TLC: \( R_f = 0.46 \) (PE/EtOAc = 95/5), [\( p \)-anisaldehyde]. \(^1\)H-NMR (200 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 3.87 – 3.67 (m, 2H), 2.10 – 1.86 (m, 3H), 1.85 – 1.66 (m, 3H), 1.46 (s, 3H), 1.42 – 1.32 (m, 1H), 1.31 (s, 3H), 1.12 (s, 3H), 0.94 (s, 3H). \(^13\)C-NMR (50 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 95.30, 89.21, 79.24, 65.17, 49.73, 38.88, 37.31, 31.06, 29.35, 28.25, 26.82, 26.07, 24.38, 10.35. IR (neat): \( \tilde{\nu} \) (cm\(^{-1}\)) = 2955 (m), 2858 (w), 1467 (w), 1374 (m), 1080 (s), 1054 (m), 885 (m).

Polycyclic ether (2j)

Compound 2j was synthesised according to general procedure 4 starting from dienol 1j (100 mg, 0.39 mmol) in CH\(_2\)Cl\(_2\) at room temperature, Bi(OTf)\(_3\) (1 mol%, 2.54 mg, 0.003 mmol) were added and the mixture was stirred for 15 min. Purification by flash chromatography (P/EtO = 98:2) afforded trans-2j (58 mg, 0.23 mmol, 58%) as a pale yellow oil. TLC: \( R_f = 0.76 \) (P/EtO = 98:2), [\( p \)-anisaldehyde]. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 1.07 – 1.21 (m, 1H), 1.26 – 1.36 (m, 4H), 1.37 – 1.49 (m, 3H), 1.50 – 1.66 (m, 2H), 1.80-1.85 (m, 1H), 1.94 – 2.10 (m, 2H), 2.98 (d, \( ^1J = 3.3 \) Hz, 1H), 3.47 (m, 1H), 3.85 (m, 1H), 4.83 (s, 1H), 7.22 (m, 1H), 7.32-7.38 (m, 4H). \(^13\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 14.6, 20.7, 24.9, 26.0, 27.2, 35.4, 43.7, 65.1, 82.1, 84.5, 85.2, 124.5, 126.3, 128.1, 143.3.

Polycyclic ethers (trans-2k and cis-2k)

Compounds 2k were synthesised according to general procedure 4 starting from dienol 1k (100 mg, 0.41 mmol) in CH\(_2\)Cl\(_2\) at room temperature, Bi(OTf)\(_3\) (1 mol%, 2.69 mg, 0.004 mmol) were added and the mixture was stirred for 10 min. Purification by flash chromatography (P/EtO = 98:2) afforded trans-2k (65 mg, 0.27 mmol, 65%) as a pale yellow oil and cis-2k (23 mg, 0.09 mmol, 23%) as a pale yellow oil. The overall yield of cycloisomerisation products was 88%.

trans-2k: TLC: \( R_f = 0.76 \) (P/EtO = 98:2), [\( p \)-anisaldehyde]. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 1.14-1.20 (m, 1H), 1.27 (s, 3H), 1.67-1.79 (m, 4H), 1.83-1.89 (m, 1H), 2.02 (td, \( ^1J = 12.1 \) Hz, 3.5 Hz, 1H), 2.14-2.20 (m, 1H), 2.36 (d, \( ^1J = 3.8 \) Hz, 1H), 3.61-3.65 (m, 1H), 3.80-3.84 (m, 1H), 4.80 (s, 1H), 7.22-7.25 (m, 1H), 7.32-7.37 (m, 4H). \(^13\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 14.8, 26.7, 27.3, 28.3, 35.4, 50.6, 67.5, 82.2, 83.9, 91.7, 124.9, 126.3, 128.0, 143.1.

cis-2k: \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 1.29 (s, 3H), 1.66 – 1.75 (m, 3H), 1.76 – 1.90 (m, 4H), 1.91 – 1.97 (m, 1H), 2.36 (d, \( ^1J = 3.5 \) Hz, 1H), 3.45 – 3.52 (m, 1H), 3.68 – 3.76 (m, 1H), 4.81 (s, 1H), 7.16 – 7.21 (m, 1H), 7.28 – 7.33 (m, 2H), 7.40 – 7.42 (m, 2H). \(^13\)C-NMR (125 MHz, CDCl\(_3\)): \( \delta \) [ppm] = 14.33, 25.87, 26.92, 28.40, 34.08, 49.09, 67.74, 83.97, 84.84, 92.18, 125.72, 125.94, 127.57, 143.84.
Polycyclic ether (2l)

Compound 2l was synthesised according to general procedure 4 starting from dienol 1l (100 mg, 0.36 mmol) in CH$_2$Cl$_2$ at room temperature, Bi(OTf)$_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et$_2$O = 95/5) afforded a mixture of endo and exo compounds 2l which were not separated (50 mg, 0.18 mmol, 50%) as a pale yellow oil. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 5.11 (ddt, $^3J = 7.1, 5.6, 1.4$ Hz, 1H), 5.07 (ddt, $^3J = 7.1, 5.7, 1.4$ Hz, 1H), 3.83 – 3.78 (m, 1H), 3.78 – 3.76 (m, 1H), 3.45 (tdd, $^3J = 12.0, 6.4, 2.6$ Hz, 2H), 2.42 (d, $^3J = 3.3$ Hz, 1H), 2.39 (d, $^3J = 1.8$ Hz, 1H), 2.19 – 1.89 (m, 5H), 1.86 – 1.47 (m, 3H), 1.37 (ddd, $^3J = 13.6, 12.2, 5.2$ Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.08 (s, 6H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ [ppm] = 131.65, 131.54, 124.62, 124.55, 87.02, 86.94, 85.16, 84.92, 79.67, 79.29, 64.93, 64.86, 46.73, 46.02, 41.82, 40.84, 34.32, 34.26, 27.53, 27.23, 26.61, 26.19, 26.12, 25.86, 25.83, 24.21, 22.44, 21.31, 21.21, 21.16, 17.87, 17.73, 15.31, 15.24.

Polycyclic ether (exo-2l)

Compound exo-2l was synthesised according to general procedure 4 starting from dienol (E)-1l (100 mg, 0.36 mmol) in CH$_2$Cl$_2$ at room temperature, Bi(OTf)$_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et$_2$O = 95/5) afforded exo-2l (51 mg, 0.18 mmol, 51%) as a pale yellow oil. TLC: $R_f$ = 0.76 (P/Et$_2$O = 95/5), [p-anisaldehyde]. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 5.07 (ddt, $^3J = 8.6, 5.7, 1.4$ Hz, 1H), 3.83 – 3.78 (m, 1H), 3.45 (td, $^3J = 11.9, 2.6$ Hz, 1H), 2.40 – 2.37 (m, 1H), 2.15 – 2.06 (m, 1H), 2.05 – 1.93 (m, 3H), 1.88 – 1.80 (m, 1H), 1.80 – 1.74 (m, 1H), 1.72 – 1.63 (m, 6H), 1.63 – 1.51 (m, 7H), 1.37 (ddd, $^3J = 13.6, 12.2, 5.2$ Hz, 1H), 1.24 (s, 3H), 1.08 (s, 3H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ [ppm] = 131.65, 124.62, 87.02, 86.94, 85.16, 79.29, 64.93, 64.86, 46.73, 46.02, 41.82, 40.84, 34.32, 27.53, 27.23, 26.61, 26.19, 26.12, 25.86, 25.83, 24.21, 22.44, 21.31, 21.21, 21.16, 17.87, 17.73, 15.31, 15.24. IR (neat): $\tilde{\nu}$ (cm$^{-1}$) = 2966 (m), 2931 (m), 2854 (w), 2358 (s), 2341 (s), 1442 (w), 1373 (w), 1185 (m), 1075 (m), 989 (m), 910 (m).

Polycyclic ether (endo-2l)

Compound endo-2l was synthesised according to general procedure 4 starting from dienol (Z)-1l (100 mg, 0.36 mmol) in CH$_2$Cl$_2$ at room temperature, Bi(OTf)$_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et$_2$O = 95/5) afforded endo-2l (53 mg, 0.19 mmol, 53%) as a pale yellow oil. TLC: $R_f$ = 0.74 (P/Et$_2$O = 95/5), [p-anisaldehyde]. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 5.11 (ddt, $^3J$
Polycyclic ether (4a)

Compound 4a was synthesised according to general procedure 4 starting from dienol 3a (100 mg, 0.55 mmol) and Bi(OTf)₃ (1 mol%, 3.6 mg, 0.005 mmol) in CH₃NO₂ stirred at room temperature for 5 min. Purification by flash chromatography (P/EtO = 95/5) afforded 4a as a pale yellow oil (79 mg, 0.43 mmol, 79%). ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 3.88 – 3.67 (m, 2H), 2.38 (ddd, 3J = 11.5, 8.9, 4.5 Hz, 1H), 2.16 (ddd, 3J = 12.1, 7.7, 5.5 Hz, 1H), 1.98 – 1.77 (m, 3H), 1.74 – 1.41 (m, 5H), 1.37 (s, 3H), 1.31 (s, 3H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 90.90, 86.11, 83.63, 67.79, 52.90, 37.74, 36.07, 32.84, 25.81, 21.98, 17.21. IR (neat): ν (cm⁻¹) = 2966 (m), 2932 (m), 2868 (w), 1445 (w), 1375 (m), 1207 (m), 1095 (s), 1073 (s). ESI-HRMS: m/z calcd. for C₁₁H₁₈O₅ [MH⁺]: 183.1385, found: 183.1382.

Polycyclic ether (4b)

Compound 4b was synthesised according to general procedure 4 starting from dienol 3b (100 mg, 0.51 mmol) and Bi(OTf)₃ (1 mol%, 3.3 mg, 0.005 mmol) in CH₃NO₂ stirred at room temperature for 5 min. Purification by flash chromatography (P/EtO = 95/5) afforded 4b as a pale yellow oil (78 mg, 0.40 mmol, 78%). TLC: Rf = 0.57 (PE/ETOAc = 95/5, [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 8.72, 83.53, 83.22, 65.76, 46.03, 38.12, 32.48, 31.95, 26.25, 22.24, 19.14, 17.20. IR (neat): ν (cm⁻¹) = 2935 (m), 2860 (w), 1443 (w), 1375 (m), 1233 (m), 1207 (m), 1132 (m), 1083 (s), 1067 (s), 1036 (m), 998 (m), 902 (m), 861 (s). ESI-HRMS: m/z calcd. for C₁₂H₂₀O₃ [MH⁺]: 197.1537, found: 197.1536.

Polycyclic ether (4c)

Compound 4c was synthesised according to general procedure 4 starting from dienol 3c (100 mg, 0.41 mmol) and Bi(OTf)₃ (1 mol%, 2.7 mg, 0.004 mmol) in CH₃NO₂ stirred at room temperature for 15 min. Purification by flash chromatography (P/EtO = 95/5) afforded 4c as a pale yellow oil (95 mg, 0.39 mmol, 79%). TLC: Rf = 0.8 (PE/ETO = 95/5, [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 7.53 – 7.17 (m, 5H), 3.85 – 3.56 (m, 2H), 3.04 – 2.83 (m, 1H), 2.02 – 1.37 (m, 8H), 1.49 (s, 3H), 1.18 – 0.96 (m, 1H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 140.90, 127.77, 126.84, 125.79, 98.21, 93.33, 90.10, 83.64, 68.59, 53.59, 37.58, 37.46, 32.61, 25.56, 22.11. IR (neat): ν (cm⁻¹) = 2965 (m),
Polycyclic ether (4d)

Compound 4d was synthesised according to general procedure 4 starting from dienol 3d (100 mg, 0.39 mmol) and Bi(OTf)₃ (1 mol%, 2.5 mg, 0.004 mmol) in CH₃NO₂ stirred at room temperature for 15 min. Purification by flash chromatography (P/EtO = 95/5) afforded 4d as a white powder (83 mg, 0.32 mmol, 83%). TLC: Rf = 0.78 (PE/EtO = 95/5), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 7.73 – 7.21 (m, 5H), 4.07 – 3.85 (m, 1H), 3.53 (ddd, ³J = 11.4, 9.0, 4.9 Hz, 1H), 3.18 – 2.85 (m, 1H), 1.97 – 1.32 (m, 10H), 1.60 (s, 3H), 1.04 – 0.76 (m, 1H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 141.26, 127.75, 126.60, 125.78, 91.27, 84.29, 83.67, 65.83, 46.21, 38.00, 31.94, 26.05, 22.43, 19.01. IR (neat): ν (cm⁻¹) = 2941 (m), 2858 (w), 1449 (m), 1121 (m), 1071 (s), 1044 (s), 1021 (s), 988 (m), 761 (s), 701 (s).

X-ray crystal structure of 4d (CCDC number 1452480)

Polycyclic ether (5a)

Compound 5a was synthesised according to general procedure 4 starting from dienol 3a (100 mg, 0.55 mmol) and Bi(OTf)₃ (1 mol%, 3.6 mg, 0.005 mmol) in CH₂Cl₂ stirred at room temperature for 5 min. Purification by flash chromatography (P/EtO = 95/5) afforded 4a (23 mg, 0.13 mmol, 23%) as a pale yellow oil and 5a (50 mg, 0.27 mmol, 53%). 5a: TLC: Rf = 0.27 (PE/EtOAc = 9/1), [p-anisaldehyde]. ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 1.23 (s, 3H), 1.37-1.58 (m, 1H), 1.59-1.72 (m, 3H), 1.82-2.30 (m, 7H), 3.85 (m, 2H), 5.27 (m, 1H). ¹³C-NMR (50 MHz, CDCl₃): δ [ppm] = 23.20, 23.25, 26.27, 30.77, 38.41, 41.88, 68.59, 72.09, 86.02, 119.57, 132.59. IR (neat): ν (cm⁻¹) = 3465 (b, OH), 2967 (m), 2901 (m), 1441 (m), 1366 (m), 1128 (m), 1108 (m), 1065 (s).

3 References


4 NMR spectra

1a

NMR spectrum with peaks at various ppm values.

1a

NMR spectrum with peaks at various ppm values.
trans-2a

trans-2a
trans-2h

trans-2h