Supporting Information

Rhodium-Catalyzed Cyclization of Terminal and Internal Allenols: An Atom Economic and Highly Stereoselective Access Towards Tetrahydropyrans

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Abstract: A comprehensive study of a diastereoselective Rh-catalyzed cyclization of terminal and internal allenols is reported. The methodology allows an atom economic and highly syn-selective access to synthetically important 4,6-disubstituted, respectively 2,4,6-trisubstituted tetrahydropyrans (THP). Furthermore, it demonstrates its utility and versatility through a great functional group compatibility and the possibility to enable the stereoselective access of THP compounds.

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1 General and Materials

FCC (Flash Column Chromatography) was accomplished using MACHEREY-NAGEL silica gel 60 ® (230-400 mesh).

TLC (Thin Layer Chromatography) was performed on aluminum plates pre-coated with silica gel (MERCK, 60F254), which were visualized by UV fluorescence (λ\text{max} = 254 nm) and/or by staining with 1% w/v KMnO₄ in 0.5 M aqueous K₂CO₃.

NMR (Nuclear Magnetic Resonance) spectra were acquired on a BRUKER Avance 400 spectrometer (400 MHz and 100.6 MHz for \(^1\)H and \(^{13}\)C respectively) and/or on a VARIAN Mercury (300 MHz and 75.5 MHz for \(^1\)H and \(^{13}\)C respectively). All \(^1\)H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm (CHCl₃). All \(^{13}\)C-NMR spectra were reported in ppm relative to residual CHCl₃ (77.16 ppm) and were obtained with \(^1\)H-decoupling. Data for \(^1\)H-NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. Data for \(^{13}\)C-NMR spectra are described in terms of chemical shift (δ in ppm).

High resolution mass spectra (HR-MS) were obtained on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument (APCI/MeOH: spray voltage 4-5 kV, ion transfer tube: 250-300 °C, vaporizer: 300-400 °C).

Chiral HPLC was performed on a MERCK HITACHI HPLC apparatus (pump: L-7100, UV detector: D-7400, oven: L-7360; columns: Chiralpak AD-3, AD-H, Chiralcel OD-3, 25 cm, 4.6 mm, DAICEL; Lux A-2, C-1, C-2, C-4, 50 cm, 4.6 mm, PHENOMENEX; carrier gas: He).

GC
Chiral GC was performed on an Agilent Technologies 6890N network GC-System [Inlet: 200 °C, 1.13 bar; Column: Hydrodex-B-TBDAc 25m x 0.25mm, carrier gas He (constant flow 1 mL/min).

Optical Rotation
The optical rotation of chiral compounds was determined on an A. KRÜSS Optronic P8000 T apparatus and transformed for a given temperature according to the following formula

\[
\left[\alpha\right]_D = \frac{\alpha \cdot 100}{c \cdot d}
\]
α: measured value for optical rotation; c: concentration in g/100 ml; d: length of the cuvette in dm; T: temperature in °C.

**Solvents:** 1,2-Dichloroethane (DCE) was freshly distilled over CaH$_2$ and degassed with argon prior to use. Toluene was freshly distilled over Sodium/Benzophenone and degassed with argon prior to use. Terahydrofuran (THF) was purchased in HPLC grade quality and was purified by continuous distillation over potassium under argon. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled by rotary evaporator before use.

**Ligand and Metal catalyst:** The ligands were purchased from Sigma-Aldrich, ABCR, Alfa Aesar, TCI, ChemPur and used without further purification. Josiphos was either purchased from Sigma-Aldrich or received as a gift from Solvias. [Rh(COD)Cl]$_2$ and Pd(dba)$_2$ were purchased from Sigma-Aldrich
2 Experimental Procedures Substart Synthesis

2.1 Preparation terminal allenes.

2.1.1 General Procedure terminal allene

General procedure GRIGNARD synthesis (GP1):
To a suspension of magnesium (1.2 equiv.) and iodide (catalytic amount) in THF (1.0 M) corresponding bromide (15 mmol) was added dropwise. After the reaction stopped refluxing, the mixture was heated to 80 °C for 1 h. Afterwards the solution was cooled to room temperature and directly used in the substrate synthesis or was stored in the freezer.

General procedure 2: 1,4-Addition:

A mixture of CuI (10 mol%) and LiBr (20 mol%) was carefully dried and cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus, before extra dry or freshly distilled THF (1.0 M) was added. The mixture was stirred at room temperature for 15 min and then cooled to −78 °C to −30 °C. A solution of ethyl (E)-hepta-2,5,6-trienoate (1.0 equiv.) in extra dry or freshly distilled THF (0.3 M) and TMSCl (1.1 equiv.) was added at this temperature. The mixture was stirred for 15 min before the GRIGNARD reagent in THF (1.5 equiv.) was added dropwise, stirred for 30 minutes at −78 °C and then slowly warmed to −30 °C. The reaction was quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O (4 × 30 mL), the combined organic layer were washed with brine (40 mL) and dried over Na₂SO₄. The solvent was removed and the residue was purified by flash chromatography on silica gel using a mixture of pentane and ether.
**General procedure 3: LAH-reduction:**

A suspension of LAH (1.5 equiv.) in dry Et₂O was cooled to 0 °C then a solution of 3-ethylhepta-5,6-dienoate in Et₂O (0.5 M) was added dropwise. The reaction was stirred at this temperature for 1 h and then warmed to room temperature and stirred for another hour. The mixture was quenched through the addition of H₂O and aqueous HCl (2.0 M). The layers were separated, the organic layer was washed with H₂O (20 mL) and brine (20 mL). The aqueous layer was extracted with Et₂O (4 × 20 mL). The combined organic layer were dried over Na₂SO₄, the solvent was removed. The crude product was used without further purification.

**General procedure 4:**

I) A mixture of CuI (10 mol%) and LiBr (20 mol%) was carefully dried and cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus, before extra dry or freshly distilled THF (1.0 M) was added. The mixture was stirred at room temperature for 15 min and then cooled to −78 °C to −30 °C. A solution of ethyl (E)-hepta-2,5,6-trienoate (1.0 equiv.) in extra dry or freshly distilled THF (0.3 M) and TMSCl (1.1 equiv.) was added at this temperature. The mixture was stirred for 15 min before the GRIGNARD reagent in THF (1.5 equiv.) was added dropwise, stirred for 30 minutes at −78 °C and then slowly warmed to −30 °C. The reaction was quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O (4 × 30 mL), the combined organic layer were washed with brine (40 mL) and dried over Na₂SO₄. The solvent was removed and the residue was filtered over a short silica pad.

II) The crude product was dissolved in Et₂O (0.5 M) and added dropwise to a suspension of LAH (1.5 equiv.) in dry Et₂O at 0 °C. The reaction was stirred at this temperature for 1 h and then warmed to room temperature and stirred for another hour. The mixture was quenched through the addition of H₂O and aqueous HCl (2.0 M). The layers were separated, the organic layer was washed with H₂O (20 mL) and brine (20 mL). The aqueous layer was extracted with Et₂O (4 × 20 mL). The combined organic layer were dried over Na₂SO₄, the solvent was removed. The solvent was removed and the residue was purified by flash chromatography on silica gel using a mixture of pentane and ether.
2.1.2 Synthesis and characterization of terminal allenes

Synthesis of ethyl (E)-hepta-2,5,6-trienoate

Prepared in analogy to a literature procedure.[1]

To a solution of propargyl alcohol (9.0 mL, 8.7 g, 0.16 mol, 0.5 equiv.) in triethyl orthoacetate (60 mL, 53 g, 0.32 mol, 1.0 equiv.) was added dropwise propionic acid (0.80 mL, 0.80 g, 11 mmol, 4.0 mol%) at 100 °C. The mixture was heated to 160 °C and resulting EtOH was continuously distilled off under atmospheric pressure for 1 h. Then another aliquot of propargyl alcohol (9.0 mL, 8.7 g, 0.16 mol, 0.5 equiv.) and propionic acid (0.80 mL, 0.80 g, 11 mmol, 4.0 mol%) were added dropwise and the mixture was stirred for another 1 h before a third portion of propionic acid (0.80 mL, 0.80 g, 11 mmol, 4.0 mol%) was added. The reaction was stirred for an additional hour and then cooled to room temperature and quenched by addition of aqueous HCl-solution (2 M, 100 mL). The organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 100 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by fractional distillation under reduced pressure (bp₄₆ mbar: 75 °C). The title compound was obtained as colorless liquid (23 g, 0.24 mol, 76 %).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.27\) (t, \(J = 7.1\) Hz, 3H), 3.07 (dt, \(J = 7.4\) Hz, \(J = 3.0\) Hz, 2H), 4.16 (q, \(J = 7.1\) Hz, 2H), 4.76 (dt, \(J = 2.9\) Hz, \(J = 6.7\) Hz, 2H), 5.27 (m, 1H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.3, 34.7, 60.9, 75.8, 83.6, 171.4, 209.5\) ppm.

APCI-HRMS: \(m/z\) calcd for C₇H₁₀O₂ [M+H]⁺ 127.0759, found 127.0759.
Preparing in analogy to a literature procedure,[1] a solution of DIBAL-H (189 mL 189 mmol, 1.4 equiv., 1.0 M in CH₂Cl₂) was added dropwise over 90 min to a solution of ethylpenta-3,4-dienoate (17.1 g, 136 mmol, 1.0 equiv.) in CH₂Cl₂ (85 mL). The reaction mixture was stirred for 1 h and then transferred to an ice cold aqueous solution of HCl (2.0 M, 500 mL) at 0°C. The layers were separated, the organic layer was washed with HCl (2.0 M, 2 × 500 mL) and the aqueous layer was extracted with CH₂Cl₂ (2 × 300 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, filtered over a silica pad and concentrated under reduced pressure. The title compound 123 was obtained as colorless liquid (5.47 g, 63.5 mmol, 47%).

Analytical Data:

¹H-NMR (400.1 MHz, CDCl₃): δ = 3.11 (dtd, J = 7.7, 3.0, 1.8 Hz, 2H), 4.79 (dt, J = 6.8, 3.0 Hz, 2H), 5.25 (m, 1H), 9.71 (t, J = 1.9 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 42.8, 76.0, 81.1, 199.2, 210.1 ppm.

APCI-HRMS: m/z calcld for C₅H₆O [M+NH₄]⁺ 100.0762, found 100.0757.
Synthesis of ethyl (E)-hepta-2,5,6-trienoate 62

Prepared in analogy to a literature procedure.\[^2\]

A suspension of NaH (60% in mineral oil, 1.1 g, 27 mmol, 1.1 equiv.) in dry THF (100 mL) was cooled to 0 °C and triethyl phosphonoacetate (6.9 g, 6.2 mL, 31 mmol, 1.3 equiv.) was added dropwise to the reaction mixture. After complete addition, the suspension was stirred for 1 h at 0 °C and was then cooled to −78 °C. A solution of penta-4,5-dienal (2.0 g, 24 mmol, 1.0 equiv.) in dry THF (20 mL) was added dropwise to the reaction mixture at this temperature. The mixture was slowly warmed to −20 °C over 3 h and then quenched by the addition of aqueous saturated NH₄Cl-solution (50 mL). The layers were separated, the aqueous layer was extracted with Et₂O (3 × 100 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (60:1 Pentane:Et₂O). The title compound was obtained as colorless liquid (3.2 g, 21 mmol, 85 %).

Analytical Data:

\[^1\]H-NMR (400.1 MHz, CDCl₃): δ = 1.29 (t, J = 7.0 Hz, 3H), 2.87 – 2.93 (m, 2H), 4.19 (q, J = 7.0 Hz, 2H), 4.74 (dt, J = 6.8, 3.1 Hz, 2H), 5.12 (tt, J = 6.9 Hz, 1H), 5.89 (dt, J = 15.7, 1.7 Hz, 1H), 6.97 (dt, J = 15.6, 6.4 Hz, 1H) ppm.

\[^13\]C-NMR (100.6 MHz, CDCl₃): δ = 14.3, 31.2, 60.3, 75.8, 86.4, 122.2, 146.3, 166.5, 209.3 ppm.

APCI-HRMS: m/z calcld for C₉H₁₃O₂ [M+H]⁺ 153.0910, found 153.0909.
Synthesis of ethyl 3-methylhepta-5,6-dienoate 63

The reaction was performed according to general procedure 3 with (E)-hepta-2,5,6-trienoate (1.0 g, 6.6 mmol, 1.0 equiv.) and methyl magnesium bromide in THF (3.3 mL, 9.9 mmol, 3.0 M). The desired product was obtained as a colourless liquid (0.98 g, 5.8 mmol, 88%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.98$ (d, $J = 6.4$, 3H), 1.25 (t, $J = 7.1$, 3H), 1.95 – 2.16 (m, 4H), 2.30 – 2.41 (m, 1H), 4.09 – 4.17 (m, 2H), 4.65 (dt, $J = 6.7$, 2.7, 2.7, 2H), 5.00 – 5.11 (m, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.4$, 19.6, 30.7, 35.7, 41.2, 60.2, 74.4, 87.7, 173.1, 209.4 ppm.

APCI-HRMS: $m/z$ calcd for C$_{10}$H$_{20}$O$_2$N [M+NH$_4$]$^+$ 186.1489 found 186.1489

GC: Hydrodex-B-TBDAc 25m x 0.25mm, 80 °C, isothermal [50% ee. $t_R = 29.0$ min (minor), 30.0 min (major)]

Synthesis of 3-methylhepta-5,6-dien-1-ol 53rac

The reaction was performed according to general procedure 4 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and methyl magnesium bromide (2.6 mL, 7.8 mmol, 3.0 M). The crude product from step I was treated with LAH (0.30 g, 7.8 mmol, 1.5 equiv.) The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et$_2$O). The desired product was obtained as a colorless liquid (0.63 g, 3.3 mmol, 63%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.95$ (d, $J = 6.7$ Hz, 3H), 1.27 (s, 1H), 1.36 – 1.47 (m, 1H), 1.63 – 1.77 (m, 2H), 1.85 – 1.97 (m, 1H), 2.04 (dddd, $J = 14.1$, 7.3, 5.8, 3.0, 3.0 Hz, 1H), 3.64 – 3.76 (m, 2H), 4.64 (ddd, $J = 6.7$, 2.9, 2.9 Hz, 2H), 5.06 (ddd, $J = 7.4$, 7.4, 6.6, 6.6 Hz 1H), ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 19.6$, 30.0, 36.1, 39.4, 61.2, 74.2, 88.1, 209.3 ppm.

APCI-HRMS: $m/z$ calcd for C$_8$H$_{14}$O [M+H]$^+$ 127.1117 found 127.1119.
Synthesis of 3-(buta-2,3-dien-1-yl)tetradecanol 64

The reaction was performed according to **general procedure 4** with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and undecyl magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product from step I was treated with LAH (0.30 g, 7.8 mmol, 1.5 equiv.) The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.9 g, 3.4 mmol, 65%).

**Analytical Data**

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 0.84 – 0.92\) (m, 3H), \(1.26\) (m, 21H), \(1.50 – 1.64\) (m, 3H), \(1.96 – 2.11\) (m, 2H), \(3.68\) (t, \(J = 6.8, 2H\)), \(4.64\) (dd, \(J = 6.7, 2.9, 2H\)), \(4.94 – 5.09\) (m, 1H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.2, 22.8, 26.7, 29.4, 29.7, 29.8, 30.1, 32.0, 32.8, 33.7, 34.7, 36.8, 61.2, 74.2, 87.9, 209.3\) ppm.

**APCI-HRMS:** \(m/z\) calcd for C₁₈H₃₅O \([\text{M+H}]^+\) 267.2682 found 267.2682.

Synthesis of 3-neopentylhepta-5,6-dien-1-ol 65

The reaction was performed according to **general procedure 4** with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (3,3-dimethylbutyl) magnesium bromide (7.2 mL, 7.2 mmol, 1.0 M). The crude product from step I was treated with LAH (0.30 g, 7.8 mmol, 1.5 equiv.) The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.52 g, 2.9 mmol, 55%).

**Analytical Data**

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 0.90\) (s, 9H), \(1.13 – 1.18\) (m, 1H), \(1.24 – 1.29\) (m, 2H), \(1.50 – 1.68\) (m, 3H), \(1.95 – 2.13\) (m, 2H), \(3.62 – 3.72\) (m, 2H), \(4.65\) (ddd, \(J = 6.7, 2.9, 2.9\) Hz 2H), \(5.04\) (ddd, \(J = 7.5, 6.7, 6.7\) Hz 1H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 30.0, 31.0, 31.3, 35.2, 39.0, 47.9, 61.2, 74.2, 88.0, 209.5\) ppm.

**APCI-HRMS:** \(m/z\) calcd for C₁₂H₂₃O \([\text{M+H}]^+\) 183.1743 found 183.1743.
Synthesis of ethyl 3-cyclopropylhepta-5,6-dienoate 66

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and cyclopropylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.58 g, 3.0 mmol, 58%).

Analytical Data

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.13 – 0.16 (m, 2H), 0.39 – 0.51 (m, 2H), 0.59 – 0.68 (m, 1H), 1.18 – 1.27 (m, 4H), 2.11 (dddd, J = 14.1, 8.1, 7.2, 2.5 Hz, 1H), 2.22 (ddddd, J=14.2, 7.3, 5.8, 3.0, 3.0 Hz, 1H), 2.34 (dd, J = 14.6, 7.2 Hz, 1H), 2.44 (dd, J = 14.6, 6.8 Hz, 1H), 4.12 (dddd, J = 7.1, 7.1, 7.1, 1.5 Hz, 2H), 4.60 – 4.67 (m, 2H), 5.09 (dddd, J = 8.1, 6.7, 6.7, 6.7 Hz, 1H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 4.0, 4.2, 14.3, 15.9, 34.2, 39.6, 41.5, 60.2, 74.2, 87.5, 173.2, 209.4 ppm.

APCI-HRMS: m/z calcd for C₁₂H₁₉O₂ [M+H]^+ 195.1380 found 195.1379.

Synthesis of 3-cyclopropylethta-5,6-dienol 67

The reaction was performed according to general procedure 3 with ethyl 3-(3-phenylpropyl)hepta-5,6-dienoate (0.58 g, 3.0 mmol.) and LAH (0.17 g, 4.5 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.45 g, 0.29 mmol, 99%).

Analytical Data

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.05 – 0.19 (m, 2H), 0.41 – 0.52 (m, 2H), 0.52 – 0.65 (m, 1H), 0.79 – 0.87 (m, 1H), 1.40 (s, 1H), 1.66 (dddd, J = 13.7, 7.6, 6.9, 6.9 Hz, 1H), 1.77 (ddddd, J = 13.9, 6.9, 6.9, 6.0 Hz, 1H), 2.09 (ddddd, J = 14.1, 7.9, 7.0, 2.6, 2.6 Hz, 1H), 2.19 (ddddd, J = 14.2, 7.3, 5.4, 3.0, 3.0 Hz, 1H), 3.75 – 3.80 (m, 2H), 4.61 – 4.66 (m, 2H), 5.08 – 5.16 (m, 1H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 3.8, 4.6, 16.0, 34.4, 37.7, 41.0, 61.3, 74.1, 88.0, 209.2 ppm.

APCI-HRMS: m/z calcd for C₁₂H₁₃O [M+H]^+ 153.1274 found 153.1274.
Synthesis of ethyl 3-cyclohexylhepta-5,6-dienoate 68

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and cyclopropylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et2O). The desired product was obtained as a colorless liquid (0.58 g, 3.0 mmol, 58%).

1H-NMR (400.1 MHz, CDCl3): δ = 5.05 – 4.97 (m, 1H), 4.63 (ddd, J = 6.7, 3.1, 2.4 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 2.32 (dd, J = 15.3, 6.2 Hz, 1H), 2.22 (dd, J = 15.4, 7.2 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.92 – 1.83 (m, 1H), 1.77 – 1.58 (m, 7H), 1.25 (t, J = 7.1 Hz, 4H), 1.21 – 1.05 (m, 3H), 1.05 – 0.92 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 209.3, 173.9, 88.3, 74.3, 60.2, 40.6, 40.5, 36.2, 30.7, 30.0, 29.9, 26.8, 26.8, 14.3 ppm.

HRMS (pos. APCI): [M+H+] calculated for 237.1849, found 237.1846.

Synthesis of 3-cyclohexylhepta-5,6-dien-1-ol 69

The reaction was performed according to general procedure 3 with ethyl 3-(3-phenylpropyl)hepta-5,6-dienoate (0.58 g, 3.0 mmol.) and LAH (0.17 g, 4.5 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.45 g, 0.29 mmol, 99%).

1H-NMR (400.1 MHz, CDCl3): δ = 5.11 – 4.99 (m, 1H), 4.64 (dt, J = 6.7, 2.9 Hz, 2H), 3.74 – 3.60 (m, 2H), 2.09 (dddt, J = 14.5, 7.2, 5.5, 3.1 Hz, 1H), 1.94 (dddt, J = 14.5, 7.6, 6.8, 2.8 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.69 – 1.57 (m, 4H), 1.50 (dt, J = 13.5, 7.3, 6.1 Hz, 1H), 1.43 – 1.32 (m, 4H), 1.28 – 1.14 (m, 3H), 1.11 (dt, J = 12.6, 3.4 Hz, 1H), 1.08 – 0.96 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 209.1, 88.9, 74.3, 61.9, 40.5, 40.1, 34.0, 30.3, 29.9, 29.8, 26.9, 26.9, 26.9 ppm.

APCI-HRMS: m/z calcd for C13H23O [M+H]+ 195.1743, found 195.1743
Synthesis of ethyl 3-(3-phenylpropyl)hepta-5,6-dienoate 70

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (3-phenylpropyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.92 g, 3.4 mmol, 65%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.24 \text{ (t, } J = 7.1 \text{ Hz, 3H), 1.35 – 1.47 (m, 2H), 1.60 – 1.69 (m, 2H), 1.97 – 2.12 (m, 3H), 2.21 – 2.36 (m, 2H), 2.60 \text{ (dd, } J = 7.7 \text{ Hz, 2H), 4.12 (dddd, } J = 7.1 \text{ Hz, 2H), 4.59 – 4.66 (m, 2H), 5.01 \text{ (ddd, } J = 7.2, 6.6 \text{ Hz, 1H), 7.15 – 7.20 (m, 3H), 7.25 – 7.29 (m, 2H).ppm.}

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.3, 28.5, 32.9, 33.3, 35.3, 36.1, 38.8, 60.2, 74.4, 87.3, 125.8, 128.3, 128.4, 142.5, 173.2, 209.4 \text{ ppm.}

APCI-HRMS: \(m/z \) calcd for C₁₅H₂₅O₂ [M+H]⁺ 273.1849 found 273.1852.

Synthesis of 3-(3-phenylpropyl)hepta-5,6-dienol 71

The reaction was performed according to general procedure 3 with ethyl 3-(3-phenylpropyl)hepta-5,6-dienoate (0.92 g, 3.4 mmol, 1.0 equiv.) and LAH (0.19 g, 5.1 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.78 g, 3.3 mmol, 98%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.29 \text{ (s, 1H), 1.34 – 1.42 (m, 2H), 1.54 – 1.69 (m, 5H), 2.03 \text{ (dddd, } J = 7.5, 5.7, 2.9, 1.0 \text{ Hz, 2H), 2.57 – 2.64 (m, 2H), 3.67 \text{ (dd, } J = 6.8, 6.8 \text{ Hz, 2H), 4.63 \text{ (dd, } J = 6.7, 2.9, 2.9 \text{ Hz, 2H), 4.93 – 5.07 (m, 1H), 7.15 – 7.20 (m, 3H), 7.26 – 7.30 (m, 2H).ppm.}

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 28.6, 32.7, 33.2, 34.5, 36.3, 36.7, 61.1, 74.2, 87.7, 125.8, 128.3, 128.4, 142.6, 209.3 \text{ ppm.}

APCI-HRMS: \(m/z \) calcd for C₁₄H₂₆ON [M+NH₄]⁺ 248.2009 found 248.2007.
Synthesis of ethyl 3-phenylhepta-5,6-dienoate 72

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and phenylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.66 g, 2.9 mmol, 55%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): δ = 1.14 (t, J = 7.1 Hz, 3H), 2.36 (ddt, J = 7.3, 7.1, 2.8 Hz, 2H), 2.58 (dd, J = 15.3, 8.4 Hz, 1H), 2.73 (dd, J = 15.3, 6.7 Hz, 1H), 3.19 – 3.31 (m, 1H), 4.03 (q, J = 7.2 Hz, 2H), 4.60 (dt, J = 6.7, 4.0 Hz 2H), 4.95 (ddt, J = 7.1, 4.0, 2.8 Hz, 1H), 7.16 – 7.24 (m, 3H), 7.26 – 7.33 (m, 2H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 35.5, 40.7, 42.2, 60.3, 74.7, 87.5, 126.7, 127.6, 128.5, 143.5 172.3, 209.4 ppm.

APCI-HRMS: m/z calcd for C₁₅H₂₂O₂N [M+NH₄]^+ 248.1645 found 248.1647

Synthesis of 3-phenylhepta-5,6-dien-1-ol 73

The reaction was performed according to general procedure 3 with ethyl 3-phenylhepta-5,6-dienoate (0.66 g, 2.9 mmol, 1.0 equiv.) and LAH (0.17 g, 4.4 mmol, 1.5 equiv., ). The desired product was obtained as a colorless liquid (0.54 g, 2.9 mmol, 99%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): δ = 1.37 (s, 1H), 1.83 (dddd, J = 13.7, 10.1, 6.4, 5.4 Hz, 1H), 2.04 (dddd, J = 13.7, 7.6, 7.0, 4.8 Hz, 1H), 2.30 – 2.40 (m, 2H), 2.84 (dt, J = 10.0, 7.3, 4.8 Hz, 1H), 3.42 – 3.59 (m, 2H), 4.54 – 4.64 (m, 2H), 4.95 (ddd, J = 14.0, 7.3, 6.7 Hz, 1H), 7.16 – 7.24 (m, 3H), 7.27 – 7.33 (m, 2H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): δ = 29.8, 36.0, 38.7, 42.6, 61.1, 74.5, 88.0, 126.5, 127.8, 128.5, 144.4, 209.2 ppm.

APCI-HRMS: m/z calcd for C₁₃H₂₀ON [M+NH₄]^+ 206.1541 found 206.1541
Synthesis of ethyl 3-(naphthalene-2-yl)hepta-5,6-dienoate 74

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and naphthalene-2-ylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.76 g, 2.7 mmol, 52%).

Analytical Data

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.12 (t, J = 7.1 Hz, 3H), 2.40 – 2.54 (m, 2H), 2.70 (dd, J = 15.4, 8.5 Hz, 1H), 2.82 (dd, J = 15.4, 6.6 Hz, 1H), 3.43 (ddd, J = 8.5, 7.1, 7.1 Hz, 1H), 4.02 (ddd, J = 7.1, 7.1, 3.0 Hz, 2H), 4.54 – 4.66 (m, 2H), 4.97 (ddd, J = 7.5, 6.8, 6.8 Hz 1H), 7.36 (m, 1H), 7.42 – 7.47 (m, 2H), 7.65 (m, 1H), 7.78 – 7.82 (m, 3H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 35.4, 40.7, 42.3, 60.4, 74.8, 87.5, 125.5, 125.9, 126.0, 126.2, 127.7, 127.8, 128.2, 132.5, 133.6, 141.0, 172.2, 209.4 ppm.

APCI-HRMS: m/z calcd for C₁₉H₂₄O₂N [M+NH₄]⁺ 298.1802 found 298.1798.
Synthesis of ethyl 3-[(1,1'-biphenyl)-4-yl]hepta-5,6-dienoate 75

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and [1,1'-biphenyl]-4-ylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.75 g, 2.4 mmol, 47%).

\[ ^1H\text{-NMR (400.1 MHz, CDCl}_3\text{): 2.44 - 2.35 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H), 2.63 (dd, J = 15.3, 8.5 Hz, 1H), 2.77 (dd, J = 15.3, 6.6 Hz, 1H), 3.30 (dq, J = 8.5, 7.1 Hz, 1H) 4.06 (qd, J = 7.2, 0.7Hz, 2H), 4.63 (ddt, J = 6.3, 3.6, 2.7 Hz, 2H), 5.03 - 4.95 (m, 1H), 7.30 - 7.28 (m, 1H), 7.28 - 7.26 (m, 1H), 7.36 - 7.30 (m, 1H), 7.46 - 7.41 (m, 2H), 7.53 - 7.52 (m, 1H), 7.55 (d, J = 4.1 Hz,1H) 7.59 - 7.57 (m, 1H), 7.61 - 7.59 (m, 1H)ppm.} \]

\[ ^13C\text{-NMR (100.6 MHz, CDCl}_3\text{): } \delta = 14.2, 35.5, 40.7, 41.8, 60.4, 74.8, 87.5, 127.1, 127.2, 127.2, 128.0, 128.8, 142.6, 172.3, 209.4 \text{ ppm.} \]

ESI-HRMS: m/z calcd for C₂₁H₂₂O₂Na [M+Na]⁺ 329.1512 found 329.1508.

Synthesis of 3-[(1,1'-biphenyl)-4-yl]hepta-5,6-dien-1-ol 76

The reaction was performed according to general procedure 3 with ethyl 3-[(1,1'-biphenyl)-4-yl]hepta-5,6-dienoate (0.75 g, 2.4 mmol, 1.0 equiv.) and LAH (0.14 g, 3.6 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.62 g, 2.4 mmol, 98%).

\[ ^1H\text{-NMR (400.1 MHz, CDCl}_3\text{): 1.36 (s, 1H), 1.87 (dddd, J = 13.7, 10.0, 6.4, 5.4 Hz, 1H), 2.07 (dddd, J = 13.8, 7.6, 7.0, 4.8 Hz, 1H), 2.38 (tt, J = 7.3, 2.8 Hz, 2H), 2.90 (dt, J = 10.0, 7.3, 4.8 Hz, 1H), 3.48 - 3.70 (m, 2H), 4.52 - 4.67 (m, 2H), 4.91 - 5.07 (m, 1H), 7.23 - 7.26 (m, 1H), 7.26 - 7.29 (m, 1H), 7.30 - 7.38 (m, 1H), 7.40 - 7.51 (m, 2H), 7.51 - 7.66 (m, 4H) ppm.} \]

\[ ^13C\text{-NMR (100.6 MHz, CDCl}_3\text{): } \delta = 36.0, 38.7, 42.2, 61.1, 74.6, 88.0, 127.0, 127.2, 127.2, 128.2, 128.8, 139.4, 141.0, 143.5, 209.2 \text{ ppm.} \]

APCI-HRMS: m/z calcd for C₁₉H₂₄ON [M+NH₄]⁺ 282.1852 found 282.1855.
Synthesis of ethyl 3-(p-tolyl)hepta-5,6-dienoate 77

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and p-tolylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.76 g, 3.1 mmol, 60%).

Analytical Data

`^1`H-NMR (400.1 MHz, CDCl₃): δ = 1.15 (t, J = 7.1 Hz, 3H), 2.31 (s, 3H), 2.32–2.37 (m, 2H), 2.56 (dd, J = 15.3, 8.4 Hz, 1H), 2.71 (dd, J = 15.3, 6.7 Hz, 1H), 3.20 (dd, J = 8.4, 6.9 Hz, 1H), 4.04 (dd, J = 7.2, 1.4 Hz, 1H), 4.61 (m, 2H), 4.85–5.02 (m, 1H), 7.09 (d, J = 0.7 Hz, 4H) ppm.

`^{13}`C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 21.1, 35.5, 40.8, 41.8, 60.3, 74.6, 87.6, 127.4, 129.2, 136.1, 140.5, 172.4, 209.3 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₅O₂N [M+NH₄]²⁺ 262.1802 found 262.1801.

Synthesis of 3-(p-tolyl)hepta-5,6-dien-1-ol 78

The reaction was performed according to general procedure 3 with ethyl 3-(p-tolyl)hepta-5,6-dienoate (0.76 g, 3.1 mmol, 1.0 equiv.) and LAH (0.17 g, 4.7 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.61 g, 3.0 mmol, 98%).

Analytical Data

`^1`H-NMR (400.1 MHz, CDCl₃): δ = 1.32 (s, 1H), 1.80 (dddd, J = 13.7, 10.1, 6.4, 5.4 Hz, 1H), 2.02 (ddddd, J = 14.0, 7.5, 7.0, 4.8 Hz, 1H), 2.30–2.35 (m, 5H), 2.79 (ddtd, J = 10.0, 7.3, 4.7 Hz, 1H), 3.45–3.61 (m, 2H), 4.50–4.74 (m, 2H), 4.95 (dddd, J = 14.0, 7.3, 6.7, 1H), 7.05–7.14 (m, 4H) ppm.

`^{13}`C-NMR (100.6 MHz, CDCl₃): δ = 21.1, 36.1, 38.7, 42.2, 61.2, 74.5, 88.1, 127.6, 129.2, 135.9, 141.3, 209.2 ppm.

APCI-HRMS: m/z calcd for C₁₄H₂₁O₂ [M+HO₂]²⁺ 221.1536 found 221.1531.
Synthesis of ethyl 3-((m-tolyl)hepta-5,6-dienoate 79

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and m-tolylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.67 g, 2.8 mmol, 54%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.15 (t, J = 7.1 \text{ Hz}, 3\text{H}), 2.32 – 2.37 (m, 5\text{H}), 2.57 (dd, J = 15.3, 8.3 \text{ Hz}, 1\text{H}), 2.71 (dd, J = 15.3, 6.7 \text{ Hz}, 1\text{H}), 3.20 (dq, J = 8.4, 7.1 \text{ Hz}, 1\text{H}), 4.04 (m, 2\text{H}), 4.53 – 4.68 (m, 2\text{H}), 4.95 (m, 1\text{H}), 6.96 – 7.06 (m, 3\text{H}), 7.13 – 7.25 (m, 1\text{H}) \text{ ppm.}

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.2, 21.5, 35.5, 40.7, 42.1, 60.3, 74.6, 87.6, 124.5, 127.4, 128.3, 128.4, 137.9, 143.5, 172.4, 209.3 \text{ ppm.}

APCI-HRMS: \(m/z \) calcd for C₁₈H₂₄O₂N [M+NH₄]⁺ 262. 1802 found 262.1799.

Synthesis of 3-(m-tolyl)hepta-5,6-dien-1-ol 80

The reaction was performed according to general procedure 3 with ethyl 3-(m-tolyl)hepta-5,6-dienoate (0.67 g, 2.8 mmol, 1.0 equiv.) and LAH (0.16 g, 4.2 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.55 g, 2.7 mmol, 98%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.31 (s, 1\text{H}), 1.82 (dddd, J = 13.7, 10.1, 6.4, 5.4 \text{ Hz}, 1\text{H}), 2.02 (dddd, J = 13.7, 7.4, 6.9, 4.8 \text{ Hz}, 1\text{H}), 2.28 – 2.38 (m, 5\text{H}), 2.79 (ddd, J = 10.0, 7.3, 4.8 \text{ Hz}, 1\text{H}), 3.41 – 3.60 (m, 2\text{H}), 4.55 – 4.72 (m, 2\text{H}), 4.91 – 5.03 (m, 1\text{H}), 6.93 – 7.07 (m, 3\text{H}), 7.19 (m, 1\text{H}) \text{ ppm.}

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 21.6, 36.0, 38.7, 42.5, 61.2, 74.5, 88.1, 124.7, 127.2, 128.4, 128.5, 138.1, 144.3, 209.2 \text{ ppm.}

APCI-HRMS: \(m/z \) calcd for C₁₄H₁₈O [M+NH₄]⁺ 220.1696 found 220.1691.
Synthesis of 3-(o-tolyl)hepta-5,6-dienoate 81

![Chemical Structure](image)

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and o-tolylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.74 g, 3.0 mmol, 58%).

**Analytical Data**

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.13 \) (t, \(J = 7.1\) Hz, 3H), 2.32 (ddd, \(J = 9.7, 7.7, 2.8\) Hz, 2H), 2.38 (s, 3H), 2.60 (dd, \(J = 15.4, 8.2\) Hz, 1H), 2.72 (dd, \(J = 15.4, 6.9\) Hz, 1H), 3.55 (d, \(J = 8.2, 7.1, 7.1\) Hz, 1H), 4.03 (m), 2H), 4.60 (ddd, \(J = 6.6, 2.7, 1.3\) Hz, 2H), 4.94 (m, 1H), 7.06 – 7.17 (m, 4H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.2, 19.8, 35.2, 36.9, 40.2, 60.3, 74.6, 87.5, 125.7, 126.2, 126.3, 130.5, 136.1, 141.7, 172.4, 209.3\) ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₄O₂N [M+NH₄]⁺ 262.1802 found 262.1801

Synthesis of 3-(o-tolyl)hepta-5,6-dien-1-ol 82

![Chemical Structure](image)

The reaction was performed according to general procedure 3 with ethyl 3-(o-tolyl)hepta-5,6-dienoate (0.74 g, 3.0 mmol, 1.0 equiv.) and LAH (0.17 g, 4.5 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.59 g, 2.9 mmol, 97%).

**Analytical Data**

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.22 – 1.30\) (m, 1H), 1.87 (dddd, \(J = 13.7, 9.6, 6.5, 5.5\) Hz, 1H), 2.04 (dddd, \(J = 13.8, 7.4, 6.9, 5.1\) Hz, 1H), 2.28 – 2.34 (m, 2H), 2.34 (s, 3H), 3.19 (dddd, \(J = 9.6, 7.2, 5.1\) Hz, 1H), 3.40 – 3.64 (m, 2H), 4.52 – 4.65 (m, 2H), 4.95 (ddd, \(J = 14.0, 7.4, 6.7\) Hz, 1H), 7.04 – 7.19 (m, 4H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 20.0, 35.7, 36.9, 38.5, 61.1, 74.4, 88.0, 125.9, 126.0, 126.3, 130.4, 136.3, 142.6, 209.1\) ppm.

APCI-HRMS: m/z calcd for C₁₄H₂₂O₂N [M+NH₄]⁺ 220.1696 found 220.1691.
Synthesis of ethyl 3-mesitylhepta-5,6-dienoate 83

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and mesitylmagnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.72 g, 2.7 mmol, 51%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 1.14 (t, J = 7.1 Hz, 3H), 2.22 (s, 3H), 2.36 (s, 6H), 2.42 – 2.49 (m, 2H), 2.67 – 2.87 (m, 2H), 3.79 (m, 1H), 4.03 (m, 2H), 4.53 – 4.67 (m, 2H), 4.80 – 5.07 (m, 1H), 6.79 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 20.7, 21.5, 21.7, 33.1, 37.1, 38.8, 60.3, 74.6, 88.2, 129.3, 131.1, 135.6, 136.4, 172.9, 209.0 ppm.

APCI-HRMS: m/z calcd for C₁₉H₂₈O₂N [M+NH₄]⁺ 290.2115 found 290.2118.

Synthesis of 3-mesitylhepta-5,6-dien-1-ol 84

The reaction was performed according to general procedure 3 with ethyl 3-mesitylhepta-5,6-dienoate (0.72 g, 2.7 mmol, 1.0 equiv.) and LAH (0.15 g, 4.1 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.60 g, 2.6 mmol, 97%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 1.19 – 1.32 (m, 1H), 1.98 – 2.12 (m, 2H), 2.24 (s, 3H), 2.32 (s, 3H), 2.36 (s, 3H), 2.42 – 2.50 (m, 2H), 3.38 (ddd, J = 9.0, 7.9, 6.1 Hz, 1H), 3.47 – 3.63 (m, 2H), 4.53 – 4.70 (m, 2H), 4.97 (ddd, J = 7.8, 6.8, 6.8 Hz 1H), 6.69 – 6.88 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 20.7, 21.5, 21.9, 33.5, 36.7, 37.4, 62.0, 74.6, 88.8, 129.3, 131.3, 135.4, 136.2, 137.1, 137.2, 208.8 ppm.

APCI-HRMS: m/z calcd for C₁₀H₂₀O₃N [M+NH₄]⁺ 248.2009 found 248.2009.
Synthesis of ethyl 3-(4-vinylphenyl)hepta-5,6-dienoate 85.

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (4-vinylphenyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.83 g, 3.2 mmol, 62%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.15$ (t, $J = 7.1$ Hz, 3H), 2.35 (dd, $J = 7.3$, 2.8 Hz, 2H), 2.57 (dd, $J = 15.3$, 8.5 Hz, 1H), 2.72 (dd, $J = 15.4$, 6.6 Hz, 1H), 3.24 (m, 1H), 4.04 (dd, $J = 7.1$, 1.5 Hz, 2H), 4.54 – 4.66 (m, 2H), 4.94 (ddd, $J = 7.4$, 6.6, 6.6 Hz, 1H), 5.20 (dd, $J = 10.9$, 1.0 Hz, 1H), 5.71 (dd, $J = 17.6$, 1.0 Hz, 1H), 6.69 (dd, $J = 17.6$, 10.9, 0.4, 1H), 7.12 – 7.21 (m, 2H), 7.32 – 7.37 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2$, 35.4, 40.6, 41.9, 60.4, 74.8, 87.5, 113.4, 126.3, 127.8, 136.1, 136.7, 136.9, 143.2, 172.2, 209.4 ppm.

APCI-HRMS: $m/z$ calcd for C$_{17}$H$_{20}$O$_2$Nan[M+Na]$^+$ 279.1356 found 279.1359.

Synthesis of 3-(4-vinylphenyl)hepta-5,6-dien-1-ol 86.

The reaction was performed according to general procedure 3 with ethyl 3-(4-vinylphenyl)hepta-5,6-dienoate (0.83 g, 3.2 mmol, 1.0 equiv.) and LAH (0.18 g, 4.8 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.67 g, 3.1 mmol, 97%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.34$ (s, 1H), 1.82 (dddd, $J = 13.7$, 10.0, 6.3, 5.3 Hz, 1H), 2.03 (dddd, $J = 13.7$, 7.6, 6.9, 4.8 Hz, 1H), 2.25 – 2.39 (m, 2H), 2.84 (dd, $J = 9.9$, 7.3, 4.7 Hz, 1H), 3.42 – 3.62 (m, 2H), 4.53 – 4.66 (m, 2H), 4.95 (dd, $J = 14.0$, 7.3, 6.7 Hz, 1H), 5.21 (dd, $J = 10.9$, 1.0 Hz, 1H), 5.72 (dd, $J = 17.6$, 1.0 Hz, 1H), 6.64 – 6.76 (m, 1H), 7.11 – 7.17 (m, 2H), 7.30 – 7.39 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 35.9$, 38.6, 42.3, 61.1, 74.6, 88.0, 113.3, 126.4, 127.9, 135.9, 136.7, 144.1, 209.2 ppm.

ESI-HRMS: $m/z$ calcd for C$_{17}$H$_{18}$ONa [M+Na]$^+$ 237.2972 found 237.2968.
Synthesis of ethyl 3-(4-trifluoromethyl)phenyl)hepta-5,6-dienoate 87.

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (4-trifluoromethyl)phenyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et<sub>2</sub>O). The desired product was obtained as a colorless liquid (0.70 g, 2.3 mmol, 45%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl<sub>3</sub>): $\delta = 1.14$ (t, J = 7.1 Hz, 3H), 2.29 – 2.42 (m, 2H), 2.59 (dd, J = 15.5, 8.7 Hz, 1H), 2.75 (dd, J = 15.5, 6.3 Hz, 1H), 3.31 (ddd, J = 8.9, 7.0, 7.0 Hz, 1H), 3.99 – 4.06 (m, 2H), 4.52 – 4.66 (m, 2H), 4.85 – 4.98 (m, 2H), 7.30 dd, J = 8.0, 1.4, 1.4, 0.8 Hz, 2H), 7.49 – 7.60 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl<sub>3</sub>): $\delta = 14.2, 35.2, 40.4, 42.0, 60.5, 75.1, 87.1, 125.4, 125.4, 125.7, 128.0, 147.6, 171.8, 209.4$ ppm.

APCI-HRMS: m/z calcd for C<sub>16</sub>H<sub>21</sub>O<sub>2</sub>NF<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup> 316.1519 found 316.1518.

Synthesis of 3-(4-trifluoromethyl)phenyl)hepta-5,6-dienol 88.

The reaction was performed according to general procedure 3 with Ethyl 3-(4-trifluoromethyl)phenyl)hepta-5,6-dienoate (0.70 g, 2.3 mmol, 1.0 equiv.) and LAH (0.13 mg, 3.5 mmol, 1.5 equiv. ). The desired product was obtained as a colorless liquid (0.55 g, 2.2 mmol, 95%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl<sub>3</sub>): $\delta = 1.37$ (s, 1H), 1.83 (dddd, J = 13.8, 9.9, 6.3, 5.2 Hz, 1H), 2.06 (dddd, J = 13.9, 7.8, 6.9, 5.0 Hz, 1H), 2.27 – 2.45 (m, 2H), 2.95 (dddd, J = 9.8, 8.0, 6.4, 4.9 Hz, 1H), 3.46 (ddd, J = 10.6, 7.8, 6.3 Hz, 1H), 3.57 (dddd, J = 10.6, 6.9, 5.3, 0.3 Hz, 1H), 4.49 – 4.65 (m, 2H), 4.86 – 4.99 (m, 2H), 7.30 (m, 2H), 7.52 – 7.61 (m, 2H).ppm.

$^{13}$C-NMR (100.6 MHz, CDCl<sub>3</sub>): $\delta = 35.6, 38.5, 42.2, 60.7, 74.9, 87.6, 125.4, 125.5, 128.2, 129.0, 148.6, 209.3$ ppm.

APCI-HRMS: m/z calcd for C<sub>14</sub>H<sub>19</sub>ONF<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup> 274.1413 found 274.1412
Synthesis of ethyl 3-(4-bromophenyl)hepta-5,6-dienoate 89.

The reaction was performed according to **general procedure 2** with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (4-bromophenyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.69 g, 2.2 mmol, 43%).

**Analytical Data**

**¹H-NMR (400.1 MHz, CDCl₃)**: δ = 1.19 (t, J = 7.0 Hz, 3H), 2.30 – 2.45 (m, 2H), 2.56 (ddd, J = 17.4, 15.3, 8.5 Hz, 1H), 2.72 (ddd, J = 15.4, 7.3, 6.5 Hz, 1H), 3.16 – 3.25 (m, 1H), 4.03 (ddd, J = 7.1, 7.1 1.4 Hz, 2H), 4.52 – 4.65 (m, 2H), 4.93 (ddd, J = 14.0, 8.7, 7.3, 6.6 Hz, 1H), 7.03 – 7.11 (m, 1H), 7.38 – 7.46 (m, 1H) ppm.

**¹³C-NMR (100.6 MHz, CDCl₃)**: δ = 14.2, 35.3, 40.5, 41.6, 60.5, 74.9, 87.2, 127.6, 128.5, 129.4, 131.6, 142.5, 172.0, 209.4 ppm.

**APCI-HRMS**: m/z calcd for C₁₅H₁₈O₂Br [M+H]⁺ 309.0485 found 309.0486.

Synthesis of 3-(4-bromophenyl)hepta-5,6-dienol 90.

The reaction was performed according to **general procedure 3** with Ethyl 3-(4-bromophenyl)hepta-5,6-dienoate (0.69 g, 2.2 mmol, 1.0 equiv.) and LAH (0.13 mg, 3.3 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.58 g, 2.2 mmol, 98%).

**Analytical Data**

**¹H-NMR (400.1 MHz, CDCl₃)**: δ = 1.30 (s, 1H), 1.72 – 1.91 (m, 1H), 1.95 – 2.09 (m, 1H), 2.24 – 2.38 (m, 2H), 2.70 – 2.89 (m, 1H), 3.41 – 3.50 (m, 1H), 3.50 – 3.61 (m, 1H), 4.49 – 4.63 (m, 2H), 4.80 – 5.08 (m, 1H), 7.05 – 7.07 (m, 1H), 7.17 – 7.32 (m, 2H), 7.41 – 7.44 (m, 1H) ppm.

**¹³C-NMR (100.6 MHz, CDCl₃)**: δ = 35.8, 38.6, 41.9, 60.8, 74.7, 87.7, 120.1, 127.8, 128.5, 129.6, 131.6, 143.4, 209.2 ppm.

**APCI-HRMS**: m/z calcd for C₁₃H₁₇O⁺BrCl [M+Cl]⁻ 302.9980 found 302.9980.
Synthesis of ethyl 3-(methoxyphenyl)hepta-5,6-dienoate 91.

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and 4-bromoanisole (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.88 g, 3.4 mmol, 65%).

Analytical Data

1H-NMR (400.1 MHz, CDCl₃): δ = 1.15 (t, J = 7.1, 3H), 2.32 (dd, J = 7.3, 2.8 Hz 2H), 2.54 (dd, J = 15.2, 8.5 Hz, 1H), 2.70 (dd, J = 15.2, 6.6 Hz, 1H), 3.19 (ddd, J=8.6, 7.1, 7.1 Hz, 1H), 3.78 (s, 3H), 4.53 – 4.68 (m, 2H), 4.94 (ddd, J=7.2, 6.6, 6.6 Hz 1H), 6.81 – 6.86 (m, 2H), 7.08 – 7.14 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 35.6, 40.9, 41.4, 55.3, 60.3, 74.6, 87.6, 113.9, 128.5, 135.6, 158.3, 172.4, 209.3 ppm.

ESI-HRMS: m/z calcd for C₁₆H₂₀O₃Na [M+Na]⁺ 283.1305 found 283.1302.

Synthesis of 3-(4-methoxyphenyl)hepta-5,6-dienol 92.

The reaction was performed according to general procedure 3 with ethyl 3-(methoxyphenyl)hepta-5,6-dienoate (0.88 g, 3.4 mmol, 1.0 equiv.) and LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.73 g, 3.3 mmol, 98%).

Analytical Data

1H-NMR (400.1 MHz, CDCl₃): δ = 1.30 (s, 1H), 1.78 (dddd, J = 13.7, 10.1, 6.3, 5.4 Hz, 1H), 2.01 (dddd, J = 13.8, 7.5, 6.9, 4.8 Hz, 1H), 2.25 – 2.36 (m, 2H), 2.78 (dddd, J = 10.1, 7.3, 4.8 Hz, 1H), 3.42 – 3.63 (m, 2H), 3.79 (s, 3H), 4.52 – 4.68 (m, 2H), 4.87 – 5.05 (m, 1H), 6.82 – 6.88 (m, 2H), 7.07 – 7.13 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 36.2, 38.8, 41.8, 55.3, 61.2, 74.5, 88.1, 114.0, 128.6, 136.3, 158.2, 209.2 ppm.

ESI-HRMS: m/z calcd for C₁₄H₁₈O₃Na [M+Na]⁺ 241.1199 found 241.1197.
Synthesis of ethyl 3-(4-methylthio)phenyl)hepta-5,6-dienoate 93.

The reaction was performed according to general procedure 2 with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (4-methylthio)phenyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.88 g, 3.2 mmol, 61%).

Analytical Data

**¹H-NMR (400.1 MHz, CDCl₃):** δ = 1.15 (t, J=7.1, 3H), 2.33 (dd, J = 7.3, 2.8, 2H), 2.46 (s, 3H), 2.55 (dd, J = 15.4, 8.7 Hz, 1H), 2.71 (dd, J = 15.3, 6.5 Hz, 1H), 3.20 (dd, J = 8.6, 7.1, 7.1 Hz, 1H), 4.04 (dd, J = 7.1, 1.4, 1.4 Hz, 2H), 4.61 (dd, J=6.5, 2.8, 2.8 Hz 2H), 4.93 (dd, J=7.3, 7.3, 6.7, 6.7 Hz, 1H), 7.10 – 7.14 (m, 2H), 7.18 – 7.22 (m, 2H) ppm.

**¹³C-NMR (100.6 MHz, CDCl₃):** δ = 14.2, 16.1, 35.4, 40.6, 41.7 , 60.4, 74.8, 87.4, 127.0, 128.1, 136.3, 140.6, 172.2, 209.4 ppm.

**APCI-HRMS:** m/z calcd for C₁₆H₂₀O₂SNa⁺ [M+Na]⁺ 299.1076 found 299.1075.

Synthesis of 3-(4-methylthio)phenyl)hepta-5,6-dienol 94.

The reaction was performed according to general procedure 3 with Ethyl 3-(4-methylthio)phenyl)hepta-5,6-dienoate (0.88 g, 3.2 mmol, 1.0 equiv.) and LAH (0.18 mg, 4.8 mmol, 1.5 equiv). The desired product was obtained as a colorless liquid (0.74 g, 3.2 mmol, 99%).

Analytical Data

**¹H-NMR (400.1 MHz, CDCl₃):** δ = 1.32 (s, 1H), 1.79 (dddd, J = 13.7, 10.0, 6.4, 5.3 Hz, 1H), 2.01 (ddddd, J = 13.8, 7.7, 6.9, 4.9 Hz, 1H), 2.28 – 2.35 (m, 2H), 2.47 (s, 3H), 2.75 – 2.88 (m, 1H), 3.47 (dd, J = 10.6, 7.7, 6.4 Hz, 1H), 3.56 (ddddd, J = 10.6, 7.0, 5.3, 0.3 Hz, 1H), 4.53 – 4.65 (m, 2H), 4.88 – 4.98 (m, 1H), 7.09 – 7.13 (m, 2H), 7.19 – 7.23 (m, 2H) ppm.

**¹³C-NMR (100.6 MHz, CDCl₃):** δ = 16.2, 35.9, 38.6, 42.0, 61.0, 74.6, 87.9, 127.2, 128.3, 136.0, 141.4, 209.2 ppm.

**APCI-HRMS:** m/z calcd for C₁₆H₂₁O₂S [M+H₂O]⁺ 277.1257 found 277.1256.
Synthesis of ethyl 3-(4-methoxyphenyl)-4-dimethylhepta-5,6-dienoate 95.

The reaction was performed according to \textit{general procedure 2} with (E)-hepta-2,5,6-trienoate (0.8 g, 5.2 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (13 mL, 13 mmol, 1.0 M). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et\textsubscript{2}O). The desired product was obtained as a colorless liquid (0.97 g, 3.4 mmol, 65%).

\textbf{Analytical Data}

\textsuperscript{1}H-NMR (400.1 MHz, CDCl\textsubscript{3}) \(\delta = 0.92 \text{ (s, 3H), 0.99 \text{ (s, 3H), 1.04 \text{ (t, } J = 7.1 \text{ Hz, 3H), 2.66 \text{ (dd, } J = 15.3, 11.2 \text{ Hz, 1H), 2.80 \text{ (dd, } J = 15.4, 4.4 \text{ Hz, 1H), 3.02 \text{ (dd, } J = 11.2, 4.5 \text{ Hz, 1H), 3.78 \text{ (s, 3H), 3.86 – 3.99 (m, 2H), 4.69 – 4.77 (m, 2H), 5.08 \text{ (dd, } J = 6.6, 6.6 \text{ Hz, 1H), 6.76 – 6.83 (m, 2H), 7.06 – 7.14 (m, 2H) ppm.}\)

\textsuperscript{13}C-NMR (100.6 MHz, CDCl\textsubscript{3}): \(\delta = 14.1, 24.7, 27.7, 36.5, 37.6, 51.4, 55.2, 60.2, 98.9, 113.1, 130.4, 132.8, 158.3, 207.3\) ppm.

\textsuperscript{APCI}-HRMS: \(m/z\) calcd for C\textsubscript{18}H\textsubscript{28}O\textsubscript{3}N [M+NH\textsubscript{4}]\textsuperscript{+} 306.2064 found 306.2065.

Synthesis of 3-(4-methoxyphenyl)-4-dimethylhepta-5,6-dienol 96.

The reaction was performed according to \textit{general procedure 3} with 3-(4-methoxyphenyl)-4-dimethylhepta-5,6-dienoate (0.97 g, 3.4 mmol, 1.0 equiv.) and LAH (0.19 g, 5.1 mmol, 1.5 equiv.). The desired product was obtained as a colorless liquid (0.83 g, 3.4 mmol, 99%).

\textbf{Analytical Data}

\textsuperscript{1}H-NMR (400.1 MHz, CDCl\textsubscript{3}): \(\delta = 0.91 \text{ (s, 3H), 0.98 \text{ (s, 3H), 1.28 \text{ (s, 1H), 1.89 \text{ (dddd, } J = 13.6, 12.2, 6.6, 4.6 \text{ Hz, 1H), 2.03 – 2.13 (m, 1H), 2.53 \text{ (dd, } J = 12.2, 2.9 \text{ Hz, 1H), 3.35 \text{ (dddd, } J = 10.5, 8.1, 6.6 \text{ Hz, 1H), 3.47 \text{ (dddd, } J = 10.5, 7.5, 4.6 \text{ Hz, 1H), 3.79 \text{ (s, 3H), 4.71 \text{ (d, } J = 6.7 \text{ Hz, 2H), 5.10 \text{ (dd, } J = 6.7, 6.7 \text{ Hz, 1H), 6.76 – 6.85 (m, 2H), 7.05 – 7.12 (m, 2H) ppm.}\)

\textsuperscript{13}C-NMR (100.6 MHz, CDCl\textsubscript{3}): \(\delta = 25.0, 27.9, 33.2, 37.7, 52.0, 55.3, 62.0, 99.4, 113.3, 130.4, 133.4, 158.2, 207.3\) ppm.

\textsuperscript{APCI}-HRMS: \(m/z\) calcd for C\textsubscript{16}H\textsubscript{26}O\textsubscript{2}N [M+NH\textsubscript{4}]\textsuperscript{+} 264.3885 found 264.3886.
2.2 Preparation of internal allenes

2.2.1 General procedure for internal allenes

**General procedure 5: Synthesis of ethyl 3,4-dienoate derivative:**

I) A solution of the aldehyde (1.0 equiv.) in THF (0.5 M) was added to ethynylmagnesium bromide (0.5 M in THF, 1.1 equiv.) within 1 h at 0 °C. The reaction mixture was then stirred for 1 h at room temperature and quenched via addition of saturated aqueous NH₄Cl solution. The phases were separated and the aqueous phase was extracted with Et₂O. The combined organic layers were dried over Na₂SO₄, filtered over a short silica pad and concentrated.

II) To a solution of the crude alcohol (step I) (0.5 equiv.) in triethyl orthoacetate (1.05 equiv.) was added dropwise propionic acid (4.0 mol%) at 100 °C. The mixture was heated to 160 °C and resulting EtOH was continuously distilled off under atmospheric pressure for 1 h. Then another aliquot of crude alcohol (step I) (0.5 equiv.) and propionic acid (0.80 mL, 0.80 g, 11 mmol, 4.0 mol%) were added dropwise and the mixture was stirred for another 1 h before a third portion of propionic acid (4.0 mol%) was added. The reaction was stirred for an additional hour and then cooled to room temperature and quenched by addition of aqueous HCl-solution (2 M). The organic layer was separated and the aqueous layer was extracted with Et₂O (× 3). The combined organic layers were washed with brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The residue was either purified by fractional distillation under reduced pressure or by flash column chromatography eluting with pentane:ether.

**General procedure 6: Synthesis of ethyl (E)-2,5,6-trienoate derivative:**

I) At −80°C a solution of DIBAL-H (1.4 equiv., 1.0 M in CH₂Cl₂) was added dropwise over 90 min to a solution of ethylpenta-3,4-dienoate (1.0 equiv.) in CH₂Cl₂ (1.6 M). The reaction mixture was stirred for 1 h and then transferred to an ice cold aqueous solution of HCl (2.0 M) at 0 °C. The layers were separated, the organic layer was washed with HCl (2.0 M, × 2) and the aqueous layer was extracted with CH₂Cl₂ (× 2). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered over a silica pad and concentrated under reduced pressure.

II) A suspension of NaH (60% in mineral oil, 1.1 equiv.) in dry THF (0.25 M) was cooled to 0 °C and triethyl phosphonoacetate (1.3 equiv.) was added dropwise to the reaction mixture. After complete
addition, the suspension was stirred for 1 h at 0 °C and was then cooled to −78 °C. A solution of penta-4,5-dienal (1.0 equiv.) was added to the reaction mixture at this temperature. The mixture was slowly warmed to −20 °C over 3 h and then quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O, the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Pentane:Et₂O).

**General procedure 7: 1,4-Addition and reduction:**

I) A mixture of CuI (10 mol%) and LiBr (20 mol%) was carefully dried and cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus, before extra dry or freshly distilled THF (1.0 M) was added. The mixture was stirred at room temperature for 15 min and then cooled to −78 °C. A solution of ethyl (E)-hepta-2,5,6-trienoate derivative (1.0 equiv) in extra dry or freshly distilled THF (0.3 M) and TMSCl (1.1 equiv.) was added at this temperature. The mixture was stirred for 15 min before the GRIGNARD reagent in THF (1.5 equiv.) was added dropwise, stirred for 30 minutes at −78 °C and then slowly warmed to −30 °C over 3 h. The reaction was quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O (× 4), the combined organic layer were washed with brine and dried over Na₂SO₄. The solvent was removed and the residue was filtered over a shirt silica pad.

II) The crude product was dissolved in Et₂O () and added dropwise to a suspension of LAH () in dry Et₂O at 0 °C. The reaction was stirred at this temperature for 1 h and then warmed to room temperature and stirred for another hour. The mixture was quenched through the addition of H₂O and aqueous HCl (2.0 M). The layers were separated, the organic layer was washed with H₂O and brine. The aqueous layer was extracted with Et₂O (× 4). The combined organic layer were dried over Na₂SO₄, the solvent was removed. The solvent was removed and the residue was purified by flash chromatography on silica gel using a mixture of pentane and ether.
2.2.2 Synthesis and characterization of internal allenenes

Synthesis of ethyl undeca-3,4-dienoate 97.

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O
\( \text{EtOH} \)
\( \text{C}_{13}\text{H}_{22}\text{O}_2 \)
210.32
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The reaction was performed according to **general procedure 5**.

I) Heptanal (21.0 g, 26.0 mL 184 mmol, 1.0 equiv.) and ethinyl magnesium bromide (400 mL, 200 mmol, 0.5 M in THF). The crude product was filtered over a short silica pad (2:1 pentane/Et\(_2\)O). Non-1-yn-3-ol was obtained as a yellow liquid (24.9 g, 178 mmol, 97\%)

II) Crude non-1-yn-3-ol (step I) (24.9 g, 178 mmol), triethyl orthoacetate (30.4 g, 34.3 mL, 187 mmol), propionic acid (3 × 4 mol\%). The crude product was purified by fractional distillation under reduced pressure (110 °C, 4 mbar) to obtain the desired product (22.9 g, 109 mmol, 61\%) as a colorless liquid.

**Analytical Data**

\(^1\text{H}-\text{NMR} (400.1 \text{ MHz, CDCl}_3)\): \( \delta = 0.89 (t, J = 6.8 \text{ Hz, 3H}), 1.27 (m, 10H), 1.35 – 1.45 (m, 3H), 1.99 (ddd, J = 7.6, 6.6, 3.1 \text{ Hz, 2H}), 3.01 (dd, J = 7.1, 2.9 \text{ Hz, 2H}), 4.16 (ddd, J = 7.2 \text{ Hz, 2H}), 5.12 – 5.28 (m, 2H) \text{ ppm.} \)

\(^{13}\text{C}-\text{NMR} (100.6 \text{ MHz, CDCl}_3)\): \( \delta = 14.1, 14.3, 22.7, 28.6, 28.8, 29.1, 31.8, 35.2, 60.7, 84.2, 92.3, 171.7, 205.1 \text{ ppm.} \)

**ESI-HRMS**: \( m/z \) calcd for \( \text{C}_{13}\text{H}_{22}\text{O}_2\text{Na} [\text{M+N}]^+ \) 233.1512 found 233.1513.
Synthesis of ethyl (E)-trideca-2,5,6-trienoate 98.

The reaction was performed according to general procedure 6.

I) Ethyl undeca-3,4-dienoate (22.9 g, 109 mmol, 1.0 equiv.) and DIBAL-H (158 mL, 158 mmol, 1.45 equiv., 1.1 M in DCM). The crude product was filtered over a short silica pad (DCM). Undeca-3,4-dienal was obtained as a yellow liquid (16.3 g, 98.1 mmol, 90%).

II) Crude undeca-3,4-dienal (step I) (7.0 g, 42 mmol), NaH (60% in mineral oil, 1.8 g, 46 mmol, 1.1 equiv.) in dry THF (168 mL) and triethyl phosphonoacetate (12 g, 11 mL, 55 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:EtO). The title compound was obtained as colorless liquid (7.1 g, 30 mmol, 72%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.87 - 0.90$ (m, 3H), 1.27 - 1.31 (m, 10H), 1.95 - 2.04 (m, 2H), 2.88 (ddd, $J = 6.6$, 2.8, 1.7 Hz, 2H), 4.19 (ddd, $J = 7.2$ Hz, 2H), 5.08 (ddd, $J = 6.6$ Hz, 3.4, 1H), 5.12 - 5.21 (m, 1H), 5.88 (ddd, $J = 15.6$ Hz, 1.7, 1H), 6.97 (ddd, $J = 15.7$, 6.5 Hz, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2$, 14.4, 28.8, 28.8, 29.1, 29.8, 31.8, 32.1, 60.3, 87.1, 92.3, 122.0, 146.9, 166.6, 204.9ppm.

ESI-HRMS: $m/z$ calcd for C$_{15}$H$_{25}$O$_2$ [M+H]$^+$ 237.1849 found 237.1849.
Synthesis of 3-methyltrideca-5,6-dien-1-ol 99.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and methylmagnesium bromide (1.7 mL, 5.1 mmol, 3.0 M in Et₂O). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.74 g, 3.54 mmol, 68%).

Analytical Data[3]

^1^H-NMR (400.1 MHz, CDCl₃): δ = 0.88 (d, J = 7.1 Hz, 3H), 0.95 (m, 3H), 1.25 – 1.33 (m, 7H), 1.37 – 1.45 (m, 3H), 1.61 – 1.74 (m, 2H), 1.83 – 1.95 (m, 1H), 1.95 – 2.06 (m, 3H), 3.63 – 3.74 (m, 2H), 4.94 – 5.11 (m, 2H) ppm.

^13^C-NMR (125.6 MHz, CDCl₃): δ = 28.9, 29.1, 29.3, 29.3, 30.0, 31.8, 36.8, 36.9, 39.4, 39.5, 61.3, 77.4, 88.8, 90.6, 204.7 ppm.

ESI-HRMS: m/z calcd for C_{14}H_{27}O [M+H]^+ found.

Synthesis of 3-(deca-2,3-dien-1-yl)pentadecan-1-ol 100.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and dodecylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.68 g, 1.9 mmol, 55%).

Analytical Data[3]

^1^H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.91 (m, 6H), 1.22 – 1.36 (m, 31H), 1.57 (ddd, J = 4.5, 1.2 Hz, 3H), 1.98 (ddddd, J = 10.8, 9.7, 5.4, 2.9 Hz, 4H), 3.65 – 3.73 (m, 2H), 4.94 – 5.11 (m, 2H) ppm.

^13^C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 14.2, 22.7, 22.8, 26.7, 26.8, 28.9, 29.1, 29.4, 29.5, 29.8, 29.8, 30.1, 31.8, 32.0, 33.4, 33.6, 33.7, 33.7, 34.6, 36.9, 61.3, 61.3, 88.5, 88.6, 90.5, 90.6, 204.7, 204.8 ppm.

ESI-HRMS: m/z calcd for C_{25}H_{48}OCl [M+Cl]^+ 399.3399 found 399.3394.
Supporting Information

Synthesis of 3-neopentyltrideca-5,6-dien-1-ol 101.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and neopentylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.44 g, 1.7 mmol, 49%).

Analytical Data[3]

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.84 – 0.92 (m, 11H), 1.13 (ddd, J = 14.1, 4.0 Hz, 1.5, 1H), 1.22 – 1.36 (m, 9H), 1.36 – 1.44 (m, 2H), 1.50 – 1.68 (m, 3H), 1.91 – 2.10 (m, 4H), 3.63 – 3.71 (m, 2H), 5.00 (dddd, J = 10.5, 5.3, 4.2, 2.5 Hz, 1H), 5.02 – 5.10 (m, 1H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 29.1, 29.4, 30.0, 30.0, 30.9, 31.1, 31.3, 31.8, 35.9, 36.0, 39.0, 39.1, 47.8, 47.8, 61.2, 88.7, 88.8, 90.5, 90.6, 204.9, 204.9 ppm.

ESI-HRMS: m/z calcd for C₁₉H₃₃OCl [M+Cl]^+ 252.2443 found 252.2451.

Synthesis of 3-cyclopropyltrideca-5,6-dien-1-ol 102.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and cyclopropylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.50 g, 2.1 mmol, 63%).

Analytical Data[3]

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.07 – 0.17 (m, 2H), 0.42 – 0.53 (m, 2H), 0.58 (dddd, J = 15.7, 9.7, 5.0, 2.5 Hz, 1H), 0.73 – 0.85 (m, 1H), 0.86 – 0.92 (m, 3H), 1.23 – 1.43 (m, 9H), 1.60 – 1.71 (m, 1H), 1.72 – 1.83 (m, 1H), 1.93 – 2.01 (m, 2H), 2.02 – 2.13 (m, 1H), 2.13 – 2.22 (m, 1H), 3.72 – 3.82 (m, 2H), 5.01 – 5.11 (m, 2H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 3.8, 3.9 , 4.6, 4.7, 14.2, 16.0, 16.1, 22.7, 28.9, 29.1, 29.3, 29.4, 31.8, 35.1, 35.2, 37.7, 37.7, 41.1, 41.1, 61.4, 61.5, 88.8, 88.8, 90.5, 204.6, 204.7 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₉O [M+H]^+ 237.2213 found 237.2212.
Synthesis of 3-cyclohexyltrideca-5,6-dien-1-ol 103.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and cyclohexylmagnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.5 g, 1.8 mmol, 62%).

Analytical Data[3]

1H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.91 (m, 3H), 1.00 – 1.24 (m, 5H), 1.24 – 1.35 (m, 8H), 1.35 – 1.43 (m, 4H), 1.44 – 1.55 (m, 1H), 1.56 – 1.70 (m, 2H), 1.70 – 1.78 (m, 2H), 1.87 – 2.12 (m, 4H), 3.56 – 3.76 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 26.9, 26.9, 27.0, 28.9, 29.1, 29.1, 29.4, 29.4, 29.5, 29.8, 30.1, 30.1, 31.0, 31.2, 31.8, 34.0, 34.1, 40.1, 40.3, 40.4, 40.5, 62.0, 89.6, 89.7, 90.7, 90.8, 204.5, 204.6 ppm.

APCI-HRMS: m/z calcd for C₁₉H₃₉O [M+H]+ 279.2672 found 279.2674.

Synthesis of 3-(3-phenylpropyl)trideca-5,6-dien-1-ol 104.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and (3-phenylpropyl)magnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.48 g, 1.5 mmol, 53%).

Analytical Data[3]

1H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.92 (m, 3H), 1.24 – 1.45 (m, 11H), 1.53 – 1.72 (m, 5H), 1.91 – 2.04 (m, 4H), 2.60 (td, J=7.6, 1.8, 2H), 3.62 – 3.69 (m, 2H), 4.88 – 5.10 (m, 2H), 7.12 – 7.22 (m, 3H), 7.25 – 7.30 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.6, 28.7, 28.9, 29.1, 29.4, 31.8, 33.3, 33.3, 33.4, 33.5, 34.5, 34.6, 36.3, 36.8, 61.2, 61.2, 88.4, 88.5, 90.6, 90.7, 125.7, 128.3, 128.4, 142.7, 204.8, 204.8 ppm.

APCI-HRMS: m/z calcd for C₂₂H₃₉ON [M+NH₄]+ 332.2948 found 332.2950.
Synthesis of 3-phenyltrideca-5,6-dien-1-ol 105.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and phenylmagnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.51 g, 0.19 mmol, 65%).

**Analytical Data**[3]

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.87 – 0.91 (m, 3H), 1.20 – 1.41 (m, 9H), 1.78 – 1.96 (m, 3H), 1.99 – 2.09 (m, 1H), 2.24 – 2.40 (m, 2H), 2.82 (dddd, J = 14.4, 9.9, 7.0, 4.8, 1H), 3.44 – 3.61 (m, 2H), 4.86 – 4.96 (m, 1H), 4.96 – 5.04 (m, 1H), 7.16 – 7.23 (m, 3H), 7.27 – 7.33 (m, 2H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 28.9, 28.9, 29.2, 29.2, 31.8, 31.8, 36.6, 36.9, 38.8, 38.9, 42.6, 42.8, 61.2, 88.7, 88.8, 90.9, 91.0, 126.4, 126.4, 127.8, 128.5, 144.6, 204.7, 204.7 ppm.

**APCI-HRMS:** m/z calcd for C₁₉H₂₈OCl [M+Cl]^+ 307.1833 found 307.1834.
Synthesis of 3-(naphthalen-2-yl)trideca-5,6-dien-1-ol 106.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.80 g, 3.4 mmol, 1.0 equiv.) and naphthalen-2-ylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.74 g, 2.3 mmol, 68%).

Analytical Data[3]

^1^H-NMR (400.1 MHz, CDCl₃): δ = 0.88 (ddd, J = 7.0, 4.8 Hz, 3H), 1.15 – 1.32 (m, 9H), 1.75 (dddd, J = 8.1, 6.7, 6.0, 3.0 Hz, 1H), 1.81 – 1.89 (m, 1H), 1.89 – 1.99 (m, 1H), 2.06 – 2.18 (m, 1H), 2.42 (dddd, J = 10.1, 4.5, 3.6, 2.6 Hz, 2H), 3.01 (dddd, J = 9.8, 7.1, 4.8 Hz, 1H), 3.47 – 3.63 (m, 2H), 4.88 – 5.04 (m, 2H), 7.35 (ddd, J = 8.5, 1.6 Hz, 1H), 7.40 – 7.48 (m, 2H), 7.62 (d, J = 1.7 Hz, 1H), 7.77 – 7.82 (m, 3H).ppm.

^1^3^C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 14.2, 22.7, 22.7, 28.8, 28.9, 28.9, 29.2, 29.2, 31.7, 31.8, 36.5, 36.9, 38.7, 38.8, 42.6, 42.9, 61.2, 61., 88.7, 88.8, 90.9, 91.1, 125.4, 126.0, 126.0, 126.0, 126.5, 126.6, 127.6, 127.7, 128.2, 132.5, 132.5, 133.6, 142.0, 142.0, 204.7, 204.7 ppm.

ESI-HRMS: m/z calcd for C₂₃H₃₀ON [M+NH₄]^+ 340.2635 found 340.2638.
**SUPPORTING INFORMATION**

**Synthesis of 3-([1,1'-biphenyl]-4-yl)trideca-5,6-dien-1-ol 107**

![Chemical Structure](image)

The reaction was performed according to **general procedure 7** with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and [1,1'-biphenyl]-4ymagnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from **step I** was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from **step II** was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.59 g, 1.7 mmol, 59%).

**Analytical Data**[3]

**1H-NMR (400.1 MHz, CDCl₃):** δ = 0.80 – 0.92 (m, 3H), 1.15 – 1.34 (m, 9H), 1.77 – 1.99 (m, 3H), 1.99 – 2.15 (m, 1H), 2.27 – 2.46 (m, 2H), 2.82 – 2.95 (m, 1H), 3.47 – 3.67 (m, 2H), 4.91 – 5.05 (m, 2H), 7.23 – 7.26 (m, 1H), 7.27 (d, J=0.5, 1H), 7.29 – 7.36 (m, 1H), 7.40 – 7.45 (m, 2H), 7.51 – 7.56 (m, 2H), 7.56 – 7.61 (m, 2H) ppm.

**13C-NMR (100.6 MHz, CDCl₃):** δ = 14.1, 14.2, 22.7, 22.7, 28.9, 28.9, 28.9, 28.9, 29.2, 29.3, 31.8, 31.8, 36.6, 36.9, 38.8, 38.9, 42.2, 42.4, 61.2, 88.7, 88.8, 90.9, 91.1, 127.0, 127.1, 127.2, 128.2, 128.8, 139.3, 139.3, 141.1, 143.7, 143.7, 204.7, 204.8 ppm.

**ESI-HRMS:** m/z calcd for C₂₂H₃₂ON [M+NH₄]⁺ 366.2791 found 366.2795.
Synthesis of 3-(p-tolyl)trideca-5,6-dien-1-ol 108.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and p-tolylmagnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.48 g, 1.7 mmol, 58%).

Analytical Data[3]

¹HNMR (400.1 MHz, CDCl₃): δ = 0.85 – 0.94 (m, 3H), 1.23 – 1.36 (m, 9H), 1.74 – 1.86 (m, 2H), 1.90 (dd, J = 9.6, 7.4, 4.8, 1H), 1.96 – 2.07 (m, 1H), 2.26 – 2.31 (m, 2H), 2.32 (m, 3H), 2.78 (dd, J = 14.5, 10.0, 7.0, 4.7, 1H), 3.45 – 3.62 (m, 2H), 4.86 – 4.96 (m, 1H), 4.96 – 5.05 (m, 1H), 7.05 – 7.13 (m, 4H) ppm.

¹³CNMR (100.6 MHz, CDCl₃): δ = 14.2, 21.1, 22.7, 28.9, 28.9, 29.0, 29.2, 29.3, 31.8, 31.8, 36.7, 37.0, 38.8, 38.9, 42.2, 42.4, 61.3, 61.3, 88.8, 88.9, 90.8, 90.9, 127.6, 127.7, 129.2, 135.8, 141.5, 141.5, 204.6, 204.7 ppm.

APCI-HRMS: m/z calcd for C₂₀H₃₄O⁺ [M+NH₄]⁺ 304.2635 found 304.2634.
Synthesis of 3-(m-tolyl)trideca-5,6-dien-1-ol 109.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and m-tolylmagnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.50 g, 1.8 mmol, 61%).

Analytical Data

1H-NMR (400.1 MHz, CDCl₃): δ = 0.85 – 0.92 (m, 3H), 1.23 – 1.35 (m, 9H), 1.77 – 1.95 (m, 3H), 1.98 – 2.07 (m, 1H), 2.27 – 2.33 (m, 2H), 2.33 (s, 3H), 2.78 (dddd, J = 10.1, 7.3, 4.8, 1H), 3.45 – 3.59 (m, 2H), 4.87 – 4.97 (m, 1H), 4.97 – 5.04 (m, 1H), 6.93 – 7.03 (m, 3H), 7.16 – 7.20 (m, 1H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 21.6, 22.7, 28.9, 28.9, 28.9, 29.0, 29.2, 31.8, 31.8, 36.7, 37.0, 38.8, 38.9, 42.5, 42.8, 61.3, 88.9, 90.8, 91.0, 124.8, 124.8, 127.1, 128.4, 128.6, 128.6, 138.0, 144.6, 204.7 ppm.

APCI-HRMS: m/z calcd for C₂₀H₃₄ON [M+NH₄]⁺ 304.2635 found 304.2635.
Synthesis of 3-(o-tolyl)trideca-5,6-dien-1-ol 110.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and o-tolylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.58 g, 2.0 mmol, 60%).

Analytical Data\textsuperscript{[3]}

\textsuperscript{1}H-NMR (400.1 MHz, CDCl\textsubscript{3}): δ = 0.87 – 0.90 (m, 3H), 1.23 – 1.32 (m, 9H), 1.78 – 1.93 (m, 3H), 1.99 – 2.09 (m, 1H), 2.27 – 2.33 (m, 2H), 2.34 (dd, J = 1.2, 0.7 Hz, 3H), 3.17 (dddd, J = 12.9, 9.4, 5.1, 2.0 Hz, 1H), 3.49 (dddd, J = 10.6, 7.4, 6.5, 3.5 Hz, 1H), 3.58 (dddd, J = 10.6, 6.9, 5.5, 2.8 Hz, 1H), 4.87 – 4.96 (m, 1H), 4.96 – 5.04 (m, 1H), 7.05 – 7.10 (m, 1H), 7.11 – 7.17 (m, 2H), 7.18 (t, J = 1.1 Hz, 1H).ppm.

\textsuperscript{13}C-NMR (100.6 MHz, CDCl\textsubscript{3}): δ = 14.2, 20.0, 20.0, 22.7, 28.9, 28.9, 29.2, 29.2, 31.8, 31.8, 36.3, 36.8, 36.8, 37.1, 38.7, 38.7, 61.2, 61.3, 88.7, 88.8, 90.8, 91.0, 125.9, 125.9, 126.0, 126.3, 126.3, 130.3, 130.4, 136.2, 136.3, 142.8, 142.9, 204.6, 204.7 ppm.

APCI-HRMS: m/z calcd for C\textsubscript{20}H\textsubscript{34}ON [M+NH\textsubscript{4}]\textsuperscript{+} 304.2635 found 304.2635.
Synthesis of 3-mesityltrideca-5,6-dien-1-ol 111.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and mesitylmagnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 4:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.55 g, 1.7 mmol, 51%).

**Analytical Data**[3]

**1H-NMR (400.1 MHz, CDCl₃):** δ = 0.87 – 0.92 (m, 3H), 1.24 – 1.37 (m, 9H), 1.78 – 1.86 (m, 1H), 1.92 – 1.97 (m, 1H), 2.01 – 2.08 (m, 2H), 2.23 (s, 3H), 2.33 (s, 3H), 2.36 (s, 3H), 2.40 – 2.49 (m, 2H), 3.32 – 3.42 (m, 1H), 3.48 – 3.61 (m, 2H), 4.92 – 4.99 (m, 1H), 4.99 – 5.06 (m, 1H), 6.76 – 6.85 (m, 2H) ppm.

**13C-NMR (100.6 MHz, CDCl₃):** δ = 14.2, 20.7, 21.5, 21.9, 22.7, 28.9, 29.0, 29.1, 29.3, 29.3, 31.8, 31.8, 34.2, 34.4, 36.7, 36.8, 37.3, 37.6, 62.0, 89.5, 89.7, 90.9, 91.1, 129.3, 129.3, 131.2, 135.3, 137.0, 137.4, 204.2 ppm.

**APCI-HRMS:** m/z calcd for C₂₂H₃₈O₄N [M+NH₄]⁺ 332.2948 found 332.2944.
Synthesis of 3-(4-vinylphenyl)trideca-5,6-dien-1-ol 112.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and (4-vinylphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.64 g, 2.1 mmol, 63%).

Analytical Data[3]

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.94 (m, 3H), 1.21 – 1.35 (m, 9H), 1.81 (dddd, J = 13.7, 10.0, 6.4, 5.5 Hz, 2H), 1.90 (dddd, J = 7.0, 7.0, 7.0, 3.0 Hz, 1H), 1.95 – 2.09 (m, 1H), 2.21 – 2.41 (m, 2H), 2.82 (dddd, J = 10.5, 7.7, 7.7, 4.9 Hz, 1H), 3.39 – 3.64 (m, 2H), 4.86 – 4.97 (m, 1H), 4.97 – 5.08 (m, 1H), 5.20 (ddd, J = 10.9, 1.0, 1.0 Hz, 1H), 5.71 (dd, J = 17.6, 1.2, 1.2 Hz, 1H), 6.69 (ddd, J = 17.6, 10.9, 1.2 Hz, 1H), 7.05 – 7.20 (m, 2H), 7.32 – 7.42 (m, 2H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 28.9, 29.2, 29.2, 31.8, 31.8, 36.5, 36.9, 38.8, 38.8, 42.3, 42.5, 61.2, 61.2, 88.7, 88.7, 90.9, 91.1, 113.2, 113.2, 126.4, 128.0, 135.8, 135.8, 136.7, 144.3, 144.4, 204.7, 204.7 ppm.

APCI-HRMS: m/z calcd for C₂₁H₃₁O [M+H]^⁺ 299.2369 found 299.2371.
Synthesis of 3-(4-bromophenyl)trideca-5,6-dien-1-ol 113

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.7 g, 2.9 mmol, 1.0 equiv.) and (4-bromophenyl)magnesium bromide (4.4 mL, 4.4 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.43 g, 1.2 mmol, 43%).

Analytical Data[3]

^1H-NMR (400.1 MHz, CDCl₃): δ = 0.87 – 0.91 (m, 3H), 1.22 – 1.34 (m, 9H), 1.75 – 1.96 (m, 3H), 1.96 – 2.12 (m, 1H), 2.23 – 2.39 (m, 2H), 2.72 – 2.88 (m, 1H), 3.44 – 3.62 (m, 2H), 4.87 – 4.96 (m, 1H), 4.96 – 5.04 (m, 1H), 7.17 – 7.21 (m, 2H), 7.27 – 7.33 (m, 2H) ppm.

^13C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 28.9, 28.9, 29.2, 29.2, 31.8, 31.8, 36.6, 37.0, 38.8, 38.9, 42.6, 42.8, 61.3, 88.7, 88.8, 90.9, 91.0, 126.4, 126.4, 127.8, 128.5, 129.6, 144.6, 144.6, 204.7, 204.7 ppm.

APCI-HRMS: m/z calcd for C₁₉H₂₉O₂Br [M+H]^+ 352.1318 found 352.1318.
Synthesis of 3-(4-methoxyphenyl)trideca-5,6-dien-1-ol 114.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.68 g, 2.2 mmol, 66%).

Analytical Data[3]

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.91 (m, 3H), 1.23 – 1.34 (m, 9H), 1.72 – 1.87 (m, 2H), 1.87 – 1.96 (m, 1H), 1.96 – 2.09 (m, 1H), 2.19 – 2.38 (m, 2H), 2.71 – 2.85 (m, 1H), 3.44 – 3.52 (m, 1H), 3.56 (dddd, J = 10.6, 6.8, 5.5, 1.3 Hz, 1H), 3.79 (s, 1.4H), 3.79 (s, 1.6), 4.86 – 4.97 (m, 1H), 4.97 – 5.04 (m, 1H), 6.81 – 6.87 (m, 2H), 7.07 – 7.13 (m, 2H).ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 28.9, 29.0, 29.2, 29.3, 31.8, 31.8, 36.8, 37.1, 38.9, 39.0, 41.8, 42.0, 55.3, 61.3, 88.8, 88.8, 90.8 90.9, 113.9, 128.7, 136.6, 136.6, 158.1, 158.2, 204.6, 204.7 ppm.

ESI-HRMS: m/z calcd for C₂₀H₂₉O₂ [M+H] 301.2162 found 301.2162.
Synthesis of 3-(4-(methylthio)phenyl)trideca-5,6-dien-1-ol 115.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.70 g, 3.0 mmol, 1.0 equiv.) and (4-(methylthio)phenyl)magnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.17 mg, 4.5 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.60 g, 1.9 mmol, 63%).

Analytical Data[3]

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 0.89 \text{ (m, } 3\text{H} ), 1.24 - 1.33 \text{ (m, } 9\text{H} ), 1.73 - 1.86 \text{ (m, } 2\text{H} ), 1.86 - 1.96 \text{ (m, } 1\text{H} ), 1.96 - 2.08 \text{ (m, } 1\text{H} ), 2.23 - 2.36 \text{ (m, } 2\text{H} ), 2.47 \text{ (d, } J=1.5, \text{ 3H} ), 2.79 \text{ (ddddd, } J=13.2, 8.4, 6.8, 4.8 \text{ Hz, } 1\text{H} ), 3.42 - 3.51 \text{ (m, } 1\text{H} ), 3.56 \text{ (ddddd, } J=10.6, 6.9, 5.3, 1.6 \text{ Hz, } 1\text{H} ), 4.90 \text{ (ddddd, } J=12.3, 9.2, 7.3, 6.1, 3.0 \text{ Hz, } 1\text{H} ), 4.99 \text{ (dddd, } J=6.5, 6.5, 4.0, 2.6, 2.5 \text{ Hz, } 1\text{H} ), 7.08 - 7.13 \text{ (m, } 2\text{H} ), 7.19 - 7.22 \text{ (m, } 2\text{H} ) \text{ ppm.}

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.2, 16.3, 22.8, 28.9, 29.2, 29.3, 31.8, 31.8, 36.6, 36.9, 38.7, 38.8, 42.0, 61.1, 88.7, 91.1, 127.1, 128.4, 135.9, 141.6, 204.6 \text{ ppm.}

APCI-HRMS: \(m/z \text{ calcd for C}_{20}\text{H}_{31}\text{OS} [M+H]^+ 319.2096 \text{ found 319.2087.} \)
Synthesis of 3-(4-(trifluoromethyl)phenyl)trideca-5,6-dien-1-ol 116.

The reaction was performed according to general procedure 7 with ethyl (E)-trideca-2,5,6-trienoate (0.70 g, 3.0 mmol, 1.0 equiv.) and (4-(trifluoromethyl)phenyl)magnesium bromide (4.5 mL, 4.5 mmol, 1.5 equiv. 1.0 M). The crude product from step I was treated with LAH (0.17 mg, 4.5 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 3:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.46 g, 1.4 mmol, 45%).

Analytical Data[3]

1H-NMR (400.1 MHz, CDCl₃): δ = 0.86 – 0.93 (m, 3H), 1.14 (s, 1H), 1.23 – 1.31 (m, 8H), 1.75 – 1.90 (m, 3H), 1.98 – 2.13 (m, 1H), 2.26 – 2.42 (m, 2H), 2.94 (ddd, J = 14.5, 9.6, 6.4 Hz, 1H), 3.46 (ddddd, J = 10.6, 7.5, 6.3, 0.9 Hz, 1H), 3.57 (ddddd, J = 10.6, 6.8, 5.3, 1.5 Hz, 1H), 4.84 – 4.94 (m, 1H), 4.94 – 5.03 (m, 1H), 7.27 – 7.32 (m, 2H), 7.53 – 7.57 (m, 2H) ppm.

13C-NMR (100.6 MHz, CDCl₃): δ = 14.1, 14.1, 22.7, 28.8, 28.9, 29.2, 29.2, 31.7, 31.8, 36.2, 36.6, 38.7, 38.7, 42.2, 42.5, 60.8, 60.8, 88.2, 88.3, 91.2, 91.3, 125.4, 125.4, 125.4, 128.2, 204.8 ppm.

APCI-HRMS: m/z calcd for C₂₀H₂₉OF₃ [M+H]+ 341.2092 found 341.2089.
Synthesis of 4-(4-methoxyphenyl)-2-methyltetradeca-6,7-dien-2-ol 117.

A solution of MeMgBr (2.5 mL, 7.3 mmol, 2.5 equiv, 3 M in Et₂O) in THF (10 mL) was cooled to 0 °C and the crude ethyl 3-(4-methoxyphenyl)trideca-5,6-dienoate (1.0 g, 2.9 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise. The mixture was stirred for 30 minutes and then warmed to room temperature and stirred for 2 hours. Saturated ammonium chloride (20 mL) was added and the aqueous layer was separated and extracted with Et₂O (2 × 30 mL). The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the two Diastereomers were separated by flash Chromatography (SiO₂, pentane/Et₂O = 2/1). The title compound was obtained (0.85 g, 2.6 mmol, 89%) as a colorless oil.

Analytical Data (syn-product)[31]

$^1$H-NMR (400.1 MHz, CDCl₃): $\delta = 0.86 – 0.92$ (m, 3H), 1.11 (m, 3H), 1.14 (m, 3H), 1.23 – 1.39 (m, 9H), 1.79 – 1.86 (m, 1H), 1.89 – 1.97 (m, 3H), 2.15 – 2.32 (m, 2H), 2.83 (m, 1H), 3.78 (m, 3H), 4.82 – 4.93 (m, 1H), 4.96 – 5.05 (m, 1H), 5.81 – 5.88 (m, 2H), 7.11 – 7.17 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): $\delta = 14.2, 22.7, 28.9, 28.9, 28.9, 29.0, 29.2, 29.9, 30.3, 30.3, 31.8, 31.8, 38.8, 39.1, 41.5, 41.7, 48.8, 49.0, 55.3, 55.5, 71.5, 88.9, 88.9, 90.8, 90.9, 114.1, 128.8, 128.9, 158.2 ppm.

ESI-HRMS: m/z calcd for C₂₂H₃₈O₂ [M+NH₄]⁺ 348.2897 found 348.2893.

Synthesis of 7-cyclohexyl-3-(4-methoxyphenyl)hepta-5,6-dien-1-ol
Synthesis of ethyl 5-cyclohexylpenta-3,4-dienoate 118.

The reaction was performed according to general procedure 5.

I) Cyclohexanecarbaldehyde (11 g, 93 mmol, 1.0 equiv.) and ethinyl magnesium bromide (200 mL, 100 mmol, 0.5 M in THF, 1.08 equiv.). The crude product was filtered over a short silica pad (2:1 pentane/Et₂O). 1-cyclohexylprop-2-yn-1-ol was obtained as a yellow liquid (12 g, 88 mmol, 95%).

II) Crude 1-cyclohexylprop-2-yn-1-ol (step I) (14 g, 86 mmol, 1.0 equiv.), triethyl orthoacetate (15 g, 17 mL, 90 mmol, 1.05 equiv.), propionic acid (3 × 5 mol%). The crude product was purified by flash chromatography on silica gel (40:1 pentane/Et₂O) to obtain the title compound (12 g, 54 mmol, 63%) as a colorless liquid.

Analytical Data

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.02 – 1.23 (m, 4H), 1.24 – 1.27 (m, 4H), 1.61 (dddd, J = 10.9, 4.0, 3.0, 1.6 Hz, 1H), 1.67 – 1.75 (m, 4H), 1.97 (ddd, J = 11.0, 6.0, 3.1 Hz, 1H), 2.99 (dd, J = 7.2, 2.8 Hz, 2H), 4.14 (q, J = 7.1, 2H), 5.16 (ddd, J = 8.9, 5.9, 2.7 Hz, 1H), 5.24 (dd, J = 7.2, 6.3, 3.0 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.3, 26.0, 26.0, 26.2, 33.0, 33.0, 37.0, 60.7, 85.0, 98.2, 171.7, 204.0 ppm.

APCI-HRMS: m/z calcd for C₁₃H₁₂O₂ [M+H]+ 200.0837 found 200.0838.

Synthesis of ethyl (E)-7-cyclohexylhepta-2,5,6-trienoat 119.

The reaction was performed according to general procedure 6.

I) ethyl 5-cyclohexylpenta-3,4-dienoate (12 g, 54 mmol, 1.0 equiv.) and DIBAL-H (78 mL, 78 mmol, 1.45 equiv., 1.0 M in DCM). The crude product was filtered over a short silica pad (DCM). 5-cyclohexylpenta-3,4-dienal was obtained as a yellow liquid (7.9 g, 49 mmol, 90%).

II) Crude 7-phenylhepta-3,4-dienal (step I) (7.9 g, 49 mmol), NaH (60% in mineral oil, 2.2 g, 54 mmol, 1.1 equiv.) in dry THF (200 mL) and triethyl phosphonoacetate (14.4 g, 12.7 mL, 64.0 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:Et₂O). The title compound was obtained as colorless liquid (6.8 g, 29 mmol, 59%).
SUPPORTING INFORMATION

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 1.03 – 1.24 (m, 4H), 1.29 (t, $J$ = 7.1 Hz, 3H), 1.62 (ddtd, $J$ = 10.8, 5.0, 2.4, 1.2 Hz, 1H), 1.67 – 1.78 (m, 5H), 1.92 – 2.03 (m, 1H), 2.88 (tdd, $J$ = 6.5, 3.0, 1.7 Hz, 2H), 4.19 (q, $J$ = 7.1 Hz, 2H), 5.08 – 5.20 (m, 2H), 5.87 (dt, $J$=15.6, 1.6, 1H), 6.97 (dtd, $J$ = 15.7, 6.5, 0.3 Hz, 1H). ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.4, 26.1, 26.1, 26.2, 32.1, 33.1, 33.1, 37.2, 60.3, 88.0, 98.3, 122.0, 146.9, 166.6, 203.8 ppm.

APCI-HRMS: $m/z$ calcd for C$_{15}$H$_{23}$O$_2$ [M+H]$^+$ 235.1693 found 235.1692.

Synthesis of 7-cyclohexyl-3-(4-methoxyphenyl)hepta-5,6-dien-1-ol 120.

The reaction was performed according to general procedure 7 with ethyl (E)-7-cyclohexylhepta-2,5,6-trienoat (0.8 g, 3.4 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et$_2$O). The desired product was obtained as a colorless liquid (0.62 g, 2.1 mmol, 61 %).

Analytical Data$^{[3]}$

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.83 – 1.08 (m, 2H), 1.13 – 1.32 (m, 4H), 1.54 – 1.72 (m, 5H), 1.74 – 1.93 (m, 2H), 1.93 – 2.11 (m, 1H), 2.21 – 2.39 (m, 2H), 2.70 – 2.85 (m, 1H), 3.43 – 3.60 (m, 2H), 3.79 (m, 3H), 4.90 – 5.03 (m, 2H), 6.81 – 6.87 (m, 2H), 7.07 – 7.12 (m, 2H). ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 26.1, 26.1, 26.2, 26.3, 33.1, 33.1, 33.2, 37.0, 37.2, 37.3, 37.5, 38.9, 39.1, 41.8, 42.1, 55.3, 55.3, 61.3, 61.3, 89.7, 89.8, 96.8, 97.0, 113.9, 113.9, 128.7, 128.7, 158.2, 158.2, 203.4, 203.5 ppm.

APCI-HRMS: $m/z$ calcd for C$_{20}$H$_{32}$O$_2$N [M+NH$_4$]$^+$ 318.2433 found 318.2433.
Synthesis of 3-(4-methoxyphenyl)-9-phenylnona-5,6-dien-1-ol.

The reaction was performed according to general procedure 5.

I) 3-Phenylpropanal (12 g, 12 mL 93 mmol, 1.0 equiv.) and ethinyl magnesium bromide (200 mL, 100 mmol, 0.5 M in THF, 1.08 equiv.). The crude product was filtered over a short silica pad (2:1 pentane/Et₂O). 5-phenylpent-1-yn-3-ol was obtained as a yellow liquid (14 g, 86 mmol, 93%)

II) Crude phenylpent-1-yn-3-ol (step I) (14 g, 86 mmol, 1.0 equiv.), triethyl orthoacetate (15 g, 17 mL, 90 mmol, 1.05 equiv.), propionic acid (3 × 5 mol%). The crude product was purified by fractional distillation under reduced pressure (110 °C, 2 mbar) to obtain the title product (12 g, 54 mmol, 63%) as a colorless liquid.

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.27\) (t, \(J = 7.1\) Hz, 3H), 2.28 – 2.38 (m, 2H), 2.70 – 2.77 (m, 2H), 2.91 – 2.98 (m, 2H), 4.15 (q, \(J = 7.2\) Hz, 2H), 5.18 – 5.28 (m, 2H), 7.17 – 7.20 (m, 3H), 7.26 – 7.31 (m, 2H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.3, 30.2, 35.0, 35.3, 60.8, 84.8, 91.5, 125.9, 128.4, 128.6, 141.7, 1071.6, 205.3\) ppm.

ESI-HRMS: \(m/z\) calcd for \(C_{15}H_{19}O_2\) [M+H]̕ 231.1380 found 231.1383.
Synthesis of ethyl (E)-9-phenylnona-2,5,6-trienoate 122.

The reaction was performed according to general procedure 6.
I) Ethyl 7-phenylocta-3,4-dienoate (12 g, 54 mmol, 1.0 equiv.) and DIBAL-H (78 mL, 78 mmol, 1.45 equiv., 1.0 M in DCM). The crude product was filtered over a short silica pad (DCM). Undeca-3,4-dienal was obtained as a yellow liquid (8.4 g, 50 mmol, 93%).
II) Crude 7-phenylocta-3,4-dienal (step I) (8.4 g, 50 mmol), NaH (60% in mineral oil, 2.2 g, 55 mmol, 1.1 equiv.) in dry THF (200 mL) and triethyl phosphonoacetate (16 g, 14 mL, 72 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:Et₂O). The title compound was obtained as colorless liquid (11 g, 43 mmol, 79%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 1.29 (t, J = 7.1 Hz, 3H), 2.29 – 2.36 (m, 2H), 2.72 (t, J = 7.7 Hz, 2H), 2.82 (ddd, J = 6.7, 2.8, 1.7 Hz, 2H), 4.18 (q, J = 7.1, 2H), 5.04 – 5.14 (m, 1H), 5.17 – 5.28 (m, 1H), 5.86 (dd, J = 15.6, 1.7 Hz, 1H), 6.89 – 7.01 (m, 1H), 7.17 – 7.21 (m, 3H), 7.27 – 7.34 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 14.4, 30.4, 31.9, 35.4, 60.3, 87.7, 91.5, 122.0, 125.9, 128.4, 128.6, 141.7, 146.7, 166.6, 205.1 ppm.

APCI-HRMS: m/z calcd for C₁₇H₂₄O₂N [M+NH₄]+ 274.1802 found 274.1801.

Synthesis of 3-(4-methoxyphenyl)-9-phenylnona-5,6-dien-1-ol 123.

The reaction was performed according to general procedure 7 with ethyl ethyl (E)-9-phenylnona-2,5,6-trienoate (0.8 g, 3.4 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.64 g, 1.9 mmol, 58%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 1.76 (dddd, J = 13.9, 10.1, 6.3, 5.4 Hz, 1H), 1.98 (dddd, J = 13.8, 7.5, 6.9, 4.8 Hz, 1H), 2.12 – 2.20 (m, 1H), 2.21 – 2.30 (m, 3H), 2.56 (dd, J = 7.9, 7.9, 2.4 Hz, 1H), 2.64 (dd,
SUPPORTING INFORMATION

$J = 7.5, 7.5$ Hz, 1H), 2.74 (dddd, $J = 14.5, 9.8, 4.8, 2.2$ Hz, 1H), 3.44 – 3.59 (m, 2H), 3.72 (s, 1H), 3.78 (s, 2H), 4.88 – 5.00 (m, 1H), 5.00 – 5.10 (m, 1H), 6.81 – 6.86 (m, 2H), 7.05 – 7.11 (m, 2H), 7.13 – 7.22 (m, 3H), 7.26 – 7.31 (m, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta =$ 30.5, 30.5, 35.4, 35.4, 36.6, 37.0, 38.9, 39.1, 41.7, 41.9, 55.2, 55.3, 61.2, 61.2, 89.4, 89.5, 90.1, 90.2, 113.9, 125.8, 125.9, 128.3, 128.3, 128.6, 128.6, 128.7, 128.7, 136.4, 136.5, 142.0, 142.0, 158.1, 158.2, 204.8 ppm.

APCI-HRMS: m/z calcd for C$_{23}$H$_{30}$O$_2$N [M+NH$_4$]$^+$ 340.2271 found 340.2272.
Synthesis of 3-(4-methoxyphenyl)-8-phenylocta-5,6-dien-1-ol.

The reaction was performed according to general procedure 5. 
I) 2-phenylacetaldehyde (g, 11.2 mL 93 mmol, 1.0 equiv.) and ethinyl magnesium bromide (200 mL, 100 mmol, 0.5 M in THF, 1.08 equiv.). The crude product was filtered over a short silica pad (2:1 pentane/Et₂O). 1-phenylbut-3-yn-2-ol was obtained as a yellow liquid (13 g, 89 mmol, 96%)
II) Crude 1-phenylbut-3-yn-2-ol (step I) (13 g, 89 mmol, 1.0 equiv.), triethyl orthoacetate (15 g, 17 mL, 90 mmol, 1.05 equiv.), propionic acid (3 × 5 mol%). The crude product was purified by fractional distillation under reduced pressure (110 °C, 2 mbar) to obtain the title compound (11 g, 61 mmol, 55%) as a colorless liquid.

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl₃): \(\delta = 1.27 (t, J = 7.1 \text{ Hz}, 3\text{H}), 3.03 (dd, J = 7.2, 2.7 \text{ Hz}, 2\text{H}), 3.36 (dd, J = 7.2, 2.8 \text{ Hz}, 2\text{H}), 4.15 (q, J = 7.1 \text{ Hz}, 2\text{H}), 5.25 – 5.33 (m, 1\text{H}), 5.33 – 5.40 (m, 1\text{H}), 7.20 – 7.24 (m, 3\text{H}), 7.27 – 7.32 (m, 2\text{H}). \text{ ppm.}

\(^13\)C-NMR (100.6 MHz, CDCl₃): \(\delta = 14.3, 35.0, 35.4, 60.8, 84.8, 91.7, 126.3, 128.5, 128.5, 140.2, 171.5, 205.6 \text{ ppm.}

APCI-HRMS: \(m/z\) calcd for C₁₄H₂₀O₂N [M+NH₄]+ 234.1489 found 234.1488.
Synthesis of ethyl (E)-8-phenylocta-2,5,6-trienoate 125.

The reaction was performed according to general procedure 6.

I) Ethyl 6-phenylhexa-3,4-dienoate (11 g, 61 mmol, 1.0 equiv.) and DIBAL-H (89 mL, 89 mmol, 1.45 equiv., 1.0 M in DCM). The crude product was filtered over a short silica pad (DCM). 6-phenylhexa-3,4-dienal was obtained as a yellow liquid (9.5 g, 55 mmol, 90%).

II) Crude 6 phenylhexa-3,4-dienal (step I) (9.5 g, 55 mmol), NaH (60% in mineral oil, 2.4 g, 61 mmol, 1.1 equiv.) in dry THF (150 mL) and triethyl phosphonoacetate (16 g, 14 mL, 72 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:Et₂O). The title compound was obtained as colorless liquid (5.9 g, 28 mmol, 50%).

Analytical Data

\[ ^{1}H\text{-NMR (400.1 MHz, CDCl}_3\text{): } \delta = 1.29 \text{ (t, } J = 7.1 \text{ Hz, 3H)}, 2.87 \text{ (ddd, } J = 6.7, 2.8, 1.7 \text{ Hz, 2H)}, 3.03 \text{ (dd, } J = 7.2, 2.7 \text{ Hz, 1H)}, 3.35 \text{ (td, } J = 6.6, 2.8 \text{ Hz, 2H)}, 4.18 - 4.22 \text{ (m, 2H)}, 5.10 - 5.17 \text{ (m, 1H)}, 5.33 - 5.36 (m, 1H), 5.84 (dt, } J = 15.6, 1.7 \text{ Hz, 1H}), 6.94 (dtd, } J = 15.6, 6.5 \text{ Hz, 0.3, 1H}), 7.22 - 7.24 \text{ (m, 2H)}, 7.27 - 7.29 \text{ (m, 2H) ppm.}

\[ ^{13}C\text{-NMR (100.6 MHz, CDCl}_3\text{): } \delta = 14.4, 31.8, 35.0, 35.6, 60.3, 60.8, 84.8, 87.9, 91.8, 122.2, 126.3, 128.6, 146.4, 205.4 \text{ ppm.}

APCI-HRMS: m/z calcd for C₁₆H₂₂O₂N [M+NH₄]^+ 260.1651 found 260.1652.

Synthesis of 3-(4-methoxyphenyl)-8-phenylocta-5,6-dien-1-ol 126.

The reaction was performed according to general procedure 7 with ethyl ethyl (E)-8-phenylocta-2,5,6-trienoate (0.82 g, 3.4 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.55 g, 1.8 mmol, 52%).
Analytical Data\[^3\]

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 1.22\ (s, 1H), 1.67 – 1.82\ (m, 1H), 1.88 – 2.02\ (m, 1H), 2.25 – 2.34\ (m, 2H), 2.73\ (dddd, \(J = 22.1, 10.0, 7.3, 6.8, 4.8\) Hz, 1H), 3.19\ (ddd, \(J = 7.5, 2.0, 2.0\) Hz, 1H), 3.27\ (dd, \(J = 7.0, 2.9\) Hz, 1H), 3.41 – 3.57\ (m, 2H), 3.77\ (mc, 3H), 4.98\ (dddd, \(J = 8.4, 7.4, 5.6, 3.9\) Hz, 1H), 5.14 – 5.25\ (m, 1H), 6.82 – 6.84\ (m, 2H), 7.05 – 7.09\ (m, 2H), 7.16 – 7.22\ (m, 3H), 7.20 – 7.30\ (m, 2H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 35.7, 35.7, 36.8, 36.9, 38.8, 41.7, 41.8, 55.3, 61.2, 61.2, 89.4, 89.6, 90.2, 90.3, 113.9, 114.0, 126.1, 128.4, 128.5, 128.6, 128.6, 136.4, 136.5, 158.2, 205.3, 205.3\ ppm.

APCI-HRMS: m/z calcd for C\(_{21}\)H\(_{28}\)O\(_2\)N [M+NH\(_4\)]\(^+\) 326.2115 found 326.2116.

Synthesis of 3-(4-methoxyphenyl)-10-(methylthio)deca-5,6-dien-1-ol

The reaction was performed according to general procedure 5.

I) 3-(methylthio)propanal (10 g, 85 mmol, 1.0 equiv.) and ethinyl magnesium bromide (180 mL, 90 mmol, 0.5 M in THF, 1.08 equiv.). The crude product was filtered over a short silica pad (2:1 pentane/Et\(_2\)O). 5-(methylthio)pent-1-yn-3-ol was obtained as a yellow liquid (12 g, 79 mmol, 93%)

II) Crude 5-(methylthio)pent-1-yn-3-ol (step I) (11 g, 87 mmol 1.0 equiv.), triethyl orthoacetate (15 g, 17 mL, 91 mmol, 1.05 equiv.), propionic acid (3 \times 5 mol%). The crude product was purified by flash chromatography on silica gel (40:1pentane/Et\(_2\)O) to obtain the title compound (11 g, 52 mmol, 60%) as a colorless liquid.
Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \( \delta = 1.27 \) (t, \( J = 7.1 \) Hz, 3H), 2.11 (s, 3H), 2.26 – 2.33 (m, 2H), 2.55 – 2.59 (m, 2H), 3.03 (dd, \( J = 7.1, 2.9 \) Hz, 2H), 4.16 (q, \( J = 7.2 \) Hz, 2H), 5.21 – 5.33 (m, 2H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl\(_3\)): \( \delta = 14.3, 15.6, 28.4, 33.6, 34.9, 60.8, 85.2, 90.6, 171.5, 205.3 \) ppm.

APCI-HRMS: m/z calcd for C\(_{10}\)H\(_{17}\)O\(_2\)S [M+H]\(^+\) 201.0944 found 201.0945.

Synthesis of ethyl (E)-9-(methylthio)nona-2,5,6-trienoate 128.

The reaction was performed according to general procedure 6.

I) ethyl 7-(methylthio)hepta-3,4-dienoate (11 g, 52 mmol, 1.0 equiv.) and DIBAL-H (75 mL, 75 mmol, 1.45 equiv., 1.0 M in DCM). The crude product was filtered over a short silica pad (DCM). 7-(methylthio)hepta-3,4-dienal was obtained as a yellow liquid (7.3 g, 43 mmol, 83%).

II) Crude 7-(methylthio)hepta-3,4-dienal (step I) (7.3 g, 48 mmol), NaH (60% in mineral oil, 2.1 g, 53 mmol, 1.1 equiv.) in dry THF (200 mL) and triethyl phosphonoacetate (15 g, 13 mL, 69 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:Et\(_2\)O). The title compound was obtained as colorless liquid (7.9 g, 33 mmol, 62%).

Analytical Data 10

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \( \delta = 1.28 \) (t, \( J = 7.1 \) Hz, 3H), 2.11 (s, 3H), 2.25 – 2.34 (m, 2H), 2.53 – 2.59 (m, 2H), 2.90 (tdd, \( J = 6.6, 2.8, 1.7 \) Hz, 2H), 4.16 – 4.22 (m, 2H), 5.11 – 5.18 (m, 1H), 5.22 (qt, \( J = 6.5, 2.8 \) Hz, 1H), 5.88 (dt, \( J = 15.6, 1.7 \) Hz, 1H), 6.96 (ddt, \( J = 15.7, 6.5, 0.3 \) Hz, 1H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl\(_3\)): \( \delta = 14.3, 15.6, 28.6, 31.8, 33.7, 60.3, 88.1, 90.7, 122.1, 146.5, 166.5, 205.1 \) ppm.

APCI-HRMS: m/z calcd for C\(_{12}\)H\(_{19}\)O\(_2\)S [M+OH]\(^-\) 243.1049 found 243.1047.
Synthesis of 3-(4-methoxyphenyl)-9-(methylthio)nona-5,6-dien-1-ol 129.

The reaction was performed according to general procedure 7 with ethyl (E)-10-(methylthio)deca-2,5,6-trienoate (0.82 g, 3.4 mmol, 1.0 equiv.) and (4-methoxyphenyl)magnesium bromide (5.1 mL, 5.1 mmol, 1.0 M). The crude product from step I was treated with LAH (0.19 mg, 5.1 mmol, 1.5 equiv.). The crude product from step II was purified by flash chromatography on silica gel (10:1 to 5:1 pentane/Et₂O). The desired product was obtained as a colorless liquid (0.68 g, 2.2 mmol, 65%).

Analytical Data \[^3\]

\(^1\)H-NMR (400.1 MHz, CDCl₃): δ = 1.27 (s, 1H), 1.78 (dddt, J = 13.7, 10.0, 6.3, 5.5 Hz, 1H), 1.94 – 2.05 (m, 1H), 2.08 (m, 3H), 2.11 – 2.17 (m, 1H), 2.17 – 2.23 (m, 1H), 2.28 – 2.34 (m, 2H), 2.36 – 2.42 (m, 1H), 2.43 – 2.49 (m, 1H), 2.73 – 2.86 (m, 1H), 3.48 (dddt, J = 10.6, 7.6, 6.3, 2.2 Hz, 1H), 3.56 (dddd, J = 10.6, 6.8, 5.4, 2.3 Hz, 1H), 3.79 (m, 3H), 4.92 – 5.11 (m, 2H), 6.81 – 6.87 (m, 2H), 7.07 – 7.12 (m, 2H) ppm.

\(^13\)C-NMR (100.6 MHz, CDCl₃): δ = 15.5, 15.6, 28.7, 28.7, 33.6, 33.7, 36.4, 37.0, 39.0, 39.1, 41.5, 41.9, 55.3, 61.2, 61.2, 89.2, 89.4, 89.8, 89.9, 113.9, 128.6, 128.7, 136.4, 204.8 ppm.

APCI-HRMS: m/z calcd for C₁₇H₂₅O₂S [M+H]⁺ 293.1575 found 293.1576.

2.3 Synthesis and characterization of 1,3-substituted allenols

Synthesis of syn and anti - 4-(4-methoxyphenyl)octa-6,7-dien-2-ol 45, 49

\[\text{I} \] At −80°C a solution of DIBAL-H (5.3 mL, 5.3 mmol, 1.4 equiv., 1.0 M in CH₂Cl₂) was added dropwise over 90 min to a solution of ethyl 3-(4-methoxyphenyl)hepta-5,6-dienoate (1.0 g, 3.8 mmol, 1.0 equiv.) in CH₂Cl₂ (5 mL). The reaction mixture was stirred for 1 h and then transferred to an ice-cold aqueous solution of HCl (2.0 M, 50 mL). The layers were separated, the organic layer was washed with HCl (2.0 M, 2 × 10 mL) and the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered over a silica pad (DCM) and concentrated under...
reduced pressure. The crude 7 3-(4-methoxyphenyl)hepta-5,6-dienal was obtained as a yellow liquid (0.78 g, 3.6 mmol, 95%).

II) A solution of MeMgBr (1.8 mL, 5.4 mmol, 1.5 equiv, 3 M in Et₂O) in THF (5 mL) was cooled to 0 °C and the crude 7 3-(4-methoxyphenyl)hepta-5,6-dienal (0.78 g, 3.6 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 30 minutes and then warmed to room temperature. Saturated ammonium chloride (10 mL) was added and the aqueous layer was separated and extracted with Et₂O (2 × 20 mL). The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the two diastereomers were separated by flash Chromatography (SiO₂, pentane/Et₂O = 4/1). The syn-diastereomer was obtained as a single diastereomer (0.40 g, 1.7 mmol, 48 %). The anti diastereomer was obtained (syn/anti = 25/75, 0.20 g, 0.86 mmol, 24 %) as colorless liquid.

Analytical Data (syn-product) syn-45

^1^H-NMR (400.1 MHz, CDCl₃): δ = 1.12 (d, J = 6.2 Hz, 3H), 1.31 (s, 1H), 1.64 (ddd, J = 14.0, 11.1, 3.1 Hz, 1H), 1.80 (ddd, J = 13.8, 9.6, 4.1 Hz, 1H), 2.28 (ddddd, J = 7.7, 7.3, 3.0, 2.8 Hz, 2H), 2.89 (ddddd, J = 11.4, 7.3, 7.2, 3.7 Hz, 1H), 3.53 (m, 1H), 3.79 (s, 3H), 4.53 – 4.64 (m, 2H), 4.90 – 4.98 (m, 1H), 6.82 – 6.87 (m, 2H), 7.08 – 7.13 (m, 2H) ppm.

^13^C-NMR (100.6 MHz, CDCl₃): δ = 24.5, 36.6, 41.7, 45.5, 55.3, 65.7, 74.4, 88.2, 113.9, 128.8, 136.5, 158.2, 209.2 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₂O₂ [M+H]^+ 233.1534 found 233.1536.

Analytical Data (anti-product) anti-49

^1^H-NMR (400.1 MHz, CDCl₃): δ = 1.17 (d, J = 6.2 Hz, 3H), 1.28 (s, 1H), 1.78 – 1.85 (m, 1H), 2.21 – 2.39 (m, 2H), 2.72 (ddddd, J = 8.2, 8.1, 5.7, 5.5 Hz, 1H), 3.44 – 3.61 (m, 1H), 3.71 (m, 1H), 3.79 (s, 3H), 4.53 – 4.64 (m, 2H), 4.88 – 4.98 (m, 1H), 6.82 – 6.87 (m, 2H), 7.08 – 7.13 (m, 2H) ppm.

^13^C-NMR (100.6 MHz, CDCl₃): δ = 23.4, 36.3, 42.5, 45.6, 55.3, 66.8, 74.5, 88.0, 114.1, 128.6, 136.5, 158.3, 209.1 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₂O [M+H]^+ 265.1692 found 265.1693.
Synthesis of syn and anti - 4-(4-methoxyphenyl)octa-6,7-dien-2-ol 46, 50

I) At −80°C a solution of DIBAL-H (5.3 mL, 5.3 mmol, 1.4 equiv., 1.0 M in CH₂Cl₂) was added dropwise over 90 min to a solution of ethyl 3-(4-methoxyphenyl)hepta-5,6-dienoate (1.0 g, 3.8 mmol, 1.0 equiv.) in CH₂Cl₂ (5 mL). The reaction mixture was stirred for 1 h and then transferred to an ice-cold aqueous solution of HCl (2.0 M, 50 mL). The layers were separated, the organic layer was washed with HCl (2.0 M, 2 × 10 mL) and the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered over a silica pad (DCM) and concentrated under reduced pressure. The crude 7 3-(4-methoxyphenyl)hepta-5,6-dienal was obtained as a yellow liquid (0.78 g, 3.6 mmol, 96%).

II) A solution of PhMgBr (5.4 mL, 5.4 mmol, 1.5 equiv, 1 M in THF) in THF (5 mL) was cooled to 0 °C and the crude 7 3-(4-methoxyphenyl)hepta-5,6-dienal (0.78 g, 3.6 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 30 minutes and then warmed to room temperature. Saturated ammonium chloride (10 mL) was added and the aqueous layer was separated and extracted with Et₂O (2 × 20 mL). The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the two Diastereomers were separated by flash Chromatography (SiO₂, pentane/Et₂O = 4/1). The syn-diastereomer was obtained as a single diastereomer (0.39 g, 1.3 mmol, 37%). The anti-diastereomer was obtained in a single diastereomer (0.21 g, 0.71 mmol, 20%).

Analytical Data (syn-product) syn-46[4]

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.68 (s, 1H), 1.87 (ddd, J = 14.1, 11.1, 2.9 Hz, 1H), 2.14 (ddd, J = 14.2, 10.2, 4.1 Hz, 1H), 2.27 – 2.39 (m, 2H), 3.03 (ddd, J = 11.3, 7.4, 7.3, 4.0 Hz, 1H), 3.82 (s, 3H), 4.39 (dd, J = 10.2, 2.9 Hz, 1H), 4.53 – 4.63 (m, 2H), 4.91 – 5.00 (m, 1H), 6.86 – 6.91 (m, 2H), 7.14 – 7.19 (m, 2H), 7.22 – 7.26 (m, 3H), 7.28 – 7.34 (m, 2H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 36.6, 41.8, 45.7, 55.3, 72.0, 74.4, 88.1, 114.0, 125.6, 127.4, 128.5, 128.9, 136.2, 145.4, 158.2, 209.2 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₂O₂ [M+H]+ 295.1692 found 295.1693.

Analytical Data (anti-product) anti-50[4]

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.71 (s, 1H), 2.15 (ddd, J = 7.2, 6.7, 1.4 Hz, 2H), 2.21 – 2.35 (m, 2H), 2.54 (ddd, J = 8.0, 7.9, 6.5, 6.1 Hz, 1H), 3.81 (s, 3H), 4.50 – 4.60 (m, 3H), 4.86 (mc, 1H), 6.85 – 6.89 (m, 2H), 7.06 – 7.12 (m, 2H), 7.26 – 7.31 (m, 3H), 7.32 – 7.38 (m, 2H) ppm.
SUPPORTING INFORMATION

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 36.4, 41.8, 44.8, 55.3, 73.2, 74.4, 87.8, 114.0, 126.4, 127.8, 128.6, 128.8, 136.4, 144.3, 158.2, 209.1$ ppm.

APCI-HRMS: $m/z$ calcd for C$_{16}$H$_{22}$O$_2$ [M+H]$^+$ 295.1692 found 295.1693.

Synthesis of syn and anti - 4-(4-methoxyphenyl)tetradeca-6,7-dien-2-ol 47, 51

I) At −80°C a solution of DIBAL-H (4.2 mL, 4.2 mmol, 1.4 equiv., 1.0 M in CH$_2$Cl$_2$) was added dropwise over 90 min to a solution of ethyl 3-(4-methoxyphenyl)trideca-5,6-dienoate (1.0 g, 2.9 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was stirred for 1 h and then transferred to an ice-cold aqueous solution of HCl (2.0 M, 50 mL). The layers were separated, the organic layer was washed with HCl (2.0 M, 2 × 10 mL) and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 20 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered over a silica pad (DCM) and concentrated under reduced pressure. The crude 3-(4-methoxyphenyl)trideca-5,6-dienal was obtained as a yellow liquid (0.85 g, 2.8 mmol, 98%).

II) A solution of MeMgBr (1.4 mL, 4.2 mmol, 1.5 equiv, 3 M in Et$_2$O) in THF (5 mL) was cooled to 0 °C and the crude 3-(4-methoxyphenyl)trideca-5,6-dienal (0.85 g, 2.8 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 30 minutes and then warmed to room temperature. Saturated ammonium chloride (10 mL) was added and the aqueous layer was separated and extracted with Et$_2$O (2 × 20 mL). The combined organic layers were dried over Na$_2$SO$_4$, the solvent was removed under reduced pressure and the two Diastereomers were separated by flash Chromatography (SiO$_2$, pentane/Et2O = 4/1). The syn-diastereomer was obtained in (0.39 g, 1.2 mmol, 41 %) yield. The anti diastereomer was obtained in (0.25 g, 0.79 mmol, 33 %) yield.

Analytical Data (syn-product) syn-47

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 7.1$ Hz, 3H), 1.11 (dd, $J = 6.2, 1.0$ Hz, 3H), 1.22 – 1.38 (m, 9H), 1.64 (dddd, $J = 14.0, 11.0, 7.7, 3.1$ Hz, 1H), 1.81 (dddd, $J = 13.7, 9.5, 9.4, 4.2$ Hz, 2H), 1.86 – 1.97 (m, 1H), 2.20 – 2.31 (m, 2H), 2.88 (dddd, $J = 10.8, 7.5, 7.4, 3.8, 3.5$ Hz, 1H), 3.53 (dddd, $J = 9.4, 6.2, 6.0, 3.4, 3.1, 2.0$ Hz, 1H), 3.79 (s, 3H), 4.86 – 4.95 (m, 1H), 4.95 – 5.04 (m, 1H), 6.81 – 6.87 (m, 2H), 7.07 – 7.14 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2, 22.7, 24.4, 28.9, 28.9, 29.0, 29.2, 31.8, 31.8, 37.3, 37.5, 41.7, 41.8, 45.6, 45.7, 55.3, 65.7, 65.8, 88.9, 89.0, 90.7, 113.9, 128.8, 136.7, 158.1, 204.7$ ppm.

ESI-HRMS: $m/z$ calcd for C$_{21}$H$_{33}$O [M+H]$^+$ 317.2475 found 317.2476.
**Analytical Data (anti-product) anti-51**

**$^1$H-NMR (400.1 MHz, CDCl$_3$):** $\delta = 0.90$ (t, $J = 6.1$ Hz, 3H), 1.16 (d, $J = 6.2$ Hz, 2H), 1.24 – 1.34 (m, 9H), 1.75 – 1.89 (m, 3H), 1.91 (dddd, $J = 5.5, 5.3, 4.4, 3.7, 2.4$ Hz, 1H), 2.18 – 2.36 (m, 2H), 2.67 – 2.81 (m, 1H), 3.44 – 3.62 (m, 1H), 3.71 (m, 1H), 3.79 (m, 3H), 4.84 – 4.95 (m, 1H), 4.95 – 5.05 (m, 1H), 6.82 – 6.89 (m, 2H), 7.07 – 7.14 (m, 2H) ppm.

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** $\delta =$ 14.2, 22.7, 23.4, 28.9, 28.9, 29.2, 29.3, 31.8, 31.8, 37.0, 37.3, 42.6, 42.7, 45.7, 45.7, 55.3, 61.3, 66.9, 66.9, 88.7, 88.8, 90.8, 90.9, 91.0, 113.9, 114.0, 128.6, 128.6, 128.7, 136.8, 158.2 ppm.

**ESI-HRMS:** m/z calcd for C$_{21}$H$_{33}$O [M+H]$^+$ 317.2475 found 317.2476.

**Synthesis of syn and anti - 3-(4-methoxyphenyl)-1-phenyltrideca-5,6-dien-1-ol 48,52**

**I)** At $-80^\circ$C a solution of DIBAL-H (4.2 mL, 4.2 mmol, 1.4 equiv., 1.0 M in CH$_2$Cl$_2$) was added dropwise over 90 min to a solution of ethyl 3-(4-methoxyphenyl)trideca-5,6-dienoate (1.0 g, 2.9 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was stirred for 1 h and then transferred to an ice-cold aqueous solution of HCl (2.0 M, 50 mL). The layers were separated, the organic layer was washed with HCl (2.0 M, 2 x 10 mL) and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 20 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered over a silica pad (DCM) and concentrated under reduced pressure. The crude 3-(4-methoxyphenyl)trideca-5,6-dienal was obtained as a yellow liquid (0.85 g, 2.8 mmol, 98%).

**II)** A solution of PhMgBr (4.2 mL, 4.2 mmol, 1.5 equiv, 1 M in THF) in THF (5 mL) was cooled to 0 °C and the crude 3-(4-methoxyphenyl)trideca-5,6-dienal (0.85 g, 2.8 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 30 minutes and then warmed to room temperature. Saturated ammonium chloride (10 mL) was added and the aqueous layer was separated and extracted with Et$_2$O (2 x 20 mL). The combined organic layers were dried over Na$_2$SO$_4$, the solvent was removed under reduced pressure and the two Diastereomers were separated by flash Chromatography (SiO$_2$, pentane/Et$_2$O = 4/1). The syn-diastereomer was obtained in (0.42 g, 1.1 mmol, 40%) yield. The anti diastereomer was obtained in (0.29 g, 0.77 mmol, 28%) yield.
Analytical Data (syn-product) syn-48

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.90$ (t, $J = 6.0$ Hz, 3H), 1.16 – 1.38 (m, 9H), 1.56 (s, 1H), 1.80 – 1.94 (m, 3H), 2.15 (dddd, $J = 14.3$, 10.3, 10.0, 4.1 Hz, 1H), 2.29 (dddd, $J = 9.5$, 4.8, 3.4, 2.0 Hz, 2H), 2.95 – 3.08 (m, 1H), 3.81 (m, 3H), 4.40 (dt, $J = 10.2$, 2.5 Hz, 1H), 4.87 – 4.95 (m, 1H), 4.99 (m, 1H), 6.86 – 6.89 (m, 2H), 7.12 – 7.19 (m, 2H), 7.21 – 7.26 (m, 3H), 7.27 – 7.33 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta =$ 14.2, 22.7, 28.9, 28.9, 28.9, 29.0, 29.2, 29.2, 31.8, 31.8, 37.3, 37.5, 41.8, 41.9, 45.7, 45.8, 55.3, 55.3, 72.0, 88.8, 88.9, 90.8, 90.8, 114.0, 115.4, 125.6, 125.6, 127.4, 128.5, 128.9, 128.9, 145.4, 204.7 ppm.

APCI-HRMS: $m/z$ calcd for C$_{26}$H$_{38}$O$_2$N$[\text{M}+\text{NH}_4]^+$ 396.2897 found 396.2898.

Analytical Data (anti-product) anti-52

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.82 – 0.93$ (m, 3H), 1.23 – 1.29 (m, 8H), 1.66 (s, 1H), 1.80 (m, 1H), 1.88 (m, 1H), 2.09 – 2.19 (m, 2H), 2.19 – 2.37 (m, 2H), 2.53 (dddd, $J = 14.6$, 12.6, 8.5, 6.4 Hz, 1H), 3.81 (s, 3H), 4.53 (m, 1H), 4.76 – 4.88 (m, 1H), 4.95 (dddd, $J = 13.5$, 9.2, 6.6, 3.4 Hz, 1H), 6.84 – 6.89 (m, 2H), 7.05 – 7.11 (m, 2H), 7.26 – 7.31 (m, 3H), 7.31 – 7.37 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta =$ 14.2, 22.7, 28.9, 28.9, 29.2, 29.2, 31.7, 37.1, 37.5, 41.9, 42.2, 44.8, 45.0, 55.3, 73.3, 88.6, 90.7, 90.9, 114.0, 126.4, 126.4, 127.8, 127.8, 128.6, 128.8, 128.8, 144.4, 158.2, 204.7 ppm.

APCI-HRMS: $m/z$ calcd for C$_{26}$H$_{38}$O$_2$N$[\text{M}+\text{NH}_4]^+$ 396.2897 found 396.2898.
3 Experimental Procedures Catalysis

3.1 General Procedure catalysis

**General Procedure 8: Rh-catalyzed cyclisation of terminal allenols:**

A 10 mL screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon (Argon 5.0 Sauerstoffwerk Friedrichshafen) using a standard SCHLENK line apparatus. The screw-cap flask was charged with the corresponding δ-hydroxy allene (0.3 mmol, 1.0 equiv.), evacuated for 15 min and then backfilled with argon three times. Then \([\text{Rh(COD)Cl}]_2\) (3.7 mg, 0.0075 mmol, 2.5 mol%), dppf (8.3 mg, 0.015 mmol, 5.0 mol%) and diphenyl phosphate (12.1 mg, 0.06 mmol, 20 mol%) was added under a flow of argon followed by freshly distilled DCM (0.3 M). The flask was sealed and stirred at 80 °C overnight. The reaction mixture was filtered over silica and concentrated under reduced pressure. The residue was analyzed by \(^1\text{H}-\text{NMR} \) spectroscopy. If desired, the crude product was purified by flash chromatography on silica gel using a mixture of pentane/ether.

**General Procedure 9: Rh-catalyzed cyclisation of internal allenols:**

A 10 mL screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon (Argon 5.0 Sauerstoffwerk Friedrichshafen) using a standard SCHLENK line apparatus. The screw-cap flask was charged with the corresponding internal δ-hydroxy allene (0.3 mmol, 1.0 equiv.), evacuated for 15 min and then backfilled with argon three times. Then \([\text{Rh(COD)Cl}]_2\) (3.7 mg, 0.0075 mmol, 2.5 mol%), L5 (12.6 mg, 0.015 mmol, 5.0 mol%) and PTSA (18 mg, 0.09 mmol, 30 mol%) was added under a flow of argon followed by freshly distilled PhF (1.0 mL, 0.3 M). The flask was sealed and stirred at 80 °C overnight. The reaction mixture was filtered over silica and concentrated under reduced pressure. The residue was analyzed by \(^1\text{H}-\text{NMR} \) spectroscopy. If desired, the crude product was purified by flash chromatography on silica gel using a mixture of pentane/ether.
To determine the syn/anti ratio the crude $^1$H-NMR was measured in CDCl$_3$.

Calculation:

d.r. = H-syn/(H-anti + H-syn)
General procedure determination of d.r ratio: Catalysis Internal allene

To determine the syn/anti ratio the crude $^1$H-NMR was measured in CDCl$_3$.

Calculation:

d.r. = H-syn/(H-anti + H-syn)
General procedure determination of E/Z-ratio: Catalysis internal allene

To determine the E/Z-ratio the crude ¹H-NMR was measured in toluene d-8.

Calculation:

\[
\frac{E}{Z} = \frac{\text{H-E-compound}}{\text{H-Z-compound} + \text{H-E-compound}}
\]
4 Condition screening

The condition screening was executed employing the general procedure 7 for terminal allenes and general procedure 8 for internal allenes. The general procedures were adapted towards the conditions shown in the corresponding tables. All reactions were performed in a 0.3 mmol scale.

4.1 Condition screening terminal allenes

Ligand-Screening:

\[
\text{[Rh(COD)Cl]_2 (2.5 mol\%)} \rightarrow \text{Ligand (5.0 mol\%)} \rightarrow \text{CICH_2CO_2H (20 mol\%)} \rightarrow \text{PhCH(OH)CH=CH_2, add. (1 mol\%)} \rightarrow \text{PhCH(O)CH=CH_2, DCE (0.3 M), 80 °C, 14 h}
\]

| #  | Ligand     | Yield /%\(^{(a,b)}\) | d.r. (syn/anti)\(^{(b)}\) |
|----|------------|-----------------------|--------------------------|
| 1  | DPEPhos    | 68                    | 86/14                    |
| 2  | Xantphos   | traces                | n.d.                     |
| 3  | rac-BINAP  | 70                    | 84/16                    |
| 4  | DPPF       | 92                    | 83/17                    |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by \(^1\)H-NMR analysis of the crude product.

Additive-Screening:

\[
\text{[Rh(COD)Cl]_2 (2.5 mol\%)} \rightarrow \text{DPPF (5.0 mol\%)} \rightarrow \text{Additive (20 mol\%)} \rightarrow \text{PhCH(OH)CH=CH_2, DCE (0.3 M), 80 °C, 14 h}
\]

| #  | Additive           | Yield /%\(^{(a)}\) | d.r. (syn/anti)\(^{(b)}\) |
|----|--------------------|---------------------|--------------------------|
| 1  | -                  |                     |                          |
| 2  | Chloroacetic acid  | 92                  | 87/13                    |
| 3  | PhCMe_2CO_2H       | 68                  | 34/66                    |
| 4  | PPTS               | 80                  | 92/8                     |
| 5  | Phenylacetic acid  | 31                  | 71/29                    |
| 6  | Diphenyl phosphate | 87                  | 93/7                     |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by \(^1\)H-NMR analysis of the crude product.
Additive concentration screening:

| #  | xx mol% | Yield /%<sup>(a)</sup> | d.r. (syn/anti)<sup>(b)</sup> |
|----|---------|-------------------------|------------------------------|
| 1  | 5.0     | 68                      | 94/6                         |
| 2  | 10      | 73                      | 94/6                         |
| 3  | 20      | 87                      | 93/7                         |
| 4  | 40      | 60                      | 97/3                         |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by ¹H-NMR analysis of the crude product.

Temperature screening:

| #  | Temp. / °C | Yield /%<sup>(a)</sup> | d.r. (syn/anti)<sup>(b)</sup> |
|----|------------|-------------------------|------------------------------|
| 1  | 90         | 78                      | 91/9                         |
| 2  | 80         | 87                      | 93/7                         |
| 3  | 60         | 84                      | 90/10                        |
| 4  | 40         | 80                      | 93/7                         |
| 5  | rt         | 56                      | 87/13                        |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by ¹H-NMR analysis of the crude product.
**Reactivity time screening:**

\[
\text{[Rh(COD)Cl]_2 (2.5 mol\%)} \quad \text{dpdp (5.0 mol\%)} \quad \text{diphenyl phosphate (20 mol\%)}
\]

\[
\text{DCE, 80 °C, Time}
\]

| #  | Time / h | Yield / %\(^{(a)}\) | d.r. (syn/anti)\(^{(b)}\) |
|----|----------|---------------------|--------------------------|
| 1  | 2        | 69                  | 90/10                    |
| 2  | 4        | 70                  | 93/7                     |
| 3  | 8        | 71                  | 95/5                     |
| 4  | 14       | 87                  | 93/7                     |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by \(^1\)H-NMR analysis of the crude product.
Solvent Screening:

| #  | Solvent | Yield / (%)<sup>a</sup> | d.r. (<i>syn</i>/<i>anti</i>)<sup>b</sup> |
|----|---------|--------------------------|-------------------------------------|
| 1  | DCE     | 87                       | 93/7                                |
| 2  | DCM     | 92                       | 95/5                                |
| 3  | Toluene | 80                       | 92/8                                |
| 4  | THF     | 80                       | 92/8                                |
| 5  | PhF     | 77                       | 93/7                                |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by <sup>1</sup>H-NMR analysis of the crude product.

4.2 Condition screening internal allenes

Ligand Screening:

| #  | Ligand | Yield / (%)<sup>a</sup> | d.r. (<i>anti</i>/<i>syn</i>)<sup>b</sup> | E/Z<sup>b</sup> |
|----|--------|--------------------------|-------------------------------------|----------------|
| 1  | DPEPhos| 86                       | 82/18                               | 75/25          |
| 2  | dppf   | 98                       | 70/30                               | 79/21          |
| 3  | XanPhos| 86                       | 82/18                               | 71/29          |
| 4  | rac-Binap | 55                     | 76/24                               | 73/27          |
| 5  | Segphos| 83                       | 64/36                               | 79/21          |
| 6  | dppp   | 75                       | 70/30                               | 67/33          |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by <sup>1</sup>H-NMR analysis of the crude product.
**Additive-Screening DPEPhos:**

| #  | Additive            | Yield /%\(^{(a)}\) | d.r. (syn/anti)\(^{(b)}\) | E/Z \(^{(b)}\) |
|----|---------------------|---------------------|---------------------------|---------------|
| 1  | -                   | traces              | -                         | -             |
| 2  | Diphenyl phosphate  | 86                  | 82/18                     | 75/25         |
| 3  | Cl\(\text{CH}_2\text{CO}_2\text{H}\) | 47                  | 91/9                      | n.d.          |
| 4  | PPTS                | 83                  | 88/12                     |               |
| 5  | (-)-Binol phospahte | 82                  | 80/20                     |               |
| 6  | Phenylacetic acid   | 52                  | 78/22                     |               |
| 7  | TFA                 | 78                  | 81/19                     | 60/40         |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by \(^1\)H-NMR analysis of the crude product

**Additive-Screening dppf:**

| #  | Additive            | Yield /%\(^{(a)}\) | d.r. (syn/anti)\(^{(b)}\) | E/Z \(^{(b)}\) |
|----|---------------------|---------------------|---------------------------|---------------|
| 1  | -                   | traces              | -                         | -             |
| 2  | Diphenyl phosphate  | 98                  | 70/30                     | 79/21         |
| 3  | Cl\(\text{CH}_2\text{CO}_2\text{H}\) | 84                  | 69/31                     | 74/26         |
| 4  | PPTS                | 86                  | 70/30                     | n.d.          |
| 5  | PTSA                | 98                  | 92/8                      | 70/30         |
| 6  | PPTS derivate       | 70                  | 70/30                     | 85/15         |
| 7  | PPTS derivate       | 68                  | 70/30                     | 84/16         |
| 8  | TFA                 | 80                  | 85/15                     | 65/35         |
| 9  | Benzosulfonsäure    | 88                  | 94/6                      | 72/28         |
| 10 | (-) Campfersulfonsäure | 25              | 68/32                     | 79/11         |
| 11 | (+) Campfersulfonsäure | 23              | 70/30                     | 80/20         |
All reactions were performed on a 0.3 mmol scale. (a) NMR-Yield; (b) determined by $^1$H-NMR analysis of the crude product

**Extended ligand screening**

![Diagram of reaction](image)

| #  | Ligand | Yield /%$^{(a)}$ | d.r.$^{(b)}$ | E/Z$^{(b)}$ |
|----|--------|-----------------|-------------|-------------|
| 1  | dpff   | 98              | 92/8        | 70/30       |
| 2  | L1     | -               | -           | -           |
| 3  | L2     | 40              | 88/12       | 63/27       |
| 4  | L3     | 89              | 94/6        | 65/35       |
| 5  | L4     | 91              | 96/4        | 68/32       |
| 6  | L5     | 96              | 91/9        | 86/14       |
| 7  | L6     | 65              | 92/8        | 80/20       |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by $^1$H-NMR analysis of the crude product.
### Temperature-Screening:

| #  | Temp. / °C | Yield / %<sup>(a)</sup> | d.r. (syn/anti)<sup>(b)</sup> | E/Z<sup>(b)</sup> |
|----|------------|--------------------------|-------------------------------|----------------|
| 1  | Rt         | 95                       | 73/27                         | 68/32           |
| 2  | 50         | 97                       | 72/28                         | 67/33           |
| 3  | 70         | 94                       | 77/23                         | 82/18           |
| 4  | 80         | 98                       | 92/8                          | 70/30           |
| 5  | 90         | 97                       | 91/9                          | 78/22           |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by <sup>1</sup>H-NMR analysis of the crude product.

### Solvent-Screening:

| #  | Solvent | Yield / %<sup>(a)</sup> | d.r. (syn/anti)<sup>(b)</sup> | E/Z<sup>(b)</sup> |
|----|---------|--------------------------|-------------------------------|----------------|
| 1  | THF     | 81                       | 78/22                         | 73/27           |
| 2  | Toluol  | 75                       | 75/25                         | 75/25           |
| 3  | DCM     | 95                       | 77/23                         | 85/15           |
| 4  | PhF     | 94                       | 90/10                         | 83/17           |

All reactions were performed on a 0.3 mmol scale. (a) isolated yield of diastereomer mixture; (b) determined by <sup>1</sup>H-NMR analysis of the crude product.
5 Proposed Mechanism

The cyclisation of allenols could only be achieved by adding an acidic additive. This observation suggests that these substrates are not able to form a Rh(III) allyl species on their own. Hence, the following mechanistic scheme can be proposed (Scheme 1). The role of the acid Additive may be the generation of a rhodium-hydride species (A) to initiate the catalytic cycle. After hydrometallation of the allene the rhodium-allyl species C is formed. The desired product is then formed via Ligand exchange and a reductive reductive elimination process.
6 Synthesis and characterization of syn-tetrahydropyrans

Synthesis of 4-methyl-2-vinyltetrahydro-2H-pyran 5

The reaction was performed according to general procedure 8 with 3-methylhepta-5,6-dien-1-ol (38 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (34 mg, 0.27 mmol, 90%).

Analytical Data[6]

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.95 (d, $J$ = 6.4, 3H), 0.99 – 1.07 (m, 1H), 1.22 (dddd, $J$ = 13.2, 12.5, 11.6, 4.6 Hz, 1H), 1.50 – 1.58 (m, 1H), 1.63 – 1.72 (m, 2H), 3.47 (ddd, $J$ = 12.5, 11.4, 2.3 Hz, 1H), 3.74 – 3.82 (m, 1H), 4.03 (ddd, $J$ = 11.4, 4.5, 1.6 Hz, 1H), 5.08 (dt, $J$ = 10.6, 1.5 Hz, 1H), 5.22 (ddd, $J$ = 17.3, 1.6, 1.6 Hz, 1H), 5.85 (ddd, $J$ = 17.3, 10.6, 5.5, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 22.4, 30.3, 34.5, 40.6, 68.1, 114.5, 139.5 ppm.

APCI-HRMS: m/z calcd for C$_8$H$_{15}$O [M+H]$^+$ 127.1118 found 127.1118.

Synthesis of syn- 4-dodecyl-2-vinyltetrahydro-2H-pyran 6

The reaction was performed according to general procedure 8 with 3-(buta-2,3-dien-1-yl)pentadecan-1-ol (85 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (79 mg, 0.28 mmol, 94%).

Analytical Data[6]

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.86 – 0.91 (m, 3H), 1.00 (dd, $J$ = 13.0, 11.4, 11.4 Hz, 1H), 1.26 (s, 23H), 1.45 – 1.55 (m, 1H), 1.55 – 1.61 (m, 1H), 1.67 – 1.75 (m, 1H), 3.46 (ddd, $J$ = 12.6, 11.4, 2.1 Hz, 1H), 3.77 (dddd, $J$ = 11.3, 5.3, 2.4, 1.3 Hz, 1H), 4.04 (ddd, $J$ = 11.4, 4.6, 1.5 Hz, 1H), 5.08 (ddd, $J$ = 10.6, 1.5, 1.5 Hz, 1H), 5.23 (ddd, $J$ = 17.3, 1.6, 1.6 Hz, 1H), 5.85 (ddd, $J$ = 17.4, 10.6, 5.5 Hz, 1H) ppm.

$^{13}$C-NMR (1006 MHz, CDCl$_3$): $\delta$ = 14.2, 22.8, 26.5, 29.4, 29.7, 29.8, 29.9, 32.0, 32.8, 35.3, 37.1, 38.8, 68.1, 78.3, 114.5, 139.6 ppm.

APCI-HRMS: m/z calcd for C$_{19}$H$_{38}$O [M+H]$^+$ 281.2841 found 281.2842.
Synthesis of syn-4-neopentyl-2-vinyltetrahydro-2H-pyran 7

The reaction was performed according to general procedure 8 with 3-neopentylhepta-5,6-dien-1-ol (55 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 85/15) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (51 mg, 0.28 mmol, 93%).

Analytical Data\cite{5}

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.92$ (s, 9H), 1.07 (dd, $J = 13.0$, 11.4 Hz, 1H), 1.16 (dd, $J = 5.0$, 2.1 Hz, 2H), 1.25 – 1.31 (m, 1H), 1.57 – 1.62 (m, 1H), 1.67 – 1.74 (m, 1H), 3.48 (ddd, $J = 12.4$, 11.5, 2.1, 1H), 3.79 (ddd, $J = 11.3$, 5.4, 2.4, 1.4 Hz, 1H), 4.01 (ddd, $J = 11.6$, 4.5, 1.6 Hz, 1H), 5.08 (ddd, $J = 10.6$, 1.3 Hz, 1H), 5.22 (dt, $J = 17.4$, 1.6 Hz, 1H), 5.84 (ddd, $J = 17.4$, 10.6, 5.5 Hz, 1H).ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 29.8$, 30.2, 31.2, 32.0, 35.1, 41.0, 51.4, 68.1, 78.3, 114.5, 139.5 ppm.

APCI-HRMS: m/z calcd for C$_{12}$H$_{23}$O [M+H]$^+$ 183.1742 found 183.1742.

Synthesis of syn-4-cyclopropyl-2-vinyltetrahydro-2H-pyran 8

The reaction was performed according to general procedure 8 with 3-cyclopropylhepta-5,6-dien-1-ol (46 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 92/8) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (40 mg, 0.26 mmol, 88%).

Analytical Data\cite{5}

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.05 – 0.13$ (m, 2H), 0.35 – 0.45 (m, 2H), 0.47 – 0.60 (m, 1H), 0.81 (ddd, $J = 12.1$, 8.6, 3.9 Hz, 1H), 1.18 (ddd, $J = 13.1$, 11.9, 11.3 Hz, 1H), 1.32 – 1.47 (m, 1H), 1.64 (ddd, $J = 13.3$, 3.9, 2.0 Hz, 1H), 1.73 – 1.83 (m, 1H), 3.40 (ddd, $J = 12.5$, 11.4, 2.3 Hz, 1H), 3.71 (ddd, $J = 11.3$, 5.2, 2.5, 1.4 Hz, 1H), 4.05 (ddd, $J = 11.4$, 4.6, 1.6 Hz, 1H), 5.04 – 5.13 (m, 1H), 5.23 (dd, $J = 17.3$, 1.6 Hz, 1H), 5.86 (ddd, $J = 17.4$, 10.7, 5.5 Hz, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 2.8$, 2.9, 17.2, 32.3, 38.3, 40.6, 68.1, 78.2, 114.5, 139.5 ppm.

APCI-HRMS: m/z calcd for C$_{10}$H$_{16}$ONaS [M+] $^+$ 153.1273 found 153.1273.
Synthesis of syn-4-cyclohexyl-2-vinyltetrahydro-2H-pyran 9

The reaction was performed according to general procedure 8 with 3-cyclohexylhepta-5,6-dien-1-ol (58 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 97/3) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (47 mg, 0.24 mmol, 81%).

Analytical Data[5]
¹H-NMR (400.1 MHz, CDCl₃): δ = 0.87 – 1.01 (m, 2H), 1.04 – 1.30 (m, 7H), 1.53 – 1.59 (m, 1H), 1.64 – 1.76 (m, 6H), 3.44 (dddd, J = 12.0, 11.4, 2.3 Hz, 1H), 3.75 (ddddd, J = 11.2, 5.2, 2.5, 1.4 Hz, 1H), 4.06 (dddd, J = 11.2, 4.3, 1.7 Hz, 1H), 5.06 – 5.10 (m, 1H), 5.22 (dddd, J = 17.3, 1.6 Hz, 1H), 5.85 (dddd, J = 17.3, 10.6, 5.5 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 26.7, 26.8, 29.8, 30.0, 30.1, 35.9, 40.9, 42.9, 68.3, 78.5, 114.4, 139.7 ppm.

APCI-HRMS: m/z calcd for C₁₃H₂₂O [M+H]+ 195.1743 found 195.1743.

Synthesis of syn-4-(3-phenylpropyl)-2-vinyltetrahydro-2H-pyran 10

The reaction was performed according to general procedure 8 with 3-(3-phenylpropyl)hepta-5,6-dien-1-ol (69 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 96/4) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (66 mg, 0.29 mmol, 96%).

Analytical Data[5]
¹H-NMR (400.1 MHz, CDCl₃): δ = 1.01 (dd, J = 13.1, 11.4, 1H), 1.19 – 1.34 (m, 3H), 1.55 – 1.75 (m, 5H), 2.58 – 2.64 (m, 2H), 3.46 (dddd, J = 12.6, 11.4, 2.1 Hz, 1H), 3.77 (dddddd, J = 11.3, 5.2, 2.4, 1.4 Hz, 1H), 4.04 (dddd, J = 11.5, 4.6, 1.5 Hz, 1H), 5.06 – 5.10 (m, 1H), 5.23 (dd, J = 17.3, 1.6 Hz, 1H), 5.85 (dddd, J = 17.3, 10.6, 5.5 Hz, 1H), 7.16 – 7.21 (m, 3H), 7.26 – 7.31 (m, 2H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 28.4, 32.7, 35.2, 36.2, 36.7, 38.7, 68.1, 78.2, 114.5, 125.8, 128.4, 128.4, 139.5, 142.6 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₆ON [M+NH₄]+ 248.2014 found 248.2009.
Synthesis of \( \text{syn}-4\)-phenyl-2-vinyltetrahydro-2H-pyran 2

The reaction was performed according to \textit{general procedure 8} with 3-phenylhepta-5,6-dien-1-ol (56 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) was determined by \(^1\)H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (49 mg, 0.26 mmol, 87%).

**Analytical Data**\(^5\)

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 1.57\) (ddd, \(J = 13.2, 12.3, 11.1\) Hz, 2H), 1.76 – 1.84 (m, 2H), 1.89 – 1.95 (m, 1H), 2.79 – 2.90 (m, 1H), 3.61 – 3.69 (m, 1H), 3.96 (ddd, \(J = 11.1, 5.2, 2.4\) Hz, 1H), 4.18 (ddd, \(J = 11.5, 4.0, 2.3\) Hz, 1H), 5.13 (dd, \(J = 10.7, 1.5\) Hz, 1H), 5.29 (dd, \(J = 17.3, 1.6\) Hz, 1H), 5.91 (dd, \(J = 17.3, 10.6, 5.4\) Hz, 1H), 7.22 – 7.25 (m, 3H), 7.30 – 7.35 (m, 2H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 33.4, 39.4, 41.8, 68.2, 78.3, 114.9, 126.5, 126.8, 128.5, 139.1, 145.7\) ppm.

APCI-HRMS: \(m/z\) calcd for C\(_{13}\)H\(_{15}\)O \([M+H]^+\) 189.1274 found 189.1273.

Synthesis of \( \text{syn}-4\)-(naphthalen-2-yl)-2-vinyltetrahydro-2H-pyran 11

The reaction was performed according to \textit{general procedure 8} with 3-(naphthalen-2-yl)hepta-5,6-dien-1-ol (72 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by \(^1\)H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (69 mg, 0.29 mmol, 97%).

**Analytical Data**\(^5\)

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 1.67\) (ddd, \(J = 13.2, 12.2, 11.1\) Hz, 1H), 1.82 – 1.94 (m, 1H), 1.97 – 2.05 (m, 1H), 2.96 – 3.05 (m, 1H), 3.66 – 3.74 (m, 1H), 4.01 (ddd, \(J = 11.1, 5.2, 1.4\) Hz, 1H), 4.23 (ddd, \(J = 11.6, 4.2, 2.1\) Hz, 1H), 5.15 (dd, \(J = 10.6, 1.5\) Hz, 1H), 5.31 (dd, \(J = 17.4, 1.5\) Hz, 1H), 5.94 (dd, \(J = 17.3, 10.7, 5.4\) Hz, 1H), 7.36 – 7.51 (m, 3H), 7.64 – 7.67 (m, 1H), 7.78 – 7.84 (m, 3H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 33.4, 39.3, 41.9, 68.3, 78.4, 115.0, 124.8, 125.5, 125.7, 126.1, 127.7, 128.2, 132.4, 133.7, 139.1, 143.1\) ppm.

APCI-HRMS: \(m/z\) calcd for C\(_{17}\)H\(_{22}\)O\(_n\) [M+NH\(_4\)]\(^+\) 256.1697 found 256.1697.
Synthesis of syn-4-((1,1'-biphenyl)-4-yl)-2-vinyltetrahydro-2H-pyran 12

The reaction was performed according to general procedure 8 with 3-((1,1'-biphenyl)-4-yl)hepta-5,6-dien-1-ol (79 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (70 mg, 0.26 mmol, 88%).

Analytical Data\[5\]

1H-NMR (400.1 MHz, CDCl3): δ = 1.57 – 1.66 (m, 1H), 1.79 – 1.88 (m, 2H), 1.93 – 1.99 (m, 1H), 2.85 – 2.94 (m, 1H), 3.63 – 3.71 (m, 1H), 3.98 (ddd, J = 11.2, 5.2, 2.5 Hz, 1H), 4.21 (ddd, J = 11.5, 4.1, 2.4 Hz, 1H), 5.15 (dd, J = 10.6, 1.5 Hz, 1H), 5.31 (dd, J = 17.4, 1.5 Hz, 1H), 5.93 (dd, J = 17.3, 10.6, 5.4 Hz, 1H), 7.30 – 7.33 (m, 2H), 7.33 – 7.37 (m, 1H), 7.42 – 7.46 (m, 2H), 7.55 – 7.61 (m, 4H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 33.4, 39.4, 41.4, 68.2, 78.3, 114.9, 127.1, 127.2, 127.2, 127.4, 128.8, 139.1, 139.5, 141.0, 144.7 ppm.

APCI-HRMS: m/z calcd for C19H21O [M+H]+ 265.1587 found 265.1586.

Synthesis of syn-4-(p-tolyl)-2-vinyltetrahydro-2H-pyran 13

The reaction was performed according to general procedure 8 with 3-(p-tolyl)hepta-5,6-dien-1-ol (61 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 96/4) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (57 mg, 0.28 mmol, 94%).

Analytical Data\[5\]

1H-NMR (400.1 MHz, CDCl3): δ = 1.55 (ddd, J = 13.2, 12.3, 11.1 Hz, 1H), 1.74 – 1.81 (m, 2H), 1.87 – 1.93 (m, 1H), 2.34 (s, 3H), 2.80 (ddd, J = 12.4, 11.0, 5.7, 3.7 Hz, 1H), 3.60 – 3.68 (m, 1H), 3.95 (ddddd, J = 11.2, 5.2, 2.5, 1.4 Hz, 1H), 4.18 (dddd, J = 11.5, 4.3, 2.4 Hz, 1H), 5.13 (dd, J = 10.6, 1.5 Hz, 1H), 5.28 (dd, J = 17.4, 1.6 Hz, 1H), 5.91 (dd, J = 17.3, 10.6, 5.4 Hz, 1H), 7.13 (mc, 4H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 21.0, 33.5, 39.5, 41.3, 68.3, 78.3, 114.8, 126.7, 129.3, 136.0, 139.1, 142.7 ppm.

APCI-HRMS: m/z calcd for C14H19O [M+H]+ 203.1430 found 203.1429.
Synthesis of syn-4-(m-tolyl)-2-vinyltetrahydro-2H-pyran 14

The reaction was performed according to general procedure 8 with 3-(m-tolyl)hepta-5,6-dien-1-ol (61 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (57 mg, 0.28 mmol, 93%).

Analytical Data[5]

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.47 – 1.64 (m, 1H), 1.73 – 1.83 (m, 2H), 1.86 – 1.95 (m, 1H), 2.35 (s, 3H), 2.74 – 2.86 (m, 1H), 3.59 – 3.70 (m, 1H), 3.95 (dddd, J = 11.1, 5.2, 2.5, 1.4 Hz, 1H), 4.18 (ddd, J = 11.5, 4.1, 2.2 Hz, 1H), 5.13 (dd, J = 10.6, 1.5 Hz, 1H), 5.28 (dd, J = 17.3, 1.6 Hz, 1H), 5.91 (ddd, J = 17.4, 10.7, 5.4 Hz, 1H), 7.01 – 7.06 (m, 3H), 7.19 – 7.24 (m, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 21.6, 33.4, 39.4, 41.7, 68.3, 78.3, 114.8, 123.8, 127.2, 127.6, 128.5, 138.2, 139.1, 145.7 ppm.

APCI-HRMS: m/z calcd for C₁₄H₂₂ON [M+NH₄]⁺ 220.1696 found 220.1693.
Synthesis of syn-4-(o-tolyl)-2-vinyltetrahydro-2H-pyran 15

The reaction was performed according to general procedure 8 with 3-(o-tolyl)hepta-5,6-dien-1-ol (61 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (54 mg, 0.27 mmol, 89%).

Analytical Data[5]

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 1.57 (ddd, $J$ = 13.2, 12.1, 11.1 Hz, 1H), 1.70 (ddd, $J$ = 13.3, 4.0, 2.1 Hz, 1H), 1.78 – 1.87 (m, 2H), 2.37 (s, 3H), 3.07 (ddd, $J$ = 12.0, 3.7 Hz, 1H), 3.61 – 3.74 (m, 1H), 3.99 (ddddd, $J$ = 11.1, 5.4, 2.3, 1.3 Hz, 1H), 4.17 – 4.24 (m, 1H), 5.13 (dd, $J$ = 10.6, 1.5 Hz, 1H), 5.29 (dd, $J$ = 17.3, 1.5 Hz, 1H), 5.91 (ddd, $J$ = 17.4, 10.7, 5.4 Hz, 1H), 7.11 – 7.22 (m, 4H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ =19.4, 32.7, 37.4, 38.6, 68.5, 114.9, 125.6, 126.1, 126.5, 130.5, 135.1, 139.1, 143.4 ppm.

APCI-HRMS: m/z calcd for C$_{14}$H$_{22}$ON [M+NH$_4$]$^+$ 220.1696 found 220.1693.
Synthesis of syn-4-mesityl-2-vinyltetrahydro-2H-pyran 16

The reaction was performed according to general procedure 8 with 3-mesitylhepta-5,6-dien-1-o (69 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 97/3) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (63 mg, 0.27 mmol, 91%).

Analytical Data$^5$

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.5$ (dd, $J = 13.4$, 4.0, 1.8 Hz, 1H), 1.7 (dddd, $J = 13.3$, 3.9, 2.3, 1.7 Hz, 1H), 2.0 (dd, $J = 12.9$, 10.9 Hz, 1H), 2.2 (s, 3H), 2.3 – 2.3 (m, 1H), 2.4 (s, 6H), 3.3 (dddd, $J = 12.6$, 3.8 Hz, 1H), 3.6 (dddd, $J = 12.0$, 11.4, 2.4 Hz, 1H), 3.9 (dddd, $J = 10.7$, 5.3, 2.6, 1.4 Hz, 1H), 4.2 – 4.2 (m, 1H), 5.1 (dd, $J = 10.7$, 1.5 Hz, 1H), 5.3 (dd, $J = 17.4$, 1.6 Hz, 1H), 5.9 (dddd, $J = 17.3$, 10.7, 5.3 Hz, 1H), 6.8 (m, 2H).ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 20.7, 21.8, 29.8, 35.8, 38.3, 69.1, 79.2, 114.8, 135.5, 136.3, 137.6, 139.2$ ppm.

APCI-HRMS: $m/z$ calcd for C$_{16}$H$_{32}$O [M+H]$^+$ 231.1743 found 231.1741.
Synthesis of syn-2-vinyl-4-(4-vinylphenyl)tetrahydro-2H-pyran 17

The reaction was performed according to **general procedure 8** with 2-vinyl-4-(4-vinylphenyl)tetrahydro-2H-pyran (64 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the **d.r. ratio (d.r. = 95/5)** was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (56 mg, 0.26 mmol, 88%).

**Analytical Data**[5]

**$^1$H-NMR (400.1 MHz, CDCl$_3$):** $\delta$ = 1.55 (ddd, $J$ = 13.2, 12.3, 11.1 Hz, 1H), 1.74 – 1.81 (m, 2H), 1.86 – 1.94 (m, 1H), 2.78 – 2.89 (m, 1H), 3.59 – 3.68 (m, 1H), 3.95 (dddd, $J$ = 11.1, 5.2, 2.5, 1.4 Hz, 1H), 4.18 (dddd, $J$ = 11.5, 4.2, 2.4 Hz, 1H), 5.13 (dd, $J$ = 10.6, 1.5 Hz, 1H), 5.21 (dd, $J$ = 10.9, 1.0 Hz, 1H), 5.28 (dd, $J$ = 17.3, 1.5 Hz, 1H), 5.72 (dd, $J$ = 17.6, 1.0 Hz, 1H), 5.90 (dddd, $J$ = 17.3, 10.6, 5.4 Hz, 1H), 6.66 – 6.76 (m, 1H), 7.16 – 7.23 (m, 2H), 7.34 – 7.40 (m, 2H).ppm.

**$^{13}$C-NMR (100.6 MHz, CDCl$_3$):** $\delta$ = 33.3, 39.3, 41.5, 68.2, 78.3, 113.4, 114.9, 126.5, 127.0, 136.0, 136.6, 139.1, 145.3 ppm.

**ESI-HRMS:** m/z calcd for C$_{15}$H$_{19}$O [M+H]$^+$ 215.1433 found 215.1430.
Synthesis of syn-4-(4-(trifluoromethyl)phenyl)-2-vinyltetrahydro-2H-pyran 18

The reaction was performed according to general procedure 8 with 3-(4-(trifluoromethyl)phenyl)hepta-5,6-dien-1-ol (77 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (74 mg, 0.29 mmol, 98%).

Analytical Data[5]
¹H-NMR (400.1 MHz, CDCl₃): δ = 1.52 – 1.61 (m, 1H), 1.75 – 1.81 (m, 2H), 1.88 – 1.96 (m, 1H), 2.85 – 2.96 (m, 1H), 3.60 – 3.69 (m, 1H), 3.92 – 4.00 (m, 1H), 4.14 – 4.25 (m, 1H), 5.14 (dd, J = 10.6, 1.4 Hz, 1H), 5.29 (dd, J = 17.3, 1.5 Hz, 1H), 5.90 (ddd, J = 17.4, 10.7, 5.4 Hz, 1H), 7.34 (d, J = 8.1, 0.7 Hz, 2H), 7.57 (dd, J = 8.0, 0.8 Hz, 2H) ppm.
¹³C-NMR (100.6 MHz, CDCl₃): δ = 33.1, 39.1, 41.7, 68.0, 78.2, 115.2, 125.5, 125.6, 127.2, 138.8, 149.6 ppm.
APCI-HRMS: m/z calcd for C₁₄H₁₆F₃O [M+H]⁺ 257.1145 found 257.1144.

Synthesis of syn-4-(4-bromophenyl)-2-vinyltetrahydro-2H-pyran 19

The reaction was performed according to general procedure 8 with 3-(4-bromophenyl)hepta-5,6-dien-1-ol (80 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 96/4) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (77 mg, 0.29 mmol, 98%).

Analytical Data[5]
¹H-NMR (400.1 MHz, CDCl₃): δ = 1.52 – 1.61 (m, 1H), 1.76 – 1.83 (m, 2H), 1.86 – 1.96 (m, 1H), 2.79 – 2.91 (m, 1H), 3.60 – 3.70 (m, 1H), 3.96 (dddd, J = 11.1, 5.2, 2.5, 1.4 Hz, 1H), 4.19 (dddd, J = 11.6, 4.0, 2.4 Hz, 1H), 5.12 – 5.15 (m, 1H), 5.29 (dd, J = 17.3, 1.5 Hz, 1H), 5.91 (dddd, J = 17.4, 10.7, 5.4 Hz, 1H), 7.22 – 7.24 (m, 2H), 7.30 – 7.35 (m, 2H) ppm.
¹³C-NMR (100.6 MHz, CDCl₃): δ = 33.4, 39.4, 41.8, 68.2, 78.3, 114.9, 126.5, 126.8, 128.6, 139.1, 145.7 ppm.
ESI-HRMS: m/z calcd for C₁₃H₁₀OBr [M+H]⁺ 267.0380 found 267.0380.
Synthesis of syn-4-(4-methoxyphenyl)-2-vinyltetrahydro-2H-pyran 20

The reaction was performed according to general procedure 8 with 3-(4-methoxyphenyl)hepta-5,6-dien-1-ol (66 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 96/4) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (63 mg, 0.28 mmol, 96%).

Analytical Data\textsuperscript{[5]}

$^1$H-NMR (400.1 MHz, CDCl\textsubscript{3}): $\delta = 1.52$ (ddd, $J = 13.1, 12.3, 11.1$ Hz, 1H), $1.72 - 1.79$ (m, 2H), $1.89$ (dddd, $J = 13.3, 3.8, 2.2, 1.6, 0.6$ Hz, 1H), $2.74 - 2.84$ (m, 1H), $3.59 - 3.67$ (m, 1H), $3.80$ (s, 3H), $3.91 - 3.98$ (m, 1H), $5.12$ (dd, $J = 10.6, 1.5$ Hz, 1H), $5.28$ (dd, $J = 17.3, 1.5$ Hz, 1H), $5.90$ (ddd, $J = 17.4, 10.7, 5.4$ Hz, 1H), $6.84 - 6.90$ (m, 2H), $7.13 - 7.17$ (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl\textsubscript{3}): $\delta = 33.6, 39.7, 40.9, 55.4, 68.3, 78.3, 114.0, 114.8, 127.7, 137.9, 139.1, 158.2$ ppm.

APCI-HRMS: \textit{m/z} calcd for C\textsubscript{14}H\textsubscript{19}O\textsubscript{2} [M+H]$^+$ 219.1385 found 219.1385.

Synthesis of syn-4-(4-(methylthio)phenyl)-2-vinyltetrahydro-2H-pyran 21

The reaction was performed according to general procedure 8 with 3-(4-(methylthio)phenyl)hepta-5,6-dien-1-ol (70 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (64 mg, 0.28 mmol, 92%).

Analytical Data\textsuperscript{[5]}

$^1$H-NMR (400.1 MHz, CDCl\textsubscript{3}): $\delta = 1.52$ (ddd, $J = 13.1, 12.3, 11.1$ Hz, 1H), $1.72 - 1.79$ (m, 2H), $1.85 - 1.92$ (m, 1H), $2.47$ (s, 3H), $2.74 - 2.85$ (m, 1H), $3.58 - 3.67$ (m, 1H), $3.94$ (dddd, $J = 11.1, 5.2, 2.5, 1.4$ Hz, 1H), $4.14 - 4.20$ (m, 1H), $5.13$ (dd, $J = 10.7, 1.5$ Hz, 1H), $5.28$ (dd, $J = 17.3, 1.6$ Hz, 1H), $5.89$ (ddd, $J = 17.4, 10.7, 5.4$ Hz, 1H), $7.13 - 7.17$ (m, 2H), $7.21 - 7.25$ (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl\textsubscript{3}): $\delta = 16.3, 33.4, 39.4, 41.3, 68.2, 78.3, 114.9, 127.4, 136.1, 139.0, 142.8$ ppm.

ESI-HRMS: \textit{m/z} calcd for C\textsubscript{14}H\textsubscript{19}OS [M+H]$^+$ 235.1153 found 235.1151.
Synthesis of syn-4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 22

The reaction was performed according to general procedure 8 with 3-(4-methoxyphenyl)-4,4-dimethylhepta-5,6-dien-1-ol (74 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 75/25) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (71 mg, 0.28 mmol, 95%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.72 (s, 3H), 0.80 (s, 3H), 1.48 (dddd, $J$ = 13.5, 3.8, 2.5, 1.4 Hz, 1H), 2.29 (dddd, $J$ = 13.3, 12.4, 4.9 Hz, 1H), 2.56 (dd, $J$ = 13.1, 3.5 Hz, 1H), 3.59 – 3.67 (m, 2H), 3.80 (s, 3H), 4.17 (ddd, $J$ = 11.3, 4.9, 1.4 Hz, 1H), 5.21 (ddd, $J$ = 10.6, 2.0, 1.0 Hz, 1H), 5.27 (ddd, $J$ = 17.3, 2.1, 1.3 Hz, 1H), 5.87 (ddd, $J$ = 17.2, 10.6, 6.6 Hz, 1H), 6.82 – 6.87 (m, 2H), 7.07 – 7.11 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.3, 24.7, 28.8, 37.5, 51.9, 55.3, 68.9, 88.1, 113.1, 117.3, 130.5, 133.8, 135.6, 158.3 ppm.

APCI-HRMS: $m/z$ calcd for C$_{16}$H$_{26}$O$^{[M+NH_4]^+}$ 264.1959 found 264.1958.

Synthesis of (2R,4S)-4-methyl-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 23

The reaction was performed according to general procedure 8 with 3-methyltrideca-5,6-dien-1-ol (63 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) and the E/Z ratio ($E/Z = 80/20$) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (58 mg, 0.28 mmol, 93%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.88 (d, $J$ = 6.8 Hz, 3H), 0.94 (m, 3H), 0.97 – 1.09 (m, 1H), 1.25 – 1.31 (m, 6H), 1.33 – 1.43 (m, 2H), 1.50 (m,c, 1H), 1.52 – 1.56 (m, 1H), 1.59 – 1.67 (m, 2H), 1.98 – 2.05 (m, 2H), 3.45 (dddd, $J$ = 12.4, 11.4, 2.3 Hz, 1H), 3.72 (dddt, $J$ = 12.1, 7.1, 1.9, 0.8 Hz, 1H), 4.01 (ddd, $J$ = 11.4, 4.6, 1.6 Hz, 1H), 5.46 (ddt, $J$ = 15.5, 6.3, 1.5 Hz, 1H), 5.67 (dd, $J$ = 15.5, 6.7, 1.1 Hz, 1H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.4, 22.7, 29.0, 29.2, 30.4, 31.8, 32.4, 34.6, 41.0, 68.1, 78.2, 131.2, 132.0 ppm.

APCI-HRMS: $m/z$ calcd for C$_{14}$H$_{27}$O$^{[M+H]^+}$ 365.3778 found 365.3774.
Synthesis of syn-4-dodecyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 24

The reaction was performed according to general procedure 9 with 3-(deca-2,3-dien-1-yl)pentadecan-1-ol (109 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio (E/Z = 86/14) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (96 mg, 0.26 mmol, 88%).

Analytical Data[6]
1H-NMR (400.1 MHz, CDCl3): δ = 0.85 – 0.89 (m, 6H), 1.21 – 1.32 (m, 30H), 1.45 – 1.54 (m, 2H), 1.54 – 1.58 (m, 1H), 1.58 – 1.66 (m, 1H), 1.80 – 1.87 (m, 1H), 1.97 – 2.05 (m, 2H), 3.47 (td, J = 11.5, 2.6 Hz, 1H), 3.71 – 3.77 (m, 1H), 3.97 – 4.03 (m, 1H), 5.46 (dddd, J = 15.5, 6.2, 6.1, 1.4 Hz, 1H), 5.66 (dd, J = 15.5, 6.7, 1.1 Hz, 1H).
13C-NMR (100.6 MHz, CDCl3): δ = 14.2, 14.2, 22.7, 22.8, 26.7, 26.8, 28.9, 29.1, 29.4, 29.5, 29.8, 29.8, 30.1, 31.8, 32.0, 33.4, 33.6, 33.7, 37.3, 34.6, 36.9, 61.3, 78.4, 131.3, 132 ppm.
APCI-HRMS: m/z calcd for C25H49O [M+H]+ 365.3778 found 365.3774.

Synthesis of syn-4-neopentyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 25

The reaction was performed according to general procedure 9 with 3-neopentyltrideca-5,6-dien-1-ol (80 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 92/8) and the E/Z ratio (E/Z = 74/26) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (76 mg, 0.29 mmol, 95%).

Analytical Data[6]
1H-NMR (400.1 MHz, CDCl3): δ = 0.88 (d, J = 6.8 Hz, 3H), 0.91 (s, 9H), 1.07 (dd, J = 12.6, 11.2 Hz, 1H), 1.15 (dd, J = 4.9, 2.4 Hz, 2H), 1.23 – 1.31 (m, 7H), 1.33 – 1.39 (m, 2H), 1.53 – 1.61 (m, 2H), 1.66 (ddd, J = 12.0, 3.6, 1.6 Hz, 1H), 1.98 – 2.04 (m, 2H), 3.47 (ddd, J = 12.3, 11.4, 2.1 Hz, 1H), 3.73 (ddd, J = 11.3, 6.3, 2.1, 1.1 Hz, 1H), 3.98 (ddd, J = 11.5, 4.6, 1.6 Hz, 1H), 5.44 (ddd, J = 15.5, 6.3, 1.5 Hz, 1H), 5.67 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H) ppm.
13C-NMR (100.6 MHz, CDCl3): δ = 14.2, 22.7, 29.0, 29.2, 30.3, 31.2, 31.8, 32.0, 32.4, 35.1, 41.5, 51.5, 68.1, 78.2, 131.2, 132.0 ppm.
ESI-HRMS: m/z calcd for C19H35O [M+H]+ 267.2668 found 267.2668.
Synthesis of syn-4-cyclopropyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 26

The reaction was performed according to general procedure 9 with 3-cyclopropyltrideca-5,6-dien-1-ol (71 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) and the E/Z ratio (E/Z = 78/22) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (67 mg, 0.28 mmol, 94%).

Analytical Data[6]

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.06 – 0.10 (m, 2H), 0.37 – 0.42 (m, 2H), 0.49 – 0.58 (m, 1H), 0.79 (ddd, J = 12.2, 8.7, 3.9 Hz, 1H), 0.86 – 0.89 (m, 3H), 1.19 (ddd, J = 13.2, 11.9, 11.2 Hz, 1H), 1.25 – 1.40 (m, 9H), 1.62 (dddd, J = 13.3, 3.9, 1.9 Hz, 1H), 1.74 (ddd, J = 13.2, 3.8, 2.0 Hz, 1H), 1.98 – 2.05 (m, 2H), 3.39 (ddd, J = 12.5, 11.4, 2.3 Hz, 1H), 3.66 (ddd, J = 11.2, 6.2, 2.2, 1.1 Hz, 1H), 4.03 (ddd, J = 11.5, 4.6, 1.6 Hz, 1H), 5.47 (ddd, J = 15.5, 6.3, 1.4 Hz, 1H), 5.67 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 2.8, 2.9, 14.2, 17.2, 22.7, 29.0, 29.2, 31.8, 32.4, 32.4, 38.7, 40.6, 68.1, 78.2, 131.1, 132.0 ppm.

APCI-HRMS: m/z calcd for C₁₆H₂₉O [M+H]+ 237.2210 found 237.2210.
Synthesis of syn-4-cyclohexyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 27

The reaction was performed according to general procedure 9 with 3-cyclohexyltrideca-5,6-dien-1-ol (84 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 91/9) and the E/Z ratio (E/Z = 82/18) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (78 mg, 0.28 mmol, 93%).

Analytical Data[6]

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.88 (t, J = 6.9 Hz, 3H), 0.95 (ddd, J = 14.2, 8.2, 4.0 Hz, 2H), 1.05 – 1.11 (m, 2H), 1.13 – 1.23 (m, 3H), 1.25 – 1.38 (m, 10H), 1.52 – 1.57 (m, 1H), 1.66 (dddd, J = 11.5, 5.0, 3.2, 2.0 Hz, 2H), 1.70 – 1.77 (m, 4H), 1.97 – 2.05 (m, 2H), 3.43 (ddd, J = 12.0, 11.4, 2.3 Hz, 1H), 3.70 (dddd, J = 11.1, 6.3, 2.2, 1.0 Hz, 1H), 4.04 (ddd, J = 11.2, 4.3, 1.7 Hz, 1H), 5.46 (ddd, J = 15.5, 6.3, 1.5 Hz, 1H), 5.67 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 26.7, 26.9, 29.0, 29.2, 29.8, 30.0, 30.1, 31.8, 32.4, 36.3, 40.9, 43.0, 68.3, 78.4, 131.3, 131.9 ppm.

APCI-HRMS: m/z calcd for C₁₉H₉₅O [M+H]⁺ 279.2687 found 279.2687.
Synthesis of syn-2-(E)-oct-1-en-1-yl)-4-(3-phenylpropyl)tetrahydro-2H-pyran 28

The reaction was performed according to general procedure 9 with 3-(3-phenylpropyl)trideca-5,6-dien-1-ol (94 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 92/8) and the E/Z ratio (E/Z = 79/21) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (93 mg, 0.29 mmol, 98%).

Analytical Data[6]
1H-NMR (400.1 MHz, CDCl3): δ = 0.86 – 0.90 (m, 3H), 1.01 (dd, J = 13.1, 11.4 Hz, 1H), 1.22 – 1.39 (m, 11H), 1.48 – 1.60 (m, 3H), 1.63 – 1.69 (m, 2H), 1.97 – 2.05 (m, 2H), 2.56 – 2.64 (m, 2H), 3.45 (ddd, J = 12.6, 11.4, 2.1 Hz, 1H), 3.71 (dddd, J = 11.2, 6.3, 2.2, 1.1 Hz, 1H), 4.02 (ddd, J = 11.4, 4.6, 1.5 Hz, 1H), 5.45 (ddd, J = 15.5, 6.3, 1.5 Hz, 1H), 5.67 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H), 7.14 – 7.20 (m, 3H), 7.26 – 7.30 (m, 2H) ppm.
13C-NMR (100.6 MHz, CDCl3): δ = 14.2, 22.7, 28.4, 29.0, 29.2, 31.8, 32.4, 32.7, 35.3, 36.2, 36.8, 39.1, 68.1, 78.2, 125.8, 128.3, 128.4, 131.1, 132.0, 142.7 ppm.
APCI-HRMS: m/z calcd for C22H38O [M+NH4]+ 332.2948 found 332.2947.

Synthesis of syn-2-(E)-oct-1-en-1-yl)-4-phenyltetrahydro-2H-pyran 29

The reaction was performed according to general procedure 9 with 3-phenyltrideca-5,6-dien-1-ol (82 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio (E/Z = 83/17) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (78 mg, 0.29 mmol, 96%).

Analytical Data[6]
1H-NMR (400.1 MHz, CDCl3): δ = 0.85 – 0.90 (m, 3H), 1.28 (dddd, J = 10.2, 4.7, 2.7, 1.6 Hz, 6H), 1.34 – 1.40 (m, 2H), 1.52 – 1.61 (m, 1H), 1.73 – 1.78 (m, 2H), 1.84 – 1.90 (m, 1H), 1.99 – 2.08 (m, 2H), 2.77 – 2.87 (m, 1H), 3.59 – 3.67 (m, 1H), 3.90 (dddd, J = 10.9, 6.1, 2.1, 1.1 Hz, 1H), 4.16 (ddd, J = 11.5, 4.0, 2.3 Hz, 1H), 5.52 (ddd, J = 15.5, 6.2, 1.4 Hz, 1H), 5.72 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H), 7.20 – 7.24 (m, 3H), 7.29 – 7.34 (m, 2H) ppm.
Synthesis of syn-4-(naphthalen-2-yl)-2-(E)-oct-1-en-1-yl)-2H-pyran 30

The reaction was performed according to general procedure 9 with 3-(naphthalen-2-yl)trideca-5,6-dien-1-ol (97 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) and the E/Z ratio (E/Z = 81/19) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (89 mg, 0.28 mmol, 92%).

Analytical Data[6]

1H-NMR (400.1 MHz, CDCl3): δ = 0.87 – 0.90 (m, 3H), 1.26 – 1.33 (m, 6H), 1.35 – 1.44 (m, 2H), 1.68 (ddd, J = 13.1, 12.2, 11.0 Hz, 1H), 1.81 – 1.89 (m, 2H), 1.97 (ddd, J = 13.2, 3.5, 1.9 Hz, 1H), 2.01 – 2.09 (m, 2H), 2.99 (ddd, J = 11.7, 4.1 Hz, 1H), 3.65 – 3.74 (m, 1H), 3.96 (ddd, J = 11.1, 6.2, 2.1, 1.1 Hz, 1H), 4.20 (ddd, J = 11.5, 4.2, 2.0 Hz, 1H), 5.55 (ddd, J = 15.5, 6.2, 1.5 Hz, 1H), 5.76 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H), 7.37 – 7.49 (m, 3H), 7.65 (dd, J = 1.8, 0.8 Hz, 1H), 7.79 – 7.83 (m, 3H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 14.2, 22.7, 29.0, 29.2, 31.8, 32.4, 33.4, 39.8, 41.9, 68.3, 78.4, 124.8, 125.4, 125.8, 126.1, 127.7, 127.7, 128.2, 130.8, 132.5, 143.2 ppm.

APCI-HRMS: m/z calcd for C23H31O [M+H]+ 323.2369 found 323.2368.
Synthesis of syn-4-[[1,1'-biphenyl]-4-yl]-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 31

The reaction was performed according to general procedure 9 with 3-[[1,1'-biphenyl]-4-yl]trideca-5,6-dien-1-ol (105 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio (E/Z = 77/23) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (96 mg, 0.28 mmol, 92%).

**Analytical Data**

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.89 (t, $J$ = 6.8 Hz, 3H), 1.26 – 1.31 (m, 6H), 1.36 – 1.41 (m, 2H), 1.56 – 1.65 (m, 1H), 1.76 – 1.83 (m, 2H), 1.91 (dd, $J$ = 11.5, 3.8, 1.9 Hz, 1H), 2.00 – 2.08 (m, 2H), 2.87 (dd, $J$ = 16.1, 10.5, 3.9 Hz, 1H), 3.62 – 3.69 (m, 1H), 3.93 (dddd, $J$ = 11.0, 6.2, 2.2 Hz, 1.1, 1H), 4.18 (dd, $J$ = 11.5, 4.1, 2.4 Hz, 1H), 5.53 (dd, $J$ = 15.5, 6.2, 1.5 Hz, 1H), 5.74 (dd, $J$ = 15.5, 6.7, 1.1 Hz, 1H), 7.29 – 7.32 (m, 2H), 7.33 – 7.36 (m, 1H), 7.41 – 7.46 (m, 2H), 7.54 – 7.60 (m, 4H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.7, 29.0, 29.2, 31.8, 32.4, 33.4, 39.9, 41.5, 68.2, 78.3, 127.1, 127.2, 127.3, 128.8, 130.7, 132.5, 139.4, 141.1, 144.9 ppm.

APCI-HRMS: m/z calcd for C$_{23}$H$_{31}$O [M+H]$^+$ 349.2526 found 349.2524.

Synthesis of syn-2-((E)-oct-1-en-1-yl)-4-(p-tolyl)tetrahydro-2H-pyran 32

The reaction was performed according to general procedure 7 with 3-(p-tolyl)trideca-5,6-dien-1-ol (86 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio (E/Z = 83/17) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (83 mg, 0.29 mmol, 97%).

**Analytical Data**

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.88 (d, $J$ = 6.8 Hz, 3H), 1.25 – 1.31 (m, 6H), 1.33 – 1.40 (m, 2H), 1.51 – 1.57 (m, 1H), 1.71 – 1.79 (m, 2H), 1.82 – 1.89 (m, 1H), 1.99 – 2.07 (m, 2H), 2.33 (s, 3H), 2.72 – 2.83 (m, 1H), 3.58 – 3.66 (m, 1H), 3.89 (dddd, $J$ = 11.0, 6.1, 2.2, 1.1 Hz, 1H), 4.15 (dd, $J$ = 11.5, 4.0, 2.4 Hz, 1H), 5.51 (dd, $J$ = 15.5, 6.2, 1.4 Hz, 1H), 5.72 (dd, $J$ = 15.5, 6.7, 1.1 Hz, 1H), 7.12 (m, 4H) ppm.
SUPPORTING INFORMATION

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 14.2, 21.6, 22.7, 28.9, 29.2, 31.8, 32.4, 33.4, 39.9, 41.8, 68.3, 123.8, 127.1, 127.7, 128.5, 130.8, 132.4, 145.8\) ppm.

APCI-HRMS: \(m/z\) calcd for C\(_{20}\)H\(_{31}\)O [M+H]\(^+\) 287.2376 found 287.2377.

Synthesis of syn-2-((E)-oct-1-en-1-yl)-4-(m-tolyl)tetrahydro-2H-pyran 33

The reaction was performed according to general procedure 9 with 3-(m-tolyl)trideca-5,6-dien-1-ol (86 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio \((E/Z = 80/20)\) was determined by \(^1\)H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (80 mg, 0.28 mmol, 93%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 0.86 – 0.90\) (m, 3H), \(1.26 – 1.31\) (m, 6H), \(1.33 – 1.40\) (m, 2H), \(1.52 – 1.59\) (m, 1H), \(1.73 – 1.77\) (m, 2H), \(1.83 – 1.89\) (m, 1H), \(2.03\) (ddd, \(J = 8.7, 6.7, 0.8\) Hz, 2H), \(2.35\) (8, 3H), \(2.73 – 2.82\) (m, 1H), \(3.58 – 3.67\) (m, 1H), \(3.89\) (ddddd, \(J = 11.1, 6.2, 2.1, 1.0\) Hz, 1H), \(4.15\) (ddd, \(J = 11.5, 4.1, 2.1\) Hz, 1H), \(5.52\) (ddd, \(J = 15.5, 6.2, 1.4\) Hz, 1H), \(5.72\) (ddd, \(J = 15.6, 6.7, 1.1\) Hz, 1H), \(7.03\) (ddd, \(J = 8.3, 1.2, 0.6\) Hz, 3H), \(7.21\) (dd, \(J = 7.3, 1.2\) Hz, 1H).

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = \delta = 14.2, 21.6, 22.7, 28.9, 29.2, 31.8, 32.4, 33.4, 39.9, 41.8, 68.3, 123.8, 127.1, 127.7, 128.5, 130.8, 132.4, 145.8\) ppm

APCI-HRMS: \(m/z\) calcd for C\(_{20}\)H\(_{31}\)O [M+H]\(^+\) 287.2369 found 287.2365.

Synthesis of syn-2-((E)-oct-1-en-1-yl)-4-(o-tolyl)tetrahydro-2H-pyran 34

The reaction was performed according to general procedure 9 with 3-(o-tolyl)trideca-5,6-dien-1-ol (86 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) and the E/Z ratio \((E/Z = 81/19)\) was determined by \(^1\)H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (78 mg, 0.27 mmol, 91%).

Analytical Data

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 0.86 – 0.90\) (m, 3H), \(1.27\) (ddd, \(J = 5.1, 2.0, 1.3\) Hz, 6H), \(1.34 – 1.42\) (m, 2H), \(1.53 – 1.61\) (m, 1H), \(1.67\) (ddddd, \(J = 13.3, 4.1, 2.1\) Hz, 1H), \(1.76 – 1.82\) (m, 2H), \(2.00 – 2.07\) (m,
2H), 2.36 (s, 3H), 3.04 (dd, \( J = 12.0, 3.6 \) Hz, 1H), 3.62 – 3.69 (m, 1H), 3.93 (dddd, \( J = 11.0, 6.1, 2.2, 1.0 \) Hz, 1H), 5.52 (ddd, \( J = 15.5, 6.2, 1.5 \) Hz, 1H), 5.73 (dd, \( J = 15.5, 6.7, 1.1 \) Hz, 1H), 7.08 – 7.24 (m, 4H) ppm.

\( ^{13} \text{C-NMR (100.6 MHz, CDCl}_3 \): \( \delta = 14.2, 19.4, 22.7, 29.0, 29.2, 31.8, 32.4, 32.7, 37.5, 39.1, 68.5, 78.5, 125.6, 126.1, 126.4, 130.5, 130.8, 132.4, 135.1, 143.6 \) ppm.

APCI-HRMS: \( m/z \) calcd for \( \text{C}_20\text{H}_{31}\text{O} [\text{M}+\text{H}]^+ 287.2369 \) found 287.2367.

**Synthesis of syn-4-mesityl-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 35**

The reaction was performed according to **general procedure 9** with 3-mesityltribeca-5,6-dien-1-ol (94 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the \( \text{d.r.} = 95/5 \) and the \( E/Z \) ratio (\( E/Z = 80/20 \)) was determined by \( ^1\text{H-NMR} \) spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (83 mg, 0.26 mmol, 88\%).

**Analytical Data**\[^6\]

\( ^1\text{H-NMR (400.1 MHz, CDCl}_3 \): \( \delta = 0.86 – 0.90 \) (m, 3H), 1.26 – 1.32 (m, 6H), 1.37 (m, 2H), 1.51 – 1.66 (m, 2H), 1.97 – 2.09 (m, 3H), 2.24 (s, 3H), 2.40 (s, 6H), 3.29 (ddd, \( J = 12.7, 3.8 \) Hz, 1H), 3.57 – 3.65 (m, 1H), 3.83 – 3.91 (m, 1H), 4.17 (dd, \( J = 11.4, 4.5 \) Hz, 1H), 5.48 – 5.56 (m, 1H), 5.67 – 5.76 (m, 1H), 6.83 (m, 2H) ppm.

\( ^{13} \text{C-NMR (100.6 MHz, CDCl}_3 \): \( \delta = 14.2, 20.7, 21.8, 22.7, 28.9, 29.2, 29.8, 31.8, 32.4, 36.2, 38.4, 69.1, 79.3, 130.9, 132.3, 135.4, 136.3, 137.8 \) ppm.

APCI-HRMS: \( m/z \) calcd for \( \text{C}_{22}\text{H}_{35}\text{O} [\text{M}+\text{H}]^+ 315.2682 \) found 315.2681.
Synthesis of syn-2-((E)-oct-1-en-1-yl)-4-(4-vinylphenyl)tetrahydro-2H-pyran 36

The reaction was performed according to general procedure 9 with 3-(4-vinylphenyl)trideca-5,6-dien-1-ol (89 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) and the E/Z ratio (E/Z = 78/22) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (82 mg, 0.28 mmol, 92%).

Analytical Data[6]

1H-NMR (400.1 MHz, CDCl3): δ = 0.85 – 0.88 (m, 3H), 1.24 – 1.28 (m, 6H), 1.34 – 1.38 (m, 2H), 1.42 – 1.46 (m, 2H), 1.72 – 1.76 (m, 2H), 1.80 – 1.89 (m, 1H), 1.99 – 2.05 (m, 2H), 2.72 – 2.83 (m, 1H), 3.58 – 3.64 (m, 1H), 3.84 – 3.94 (m, 1H), 4.14 (ddd, J = 11.4, 4.1, 2.3 Hz, 1H), 5.50 (dddd, J = 15.5, 6.2, 1.5 Hz, 1H), 5.67 – 5.76 (m, 1H), 6.28 – 6.44 (m, 1H), 7.11 – 7.25 (m, 4H), 7.28 – 7.32 (m, 1H) ppm.

13C-NMR (100.6 MHz, CDCl3): δ = 14.2, 21.3, 29.2, 31.8, 33.3, 33.4, 39.7, 39.9, 41.3, 42.2, 68.2, 78.3, 126.4, 126.9, 127.0, 127.5, 128.1, 132.5, 134.9, 135.8, 143.7, 144.7 ppm.

APCI-HRMS: m/z calcd for C21H34O [M+NH4]+ 316.2635 found 316.2632.

Synthesis of syn-4-(4-bromophenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 37

The reaction was performed according to general procedure 9 with 3-(4-bromophenyl)trideca-5,6-dien-1-ol (105 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 90/10) and the E/Z ratio (E/Z = 71/29) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (83 mg, 0.24 mmol, 79%).

Analytical Data[6]

1H-NMR (400.1 MHz, CDCl3): δ = 0.85 – 0.90 (m, 3H), 1.25 – 1.31 (m, 6H), 1.34 – 1.40 (m, 2H), 1.53 – 1.60 (m, 1H), 1.74 – 1.78 (m, 2H), 1.83 – 1.91 (m, 1H), 1.98 – 2.07 (m, 2H), 2.77 – 2.87 (m, 1H), 3.59 – 3.67 (m, 1H), 3.90 (dddd, J = 10.9, 6.2, 2.2 Hz, 1.1, 1H), 4.16 (ddd, J = 11.5, 4.0, 2.3 Hz, 1H), 5.51 (dd, J = 15.5, 6.2, 1.4 Hz, 1H), 5.72 (ddd, J = 15.5, 6.7, 1.1 Hz, 1H), 7.21 – 7.23 (m, 2H), 7.29 – 7.34 (m, 2H) ppm.
**SUPPORTING INFORMATION**

\[^{13}\text{C}-\text{NMR (100.6 MHz, CDCl}_3\): } \delta = 14.2, 22.7, 29.0 29.2, 31.8, 32.4, 33.4, 39.9, 41.8, 68.2, 78.3, 126.4, 126.8, 128.6, 130.8, 132.4, 145.8 ppm.**

**APCI-HRMS:** m/z calcd for C_{19}H_{31}ON [M+NH\textsubscript{4}]\textsuperscript{+} 370.1569 found 370.1570.

**Synthesis of syn-4-(4-methoxyphenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 4**

![Chemical structure of 4](image)

The reaction was performed according to general procedure 9 with 3-(4-bromophenyl)trideca-5,6-dien-1-ol (91 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) and the E/Z ratio (E/Z = 85/15) was determined by \(^1\text{H}-\text{NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (86 mg, 0.29 mmol, 95%).**

**Analytical Data**\[^6\]

\(^1\text{H}-\text{NMR (500 MHz, Toluene-d}_8\): } \delta = 0.88 (t, J = 6.9 Hz, 3H), 1.22 – 1.28 (m, 6H), 1.33 – 1.37 (m, 2H), 1.43 – 1.47 (m, 1H), 1.48 – 1.51 (m, 1H), 1.60 (ddd, J = 13.0, 12.2, 4.5 Hz, 1H), 1.73 (ddd, J = 13.0, 3.9, 2.1 Hz, 1H), 1.99 – 2.04 (m, 2H), 2.09 (dd, J = 4.4, 2.2 Hz, 2H), 2.50 (dd, J = 12.3, 3.9 Hz, 1H), 3.37 (s, 3H), 3.78 (dddd, J = 11.0, 5.4, 1.2 Hz, 1H), 4.02 (ddd, J = 11.3, 4.5, 1.6 Hz, 1H), 5.61 (ddd, J = 15.5, 5.4, 1.4 Hz, 1H), 5.73 – 5.80 (m, 1H), 6.75 – 6.77 (m, 2H), 6.94 – 6.96 (m, 2H) ppm.

\[^{13}\text{C}-\text{NMR (126 MHz, Toluene-d}_8\): } \delta = 14.3, 23.1, 29.4, 29.8, 32.2, 32.9, 34.2, 40.8, 41.4, 54.7, 68.1, 78.2, 114.2, 130.6, 132.1, 137.4, 138.3, 158.7 ppm.

**APCI-HRMS:** m/z calcd for C_{20}H_{30}O_2 [M+H]^+ 302.2246 found 302.2246.
Synthesis of \( \text{syn-4-(4-(methylthio)phenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran} \)

The reaction was performed according to \textit{general procedure 9} with 3-(4-(methylthio)phenyl)trideca-5,6-dien-1-ol (96 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the \textit{d.r.} ratio (\textit{d.r.} = 94/6) and the \textit{E/Z} ratio (\( \text{E/Z} = 83/17 \)) was determined by \( ^1 \text{H-NMR} \) spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (91 mg, 0.29 mmol, 96%).

\textbf{Analytical Data}\[6\]

\( ^1 \text{H-NMR (400.1 MHz, CDCl}_3\):} \( \delta = 0.88 \) (t, \( J = 6.8 \) Hz 3H), 1.23 - 1.27 (m, \( J = 3.4, 1.6 \) Hz, 6H), 1.34 – 1.40 (m, 2H), 1.47 – 1.54 (m, 1H), 1.71 – 1.77 (m, 2H), 1.81 – 1.87 (m, 1H), 2.00 – 2.06 (m, 2H), 2.47 (s, 3H), 2.77 (dddt \( J = 11.9, 8.7, 4.3 \) Hz, 1H), 3.58 – 3.65 (m, 1H), 3.88 (dddd, \( J = 11.0, 6.2, 2.2, 1.1 \) Hz, 1H), 4.11 – 4.18 (m, 1H), 5.50 (dddd, \( J = 15.5, 6.2, 1.5 \) Hz, 1H), 5.72 (dddd, \( J = 15.5, 6.7, 1.1 \) Hz, 1H), 7.13 – 7.16 (m, 2H), 7.21 – 7.24 (m, 2H) ppm.

\( ^{13} \text{C-NMR (100.6 MHz, CDCl}_3\):} \( \delta = 14.2, 16.4, 22.7, 28.9, 29.2, 31.8, 32.4, 33.4, 39.8, 41.3, 68.2, 78.3, 127.4, 130.7, 132.5, 136.0, 143.0 \) ppm.

\textit{ESI-HRMS:} \( m/z \) calcd for C\( _{16} \)H\( _{22} \)O\( _3 \)NNaS [M+\]/ found

Synthesis of \( \text{syn-2-((E)-oct-1-en-1-yl)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran} \)

The reaction was performed according to \textit{general procedure 9} with 3-(4-(trifluoromethyl)phenyl)trideca-5,6-dien-1-ol (96 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the \textit{d.r.} ratio (\textit{d.r.} = 94/6) and the \textit{E/Z} ratio (\( \text{E/Z} = 81/19 \)) was determined by \( ^1 \text{H-NMR} \) spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (95 mg, 0.28 mmol, 93%).

\textbf{Analytical Data}\[6\]

\( ^1 \text{H-NMR (400.1 MHz, CDCl}_3\):} \( \delta = 0.88 \) (t, \( J = 6.7 \) Hz 3H), 1.26 – 1.31 (m, 6H), 1.35 – 1.41 (m, 2H), 1.54 – 1.59 (m, 1H), 1.76 (dddd, \( J = 6.1, 4.7, 1.7 \) Hz, 2H), 1.85 – 1.89 (m, 1H), 2.01 – 2.07 (m, 2H), 2.85 – 2.93 (m, 1H), 3.60 – 3.67 (m, 1H), 3.91 (dddd, \( J = 10.8, 6.1, 2.1, 1.1 \) Hz, 1H), 4.17 (dddd, \( J = 11.6, 4.1, 2.4 \) Hz, 1H), 5.51 (dddd, \( J = 15.4, 6.2, 1.4 \) Hz, 1H), 5.73 (dddd, \( J = 15.5, 6.7, 1.1 \) Hz, 1H), 7.32 – 7.35 (m, 2H), 7.56 – 7.58 (m, 2H) ppm.
Supporting Information

C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 29.2, 31.8, 32.4, 33.1, 39.5, 41.7, 68.0, 74.1, 78.2, 125.6, 125.6, 127.2, 130.5, 132.7, 149.7 ppm.

APCI-HRMS: m/z calcd for C₂₀H₃₁OF₃N [M+NH₄]⁺ 358.2358 found 358.2358.

Synthesis of syn-2,2-dimethyl-6-((E)-oct-1-en-1-yl)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran 40

The reaction was performed according to general procedure 9 with 4-(4-methoxyphenyl)-2-methyltetradeca-6,7-dien-2-ol (96 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 85/15) and the E/Z ratio (E/Z = 70/30) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (90 mg, 0.27 mmol, 91%).

Analytical Data:

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.24 – 1.29 (m, 5H), 1.30 (s, 3H), 1.33 (s, 3H), 1.33 – 1.41 (m, 3H), 1.41 – 1.58 (m, 2H), 1.66 (ddd, J = 13.1, 3.8, 1.9 Hz, 1H), 1.79 (ddd, J = 12.9, 3.9, 2.1 Hz, 1H), 1.95 – 2.10 (m, 2H), 2.93 (ddd, J = 12.6, 3.7 Hz, 1H), 3.79 (s, 3H), 4.15 (ddd, J = 11.4, 6.5, 2.3, 0.9 Hz, 1H), 5.49 (ddd, J = 15.4, 6.5, 1.4 Hz, 1H), 5.68 (ddd, J = 15.5, 6.6, 1.0 Hz, 1H), 6.83 – 6.88 (m, 2H), 7.11 – 7.16 (m, 2H) ppm.

C-NMR (100.6 MHz, CDCl₃): δ = 14.2, 22.6, 22.7, 29.0, 29.1, 31.8, 32.0, 32.4, 36.9, 39.9, 44.1, 55.4, 71.8, 72.4, 114.0, 127.7, 131.6, 132.2, 138.2, 158.1 ppm.

APCI-HRMS: m/z calcd for C₂₂H₆₅O₂[M+H]⁺ 331.2629 found 331.2629.

Synthesis of syn-2-((E)-2-cyclohexylvinyl)-4-(4-methoxyphenyl)tetrahydro-2H-pyran 41

The reaction was performed according to general procedure 9 with 7-cyclohexyl-3-(4-methoxyphenyl)hepta-5,6-dien-1-ol (90 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) and the E/Z ratio (E/Z = 88/12) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (70 mg, 0.23 mmol, 78%).
**Analytical Data**[6]

**1H-NMR (400.1 MHz, CDCl3):** δ = 1.02 – 1.32 (m, 6H), 1.51 (ddd, J = 13.1, 12.2, 11.0 Hz, 1H), 1.64 (dtt, J = 12.4, 3.3, 1.7 Hz, 1H), 1.68 – 1.74 (m, 5H), 1.82 – 1.88 (m, 1H), 1.95 (dddd, J = 11.5, 8.4, 5.0, 2.1 Hz, 1H), 2.76 (ddd, J = 16.0, 8.7, 3.8 Hz, 1H), 3.57 – 3.65 (m, 1H), 3.79 (s, 3H), 3.85 – 3.91 (m, 1H), 4.12 – 4.18 (m, 1H), 5.47 (ddd, J = 15.7, 6.1, 1.3 Hz, 1H), 5.67 (ddd, J = 15.7, 6.5, 1.1 Hz, 1H), 6.84 – 6.88 (m, 2H), 7.13 – 7.16 (m, 2H) ppm.

**13C-NMR (100.6 MHz, CDCl3):** δ = 26.1, 26.3, 32.9, 33.6, 40.2, 40.4, 41.0, 55.4, 68.3, 78.5, 114.0, 127.7, 128.4, 137.9, 138.1, 158.2 ppm.

**APCI-HRMS:** m/z calcd for C20H29O2 [M+H]+ 301.2162 found 301.2169.

**Synthesis of syn-4-(4-methoxyphenyl)-2-((E)-4-phenylbut-1-en-1-yl)tetrahydro-2H-pyran 42**

![Chemical structure of syn-4-(4-methoxyphenyl)-2-((E)-4-phenylbut-1-en-1-yl)tetrahydro-2H-pyran 42](image)

The reaction was performed according to **general procedure 9** with 3-(4-methoxyphenyl)-9-phenylnona-5,6-dien-1-ol (97 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the **d.r.** ratio (**d.r. = 93/7**) and the **E/Z** ratio (**E/Z = 78/22**) was determined by **1H-NMR** spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (89 mg, 0.28 mmol, 93%).

**Analytical Data**[6]

**1H-NMR (400.1 MHz, CDCl3):** δ = 1.43 – 1.56 (m, 1H), 1.73 (ddd, J = 9.6, 5.2, 3.9 Hz, 2H), 1.83 (dddd, J = 13.1, 3.3, 1.4 Hz, 1H), 2.33 – 2.39 (m, 2H), 2.70 (dd, J = 8.6, 7.1 Hz, 2H), 2.73 – 2.80 (m, 1H), 3.58 – 3.64 (m, 1H), 3.80 (s, 3H), 3.86 – 3.92 (m, 1H), 4.12 – 4.20 (m, 1H), 5.57 (dddd, J = 15.5, 6.1, 1.4 Hz, 1H), 5.77 (ddd, J = 15.5, 6.6 Hz, 1.1, 1H), 6.84 – 6.89 (m, 2H), 7.12 – 7.20 (m, 5H), 7.26 – 7.29 (m, 2H) ppm.

**13C-NMR (100.6 MHz, CDCl3):** δ = 33.7, 34.3, 35.7, 40.0, 40.9, 55.4, 68.3, 78.2, 114.0, 125.9, 127.7, 128.4, 128.5, 131.2, 131.5, 138.0, 141.9, 158.2 ppm.

**APCI-HRMS:** m/z calcd for C22H27O2 [M+H]+ 323.2006 found 323.2008.
Synthesis of syn-4-(4-methoxyphenyl)-2-((E)-3-phenylprop-1-en-1-yl)tetrahydro-2H-pyran 43

The reaction was performed according to general procedure 9 with 3-(4-methoxyphenyl)-8-phenylocta-5,6-dien-1-ol (93 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) and the E/Z ratio (E/Z = 80/20) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (83 mg, 0.27 mmol, 90%).

**Analytical Data**[6]

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.44 – 1.57$ (m, 1H), $1.72 – 1.77$ (m, 2H), $1.84 – 1.89$ (m, 1H), 2.76 (ddd, $J = 12.2, 8.4, 4.4$ Hz, 1H), 3.35 – 3.40 (m, 2H), 3.56 – 3.66 (m, 1H), 3.79 (s, 3H), 3.90 – 3.96 (m, 1H), 4.11 – 4.17 (m, 1H), 5.54 – 5.62 (m, 1H), 5.88 (ddd, $J = 15.5, 6.7, 1.2$ Hz, 1H), 7.12 – 7.22 (m, 6H), 7.26 – 7.32 (m, 3H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 33.6, 38.8, 40.1, 40.9, 55.4, 68.3, 78.1, 114.0, 114.0, 126.1, 127.7, 127.7, 128.5, 128.7, 130.6, 132.3, 138.0, 140.1, 158.2$ ppm.

APCI-HRMS: m/z calcd for C$_{21}$H$_{25}$O$_2$ [M+H]$^+$ 309.1849 found 309.1854.

Synthesis of syn-4-(4-methoxyphenyl)-2-((E)-5-(methylthio)pent-1-en-1-yl)tetrahydro-2H-pyran 44

The reaction was performed according to general procedure 9 with 3-(4-methoxyphenyl)-8-phenylocta-5,6-dien-1-ol (91 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) and the E/Z ratio (E/Z = 89/11) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (81 mg, 0.27 mmol, 89%).

**Analytical Data**[6]

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.43 – 1.56$ (m, 1H), $1.71 – 1.76$ (m, 2H), $1.83 – 1.89$ (m, 1H), 2.10 (s, 3H), 2.30 – 2.37 (m, 2H), 2.52 – 2.57 (m, 2H), 2.71 – 2.80 (m, 1H), 3.58 – 3.65 (m, 1H), 3.79 (s, 3H), 3.90 (ddd, $J = 11.0, 5.8, 2.1, 1.0$ Hz, 1H), 4.12 – 4.17 (m, 1H), 5.56 – 5.63 (m, 1H), 5.75 (ddd, $J = 15.5, 6.6, 1.2$ Hz, 1H), 6.84 – 6.88 (m, 2H), 7.12 – 7.15 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 15.6, 32.2, 33.6, 33.9, 40.0, 40.9, 55.4, 68.3, 78.0, 78.0, 114.0, 127.7, 129.7, 132.4, 137.9, 158.2$ ppm.

APCI-HRMS: m/z calcd for C$_{17}$H$_{24}$O$_2$S [M+H]$^+$ 293.1575 found 293.1575.
6.1 Large scale catalysis

Synthesis of syn-4-(4-methoxyphenyl)-2-vinyltetrahydro-2H-pyran 20

A screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus. The screw-cap flask was charged with 3-(4-methoxyphenyl)hepta-5,6-dien-1-ol (306 mg, 1.40 mmol, 1.0 equiv.) the flask was evacuated for 15 min and backfilled with argon three times. Then [Rh(COD)Cl]₂ (17.3 mg, 0.035 mmol, 2.5 mol%), dppf (38.8 mg, 0.700 mmol, 5.0 mol%) and diphenyl phosphate (70 mg, 0.28 mmol, 20 mol%) was added under a flow of argon followed by freshly distilled DCM (5 mL). The flask was sealed and stirred at room temperature overnight. The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (DCM) the product was obtained as a colorless solid (287 mg, 1.32 mmol, 94%).

Analytical Data[^5]

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.52 (ddd, J = 13.1, 12.3, 11.1 Hz, 1H), 1.72 – 1.79 (m, 2H), 1.89 (ddddd, J = 13.3, 3.8, 2.2, 1.6, 0.6 Hz, 1H), 2.74 – 2.84 (m, 1H), 3.59 – 3.67 (m, 1H), 3.80 (s, 3H), 3.91 – 3.98 (m, 1H), 4.14 – 4.20 (m, 1H), 5.12 (dd, J = 10.6, 1.5 Hz, 1H), 5.28 (dd, J = 17.3, 1.5 Hz, 1H), 5.90 (dd, J = 17.4, 10.7, 5.4 Hz, 1H), 6.84 – 6.90 (m, 2H), 7.13 – 7.17 (m, 2H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 33.6, 39.7, 40.9, 55.4, 68.3, 78.3, 114.0, 114.8, 127.7, 137.9, 139.1, 158.2 ppm.

APCI-HRMS: m/z calcd for C₁₄H₁₉O₂ [M+H]^⁺ 219.1385 found 219.1385
Synthesis of syn-4-(4-methoxyphenyl)-2-vinyltetrahydro-2H-pyran 4

A screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus. The screw-cap flask was charged with 3-(4-methoxyphenyl)trideca-5,6-dien-1-ol (423 mg, 1.40 mmol, 1.0 equiv.) the flask was evacuated for 15 min and backfilled with argon three times. Then [Rh(COD)Cl]₂ (17.3 mg, 0.035 mmol, 2.5 mol%), dppf (38.8 mg, 0.700 mmol, 5.0 mol%) and PTSA (80 mg, 0.42 mmol, 30 mol%) was added under a flow of argon followed by freshly distilled PhF (5 mL). The flask was sealed and stirred at room temperature overnight. The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) and E/Z ratio (E/Z = 83/17) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (DCM) the product was obtained as a colorless solid (394 mg, 1.3 mmol, 93%).

Analytical Data[6]
¹H-NMR (500 MHz, Toluene-d₈) δ = 0.88 (t, J = 6.9 Hz, 3H), 1.22 – 1.28 (m, 6H), 1.33 – 1.37 (m, 2H), 1.43 – 1.47 (m, 1H), 1.48 – 1.51 (m, 1H), 1.60 (ddd, J = 13.0, 12.2, 4.5 Hz, 1H), 1.73 (ddd, J = 13.0, 3.9, 2.1 Hz, 1H), 1.99 – 2.04 (m, 2H), 2.09 (dd, J = 4.4, 2.2 Hz, 2H), 2.50 (dd, J = 12.3, 3.9 Hz, 1H), 3.37 (s, 3H), 3.78 (ddd, J = 11.0, 5.4, 1.2 Hz, 1H), 4.02 (ddd, J = 11.3, 4.5, 1.6 Hz, 1H), 5.61 (ddd, J = 15.5, 5.4, 1.4 Hz, 1H), 5.73 – 5.80 (m, 1H), 6.75 – 6.77 (m, 2H), 6.94 – 6.96 (m, 2H) ppm.
¹³C-NMR (126 MHz, Toluene-d₈): δ = 14.3, 23.1, 29.4, 29.8, 32.2, 32.9, 34.2, 40.8, 41.4, 54.7, 68.1, 78.2, 114.2, 130.6, 132.1, 137.4, 138.3, 158.7 ppm.
APCI-HRMS: m/z calcd for C₂₀H₂₉O₂ [M+H]+ 302.2246 found 302.2246

6.2 Catalysis of 1, 3-substituted δ-allenols

Synthesis of 4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 45A

The reaction was performed according to general procedure 6 with syn-4-(4-methoxyphenyl)octa-6,7-dien-2-ol (70 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (65 mg, 0.28 mmol, 93%).
**Analytical Data**

\[ {^1}H\text{-NMR (500.1 MHz, CDCl}_3\text{): } \delta = 1.28 (d, J = 6.1 \text{ Hz, 3H}), 1.33 – 1.50 (m, 2H), 1.83 (dddd, J = 6.3, 13.1, 3.9, 2.0 \text{ Hz, 2H}), 2.80 (dddd, J = 12.3, 12.2, 3.7, 3.8 \text{ Hz, 1H}), 3.62 – 3.70 (m, 1H), 3.79 (s, 3H), 3.99 (dddt, J = 11.0, 5.7, 2.4, 1.4 \text{ Hz, 1H}), 5.13 (dd, J = 10.6, 1.4 \text{ Hz, 1H}), 5.29 (dd, J = 17.3, 1.5 \text{ Hz, 1H}), 5.92 (ddd, J = 17.3, 10.6, 5.4 Hz, 1H), 6.84 – 6.88 (m, 2H), 7.10 – 7.16 (m, 2H) ppm. \]

\[ {^13}C\text{-NMR (125.6 MHz, CDCl}_3\text{): } \delta = 22.1, 40.9, 40.9, 55.4, 73.7, 78.2, 114.0, 115.1, 127.7, 137.9, 139.2, 158.1 \text{ ppm.} \]

**APCI-HRMS:** m/z calcd for C\(_{15}\)H\(_{21}\)O\(_2\) [M+H]\(^+\) 233.1536 found 233.1534.

**Synthesis of 4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 49A, 49B**

The reaction was performed according to **general procedure 8** with anti-4-(4-methoxyphenyl)octa-6,7-dien-2-ol (70 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by \(^1\)H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (71 mg, 0.28 mmol, 92%).

**Analytical Data (major compound) 49A**

\[ {^1}H\text{-NMR (400.1 MHz, CDCl}_3\text{): } \delta = 1.40 (s, 1H), 1.43 – 1.56 (m, 1H), 1.64 (dddd, J = 13.2, 3.5, 2.0, 1.4 Hz, 1H), 1.72 – 1.78 (m, 1H), 1.82 – 1.88 (m, 1H), 1.89 – 1.97 (m, 1H), 3.01 (dddd, J = 12.6, 12.5, 3.7, 3.6 Hz 1H), 3.79 (s, 3H), 4.26 dddd, J = 11.1, 5.4, 2.6, 1.4, 1.4 Hz 1H), 4.41 (dddd, J = 7.3, 7.2, 5.8, 5.6 Hz, 1H), 5.11 (ddd, J = 10.5, 1.5 Hz, 1H), 5.26 (ddd, J = 17.3, 1.5 Hz, 1H), 5.87 (ddd, J = 17.3, 10.5, 5.6 Hz, 1H), 6.85 – 6.88 (m, 2H), 7.13 – 7.17 (m, 2H) ppm. \]

\[ {^13}C\text{-NMR (100.6 MHz, CDCl}_3\text{): } \delta = 17.3, 34.9, 37.3, 39.8, 55.3, 68.3, 69.4, 70.0, 78.3, 114.0, 114.8, 139.6, 158.1 \text{ ppm.} \]

**APCI-HRMS:** m/z calcd for C\(_{15}\)H\(_{21}\)O\(_2\) [M+H]\(^+\) 233.1536 found 233.1534.
Analytical Data (minor compound) 49B

$^1$H-NMR (400.1 MHz, CDCl$_3$): 1.21 (d, $J = 6.1$ Hz, 3H), 1.59 (s, 1H), 1.79 (dddd, $J = 44.9$, 13.9, 11.6, 5.5 Hz, 3H), 2.08 (ddddd, $J = 18.4$, 13.9, 2.2 Hz, 2H), 3.25 − 3.30 (m, 1H), 3.72 − 3.79 (m, 1H), 3.81 (s, 3H), 4.04 − 4.12 (m, 1H), 5.11 (ddd, $J = 10.6$, 1.4 Hz, 1H), 5.25 (ddd, $J = 17.3$, 2.0, 1.5 Hz, 1H), 5.87 (dd, $J = 17.4$, 10.6, 5.8 Hz, 1H), 6.87 − 6.91 (m, 2H), 7.23 − 7.26 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 22.4$, 34.2, 35.5, 37.3, 55.3, 68.9, 73.7, 115.1, 127.7, 128.8, 135.9, 139.6, 157.6 ppm.

APCI-HRMS: $m/z$ calcd for C$_{15}$H$_{21}$O$_2$ [M+H]$^+$ 233.1536 found 233.1534.

Synthesis of 4-(4-methoxyphenyl)-2-phenyl-6-vinyltetrahydro-2H-pyran 46A

![Chemical Structure](image)

The reaction was performed according to general procedure 8 with syn-3-(4-methoxyphenyl)-1-phenylhepta-5,6-dien-1-ol (88 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (85 mg, 0.29 mmol, 96%).

Analytical Data

$^1$H-NMR (500.1 MHz, CDCl$_3$): $\delta = 1.58$ (dd, $J = 12.8$, 11.6 Hz, 1H), 1.64 − 1.77 (m, 1H), 2.03 (dddd, $J = 52.8$, 13.2, 4.0, 2.1 Hz, 2H), 3.00 (dddd, $J = 12.4$, 12.3, 4.5, 3.7 Hz, 1H), 3.79 (s, 3H), 4.20 (dd, $J = 10.9$, 5.3, 1.8 Hz, 1H), 4.60 (dd, $J = 11.2$, 2.2 Hz, 1H), 5.16 (ddd, $J = 10.7$, 1.5, 0.7 Hz, 1H), 5.37 (dd, $J = 17.4$, 1.6, 0.7 Hz, 1H), 6.01 (dddd, $J = 17.2$, 10.6, 5.3, 0.6 Hz, 1H), 6.84 − 6.89 (m, 2H), 7.15 − 7.18 (m, 2H), 7.24 − 7.28 (m, 1H), 7.32 − 7.37 (m, 2H), 7.43 (ddd, $J = 8.3$, 1.4, 0.7 Hz, 2H) ppm.

$^{13}$C-NMR (110.6 MHz, CDCl$_3$): $\delta = 39.2$, 41.2, 41.3, 55.4, 78.5, 79.5, 114.0, 114.8, 125.9, 127.4, 127.7, 128.3, 137.6, 139.1, 142.9, 158.2 ppm.

ESI-HRMS: $m/z$ calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+Na]$^+$ found
The reaction was performed according to general procedure 8 with anti-3-(4-methoxyphenyl)-1-phenylhepta-5,6-dien-1-ol (88 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 85/15) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (71 mg, 0.28 mmol, 94%).

### Analytical Data (major compound) 50A

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 1.59 – 1.67 (m, 1H), 1.80 (ddd, $J = 12.8, 4.0, 2.2$ Hz, 1H), 2.19 (ddd, $J = 13.8, 12.8, 5.5$ Hz, 1H), 2.53 (ddd, $J = 13.9, 3.9, 3.5, 1.8$ Hz, 1H), 2.89 (ddd, $J = 12.9, 12.5, 3.9, 3.5$ Hz, 1H), 3.81 (s, 3H), 3.92 (ddd, $J = 14.0, 11.7, 5.4$ Hz, 1H), 2.93 (ddd, $J = 14.1, 1.1, 0.5$ Hz, 1H), 3.39 (m, 1H), 3.84 (s, 3H), 4.12 (ddd, $J = 12.8, 2.2$ Hz, 1H), 5.00 (d, $J = 9.9$, 1.5 Hz, 1H), 5.23 (d, $J = 6.9$ Hz, 2H), 5.92 (ddd, $J = 17.3, 10.6, 6.5$ Hz, 1H), 6.85 – 6.92 (m, 2H), 7.15 – 7.20 (m, 2H), 7.30 – 7.35 (m, 2H), 7.50 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 34.0, 35.6, 39.6, 55.4, 71.1, 73.7, 114.1, 114.9, 126.7, 126.9, 127.7, 128.8, 137.8, 139.2, 140.4, 158.2 ppm.

ESI-HRMS: m/z calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+]$^+$ found

### Analytical Data (minor product) 50B

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 1.96 (ddd, $J = 14.0, 11.7, 5.4$ Hz, 1H), 2.06 (ddd, $J = 14.1, 11.8, 5.3, 1$ Hz), 2.24 (dd, $J = 14.0, 2.5, 2.3$ Hz, 1H), 2.33 (ddd, $J = 14.1, 2.6$ Hz, 1H), 3.39 (m, 1H), 3.84 (s, 3H), 4.26 – 4.32 (m, 1H), 4.68 (dd, $J = 11.8, 2.2$ Hz, 1H), 5.14 (dd, $J = 10.6, 1.5$ Hz, 1H), 5.32 (dd, $J = 17.3, 1.6$ Hz, 1H), 5.95 (ddd, $J = 17.3, 10.6, 5.3$ Hz, 1H), 6.92 – 6.97 (m, 2H), 7.24 – 7.26 (m, 1H), 7.31 – 7.36 (m, 4H), 7.39 (ddd, $J = 7.8, 1.5, 0.7$ Hz, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 34.4, 35.4, 37.9, 55.4, 74.0, 74.9, 114.0, 114.9, 125.9, 127.3, 128.3, 128.8, 135.3, 139.5, 143.3, 157.7 ppm.

ESI-HRMS: m/z calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+]$^+$ found
Synthesis of syn-4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 47

The reaction was performed according to general procedure 9 with syn-4-(4-methoxyphenyl)tetradeca-6,7-dien-2-ol (95 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (86 mg, 0.27 mmol, 91%).

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.85 – 0.90$ (m, 3H), 1.24 – 1.31 (m, 9H), 1.32 – 1.41 (m, 3H), 1.41 – 1.50 (m, 1H), 1.75 – 1.85 (m, 2H), 1.98 – 2.07 (m, 2H), 2.78 (dddd, $J = 12.5, 12.3, 4.1, 3.8$ Hz, 1H), 3.64 (m, 1H), 3.79 (s, 3H), 3.91 – 3.97 (m, 1H), 5.53 (dddd, $J = 15.5, 6.5, 1.5$ Hz, 1H), 5.71 (dddd, $J = 15.5, 6.7, 1.1$ Hz, 1H), 6.83 – 6.88 (m, 2H), 7.11 – 7.15 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2, 22.2, 22.7, 29.0, 29.1, 31.8, 32.5, 39.5, 40.9, 55.4, 73.6, 78.3, 114.0, 127.7, 130.9, 132.5, 138.1, 158.1$ ppm.

ESI-HRMS: m/z calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+]$^+$ found

Synthesis of syn-4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 51A, 51B

The reaction was performed according to general procedure 9 with trans-4-(4-methoxyphenyl)tetradeca-6,7-dien-2-ol (95 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 80/20) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (86 mg, 0.27 mmol, 92%).

Analytical Data (major product) 51A

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.87$ (t, $J = 5.4$ Hz, 3H), 1.25 – 1.30 (m, 10H), 1.35 – 1.38 (m, 2H), 1.51 (dddd, $J = 13.1, 12.3, 11.0$ Hz, 2H), 1.71 – 1.74 (m, 2H), 1.82 – 1.86 (m, 1H), 1.99 – 2.03 (m, 2H), 2.70 – 2.80 (m, 1H), 3.58 – 3.65 (m, 1H), 3.85 – 3.91 (m, 1H), 4.10 – 4.17 (m, 1H), 5.47 – 5.53 (m, 1H), 5.71 (dddd, $J = 15.5, 6.7, 1.1$ Hz, 1H), 6.83 – 6.88 (m, 2H), 7.13 – 7.15 (m, 2H) ppm.
**SUPPORTING INFORMATION**

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2, 22.7, 29.0, 29.2, 32.4, 33.6, 40.1, 40.9, 55.4, 68.3, 78.4, 114.0, 127.7, 128.7, 130.8, 132.4, 138.1, 158.1$ ppm.

ESI-HRMS: $m/z$ calcd for C$_{15}$H$_{22}$O$_3$NaS [M+]$^+$ found

Analytical Data$^3$ (minor product) 51B

$^1$H-NMR (500.1 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 5.2$ Hz, 3H), 1.20 (d, $J = 6.2$, 3H), 1.25 – 1.30 (m, 7H), 1.34 – 1.39 (m, 2H), 1.73 (ddd, $J = 14.1, 11.4, 5.6$ Hz, 1H), 1.79 – 1.88 (m, 1H), 2.03 (ddd, $J = 9.2, 4.9, 1.7$ Hz, 3H), 3.25 (m, 1H), 3.73 (ddd, $J = 12.5, 6.2, 1.9$ Hz, 1H), 3.81 (s, 3H), 4.01 – 4.10 (m, 1H), 5.48 (ddd, $J = 15.5, 6.6, 1.5$ Hz, 1H), 5.67 (ddd, $J = 15.5, 6.7, 1.1$ Hz, 1H), 6.87 – 6.90 (m, 2H), 7.22 – 7.26 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2, 22.4, 22.7, 29.1, 32.5, 34.3, 35.8, 37.4, 40.9, 55.3, 68.8, 73.7, 78.3, 113.8, 114.0, 127.7, 128.8, 131.2, 132.5, 136.1, 157.6$ ppm.

ESI-HRMS: $m/z$ calcd for C$_{15}$H$_{22}$O$_3$NaS [M+]$^+$ found

Synthesis of 4-(4-methoxyphenyl)-2-((E)-oct-1-en-1-yl)-6-phenyltetrahydro-2H-pyran 48A

The reaction was performed according to general procedure 9 with syn-3-(4-methoxyphenyl)-1-phenylocta-5,6-dien-1-o (114 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 95/5) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (102 mg, 0.27 mmol, 90%).

Analytical Data$^3$

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 0.88$ (t, $J = 4.8$ Hz, 3H), 1.26 – 1.31 (m, 7H), 1.35 – 1.40 (m, 2H), 1.58 – 1.72 (m, 2H), 1.92 (ddd, $J = 13.2, 4.0, 2.0$ Hz, 1H), 2.03 – 2.07 (m, 2H), 2.97 (ddd, $J = 12.8, 12.3, 4.0, 3.7$ Hz, 1H), 3.79 (s, 3H), 4.14 (ddd, $J = 11.1, 6.0, 2.2, 1.1$ Hz, 1H), 4.57 (dd, $J = 11.2, 2.2$ Hz, 1H), 5.61 (ddd, $J = 15.5, 6.1, 1.4$ Hz, 1H), 5.76 (ddd, $J = 15.5, 6.6, 1.1$ Hz, 1H), 6.84 – 6.87 (m, 2H), 7.14 – 7.18 (m, 2H), 7.22 – 7.26 (m, 1H), 7.31 – 7.34 (m, 2H), 7.39 – 7.43 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 14.2, 22.7, 29.0, 29.2, 31.8, 32.5, 39.7, 41.3, 55.4, 78.7, 79.6, 114.0, 126.1, 127.4, 127.7, 128.3, 128.3, 130.8, 132.1, 137.7, 143.0, 158.2 ppm

ESI-HRMS: $m/z$ calcd for C$_{15}$H$_{22}$O$_3$NaS [M+]$^+$ found
Synthesis of 4-(4-methoxyphenyl)-2-((E)-oct-1-en-1-yl)-6-phenyltetrahydro-2H-pyran 52A, 52B

The reaction was performed according to general procedure 9 with trans-3-(4-methoxyphenyl)-1-phenylocta-5,6-dien-1-ol (114 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 73/27) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 60/1 to 40/1) the product was obtained as colorless liquid (99 mg, 0.26 mmol, 88%).

Analytical Data$^3$ (major product) 52A

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.87 (t, $J$ = 7.1 Hz, 3H), 1.26 – 1.29 (m, 6H), 1.36 – 1.41 (m, 2H), 1.59 – 1.68 (m, 1H), 1.74 – 1.80 (m, 1H), 2.02 – 2.07 (m, 2H), 2.14 – 2.22 (m, 1H), 2.50 (ddd, $J$ = 13.9, 3.5, 1.8 Hz, 1H), 2.86 (ddddd, $J$ = 13.3, 12.5, 3.9, 3.5 Hz, 1H), 3.60 (s, 3H), 4.04 – 4.09 (m, 1H), 5.28 – 5.31 (m, 1H), 5.54 (ddd, $J$ = 15.5, 6.1, 1.5 Hz, 1H), 5.70 (ddd, $J$ = 15.5, 6.7, 1.1 Hz, 1H), 6.86 – 6.89 (m, 2H), 7.15 – 7.18 (m, 2H), 7.27 – 7.31 (m, 1H), 7.40 – 7.44 (m, 2H), 7.48 – 7.50 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.7, 29.0, 29.2, 31.8, 32.5, 34.1, 35.7, 40.0, 55.4, 71.1, 73.8, 114.0, 126.7, 126.9, 127.7, 128.7, 130.8, 132.4, 138.0, 140.6, 158.2 ppm.

ESI-HRMS: m/z calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+]+ found

Analytical Data$^3$ (minor product) 52B

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.89 (t, $J$ = 6.5 Hz, 3H), 1.24 – 1.33 (m, 7H), 1.35 – 1.39 (m, 2H), 1.92 – 1.99 (m, 1H), 2.02 – 2.06 (m, 3H), 2.17 – 2.23 (m, 1H), 2.28 – 2.33 (m, 1H), 3.37 (dd, $J$ = 5.7, 3.1 Hz, 1H), 3.83 – 3.84 (m, 3H), 4.20 – 4.26 (m, 1H), 4.62 – 4.66 (m, 1H), 5.56 (ddd, $J$ = 15.5, 6.2, 1.5 Hz, 1H), 5.72 (ddd, $J$ = 15.4, 6.6, 1.1 Hz, 1H), 6.93 – 6.95 (m, 2H), 7.30 – 7.35 (m, 5H), 7.36 – 7.39 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.7, 29.0, 29.1, 31.8, 32.5, 34.5, 35.8, 37.9, 55.4, 70.2, 74.1, 75.0, 114.0, 126.1, 127.3, 128.8, 131.1, 132.1, 135.5, 143.4, 157.7 ppm.

ESI-HRMS: m/z calcd for C$_{15}$H$_{22}$O$_3$NNaS [M+]+ found
7 Stereoselective synthesis

Stereoselective synthesis of (2S,4R)-4-methyl-2-vinyltetrahydro-2H-pyr

Cul (1.0 mol%) and S-Tol-Binap (20 mol%) was dissolved in t-BuOMe (40 mL) and stirred under argon at room Temperature for 1 h until a yellow suspension was observe. The mixture was cooled to −50 °C and ethyl (E)-hepta-2,5,6-trienoate (2.0 g, 13 mmol) was added and stirred for 15 min. Then MeMgBr in THF (6.5 mL, 20 mmol, 3.0 M, 1.5 equiv.) was added dropwise. The mixture was stirred at −50 °C for 2 h, then quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O (4 × 30 mL), the combined organic layers were washed with brine (40 mL) and dried over Na₂SO₄. The solvent was removed and the residue was purified by flash chromatography on silica gel (Pentane:Et₂O = 60:1). The Product was obtained as a colorless oil (1.0 g, 6.2 mmol, 48 %).

Analytical Data

¹H-NMR (400.1 MHz, CDCl₃): \( \delta = 0.98 \) (d, \( J = 6.4 \), 3H), \( 1.25 \) (t, \( J = 7.1 \), 3H), \( 1.95 - 2.16 \) (m, 4H), \( 2.30 - 2.41 \) (m, 1H), \( 4.09 - 4.17 \) (m, 2H), \( 4.65 \) (dt, \( J = 6.7 \), 2.7, 2.7, 2H), \( 5.00 - 5.11 \) (m, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): \( \delta = \delta = 14.4, 19.6, 30.7, 35.7, 41.2, 60.2, 74.4, 87.7, 173.1, 209.4 \) ppm.

APCI-HRMS: \( m/z \) calcd for C₁₀H₂₀O₂N [M+NH₄]⁺ 186.1489 found 186.1489

GC: Hydrodex-B-TBDAc 25m x 0.25mm, 80 °C, isothermal [94% ee. \( t_R = 28.9 \) min (minor), 29.7 min (major)], \( [\alpha]_D^{25} = -12 \) (c = 0.59 CHCl₃).
A suspension of LAH (LAH) in dry Et₂O was cooled to 0 °C then a solution of 3-ethylhepta-5,6-dienoate in Et₂O (2 mL) was added dropwise. The reaction was stirred at this temperature for 1 h and then warmed to room temperature and stirred for another hour. The mixture was quenched through the addition of H₂O and aqueous HCl (2.0 M). The layers were separated, the organic layer was washed with H₂O (20 mL) and brine (20 mL). The aqueous layer was extracted with Et₂O (4 × 20 mL). The combined organic layer were dried over Na₂SO₄, the solvent was removed. The crude product was used without further purification.

**Analytical Data**

\(^1\text{H}-\text{NMR} (400.1 \text{ MHz, CDCl}_3): \delta = 0.95 \text{ (d, J = 6.7 Hz, 3H)}, 1.27 \text{ (s, 1H)}, 1.38 - 1.48 \text{ (m, 1H)}, 1.61 - 1.77 \text{ (m, 2H)}, 1.86 - 1.98 \text{ (m, 1H)}, 2.04 \text{ (ddddd, J = 14.1, 7.3, 5.8, 3.0 Hz, 1H)}, 3.64 - 3.77 \text{ (m, 2H)}, 4.64 \text{ (ddd, J = 6.7, 2.9 Hz, 2H)}, 5.06 \text{ (dddt, J = 7.4, 6.6, 2.8 Hz, 1H)} \text{ ppm.}

\(^{13}\text{C}-\text{NMR} (100.6 \text{ MHz, CDCl}_3): \delta = 19.6, 30.0, 36.1, 39.4, 61.2, 74.2, 88.1, 209.3 \text{ ppm.}

APCI-HRMS: m/z calcd for C₈H₁₈O \([\text{M+NH}_4]^+\) 144.1388 found 144.1383.

**Synthesis of (2S,4R)-4-methyl-2-vinyltetrahydro-2H-pyran 5ee**

The reaction was performed according to general procedure 8 with (S)-3-methylhepta-5,6-dien-1-ol (38 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the \text{d.r.} ratio (\text{d.r.} = 96/4) was determined by \(^1\text{H}-\text{NMR} \) spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (63 mg, 0.28 mmol, 96%).

**Analytical Data**

\(^1\text{H}-\text{NMR} (400.1 \text{ MHz, CDCl}_3): \delta = 0.95 \text{ (d, J = 6.4 Hz, 3H)}, 0.99 - 1.08 \text{ (m, 1H)}, 1.16 - 1.30 \text{ (m, 1H)}, 1.50 - 1.58 \text{ (m, 1H)}, 1.63 - 1.72 \text{ (m, 2H)}, 3.47 \text{ (dddd, J = 12.5, 11.4, 2.3 Hz, 1H)}, 3.73 - 3.82 \text{ (m, 1H)}, 4.03 \text{ (dddd, J = 11.4, 4.5, 1.6 Hz, 1H)}, 5.08 \text{ (dt, J = 10.6, 1.5, 1H)}, 5.22 \text{ (dddd, J = 17.3, 1.6 Hz, 1H)}, 5.85 \text{ (dddd, J = 17.3, 10.6, 5.5 Hz, 1H)} \text{ ppm.}

\(^{13}\text{C}-\text{NMR} (100.6 \text{ MHz, CDCl}_3): \delta = 22.4, 30.3, 34.5, 40.6, 68.1, 78.2, 114.5, 139.5 \text{ ppm.}

APCI-HRMS: m/z calcd for C₈H₁₅O \([\text{M+H}]^+\) 127.1123 found 127.1117.
**GC:** Hydrodex-B-TBDAc 25m x 0.25mm, 80 °C, isothermal [94% ee. \( t_R = 4.34 \text{ min (major)}, 4.57 \text{ min (major)} \). [\( \alpha \) ]\text{D}^{25} = -12 (c = 0.59 CHCl₃).

**Stereoselective synthesis of (2S,4R)-2-((E)-but-1-en-1-yl)-4-methyltetrahydro-2H-pyran**

The reaction was performed according to **general procedure 5.**

I) Butyraldehyde (4.3 g, 5.4 mL, 60 mmol, 1.0 equiv.) and ethinyl magnesium bromide (130 mL, 65 mmol, 0.5 M in THF, 1.08 equiv.). The crude product was filtered over a short silica pad (2:1 pentane/Et₂O). hex-1-yn-3-ol was obtained as a yellow liquid (5.6 g, 57 mmol, 95%)

II) Crude hex-1-yn-3-ol (step I) (5.6 g, 57 mmol, 1.0 equiv.), triethyl orthoacetate (15 g, 17 mL, 90 mmol, 1.05 equiv.), propionic acid (3 × 5 mol%). The crude product was purified by fractional distillation under reduced pressure (75 - 78 °C, 10 mbar) to obtain the title product (5.6 g, 36 mmol, 63%) as a colorless liquid.

**Analytical Data**

\(^1\text{H-NMR (400.1 MHz, CDCl}_3\)): \( \delta = 0.99 \) (t, \( J = 7.4 \text{ Hz, 3H} \)), 1.26 (t, \( J = 7.1 \text{ Hz, 3H} \)), 1.97 – 2.04 (m, 2H), 2.99 – 3.02 (m, 2H), 4.15 (q, \( J = 7.2 \text{ Hz, 2H} \)), 5.21 – 5.29 (m, 2H) ppm.

\(^{13}\text{C-NMR (100.6 MHz, CDCl}_3\)): \( \delta = 13.3, 14.3, 21.7, 35.2, 60.7, 84.9, 94.0, 171.7, 204.8 \text{ ppm.} \)

**APCI-HRMS:** \( m/z \) calcd for C₉H₁₄O₂ [M+H]⁺ 155.1067 found 155.1067.

**Synthesis of ethyl (E)-nona-2,5,6-trienoate 132.**
The reaction was performed according to **general procedure 6**.

I) Ethyl hepta-3,4-dienoate (5.6 g, 36 mmol, 1.0 equiv.) and DIBAL-H (52 mL, 52 mmol, 1.45 equiv., 1.0 M in DCM). The crude product was filtered over a short silica pad (DCM). Hepta-3,4-dienal was obtained as a yellow liquid (3.7 g, 33 mmol, 92%).

II) Crude hepta-3,4-dienal (step I) (3.7 g, 33 mmol), NaH (60% in mineral oil, 1.4 g, 61 mmol, 1.1 equiv.) in dry THF (100 mL) and triethyl phosphonoacetate (9.6 g, 8.5 mL, 43 mmol, 1.3 equiv.). The crude product was purified by flash chromatography on silica gel (40:1 Pentane:Et2O). The title compound was obtained as colorless liquid (4.5 g, 25 mmol, 75%).

**Analytical Data10**

**1H-NMR (400.1 MHz, CDCl3):** $\delta = 1.0$ (t, $J = 7.4$ Hz, 3H), 1.3 (t, $J = 7.1$ Hz, 3H), 2.0 (qdd, $J = 7.4$, 6.2, 3.2 Hz, 2H), 2.9 (tdd, $J = 6.6$, 2.8, 1.7 Hz, 2H), 4.2 (q, $J = 7.1$ Hz, 2H), 5.1 – 5.2 (m, 1H), 5.2 (qt, $J = 6.3$, 2.8 Hz, 1H), 5.9 (dt, $J = 15.6$, 1.7 Hz, 1H), 7.0 (dt, $J = 15.6$, 6.5, 0.4 Hz, 1H) ppm.

**13C-NMR (100.6 MHz, CDCl3):** $\delta = 13.4$, 14.4, 21.9, 32.1, 60.3, 87.8, 94.0, 122.0, 146.8, 166.6, 204.5 ppm.

**APCI-HRMS:** m/z calcd for $C_{11}H_{17}O_2$ [M+H]$^+$ 181.1225 found 181.1225.
Synthesis of ethyl (3S)-3-methylnona-5,6-dienoate 133.

Cul (1.0 mol%) and S-Tol-Binap (20 mol%) was dissolved in t-BuOMe (40 mL) and stirred under argon at room Temperature for 1 h until a yellow suspension was observe. The mixture was cooled to −50 °C and ethyl (E)-nona-2,5,6-trienoate (1.8 g, 10 mmol) was added and stirred for 15 min. Then MeMgBr in THF (5.0 mL, 25 mmol, 3.0 M, 1.5 equiv.) was added dropwise. The mixture was stirred at −50 °C for 2 h, then quenched by the addition of aqueous saturated NH₄Cl-solution. The layers were separated, the aqueous layer was extracted with Et₂O (4 × 30 mL), the combined organic layers were washed with brine (40 mL) and dried over Na₂SO₄. The solvent was removed and the residue was purified by flash chromatography on silica gel (Pentane:Et₂O = 60:1). The Product was obtained as a colorless oil (0.88 g, 4.5 mmol, 45 %).

Analytical Data[3]

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.93 – 0.98 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H), 1.25 (dd, J = 7.1, 6.9 Hz 3H), 1.90 – 2.14 (m, 7H), 2.35 – 2.42 (m, 1H), 4.13 (qd, J = 7.2, 1.2 Hz, 2H), 5.04 (dddd, J = 9.3, 6.2, 4.0, 3.2, 2.1 Hz, 1H), 5.10 – 5.16 (m, 1H). ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 7.9, 13.6, 14.4, 19.6, 19.7, 22.1, 27.7, 30.7, 30.8, 36.5, 36.6, 41.2, 41.2, 60.2, 89.1, 89.2, 92.5, 102.5, 173.2, 204.4 ppm.

APCI-HRMS: m/z calcd for C₁₂H₂₂O₂ [M+H]+ 197.1541 found 197.1537.

GC: Hydrodex-B-TBDAc 25m x 0.25mm, 75 °C, isothermal [97% ee. tᵣ = 132.02 min (minor), 136.50 min (major)].
Synthesis of (S)-3-methylhepta-5,6-dien-1-ol 54.

A suspension of LAH (1) in dry Et₂O was cooled to 0 °C then a solution of 3-ethylhepta-5,6-dienoate in Et₂O (2 mL) was added dropwise. The reaction was stirred at this temperature for 1 h and then warmed to room temperature and stirred for another hour. The mixture was quenched through the addition of H₂O and aqueous HCl (2.0 M). The layers were separated, the organic layer was washed with H₂O (20 mL) and brine (20 mL). The aqueous layer was extracted with Et₂O (4 × 20 mL). The combined organic layer were dried over Na₂SO₄, the solvent was removed. The crude product was used without further purification.

Analytical Data[3]

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 0.94 – 0.97 (m, 3H), 1.01 (t, $J = 7.4$ Hz, 3H), 1.33 (s, 1H), 1.39 – 1.48 (m, 1H), 1.63 – 1.75 (m, 2H), 1.83 – 1.95 (m, 1H), 1.96 – 2.08 (m, 3H), 3.64 – 3.76 (m, 2H), 5.01 – 5.15 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 13.6, 13.6, 19.6, 22.1, 22.1, 30.0, 36.8, 36.9, 39.4, 39.5, 61.3, 89.5, 89.6, 92.2, 92.3, 204.3 ppm.

APCI-HRMS: m/z calcd for C₁₀H₁₉O [M+H]$^+$ 155.1430 found 155.1430.

Synthesis of (2S,4R)-2-((E)-but-1-en-1-yl)-4-methyltetrahydro-2H-pyran 55ee.

The reaction was performed according to general procedure 9 with (S)-3-methylhepta-5,6-dien-1-ol (46 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 75/25) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (63 mg, 0.28 mmol, 96%).

Analytical Data[6]

$^1$H-NMR (400.1 MHz, CDCl₃): δ = 0.94 (d, $J = 6.4$ Hz, 3H), 0.97 – 1.01 (m, 3H), 1.17 – 1.28 (m, 2H), 1.49 – 1.55 (m, 1H), 1.58 – 1.68 (m, 2H), 1.99 – 2.16 (m, 2H), 3.40 – 3.54 (m, 1H), 3.61 – 3.84 (m, 1H), 4.00 (ddddd, $J = 11.1$, 6.5, 4.5, 1.6 Hz, 1H), 5.40 – 5.50 (m, 1H), 5.72 (ddddd, $J = 15.5$, 6.3, 6.2, 1.1 Hz, 1H).ppm.

$^{13}$C-NMR (100.6 MHz, CDCl₃): δ = 13.4, 14.4, 21.3, 22.4, 25.3, 30.3, 30.3, 34.5, 34.6, 40.9, 41.0, 67.9, 68.1, 130.3, 130.5, 133.5 ppm.
8 Catalysis followed by in situ hydration

General Procedure 10

A 10 mL screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon (Argon 5.0 Sauerstoffwerk Friedrichshafen) using a standard SCHLENK line apparatus. The screw-cap flask was charged with the corresponding internal δ-hydroxy allene (0.3 mmol, 1.0 equiv.), evacuated for 15 and then backfilled with argon three times. Then [Rh(COD)Cl]₂ (3.7 mg, 0.0075 mmol, 2.5 mol%), dppf (8.3 mg, 0.015 mmol, 5.0 mol%) and PTSA (17.1 mg, 0.09 mmol, 30 mol%) was added under a flow of argon followed by freshly distilled PhF (0.3 M). The flask was sealed and stirred at 80 °C overnight. The reaction mixture was diluted with MeOH (0.3 M) and Pd/C (5%, 30 mol%) was added. The mixture was hydrogenated at room temperature for 6 hours. The suspension was filtered and the solvent was evaporated to obtain the crude product. The residue was analyzed by ¹H-NMR spectroscopy. The crude product was purified by flash chromatography on silica gel using a mixture of pentane/ether.

Synthesis of syn-(4-cyclopropyl-2-octyltetrahydro-2H-pyran 56

The reaction was performed according to general procedure 10 with 3-cyclopropyltrideca-5,6-dien-1-ol (71 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) was determined by ¹H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (67 mg, 0.28 mmol, 94%).

Analytical Data

¹H-NMR (400.1 MHz, CDCl₃): δ = 0.05 – 0.09 (m, 2H), 0.36 – 0.42 (m, 2H), 0.47 – 0.57 (m, 1H), 0.69 – 0.79 (m, 1H), 0.88 (s, 3H), 1.05 (dd, J = 13.1, 11.9, 11.0 Hz, 1H), 1.25 – 1.30 (m, 1H), 1.35 – 1.43 (m, 3H), 1.47 – 1.54 (m, 1H), 1.59 – 1.64 (m, 1H), 1.71 (dddd, J = 13.0, 3.9, 2.0 Hz, 1H), 3.14 (dddd, J = 11.0, 7.2, 4.9, 2.1 Hz, 1H), 3.32 (ddd, J = 12.5, 11.4, 2.3 Hz, 1H), 3.99 (ddd, J = 11.4, 4.6, 1.6 Hz, 1H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 2.8, 14.2, 17.3, 22.8, 25.7, 29.4, 29.7, 29.9, 32.0, 32.7, 36.7, 38.5, 40.7, 68.2, 77.8 ppm.

APCI-HRMS: m/z calcd for C₁₆H₃₉O [M+H]^+ 239.2375 found 239.2369.
Synthesis of **syn 2-octyl-4-(4-phenylbutyl)tetrahydro-2H-pyran 57**

The reaction was performed according to **general procedure 10** with 3-(3-phenylpropyl)trideca-5,6-dien-1-ol (98 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 92/8) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (96 mg, 0.29 mmol, 98%).

**Analytical Data**

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.87 – 0.91 (m, 3H), 1.13 – 1.21 (m, 1H), 1.25 – 1.29 (m, 14iii), 1.34 – 1.42 (m, 2H), 1.44 – 1.53 (m, 2H), 1.56 (ddd, $J$ = 12.8, 4.1, 2.0 Hz, 1H), 1.60 – 1.69 (m, 3H), 2.58 – 2.63 (m, 2H), 3.20 (dddd, $J$ = 11.0, 7.1, 4.8, 2.0 Hz, 1H), 3.38 (ddd, $J$ = 12.5, 11.4, 2.2 Hz, 1H), 3.99 (ddd, $J$ = 11.4, 4.6, 1.6 Hz, 1H), 7.16 – 7.20 (m, 3H), 7.26 – 7.31 (m, 2H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.8, 25.6, 28.4, 29.4, 29.7, 29.9, 32.0, 33.1, 35.4, 36.2, 36.8, 36.9, 38.9, 68.2, 77.7, 125.7, 128.3, 128.4, 142.7 ppm.

APCI-HRMS: m/z calcld for C$_{22}$H$_{37}$O [M+H]$^+$ 317.2838 found 317.2838.

**Synthesis of syn-4-[[1,1'-biphenyl]-4-yl]-2-octyltetrahydro-2H-pyran 58**

The reaction was performed according to **general procedure 10** with 3-[[1,1'-biphenyl]-4-yl]trideca-5,6-dien-1-ol (105 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 94/6) was determined by $^1$H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (97 mg, 0.28 mmol, 92%).

**Analytical Data**

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta$ = 0.87 – 0.91 (m, 3H), 1.25 – 1.35 (m, 11H), 1.42 – 1.52 (m, 3H), 1.53 – 1.64 (m, 1H), 1.77 – 1.84 (m, 2H), 1.85 – 1.91 (m, 1H), 2.77 – 2.87 (m, 1H), 3.41 (dddd, $J$ = 12.0, 7.0, 4.8, 2.0 Hz, 1H), 3.55 – 3.64 (m, 1H), 4.12 – 4.17 (m, 1H), 7.29 – 7.32 (m, 2H), 7.33 – 7.36 (m, 1H), 7.40 – 7.46 (m, 2H), 7.54 – 7.60 (m, 4H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta$ = 14.2, 22.8, 25.6, 28.4, 29.7, 29.9, 32.0, 33.8, 36.7, 39.7, 41.7, 68.3, 78.0, 127.1, 127.2, 127.3, 128.8, 139.4, 141.1, 145.2 ppm.

APCI-HRMS: m/z calcld for C$_{25}$H$_{35}$O [M+H]$^+$ 351.2681 found 351.2682.
Synthesis of syn-4-(4-methoxyphenyl)-2-(4-phenylbutyl)tetrahydro-2H-pyran 59

The reaction was performed according to general procedure 10 with 3-(4-methoxyphenyl)-9-phenylnona-5,6-dien-1-ol (97 mg, 0.3 mmol, 1.0 equiv.). The reaction mixture was filtered, concentrated and the d.r. ratio (d.r. = 93/7) was determined by 1H-NMR spectroscopy of the crude product. After purification by flash chromatography on silica gel (pentane/ether 80/1 to 40/1) the product was obtained as colorless liquid (87 mg, 0.28 mmol, 93%).

Analytical Data

1H-NMR (500.1 MHz, CDCl3): δ = 1.34 – 1.53 (m, 4H), 1.64 (dddd, J = 11.9, 7.3, 3.6, 1.7 Hz, 2H), 1.72 (ddd, J = 10.8, 8.5, 3.7 Hz, 2H), 1.79 (ddd, J = 13.1, 3.8, 1.5 Hz, 1H), 2.62 (dd, J = 7.8, 6.9 Hz, 2H), 2.66 – 2.76 (m, 1H), 3.36 (dd, J = 4.7, 2.4 Hz, 1H), 3.51 – 3.58 (m, 1H), 3.80 (s, 3H), 4.08 – 4.14 (m, 1H), 6.84 – 6.88 (m, 2H), 7.12 – 7.16 (m, 2H), 7.16 – 7.19 (m, 3H), 7.26 – 7.29 (m, 2H) ppm.

13C-NMR (125.6 MHz, CDCl3): δ = 25.4, 31.7, 34.0, 36.0, 36.5, 39.9, 41.0, 55.4, 68.3, 77.8, 114.0, 125.7, 127.7, 128.3, 128.5, 138.3, 142.8, 158.1 ppm.

APCI-HRMS: m/z calcd for C22H29O2 [M+H]+ 325.2168 found 325.2169.
9 Total synthesis of (-)-centrolobine

Synthesis of 5-(4-methoxyphenyl)-5-oxopentanal 61

A solution of 1-(cyclopent-1-en-1-yl)-4-methoxybenzene\(^1\) (5.0 g, 29 mmol) in MeOH (200 mL) was cooled to \(-78\, ^\circ\text{C}\). Ozone was bubbled through the solution until the solution showed a blue colour (approx. 30 min) then, the reaction vessel was degassed with nitrogen until disappearance of the blue colour occurred. Me\(_2\)S (15 mL, 10 equiv.) was added and the reaction mixture was allowed to warm to room temperature over night. The solution was concentrated under recued pressure crude product was purified by flash chromatography on silica gel (pentane/ether 10/1 to 4/1). The desired product as obtained as white solid (5.0 g, 24 mmol, 83%).

**Analytical Data**

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\)): \(\delta = 2.07\) (tt, \(J = 7.0, 7.1\) Hz, 2H), 2.58 (td, \(J = 7.1, 1.4\) Hz, 2H), 2.99 (t, \(J = 7.1\) Hz, 2H), 3.87 (s, 3H), 6.90 – 6.97 (m, 2H), 7.91 – 7.98 (m, 2H), 9.80 (s, 1H) ppm.

\(^{13}\)C-NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 16.8, 37.0, 43.3, 55.6, 113.8, 130.4, 130.4, 163.6, 198.0, 202.1\) ppm.

**ESI-HRMS**: \(m/z\) calcd for C\(_{12}\)H\(_{15}\)O\(_3\) [M+H]\(^+\) 207.1016 found 207.1013.

\(^1\) L. En-Chih, J. Topczewski, *J. Am. Chem. Soc.* 2019, 14, 5135-5138.
Synthesis of 7-(4-methoxyphenyl)-7-oxohept-1-yn-3-yl acetate

Ethynylmagnesium bromide (0.5 M in THF, 15 mL, 7.8 mmol, 1.0 equiv.) was cooled to 0 °C. 5-(4-methoxyphenyl)-5-oxopentanal (1.6 g, 7.8 mmol) was added dropwise and the solution was stirred for 1 h at rt. Then cooled to 0 °C and acetyl chloride (0.6 mL, 8.5 mmol) was added dropwise. The solution was warmed to rt. And stirred for 1 h. The reaction was quenched with H₂O (10 mL) and the aqueous layer was extracted with Et₂O (3 × 25 mL). The combined organic layer was dried over Na₂SO₄, the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography on silica gel (pentane/ether 10/1 to 4/1). The desired product as obtained as colorless oil (1.9 g, 19 mmol, 85%)

Analytical Data

¹H-NMR (400.1 MHz, CDCl₃): δ = 1.84 – 1.95 (m, 4H), 2.07 (s, 3H), 2.46 (d, J = 2.2 Hz ppm, 1H), 2.90 – 3.01 (m, 2H), 3.86 (s, 3H), 5.36 – 5.42 (m, 1H), 6.90 – 6.97 (m, 2H), 7.90 – 7.97 (m, 2H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 19.8, 21.0, 34.1, 37.4, 55.5, 63.5, 73.8, 81.1, 113.8, 130.1, 130.3, 163.5, 169.9, 198.0 ppm.

ESI-HRMS: m/z calcd for C₁₆H₁₉O₄ [M+H]⁺ 275.1278 found 275.1280.
Synthesis of 7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hept-5,6-dien-1-one 62

To a solution of 7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hept-5,6-dien-1-one (1.0 M in THF, 4.1 mL, 4.1 mmol, 1.1 equiv.), CuBr (61 mg, 0.4 mmol, 10 mol%) in THF (10 mL) was cooled to 0 °C. At this temperature (4-(benzyloxy)phenyl)magnesium bromide (1.1 g, 4.0 mmol, 1.0 equiv.) was added dropwise. The reaction was allowed to warm to rt. and stirred for 2 h. Saturated ammonium chloride (10 mL) was added and the aqueous layer was separated and extracted with Et₂O (2 × 20 mL). The combined organic layers were dried over Na₂SO₄, the solvent was removed under reduced pressure and the two Diastereomers were separated by flash Chromatography (SiO₂, pentane/Et₂O = 10/1 to 2/1). The desired product was obtained as colorless oil (0.78 g, 2.0 mmol, 48%)

Analytical Data

\[ ^1H-NMR \ (400.1 \text{ MHz, CDCl}_3) \delta = 1.89 – 1.98 \ (m, 2H), 2.19 – 2.28 \ (m, 2H), 2.95 – 3.03 \ (m, 2H), 3.85 \ (s, 3H), 5.05 \ (s, 2H), 5.55 – 5.78 \ (m, 1H), 6.11 \ (dt, J = 6.2, 3.0 Hz, 1H), 6.89 – 6.93 \ (m, 4H), 7.21 \ (dt, J = 8.9, 0.5 Hz, 2H), 7.31 – 7.47 \ (m, 6H), 7.89 – 7.92 \ (m, 2H) \text{ ppm.} \]

\[ ^{13}C-NMR \ (100.6 \text{ MHz, CDCl}_3) \delta = 23.8, 28.6, 37.6, 55.5, 70.2, 94.4, 94.5, 113.8, 115.2, 127.5, 127.6, 127.8, 128.0, 128.6, 130.3, 130.4, 137.1, 158.0, 163.4, 198.7, 204.9 \text{ ppm.} \]

ESI-HRMS: \( m/z \) calcd for C₁₂H₁₅O₃ [M+H]^+ 207.1016 found 207.1013.
Synthesis of (1S)-7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hepta-5,6-dien-1-ol 63

7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hepta-5,6-dien-1-one (0.42 g, 1.1 mmol, 1.0 equiv.) was solved in THF (7 mL) and (+)-CBS-Cat. (1 M in toluene, 1.0 mL, 2.0 mmol, 1.0 equiv.) was added before it was cooled to −20 °C. Then BH$_3$-THF (1 M, 2.2 mL, 2.2 mml, 2.0 equiv.) was added dropwise at −20 °C and the solution was stirred for 5 h. Afterwards, MeOH (2 mL) was added and the reaction was warmed to room temperature. The mixture was quenched by adding aq. HCl (1 M, 10 mL) and the layers were separated. The aqueous layer was extracted with Et$_2$O (3 × 50 mL) and the combined organic layers were dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (pentane: Et$_2$O = 2:1) to afford the desired product (374 mg, 0.94 mmol, 85 %) as a yellow liquid.

Analytical Data

$^1$H-NMR (400.1 MHz, CDCl$_3$): $\delta = 1.44 – 1.92$ (m, 6H), 2.15 (dddd, $J = 7.2, 7.2, 7.1, 3.0$ Hz, 2H), 3.80 (d, $J = 0.9$ Hz, 3H), 4.62 (dddd, $J = 7.9, 5.7$ Hz, 2.8, 1H), 5.06 (s, 2H), 5.45 – 5.56 (m, 1H), 6.08 (dddd, $J = 7.2, 7.2, 7.1, 3.0$ Hz, 2H), 4.62 – 4.94 (m, 4H), 7.17 – 7.26 (m, 4H), 7.29 – 7.48 (m, 5H) ppm.

$^{13}$C-NMR (100.6 MHz, CDCl$_3$): $\delta = 25.5, 25.5, 28.8, 38.5, 55.4, 70.2, 74.1, 74.2, 94.3, 94.7, 113.9, 113.9, 115.2, 127.2, 127.5, 127.7, 127.8, 128.0, 128.6, 137.0, 157.9, 204.7, 205.7$ ppm.

$^1$H-NMR (400.13 MHz, CDCl$_3$):

HR-MS (C$_{27}$H$_{28}$O$_3$; [M+Na]$^+$, pos. ESI): calculated: 423.1931, found: 423.1935.
Synthesis of (-)-Centrolobine

I) A screw-cap flask was flame-dried, cooled to room temperature under vacuum and backfilled with argon using a standard SCHLENK line apparatus. The screw-cap flask was charged with (1S)-7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hepta-5,6-dien-1-ol 63 (120 mg, 0.3 mmol, 1.0 equiv.) the flask was evacuated for 15 min and backfilled with argon three times. Then [Rh(COD)Cl]₂ (3.7 mg, 0.075 mmol, 2.5 mol%), dppf (8.3 mg, 0.015 mmol, 5.0 mol%) and HOAcCl (19 mg, 0.09 mmol, 30 mol%) was added under a flow of argon followed by freshly distilled DCE. The flask was sealed and stirred at 80 °C overnight. The reaction mixture concentrated and the d.r. ratio (d.r. = 90/10) was determined by ¹H-NMR spectroscopy of the crude product. The product was obtained as yellow oil (99 mg, 0.25 mmol, 83%).

II) (2R,6S)-2-((E)-4-(benzyloxy)styryl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran (99.0 mg, 0.25 mmol, 1.0 equiv.) and Pd (5 wt% on carbon, 5.0 mol%) were stirred in MeOH (1.1 mL) under a H₂-atomosphere (1 atm) at room temperature for 72 h. The reaction mixture was then filtrated over a pad of celite, rinsed with Et₂O (5 mL) and concentrated under reduced pressure. The residue was purified by column chromatography (SiO₂, pentane:Et₂O = 5:1 → 1:1) to afford the desired product (64 mg, 0.21 mmol, 80%).

Analytical data:

¹H-NMR (400.13 MHz; CDCl₃): δ = 0.83 – 0.90 (m, 2H), 1.00 – 1.22 (m, 3H), 1.47 (m, 3H), 1.77 (m, 1H), 2.23 – 2.33 (m, 1H), 2.44 – 2.56 (m, 1H), 3.22 (s, 1H), 3.77 (s, 3H), 4.31 (m, 1H), 6.76 – 6.86 (m, 4H), 7.09 – 7.22 (m, 4H) ppm.

¹³C-NMR (100.6 MHz, CDCl₃): δ = 24.2, 30.9, 31.4, 33.5, 38.4, 55.4, 113.7, 115.2, 127.1, 129.6, 134.9, 136.0, 153.6, 158.8.

HR-MS (C₂₀H₂₄O₃; [M+Na]⁺, pos. ESI): calculated: 335.1618, found: 335.1617.
10 Determination of relative configuration

Exemplary determination of the relative configuration of 4-phenyl-2-vinyltetrahydro-2H-pyran

**NOE-Experiment syn-Product; (major compound)**

**NOE-Experiment anti-Product; (minor compound)**
Exemplary determination of the relative configuration of 2,4-diphenyl-6-vinyltetrahydro-2H-pyran
Exemplary determination of the relative configuration of (E)-2-(oct-1-en-1-yl)-4,6-diphenyltetrahydro-2H-pyran
11 Ligand synthesis

Synthesis of 1, 1'-Bis[bis[4-(trifluoromethyl)phenyl]phosphino]ferrocene

Synthesis of bis(4-(trifluoromethyl)phenyl)phosphine oxide

I) To a suspension of magnesium (2.60 g, 108 mmol, 2.1 equiv.) and iodide (catalytic amount) in Et₂O (88 mL, 1.0 M) 1-bromo-4-(trifluoromethyl)benzene (22.1 g, 13.8 mL, 98.2 mmol, 2.0 equiv.) was added dropwise. After the reaction stopped refluxing, the mixture was heated to 80 °C for 1 h.

II) To a suspension of NaH (2.16 g, 54.0 mmol, 1.1 equiv. (60%)) in dry THF (30 mL) was carefully added diethylphosphite (67.9 g, 63.3 mL, 49.1 mmol, 1.0 equiv) dropwise. After completed addition the mixture was stirred for 1 h and then cooled to 0 °C. The Grignard solution (step I) was added the reaction was allowed to warm to room temperature and was then refluxed for 30 minutes. The reaction mixture was cooled to room temperature and stirred for 3 h before it was quenched through the addition of H₂O (100
mL) nad conc. HCl (100mL). The layers were separated, and the aqueous layer was extracted with EE (3 x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (DCM to DCM/EE = 90/10) the residue was recrystallized from Et₂O to obtain the pure title combined as white solid (12.5 g, 36.8 mol, 75%) using a mixture of pentane/ether.

Analytical Data

^1^H-NMR (500.1 MHz, CDCl₃): δ = 7.77 – 7.82 (m, 4H), 7.83 – 7.91 (m, 4H), 8.19 (d, J = 491.6 Hz 1H) ppm.

^1^3^C-NMR (125.6 MHz, CDCl₃): δ = 126.05, 126.0, 126.1, 126.1, 126.1, 131.2, 131.3, 134.5 ppm.

^1^9^F-NMR (470.5, CDCl₃): δ = -63.4 ppm.

^3^1^P-NMR (201.4, CDCl₃): δ = 17.8 ppm.

ESI-HRMS: m/z calcd for C₁₅H₁₀O₃F₃ [M+H]^+ 339.0373 found 339.0385.

Synthesis of 1, 1’-Bis[bis[4-(trifluoromethyl)phenyl]phosphino]ferrocene

I) To a solution of bis(4-(trifluoromethyl)phenyl)phosphine oxide (548 mg, 1.62 mmol, 1.0 equiv.) in dry DCM (10 mL) was added PCl₅ (111mg, 71 μL, 0.81 mmol, 0.50 equiv.) at room temperature. The mixture was stirred at this temperature until the reaction was complete as indicated by TLC. The solvent was removed under reduced pressure and the crude chlorobis(4-(trifluoromethyl)phenyl)phosphane was used without further purification in the net reaction step.

II) N,N,N’,N’-Tetramethylethylenediamine (290 μL, 1.34 mmol, 2.50 equiv.) and n-BuLi (2.5 M in Hexane, 480 μL, 1.19 mmol, 2.2 equiv.) were added dropwise to a stirred solution of (C₅H₅)₂Fe (100 mg, 0.540 mmol, 1.0 equiv.) in hexane (10 mL) under a argon atmosphere at room temperature. The solution was stirred at room temperature overnight. The orange slurry was allowed to settle, and the hexane layer was removed with a syringe. The remaining orange powder was washed with dry hexane (5 mL) and dissolved in dry THF (10 mL). Chlorobis(4-(trifluoromethyl)phenyl)phosphane (578 mg, 1.62 mmol, 3.0
equiv.) was diluted with dry THF (2 mL) and added to the orange solution at −78 °C. The solution was slowly warmed to room temperature and stirred for 4 hours. The reaction was quenched with water and diluted with DCM (10 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (pentane/Et₂O = 60/1) the orange residue was recrystallized in heptane to obtain the pure title combined as orange needles (149 mg, 0.178 mmol, 33%) using a mixture of pentane/ether.

Analytical Data

^1H-NMR (500.1 MHz, CDCl₃): δ = 3.99 (t, J = 1.8 Hz, 2H), 4.29 – 4.37 (m, 2H), 7.38 (d, J = 8.2 Hz, 4H), 7.55 (d, J = 8.1 Hz, 4H) ppm.

^13C-NMR (125.6 MHz, CDCl₃): δ = 72.9, 72.9, 74.0, 75.0, 125.1, 125.1, 125.2, 125.2, 131.2, 133.6, 133.8, 142.9, 143.0 ppm.

^19F-NMR (470.5 MHz, CDCl₃): δ = -62.8 ppm.

^31P-NMR (201.4 MHz, CDCl₃): δ = -17.2 ppm.

ESI-HRMS: m/z calcd for C₃₈H₃₅O₂F₁₂FeP₂ [M+H]^+ 827.0589 found 827.0561.

Synthesis of 1, 1´-Bis[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]ferrocene

Synthesis of bis(3,5-bis(trifluoromethyl)phenyl)phosphine oxide 135

I) To a suspension of magnesium (2.60 g, 108 mmol, 2.1 equiv.) and iodide (catalytic amount) in Et₂O (88 mL, 1.0 M) 1-bromo-3,5-bis(trifluoromethyl)benzene (28.7 g, 18.6 mL, 98.2 mmol, 2.0 equiv.) was added dropwise. After the reaction stopped refluxing, the mixture was heated to 80 °C for 1 h.

II) To a suspension of NaH (2.16 g, 54.0 mmol, 1.1 equiv. (60%)) in dry THF (30 mL) was carefully added diethylphosphite (67.9 g, 63.3 mL, 49.1 mmol, 1.0 equiv) dropwise. After completed addition the mixture was stirred for 1 h and then cooled to 0 °C. The Grignard solution (step I) was added the reaction was allowed to warm to room temperature and was then refluxed for 30 minutes. The reaction mixture was cooled to room temperature and stirred for 3 h before it was quenched through the addition of H₂O (100 mL) and conc. HCl (100 mL). The layers were separated, and the aqueous layer was extracted with EE (3 x 50 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (DCM to
DCM/EE = 90/10) the residue was recrystallized from Et₂O to obtain the pure title combined as white solid (16.3g, 34.7 mol, 70%) using a mixture of pentane/ether.

Analytical Data

**1H-NMR** (500.1 MHz, CDCl₃): δ = 8.3 (d, J = 504.4 Hz, 1H), 8.13 – 8.16 (m, 2H), 8.21 (d, J = 1.6 Hz, 2H), 8.81 (s, 1H) ppm.

**13C-NMR** (125.6 MHz, CDCl₃): δ = 19.3, 121.5, 123.6, 125.8, 127.3, 127.4, 130.8, 130.9, 130.9, 132.7, 133.5 ppm.

**19F-NMR** (470.5 MHz, CDCl₃): δ = -63.1 ppm.

**31P-NMR** (201.4 MHz, CDCl₃): δ = -14.3 ppm.

**ESI-HRMS:** m/z calcd for C₁₆H₈OF₃P [M+H]+ 475.01116 found 475.01113.

**Synthesis of 1,1′-Bis[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]ferrocen (L5) 136**

**I)** To a solution of bis(3,5-bis(trifluoromethyl)phenyl)phosphine oxide (769 mg, 1.62 mmol, 1.0 equiv.) in dry DCM (10 mL) was added PCl₃ (111 mg, 71 μL, 0.81 mmol, 0.50 equiv.) at room temperature. The mixture was stirred at this temperature until the reaction was complete as indicated by TLC. The solvent was removed under reduced pressure and the crude bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphane was used without further purification in the net reaction step.

**II)** N,N,N′,N′-Tetramethylethylenediamine (290 μL, 1.34 mmol, 2.50 equiv.) and n-BuLi (2.5 M in Hexane, 480 μL, 1.19 mmol, 2.2 equiv.) were added dropwise to a stirred solution of (C₅H₅)₂Fe (100 mg, 0.540 mmol, 1.0 equiv.) in hexane (10 mL) under a argon atmosphere at room temperature. The solution was stirred at room temperature overnight. The orange slurry was allowed to settle, and the hexane layer was removed with a syringe. The remaining orange powder was washed with dry hexane (5 mL) and dissolved in dry THF (10 mL). Bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphane (798 mg, 1.62 mmol, 3.0 equiv.) was diluted with dry THF (2 mL) and added to the orange solution at −78 °C. The solution
was slowly warmed to room temperature and stirred for 4 hours. The reaction was quenched with water and diluted with DCM (10 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic phases were dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (pentane/Et$_2$O = 60/1) the orange residue was recrystallized in heptane to obtain the pure title combined as orange needles (178 mg, 0.162 mmol, 30%) using a mixture of pentane/ether.

$^{1}$H NMR (500.1 MHz, CDCl$_3$): $\delta$ = 4.01 (m, 4H), 4.43 – 4.45 (m, 4H), 7.69 (d, $J = 1.6$ Hz, 4H), 7.70 (d, $J = 1.6$ Hz, 4H), 7.88 – 7.90 (m, 4H) ppm.

$^{13}$C NMR (125.6 MHz, CDCl$_3$): $\delta$ = 73.4, 73.7, 73.9, 119.8, 121.9, 123.4, 123.5, 123.5, 123.5, 123.5, 123.6, 124.1, 126.3, 131.8, 132.0, 132.1, 132.3, 132.3, 132.6, 132.9, 133.0, 133.1, 133.1, 140.3.

$^{19}$F NMR (470.5 MHz, CDCl$_3$): $\delta$ = -63.0 ppm.

$^{31}$P NMR (201.4 MHz, CDCl$_3$) $\delta$ = -15.6 ppm.

ESI-HRMS: $m/z$ calcd for C$_{42}$H$_{25}$O$_2$F$_4$FeP$_2$ [M+H]$^+$ 1130.9977 found 1130.9980.
12 NMR

ethyl penta-3,4-dienoate 60

$^{1}$H-NMR

$^{13}$C-NMR
penta-3,4-dienal 61

$^1$H-NMR

$^{13}$C-NMR
ethyl (E)-hepta-2,5,6-trienoate 62

$^{1}$H-NMR

$^{13}$C-NMR
**Supporting Information**

**ethyl 3-methylhepta-5,6-dienoate 63**

$^1$H-NMR

$^1$C-NMR
3-methylhepta-5,6-dien-1-ol 53rac

$^1$H-NMR

$^{13}$C-NMR
3-(buta-2,3-dien-1-yl)tetradecanol 64

$^1$H-NMR

$^{13}$C-NMR
3-neopentylhepta-5,6-dien-1-ol 65

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-cyclopropylhepta-5,6-dienoate 66

$\text{C}_{13}\text{H}_{18}\text{O}_2$

194.27
3-cyclopropylepta-5,6-dienol 67

$^{13}$C-NMR
ethyl 3-(3-phenylpropyl)hepta-5,6-dienoate 69

$^1$H-NMR

$^{13}$C-NMR
3-(3-phenylpropyl)hepta-5,6-dienol 70

$^{1}H$-NMR

$^{13}C$-NMR
ethyl 3-phenylhepta-5,6-dienoate 71

$^1$H-NMR

$^{13}$C-NMR
3-phenylhepta-5,6-dien-1-ol 72

$^{1}H$-NMR

$^{13}C$-NMR
ethyl 3-(naphthalene-2-yl)hepta-5,6-dienoate 73

$\text{C}_{18}\text{H}_{20}\text{O}_2$

280.37

$^1\text{H}-\text{NMR}$

$^{13}\text{C}-\text{NMR}$
ethyl 3-((1,1'·biphenyl)-4-yl)hepta-5,6-dienoate 75

$^{1}H$-NMR

$^{13}C$-NMR
3-[[1,1'-biphenyl]-4-yl]hepta-5,6-dien-1-ol 76

$\text{C}_{18}\text{H}_{20}\text{O}$

$264.37$

$^1\text{H-NMR}$

$^1\text{H-NMR}$

$^1\text{C-NMR}$
ethyl 3-(p-tolyl)hepta-5,6-dienoate 77

$^1$H-NMR

$^{13}$C-NMR
3-(p-tolyl)hepta-5,6-dien-1-ol 78

$^1$H-NMR

$^1$C-NMR
ethyl 3-(m-tolyl)hepta-5,6-dienoate 79

$^1$H-NMR

$^{13}$C-NMR
3-(m-tolyl)hepta-5,6-dien-1-ol 80

$^1$H-NMR

$^{13}$C-NMR
3-(o-tolyl)hepta-5,6-dienoate 81

$^1$H-NMR

$^{13}$C-NMR
3-(o-tolyl)hepta-5,6-dien-1-ol 82

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-mesitylhepta-5,6-dienoate 83

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-(4-vinylphenyl)hepta-5,6-dienoate 85

$^{1}H$-NMR

$^{13}C$-NMR
3-(4-vinylphenyl)hepta-5,6-dien-1-ol 86

$^{1}H$-NMR

$^{13}C$-NMR
ethyl 3-(4-trifluoromethyl)phenyl)hepta-5,6-dienoate 87

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-(4-bromophenyl)hepta-5,6-dienoate 89

$\text{C}_{15}\text{H}_{17}\text{BrO}_2$

309.20
3-(4-bromophenyl)hepta-5,6-dienol 90

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-(methoxyphenyl)hepta-5,6-dienoate 91

$^{1}H$-NMR

$^{13}C$-NMR

C$_{16}$H$_{20}$O$_{3}$

260.33
3-(4-methoxyphenyl)hepta-5,6-dienol 92

$^{1}$H-NMR

C$_{14}$H$_{19}$O$_{2}$
218.30

$^{13}$C-NMR
3-(4-methylthio)phenyl)hepta-5,6-dienol 94

$^1$H-NMR

$^{13}$C-NMR
ethyl 3-(4-methoxyphenyl)-4-dimethylhepta-5,6-dienoate 95

$^1$H-NMR

$^{13}$C-NMR
Supporting Information

3-(4-methoxyphenyl)-4-dimethylhepta-5,6-dienol 96

$^1$H-NMR

$^{13}$C-NMR
ethyl undeca-3,4-dienoate 97

$^1$H-NMR

C$_{13}$H$_{22}$O$_2$
210.32

$^{13}$C-NMR
ethyl (E)-trideca-2,5,6-trienoate 98

$^1$H-NMR

$^{13}$C-NMR

$C_{15}H_{24}O_2$

236.36
3-methyltrideca-5,6-dien-1-ol 99

$^{1}H$-NMR

Me

OC

$C_{14}H_{26}O$

210.36

$^{13}C$-NMR
3-(deca-2,3-dien-1-yl)pentadecan-1-ol 100
3-neopentyltrideca-5,6-dien-1-ol 101

$^1$H-NMR

$^{13}$C-NMR
3-cyclopropyltrideca-5,6-dien-1-ol 102

$^1$H-NMR

$^{13}$C-NMR
3-cyclohexyltrideca-5,6-dien-1-ol 103

$^{1}H$-NMR

$^{13}C$-NMR
3-(3-phenylpropyl)trideca-5,6-dien-1-ol 104

$^1$H-NMR

$^{13}$C-NMR
3-phenyltrideca-5,6-dien-1-ol 105

$^1$H-NMR

$^{13}$C-NMR
3-(naphthalen-2-yl)trideca-5,6-dien-1-ol 106

\[ \text{C}_{23}\text{H}_{39}\text{O} \]

322.49
3-((1,1'-biphenyl)-4-yl)trideca-5,6-dien-1-ol 107

$^{1}H$-NMR

$^{13}C$-NMR
3-(p-tolyl)trideca-5,6-dien-1-ol 108

\[ \text{C}_{20}\text{H}_{30}\text{O} \]

286.46

$^1$H-NMR

$^{13}$C-NMR
3-(m-tolyl)trideca-5,6-dien-1-ol 109

$^1$H-NMR

$^{13}$C-NMR
3-(o-tolyl)trideca-5,6-dien-1-ol 110

**^1H-NMR**

**^{13}C-NMR**
3-mesityltrideca-5,6-dien-1-ol 111

$^{1}H$-NMR

$^{13}C$-NMR

$C_{22}H_{34}O$

314.51
3-(4-vinylphenyl)trideca-5,6-dien-1-ol 112

$^1$H-NMR

$^{13}$C-NMR
3-(4-methoxyphenyl)trideca-5,6-dien-1-ol 114

$^1$H-NMR

$^{13}$C-NMR
3-(4-(methylthio)phenyl)trideca-5,6-dien-1-ol 115

$^{1}$H-NMR

$^{13}$C-NMR

C$_{29}$H$_{36}$OS

318.52
3-(4-(trifluoromethyl)phenyl)trideca-5,6-dien-1-ol 116

$^{1}$H-NMR

$^{13}$C-NMR
3-(4-(trifluoromethyl)phenyl)trideca-5,6-dien-1-ol 117

$\text{C}_{22}\text{H}_{34}\text{O}_2$

$M = 330.51$

$^1\text{H-NMR}$

$^1\text{C-NMR}$
ethyl 5-cyclohexylpenta-3,4-dienoate. 118

$^{1}$H-NMR

C$_{13}$H$_{20}$O$_{2}$
208.30

$^{13}$C-NMR
ethyl (E)-7-cyclohexylhepta-2,5,6-trienoate 119

$^{1}H$-NMR

$^{13}C$-NMR
7-cyclohexyl-3-(4-methoxyphenyl)hepta-5,6-dien-1-ol 120

$^1$H-NMR

$^1$C-NMR

C$_{20}$H$_{28}$O$_2$
300.44
ethyl 7-phenylehepta-3,4-dienoate 121

$^{1}H$-NMR

$C_{15}H_{18}O_{2}$

230.31

$^{13}C$-NMR
ethyl (E)-9-phenylnona-2,5,6-trienoate 122

$^1$H-NMR

$^{13}$C-NMR

$C_{15}H_{29}O_2$

256.35
3-(4-methoxyphenyl)-9-phenylnona-5,6-dien-1-ol 123

$^1$H-NMR

$^{13}$C-NMR
ethyl 6-phenylhexa-3,4-dienoate 124
**Supporting Information**

**ethyl (E)-8-phenylocta-2,5,6-trienoate 125**

**1H-NMR**

\[ C_{18}H_{18}O_2 \]

242.32

**13C-NMR**

\[ 205.45 \]

\[ 166.49 \]

\[ 152.59 \]

\[ 132.17 \]

\[ 72.76 \]

\[ 54.80 \]

\[ 31.80 \]

\[ 14.37 \]
3-(4-methoxyphenyl)-8-phenylocta-5,6-dien-1-ol 126

$^1$H-NMR

$^{13}$C-NMR
ethyl 7-(methylthio)hepta-3,4-dienoate 127

$^1$H-NMR

$^{13}$C-NMR
ethyl (E)-9-(methylthio)nona-2,5,6-trienoate 128

$\text{C}_{13}\text{H}_{26}\text{O}_{2}\text{S}$

240.36

$^1\text{H-NMR}$

$^13\text{C-NMR}$
3-(4-methoxyphenyl)-9-(methylthio)nona-5,6-dien-1-ol 129

$^1$H-NMR

$^{13}$C-NMR
Syn-4-(4-methoxyphenyl)octa-6,7-dien-2-ol 45

$^1$H-NMR

$^{13}$C-NMR

C$_{19}$H$_{20}$O$_2$

232.32

200
**SUPPORTING INFORMATION**

**syn - 4-(4-methoxyphenyl)octa-6,7-dien-2-ol 46**

\(^1\)H-NMR

\[^13\]C-NMR

```
Ph
OH
MeO
```

C\(_{29}\)H\(_{22}\)O\(_2\)

294.39
anti- 4-(4-methoxyphenyl)octa-6,7-dien-2-ol 50

$^1$H-NMR

$^{13}$C-NMR

C$_{20}$H$_{22}$O$_2$ 294.39
**SUPPORTING INFORMATION**

**syn-4-(4-methoxyphenyl)tetrada-6,7-dien-2-ol 47**

**1H-NMR**

![NMR spectrum](image)

**13C-NMR**

![NMR spectrum](image)
anti-4-(4-methoxyphenyl)tetradeca-6,7-dien-2-ol 51

**1H-NMR**

**13C-NMR**

C$_{21}$H$_{32}$O$_2$

316.49
**syn - 3-(4-methoxyphenyl)-1-phenyltrideca-5,6-dien-1-ol 48**

**1H-NMR**

**13C-NMR**
anti - 3-(4-methoxyphenyl)-1-phenyltrideca-5,6-dien-1-ol 52

$^1$H-NMR

$^{13}$C-NMR
syn-4-methyl-2-vinyltetrahydro-2H-pyran 5

$^1$H-NMR

$^{13}$C-NMR
$^{1}$H-NMR

$^{13}$C-NMR

$^{syn}$-4-dodecyl-2-vinyltetrahydro-2H-pyran 6
**SUPPORTING INFORMATION**

**syn-4-neopentyl-2-vinyltetrahydro-2H-pyran 7**

**1^H-NMR**

**13C-NMR**
**syn-4-cyclopropyl-2-vinyltetrahydro-2H-pyran 8**

**1H-NMR**

**13C-NMR**

\[ C_{10}H_{16}O \]

152.24
syn-4-cyclohexyl-2-vinyltetrahydro-2H-pyran 9

$\text{C}_{13}\text{H}_{22}\text{O}$

194.32
syn-4-(3-phenylpropyl)-2-vinyltetrahydro-2H-pyran 10
**Supporting Information**

**syn-4-phenyl-2-vinyltetrahydro-2H-pyran 2**

**$^1$H-NMR**

**$^{13}$C-NMR**

![NMR spectra](image-url)
syn-4-(naphthalen-2-yl)-2-vinyltetrahydro-2H-pyran 11

$^1$H-NMR

$^{13}$C-NMR
syn-4-[(1,1'-biphenyl)-4-yl]-2-vinyltetrahydro-2H-pyran 12

$^1$H-NMR

$^{13}$C-NMR
syn-4-(p-tolyl)-2-vinyltetrahydro-2H-pyran 13

$\text{H-NMR}$

$\text{C}_{14}\text{H}_{13}\text{O}$  
$202.30$

$\text{C-NMR}$
syn-4-(m-tolyl)-2-vinyltetrahydro-2H-pyran 14

$^1$H-NMR

$^{13}$C-NMR
$\textit{syn}$-4-(o-tolyl)-2-vinyltetrahydro-2H-pyran 15

$^{1}\text{H-NMR}$

$^{13}\text{C-NMR}$
syn-4-mesityl-2-vinyltetrahydro-2H-pyran 16

$^1$H-NMR

$^{13}$C-NMR
**syn-2-vinyl-4-(4-vinylphenyl)tetrahydro-2H-pyran 17**

**1H-NMR**

**13C-NMR**
syn-4-(4-(trifluoromethyl)phenyl)-2-vinyltetrahydro-2H-pyran 18
Supporting Information

**syn-4-(4-bromophenyl)-2-vinyltetrahydro-2H-pyran 19**

**$^{1}$H-NMR**

![1H-NMR spectrum]

**$^{13}$C-NMR**

![13C-NMR spectrum]
**syn-4-(4-methoxyphenyl)-2-vinyltetrahydro-2H-pyran 20**

1H-NMR

13C-NMR
syn-4-(4-(methylthio)phenyl)-2-vinyltetrahydro-2H-pyran 21

$^1$H-NMR

$^{13}$C-NMR
**SUPPORTING INFORMATION**

**syn-4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 22**

**¹H-NMR**

**¹³C-NMR**
syn-4-dodecyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 23

\[
\begin{align*}
\text{H-NMR} & \\
\text{C} & 210.36
\end{align*}
\]
syn-4-neopentyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 25

$^1$H-NMR

$^{13}$C-NMR
**Supporting Information**

**syn-4-cyclopropyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 26**

**1H-NMR**

**13C-NMR**

[C_18H_28O]

236.40
syn-4-cyclohexyl-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 27

$^1$H-NMR

$^{13}$C-NMR
**Supporting Information**

*syn-2-(E)-oct-1-en-1-yl)-4-(3-phenylpropyl)tetrahydro-2H-pyran 28*

**$^1$H-NMR**

**$^{13}$C-NMR**

C$_{22}$H$_{34}$O

314.51
syn-2-(E)-oct-1-en-1-yl)-4-phenyltetrahydro-2H-pyran 29

**1H-NMR**

**13C-NMR**

C_{19}H_{28}O

272.43
syn-4-(naphthalen-2-yl)-2-(E)-oct-1-en-1-yl)tetrahydro-2H-pyran 30

$^1$H-NMR

$^{13}$C-NMR
syn-4-((1,1'-biphenyl]-4-yl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 31

$^1$H-NMR

$^{13}$C-NMR
**Syn-2-((E)-oct-1-en-1-yl)-4-(p-tolyl)tetrahydro-2H-pyran 32**

**\(^1\text{H-NMR}\)**

**\(^{13}\text{C-NMR}\)**
$\text{syn-2-((E)-oct-1-en-1-yl)-4-(m-tolyl)tetrahydro-2H-pyran 33} \ $
syn-2-((E)-oct-1-en-1-yl)-4-(o-tolyl)tetracyclo-2H-pyran 34

$^1$H-NMR

$^{13}$C-NMR
**syn-2-((E)-oct-1-en-1-yl)-4-(4-vinylphenyl)tetrahydro-2H-pyran 36**

**$^1$H-NMR**

**$^{13}$C-NMR**

$$C_{29}H_{38}O\quad 298.47$$
syn-4-(4-bromophenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 37

$^1$H-NMR

$^{13}$C-NMR
syn-4-(4-methoxyphenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 4

$^1$H-NMR

C$_{20}$H$_{30}$O$_2$
302.46

$^{13}$C-NMR

128.68
127.34
126.90
124.93
124.70
123.11
78.23
58.98
54.65
48.62
46.91
45.48
42.86
39.35
39.35
34.13
syn-4-(4-(methylthio)phenyl)-2-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 38

$^1$H-NMR

$^{13}$C-NMR
syn-2-((E)-oct-1-en-1-yl)-4-(4-(trifluoromethyl)phenyl)tetrahydro-2H-pyran 39

$^1$H-NMR

$^{13}$C-NMR
syn-2,2-dimethyl-6-((E)-oct-1-en-1-yl)-4-(4-( trifluoromethyl)phenyl)tetrahydro-2H-pyran 40

$\text{C}_{22}\text{H}_{34}\text{O}_{2}$

$\delta$ 330.26

$^1$H-NMR

$^1$C-NMR

$^1$H-NMR

$^1$C-NMR
syn-2-((E)-2-cyclohexylvinyl)-4-(4-methoxyphenyl)tetrahydro-2H-pyran 41

$^1$H-NMR

$^{13}$C-NMR
syn-4-(4-methoxyphenyl)-2-((E)-4-phenylbut-1-en-1-yl)tetrahydro-2H-pyran 42
syn-4-(4-methoxyphenyl)-2-((E)-3-phenylprop-1-en-1-yl)tetrahydro-2H-pyran 43

$^1$H-NMR

$^{13}$C-NMR
syn-4-(4-methoxyphenyl)-2-((E)-5-(methylthio)pent-1-en-1-yl)tetrahydro-2H-pyran 44

$^1$H-NMR

$^{13}$C-NMR
4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 45A

$^1$H-NMR

$^{13}$C-NMR
4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 49A

$^1$H-NMR

$^{13}$C-NMR

major product
$C_{16}H_{20}O_2$

232.32
4-(4-methoxyphenyl)-3,3-dimethyl-2-vinyltetrahydro-2H-pyran 49B

**$	extsuperscript{1}$H-NMR**

![NMR spectrum](image)

**$^{13}$C-NMR**

![NMR spectrum](image)
4-(4-methoxyphenyl)-2-phenyl-6-vinyltetrahydro-2H-pyran 46A

$^1$H-NMR

$^{13}$C-NMR
4-(4-methoxyphenyl)-2-phenyl-6-vinyltetrahydro-2H-pyran 50A

**$^{1}H$-NMR**

![NMR spectrum](image)

**$^{13}C$-NMR**

![NMR spectrum](image)
4-(4-methoxyphenyl)-2-phenyl-6-vinyltetrahydro-2H-pyran 50B

$^1$H-NMR

$^{13}$C-NMR
4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 47A

$^1$H-NMR

$^{13}$C-NMR
4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 51B
4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 52A
4-(4-methoxyphenyl)-2-methyl-6-((E)-oct-1-en-1-yl)tetrahydro-2H-pyran 52B

$^1$H-NMR

$^{13}$C-NMR
SUPPORTING INFORMATION

ethyl hepta-3,4-dienoate 131

$^{1}H$-NMR

$^{13}C$-NMR
ethyl (E)-nona-2,5,6-trienoate 132

$\text{C}_{11}\text{H}_{16}\text{O}_{2}$

1H-NMR

13C-NMR
ethyl (3S)-3-methylnona-5,6-dienoate 133

$\text{C}_{19}\text{H}_{26}\text{O}_{2}$

1H-NMR

$\text{C}^1$-NMR

$\text{C}^{13}$-NMR
(2S,4R)-2-((E)-but-1-en-1-yl)-4-methyltetrahydro-2H-pyran 55ee

$^{1}H$-NMR

$^{13}$C-NMR
syn-(4-cyclopropyl-2-octyltetrahydro-2H-pyran 56

$^{1}$H-NMR

$^{13}$C-NMR
sup 2-octyl-4-(4-phenylbutyl)tetrahydro-2H-pyran 57
Supporting Information

syn-4-((1,1′-biphenyl)-4-yl)-2-octyltetrahydro-2H-pyran 58

$^1$H-NMR

$^{13}$C-NMR
*syn*-4-(4-methoxyphenyl)-2-(4-phenylbutyl)tetrahydro-2H-pyran 59

**1H-NMR**

**13C-NMR**
7-(4-methoxyphenyl)-7-oxohept-1-yn-3-yl acetate

$^1$H-NMR

$^{13}$C-NMR

C$_{16}$H$_{14}$O$_4$

274.31
7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hepta-5,6-dien-1-one 62

1H-NMR

13C-NMR
(1S)-7-(4-(benzyloxy)phenyl)-1-(4-methoxyphenyl)hepta-5,6-dien-1-ol 63

**1H-NMR**

**13C-NMR**
Bis(4-(trifluoromethyl)phenyl)phosphine oxide 134

\[ \text{\textsuperscript{1}H-NMR} \]

\[ \text{\textsuperscript{13}C-NMR} \]
1, 1'-Bis[bis[4-(trifluoromethyl)phenyl]phosphino]ferrocene 135

\(^1\)H-NMR

\[^{13}\)C-NMR
$^{19}$F-NMR

$C_{38}H_{34}F_{12}FeP_2$

836.46 g/mol

$^{31}$P-NMR
SUPPORTING INFORMATION

**bis(3,5-bis(trifluoromethyl)phenyl)phosphine oxide**

$^{1}H$-NMR

$^{13}C$-NMR

C$_{16}$H$_{12}$F$_{12}$OP

474.19
1,1'-Bis[bis[3,5-bis(trifluormethyl)phenyl]phosphino]ferrocen (L5) 137

$^{1}H$-NMR

$^{13}C$-NMR

$C_{42}H_{26}F_{24}FeP_{2}$

109838 g/mol
GC – analysis of rac and S-3-methylhepta-5,6-dienoate

| Spectra | Peak Index | t [min] | Area [%] |
|---------|------------|---------|----------|
| A       | 1          | 29.005  | 49.17    |
| A       | 2          | 30.048  | 50.83    |
| B       | 1          | 28.975  | 3.17     |
| B       | 2          | 29.748  | 96.83    |
GC – analysis of rac and R, S 4-methyl-2-vinyltetrahydro-2H-pyran

| Spectra | Peak Index | t [min] | Area [%] |
|---------|------------|---------|----------|
| A       | 1          | 4.332   | 49.28    |
| A       | 2          | 4.551   | 50.71    |
| B       | 1          | 4.338   | 97.23    |
| B       | 2          | 4.565   | 2.77     |
GC – analysis of rac and S ethyl 3-methyl nona-5,6-dienoate

| Spectra | Peak Index | t [min]  | Area [%] |
|---------|-----------|---------|----------|
| A       | 1         | 127.745 | 49.37    |
| A       | 2         | 131.272 | 23.10    |
| A       | 3         | 136.418 | 27.53    |
| B       | 1         | 132.021 | 0.78     |
| B       | 2         | 136.505 | 99.22    |
GC – analysis of rac and (2S,4R)-2-((E)-but-1-en-1-yl)-4-methyltetrahydro-2H-pyran

| Spectra | Peak Index | t [min]  | Area [%] |
|---------|------------|----------|----------|
| A       | 1          | 25.490   | 50.52    |
| A       | 2          | 26.393   | 49.82    |
| B       | 1          | 132.021  | 2.09     |
| B       | 2          | 136.505  | 97.91    |
HPLC – analysis of rac and (-)-centrolobine

![HPLC chart](image)

| Spectra | Peak Index | Area [%] | Peak Index | Area [%] |
|---------|------------|----------|------------|----------|
| A       | 1          | 50.65    | 2          | 50.65    |
| A       | 2          | 50.65    | 1          | 50.65    |
| B       | 1          | 5.21     | 1          | 1.00     |
| B       | 2          | 95.89    | 2          | 95.89    |
14 References

[1] P. Spreider, A. Haydl, M. Heinrich, B. Breit Angew. Chem. 2016, 128, 15798-15802; Angew. Chem. Int. Ed. 2015, 55, 15569-15573.
[2] J. P. Schmidt, B. Breit, Chem. Sci. 2019, 10, 3074-3079
[3] NMR-Spectra of diastereomeric mixture. Overlapping signals were discussed as multiplet.
[4] NMR-Spectra of single diastereomer.
[5] NMR-Spectra of syn-product. Some spectra are containing traces of anti-product signals from this compound were not analysed separately. Overlapping signals were discussed as multiplet.
[6] NMR-Spectra of syn-E-product. Some spectra are containing traces of syn-Z-product, signals from this compound were not analysed separately. Overlapping signals were discussed as multiplet.