Supporting information

The Ruthenium-catalyzed olefin metathesis-double bond isomerization sequence

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Syntheses and analytical data of alcohols 1

1-(2-Methoxy-phenyl)-prop-2-en-1-ol (1a): To a solution of 2-methoxy-benzaldehyde (1.20 mL, 10.0 mmol) in ether (25 mL) was added a solution of vinyl magnesiumchloride in THF (1.7 M, 7.6 mL, 13 mmol) at 0°C. The mixture was stirred for 30 min., diluted with ether and poured onto aqueous NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted twice with MTBE. The combined organic extracts were dried with MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The residue was distilled (0.1 mbar, bp 95°C) to give **1a** (1.50 g, 91%). ¹H NMR (500 MHz, CDCl₃): δ = 2.81 (s, 1 H), 3.87 (s, 3 H), 5.17 (d, *J* = 10.5 Hz, 1 H), 5.32 (d, *J* = 17.2 Hz, 1 H), 5.41 (dd, *J* = 6.2, 5.5 Hz, 1 H), 6.14 (ddd, *J* = 17.2, 10.5, 5.5 Hz, 1 H), 6.90 (d, *J* = 7.7 Hz, 1 H), 6.96 (dd, *J* = 7.5, 7.5 Hz, 1 H), 7.27 (ddd, *J* = 7.7, 7.5, 1.7 Hz, 1 H), 7.31 (dd, *J* = 7.5, 1.3 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 55.3 (3), 71.6 (1), 110.7 (1), 114.5 (2), 120.9 (1), 127.4 (1), 128.7 (1), 130.7 (0), 139.4 (1), 158.2 (0) ppm. IR (film, KBr-plates): ν = 1491 (s), 1651 (s), 3419 (s) cm⁻¹. MS (EI): *m/z* = 164 (78) [M⁺], 107 (100). C₁₀H₁₂O₂ (164.2): calcd. C 73.2, H 7.4; found: C 72.7, H 7.3.

1-(3-Methoxy-phenyl)-prop-2-en-1-ol (1b): Following the procedure for **1a**, **1b** was obtained from 3-methoxy-benzaldehyde (2.95 g, 22.0 mmol). Bp 80°C (0.05 mbar), yield: 2.65 g (73%). ¹H NMR (500 MHz, CDCl₃): δ = 2.20 (d, *J* = 3.7 Hz, 1 H), 3.78 (s, 3 H), 5.14 (dd, *J* = 6.0, 3.7 Hz, 1 H), 5.17 (d, *J* = 10.2 Hz, 1 H), 5.33 (d, *J* = 17.2 Hz, 1 H), 6.01 (ddd, *J* = 17.2, 10.2, 6.0 Hz, 1 H), 6.81 (dd, *J* = 8.0, 2.3 Hz, 1 H), 6.91 (d, *J* = 2.3 Hz, 1 H), 6.93 (d, *J* = 7.7 Hz, 1 H), 7.25 (dd, *J* = 8.0, 7.7 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 55.2 (3), 75.2 (1), 111.7 (1), 113.2 (1), 115.1 (1), 118.6 (1), 129.5 (1), 140.0 (1), 144.2 (0), 159.7 (0) ppm. IR (film, KBr-plates): ν = 1262 (s), 1488 (s), 1600 (s), 3423 (s) cm⁻¹. MS (EI): *m/z* = 164 (100) [M⁺], 109 (98), 77 (90), 55 (90). C₁₀H₁₂O₂ (164.2): calcd. C 73.2, H 7.4; found: C 72.9, H 7.5.

5-Phenyl-pent-1-en-3-ol (1c):¹ Following the procedure for **1a**, **1c** was obtained from 3-phenylpropionic aldehyde (2.70 mL, 20.0 mmol). Bp 70°C (0.15 mbar), yield: 2.43 g (75%). ¹H NMR (500 MHz, CDCl₃): δ = 1.62 (d, *J* = 3.2 Hz, 1 H), 1.81-1.89 (2 H), 2.64-2.77 (2 H), 4.12 (m, 1 H), 5.13 (d, *J* = 10.2 Hz, 1 H), 5.23 (d, *J* = 17.0 Hz, 1 H), 5.90 (ddd, *J* = 17.0, 10.2, 6.2 Hz, 1 H), 7.18 (t, *J* = 7.3 Hz, 1 H), 7.20 (d, *J* = 7.0 Hz, 2 H), 7.27 (dd, *J* = 7.3, 7.0 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 31.6 (2), 38.5 (2), 72.4 (1), 114.9 (2), 125.8 (1), 128.4 (1), 128.4 (1) 141.0 (1), 141.8 (0) ppm.

1-(5,6-Dihydro-4H-pyran-2-yl)-prop-2-en-1-ol (1d):² A solution of 2,3-dihydropyran (0.91 mL, 10.0 mmol) in THF (20 mL) is cooled to -78°C. A solution of *tert*-BuLi in pentane (11.8

mL, 20.0 mmol, 1.7 M) is added dropwise and the solution is stirred at -10°C for 1 hour. The mixture is recooled to -78°C, and acroleine (1.67 mL, 30.0 mmol) is added slowly. Stirring is continued at this temperature for another hour. The reaction is quenched by addition of saturated NH₄Cl solution; the organic layer is separated and the aqueous layer extracted with MTBE. The combined organic extracts are dried with MgSO₄, filtered, and the solvent is evaporated. The residue is purified by flash chromatography on silica (cyclohexane/MTBE 5 : 1 (v/v)). Yield: 0.64 g (42%). ¹H NMR (500 MHz, C₆D₆): δ = 1.35 – 1.45 (2 H), 1.70 – 1.80 (2 H), 2.40 (d, *J* = 5.3 Hz, 1 H), 3.65 - 3.75 (2H), 4.51 (dd, *J* = 5.5, 5.3 Hz, 1 H), 4.75 (dd, *J* = 3.7, 3.7 Hz, 1 H), 5.10 (ddd, *J* = 10.5, 1.5, 1.5 Hz, 1 H), 5.40 (ddd, *J* = 17.2, 1.5, 1.5 Hz, 1 H), 6.06 (ddd, *J* = 17.2, 10.5, 5.5 Hz, 1 H). ¹³C-NMR (125 MHz, C₆D₆): δ = 20.1 (2), 22.6 (2), 66.2 (2), 73.3 (1), 96.2 (1), 115.0 (2), 138.8 (1), 154.9 (0). IR (film, NaCl-plates): ν = 3423 (s), 2931 (s), 1676 (s), 1232 (s), 1062 (s) cm⁻¹. MS (EI): *m/z* = 140 (34) [M⁺], 55 (100).

1-Vinyl-cyclohexanol (1e): Following the procedure for **1a**, **1e** was obtained from cyclohexanone (2.90 g, 29.5 mmol). Bp 68°C (13 mbar), yield: 2.83 g (76%). ¹H NMR (500 MHz, CDCl₃): δ = 1.24 (m, 1 H), 1.40-1.65 (10 H), 4.98 (dd, *J* = 10.8, 1.3 Hz, 1 H), 5.19 (dd, *J* = 17.3, 1.3 Hz, 1 H), 5.92 (dd, *J* = 17.3, 10.8 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 22.0 (2), 25.4 (2), 37.5 (2), 71.7 (0), 111.4 (1), 146.0 (1) ppm. IR (film, KBr-plates): ν = 1448 (s), 1640 (m), 1933 (s), 3385 (s) cm⁻¹. MS (EI): *m/z* = 126 (6) [M⁺], 111 (26), 83 (100). C₈H₁₄O (126.2): calcd. C 76.1, H 11.2; found: C 75.6, H 11.2.

1-Phenyl-hex-5-en-3-ol (1f): To a solution of 3-phenyl propionaldehyde (6.60 mL, 50.0 mmol) in ether (20 mL) was added a solution of allyl magnesiumbromide in ether (1.25 M, 60 mL, 75 mmol) at 0°C. The mixture was stirred for 30 min., diluted with ether and poured onto aqueous NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted twice with MTBE. The combined organic extracts were dried with MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The residue was distilled (0.15 mbar, bp 80°C) to give **1f** (7.19 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ = 1.64 (s, 1 H), 1.74-1.81 (2 H), 2.17 (ddd, *J* = 14.1, 7.8, 7.8 Hz, 1 H), 2.31 (dm, *J* = 14.1 Hz, 1 H), 2.68 (ddd, *J* = 14.3, 8.8, 7.5 Hz, 1 H), 2.80 (ddd, *J* = 14.3, 8.8, 6.8 Hz, 1 H), 3.66 (m, 1 H), 5.10-5.16 (2 H), 5.80 (dddd, *J* = 17.6, 9.5, 8.0, 6.8 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 1 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 7.27 (dd, *J* = 7.5, 7.5 Hz, 2 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 32.0 (2), 38.4 (2), 42.0 (2), 69.9 (1), 118.3 (2), 125.8 (1), 128.4 (1), 128.4 (1), 134.6 (1), 142.0 (0) ppm. IR (film, KBr-plates): ν = 1454 (s), 1495 (s), 1603 (s), 1641 (s), 2931 (s), 3406 (s) cm⁻¹. MS (EI): *m/z* = 176 (10) [M⁺], 158 (100). C₁₂H₁₆O (176.3): calcd. C 81.8, H 9.2; found: C 81.6, H 9.1.

(*R*)-1-Phenyl-hex-5-en-3-ol ((*R*)-1f):³ To a solution of (-)-DIP-chloride (3.75 g, 11.7 mmol) in ether (20 mL) was added a solution of allylmagnesium bromide in ether (1.5 M, 7.0 mL, 10.5 mmol) at -78°C. The mixture was warmed to 20°C and stirred at this temperature for 1 hour. After re-cooling the solution to -78°C, 3-phenyl propionaldehyde (1.21 g, 9.0 mmol), dissolved in ether (5 mL), was added slowly. Stirring was continued at -78°C for 90 min. and for 10 hours at 20°C. A solution of aqueous NaOH (3N, 20 mL) and aqueous H₂O₂ (30%, 8.0 mL) was added dropwise, causing a vigorous reaction. After heating to reflux for one hour, the mixture was diluted with water (20 mL), and extracted with MTBE. The combined organic extracts were dried with MgSO₄, filtered and the solvent was evaporated in vacuo. Isopinocampheol, resulting from oxidative cleavage of the borane, was removed by distillation (0.08 mbar, 45°C). The residue was chromatographed on silica using cyclohexane/MTBE mixtures of increasing polarity as eluent, to give (*R*)-1f (820 mg, 52%). The ee was determined by HPLC analysis (Daicel Chiralcel OD, eluent: heptane/2-propanol 90:10, flow 1.0 mLmin⁻¹, 20°C) to be 90% after comparison with racemic 1f under identical conditions. $[\alpha]_D^{20} = +16.8$ (*c* 1.46, CH₂Cl₂) for 90% ee.

1-Phenyl-hexa-1,5-dien-3-ol (1g):⁴ Following the procedure for 1e, 1f was obtained from cinnam aldehyde (6.30 mL, 50.0 mmol). Bp 95°C (0.15 mbar), yield: 8.04 g (92%). ¹H NMR (400 MHz, CDCl₃): δ = 2.00 (s, 1 H), 2.28-2.43 (2 H), 4.29 (ddd, *J* = 6.3, 6.0, 6.0 Hz, 1 H), 5.11 (dm, *J* = 10.3 Hz, 1 H), 5.13 (dm, *J* = 17.1 Hz, 1 H), 5.80 (dddd, *J* = 17.1, 10.3, 7.3, 7.0 Hz, 1 H), 6.18 (dd, *J* = 15.8, 6.3 Hz, 1 H), 6.55 (d, *J* = 15.8 Hz, 1 H), 7.18 (tt, *J* = 7.0, 1.5 Hz, 1 H), 7.24 (dd, *J* = 7.3, 7.0 Hz, 2 H), 7.32 (d, *J* = 7.3 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 41.9 (2), 71.6 (1), 118.4 (2), 126.4 (1), 127.6 (1), 128.5 (1), 130.2 (1), 131.5 (1), 134.0 (1), 136.6 (0) ppm. IR (film, KBr-plates): ν = 693 (s), 749 (s), 967 (s), 1494 (s), 1641 (s), 3382 (s) cm⁻¹. MS (EI): *m/z* = 174 (2) [M⁺], 133 (100).

1-(3-Phenyl-oxiranyl)-but-3-en-1-ol (1h): To a solution of 1g (1.00 g, 5.7 mmol) in DCM (20 mL) was added VO(acac)₂ (76 mg, 5 mol%), followed by *tert*-BuOOH (5.5 M solution in decane, 1.5 mL, 8.0 mmol). The mixture was stirred until the starting material was fully consumed, as indicated by TLC (cyclohexane/MTBE 5:1), diluted with MTBE and washed with aqueous Na₂SO₃ solution. The organic extracts were dried with MgSO₄, filtered and evaporated. The residue was purified by flash chromatography on silica, followed by Kugelrohr distillation (0.08 mbar, 150°C), to give 1g (0.98 g, 90%) as an inseparable 2:1 mixture of diastereoisomers. ¹H NMR (400 MHz, CDCl₃): δ = 2.17-2.23 (1 H), 2.30-2.50 (2 H), 3.06 (dd, *J* = 4.3, 2.0 Hz, 1 H), 3.08 (dd, *J* = 3.3, 2.0 Hz, 1 H), 3.73 (m, 1 H), 3.86 (d, *J* = 2.0 Hz), 3.95 (d, *J* = 2.0 Hz), 3.97 (m, 1 H), 5.11-5.19 (2 H, =CH₂), 5.86 (dddd, *J* = 17.5,

10.0, 7.3, 7.3 Hz, 1 H), 5.88 (dddd, $J = 17.5, 10.3, 7.3, 7.3$ Hz, 1 H), 7.23-7.36 (5 H) ppm. ^{13}C NMR (100 MHz, CDCl_3) for major isomer: $\delta = 37.9$ (2), 55.0 (1), 64.3 (1), 68.1 (1), 118.3 (2), 125.6 (1), 128.2 (1), 128.4 (1), 133.4 (1), 136.7 (0) ppm. ^{13}C NMR (100 MHz, CDCl_3) for major isomer: $\delta = 39.0$ (2), 56.2 (1), 64.9 (1), 70.0 (1), 118.5 (2), 125.5 (1), 128.2 (1), 128.5 (1), 133.2 (1), 136.5 (0) ppm. IR (film, NaCl-plates): $\nu = 698$ (s), 7509 (s), 918 (s), 1463 (s), 1642 (s), 2979 (m), 3074 (m), 3442 (s) cm^{-1} . MS (EI): $m/z = 190$ (1) $[\text{M}^+]$, 107 (90), 103 (100). $\text{C}_{12}\text{H}_{14}\text{O}_2$ (190.2): calcd. C 75.8, H 7.4; found: C 75.4, H 7.8.

1-(2,2-Dimethyl-5-phenyl-[1,3]dioxolan-4-yl)-but-3-en-1-ol (1i): (2*S*, 3*R*)-2,3-Dihydroxy-3-phenyl-propionic acid methyl ester (3).⁵ To a solution of methyl cinnamate (3.40 g, 20.0 mmol) in *tert*-butanol (30 mL) and water (30 mL) was added AD-mix $\beta^{\text{®}}$ (28.0 g). The mixture was stirred at 20°C for 10 hours and then diluted with ethyl acetate (80 mL). The organic layer was separated, the aqueous layer was extracted twice with ethyl acetate, the combined organic extracts were dried, filtered and the solvent was evaporated to give **3** (3.92 g, 100%) as a colourless solid, mp 85°C, which was used in the next step without further purification. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.90$ (s, 1 H), 3.20 (s, 1 H), 3.80 (s, 3 H), 4.37 (d, $J = 2.7$ Hz, 1 H), 5.01 (d, $J = 2.7$ Hz, 1 H), 7.28-7.41 (5 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 52.8$ (3), 74.4 (1), 74.7 (1), 126.2 (81), 128.1 (1), 128.4 (1), 139.0 (0), 173.1 (0) ppm. (4*S*, 5*R*)-2,2-Dimethyl-5-phenyl-[1,3]dioxolane-4-carboxylic acid methyl ester (4).⁵ Diol **3**, 2,2-dimethoxypropane (5.00 mL, 41 mmol) and para-toluene sulfonic acid (100 mg, 2.6 mol%) were dissolved in toluene (80 mL) and heated to reflux for 1 hour. The solution was concentrated in vacuo to a volume of approximately 20 mL, and toluene (80 mL) and 2,2-dimethoxypropane (5.00 mL, 41 mmol) were added. The solution was again heated to reflux for 1 hour, all volatiles were removed in vacuo, the residue was diluted with ethyl acetate, washed with aqueous Na_2CO_3 solution, dried with MgSO_4 and filtered. Evaporation of the solvent and flash chromatography on silica (hexanes/ethyl acetate 2:1) gave **4** (3.40 g, 72% based on methyl cinnamate). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.50$ (s, 3 H), 1.54 (s, 3 H), 3.26 (s, 3 H), 4.36 (d, $J = 7.5$ Hz, 1 H), 5.29 (d, $J = 7.5$ Hz, 1 H), 7.10 (t, $J = 7.5$ Hz), 7.16 (dd, $J = 7.5, 7.5$ Hz, 2 H), 7.43 (d, $J = 7.5$ Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 26.0$ (3), 27.1 (3), 51.6 (3), 81.2 (1), 81.9 (1), 111.7 (0), 126.7 (1), 128.5 (1), 128.7 (1), 138.7 (0), 170.7 (0) ppm. **1-(2,2-Dimethyl-5-phenyl-[1,3]dioxolan-4-yl)-but-3-en-1-ol (1i):** To a solution of ester **4** (3.40 g, 14.4 mmol) in ether (30 mL) was added DIBAL-H (1.0 M solution in cyclohexane, 20.0 mmol, 20.0 mL) at -90°C. The mixture was stirred at this temperature until the ester was completely consumed, as indicated by TLC (hexane/ether 2:1). At this point allylmagnesium bromide (1.0 M solution in ether, 25.0 mmol, 25.0 mL) was added, and

the solution was allowed to warm to ambient temperature. Stirring was continued at ambient temperature for 3 hours, and the mixture was poured onto water. The inorganic precipitates were dissolved with a minimum amount of concentrated HCl (aq.), the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were dried with MgSO₄, filtered, and the solvent was evaporated. The residue was purified by flash chromatography on silica and subsequently by Kugelrohr distillation (0.1 mbar, 175°C) to give **1i** (2.90 g, 81%) as a 1.2 : 1 mixture of diastereoisomers. *NMR-data for major isomer*: ¹H NMR (400 MHz, CDCl₃): δ = 1.43 (s, 3 H), 1.50 (s, 3 H), 1.73 (d, *J* = 4.5 Hz, 1 H), 2.04-2.32 (2 H), 3.77 (m, 1 H), 3.88 (dd, *J* = 7.8, 5.3 Hz, 1 H), 4.91 (d, *J* = 10.0 Hz, 1 H), 4.95 (d, *J* = 17.0 Hz, 1 H), 5.12 (d, *J* = 7.8 Hz, 1 H), 5.64 (dddd, *J* = 17.1, 10.0, 7.0, 7.0 Hz, 1 H), 7.06-7.20 (3 H), 7.48 (d, *J* = 7.5 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.4 (3), 27.5 (3), 38.3 (2), 71.6 (1), 80.3 (1), 85.4 (1), 109.2 (0), 117.7 (2), 127.1 (1), 128.5 (1), 128.7 (1), 134.6 (1), 140.0 (0) ppm. *NMR-data for minor isomer*: ¹H NMR (400 MHz, CDCl₃): δ = 1.44 (s, 3 H), 1.51 (s, 3 H), 1.93 (d, *J* = 9.0 Hz, 1 H), 2.04-2.32 (2 H), 3.56 (m, 1 H), 3.72 (dd, *J* = 8.5, 2.0 Hz, 1 H), 4.81 (d, *J* = 17.0 Hz, 1 H), 4.96 (d, *J* = 10.2 Hz, 1 H), 5.16 (d, *J* = 8.5 Hz, 1 H), 5.71 (dddd, *J* = 17.5, 10.8, 7.3, 7.0 Hz, 1 H), 7.06-7.20 (3 H), 7.40 (d, *J* = 7.3 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 27.1 (3), 27.3 (3), 40.1 (2), 68.0 (1), 79.5 (1), 85.6 (1), 109.1 (0), 117.5 (2), 127.1 (1), 128.5 (1), 128.7 (1), 134.9 (1), 138.8 (0) ppm. IR (film, NaCl-plates): ν = 1059 (s), 1231 (s), 1371 (s), 1455 (s), 1642 (m), 2985 (s), 3477 (s) cm⁻¹. MS (EI): *m/z* = 248 (4) [M⁺], 148 (71), 43 (100). C₁₅H₂₀O₃ (248.3): calcd. C 72.6, H 8.1; found: C 72.7, H 8.1.

Non-1-en-4-ol (1j): Following the procedure for **1f**, **1j** was obtained from hexanal (2.50 mL, 20.0 mmol). Bp 60°C (8.0 mbar), yield: 2.50 g (88%). ¹H NMR (500 MHz, CDCl₃): δ = 0.86 (t, *J* = 7.0 Hz, 3 H), 1.20-1.47 (8 H), 1.63 (s (br), 1 H), 2.10 (ddd, *J* = 14.0, 7.8, 7.8 Hz, 1 H), 2.27 (dddm, *J* = 14.0, 7.2, 5.2 Hz, 1 H), 3.60 (m, 1 H), 5.07-5.13 (2 H), 5.80 (m, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 14.0 (3), 22.6, 25.3, 31.8, 36.8, 41.9 (2), 70.7 (1), 118.0 (2), 134.9 (1) ppm. IR (film, NaCl-plates): ν = 995 (s), 1641 (m), 2859 (s), 2930 (s), 2958 (s), 3077 (w), 3363 (s) cm⁻¹. MS (EI): *m/z* = 141 (4) [M⁺-1], 99 (48), 83 (55), 55 (100). C₉H₁₈O (142.2): calcd. C 76.0, H 12.8; found: C 75.8, H 13.3.

1-Furan-2-yl-but-3-en-1-ol (1k): Following the procedure for **1f**, **1k** was obtained from furan-2-carbaldehyde (9.90 mL, 120.0 mmol). Bp 90°C (12.0 mbar), yield: 13.20 g (80%). ¹H NMR (500 MHz, CDCl₃): δ = 2.30 (s, 1 H), 2.53-2.65 (2 H), 4.70 (dd, *J* = 6.7, 6.5 Hz, 1 H), 5.10 (d, *J* = 10.2 Hz, 1 H), 5.15 (d, *J* = 17.3 Hz, 1 H), 5.77 (dddd, *J* = 17.3, 10.2, 7.2, 7.0 Hz, 1 H), 6.22 (d, *J* = 3.2 Hz, 1 H), 6.30 (dd, *J* = 3.2, 1.7 Hz, 1 H), 7.35 (d, *J* = 1.7 Hz, 1 H)

ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 40.0 (2), 66.9 (1), 106.0 (1), 110.1 (1), 118.4 (2), 133.7 (1), 141.9 (1), 156.0 (0) ppm. IR (film, NaCl-plates): ν = 739 (s), 1011 (s), 1149 (s), 1504 (m), 1642 (s), 3388 (s) cm^{-1} . MS (EI): m/z = 138 (3) [M^+], 97 (100). $\text{C}_8\text{H}_{10}\text{O}_2$ (138.2): calcd. C 69.5, H 7.3; found: C 68.8, H 7.5.

1-Phenyl-but-3-en-1-ol (1f).⁶ Following the procedure for **1f**, **1f** was obtained from benzaldehyde (5.05 mL, 50.0 mmol). Bp 82°C (0.9 mbar), yield: 6.52 g (88%).

1-(2-Methoxy-naphthalen-1-yl)-but-3-en-1-ol (1m). Following the procedure for **1f**, **1m** was obtained from 2-methoxy-1-naphthaldehyde (2.00 g, 10.7 mmol). Yield: 1.92 g (79%). ^1H NMR (400 MHz, CDCl_3): δ = 2.64 (ddd, J = 14.3, 8.3, 7.5 Hz, 1 H), 2.84 (ddd, J = 14.3, 8.3, 7.5 Hz, 1 H), 3.92 (d, J = 9.5 Hz, 1 H), 3.99 (s, 3 H), 5.05 (dm, J = 10.0 Hz, 1 H), 5.13 (dm, J = 17.3 Hz, 1 H), 5.59 (ddd, J = 8.8, 7.5, 5.5 Hz, 1 H), 5.89 (dddd, J = 17.3, 10.0, 7.0, 7.0 Hz, 1 H), 7.34 (dd, J = 7.8, 7.0 Hz, 1 H), 7.47 (ddd, J = 8.5, 6.8, 1.3 Hz, 1 H), 7.78 (d, J = 9.0 Hz, 1 H), 7.78 (d, J = 9.0 Hz, 1 H), 8.08 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 42.2 (2), 56.3 (3), 69.6 (1), 113.2 (1), 117.0 (2), 123.0 (1), 123.6 (1), 123.9 (0), 126.6 (1), 128.6 (1), 129.3 (0), 129.4 (1), 131.5 (0), 135.5 (1), 154.5 (0) ppm. IR (film, NaCl-plates): ν = 1247 (s), 1596 (s), 1623 (s), 1639 (m), 2839 (s), 2939 (s), 3073 (m), 3424 (s) cm^{-1} . MS (EI): m/z = 228 (2) [M^+], 210 (16), 187 (100). $\text{C}_{15}\text{H}_{16}\text{O}_2$ (228.3): calcd. C 78.9, H 7.1; found: C 78.7, H 7.2.

1-Benzyloxy-pent-4-en-2-ol (1t). *Benzyloxy-acetic acid butyl ester (5).* Butyl glycolate (2.60 mL, 20.0 mmol) was dissolved in THF (40 mL) and NaH (1.20 g, 30 mmol, 60% dispersion in mineral oil) was added. The mixture was heated to reflux for 30 min. Benzyl bromide (3.00 mL, 25.0 mmol) was added, and the mixture was heated to reflux until the starting material was fully consumed. After aqueous workup, the residue was purified by flash chromatography on silica to give **5** (2.24 g, 53%). ^1H NMR (400 MHz, CDCl_3): δ = 0.91 (t, J = 7.5 Hz, 3 H), 1.36 ("sext", J = 7.5 Hz, 2 H), 1.62 ("pent.", J = 7.5 Hz, 2 H), 4.07 (s, 2 H), 4.15 (t, J = 6.8 Hz, 2 H), 4.62 (s, 2 H), 7.20-7.38 (5 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 13.6 (3), 19.0 (2), 30.5 (2), 64.7 (2), 67.1 (2), 73.3 (2), 127.9 (1), 128.0 (1), 128.4 (1), 137.1 (0), 170.4 (0) ppm. IR (film, NaCl-plates): ν = 739 (s), 1132 (s), 1201 (s), 1455 (s), 1755 (s), 2873 (s), 2960 (s) cm^{-1} . MS (EI): m/z = 222 (1) [M^+], 107 (53), 91 (100), 56 (93). *1-Benzyloxy-pent-4-en-2-ol (1t).*⁷ Following the procedure for **1i**, **1t** was obtained from ester **5** (2.20 g, 9.9 mmol). Bp 75°C-80°C (0.15 mbar), yield: 1.32 g (69%). ^1H NMR (400 MHz, CDCl_3): δ = 2.25 ("t", J = 7.0 Hz, 2 H), 2.34 (s, 1 H), 3.36 (dd, J = 9.5, 7.0 Hz, 1 H), 3.50 (dd, J = 9.5, 3.5 Hz, 1 H), 3.86 (dddd, J = 7.0, 7.0, 7.0, 3.5 Hz, 1 H), 4.54 (s, 2 H), 5.07 (dm, J = 10.0 Hz, 1 H), 5.10 (dm, J = 17.1 Hz, 1 H), 5.80 (dddd, J = 17.1, 10.0, 7.0, 7.0 Hz, 1 H), 7.25-7.37 (5 H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 37.8 (2), 69.6 (1), 73.3 (2), 73.8 (2), 117.7 (2), 127.7 (1), 127.7 (1), 128.4 (1), 134.2 (1), 137.9 (0) ppm.

1-(4-Methoxy-phenyl)-pent-4-en-1-ol (1u).⁸ Mg turnings (0.30 g, 12.5 mmol) were stirred in dry ether (5 mL) for 20 min. 1-Bromobutene (1.20 g, 8.8 mmol), dissolved in ether (5 mL), was added slowly. After complete addition of the bromobutene, stirring was continued at ambient temperature for 30 min. A solution of 4-methoxy benzaldehyde (1.09 g, 8.0 mmol) in ether (10 mL) was then slowly added at ambient temperature. The reaction mixture was poured onto aqueous NH_4Cl solution, the aqueous layer was extracted twice with MTBE, the combined organic extracts were dried with MgSO_4 , filtered and all volatiles were evaporated. The residue was purified by flash chromatography on silica to give **1u** (1.15 g, 68%). ^1H NMR (500 MHz, CDCl_3): δ = 1.78 (m, 1 H), 1.85-1.90 (2 H), 2.02-2.20 (2 H), 3.81 (s, 3 H), 4.64 (dd, J = 6.0, 6.0 Hz, 1 H), 4.97 (d, J = 10.2 Hz, 1 H), 5.03 (d, J = 17.2 Hz, 1 H), 5.84 (dddd, J = 17.2, 10.2, 6.7, 6.7 Hz, 1 H), 6.88 (d, J = 8.5 Hz, 2 H), 7.27 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 30.1 (2), 37.9 (2), 55.3 (3), 73.6 (1), 113.8 (1), 114.9 (2), 127.1 (1), 136.7 (0), 138.2 (1), 159.0 (0) ppm. IR (film, NaCl-plates): ν = 1248 (s), 1513 (s), 1612 (s), 2935 (s), 3406 (s) cm^{-1} . MS (EI): m/z = 192 (10) [M^+], 137 (100), 109 (40). $\text{C}_{12}\text{H}_{16}\text{O}_2$ (192.3): calcd. C 75.0, H 8.4; found: C 75.2, H 8.3.

Syntheses and analytical data of dienes 2

1-(1-Allyloxy-allyl)-2-methoxy-benzene (2a). To a solution of **1a** (1.25 g, 7.6 mmol) in THF (25 mL) was added NaH (60% dispersion in mineral oil, 0.60 g, 15.0 mmol). The mixture was heated to reflux for 30 min., the oil bath was removed, and allyl bromide (1.30 mL, 15.0 mmol) was added. The mixture was heated until the starting material was fully consumed, as indicated by TLC. After cooling to ambient temperature, the reaction mixture was poured onto aqueous NH₄Cl solution, the aqueous layer was separated and extracted twice with MTBE. The combined organic extracts were dried with MgSO₄, filtered, and the solvent was evaporated. The residue was purified by Kugelrohr distillation (0.1 mbar, 150°C). Yield: 1.50 g (95%). ¹H NMR (500 MHz, CDCl₃): δ = 3.83 (s, 3 H), 3.97-4.01 (2 H), 5.14 (dm, *J* = 10.5 Hz, 1 H), 5.17 (dm, *J* = 10.2 Hz, 1 H), 5.26-5.33 (3 H), 5.92-6.00 (2 H), 6.87 (d, *J* = 8.2 Hz, 1 H), 6.98 (dd, *J* = 7.5, 7.5 Hz, 1 H), 7.25 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1 H), 7.44 (dd, *J* = 7.5, 1.8 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 55.3 (3), 69.4 (2), 75.3 (1), 110.4 (1), 115.2 (2), 116.4 (2), 127.1 (1), 128.4 (1), 129.3 (0), 135.0 (1), 138.2 (1), 156.7 (0) ppm. IR (film, NaCl-plates): ν = 1071 (s), 1242 (s), 1490 (s), 1600 (s), 1644 (m), 2837 (m) cm⁻¹. MS (EI): *m/z* = 204 (4) [M⁺], 163 (53), 135 (100). C₁₃H₁₆O₂ (204.3): calcd. C 76.4, H 7.9; found: C 76.6, H 8.4.

1-(1-Allyloxy-allyl)-3-methoxy-benzene (2b). Following the procedure for **2a**, **2b** was obtained from **1b** (1.97 g, 12.0 mmol). Bp 70°C (0.05 mbar), yield: 2.36 g (96%). ¹H NMR (500 MHz, CDCl₃): δ = 3.80 (s, 3 H), 3.95-4.03 (2 H), 4.78 (d, *J* = 6.7 Hz, 1 H), 5.18 (dm, *J* = 10.5 Hz, 1 H), 5.19 (dm, *J* = 10.0 Hz, 1 H), 5.28 (dm, *J* = 17.2 Hz, 1 H), 5.29 (dm, *J* = 17.2 Hz, 1 H), 5.89-5.99 (2 H), 6.81 (dd, *J* = 8.0, 2.2 Hz, 1 H), 6.90-6.94 (2 H), 7.25 (dd, *J* = 8.2, 8.0 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 55.1 (3), 69.1 (2), 82.9 (1), 112.1 (1), 113.1 (1), 116.2 (2), 116.7 (2), 119.2 (1), 129.4 (1), 134.7 (1), 138.7 (1), 142.6 (0), 159.7 (0) ppm. IR (film, NaCl-plates): ν = 925 (s), 1049 (s), 1264 (s), 1586 (s), 1600 (s) cm⁻¹. MS (EI): *m/z* = 204 (6) [M⁺], 148 (100), 135 (51), 41 (58). C₁₃H₁₆O₂ (204.3): calcd. C 76.4, H 7.9; found: C 76.5, H 8.1.

(3-Allyloxy-pent-4-enyl)-benzene (2c). Following the procedure for **2a**, **2c** was obtained from **1c** (1.30 g, 8.0 mmol). Bp 60°C (0.17 mbar), yield: 1.36 g (84%). ¹H NMR (500 MHz, CDCl₃): δ = 1.80 (dddd, *J* = 13.7, 10.0, 6.5, 6.0 Hz, 1 H), 1.96 (dddd, *J* = 13.7, 9.5, 7.5, 6.0 Hz, 1 H), 2.64-2.77 (2 H), 3.70 (ddd, *J* = 7.7, 7.7, 6.0 Hz, 1 H), 3.82 (dddd, *J* = 12.7, 6.0, 1.5, 1.5 Hz, 1 H), 4.06 (dddd, *J* = 12.7, 5.2, 1.5, 1.5 Hz, 1 H), 5.14-5.23 (3 H), 5.28 (dddd, *J* = 17.2, 1.8, 1.8, 1.8, 1.8 Hz, 1 H), 5.72 (ddd, *J* = 17.2, 10.5, 7.7 Hz, 1 H), 5.93 (dddd, *J* = 17.2, 10.5, 6.0, 5.2 Hz, 1 H), 7.15-7.21 (3 H), 7.27 (dd, *J* = 7.7, 7.7 Hz, 2 H) ppm. ¹³C NMR (125

MHz, CDCl₃): δ = 31.5 (2), 37.0 (2), 69.2 (2), 79.8 (1), 116.5 (2), 117.1 (2), 125.7 (1), 128.3 (1), 128.4 (81), 135.1 (1), 138.8 (1), 142.1 (0) ppm. IR (film, NaCl-plates): ν = 924 (s), 1081 (s), 1454 (s), 1496 (s), 1603 (s), 1649 (s) cm⁻¹. MS (EI): m/z = [M⁺] not observed, 144 (41), 91 (69), 41 (100). C₁₄H₁₈O (202.3): calcd. C 83.1, H 9.0; found: C 83.1, H 9.1.

6-(1-Allyloxyallyl)-3,4-dihydro-2H-pyran (2d). Following the procedure for **2a**, **2d** was obtained from **1d** (1.00 g, 7.1 mmol). Bp 45°C (0.8 mbar), yield: 0.96 g (75%). ¹H NMR (500 MHz, C₆D₆): δ = 1.36-1.51 (2 H), 1.76-1.82 (2 H), 3.70 (ddd, J = 10.3, 7.3, 3.5 Hz, 1 H), 3.77 (ddd, J = 10.3, 6.0, 3.8 Hz, 1 H), 3.94 (ddm, J = 13.1, 5.3 Hz, 1 H), 4.02 (ddm, J = 13.1, 5.3 Hz, 1 H), 4.17 (d, J = 6.3 Hz, 1 H), 4.86 (dd, J = 3.7, 3.7 Hz, 1 H), 5.06 (dm, J = 10.3 Hz, 1 H), 5.14 (dm, J = 10.3 Hz, 1 H), 5.33 (dm, J = 17.1 Hz, 1 H), 5.39 (dm, J = 17.1 Hz, 1 H), 5.91 (dddd, J = 17.1, 10.3, 5.3, 5.3 Hz, 1 H), 6.08 (ddd, J = 17.1, 10.3, 6.3 Hz, 1 H) ppm. ¹³C NMR (125 MHz, C₆D₆): δ = 20.2 (2), 22.6 (2), 66.1 (2), 69.3 (2), 80.8 (1), 97.5 (1), 115.9 (2), 116.2 (2), 135.7 (1), 137.3 (1), 153.4 (0) ppm. IR (film, NaCl-plates): ν = 922 (s), 1064 (s), 1086 (s), 1671 (m), 2850 (m), 2931 (m) cm⁻¹. MS (EI): m/z = 180 (7) [M⁺], 124 (44), 55 (100). C₁₁H₁₆O₂ (180.2): calcd. C 73.3, H 9.0; found: C 73.1, H 9.3.

1-Allyloxy-1-vinyl-cyclohexane (2e).⁹ Following the procedure for **2a**, **2e** was obtained from **1e** (1.40 g, 11.1 mmol). Bp 55°C (8.2 mbar), yield: 1.50 g (81%).

(3-Allyloxy-hex-5-enyl)-benzene (2f). Following the procedure for **2a**, **2f** was obtained from **1f** (3.40 g, 19.3 mmol). Bp 85°C (0.15 mbar), yield: 3.17 g (76%). ¹H NMR (500 MHz, CDCl₃): δ = 1.76-1.84 (2 H), 2.24-2.37 (2 H), 2.63 (ddd, J = 14.0, 9.5, 7.0 Hz, 1 H), 2.76 (ddd, J = 14.0, 9.3, 6.5 Hz, 1 H), 3.38 ("pent.", J = 6.0 Hz, 1 H), 3.95 (dd, J = 12.6, 5.5 Hz, 1 H), 4.06 (dd, J = 12.6, 5.5 Hz, 1 H), 5.05 (dm, J = 10.3 Hz, 1 H), 5.08 (dm, J = 17.3 Hz, 1 H, =CH₂), 5.16 (dm, J = 10.3 Hz, 1 H), 5.28 (dm, J = 17.3 Hz, 1 H), 5.81 (dddd, J = 17.3, 10.3, 7.3, 7.3 Hz, 1 H), 5.93 (dddd, J = 17.3, 10.5, 5.5, 5.5 Hz, 1 H), 7.14-7.21 (3 H), 7.27 (dd, J = 7.8, 7.5 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 31.6 (2), 35.6 (2), 38.3 (2), 70.0 (2), 77.7 (1), 116.6 (2), 117.0 (2), 125.7 (1), 128.3 (1), 128.4 (1), 134.7 (1), 135.3 (1), 142.3 (0) ppm. IR (film, NaCl-plates): ν = 917 (s), 1083 (s), 1454 (s), 1496 (s), 1641 (m), 2859 (s), 2932 (s), 3078 (m) cm⁻¹. MS (EI): m/z = 216 (57) [M⁺], 175 (100), 157 (75). C₁₅H₂₀O (216.3): calcd. C 83.3, H 9.3; found: C 83.3, H 9.4.

(R)-(3-Allyloxy-hex-5-enyl)-benzene ((R)-2f). Following the procedure for **2a**, **(R)-2f** was obtained from **(R)-1f** (0.35 g, 2.0 mmol). Yield: 0.33 g (76%). [α]_D²⁰ = +17 (c 1.02, CH₂Cl₂) for 90% ee.

(3-Allyloxyhexa-1,5-dienyl)-benzene (2g). Following the procedure for **2a**, **2g** was obtained from **1g** (1.90 g, 11.0 mmol). Bp 78°C (0.07 mbar), yield: 2.04 g (86%). ¹H NMR (500 MHz,

CDCl₃): δ = 2.38 (ddd, J = 14.2, 7.0, 7.0 Hz, 1 H), 2.49 (ddd, J = 14.2, 7.0, 7.0 Hz, 1 H), 3.91 (dddd, J = 13.0, 6.0, 1.5, 1.5 Hz, 1 H), 3.95 (ddd, J = 8.0, 7.0, 7.0 Hz, 1 H), 4.10 (dddd, J = 13.0, 5.2, 1.5, 1.5 Hz, 1 H), 5.06 (dm, J = 10.2 Hz, 1 H), 5.11 (dm, J = 17.2 Hz, 1 H), 5.17 (dm, J = 10.2 Hz, 1 H), 5.28 (dm, J = 17.2 Hz, 1 H), 5.86 (dddd, J = 17.2, 10.2, 7.0, 7.0 Hz, 1 H), 5.93 (dddd, J = 17.2, 10.2, 6.0, 5.2 Hz, 1 H), 6.09 (dd, J = 16.0, 8.0 Hz, 1 H), 6.53 (dd, J = 16.0 Hz, 1 H), 7.24 (t, J = 7.5 Hz, 1 H), 7.32 (dd, J = 7.5, 7.5 Hz, 1 H), 7.39 (d, J = 7.5 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 40.3 (2), 69.2 (2), 79.7 (1), 116.7 (2), 117.0 (2), 126.5 (1), 127.7 (1), 128.5 (1), 129.9 (1), 132.3 (1), 134.4 (1), 135.0 (1), 136.5 (0) ppm. IR (film, NaCl-plates): ν = 693 (s), 750 (s), 917 (s), 968 (s), 1072 (s), 1494 (s), 1642 (m), 2855 (m), 3026 (m), 3078 (m) cm⁻¹. MS (EI): m/z = 213 (1) [M⁺-H], 173 (96), 41 (100). C₁₅H₁₈O (214.3): calcd. C 84.1, H 8.5; found: C 83.7, H 8.8.

2-(1-Allyloxy-but-3-enyl)-3-phenyl-oxirane (2h). To a solution of **1h** (0.40 g, 1.8 mmol) in THF (15 mL) was added NaH (120 mg, 3.0 mmol, 60% dispersion in mineral oil) and allyl bromide (0.26 mL, 3.0 mmol) at ambient temperature. The mixture was stirred at ambient temperature, until the starting material was fully consumed, as indicated by TLC (18 hours). Aqueous workup, followed by Kugelrohr distillation (0.3 mbar, 150°C), yields **2h** (0.75 g, 79%) as an inseparable 3:2 mixture of diastereoisomers. *NMR-data for the major isomer:* ¹H NMR (500 MHz, CDCl₃): δ = 2.35-2.53 (2 H), 2.99 (dd, J = 5.2, 2.0 Hz, 1 H), 3.46 (ddd, J = 7.0, 5.2, 5.0 Hz, 1 H), 3.89 (d, J = 2.0 Hz, 1 H), 4.06 (dd, J = 12.7, 5.7 Hz, 1 H), 4.18 (dd, J = 12.7, 5.5 Hz, 1 H), 5.08-5.23 (3 H), 5.30 (dm, J = 17.3 Hz, 1 H), 5.81-6.02 (2 H), 7.25-7.40 (5 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 37.1 (2), 57.1 (1), 63.5 (1), 71.3 (2), 77.3 (1), 117.0 (2), 117.5 (2), 125.5 (1), 128.2 (1), 128.5 (1), 133.9 (1), 134.8 (1), 137.0 (0) ppm. *Characteristic data for the minor isomer:* ¹H NMR (500 MHz, CDCl₃): δ = 3.05 (dd, J = 7.0, 2.2 Hz, 1 H), 3.27 (ddd, J = 7.0, 6.7, 6.7 Hz, 1 H), 3.66 (d, J = 2.2 Hz, 1 H), 4.15 (ddm, J = 12.7, 5.7 Hz, 1 H), 4.33 (dd, J = 12.7, 5.2 Hz, 1 H), 5.35 (dm, J = 17.2 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 37.0 (2), 55.2 (1), 64.8 (1), 70.8 (2), 79.4 (1), 117.0 (2), 117.7 (2), 125.5 (1), 128.2 (1), 128.5 (1), 133.7 (1), 134.8 (1), 136.8 (0) ppm. IR (film, NaCl-plates): ν = 698 (s), 754 (s), 919 (s), 1092 (s), 1461 (s), 1643 (m), 2860 (s), 1927 (s), 3077 (m) cm⁻¹. MS (EI): m/z = 230 (1) [M⁺], 189 (16), 91 (54), 41 (100). C₁₅H₁₈O₂ (214.3): calcd. C 78.2, H 7.9; found: C 78.4, H 8.3.

1-(2,2-Dimethyl-5-phenyl-[1,3]-dioxolan-4-yl)-but-3-en-1-ol (2i). Following the procedure for **2a**, **2i** was obtained from **1i** (2.35 g, 9.5 mmol). Kugelrohr distillation (170°C, 0.17 mbar) yields **2i** (2.54 g, 93%) as a 3:2 mixture of diastereoisomers. *NMR-data for the major isomer:* ¹H NMR (500 MHz, CDCl₃): δ = 1.58 (s, 3 H), 1.58 (s, 3 H), 2.22 (ddd, J = 14.5, 7.0, 5.5 Hz,

1 H), 2.39 (ddd, $J = 14.5, 6.7, 5.5$ Hz, 1 H), 3.67 (ddd, $J = 5.5, 5.5, 5.5$ Hz, 1 H), 4.00-4.09 (3 H), 4.16 (ddd, $J = 7.7, 4.7, 1.3$ Hz, 1 H), 4.90-5.35 (4 H), 5.73-5.94 (2 H), 7.14-7.29 (3 H), 7.56 (d, $J = 8.0$ Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 27.4$ (3), 27.5 (3), 36.0 (2), 71.6 (2), 79.1 (1), 80.5 (1), 84.4 (1), 109.1 (0), 116.1 (2), 117.3 (2), 127.4-128.7 (1, 3C), 134.7 (1), 135.4 (1), 140.1 (0) ppm. *Characteristic data for the minor isomer:* ^1H NMR (500 MHz, CDCl_3): $\delta = 1.62$ (s, 3 H), 1.63 (s, 3 H), 3.40 (ddd, $J = 6.5, 6.5, 3.2$ Hz, 1 H), 3.91 (dd, $J = 13.0, 5.5$ Hz, 1 H), 7.51 (d, $J = 7.7$ Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 27.2$ (3), 27.5 (3), 36.0 (2), 71.2 (2), 76.8 (1), 79.1 (1), 84.9 (1), 109.1 (0), 116.0 (2), 117.2 (2), 127.4-128.7 (1, 3C), 135.0 (1), 135.5 (1), 139.5 (0) ppm. IR (film, NaCl-plates): $\nu = 1063$ (s), 1370 (s), 1379 (s), 1642 (m), 2931 (s), 2985 (s) cm^{-1} . MS (EI): $m/z = 288$ (1) [M^+], 189 (24), 148 (47), 119 (57), 41 (100). $\text{C}_{18}\text{H}_{24}\text{O}_3$ (288.4): calcd. C 75.0, H 8.4; found: C 75.4, H 8.8.

4-Allyloxy-non-1-ene (2j). Following the procedure for **2a**, **2j** was obtained from **1j** (2.10 g, 14.8 mmol). Bp 58°C (3.9 mbar), yield: 2.00 g (74%). ^1H NMR (400 MHz, CDCl_3): $\delta = 0.86$ (t, $J = 6.8$ Hz, 3 H), 1.20-1.50 (8 H), 2.18-2.30 (2 H), 3.32 ("pent.", $J = 5.8$ Hz, 1 H), 3.94 (ddm, $J = 12.5, 5.5$ Hz, 1 H), 4.01 (ddm, $J = 12.5, 5.5$ Hz, 1 H), 5.02 (dm, $J = 10.3$ Hz, 1 H), 5.05 (dm, $J = 17.3$ Hz, 1 H), 5.12 (dm, $J = 10.3$ Hz, 1 H), 5.24 (dm, $J = 17.3$ Hz, 1 H), 5.80 (dddd, $J = 17.3, 10.3, 7.3, 7.0$ Hz, 1 H), 5.89 (dddd, $J = 17.3, 10.3, 5.5, 5.5$ Hz, 1 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 14.0$ (3), 22.6, 25.0, 31.9, 33.8, 38.4 (2), 70.0 (2), 78.6 (1), 116.4 (2), 116.7 (2), 135.1 (1), 135.5 (1) ppm. IR (film, NaCl-plates): $\nu = 916$ (s), 1085 (s), 1459 (m), 1642 (m), 2859 (s), 2932 (s), 2957 (s), 3078 (m) cm^{-1} . MS (EI): $m/z = [\text{M}^+]$ not observed, 141 (13), 99 (24), 41 (100). $\text{C}_{12}\text{H}_{22}\text{O}$ (182.3): calcd. C 79.0, H 12.2; found: C 78.4, H 12.4.

2-(1-Allyloxy-but-3-enyl)-furan (2k). Following the procedure for **2a**, **2k** was obtained from **1k** (2.76 g, 20.0 mmol). Bp 55°C (3.0 mbar), yield: 3.06 g (86%). ^1H NMR (400 MHz, CDCl_3): $\delta = 2.61$ (dtm, $J = 14.0, 7.0$ Hz, 1 H), 2.69 (dtm, $J = 14.0, 7.0$ Hz, 1 H), 3.86 (ddm, $J = 12.8, 5.0$ Hz, 1 H), 3.99 (ddm, $J = 12.8, 5.0$ Hz, 1 H), 4.39 ("t", $J = 7.0$ Hz, 1 H), 5.04 (dm, $J = 10.0$ Hz, 1 H), 5.09 (dm, $J = 17.1$ Hz, 1 H), 5.17 (dm, $J = 10.3$ Hz, 1 H), 5.26 (dm, $J = 17.1$ Hz, 1 H), 5.77 (ddt, $J = 17.1, 10.3, 7.0$ Hz, 1 H), 5.88 (dddd, $J = 17.1, 10.5, 6.3, 5.3$ Hz, 1 H), 6.27 (d, $J = 3.2$ Hz, 1 H), 6.34 (dd, $J = 3.3, 1.8$ Hz, 1 H), 7.40 (dd, $J = 1.8, 0.8$ Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 38.6$ (2), 69.4 (2), 73.7 (1), 107.9 (1), 109.8 (1), 117.0 (2), 117.1 (2), 134.0 (1), 134.6 (1), 142.1 (1), 154.0 (0) ppm. IR (film, NaCl-plates): $\nu = 739$ (s), 921 (s), 1012 (s), 1079 (s), 1504 (m), 1643 (m), 2861 (s), 3079 (s) cm^{-1} . MS (EI): $m/z = [\text{M}^+]$ not observed, 137 (65), 41 (100). $\text{C}_{11}\text{H}_{14}\text{O}_2$ (182.3): calcd. C 74.1, H 7.9; found: C 73.8, H 7.9.

(1-Allyloxy-but-3-enyl)-benzene (2l).¹⁰ Following the procedure for **2a**, **2l** was obtained from **1l** (3.00 g, 20.2 mmol). Bp 100°C (0.2 mbar), yield: 3.38 g (90%).

1-(1-Allyloxy-but-3-enyl)-2-methoxynaphthalene (2m). Following the procedure for **2a**, **2m** was obtained from **1m** (1.80 g, 7.9 mmol). Purification by flash chromatography on silica. Yield: 2.10 g (99%). ¹H NMR (400 MHz, CDCl₃): δ= 2.66 (dddd, *J* = 14.3, 7.3, 6.9, 1.3, 1.3 Hz, 1 H), 2.99 (dddd, *J* = 14.3, 7.8, 6.8, 1.3, 1.3 Hz, 1 H), 3.78 (dddd, *J* = 12.8, 6.0, 1.3, 1.3 Hz, 1 H), 3.85 (dddd, *J* = 12.8, 5.0, 1.5, 1.5 Hz, 1 H), 3.87 (s, 3 H), 4.95 (dm, *J* = 10.3 Hz, 1 H), 5.00 (dddd, *J* = 17.1, 1.8, 1.5, 1.5 Hz, 1 H), 5.08 (dddd, *J* = 10.5, 1.8, 1.3, 1.3 Hz, 1 H), 5.18 (dddd, *J* = 17.1, 1.8, 1.5, 1.5 Hz, 1 H), 5.53 (dd, *J* = 7.8, 6.5 Hz, 1 H), 5.79-5.92 (2 H), 7.20 (d, *J* = 9.0 Hz, 1 H), 7.30 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1 H), 7.41 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1 H), 7.73 (d, *J* = 9.3 Hz, 1 H), 7.74 (d, *J* = 7.0 Hz, 1 H), 8.72 (d, *J* = 8.8 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 40.2 (2), 56.7 (3), 69.4 (2), 74.5 (1), 113.2 (1), 116.1 (2), 116.4 (2), 121.6 (1), 123.4 (1), 125.3 (0), 125.9 (1), 128.4 (1), 129.6 (1), 129.6 (0), 132.4 (0), 135.2 (1), 136.6 (1), 155.2 (0) ppm. IR (film, NaCl-plates): ν = 1079 (s), 1248 (s), 1596 (s), 1624 (m), 1642 (m), 2838 (s), 2937 (s), 3076 (m) cm⁻¹. MS (EI): *m/z* = 268 (2) [M⁺], 227 (100), 185 (41), 158 (43). C₁₈H₂₀O₂ (268.4): calcd. C 80.6, H 7.5; found: C 80.5, H 7.8.

2-Allyloxy-2-phenyl-pent-4-enoic acid methyl ester (2n). The title compound was prepared from DL-methyl mandelate by a one-pot O-allylation/Wittig-rearrangement/O-allylation sequence following a literature procedure.¹¹

2-Allyloxy-2-phenyl-pent-4-en-1-ol (2o). The title compound was prepared from **2n** by reduction of the ester group with DIBAL-H following a literature procedure.¹¹

(1-Allyloxy-1-methoxymethyl-but-3-enyl)-benzene (2p). To a solution of **2o** (3.35 g, 15.3 mmol) in THF (30 mL) was added NaH (1.28 g, 60% dispersion in mineral oil, 32 mmol). The mixture was heated to reflux for 30 min., and methyl iodide (2.0 mL, 32 mmol) was added. Heating to reflux was continued until the starting material was fully consumed, as indicated by TLC. Aqueous workup, followed by flash chromatography on silica, yields **2p** (3.38 g, 95%). ¹H NMR (500 MHz, CDCl₃): δ= 2.65 (ddm, *J* = 14.2, 7.0 Hz, 1 H), 2.73 (ddm, *J* = 14.2, 7.3 Hz, 1 H), 3.27 (s, 3 H), 3.59 (d, *J* = 9.7 Hz, 1 H), 3.70 (d, *J* = 9.7 Hz, 1 H), 3.77-3.81 (2 H), 5.01 (dm, *J* = 10.2 Hz, 1 H), 5.04 (dm, *J* = 17.2 Hz, 1 H), 5.08 (dddd, *J* = 10.5, 1.5, 1.5, 1.5 Hz, 1 H), 5.25 (dddd, *J* = 17.2, 1.8, 1.8, 1.8 Hz, 1 H), 5.70 (dddd, *J* = 17.2, 10.2, 7.3, 7.0 Hz, 1 H), 5.87 (dddd, *J* = 17.2, 10.5, 5.2, 5.2 Hz, 1 H), 7.22 (tt, *J* = 7.0, 1.5 Hz, 1 H), 7.30 (dd, *J* = 7.2, 7.0 Hz, 1 H), 7.35 (dd, *J* = 7.2, 1.5 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 40.5 (2), 59.3 (3), 63.9 (2), 76.0 (2), 80.2 (0), 115.6 (2), 117.9 (2), 126.5 (1), 127.2 (1), 128.1 (1), 133.5 (1), 135.2 (1), 142.1 (0) ppm. IR (film, NaCl-plates): ν = 701 (s),

1116 (s), 1447 (s), 1640 (m), 2892 (s), 3076 (m) cm^{-1} . MS (EI): $m/z = [M^+]$ not observed, 191 (45) $[M^+ - \text{C}_3\text{H}_5]$, 187 (76), 105 (100). $\text{C}_{15}\text{H}_{20}\text{O}_2$ (232.3): calcd. C 77.6, H 8.7; found: C 77.5, H 9.0.

1-Allyloxy-1-phenyl-but-3-en-2-ol (2q). The title compound was prepared from DL-methyl mandelate in two steps by O-allylation and subsequent DIBAL-reduction-vinylmagnesium chloride addition to **6** as described in the literature.⁹

[1-(Allyloxy-phenyl-methyl)-allyloxy]-tert-butyldimethyl silane (2r). To a solution of **2q** (0.40 g, 2.0 mmol) in dry THF (10 mL) was added NaH (0.12 g of a 60% dispersion in mineral oil, 3.0 mmol) and the mixture was heated to reflux for 30 min. The reaction was cooled to ambient temperature and TBDMSCl (450 mg, 3.0 mmol) was added. The mixture was again heated to reflux until the starting material was fully consumed (TLC), diluted with MTBE (20 mL) and washed with brine. The organic layer was separated, dried with MgSO_4 , filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica to give **2r** (0.54 g, 85%). ^1H NMR (400 MHz, CDCl_3): δ = 0.00 (s, 3 H), 0.04 (s, 3 H), 0.88 (s, 9 H), 3.80 (dddd, J = 12.8, 6.0, 1.3, 1.3 Hz, 1 H), 3.94 (dddd, J = 12.8, 5.3, 1.5, 1.5 Hz, 1 H), 4.18 (d, J = 6.3 Hz, 1 H), 4.28 (dddd, J = 6.3, 5.3, 1.5, 1.5 Hz, 1 H), 4.97 (ddd, J = 10.6, 2.0, 1.3 Hz, 1 H), 5.08-5.14 (2 H), 5.21 (dddd, J = 17.3, 1.8, 1.8, 1.8 Hz, 1 H), 5.57 (ddd, J = 17.1, 10.6, 5.3 Hz, 1 H), 5.86 (dddd, J = 17.3, 10.5, 6.0, 5.3 Hz, 1 H), 7.21-7.31 (5 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = -4.9 (3), -4.7 (3), 18.4 (0), 25.9 (3), 69.8 (2), 76.8 (1), 85.2 (1), 115.4 (2), 116.4 (2), 127.6 (1), 127.8 (1), 128.0 (1), 135.0 (1), 137.7 (1), 139.0 (0) ppm. IR (film, NaCl-plates): ν = 700 (s), 836 (s), 1092 (s), 1140 (s), 1253 (s), 2857 (s), 2956 (s) cm^{-1} . MS (EI): $m/z = [M^+]$ not observed, 261 (10) $[M^+]$ -allyloxy, 205 (40), 147 (100). $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$ (318.5): calcd. C 71.6, H 9.5; found: C 71.7, H 9.6.

3-(Allyloxy-phenyl-methyl)-penta-1,4-dien-3-ol (2s). The title compound was prepared from DL-methyl mandelate in two steps by allylation and subsequent addition of vinylmagnesium chloride as described in the literature.¹²

(2-Allyloxy-pent-4-enyloxymethyl)-benzene (2t).¹³ Following the procedure for **2a**, **2t** was obtained from **1t** (1.32 g, 6.9 mmol). Purification by Kugelrohr distillation at 0.17 mbar and 130°C. Yield: 1.30 g (81%). ^1H NMR (600 MHz, CDCl_3): δ = 2.27-2.38 (2 H), 3.47-3.52 (2 H), 3.58 ("pent.", J = 5.5 Hz, 1 H), 4.06 (dd, J = 12.8, 5.5 Hz, 1 H), 4.12 (dd, J = 12.8, 5.5 Hz, 1 H), 4.54 (s, 2 H), 5.03 (d, J = 10.2 Hz, 1 H), 5.08 (d, J = 17.2 Hz, 1 H), 5.14 (d, J = 10.2 Hz, 1 H), 5.26 (d, J = 17.2, Hz, 1 H), 5.81 (dddd, J = 17.2, 10.2, 7.3, 7.0 Hz, 1 H), 5.91 (dddd, J = 17.2, 10.3, 5.5, 5.5 Hz, 1 H), 7.25-7.35 (5 H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 36.3 (2), 70.8 (2), 72.1 (2), 73.3 (2), 77.6 (1), 116.6 (2), 117.0 (2), 127.5 (1), 127.6 (1), 128.3 (1), 134.6

(1), 135.2 (1), 138.3 (0) ppm. IR (film, NaCl-plates): ν = 917 (s), 1099 (s), 1454 (s), 1642 (m), 2859 (s), 3076 (m) cm^{-1} . MS (EI): m/z = 232 (1) [M^+], 131 (20), 91 (100).

1-(1-Allyloxy-pent-4-enyl)-4-methoxybenzene (2u). Following the procedure for **2a**, **2u** was obtained from **1u** (0.67 g, 3.5 mmol). Purification by flash chromatography on silica. Yield: 0.73 g (90%). ^1H NMR (500 MHz, CDCl_3): δ = 1.69 (m, 1 H), 1.91 (m, 1 H), 2.00-2.16 (2 H), 3.71 (dd, J = 12.7, 5.5 Hz, 1 H), 3.79 (s, 3 H), 3.86 (dd, J = 12.7, 5.5 Hz, 1 H), 4.22 (dd, J = 6.7, 6.7 Hz, 1 H), 4.93 (d, J = 10.0 Hz, 1 H), 4.98 (d, J = 17.2 Hz, 1 H), 5.12 (d, J = 10.2 Hz, 1 H), 5.21 (d, J = 17.5 Hz, 1 H), 5.79 (dddd, J = 17.2, 10.2, 6.5, 6.5 Hz, 1 H), 5.87 (dddd, J = 17.2, 10.0, 5.5, 5.5 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 30.0 (2), 37.2 (2), 55.2 (3), 69.2 (2), 80.3 (1), 113.7 (1), 114.6 (2), 116.6 (2), 127.9 (1), 134.4 (0), 135.1 (1), 138.3 (1), 159.0 (0) ppm. IR (film, NaCl-plates): ν = 1248 (s), 1512 (s), 1612 (s), 2936 (s), 3076 (s) cm^{-1} . MS (EI): m/z = 232 (10) [M^+], 177 (100), 135 (90), 121 (80). $\text{C}_{15}\text{H}_{20}\text{O}_2$ (232.3): calcd. C 77.6, H 8.7; found: C 77.8, H 8.7.

1-Allyloxy-1-phenyl-pent-4-en-2-ol (2v). To a solution of ester **6**¹² (1.03 g, 5.0 mmol) in ether (20 mL) was added DIBAL-H (1.0 M solution in cyclohexane, 6.3 mL, 6.3 mmol) at -90°C . The solution was stirred until the starting material was fully consumed (TLC) and a solution of allylmagnesium bromide (1.0 M solution in ether, 7.5 mL, 7.5 mmol) was added. The cooling bath was removed and the reaction mixture was allowed to warm to ambient temperature. The solution was poured onto water, and the inorganic residues were dissolved with a minimum amount of aqueous HCl. The organic layer was separated, the aqueous layer was extracted with ether and the combined organic extracts were dried with MgSO_4 , filtered and evaporated. The residue was purified by flash chromatography on silica using hexane/MTBE mixtures as eluent to give **2v** (1.12 g, 90%) as a 5:1 mixture of diastereoisomers. ^1H NMR (500 MHz, CDCl_3): δ = 2.01 (ddd, J = 14.4, 7.5, 7.5 Hz, 1 H), 2.09 (dm, J = 14.4 Hz, 1 H), 2.95 (s, 1 H), 3.73-3.80 (2 H), 3.92 (dd, J = 12.7, 5.2 Hz, 1 H), 4.14 (d, J = 7.7 Hz, 1 H), 5.00 (d, J = 17.2 Hz, 1 H), 5.03 (d, J = 10.2 Hz, 1 H), 5.14 (dm, J = 10.2 Hz, 1 H), 5.20 (d, J = 17.2 Hz, 1 H), 5.76-5.92 (2 H), 7.22-7.38 (5 H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 36.5 (2), 69.6 (2), 74.4 (1), 84.6 (1), 117.1 (2), 117.2 (2), 127.7 (1), 128.3 (1), 128.4 (1), 134.4 (1), 134.5 (1), 138.4 (0) ppm. IR (film, NaCl-plates): ν = 917 (s), 1082 (s), 1453 (s), 1642 (s), 2866 (s), 3076 (s), 3464 (s) cm^{-1} . MS (EI): m/z = [M^+] not observed, 177 (10) [M^+]-allyl, 147 (80), 105 (90), 91 (100). $\text{C}_{14}\text{H}_{18}\text{O}_2$ (218.3): calcd. C 77.0, H 8.3; found: C 76.8, H 8.3.

[1-(Allyloxy-phenyl-methyl)-but-3-enyloxy]-tert-butyl-dimethyl-silane (2w). Following the procedure for **2r**, **2w** was obtained from **2v** (0.44 g, 2.0 mmol). Purification by flash chromatography on silica. Yield: 0.63 g (95%). ¹H NMR (500 MHz, CDCl₃): δ= 0.04 (s, 6 H), 0.90 (s, 9 H), 1.88 (ddd, *J* = 14.0, 7.5, 6.7 Hz, 1 H), 2.21 (dm, *J* = 14.0 Hz, 1 H), 3.78 (dddd, *J* = 13.0, 6.0, 1.8, 1.8 Hz, 1 H), 3.87 (ddd, *J* = 6.5, 6.5, 6.5 Hz), 3.93 (dddd, *J* = 13.0, 5.0, 1.8, 1.8 Hz, 1 H), 4.23 (d, *J* = 6.0 Hz, 1 H), 4.94 (dm, *J* = 17.2 Hz, 1 H), 5.00 (dm, *J* = 10.2 Hz, 1 H), 5.13 (dm, *J* = 10.4 Hz, 1 H), 5.21 (d, *J* = 17.2, Hz, 1 H), 5.81 (dddd, *J* = 17.2, 10.2, 7.7, 6.7 Hz, 1 H), 5.89 (dddd, *J* = 17.2, 10.4, 6.0, 5.2 Hz, 1 H), 7.25-7.35 (5 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ= -4.9 (3), -4.3 (3), 18.3 (0), 26.0 (3), 38.1 (2), 69.8 (2), 75.4 (1), 84.1 (1), 116.5 (2), 116.9 (2), 127.6 (1), 127.9 (1), 128.0 (1), 135.1 (1), 135.3 (1), 139.4 (0) ppm. IR (film, NaCl-plates): ν = 701 (s), 835 (s), 1109 (s), 1253 (s), 2856 (s), 2928 (s), 2954 (s) cm⁻¹. MS (EI): *m/z* = [M⁺] not observed, 291 (10), 275 (15) [M⁺]-allyloxy, 185 (100). C₂₀H₃₂O₂Si (332.6): calcd. C 72.2, H 9.7; found: C 72.2, H 9.8.

Syntheses and analytical data of dihydropyrans 7

1-(1-Allyloxyallyl)-2-methoxybenzene (7a). To a solution of **2a** (0.60 g, 2.9 mmol) in CH₂Cl₂ (10 mL) was added [Cl₂(PCy₃)₂Ru=CHPh] (70 mg, 2.9 mol%). The mixture was stirred at room temperature until complete conversion was indicated by TLC (approximately 1 h). The solvent was evaporated, and the residue was purified by Kugelrohr distillation (0.13 mbar, 125°C) to give **7a** (0.46 g, 90%). ¹H NMR (500 MHz, CDCl₃): δ= 3.84 (s, 3 H), 4.77 (dm, *J* = 12.7 Hz, 1 H), 4.85 (dddd, *J* = 12.7, 6.2, 2.0, 2.0 Hz, 1 H), 5.94 (dm, *J* = 6.2 Hz, 1 H), 5.98 (dm, *J* = 6.2 Hz, 1 H), 6.13 (m, 1 H), 6.86 (d, *J* = 8.2 Hz, 1 H), 6.95 (dd, *J* = 7.7, 7.5 Hz, 1 H), 7.23 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1 H), 7.34 (dd, *J* = 7.7, 1.7 Hz, 1 H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ= 55.3 (3), 75.5 (2), 82.4 (1), 110.2 (1), 120.7 (1), 125.8 (1), 126.4 (1), 128.4 (1), 129.4 (1), 130.5 (0), 156.1 (0) ppm. IR (film, NaCl-plates): ν = 755 (s), 1069 (s), 1241 (s), 1464 (s), 1489 (s), 1600 (s), 2838 (s) cm⁻¹. MS (EI): *m/z* = 176 (33) [M⁺], 136 (100), 77 (45). C₁₁H₁₂O₂ (176.2): calcd. C 75.0, H 6.9; found: C 74.6, H 7.0.

2-Phenethyl-3,6-dihydro-2H-pyran (7f). Following the procedure for **7a**, **7f** was obtained from **2f** (3.80 g, 17.6 mmol). Purification by flash chromatography on silica. Yield: 2.95 g (89%). ¹H NMR (400 MHz, CDCl₃): δ= 1.75 (dddd, *J* = 14.1, 9.8, 7.0, 4.5 Hz, 1 H), 1.88 (dddd, *J* = 14.1, 9.5, 8.5, 5.5 Hz, 1 H), 1.95 (dm, *J* = 17.0 Hz, 1 H), 2.04 (ddm, *J* = 17.0, 9.8 Hz, 1 H), 2.68 (ddd, *J* = 13.8, 9.3, 7.0 Hz, 1 H), 2.80 (ddd, *J* = 13.8, 9.5, 5.5 Hz, 1 H), 3.46 (dddd, *J* = 9.8, 8.5, 4.5, 3.0 Hz, 1 H), 4.12-4.25 (2 H), 5.70 (dm, *J* = 10.0 Hz, 1 H), 5.78 (dm, *J* = 10.0 Hz, 1 H), 7.17 (t, *J* = 7.3 Hz, 1 H), 7.19 (d, *J* = 7.3 Hz, 1 H), 7.27 (dd, *J* = 7.3, 7.3 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 31.0 (2), 31.7 (2), 37.6 (2), 65.9 (2), 72.6 (1), 124.2 (1), 125.7 (1), 126.3 (1), 128.3 (1), 128.5 (1), 142.1 (0) ppm. IR (film, NaCl-plates): ν = 745 (s), 1090 (s), 1181 (s), 1454 (s), 1604 (m), 2927 (s), 3029 (s) cm⁻¹. MS (EI): *m/z* = 188 (60) [M⁺], 117 (60), 91 (100). C₁₃H₁₆O (188.3): calcd. C 82.9, H 8.6; found: C 82.6, H 8.5.

2-Styryl-3,6-dihydro-2H-pyran (7g). Following the procedure for **7a**, **7g** was obtained from **2g** (0.98 g, 4.6 mmol). Purification by flash chromatography on silica. Yield: 0.96 g (90%). ¹H NMR (400 MHz, CDCl₃): δ= 2.13 (dm, *J* = 16.8 Hz, 1 H), 2.24 (ddm, *J* = 16.8, 9.8 Hz, 1 H), 4.21 (m, 1 H), 4.23-4.33 (2 H), 5.76 (dm, *J* = 10.3 Hz, 1 H), 5.86 (dm, *J* = 10.3 Hz, 1 H), 6.26 (dd, *J* = 16.1, 5.8 Hz, 1 H), 6.63 (d, *J* = 16.1 Hz, 1 H), 7.21 (t, *J* = 7.5 Hz, 1 H), 7.29 (dd, *J* = 7.5, 7.5 Hz, 2 H), 7.38 (d, *J* = 7.5 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ= 31.1 (2), 65.7 (2), 73.3 (1), 123.8 (1), 126.3 (1), 126.4 (1), 127.5 (1), 128.5 (1), 129.8 (1), 130.4 (1), 136.8 (0) ppm. IR (film, NaCl-plates): ν = 746 (s), 967 (s), 1088 (s), 1180 (s), 2825 (s), 3032 (s) cm⁻¹. MS (EI): *m/z* = 186 (11) [M⁺], 144 (19), 131 (100), 104 (85).

2-Furan-2-yl-3,6-dihydro-2H-pyran (7k).¹⁴ Following the procedure for **7a**, **7k** was obtained from **2k** (1.78 g, 10.0 mmol). Purification by flash chromatography on silica. Yield: 1.43 g (95%). ¹H NMR (400 MHz, CDCl₃): δ = 2.29 (dm, J = 17.3 Hz, 1 H), 2.62 (ddm, J = 17.1, 10.0 Hz, 1 H), 4.27 (dm, J = 16.6 Hz, 1 H), 4.37 (dm, J = 16.6 Hz, 1 H), 4.67 (dd, J = 10.0, 3.8 Hz), 5.79 (dm, J = 10.1 Hz), 5.91 (ddd, J = 10.0, 5.3, 2.5 Hz, 1 H), 6.32 (d, J = 3.3 Hz, 1 H), 6.36 (dd, J = 3.3, 1.8 Hz, 1 H), 7.42 (dd, J = 1.8, 0.8 Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 28.5 (2), 65.8 (2), 68.7 (1), 106.8 (1), 110.1 (1), 123.6 (1), 126.2 (1), 142.3 (1), 154.3 (0) ppm. IR (film, NaCl-plates): ν = 745 (m), 809 (s), 1013 (s), 1088 (s), 1264 (s), 1505 (s), 2832 (s), 2967 (s) cm⁻¹. MS (EI): m/z = 150 (33) [M⁺], 95 (100), 54 (78).

2-Phenyl-3,6-dihydro-2H-pyran (7l).¹⁰ Following the procedure for **7a**, **7l** was obtained from **2l** (0.50 g, 2.7 mmol). Purification by Kugelrohr distillation (0.2 mbar, 100°C). Yield: 0.39 g (90%).

Control experiments

Attempted isomerization of 7a with NaH. 7a (obtained by RCM of 2a) was chromatographed on silica and distilled prior to use in the control experiment, to ensure that no ruthenium residues are present. To a solution of 7a (0.30 g, 1.7 mmol) in toluene (10 mL) was added NaH (52 mg of a 60% dispersion in mineral oil, 1.3 mmol). The mixture was heated to reflux for 4 hours. A sample of the mixture (1 mL) was hydrolyzed, the organic layer was separated, dried and the solvent was evaporated. H-NMR spectroscopy of the residue revealed the presence of unreacted starting material. Reaction products could not even be detected in trace amounts. $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ (55 mg, 3.9 mol%) was then added to the mixture, and heating to reflux was continued for one hour, leading to complete conversion to 8a.

Attempted isomerization of 7a by prolonged heating in the presence of metathesis catalyst. To a solution of 2a (0.18 g, 0.9 mmol) in toluene (10 mL) was added $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ (36 mg, 4.9 mol%). The solution was stirred at ambient temperature until the starting material was fully consumed, and then heated to reflux for 4 hours. A sample (1 mL) was evaporated, and the residue was analyzed by H-NMR-spectroscopy. Only 7a could be detected. NaBH_4 (19 mg, 0.5 mmol) was then added to the rest of the reaction mixture and heating was continued for 1.5 hours. After 15 min. the isomerization product 8a could be detected by TLC. Conversion to 8a was complete after 1.5 hours.

Attempted base-induced isomerization of 7I with NaOH in alcohol-toluene mixtures. 7I was purified by chromatography and distillation prior to use in the control experiment. To a solution of 7I (0.32 g, 2.0 mmol) in toluene (10 mL) and 2-propanol (2 mL) was added NaOH (100 mg, 2.5 mmol) and the mixture was heated to reflux for 5 hours. Analysis of a sample (1 mL) by H-NMR as described above revealed the absence of any isomerization product. $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ (49 mg, 3.0 mol%) was added to the rest of the mixture, leading to a green solution. Upon heating to reflux, a colour change to orange-yellow was observed. Formation of the isomerization product 8I could be observed after 10 min.. After 2 hours, the RCM product 7I was completely converted to 8I under these conditions.

³¹P-NMR-experiments

³¹P-NMR spectra were obtained directly from the reaction mixture in undeuterated solvents: a sample (approximately 0.7 mL) was transferred via syringe under argon to a dry 5-mm-NMR-tube flushed with dry argon. A sealed lock capillary containing C₆D₆ (length 4 cm, diameter 1 mm) was added. ³¹P{¹H}-NMR spectra were obtained on a Varian-Mercury-200 at 81 MHz.

¹H-NMR-experiments: detection of Ru-H-species

Protocol d: **2p** (0.18 g, 0.8 mmol) was dissolved in toluene d-8 (8 mL) and $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ (130 mg, 20 mol%) was added. After completion of the olefin metathesis reaction (TLC), NaBH_4 (60 mg, 1.6 mmol) was added and the mixture was heated to reflux until the RCM product was completely consumed (TLC). A sample of the reaction mixture (0.7 mL) was transferred to an NMR-tube under argon. ^{31}P NMR (81 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = 47.1$ ppm. ^1H NMR (600 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = -14.24$ (t, $^2J(^{31}\text{P}-^1\text{H}) = 18.0$ Hz), -10.63 (d, $^2J(^{31}\text{P}-^1\text{H}) = 42.7$ Hz), -7.58 (s(br.)) ppm.

Figure 1. ^1H -NMR spectrum (toluene d8, 600 MHz) obtained from the reaction mixture of a tandem RCM-isomerization reaction (activation with NaBH_4)

Protocol e: **2m** (80 mg, 0.3 mmol) was dissolved in toluene d-8 (2 mL) and $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ (70 mg, 30 mol%) was added. After completion of the olefin metathesis reaction (TLC), the mixture was heated to reflux for two hours and a sample of the reaction mixture was analyzed by H-NMR spectroscopy. The isomerized product **8m** could not be detected, and no signals in the high field region of the spectrum were observed. After addition of isopropanol (34 mg) and NaOH (20 mg), the mixture was heated to reflux. TLC revealed that the isomerization reaction was complete after 30 min.. A sample of the reaction mixture (0.7 mL) was transferred to an NMR-tube under argon. ^1H NMR (500 MHz, $\text{C}_6\text{D}_5\text{CD}_3$): $\delta = -10.66$ (d, $^2J(^{31}\text{P}-^1\text{H}) = 43$ Hz), -8.35 (t, $^2J(^{31}\text{P}-^1\text{H}) = 22$ Hz) ppm.

Figure 2. ^1H -NMR spectrum (toluene d₈, 500 MHz) obtained from the reaction mixture of a tandem RCM-isomerization reaction (activation with Et₃SiH)

Protocol f: **2m** (47 mg, 0.2 mmol) was dissolved in toluene d-8 (2 mL) and [Cl₂(PCy₃)₂Ru=CHPh] (79 mg, 50 mol%) was added. After completion of the olefin metathesis reaction (TLC), Et₃SiH (42 mg, 0.36 mmol) was added and the mixture was heated to reflux. TLC revealed that the isomerization reaction was complete after 2 hours. A sample of the reaction mixture (0.7 mL) was transferred to an NMR-tube under argon. ^1H NMR (500 MHz, C₆D₅CD₃): δ = -10.71 (dd, J = 43, 8 Hz), -11.46 (d, J = 33 Hz), -13.47 (s) ppm.

Figure 3. ^1H -NMR spectrum (toluene d_8 , 500 MHz) obtained from the reaction mixture of a tandem RCM-isomerization reaction (activation with Et_3SiH)

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