Supporting Information

Bisallylation of Zirconacyclopentenes and Ring-Closing Metathesis: a Route to 8-Membered Ring Compounds.

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1. General
The following general procedures were used in all reactions unless otherwise noted. Reaction vessels were dried by heat gun under dry argon pressure. Oxygen- and moisture sensitive reactions were carried out under slight argon overpressure and in dry solvents. All commercially available reagents were purchased in the best quality and used without further purification unless otherwise noted. Solvents were purified and dried by distillation as follows: tetrahydrofuran, diethylether, and toluene from sodium/benzophenone, dichloromethane from calcium hydride. All reactions were monitored by using TLC on E. Merck silica gel 60-F254 coated aluminium plates. Unless the compound was colored, UV-active spots were detected at long wave UV (254 nm) or shortwave UV (180 nm). Column chromatography was performed on Merck Silica gel 60 (0.040-0.063 µm, 240-400 mesh). NMR spectra were recorded on Bruker AVANCE III Spectrometer ($^1$H at 600.17 MHz and $^{13}$C at 150.91 MHz). All NMR spectra were measured in CDCl$_3$ solutions and referenced to residual CDCl$_3$ signal ($^1$H, $\delta$ = 7.26; $^{13}$C, $\delta$ = 77.0, coupling constants J are given in Hz). Infrared spectra were recorded with Thermo Nicolet AVATAR 370 FT-IR spectrometer on KBr tablets of the compounds via DRIFT method and reported in wave numbers (cm$^{-1}$). High resolution mass spectra were recorded on VG-Analytical ZAB-SEQ.
2. Syntheses of nonconjugated enynes.

**General procedure for the synthesis of nonconjugated enynes 1a, 1b, and 1d-1g.** To a solution of corresponding alkyne (10.0 mmol) in dry THF (20 mL) at -78 °C, n-BuLi (1.6 M in hexanes, 6.25 mL, 10.0 mmol) was added dropwise within 10 min and the reaction mixture was stirred for 30 min. Then, 5-bromopent-1-ene (or 6-bromopent-1-ene for 1f and 1g) (12.0 mmol) and DMF (2.41 mL, 20.0 mmol) were added and reaction mixture was allowed to warm gradually to 25 °C. After 12 h the reaction mixture was quenched with a saturated solution of NH₄Cl (20 mL) and extracted with Et₂O (3×15 mL). The combined organic phases were washed with water (20 mL), brine (20 mL), dried over MgSO₄, then the solution was filtered, and concentrated under reduced pressure. Purification of the residue provided the corresponding enyne.

**Synthesis of dimethyl(tert-butyl)(but-3-ynolosilane).** The silyl ether was prepared according to procedure described by Woerpel.² Column chromatography of the residue on silica gel (hexanes) yielded 2.74 g (87 %) of the title product as a colorless liquid. The spectral characteristics are consistent with the reported data. ¹H NMR (600 MHz, CDCl₃) δ 3.75 (t, J = 7.2 Hz, 2H), 2.40 (td, J = 7.2, 2.4 Hz, 2H), 1.95 (t, J = 2.4 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 81.5, 69.3, 61.7, 25.9, 22.8, 18.3, -5.3.

**((But-3-yn-1-yloxy)methyl)benzene.** ((But-3-yn-1-yloxy)methyl)benzene was prepared according to procedure reported by Benner.³ Purification of the residue under reduced pressure (bp 90 °C, 25 torr) yielded 2.35 g (80%) of the title compound as a colorless liquid. The spectral characteristics are consistent with the reported data. ¹H NMR (600 MHz, CDCl₃) δ 7.37-7.34 (m, 4H), 7.31-7.28 (m, 1H), 4.57 (s, 2H), 3.61 (t, J = 6.6 Hz, 2H), 2.51 (dt, J = 7.2, 3.0 Hz, 2H), 2.00 (t, J = 3.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 138.0, 128.4, 127.7, 81.3, 73.0, 69.3, 68.1, 19.9.

**4,4-Dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-ol.** 4,4-Dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-ol was prepared according to procedure reported by Negishi.⁴ The spectral characteristics are consistent with the reported data. ¹H NMR (600 MHz, CDCl₃) δ 5.89-5.83 (m, 1H), 5.23-5.14 (m, 2H), 3.92 (dt, J = 7.2, 1.2 Hz, 1H), 2.22 (d, J = 16.8 Hz, 1H), 2.10 (d, J = 16.8 Hz, 1H), 0.92 (d, J = 4.2 Hz, 6H), 0.09 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 137.4, 116.8, 105.2, 87.1, 79.2, 37.8, 30.1, 23.4, 22.4, 0.1.
Hept-6-en-1-yn-1-ylbenzene (1a). Column chromatography of the residue on silica gel (hexanes) yielded 1.55 g (91%) of the title compound as a colorless liquid. $R_f$ (hexanes) = 0.45; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.40-7.38 (m, 2H), 7.29-7.25 (m, 3H), 5.87-5.80 (m, 1H), 5.10-4.99 (m, 2H), 2.42 (t, $J = 6.6$ Hz, 2H), 2.25-2.21 (m, 2H), 1.74-1.69 (m, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ 137.9, 131.5, 128.2, 127.5, 124.0, 115.2, 89.9, 80.9, 32.8, 27.9, 18.8; IR (KBr) $\nu$ max 3072, 3031, 2938, 2857, 2839, 2244, 2223, 1637, 1595, 1491, 1440, 911, 755, 689 cm$^{-1}$; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{13}$H$_{14}$ 170.1096; found 170.1098.

(Hept-6-en-1-ynyl)trimethylsilane (1b). Distillation of the residue under reduced pressure (bp 70 °C, 25 torr) yielded 0.83 g (50%) of the title product as a colorless liquid. The spectral characteristics are consistent with the reported data.$^5$ $^1$H NMR (600 MHz, CDCl$_3$) δ 5.82-5.75 (m, 1H), 5.05-4.96 (m, 2H), 2.23 (t, $J = 7.2$ Hz, 2H), 2.17-2.12 (m, 2H), 1.63-1.58 (m, 2H), 0.14 (s, 9H), $^{13}$C NMR (151 MHz, CDCl$_3$) δ 137.9, 115.1, 107.2, 84.7, 32.7, 27.8, 19.2, 0.15.

N-Benzyl-N-(3-phenylprop-2-yn-1-yl)prop-2-en-1-amine (1c). Compound 1c was prepared according to procedure reported by Whitby.$^6$ Column chromatography of the residue on silica gel (5/1 hexanes/Et$_2$O) yielded 2.19 g (84%) of the title compound as a yellow oil. The spectral characteristics are consistent with the reported data. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.52-7.50 (m, 2H), 7.44-7.42 (m, 2H), 7.38-7.35 (m, 5H), 7.31-7.29 (m, 1H), 6.00-5.93 (m, 1H), 5.37-5.33 (m, 1H), 5.25-5.22 (m, 1H), 3.76 (s, 2H), 3.57 (s, 2H), 3.30 (dt, $J = 6.61$ Hz, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ 138.7, 135.7, 131.7, 129.2, 128.3, 128.2, 128.0, 127.1, 123.4, 118.0, 85.7, 84.4, 57.4, 56.8, 42.1.

Undec-1-en-6-yne (1d). Column chromatography of the residue on silica gel (hexanes) yielded 1.04 g (70%) of the title compound as a colorless liquid. $R_f$ (hexanes) = 0.39; $^1$H NMR (600 MHz, CDCl$_3$) δ 5.83-8.77 (m, 1H), 5.05-4.95 (m, 2H), 2.18-2.12 (m, 6H), 1.60-1.55 (m, 2H), 1.49-1.44 (m, 2H), 1.43-1.47 (m, 2H) 0.92-0.89 (t, $J = 6$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) δ 137.9, 131.4, 128.9, 120.9, 115.1, 89.1, 80.9, 32.9, 28.0, 21.4, 18.8; IR (KBr) $\nu_{max}$ 3069, 2959, 2929, 2857, 2860, 1643, 1458, 1443, 1329, 991, 914 cm$^{-1}$; HRMS (TOF-MS-Cl) m/z: [M + H]$^+$ calcd for C$_{11}$H$_{19}$ 151.1487; found 151.1490.

((Non-8-en-3-yn-1-yl)oxy)methyl)benzene (1e). Column chromatography of the residue on silica gel (10/1 hexanes/Et$_2$O) yielded 1.16 g (51 %) of the title compound as a colorless liquid. $R_f$ (10/1...
hexanes/Et2O) = 0.45; 1H NMR (600 MHz, CDCl3) δ 7.36-7.33 (m, 4H), 7.31-7.27 (m, 1H), 5.83-5.76 (m, 1H), 5.05-4.96 (m, 2H), 4.56 (s, 2H), 3.57 (t, J = 7.2 Hz, 2H), 2.50-2.46 (m, 2H), 2.19-2.12 (m, 4H), 1.61-1.56 (m, 2H); 13C NMR (151 MHz, CDCl3) δ 138.2, 138.0, 128.4, 127.6, 127.7, 115.0, 81.0, 76.9, 72.9, 68.9, 32.8, 28.1, 20.2, 18.2.; IR (KBr) νmax 3066, 3031, 2974, 2929, 2905, 2857, 1640, 1497, 1365, 1102, 994, 914, 740, 701 cm−1; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C16H20O 227.1436; found 227.1435.

Oct-7-en-1-yn-1-ylbenzene (1g). To a solution of phenylacetylene (3.75 mmol,) in dry THF (15 mL) at -78 °C, n-BuLi (1.6 M in hexanes, 2.34 mL, 3.75 mmol) was added dropwise within 10 min and the reaction mixture was stirred for 30 min. Then, 6-bromopent-1-ene (4.50 mmol, 0.60 mL) and DMPU (1.08 mL, 9.00 mmol) were added and reaction mixture was allowed to warm gradually to 25 °C. After 12 h the reaction mixture was quenched with a saturated solution of NH4Cl (20 mL) and extracted with Et2O (3×15 mL). The combined organic phases were washed with water (20 mL), brine (20 mL), dried over MgSO4, then the solution was filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes) yielded 0.40 g (58%) of the title compound as a colorless liquid. Rf (hexanes) = 0.45; 1H NMR (300 MHz, CDCl3) δ 7.41-7.38 (m, 2H), 7.32-7.27 (m, 3H), 5.90-5.77 (m, 1H), 2.42 (t, J = 6.6 Hz, 2H), 2.15-2.08 (m, 2H), 1.69-1.51 (m, 4H); 13C NMR (151 MHz, CDCl3) δ 138.6, 131.5, 128.2, 127.5, 124.0, 114.6, 90.2, 80.7, 33.3, 28.2, 28.1, 19.3.; IR (KBr) νmax 3075, 2980, 2935, 2854, 2226, 1643, 1595, 1488, 1449, 991, 914, 758, 692 cm−1; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C14H16 184.1252; found 184.1251.

N-benzyl-N-(3-ethoxyprop-2-yn-1-yl)prop-2-en-1-amine (1h). Compound 1i was prepared according to modified procedure reported by Whitby. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.96 g (42 %) of the title compound as a yellow liquid. Rf (2/1 hexanes/EtOAc) = 0.54; 1H NMR (600
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MHz, CDCl3) δ 7.36-7.34 (m, 2H), 7.32-7.30 (m, 2H), 7.24 (tt, J = 6.6, 1.8 Hz, 1H), 5.92-5.90 (m, 1H), 5.27-5.24 (m, 1H), 5.16-5.14 (m, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.60 (s, 2H), 3.30 (s, 2H), 3.14 (td, J = 6.6, 1.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H); 13C NMR (151 MHz, CDCl3) δ 139.0, 136.0, 129.2, 128.2, 117.6, 93.7, 74.3, 57.1, 56.5, 40.9, 31.9, 14.4.; IR (KBr) νmax 3078, 3063, 3028, 2977, 2923, 2815, 1455, 1326, 1287, 1224, 1120, 1003, 925, 866, 740, 698 cm⁻¹; HRMS (TOF-MS-Cl) m/z: [M + H]+ calcd for C15H19NO 229.1467; found 229.1468.

tert-Butyl((4,4-dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-yl)oxy)dimethylsilane (1i). Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) yielded 0.577 g (88%) of the title compound as a colorless liquid. The spectral characteristics are consistent with the reported data.4 1H NMR (600 MHz, CDCl3) δ 7.35-7.31 (m, 4H), 7.28-7.25 (m, 1H), 5.80-5.74 (m, 1H), 5.34-5.23 (m, 2H), 4.58 (d, J = 12.0 Hz, 1H), 4.30 (d, J = 11.4 Hz, 1H), 3.61-3.59 (m, 1H), 2.33 (d, J = 16.8 Hz, 1H), 2.20 (d, J = 16.2 Hz, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.14 (s, 9H); 13C NMR (151 MHz, CDCl3) δ 139.0, 135.3, 128.2, 127.6, 127.3, 119.12 105.7, 86.4, 86.2, 70.6, 37.7, 30.4, 23.5, 22.4, 0.2.

tert-Butyl((4,4-dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-yl)oxy)dimethylsilane (1j). 4,4-dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-ol (0.470 g, 2.23 mmol) was dissolved in DCM (15 mL) and solution was cooled to – 40 °C. Then, Et3N (0.486 mL, 3.5 mmol) and TBDMSOTf (0.616 mL, 2.68 mmol) were added and reaction mixture was stirred at the same temperature for 1 h. Then, reaction mixture was quenched with EtOH (0.5 mL) and brine (25 mL) and extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO4, then the solution was filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes) yielded 0.638 g (88%) of the title compound as a colorless liquid. Rf (hexanes) = 0.50; 1H NMR (600 MHz, CDCl3) δ 5.79-5.74 (m, 1H), 5.15-5.10 (m, 2H), 3.92-3.91 (m, 1H), 2.26 (d, J = 16.2 Hz, 1H), 2.09 (d, J = 16.8 Hz, 1H), 0.92 (s, 3H), 0.90 (s, 3H), 0.89 (s, 9H), 0.16 (s, 9H), 0.06 (s, 3H), -0.01 (s, 3H); 13C NMR (151 MHz, CDCl3) δ 138.5, 116.4 105.9, 86.3, 79.6, 38.4, 30.1, 25.9, 23.1, 22.2, 18.2, 0.2, -4.0, -5.0.; IR (KBr) νmax 2950, 2929, 2893, 2857, 2172, 1473, 1248, 1075, 842, 779, 761 cm⁻¹; HRMS (TOF-MS-Cl) m/z: [M + H]+ calcd for C18H37OSi2 325.2383; found 325.2378.
3. Bisallylation reactions

**General procedure for the synthesis of bis-allylation products.** To a solution of bis(cyclopentadienyl)zirconium dichloride (0.350 g, 1.20 mmol) in dry THF (7 mL) cooled to -78°C was added dropwise n-BuLi (1.6 M in hexanes, 1.50 mL, 2.40 mmol) within 5 min and the reaction mixture was stirred for 1 h at the same temperature. An enyne (1.00 mmol) was added and the reaction mixture was allowed to warm gradually to 25°C. After 3 h, CuCl (0.20 mmol, 0.018 g), and allyl chloride (0.325 mL, 4.00 mmol) were added and the reaction mixture was left to stir at 25°C for 12 h. Then the reaction mixture was quenched with 1N HCl (10 mL) and extracted with EtOAc (3×20 mL). Combined organic phases were washed with saturated solution of NaHCO₃ (20 mL), water (2×20 mL), brine (20 mL), dried over MgSO₄, the solution was filtered, and concentrated under reduced pressure. Purification of the residue by column chromatography provided the corresponding triene.

\[(E)-(1-(2-(But-3-en-1-yl)cyclopentylidene)but-3-en-1-yl)benzene (4a)\]. Column chromatography of the residue on silica gel (hexane) yielded 0.224 g (89%) of the title compound as a colorless liquid. \(R_f\) (hexanes) = 0.36; \(^1\)H NMR (600 MHz, CDCl₃) δ 7.30-7.28 (m, 2H), 7.20-7.15 (m, 3H), 5.92-5.85 (m, 1H), 5.76-5.70 (m, 1H), 5.08-4.90 (m, 4H), 3.21-3.13 (m, 2H), 2.81-2.77 (m, 1H), 2.25-2.17 (m, 2H), 2.12-2.05 (m, 2H), 1.83-1.77 (m, 1H), 1.70-1.63 (m, 2H), 1.59-1.54 (m, 1H), 1.51-1.41 (m, 2H); \(^13\)C NMR (151 MHz, CDCl₃) δ 145.5, 143.5, 138.9, 136.6, 129.7, 128.5, 127.8, 125.9, 115.1, 114.5, 41.2, 39.0, 34.2, 32.0, 31.6, 31.2, 24.3.; IR (KBr) \(\nu_{max}\) 3072, 3052, 3019, 2977, 2950, 2929, 2863, 1643, 1595, 1494, 1440, 994, 908, 776, 701 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C₁₉H₂₅ 252.1878; found 252.1877.

\[(E)-(1-(2-(But-3-en-1-yl)cyclopentylidene)but-3-en-1-yl)trimethylsilane (4b)\]. Column chromatography of the residue on silica gel (heptane) yielded 0.160 g (65%) of the title compound as a yellow liquid. \(R_f\) (heptane) = 0.65; \(^1\)H NMR (600 MHz, CDCl₃) δ 5.85-5.76 (m, 2H), 5.02-4.92 (m, 4H), 2.96 (dd, \(J = 15.6, 5.4\) Hz, 1H), 2.85-2.82 (m, 1H), 2.70-2.66 (m, 1H), 2.36-2.28 (m, 2H), 2.14-2.08 (m, 1H), 2.03-1.96 (m, 1H), 1.74-1.69 (m, 1H), 1.67-1.58 (m, 2H), 1.56-1.45 (m, 2H), 1.31-1.25 (m, 1H), 0.10 (s, 9H); \(^13\)C NMR (151 MHz, CDCl₃) δ 160.5, 138.9, 138.5, 126.3, 114.4, 114.2, 41.8, 36.8, 33.7, 32.5, 32.2, 30.3, 24.0, 0.2.; IR (KBr) \(\nu_{max}\) 3075, 2998, 2950, 2860, 1637, 1610, 1455, 1437, 1251, 994, 908, 857, 839 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C₁₆H₂₈Si 248.1960; found 248.1961.
(Z)-1-Benzyl-3-(but-3-en-1-yl)-4-(1-phenylbut-3-en-1-ylidene)pyrrolidine (4c). Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.188 g (55%) of the title compound as a yellow liquid. \( R_f \) (2/1 hexanes/EtOAc) = 0.42; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.31-7.28 (m, 6H), 7.25-7.20 (m, 2H), 7.15-7.14 (m, 2H), 5.90-5.83 (m, 1H), 5.73-5.67 (m, 1H), 5.01-4.92 (m, 4H), 3.58 (dd, \( J = 55.2, 13.2 \) Hz, 2H), 3.26-3.24 (m, 1H), 3.18 (d, \( J = 6.0 \) Hz, 2H), 3.03 (d, \( J = 13.2 \) Hz, 1H), 2.93-2.92 (m, 1H), 2.83-2.82 (m, 1H), 2.48 (s, 1H), 2.20-2.14 (m, 1H), 2.10-2.04 (m, 1H), 1.81-1.76 (m, 1H), 1.74 (m, 1H); \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 142.3, 138.4, 135.9, 128.7, 128.2, 128.1, 128.0, 126.9, 126.4, 115.7, 114.8, 60.5, 59.2, 58.7, 40.8, 38.5, 33.7, 31.9; IR (KBr) \( \nu_{\text{max}} \) 3078, 3060, 3028, 2998, 2971, 2935, 2908, 2860, 2833, 2782, 2729, 1676, 1637, 1500, 1449, 1440, 997, 740, 701 cm\(^{-1}\); HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C\(_{25}\)H\(_{30}\)N 344.2378; found 344.2385.

(Z)-1-(But-3-en-1-yl)-2-(oct-1-en-4-ylidene)cyclopentane (4d). Column chromatography of the residue on silica gel (heptane) yielded 0.177 g (76%) of the title compound as a colorless liquid. \( R_f \) (heptane) = 0.48; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 5.86-5.80 (m, 1H), 5.78-5.72 (m, 1H), 5.03-4.93 (m, 4H), 2.84-2.73 (m, 2H), 2.62-2.58 (m, 1H), 2.24-2.20 (m, 2H), 2.14-2.08 (m, 1H), 2.03-1.93 (m, 3H), 1.72-1.55 (m, 4H), 1.45-1.39 (m, 1H), 1.34-1.25 (m, 5H), 0.89 (t, \( J = 7.2 \) Hz, 3H); \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 142.3, 139.1, 137.4, 128.0, 114.9, 114.3, 40.9, 37.1, 33.8, 32.3, 32.2, 31.1, 30.2, 29.4, 23.7, 22.8, 14.1; IR (KBr) \( \nu_{\text{max}} \) 3072, 2998, 2953, 2926, 2872, 2857, 1823, 1634, 1470, 1455, 1434, 1410, 1374, 994, 911; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C\(_{17}\)H\(_{28}\) 232.2195; found 232.2195.

(E)-(((3-(2-(But-3-en-1-yl)cyclopentylidene)hex-5-en-1-yl)oxy)methyl)benzene (4e). Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.257 g (83%) of the title compound as a yellow liquid. \( R_f \) (2/1 hexanes/EtOAc) = 0.63; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.35-7.32 (m, 4H), 7.30-7.27 (m, 1H), 5.85-5.71 (m, 2H), 5.03-4.93 (m, 4H), 4.51 (s, 2H), 3.50-3.46 (m, 2H), 2.84-2.75 (m, 2H), 2.63-2.60 (m, 1H), 2.38-2.30 (m, 2H), 2.29-2.22 (m, 2H), 2.14-2.08 (m, 1H), 2.03-1.96 (m, 1H), 1.72-1.56 (m, 4H), 1.45-1.39 (m, 1H), 1.33-1.27 (m, 1H); \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 144.9, 138.9, 138.7, 137.0, 128.3, 127.5, 127.4, 124.0, 115.3, 114.4, 72.7, 68.8, 41.0, 37.8, 33.7, 33.0, 32.2, 31.0, 29.6, 23.6. IR (KBr) \( \nu_{\text{max}} \) 3078, 3028, 2941, 2929, 2863, 1637, 1458, 1362, 1099, 997, 911, 737, 695 cm\(^{-1}\); HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C\(_{22}\)H\(_{30}\)O 310.2297; found 310.2300.
(Z)-1-(But-3-en-1-yl)-2-(oct-1-en-4-ylidene)cyclohexane (4f). Column chromatography on silica gel (heptane) yielded 0.204 g (83%) of the title compound as a colorless liquid. $R_f$ (heptane) = 0.47; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.86-5.79 (m, 1H), 5.77-5.70 (m, 1H), 5.02-4.97 (m, 2H), 4.95-4.91 (m, 2H), 2.91-2.88 (m, 1H), 2.68-2.62 (m, 2H), 2.45-2.42 (m, 1H), 2.09-2.04 (m, 1H), 2.02-1.88 (m, 3H), 1.83 (td, $J = 13.8, 3.6$ Hz, 1H), 1.79-1.74 (m, 1H), 1.69-1.65 (m, 1H), 1.62-1.38 (m, 5H), 1.34-1.26 (m, 4H), 1.24-1.16 (m, 1H), 0.89 (t, $J = 6.6$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 139.5, 137.6, 136.7, 128.0, 114.2, 114.0, 36.6, 36.4, 31.9, 31.9, 31.8, 31.5, 31.2, 28.4, 25.3, 22.9, 21.1, 14.1.; IR (KBr) $\nu_{max}$ 3072, 2956, 2923, 2857, 1820, 1634, 1443, 994, 908 cm$^{-1}$; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{18}$H$_{30}$ 246.2348; found 246.2354.

(E)-(1-(2-(But-3-en-1-yl)cyclohexylidene)but-3-en-1-yl)benzene (4g). Column chromatography of the residue on silica gel (10/1 hexanes/Et$_2$O) yielded 0.213 g (80%) of the title compound as a colorless liquid. $R_f$ (10/1 hexanes/Et$_2$O) = 0.45; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.30-7.27 (m, 2H), 7.19 (tt, $J = 7.8, 1.2$ Hz, 1H), 7.10-7.08 (m, 2H), 5.91-5.85 (m, 1H), 5.76-5.70 (m, 1H), 5.07-4.92 (m, 4H), 3.25 (dd, $J = 15.6, 6.0$ Hz, 1H), 2.98-2.93 (m, 1H), 2.86-2.81 (m, 1H), 2.14-2.03 (m, 3H), 1.82 (td, $J = 13.8, 4.2$ Hz, 1H), 1.78-1.69 (m, 2H), 1.67-1.63 (m, 1H), 1.61-1.54 (m, 3H), 1.52-1.48 (m, 1H), 1.24-1.16 (m, 1H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.1, 139.5, 139.3, 136.5, 130.6, 128.9, 127.8, 125.8, 114.7, 114.2, 38.4, 36.5, 32.0, 31.8, 31.2, 28.5, 27.2, 21.0.; IR (KBr) $\nu_{max}$ 3075, 3058, 3019, 2929, 2851, 1643, 1497, 1443, 994, 908, 779, 701 cm$^{-1}$; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{20}$H$_{26}$ 266.2035; found 266.2036.

(Z)-1-Benzyl-3-(but-3-en-1-yl)-4-(1-ethoxybut-3-en-1-ylidene)pyrrolidine (4h). Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.130 g (42%) of the title compound as a yellow liquid. $R_f$ (2/1 hexanes/EtOAc) = 0.53; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40-7.30 (m, 4H), 7.25-7.23 (m, 1H), 5.85-5.76 (m, 2H), 5.15-4.93 (m, 4H), 3.73-3.66 (m, 2H), 3.62 (s, 2H), 3.35 (d, $J = 13.2$ Hz, 1H), 3.18 (d, $J = 12.6$ Hz, 1H), 2.95-2.88 (m, 2H), 2.69-2.65 (m, 2H), 2.51-2.50 (m, 1H), 2.12-2.05 (m, 1H), 2.03-1.96 (m, 1H), 1.66-1.53 (m, 2H), 1.17 (t, $J = 6.6$ Hz, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 138.6, 134.8, 128.7, 128.2, 126.8, 116.3, 114.6, 63.7, 60.5, 59.5, 55.8, 39.4, 33.9, 33.3, 31.9, 15.5.; IR (KBr) $\nu_{max}$ 3075, 3060, 3028, 2977, 2932, 2911, 2782, 2732, 1700, 1679, 1643, 1455, 1254, 1171, 1048, 911, 740, 701; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{21}$H$_{30}$NO 312.2337; found 312.2322.
((E)-1-((2S,3R)-3-(Benzyloxy)-2-(but-3-en-1-yl)-4,4-dimethylcyclopentylidene)but-3-en-1-yl)tri-methylsilane (4i). Column chromatography of the residue on silica gel (10/1 hexanes/toluene) yielded 0.309 g (81%) of the title compound as a colorless liquid. 

\[ R_f (10/1 \text{hexanes/toluene}) = 0.41; \]

\[ ^1H \text{NMR (600 MHz, CDCl}_3) \delta 7.37-7.33 (m, 4H), 7.29-7.27 (m, 1H), 5.82-5.74 (m, 2H), 4.99-4.91 (m, 4H), 4.68 (d, \text{J = 11.4 Hz, 1H}), 4.55 (d, \text{J = 11.4 Hz, 1H}), 3.42 (d, \text{J = 6.0 Hz, 1H}), 2.91-2.88 (m, 1H), 2.80-2.76 (m, 1H), 2.71-2.68 (m, 1H), 2.22-2.13 (m, 2H), 2.09-1.99 (m, 2H); \]

\[ ^{13}C \text{NMR (151 MHz, CDCl}_3) \delta 154.6, 139.0, 138.1, 128.5, 128.3, 127.6, 127.5, 114.6, 114.4, 92.5, 73.2, 48.6, 47.9, 41.6, 36.0, 33.7, 30.6, 28.4, 20.7, 0.3. \]

IR (KBr) \[ \nu_{\text{max}} 3075, 3058, 3031, 2953, 2929, 2893, 2863, 2839, 1637, 1622, 1449, 1248, 1096, 911, 857, 836, 758, 695 \text{ cm}^{-1}; \]

HRMS (TOF-MS-CI) \[ m/z: [M + H]^+ \text{ calcd for C}_{25}H_{39}OSi 383.2770; \text{ found 383.2772.} \]

(((1R,E)-5-(But-3-en-1-yl)-2,2-dimethyl-4-(1-(trimethylsilyl)but-3-en-1-ylidene)cyclopentyl)oxy)(tert-butyl)dimethylsilane (4j). Column chromatography of the residue on silica gel (hexanes) yielded 0.308 g (76%) of the title compound as a colorless liquid. 

\[ R_f \text{(hexanes)} = 0.55; \]

\[ ^1H \text{NMR (600 MHz, CDCl}_3) \delta 5.82-5.75 (m, 2H), 5.01-4.91 (m, 4H), 3.60 (d, \text{J = 6.0 Hz, 1H}), 2.91-2.79 (m, 2H), 2.59-2.54 (m, 1H), 2.22 (dd, \text{J = 13.8, 1.2 Hz, 1H}), 2.00-1.94 (m, 3H), 1.76-1.70 (m, 1H), 1.59-1.55 (m, 1H), 1.02 (s, 3H), 0.89 (s, 9H), 0.78 (s, 3H), 0.10 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); \]

\[ ^{13}C \text{NMR (151 MHz, CDCl}_3) \delta 154.3, 139.2, 138.1, 128.8, 114.4, 114.1, 83.9, 49.4, 48.2, 41.3, 36.0, 31.1, 29.6, 26.9, 26.0, 20.2, 18.2, 0.3, -4.0, -4.1.; \]

IR (KBr) \[ \nu_{\text{max}} 3078, 2953, 2890, 2857, 1473, 1461, 1434, 1407, 1389, 1362, 1245, 1108, 911, 860, 836, 773 \text{ cm}^{-1}; \]

HRMS (TOF-MS-CI) \[ m/z: [M + H]^+ \text{ calcd for C}_{24}H_{47}OSi}_2 407.3165; \text{ found 407.3168.} \]

Ethyl (E)-2-(2-(1-phenylbut-3-en-1-ylidene)cyclopentyl)pent-4-enoate (9). To a solution of bis(cyclopentadienyl)zirconium dichloride (1.051 g, 3.60 mmol) in dry THF (15 mL) cooled to -78 °C was added dropwise n-BuLi (1.6 M in hexanes, 4.50 mL, 7.20 mmol) within 10 min and the reaction mixture was stirred for 1 h at the same temperature. Then \[ 1a \text{(3.00 mmol, 0.510 g) was added and the reaction mixture was allowed to warm gradually to 25 °C. After 3 h, reaction mixture was cooled to – 10 °C and CuCl (3.10 mmol, 0.30 g), and allyl chloride (3.10 mmol, 0.253 mL) were added and the reaction mixture was left to stir at – 10 °C for 12 h. Then ethyl chloroformate (9.00 mmol, 0.858 mL) was added and reaction mixture was stirred at 25 °C for additional 12 h. Then the reaction mixture was quenched with saturated solution of NH₄Cl (10 mL) and extracted with EtOAc (3×20 mL). Combined organic phases were washed with saturated solution of NaHCO₃ (20 mL), water (2×20 mL), brine (20 mL),
dried over MgSO₄, the solution was filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (4/1 hexanes/EtOAc) yielded 0.350 g (41%) diene 8 as a yellow liquid. Rₜ (4/1 hexanes/EtOAc) = 0.55. ¹H NMR (600 MHz, CDCl₃) δ 7.30-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.15-7.14 (m, 2H), 5.74-5.68 (m, 1H), 5.01-4.91 (m, 2H), 4.17 (q, 2H), 3.28-3.24 (m, 1H), 3.20-2.9 (t, J = 6.6 Hz, 2H), 2.57 (dd, J = 15.0, 3.6 Hz, 1H), 2.31 (dd, J = 15.0, 10.8 Hz, 1H), 2.28-2.23 (m, 1H), 2.12-2.07 (m, 1H), 1.91-1.85 (m, 1H), 1.72-1.65 (m, 1H), 1.62-1.57 (m, 1H), 1.56-1.52 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 172.8, 143.7, 143.2, 136.2, 130.9, 128.4, 127.9, 126.1, 115.4, 60.3, 39.6, 39.0, 38.6, 31.9, 31.4, 24.0, 14.3.; IR (KBr) νₘₐₓ 3383, 3075, 3055, 3019, 2956, 2869, 1745, 1676, 1443, 1386, 1263, 1006, 701 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C₁₉H₂₄O₂ 284.17763; found 284.17762. To a solution of diisopropylamine (1.72 mmol, 0.240 mL) in THF (5 mL), n-BuLi (2.5M in hexanes, 1.64 mmol, 0.655 mL) was added at –78 °C and left to stir for 15 min. Then a solution of diene (1.20 mmol, 0.350 g) in THF (2 mL) was added over period of 10 min. and left to stir for 30 min. Then allyl bromide (2.4 mmol, 0.207 mL) was added and reaction mixture was left to stir for 20 h at 25 °C. Reaction mixture was quenched with 1N HCl (10 mL) and extracted with EtOAc (3×20 mL). Combined organic phases were washed with saturated solution of NaHCO₃ (20 mL), water (2×20 mL), brine (20 mL), dried over MgSO₄, the solution was filtered, and concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (4/1 hexanes/EtOAc) yielded 0.289 g (75%) the title compound as a yellow liquid. Rₜ (4/1 hexanes/EtOAc) = 0.60. Major diastereoisomer: ¹H NMR (600 MHz, CDCl₃) δ 7.30-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.16-7.14 (m, 2H), 5.82-5.70 (m, 2H), 5.18-4.92 (m, 4H), 4.15 (dd, J = 7.8, 1.8 Hz, 1H), 3.32-3.26 (m, 1H), 3.20-3.15 (m, 2H), 2.80-2.77 (m, 1H), 2.53-2.47 (m, 1H), 2.26-2.17 (m, 3H), 2.14-2.10 (m, 1H), 1.75-1.68 (m, 3H), 1.49-1.42 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ ¹³C NMR (151 MHz, CDCl₃) δ 174.4, 143.3, 142.8, 136.4, 136.2, 131.6, 128.4, 127.8, 126.2, 116.2, 115.4, 60.2, 48.2, 43.8, 38.6, 32.4, 32.0, 27.9, 24.2, 14.3. Minor diastereoisomer: ¹H NMR (600 MHz, CDCl₃) δ 4.17-4.13 (m, 1H), 3.10-3.06 (m, 2H), 2.70-2.66 (m, 1H), 2.36-2.31 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H) – the remaining signals were overlapped by the signals of the major diastereoisomer; ¹³C NMR (151 MHz, CDCl₃) δ 174.9, 143.2, 142.5, 136.1, 135.9, 131.8, 128.4, 126.2, 116.6, 115.6, 60.2, 48.4, 43.8, 39.3, 35.5, 31.0, 28.3, 23.3, 20.5, 14.4. IR (KBr) νₘₐₓ 3072, 3055, 2971, 2953, 2872, 1733, 1643, 1443, 1227, 1180, 1030, 994, 914, 779, 704 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C₂₂H₂₉O₂ 325.21622; found 325.21621.
4. Ring closing metathesis

(6Z,9E)-9-Phenyl-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6a). Method A:

Compound 4a (0.39 mmol, 0.10 g) was dissolved in DCM (30 mL) and argon was bubbled through the solution for 15 min. Grubbs 2\textsuperscript{nd} generation catalyst (0.019 mmol, 0.017 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2\textsuperscript{nd} generation catalyst was transferred to the solution of 4a and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Without purification, \textsuperscript{1}H NMR analysis of the residue showed the title compound to be formed in 99\%. (Mesitylene, 0.39 mmol was used as internal standard). Column chromatography of the residue on silica gel (hexanes) yielded 0.057 g (64\%) of the title compound as a yellow liquid. \(R_f\) (hexanes) = 0.42; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36-7.31 (m, 2H), 7.25-7.20 (m, 3H), 5.90-5.85 (m, 1H), 5.67-5.63 (m, 1H), 3.53-3.49 (m, 1H), 3.15-3.12 (m, 1H), 2.74 (q, \(J = 6.0\) Hz, 1H), 2.51-2.45 (m, 1H), 2.43-2.37 (m, 1H), 2.20-2.11 (m, 2H), 2.06-2.01 (m, 1H), 1.80-1.75 (m, 1H), 1.68-1.63 (m, 1H), 1.47-1.39 (m, 3H); \textsuperscript{13}C NMR (151 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 145.0, 143.2, 134.3, 132.1, 130.1, 128.1, 128.0, 125.9, 43.9, 35.8, 35.3, 33.5, 33.3, 27.2, 25.1.; IR (KBr) \(\nu_{\text{max}}\) 3075, 3055, 3022, 2947, 2929, 1595, 1497, 1449, 1437, 1072, 794, 737, 698 cm\textsuperscript{-1}; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C\textsubscript{17}H\textsubscript{20} 224.1565; found 224.1564.

Method B: Compound 4a (0.39 mmol, 0.10 g) was dissolved in DCM (30 mL) and argon was bubbled through the solution for 15 min. Hoveyda-Grubbs 1\textsuperscript{st} generation catalyst (0.02 mmol, 0.012 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Hoveyda-Grubbs 1\textsuperscript{st} generation catalyst was transferred to the solution of 4a and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Without purification, \textsuperscript{1}H NMR analysis of the residue showed the title compound to be formed in 82\%. (Mesitylene, 0.39 mmol was used as internal standard).

Method C: Compound 4a (0.20 mmol, 0.05 g) was dissolved in DCM (15 mL) and argon was bubbled through the solution for 15 min. Hoveyda-Grubbs 2\textsuperscript{nd} generation catalyst (0.01 mmol, 0.0062 g) was dissolved in DCM (5 mL) and argon was bubbled through the solution also for 15 min. Solution of Hoveyda-Grubbs 2\textsuperscript{nd} generation catalyst was transferred to the solution of 4a and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Without purification, \textsuperscript{1}H NMR analysis of the residue showed the title compound to be formed in 64\%. (Mesitylene, 0.20 mmol was used as internal standard).
**Method D:** Compound 4a (0.20 mmol, 0.05 g) was dissolved in DCM (15 mL) and argon was bubbled through the solution for 15 min. Grubbs 1st generation catalyst (0.01 mmol, 0.0082 g) was dissolved in DCM (5 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 1st generation catalyst was transferred to the solution of 4a and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Without purification, $^1$H NMR analysis of the residue showed the title compound to be formed in 99%. (Mesitylene, 0.20 mmol was used as internal standard).

$((3aE,6Z)-2,3,5,8,9,9a$-Hexahydro-1H-cyclopenta[8]annulen-4-yl)trimethylsilane (6b).

Compound 4b (0.20 mmol, 0.50 g) was dissolved in DCM (15 mL) and argon was bubbled through the solution for 15 min. Grubbs 2nd generation catalyst (0.01 mmol, 0.009 g) was dissolved in DCM (5 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2nd generation catalyst was transferred to the solution of 4b and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (hexanes) yielded 0.034 g (77%) of the title compound as a colorless liquid. $R_f$ (hexanes) = 0.42; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.79-5.75 (m, 1H), 5.52-5.47 (m, 1H), 3.15-3.11 (m, 1H), 3.04-3.00 (m, 1H), 2.47-2.40 (m, 2H), 2.35-2.30 (m, 1H), 2.24-2.15 (m, 2H), 1.94-1.89 (m, 1H), 1.72-1.64 (m, 2H), 1.52-1.45 (m, 1H), 1.37-1.32 (m, 1H), 1.25-1.19 (m, 1H), 0.13 (s, 9H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 158.3, 134.2, 131.4, 128.8, 45.5, 35.6, 34.3, 33.4, 32.4, 27.3, 25.1, 0.1; IR (KBr) $\nu_{\text{max}}$ 3013, 2950, 2926, 2863, 1613, 1458, 1248, 860, 836, 755, 731 cm$^{-1}$; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{14}$H$_{24}$Si 220.1647; found 220.1648.

$((6Z,9Z)-2$-Benzyl-9-phenyl-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole (6c). Compound 4c (0.31 mmol, 0.108 g) was dissolved in DCM (25 mL) and argon was bubbled through the solution for 15 min. Grubbs 2nd generation catalyst (0.016 mmol, 0.013 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2nd generation catalyst was transferred to the solution of 4c and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.050 g (52%) of the title compound as a yellow liquid. $R_f$ (2/1 hexanes/EtOAc) = 0.40; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33-7.28 (m, 6H), 7.25-7.18 (m, 4H), 5.89-5.84 (m, 1H), 5.68-5.63 (m, 1H), 3.60 (d, $J$ = 12.6 Hz, 1H), 3.45 (td, $J$ = 13.8, 3.6 Hz, 2H), 3.30-3.25 (m, 1H), 3.16 (d, $J$ = 13.2 Hz, 1H), 3.06-3.00 (m, 2H), 2.76 (q, 6.0 Hz, 1H), 2.54-2.48 (m, 1H), 2.39-2.33 (m, 1H), 2.17 (t, $J$ = 7.8 Hz, 1H), 1.77-1.73 (m, 1H), 1.57-1.51 (m, 1H); $^{13}$C NMR (151
MHz, CDCl\textsubscript{3}) \( \delta \) 143.5, 138.8, 135.7, 131.7, 130.5, 128.8, 128.2, 128.0, 127.7, 126.9, 126.4, 62.1, 60.6, 59.9, 43.5, 34.6, 32.1, 26.8.; IR (KBr) \( \nu \)\textsubscript{max} 3075, 3058, 3025, 2998, 2974, 2929, 2860, 2788, 2726, 1679, 1640, 1494, 1455, 1440, 1126, 1033, 997, 917, 737, 701 cm\textsuperscript{-1}; HRMS (TOF-MS-CI) m/z: [M + H]\textsuperscript{+} calcd for C\textsubscript{22}H\textsubscript{26}N 316.20566; found 316.20598.

(6Z,9Z)-9-Butyl-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6d). Compound 4d (0.56 mmol, 0.130 g) was dissolved in DCM (35 mL) and argon was bubbled through the solution for 15 min. Grubbs 2\textsuperscript{nd} generation catalyst (0.028 mmol, 0.024 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2\textsuperscript{nd} generation catalyst was transferred to the solution of 4d and reaction mixture was stirred under reflux for 4 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (heptane) yielded 0.070 g (62%) of the title compound as a colorless liquid. \( R_f\) (heptane) = 0.53; \(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) 5.86-5.82 (m, 1H), 5.54-5.50 (m, 1H), 3.11-3.07 (m, 1H), 2.94-2.91 (m, 1H), 2.40 (dd, \( J = 15.0, 6.0 \) Hz, 1H), 2.32-2.16 (m, 4H), 2.07-1.93 (m, 2H), 1.89-1.83 (m, 1H), 1.67-1.61 (m, 1H), 1.60-1.49 (m, 2H), 1.42-1.25 (m, 6H), 0.91 (t, \( J = 7.8 \) Hz, 3H); \(^{13}\)C NMR (151 MHz, CDCl\textsubscript{3}) \( \delta \) 139.5, 132.7, 132.5, 129.4, 43.2, 35.8, 35.3, 33.3, 32.7, 30.9, 30.6, 27.0, 24.4, 22.8, 14.1.; IR (KBr) \( \nu \)\textsubscript{max} 3016, 2953, 2938, 2866, 2857, 1467, 1452, 1377, 967, 743 cm\textsuperscript{-1}; HRMS (TOF-MS-CI) m/z: [M + H]\textsuperscript{+} calcd for C\textsubscript{15}H\textsubscript{24} 204.1878; found 204.1886.

(6Z,9E)-9-(2-(Benzyloxy)ethyl)-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6e). Compound 4e (0.32 mmol, 0.10 g) was dissolved in DCM (25 mL) and argon was bubbled through the solution for 15 min. Grubbs 2\textsuperscript{nd} generation catalyst (0.016 mmol, 0.013 g) was dissolved in DCM (12 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2\textsuperscript{nd} generation catalyst was transferred to the solution of 4f and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 0.078 g (86%) of the title compound as a yellow liquid. \( R_f\) (2/1 hexanes/EtOAc) = 0.66; \(^1\)H NMR (600 MHz, CDCl\textsubscript{3}) \( \delta \) 7.36-7.33 (m, 4H), 7.30-7.27 (m, 1H), 5.84-5.79 (m, 1H), 5.54-5.50 (m, 1H), 4.53 (s, 2H), 3.57-3.50 (m, 2H), 3.13-3.09 (m, 1H), 2.95-2.92 (m, 1H), 2.45-2.35 (m, 3H), 2.32-2.19 (m, 4H), 1.88-1.82 (m, 1H), 1.67-1.50 (m, 3H), 1.42-1.38 (m, 1H), 1.30-1.24 (m, 1H); \(^{13}\)C NMR (151 MHz, CDCl\textsubscript{3}) \( \delta \) 142.0, 138.7, 132.0, 129.7, 128.6, 128.3, 127.5, 127.4, 72.9, 69.1, 43.2, 36.0, 35.7, 33.8, 32.4, 31.1, 26.9, 24.4.; IR (KBr) \( \nu \)\textsubscript{max} 3324, 3084, 3028, 2938, 2860, 1721, 1658, 1458, 1368, 1272, 1096, 1033, 734, 695 cm\textsuperscript{-1}; HRMS (TOF-MS-CI) m/z: [M + H]\textsuperscript{+} calcd for C\textsubscript{20}H\textsubscript{26}O 282.1984; found 282.1987.
(7Z,10E)-10-Phenyl-1,2,3,4,4a,5,6,9-octahydrobenzo[8]annulene (6g). Compound 4g (0.39 mmol, 0.10 g) was dissolved in DCM (30 mL) and argon was bubbled through the solution for 15 min. Grubbs 2nd generation catalyst (0.019 mmol, 0.016 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2nd generation catalyst was transferred to the solution of 4h and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (10/1 hexanes/Et2O) yielded 0.083 g (92%) of the title compound as a brown liquid. Rf (10/1 hexanes/Et2O) = 0.50; 1H NMR (600 MHz, CDCl3) δ 7.31-7.28 (m, 2H), 7.18-7.07 (td, J = 7.2, 1.2 Hz, 1H), 7.14-7.12 (m, 2H), 5.63-5.57 (m, 1H), 5.51-5.47 (m, 1H), 3.53 (td, J = 19.2, 2.4 Hz, 1H), 3.09-3.05 (m, 1H), 2.79 (dd, J = 19.8, 5.4 Hz, 1H), 2.52-2.44 (m, 1H), 2.32-2.28 (m, 1H), 1.91-1.85 (m, 2H), 1.78-1.72 (m, 1H), 1.65-1.44 (m, 6H), 1.26-1.15 (m, 1H); 13C NMR (151 MHz, CDCl3) δ 145.3, 138.1, 131.3, 130.3, 128.3, 128.0, 128.0, 125.7, 38.0, 35.0, 30.9, 30.2, 27.1, 26.7, 23.2, 21.5.; IR (KBr) νmax 3075, 3052, 3013, 2926, 2848, 1646, 1595, 1491, 1440, 1078, 1027, 767, 701 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]+ calcd for C18H22 238.1722; found 238.1724.

((1R,3aE,6Z,9aR)-1-(Benzyloxy)-2,2-dimethyl-2,3,5,8,9,9a-hexahydro-1H-cyclopenta[8]annulen-4-yl)trimethylsilane (6i). Compound 4i (0.16 mmol, 0.61 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution for 15 min. Grubbs 2nd generation catalyst (0.008 mmol, 0.007 g) was dissolved in DCM (6 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2nd generation catalyst was transferred to the solution of 4j and reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (10/1 hexanes/toluene) yielded 0.036 g (61%) of the title compound as a colorless solid. Mp 47.4-49.2 °C. Rf (10/1 hexanes/toluene) = 0.35; 1H NMR (600 MHz, CDCl3) δ 7.39-7.35 (m, 4H), 7.29 (tt, J = 6.6, 1.8 Hz, 1H), 5.80-5.75 (m, 1H), 5.53-5.49 (m, 1H), 4.74 (d, J = 11.4 Hz, 1H), 4.59 (d, J = 12.0 Hz, 1H), 3.09-3.06 (m, 1H), 2.90 (t, J = 9.0 Hz, 1H), 2.51-2.46 (m, 1H), 2.37 (q, J = 6.6 Hz, 1H), 2.18-2.12 (m, 2H), 2.07 (d, J = 14.4 Hz, 1H), 1.97-1.92 (m, 1H), 1.28-1.19 (m, 1H), 1.17 (s, 3H), 0.91 (s, 3H), 0.13 (s, 9H); 13C NMR (151 MHz, CDCl3) δ 153.2, 139.1, 134.1, 133.7, 129.1, 128.3, 127.6, 127.5, 94.8, 74.0, 51.8, 47.9, 40.4, 32.5, 31.5, 27.8, 27.3, 20.2, 0.2.; IR (KBr) νmax 3055, 3016, 2953, 2917, 2905, 2878, 2860, 2842, 1455, 1368, 1353, 1245, 1123, 1099, 866, 839, 734 cm⁻¹; HRMS (TOF-MS-CI) m/z: [M + H]^+ calcd for C23H34OSi 354.2379; found 354.2383.
**tert-Butyl((1R,3aE,6Z,9aS)-2,2-dimethyl-4-(trimethylsilyl)-2,3,5,8,9,9a-hexahydro-1H-cyclopenta[8]annulen-1-yl)oxy)dimethylsilane (6j).** Compound 4j (0.24 mmol, 0.10 g) was dissolved in DCM (15 mL) and argon was bubbled through the solution for 15 min. Grubbs 2\(^{\text{nd}}\) generation catalyst (0.012 mmol, 0.010 g) was dissolved in DCM (10 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2\(^{\text{nd}}\) generation catalyst was transferred to the solution of 4k and the reaction mixture was stirred under reflux for 2 h. Then, the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (hexanes) yielded 0.081 g (85%) of the title compound as a colorless solid. Mp 51.6-52.0 °C. \(R_f\) (hexanes) = 0.52; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 5.80-5.75 (m, 1H), 5.54-5.50 (m, 1H), 3.30 (d, \(J = 7.2\) Hz, 1H), 3.10-3.06 (m, 1H), 2.68 (t, \(J = 8.4\) Hz, 1H), 2.49-2.43 (m, 1H), 2.36 (q, \(J = 7.2\) Hz, 1H), 2.20-2.13 (m, 2H), 1.97 (d, \(J = 14.4\) Hz, 1H), 1.94-1.90 (m, 1H), 1.20-1.13 (m, 1H), 0.98 (s, 3H0), 0.92 (s, 9H), 0.78 (s, 3H), 0.12 (s, 9H), 0.08 (s, 6H); \(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 154.0, 134.1, 133.2, 129.1, 87.8, 53.4, 47.0, 40.5, 32.0, 31.5, 27.3, 26.6, 26.0, 19.8, 18.3, 0.2, -3.9, -4.2. IR (KBr) \(\nu_{\text{max}}\) 3016, 2956, 2929, 2893, 2854, 1461, 1245, 1129, 1102, 872, 836, 776 cm\(^{-1}\); HRMS (TOF-MS-CI) m/z: [M + H\(^+\)] calculated for C\(_{22}\)H\(_{42}\)O\(_2\)Si\(_2\) 378.2774; found 378.2775.

**Ethyl (6Z,9E)-9-phenyl-2,3,3a,4,5,8-hexahydro-1s-cyclopenta[8]annulene-4-carboxylate (10).**

Compound 9 (0.31 mmol, 0.10 g) was dissolved in DCM (25 mL) and argon was bubbled through the solution for 15 min. Grubbs 2\(^{\text{nd}}\) generation catalyst (0.015 mmol, 0.013 g) was dissolved in DCM (5 mL) and argon was bubbled through the solution also for 15 min. Solution of Grubbs 2\(^{\text{nd}}\) generation catalyst was transferred to the solution of 9 and the reaction mixture was stirred under reflux for 2 h. Then the solvent was evaporated under reduced pressure and under argon atmosphere. Column chromatography of the residue on silica gel (4/1 hexanes/Et\(_2\)O) yielded 0.084 g (92%) of the title compound as a brown liquid. \(R_f\) (4/1 hexanes/Et\(_2\)O) = 0.58. Major diastereoisomer: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.28 (m, 2H), 7.21-7.18 (m, 3H), 5.85-5.79 (m, 1H), 5.58-5.54 (m, 1H), 4.14 (dd, \(J = 7.2\), 1.8 Hz, 2H), 3.40-3.36 (m, 1H), 3.31-3.28 (m, 1H), 2.97-2.95 (m, 1H), 2.84 (q, \(J = 6.6\) Hz, 1H), 2.67 (t, \(J = 7.2\) Hz, 2H), 2.39-2.33 (m, 1H), 2.09-2.04 (m, 1H), 1.98-1.94 (m, 1H), 1.63-1.58 (m, 2H), 1.57-1.55 (m, 1H), 1.28 (t, \(J = 7.2\) Hz, 3H); Minor distereoisomer: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.17-7.15 (m, 3H), 5.54-5.50 (m, 1H), 4.20-4.16 (m, 2H), 2.89 (dd, \(J = 18.0\), 6.0 Hz, 1H), 2.78-2.74 (m, 1H), 2.48-2.43 (m, 2H), 1.29 (t, \(J = 7.2\) Hz, 3H) – the remaining signals were overlapped by the signals of the major diastereoisomer; Major diastereoisomer: \(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 174.0, 144.9, 141.5, 137.9, 129.0, 128.2, 127.9, 125.9, 125.3, 60.1, 47.4, 44.3, 35.0, 34.8, 29.3, 25.1, 21.4, 14.3
Minor distereoisomer: $^{13}$C NMR (151 MHz, CDCl$_3$) δ 195.4, 143.8, 56.8, 40.7, 37.8, 23.4, 21.5, 19.7, 12.9.- the remaining signals were overlapped by the signals of the major diastereoisomer; IR (KBr) $v_{\text{max}}$ 3075, 3055, 3025, 2953, 2866, 1733, 1598, 1446, 1263, 1177, 1159, 1096, 1069, 1036, 701 cm$^{-1}$; HRMS (TOF-MS-CI) m/z: [M + H]$^+$ calcd for C$_{20}$H$_{25}$O$_2$ 297.18495; found 297.18491.
5. References

6. Figures and Copies of $^1$H and $^{13}$C NMR spectra

**Figure 1.** $^1$H NMR spectrum of $6j$ and corresponding NOE spectra of selected signals.

**Figure 2.** $^1$H NMR spectrum of $4k$ and corresponding NOE spectra of selected signals.
Figure 3. $^1$H NMR spectrum of 10 and corresponding NOE spectra of selected signals.
((Non-8-en-3-yn-1-yloxy)methyl)benzene (1e)
*tert*-Butyl((4,4-dimethyl-7-(trimethylsilyl)hept-1-en-6-yn-3-yl)oxy)dimethylsilane (1j)
N-benzyl-N-(3-ethoxyprop-2-yn-1-yl)prop-2-en-1-amine (1i)
(E)-(1-(2-(But-3-en-1-yl)cyclopentylidene)but-3-en-1-yl)benzene (4a)
(E)-(1-(2-(But-3-en-1-yl)cyclopentylidene)but-3-en-1-yl)trimethylsilane (4b)
(Z)-1-Benzyl-3-(but-3-en-1-yl)-4-(1-phenylbut-3-en-1-ylidene)pyrrolidine (4c)
(Z)-1-(But-3-en-1-yl)-2-(oct-1-en-4-ylidene)cyclopentane (4d)
(E)-(((3-(2-(But-3-en-1-yl)cyclopentylidene)hex-5-en-1-yl)oxy)methyl)benzene (4e)
(Z)-1-(But-3-en-1-yl)-2-(oct-1-en-4-ylidene)cyclohexane (4f)
(E)-(1-(2-(But-3-en-1-yl)cyclohexylidene)but-3-en-1-yl)benzene (4g)
(Z)-1-Benzyl-3-(but-3-en-1-yl)-4-(1-ethoxybut-3-en-1-ylidene)pyrrolidine (4h)
((((1R,E)-5-(But-3-en-1-yl)-2,2-dimethyl-4-(1-(trimethylsilyl)but-3-en-1-ylidene)cyclopentyl)oxy)(tert-butyl)dimethylsilane (4j)
Ethyl (E)-2-(2-(1-phenylbut-3-en-1-ylidene)cyclopentyl)acetate (8)
Ethyl (E)-2-(2-(1-phenylbut-3-en-1-ylidene)cyclopentyl)pent-4-enoate (9)
(6Z,9E)-9-Phenyl-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6a)
((3aE,6Z)-2,3,5,8,9,9a-Hexahydro-1H-cyclopenta[8]annulen-4-yl)trimethylsilane (6b)
(6Z,9Z)-2-Benzyl-9-phenyl-2,3,3a,4,5,8-hexahydro-1H-cycloocta[c]pyrrole (6c)
(6Z,9Z)-9-Butyl-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6d)
(6Z,9E)-9-(2-(Benzylxy)ethyl)-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene (6e)
(7Z,10E)-10-phenyl-1,2,3,4,4a,5,6,9-octahydrobenzo[8]annulene (6g)
((1R,3aE,6Z,9aR)-1-(Benzyloxy)-2,2-dimethyl-2,3,5,8,9,9a-hexahydro-1H-cyclopenta[8]annulen-4-yl)trimethylsilane (6i)
tert-Butyl((1R,3aE,6Z,9aS)-2,2-dimethyl-4-(trimethylsilyl)-2,3,5,8,9,9a-hexahydro-1H-cyclopenta[8]annulen-1-yl)oxy)dimethylsilane (6j)
Ethyl(6Z,9E)-9-phenyl-2,3,3a,4,5,8-hexahydro-1H-cyclopenta[8]annulene-4-carboxylate (10)
(E)-(1-(2-methylcyclopentylidene)but-3-en-1-yl)benzene (5a)