Intramolecular [4+2] Cycloaddition of Nitroalkenes for Construction of Vicinal Quaternary Stereocenters

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SUPPORTING INFORMATION

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General Experimental

^1H and ^{13}C NMR spectra were recorded on Varian Unity-400 (400 MHz ^1H , 101 MHz ^{13}C), Unity-500 (500 MHz ^1H , 126 MHz ^{13}C) and Varian Unity Inova 500 (500 MHz ^1H) spectrometers in deuteriochloroform. Spectra were referenced to residual chloroform (7.26 ppm, ^1H ; 77.0 ppm, ^{13}C). Data are reported in the following order: chemical shift in ppm (δ); multiplicities are indicated (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants, J , are reported in hertz (Hz); integration is provided; and assignment is indicated. ^1H and ^{13}C NMR assignments are corroborated by 2D experiments (COSY, HMQC, and HMBC). Spectra are available on request from denmark@scs.uiuc.edu. Mass spectrometry was performed by the University of Illinois Mass Spectrometry Center. Electron impact (EI) spectra were performed on a Micromass 70-VSE spectrometer, chemical ionization (CI) spectra were obtained on a Micromass 70-VSE spectrometer using methane as the carrier gas, electrospray ionization (ESI) spectra were obtained from Micromass Q-TOF spectrometer. Data are reported in the form of m/z (intensity relative to base peak = 100). Infrared spectra (IR) were recorded on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with indicated intensities: s (strong, 67 – 100% absorption), m (medium, 34 –

66%), w (weak, 0 – 33%). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

Analytical thin-layer chromatography was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV light, iodine, and molybdate stain ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + \text{Ce}(\text{SO}_4)_2$ in aqueous H_2SO_4 , (CAM)). Column chromatography was performed by the method of Still¹ with silica gel (Merck). Bulb-to-bulb distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points (bp) correspond to uncorrected, air bath temperatures. Preparative HPLC were performed on Rainin Model SD 200 equipped with UV absorbance detector (Model UV 1) at a wavelength of 360 nm. Melting points (mp) were determined in sealed capillary tubes on a Thomas-Hoover melting point apparatus and are corrected.

All reactions were performed in oven-dried (140 °C) and/or flame-dried glassware under an atmosphere of dry nitrogen, unless otherwise stated. All internal reaction temperatures correspond to internal temperatures measured by Teflon-coated thermocouples. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethylether (Fisher, BHT stabilized ACS grade), and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexane (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvent acetonitrile was refluxed over CaH_2 and freshly distilled from it. Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: dichloromethane (CaCl_2); hexane (CaCl_2); ethyl acetate (K_2CO_3). Toluene, and methanol were reagent grade. DMSO was reagent grade, stored over MS 4Å. Hexamethylphosphoramide (HMPA) was distilled from CaH_2 at 0.5 mmHg and stored over MS 4Å. *n*-Butyllithium was titrated with *sec*-butanol using 9,10-phenanthroline as the indicator. Potassium hexamethyldisilazide (KHMDs) was titrated according to the method of Ireland². CuBr was purified through dissolution in 48% aqueous HBr, diluting with water, washing with water, methanol, and ether, drying in vacuo at room temperature. LiBr was dried under vacuo (0.1-1.0 mmHg) at 140 °C overnight. “Brine” refers to a saturated solution of NaCl. Diisopropylamine was refluxed over CaH_2 and freshly distilled from it. Tin tetrachloride was freshly distilled.

Literature Preparations

The following compounds were prepared by literature methods: *tert*-butyl(hex-1-en-5-yn-3-yloxy)dimethylsilane (**3**)³, 3-chloromagnesiumpropan-1-olate magnesium chloride (**9**)⁴, 1-iodo-2-methylpropene⁵, methyl-3-nitropropionate⁶, benzeneseleninyl chloride⁷.

Scheme 1. Synthesis of **2a** and **2b**. Characterized compounds not appearing in the text are shown in bold italic type.

Experimental Procedures

Preparation of (*E*)-4-(2-(*tert*-Butyldimethylsilyloxy)but-3-enyl)-7-methyl-octa-4,6-dien-1-ol (4)

A mixture of CuBr (410 mg, 2.86 mmol, 2 equiv) and LiBr (497 mg, 5.72 mmol, 4 equiv) in a 100-mL, 2-necked round-bottom flask fitted with a N₂ inlet, a rubber septum, and a magnetic stir bar was suspended in 5 mL of toluene and the solvent was removed in vacuum at room temperature with stirring. The flask was filled with nitrogen and the contents were dissolved in THF (6.0 mL). The light green solution formed was cooled down to -45 °C (external temperature) and a solution of **9** (0.33 M in THF, 8.66 mL, 2.86 mmol, 2 equiv) was added dropwise via syringe. The dark reddish-brown solution was stirred for 20 min while the external temperature reached -29 °C. The alkyne **3** was added at once via syringe, the flask was put into a cooling bath (*i*-PrOH/ice, external temperature -10 °C). The contents were allowed to warm up slowly to room temperature during 12 h, then cooled down to -34 °C (external temperature). A solution of Pd(PPh₃)₄ (50 mg, 0.043 mmol, 0.03 equiv) and 1-iodo-2-methylpropene (286 mg, 1.57 mmol, 1.1 equiv) in 4.0 mL of THF was added via cannula. The flask was rinsed with 2.0 mL of THF and the washings were also added to the reaction mixture via cannula. The reaction mixture was stirred overnight (11 h) with warming up to room temperature. The reaction was quenched with sat. aq. solution of NH₄Cl (20 mL), extracted with hexane (2x50 mL) the combined organic layers were washed with saturated aqueous solution of NH₄Cl (2x10 mL), brine (20 mL), dried (MgSO₄), filtered, and concentrated. Purification of the yellow heterogeneous oil by silica gel column chromatography (20 mm column, 10 g of silica gel, hexanes/EtOAc, gradient from 20/1 to 5/1) provided 292 mg (0.90 mmol, 61%) of **4** as yellow oil. Further purification by distillation provided **4** as a light yellow viscous oil (257 mg, 0.79 mmol, 53%).

Data for 4:

bp: 100 °C (1.5×10^{-4} mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)

6.03 (d (a part of AB system), $J = 11.4$, 1 H, HC(5)), 5.98 (doublet of apparent pentets (a part of AB system), $J = 11.2$, 1.2, 1 H, HC(6)), 5.83 (ddd, $J = 17.1$, 10.4, 5.7, 1 H, HC(12)), 5.16 (ddd, $J = 17.1$, 1.9, 1.3, 1 H, $HHC(13)$), 5.02 (ddd, $J = 10.5$, 1.8, 1.4, 1 H, $HHC(13)$), 4.16-4.22 (m, 1 H, HC(11)), 3.64 (t, $J = 6.3$, 2 H, H₂C(1)), 2.12-2.34 (m, 4 H, H₂C(10) and H₂C(3)), 1.79 (s, 3 H, H₃C(8) or H₃C(9)), 1.73 (s, 3 H, H₃C(8) or H₃C(9)), 1.63-1.73 (m, 2 H, H₂C(2)), 1.44 (s, 1 H, OH), 0.87 (s, 9 H, H₃C(17)), 0.04 (s, 3 H, H₃C(14) or H₃C(15)), 0.000 (s, 3 H, H₃C(14) or H₃C(15)).

¹³C NMR: (101 MHz, CDCl₃)

141.5 (C(12)), 135.1 (C(4)), 134.0 (C(7)), 125.0 (C(5)), 120.6 (C(6)), 113.5 (C(13)), 72.9 C(11)), 62.8 (C(1)), 46.2 (C(10)), 31.3 (C(10)), 31.3 (C(2)), 27.0 (C(3)), 26.4 (C(8) or C(9)), 25.8 (C(17)), 18.2 (C(16)), 18.1 (C(8) or C(9)), -4.6 (C(14) or C(15)), -4.9 (C(14) or C(15)).

IR: (neat)

3338 (m), 2953 (s), 2929 (s), 2857 (s), 1644 (w), 1614 (w), 1472 (s), 1462 (s), 1441 (s), 1361 (s), 1253 (s), 1123 (s), 1070 (s), 1033 (s), 991 (m), 947 (m), 920 (m), 836 (s), 776 (s).

MS: (EI, 70 eV)

324.3 (0.5, M⁺), 277 (1), 267 (2), 211 (1), 192 (3), 175 (3), 173 (7), 172 (19), 171 (100), 159 (3), 157 (3), 153 (1)

TLC: R_f 0.18 (hexanes/EtOAc, 4/1) [silica gel, UV, I₂, CAM]

Analysis: C₁₉H₃₆O₂Si (324.57)

Calcd: C, 70.31; H, 11.18

Found: C, 70.28; H, 11.21

(*E*)-tert-Butyl-(5-(3-methoxypropyl)-8-methyl-nona-1,5,7-trien-3-yloxy)dimethylsilane (10**)**

Into a 100-mL 1-neck round bottom flask equipped with a nitrogen inlet and a magnetic stir bar was placed **4** (985 mg, 3.03 mmol, 1 equiv) and 10 mL DMSO via syringe, followed by MeI (0.76 mL, 1.72 g, 12.1 mmol, 4 equiv) and ground KOH (85%, 0.80 g, 12.1 mmol, 4 equiv). The reaction mixture was stirred at room temperature for 21 h, quenched with 40 mL of sat. aq. solution of NH_4Cl , and extracted with hexane (3x50 mL). The combined organic layers were washed with 20 mL of brine, dried (MgSO_4), filtered through a short plug of SiO_2 , and concentrated. The light yellow oily material was purified by chromatography (silica gel (28 g), hexane/EtOAc, gradient 10/0 to 10/1, 30 mm column) and distillation to afford 905 mg (2.67 mmol, 88%) of **10** as a clear, colorless oil.

Data for **10:**

bp: 100 °C (1.1×10^{-4} mmHg, ABT)

^1H NMR: (400 MHz, CDCl_3)

6.03 (d (a part of AB system), $J = 11.5$, 1 H, HC(7)), 5.97 (doublet of apparent pentets (a part of AB system), $J = 11.5$, 1.2, 1 H, HC(6)), 5.83 (ddd, $J = 17.1$, 10.4, 5.7, 1 H, HC(12)), 5.16 (ddd, $J = 17.1$, 1.5, 1.2, 1 H, $\text{HHC}(1)$), 5.01 (ddd, $J = 10.4$, 1.3, 1.2, 1 H, $\text{HHC}(1)$), 4.15-4.22 (m, 1 H, HC(3)), 3.35 (t, $J = 6.4$, 2 H, $\text{H}_2\text{C}(13)$), 3.32 (s, 3 H, $\text{H}_3\text{C}(14)$), 2.10-2.30 (m, 4 H, $\text{H}_2\text{C}(4)$ and $\text{H}_2\text{C}(11)$), 1.78 (s, 3 H, $\text{H}_3\text{C}(9)$ or $\text{H}_3\text{C}(10)$), 1.72 (s, 3 H, $\text{H}_3\text{C}(9)$ or $\text{H}_3\text{C}(10)$), 1.62-1.70 (m, 2 H, $\text{H}_2\text{C}(12)$), 0.87 (s, 9 H, $\text{H}_3\text{C}(18)$), 0.002 (s, 3 H, $\text{H}_3\text{C}(15)$ or $\text{H}_3\text{C}(16)$), -0.030 (s, 3 H, $\text{H}_3\text{C}(15)$ or $\text{H}_3\text{C}(16)$).

^{13}C NMR: (101 MHz, CDCl_3)

141.6 (C(2)), 135.0 (C(5)), 133.4 (C(8)), 125.0 (C(6)), 120.9 (C(7)), 113.4 (C(1)),

72.9 (C(3)), 72.1 (C(13)), 58.5 (C(14)), 46.3 (C(4)), 28.4 (C(12)), 27.1 (C(11)), 26.4 (C(9)) or C(10)), 25.9 (C(18)), 18.2 (C(17)), 18.1 (C(9)) or C(10)), -4.6 (C(15)) or C(16)), -4.9 (C(15)) or C(16)).

IR: (neat)

2956 (s), 2929 (s), 2895 (s), 2857 (s), 1843 (w), 1644 (w), 1614 (w), 1472 (m), 1462 (m), 1448 (m), 1403 (w), 1376 (m), 1361 (m), 1253 (s), 1208 (w), 1187 (w), 1121 (s), 1075 (s), 1031 (m), 1006 (m), 991 (w), 948 (m), 920 (m), 837 (s), 736 (s)

MS: (EI, 70 eV)

338.4 (1, M⁺), 281 (2), 207 (1), 206 (6), 175 (3), 174 (1), 173 (5), 172 (15), 161 (1), 159 (2), 147 (1), 145 (4), 133 (2), 131 (2), 121 (1), 119 (3), 116 (4), 115 (25), 114 (1), 113 (1)

TLC: *R_f* 0.38 (hexane/EtOAc, 10/1) [silica gel, UV, I₂, CAM]

Analysis: C₂₀H₃₈O₂Si (338.60)

Calcd: C, 70.94%; H, 11.31%

Found: C, 71.03%; H, 11.24%

(*E*)-3-(*tert*-Butyldimethylsilyloxy)-5-(3-methoxypropyl)-8-methyl-nona-5,7-dien-1-ol (11**)**

Into a 100-mL, 1-neck round bottom flask equipped with a nitrogen inlet and a magnetic stir bar was placed **10** (1090 mg, 3.22 mmol, 1 equiv), followed by addition of 9-BBN (0.43 M solution in THF, 8.22 mL, 3.54 mmol, 1.1 equiv) via syringe. After 1 h 20 min of stirring at room temperature, 8.0 mL of water was added, followed by NaBO₃·4H₂O (2.48 g, 16.1 mmol, 5 equiv). Moderate heat evolution was observed. The heterogeneous mixture was vigorously stirred for 1 h 10 min, quenched with sat. aq. solution of NH₄Cl (30 mL), and extracted with a mixture hexane/MTBE=1/1 (3x50 mL). The combined organic layers were dried (CaCl₂),

filtered, and concentrated. The colorless oil was purified by chromatography (silica gel (20g) , hexane/EtOAc, gradient 10/1 to 4/1, 20 mm column) to afford **II** as colorless oily material (911 mg, 2.55 mmol, 79%). A sample of the analytically pure material for characterization was obtained by distillation.

Data for **II**:

bp: 115 °C (1.0 x 10⁻⁴ mmHg, ABT)

¹H NMR: (400 MHz, CDCl₃)

6.01 (d (a part of AB system), $J = 11.2$, 1 H, HC(6)), 5.95 (doublet of apparent pentets (a part of AB system), $J = 11.2$, 1.1, 1 H, HC(7)), 4.00-4.07 (m, 1 H, HC(3)), 3.86 (ddd, $J = 10.9$, 8.5, 4.2, 1 H, HHC(1)), 3.67-3.73 (m, 1 H, HHC(1)), 3.34 (t, $J = 6.4$, 2 H, H₂C(13)), 3.32 (s, 3 H, H₃C(14)), 2.35 (dd (a part of AB system), $J = 13.3$, 5.8, 1 H, HHC(4)), 2.08-2.25 (m, 3 H, HHC(4) and H₂C(11)), 1.78-1.90 (m, 1 H, HHC(2)), 1.79 (s, 3 H, H₃C(9) or H₃C(10)), 1.72 (s, 3 H, H₃C(9) or H₃C(10)), 1.54-1.70 (m, 3 H, HHC(2) and H₂C(12)), 0.88 (s, 9 H, H₃C(18)), 0.09 (s, 3 H, H₃C(15) or H₃C(16)), 0.05 (s, 3 H, H₃C(15) or H₃C(16)).

¹³C NMR: (101 MHz, CDCl₃)

135.0 (C(5)), 134.0 (C(8)), 125.0 (C(6)), 120.6 (C(7)), 72.0 (C(13)), 70.9 (C(3)), 60.3 (C(1)), 54.5 (C(14)), 45.1 (C(4)), 37.6 (C(2)), 28.5 (C(12)), 26.8 (C(11)), 26.4 (C(9) or C(10)), 25.8 (C(18)), 18.1 (C(9) or C(10)), 17.9 (C(17)), -4.5 (C(15) or C(16)), -4.9 (C(15) or C(16)).

IR: (neat)

3436 (m, br), 2951 (s), 2929 (s), 2886 (s), 1656 (w), 1614 (w), 1472 (m), 1462 (m), 1447 (m), 1408 (w), 1386 (m), 1361 (m), 1255 (m), 1209 (w), 1187 (w), 1119 (s), 1089 (s), 1020 (m), 1006 (m), 974 (w), 938 (w), 872 (w), 836 (s), 775 (s)

MS: (EI, 70 eV)

356.3 (1, M⁺), 311 (1), 299 (3), 190 (16), 189 (97), 175 (11), 149 (11), 145 (21), 133 (14), 131 (49), 121 (12), 119 (14), 115 (20), 111 (10), 109 (1), 107 (15), 105 (22), 101 (11)

TLC: R_f 0.29 (hexane/EtOAc, 2/1) [silica gel, UV, I₂, CAM]

Analysis: C₂₀H₄₀O₃Si (356.62)
 Calcd: C, 67.36%; H, 11.31%
 Found: C, 67.10%; H, 11.21%

(*E*)-tert-Butyl-(1-iodo-5-(3-methoxypropyl)-8-methylnona-5,7-dien-3-yloxy)dimethylsilane
(5)

In a 100-mL 3-neck round bottom flask fitted with a N₂ inlet, a thermocouple, a rubber septum, and a magnetic stir bar were placed PPh₃ (709 mg, 2.71 mmol, 1.15 equiv) and imidazole (320 mg, 4.7 mmol, 2.0 equiv). Acetonitrile (10.5 mL) and ether (6.5 mL) were added via syringe at room temperature to dissolve the contents, and the flask was placed in ice/water cooling bath (until the internal temperature reached +1 °C). Iodine (657 mg, 2.59 mmol, 1.1 equiv) was added at once (internal temperature was below +4 °C during the addition). A dark yellow suspension was formed within 7 min. 12 min after the iodine addition, a solution of **11** (840 mg, 2.35 mmol, 1.0 equiv) in a mixture of 3.5 mL ether and 5.0 mL of acetonitrile was added via cannula (T_{int} < 7 °C), the flask with **11** was washed with a mixture of 3.5 mL ether and 5.0 mL of acetonitrile and the washings were also cannulated into the reaction flask. After 10 min the cooling bath was removed and the contents were allowed to warm up to room temperature during 2 h. The reaction mixture was concentrated. Purification by chromatography (silica gel (21g), hexane/EtOAc, gradient 10/0 to 10/1, 20 mm column) provided **5** as a colorless oily material (969 mg, 2.07 mmol, 88%), which could not be purified further to pass the elemental analysis.

Data for **5**:

¹H NMR: (500 MHz, CDCl₃)
 5.99 (d (a part of AB system), *J* = 11.5, 1 H, HC(6)), 5.98 (doublet of apparent pentets (a part of AB system), *J* = 11.2, 1.0, 1 H, HC(7)), 3.82-3.88 (m, 1 H,

HC(3)), 3.35 (t, $J = 6.5$, 2 H, H₂C(13)), 3.33 (s, 3 H, H₃C(14)), 3.15-3.30 (m, 2 H, H₂C(1)), 2.32 (dd (a part of AB system), $J = 13.6, 5.6$, 1 H, HHC(4)), 2.19-2.27 (m, 1 H, HHC(11)), 2.10-2.18 (m, 2 H, HHC(4) and HHC(11)), 2.01 (dtd, $J = 14.4, 7.9, 3.6$, 1 H, HHC(2)), 1.85 (dtd, $J = 12.9, 7.4, 5.3$, 1 H, HHC(2)), 1.79 (s, 3 H, H₃C(9) or H₃C(10)), 1.74 (s, 3 H, H₃C(9) or H₃C(10)), 1.62-1.70 (m, 2 H, H₂C(12)), 0.88 (s, 9 H, H₃C(18)), 0.10 (s, 3 H, H₃C(15) or H₃C(16)), 0.06 (s, 3 H, H₃C(15) or H₃C(16)).

¹³C NMR: (126 MHz, CDCl₃)
135.0 (C(5)), 134.0 (C(8)), 124.9 (C(6)), 120.7 (C(7)), 72.0 (C(13)), 71.1 (C(3)), 58.5 (C(14)), 45.3 (C(4)), 40.6 (C(2)), 28.4 (C(12)), 26.9 (C(11)), 26.4 (C(9) or C(10)), 25.8 (C(18)), 18.1 (C(9) or C(10)), 18.0 (C(17)), 3.6 (C(1)), -4.3 (C(15) or C(16)), -4.5 (C(15) or C(16)).

IR: (neat)
2953 (s), 2929 (s), 2857 (s), 1741 (s), 1613 (w), 1558 (s), 1472 (w), 1461 (m), 1438 (m), 1379 (s), 1254 (s), 1204 (m), 1178(m), 1118 (s), 1090 (m), 1006 (w), 965 (w), 836 (s), 775 (s)

MS: (EI, 70 eV)
466.2 (1, M⁺), 446 (2), 410 (2), 409 (8), 334 (5), 300 (16), 299 (100), 273 (10), 243 (16), 185 (8)

TLC: R_f 0.22 (hexane/EtOAc, 4/1) [silica gel, UV, I₂, CAM]

(E)-Methyl-5-(*tert*-butyldimethylsilyloxy)-7-(3-methoxypropyl)-10-methyl-2-(nitromethyl)-undeca-7,9-dienoate (6**)**

In a 250-mL 3-neck round bottom flask fitted with a N₂ inlet, a thermocouple, a rubber septum, and a magnetic stir bar via syringe were added THF (60 mL), HMPA (14 mL), and diisopropylamine (0.705 mL, 509 mg, 5.04 mmol, 2.6 equiv). The flask was cooled down to -38 °C (internal temperature), and *n*-butyllithium (1.38 M solution in hexane, 3.65 mL, 5.04 mmol, 2.6 equiv) was added dropwise via syringe (*T*_{int} < -35 °C). The orange solution formed was stirred at -35 °C for 5 min, then cooled down to -73 °C (internal temperature) over 40 min, during which time an orange suspension formed. Methyl-3-nitropropionate was added at once (*T*_{int} < -68 °C) via syringe (309 mg, 2.33 mmol, 1.2 equiv), and the light yellow suspension was stirred at -73 °C for 1.5 h. A solution of **5** (905 mg, 1.94 mmol, 1.0 equiv) in 4 mL of THF was added to the formed dianion via cannula (*T*_{int} < -69 °C). The flask with **5** was rinsed twice with 3 mL of THF, cannulating each time into the reaction flask. The reaction mixture was stirred at -70 to -73 °C for 2.3 h, then warmed up to -30 °C during 1.5 h, and quenched with 1 mL of acetic acid, and then 50 mL of sat. aq. solution of NH₄Cl. Water (20 mL) was added to dissolve the precipitated salts and the contents were extracted with hexane (4x50 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), dried (CaCl₂), filtered and concentrated. Purification by chromatography (silica gel (25 g), hexane/EtOAc, gradient 20/1 to 10/1, 30 mm column) provided **6** (inseparable mixture of diastereomers, dr = 4/1) as a colorless oily material (604 mg, 1.28 mmol, 66%). An additional purification by chromatography using distilled solvents (silica gel (15 g), dichloromethane/EtOAc, gradient 30/1 to 20/1, 20 mm column) provided **6** as a light yellow oily material (547 mg, 1.16 mmol, 60%).

Data for 6:

¹H NMR: (500 MHz, CDCl₃). Data for the major diastereomer.

5.97 (s, br, 2 H, HC(8) and HC(9)), 4.73 (dd, $J = 14.4, 9.4$, 1 H, *HHC*(17)), 4.38 (dd, $J = 14.4, 4.7$, 1 H, *HHC*(17)), 3.73-3.81 (m, 1 H, HC(5)), 3.72 (s, 3 H, H₃C(18)), 3.34 (t, $J = 6.3$, 2 H, H₂C(15)), 3.32 (s, 3 H, H₃C(16)), 3.14-3.22 (m, 1 H, HC(2)), 2.24 (dd, $J = 13.4, 6.0$, 1 H, *HHC*(6)), 2.10-2.22 (m, 2 H, H₂C(13)), 2.08 (dd, $J = 13.4, 7.0$, 1 H, *HHC*(6)), 1.79 (s, 3 H, H₃C(11) or H₃C(12)), 1.73 (s, 3 H, H₃C(11) or H₃C(12)), 1.65-1.80 (m, 2 H, H₂C(3)), 1.55-1.70 (m, 2 H, H₂C(14)), 1.30-1.55 (m, 2 H, H₂C(5)), 0.86 (s, 9 H, H₃C(22)), 0.01 (s, 3 H, H₃C(19) or H₃C(20)), 0.00 (s, 3 H, H₃C(19) or H₃C(20)).

¹³C NMR: (126 MHz, CDCl₃). Data for the major diastereomer.

172.6 (C(1)), 135.0 (C(7)), 133.9 (C(10)), 124.9 (C(8)), 120.6 (C(9)), 75.1 (C(17)), 72.0 (C(15)), 70.2 (C(5)), 58.5 (C(16)), 52.3 (C(18)), 45.1 (C(6)), 42.7 (C(2)), 33.4 (C(4)), 28.5 (C(14)), 26.9 (C(13)), 26.4 (C(11) or C(12)), 25.8 (C(22)), 24.6 (C(3)), 18.1 (C(11) or C(12) or C(21)), 18.0 (C(11) or C(12) or C(21)), -4.4 (C(19) or C(20)), -4.7 (C(19) or C(20)).

IR: (neat)

2953 (s), 2929 (s), 2857 (s), 1741 (s), 1613 (w), 1558 (s), 1472 (w), 1461 (m), 1438 (m), 1379 (s), 1254 (s), 1204 (m), 1178 (m), 1118 (s), 1090 (s), 1006 (w), 965 (w), 836 (s), 775 (s)

MS: (EI, 70 eV)

471.3 (1, M⁺), 414 (3), 339 (1), 306 (8), 305 (22), 304 (100), 195 (67), 152 (32), 151 (46), 143 (13), 119 (87), 115 (10), 111 (11), 108 (10), 89 (13)

TLC: R_f 0.26 (hexane /EtOAc, 4/1) [silica gel, UV, I₂, CAM]

Analysis: Calc for C₂₄H₄₅NO₆Si (471.70)

Calcd: C, 61.11%; H, 9.62% N, 2.97%

Found: C, 60.96%; H, 9.73% N, 3.54%

(E)-6-(2-(3-Methoxypropyl)-5-methylhexa-2,4-dienyl)-3-(nitromethyl)-tetrahydropyran-2-one (6)

To a solution of **6** (522 mg, 1.109 mmol, 1.0 equiv) in 10 mL of acetonitrile in a polyethylene bottle with a cap and a stir bar under air was added 0.4 mL of HF (49% in water, 10 mmol, 9 equiv). The bottle was capped and the contents were stirred at room temperature for 19 h. The reaction was quenched with 10 mL of sat. aq. solution of NaHCO₃, extracted with EtOAc (4x6 mL), the combined organic layers were washed with brine (6 mL), dried (CaCl₂), filtered, and concentrated. The light yellow oil (400 mg, **7/12** = 1/4 by HPLC analysis) was dissolved in 20 mL of methylene chloride, transferred into a 250-mL round bottom flask equipped with a stir bar, Soxlet apparatus charged with anhydrous CaCl₂, and a drying tube (Drierite). Pentane (50 mL) and *p*-toluenesulfonic acid monohydrate (95 mg, 0.05 mmol, 0.05 equiv) were added, and the reaction mixture was refluxed for 4 h. The contents were concentrated and purified by chromatography (silica gel (6 g), hexane/EtOAc/AcOH, 30/40/0.5, 10 mm column) to provide **7** as white crystalline material (323 mg, 90%), which was further purified by precipitating with hexane from the solution in ether to provide **7** (271 mg, 0.83 mmol, 75%) as white crystalline inseparable mixture of diastereomers (dr = 4/1).

Data for **7**:

mp: 79-81 °C (ether/hexane)

¹H NMR: (500 MHz, CDCl₃)

6.09 (d (part of AB system), *J* = 11.3, 1 H, HC(9)), 6.00 (doublet of apparent pentets (part of AB system), *J* = 11.3, 1.2, 1 H, HC(10)), 4.84 (dd (part of AB system), *J* = 14.6, 6.1, 1 H, HHC(18)), 4.73 (dd (part of AB system), *J* = 14.6, 3.9, 0.86 H, HHC(18)), 4.48-4.55 (m, 1 H, HC(6)), 4.47 (dd (part of AB system), *J* = 14.3, 7.1, 0.24 H, HHC(18)), 3.36 (t, *J* = 6.3, 2 H, H₂C(16)), 3.33 (s, 0.55 H, H₃C(17)), 3.32 (s, 2.32 H, H₃C(17)), 3.01 (dtd, *J* = 10.2, 6.2, 4.0, 0.82 H, HC(3)), 2.61 (dd, *J* = 13.8, 5.7, 1 H, HHC(7)), 2.31 (dd, *J* = 13.9, 7.5, 1 H, HHC(7)), 2.25-

2.31 (m, 1 H, *HHC*(14)), 2.12-2.22 (m, 1 H, *HHC*(14)), 2.03-2.11 (m, 2 H, *HHC*(4) and *HHC*(5)), 1.80 (s, 3 H, H₃C(12) or H₃C(13)), 1.75 (s, 3 H, H₃C(12) or H₃C(13)), 1.71-1.84 (m, 1 H, *HHC*(4)), 1.59-1.75 (m, 3 H, *HHC*(5), H₂C(15)).

¹³C NMR: (101 MHz, CDCl₃). Data for the major diastereomer.

169.5 (C(2)), 135.1 (C(11)), 132.7 (C(8)), 125.7 (C(9)), 120.4 (C(10)), 81.0 (C(6)), 75.6 (C(18)), 71.9 (C(16)), 58.5 (C(17)), 43.8 (C(7)), 39.1 (C(3)), 28.4 (C(5) or C(15)), 28.2 (C(5) or C(15)), 27.0 (C(14)), 26.4 (C(12) or C(3)), 23.9 (C(4)), 18.2 (C(12) or C(13))

IR: (neat)

2923 (m), 2865 (m), 1730 (s), 1608 (w), 1557 (s), 1456 (w), 1442 (w), 1420 (w), 1377 (m), 1327 (w), 1283 (w), 1226 (w), 1193 (m), 1115 (m), 1079 (m), 991 (w), 930 (w), 883 (w), 852 (w), 798 (w)

MS: (EI, 70 eV)

325.2 (35, M⁺), 298 (20), 297 (99), 293 (10), 280 (13), 278 (20), 254 (21), 253 (100), 252 (12), 238 (31), 210 (17), 161 (10), 147 (16), 135 (21), 133 (13), 119 (10), 107 (13), 105 (10), 93 (11)

TLC: *R_f* 0.26 (hexane/EtOAc, 1/1) [silica gel, UV, I₂, CAM]

Analysis: Calc for C₁₇H₂₇NO₅ (325.40)

Calcd: C, 62.75%; H, 8.36%; N, 4.30%

Found: C, 62.93%; H, 8.53%; N, 4.47%

(E)-6-((E)-2-(3-Methoxypropyl)-5-methylhexa-2,4-dienyl)-3-(nitromethylene)-tetrahydropyran-2-one ((E)-1)

In a 2-neck, 50-mL pear-shaped flask equipped with a stir bar, nitrogen inlet and a rubber septum was placed **7** (325 mg, 1.00 mmol, 1.0 equiv) dissolved in 10.0 mL of THF. The flask was cooled down in -65°C cooling bath, and KHMDS (0.57 M solution in toluene, 1.84 mL, 1.05 mmol, 1.05 equiv) was added dropwise via syringe. The reaction mixture was stirred for 13 min, and then was transferred via cannula into a 3-neck, 100-mL round bottom flask equipped with a thermocouple, a stir bar, a rubber septum, and a nitrogen inlet, charged with a solution of PhSe(O)Cl (1040 mg, 5.00 mmol, 5.0 equiv) in 20 mL of THF in a -100°C cooling bath. Internal temperature during the addition was below -89°C . The flask in which the nitro enolate was formed was rinsed with 5.0 mL of THF and the solution was also transferred via cannula into the flask with PhSe(O)Cl. After 15 min the cooling bath was removed and the reaction mixture was warmed up to -45°C (internal temperature) during 8 min. The reaction was quenched with a mixture of sat. aq. solution of NaHCO_3 (20 mL) and brine (20 mL), extracted with a mixture of hexane and MTBE (1/1, 3x50 mL). The combined organic layers were washed with a mixture of sat. aq. solution of NaHCO_3 (10 mL) and brine (10 mL), dried (Na_2SO_4), filtered, and concentrated. The yellow oily crude material was purified by chromatography (silica gel (10 g), hexane/EtOAc, gradient from 5/1 to 1/1, 20 mm column) to provide fractions containing **(E)-1** (yellow oil, 182 mg, 56%, impure by $^1\text{H-NMR}$) and **(Z)-1** (light yellow oil, 57 mg, 18%, impure by $^1\text{H-NMR}$). The fraction containing **(E)-1** was further purified by chromatography (silica gel (10 g), hexane/EtOAc, gradient from 5/1 to 3/1, 20 mm column) and recrystallization from ether/hexane (three times) to provide **(E)-1** as light yellow crystals (needles, 33 mg, 0.10 mmol, 10%). **(Z)-1** could not be purified further by crystallization.

Data for (E)-1:

mp: 50-52 °C (ether/hexane)

¹H NMR: (400 MHz, CDCl₃)

7.84 (t, $J = 2.8$, 1 H, HC(18)), 6.09 (d (a part of AB system), $J = 11.2$, 1 H, HC(9)), 5.98 (doublet of apparent pentets (a part of AB system), $J = 11.3$, 1.0, 1 H, HC(10)), 4.44-4.52 (m, 1 H, HC(6)), 3.35 (t, $J = 6.3$, 2 H, H₂C(16)), 3.32 (s, 3 H, H₃C(17)), 3.25-3.29 (m, 0.5 H, HHC(4), from HMQC it follows that this signal is a doublet of multiplets and the second half of this signal is hidden below the signals for H₂C(16) and H₃C(17)), 2.99 (dddd, $J = 18.5$, 12.5, 6.3, 3.4, 1 H, HHC(4)), 2.62 (dd (a part of AB system), $J = 14.2$, 6.1, 1 H, HHC(7)), 2.33 (dd (a part of AB system), $J = 14.2$, 7.5, 1 H, HHC(7)), 2.23-2.30 (m, 1 H, HHC(14)), 2.14-2.21 (m, 1 H, HHC(14)), 2.05-2.14 (m, 1 H, HHC(5)), 1.80 (s, 3 H, H₃C(12) or H₃C(13)), 1.74 (s, 3 H, H₃C(12) or H₃C(13)), 1.58-1.74 (m, 3 H, HHC(5), H₂C(15)).

¹³C NMR: (101 MHz, CDCl₃)

163.0 (C(2)), 144.7 (C(18)), 135.5 (C(11) or C(3)), 135.2 (C(11) or C(3)), 132.2 (C(8)), 126.0 (C(9)), 120.3 (C(10)), 79.5 (C(6)), 71.8 (C(16)), 58.5 (C(17)), 42.9 (C(7)), 28.4 (C(15)), 27.0 (C(14)), 26.4 (C(12) or C(13)), 26.0 (C(5)), 24.4 (C(4)), 18.2 (C(12) or C(13))

IR: (neat)

3104 (w), 2925 (m), 2870 (m), 1724 (s), 1632 (w), 1529 (s), 1446 (w), 1420 (w), 1383 (w), 1353 (m), 1304 (s), 1250 (s), 1207 (m), 1117 (s), 1047 (w), 997 (w), 933 (w), 868 (w)

MS: (EI, 70 eV)

324.2 (8), 323.2 (37, M⁺), 276 (15), 245 (11), 199 (9), 193 (9), 189 (15), 173 (10), 162 (10), 161 (44), 159 (14), 157 (11), 147 (28), 146 (10), 145 (29), 143 (12), 136 (10), 135 (63), 134 (31), 133 (45), 132 (11), 131 (25), 129 (10), 123 (10), 121 (34)

TLC: R_f 0.37 (hexanes/EtOAc, 2/1) [silica gel, UV, I₂, CAM]

Analysis: Calc for C₁₇H₂₅NO₅ (323.38)

Calcd: C, 63.14%; H, 7.79%; N, 4.33%

Found: C, 62.87%; H, 7.66%; N, 4.47%

Selected data for (Z)-1:

¹H NMR: (400 MHz, CDCl₃)
6.90 (t, $J = 1.9$, 1 H, HC(18)), 6.09 (d (a part of AB system), $J = 11.3$, 1 H, HC(9)), 5.98 (doublet of apparent pentets (a part of AB system), $J = 11.3$, 1.2, 1 H, HC(10)), 4.40-4.48 (m, 1 H, HC(6)), 3.36 (t, $J = 6.3$, 2 H, H₂C(16)), 3.32 (s, 3 H, H₃C(17)), 1.80 (s, 3 H, H₃C(12) or H₃C(13)), 1.74 (s, 3 H, H₃C(12) or H₃C(13)).

¹³C NMR: (101 MHz, CDCl₃)
162.1, 139.6, 135.5, 132.3, 131.1, 125.9, 120.3, 78.8, 71.8, 58.5, 42.6, 28.4, 27.3, 26.9, 26.4, 24.2, 18.2.

IR: (neat)
2925 (s), 2871 (s), 1728 (s), 1640 (w), 1613 (w), 1543 (s), 1446 (m), 1380 (m), 1226 (m), 1205 (s), 1115 (s).

TLC: R_f 0.21 (hexanes/EtOAc, 1/1) [silica gel, UV, I₂, CAM]

(1*S*,4*aS*,7*R*,8*aR*)-rel, 3-Oxo-8*a*-(3-methoxypropyl)-4*a*,7-ethano-1-(2-methylprop-1-enyl)-8,8*a*-dihydropyrano[3,4-*d*][1,2]oxazin-5(1*H*,4*aH*,7*H*)-one, (**2a**); (1*R*,4*aS*,7*R*,8*aR*)-rel, 3-Oxo-8*a*-(3-methoxypropyl)-4*a*,7-ethano-1-(2-methylprop-1-enyl)-8,8*a*-dihydropyrano[3,4-*d*][1,2]oxazin-5(1*H*,4*aH*,7*H*)-one, (**2b**); and (*E*)-5-(3-Hydroxy-3-methylbut-1-enyl)-5-(3-methoxypropyl)-4-(nitromethyl)-2-oxa-bicyclo[2.2.2]octan-3-one.⁸

A 1-neck round bottom flask equipped with a nitrogen inlet and a stir bar was charged with a solution of (*E*)-**1** (155 mg, 0.48 mmol, 1.0 equiv) in 10.0 mL of methylene chloride and put into a cooling bath at $-75\text{ }^\circ\text{C}$ (external temperature). SnCl_4 (0.224 mL, 499 mg, 1.92 mmol, 4.0 equiv) was added at once via syringe. An orange solution was instantly formed, which became yellow in less than 1 min, then orange/yellow suspension (within 10 min). After 4.5 h the yellow suspension was quenched with EtOAc (1 mL), then sat. aq. solution of NaHCO_3 (30 mL), diluted with EtOAc (40 mL), filtered through a paper filter, and the aqueous layer was extracted with EtOAc (2x20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The ^1H -NMR analysis of the crude material showed that it contains **2a** and **2b** in 2.5/1 ratio, 10-15% of the unreacted (*E*)-**1**, and 10-15% of **8**. Purification by chromatography (silica gel (8 g), EtOAc, 20 mm column) provided 115 mg of a mixture of **2a**, **2b**, and **8**. Further purification by chromatography (silica gel (5 g), ether, then EtOAc, 10 mm column) provided **8** (colorless oil, 14 mg, 0.041 mmol, 9%) and a mixture of **2a** and **2b** (white crystals, **2a/2b**=2.4/1,

90 mg, 0.28 mmol, 58%). The nitronates were separated by preparative HPLC (μ Porasil[®] silica gel, 10 μ m, 19x300 mm, Waters, part # WAT 025829, EtOAc/hexane, 4/1, 5 mL/min). Crystals suitable for X-ray analysis were obtained by crystallization from EtOAc.

Data for 2a:

mp: 137-139 °C (EtOAc)

¹H NMR: (500 MHz, CDCl₃)
6.19 (s, 1 H, HC(4)), 5.22 (doublet of apparent pentets, $J = 9.0, 1.4$, 1 H, HC(11)), 4.93 (d, $J = 9.0$, 1 H, HC(1)), 4.69-4.73 (m, 1 H, HC(7)), 3.32-3.39 (m, 2 H, H₂C(17)), 3.31 (s, 3 H, H₃C(18)), 2.15-2.28 (m, 2 H, H₂C(9)), [1.87-1.96 (m, 2 H) and 1.73-1.86 (m, 4 H), H₂C(10), H₂C(15) and H₂C(16)], 1.79 (d, $J = 1.0$, 3 H, H₃C(13) or H₃C(14)), 1.72 (d, $J = 1.0$, 3 H, H₃C(13) or H₃C(14)), 1.66 (dt, $J = 15.0, 2.0$, 1 H, HHC(8)), 1.62 (dd, $J = 15.0, 2.0$, 1 H, HHC(8)).

¹³C NMR: (126 MHz, CDCl₃)
173.8 (C(5)), 142.1 (C(12)), 116.7 (C(11)), 110.5 (C(4)), 81.5 (C(1)), 73.9 (C(7)), 71.9 (C(17)), 58.7 (C(18)), 44.9 (C(4a)), 36.4 (C(8)), 32.1 (C(8a) or C(16)), 31.5 (C(8a) or C(16)), 26.0 (C(13) or C(14)), 24.4 (C(9) or C(10) or C(15)), 24.2 (C(9) or C(10) or C(15)), 23.2 (C(9) or C(10) or C(15)), 18.7 (C(13) or C(14))

IR: (neat)
3474 (w), 3064 (w), 2973 (w), 2933 (m), 2875 (m), 2829 (w), 2735 (w), 1744 (s), 1669 (w), 1622 (s), 1558 (w), 1476 (w), 1450 (m), 1366 (m), 1248 (s), 1211 (w), 1143 (w), 1120 (s), 1069 (m), 1022 (w), 968 (s), 923 (w), 892 (w), 833 (w), 790 (m)

MS: (EI, 70 eV)
323.2 (8, M⁺), 308 (5), 306 (10), 262 (10), 261 (11), 245 (10), 194 (14), 178 (11), 175 (10), 173 (10), 164 (13), 163 (12), 162 (18), 161 (45), 160 (13), 159 (16), 154 (10), 151 (11), 150 (15), 149 (14), 148 (16), 147 (26), 146 (26), 145 (32), 144 (11)

HRMS: (EI)
C₁₇H₂₅NO₅ (323.17)
Calcd: 323.173273
Found: 323.172925

TLC: R_f 0.23 (EtOAc) [silica gel, UV, I₂, CAM]

Data for 2b:

mp: 150-155 °C (EtOAc)

¹H NMR: (500 MHz, CDCl₃)
6.31 (s, 1 H, HC(4)), 5.49 (doublet of apparent pentets, $J = 9.6, 1.4$, 1 H, HC(11)), 5.04 (d, $J = 9.6$, 1 H, HC(1)), 4.70-4.73 (m, 1 H, HC(7)), 3.48-3.53 (m, 1 H, HHC(17)), 3.30-3.38 (m, 1 H, HHC(17)), 3.34 (s, 3 H, H₃C(18)), 2.28 (ddd, $J = 13.7, 10.6, 2.6$, 1 H, HHC(9)), 2.11-2.20 (m, 1 H, HHC(10)), 1.78-1.94 (m, 3 H, HHC(10) and H₂C(15)), 1.77 (d, $J = 1.0$, 3 H, H₃C(13) or H₃C(14)), 1.65 (d, $J = 1.3$, 3 H, H₃C(13) or H₃C(14)), 1.26-1.78 (m, 5 H, HHC(9) and H₂C(8) and H₂C(16)).

¹³C NMR: (126 MHz, CDCl₃)
173.8 (C(5)), 142.1 (C(12)), 116.7 (C(11)), 110.5 (C(4)), 81.5 (C(1)), 73.9 (C(7)), 71.9 (C(17)), 58.8 (C(18)), 44.9 (C(4a)), 36.4 (C(8a)), 32.1 (C(8) or C(16)), 31.5 (C(8) or C(16)), 26.0 (C(13) or C(14)), 24.4 (C(9)), 24.2 (C(10) or C(15)), 23.2 (C(10) or C(15)), 18.7 (C(13) or C(14))

IR: (neat)
3474 (w), 3071 (w), 2968 (m), 2936 (m), 2870 (m), 1742 (s), 1667 (w), 1617 (s), 1447 (m), 1365 (m), 1298 (w), 1260 (m), 1237 (m), 1193 (w), 1133 (m), 1111 (s), 1057 (m), 1043 (m), 972 (m), 947 (m), 919 (m), 857 (w), 788 (m), 752 (w)

MS: (EI, 70 eV)
323.2 (35, M⁺), 306 (16), 262 (11), 245 (7), 194 (8), 193 (11), 192 (12), 178 (18), 163 (11), 162 (14), 161 (42), 160 (15), 159 (16), 157 (10), 151 (10), 150 (12), 149 (14), 148 (12), 147 (25), 146 (23), 145 (29), 143 (10), 142 (11), 137 (12), 136 (15)

HRMS: (EI)
C₁₇H₂₅NO₅ (323.17)
Calcd: 323.173273
Found: 323.172786

TLC: *R_f* 0.19 (EtOAc) [silica gel, UV, I₂, CAM]

Data for 8:

- ¹H NMR:** (500 MHz, CDCl₃)
5.68 (d (a part of AB system), 1 H, $J = 16.0$, HC(10)), 5.46 (d (a part of AB system), 1 H, $J = 16.0$, HC(9)), 4.86 (d, 1 H, $J = 13.2$, HHC(18)), 4.76-4.79 (m, 1 H, HC(1)), 4.49 (d, 1 H, $J = 13.2$, HHC(18)), 3.33-3.42 (m, 2 H, H₂C(16)), 3.32 (s, 3 H, H₃C(17)), 2.32 (ddd, 1 H, $J = 14.1, 11.1, 5.6$, HHC(11)), 2.16-2.28 (m, 2 H, HHC(11) and HHC(6)), 2.05-2.14 (m, 1 H), 1.68-1.86 (m, 4 H), 1.65 (d, $J = 14.5$, 1 H, HHC(6)), 1.36-1.56 (m, 2 H), 1.30 (s, 6 H, H₃C(12) and H₃C(13)).
- ¹³C NMR:** (101 MHz, CDCl₃)
172.7 (C(3)), 142.1 (C(10)), 128.4 (C(9)), 75.0 (C(18)), 73.7 (C(1)), 72.4 (C(16)), 70.9 (C(11)), 58.8 (C(17)), 49.7 and 43.1 (C(4) and C(5)), 36.3 (C(6)), 30.4, 30.0 and 29.9 (C(12) and C(13)), 25.8, 25.0, 20.2.
- MS:** (CI, 130 eV, methane)
325.3 (21), 324.3 (100, M⁺-H₂O+H), 295 (35), 294 (52), 293 (16), 292 (79), 278 (11), 277 (53), 247 (14), 246 (20), 245 (85), 227 (17), 203 (10), 201 (20), 199 (23), 185 (11), 159 (12), 145 (10), 133 (12),
- HRMS:** (CI, 130 eV, methane)
Calcd. for C₁₇H₂₇NO₆-H₂O+H, 324.181098. Found, 324.181470.
- TLC:** R_f 0.14 (ether) [silica gel, I₂, CAM]

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- (8) The optimized procedure for the cycloaddition required executing the reaction at -60 to 0 °C to consume starting material and suppress the formation of **8**. The experiment described herein provided the material for X-ray analyses and also for characterization of **8**.