Useful Enantioselective Bicyclization Reactions Using an N-Protonated Chiral Oxazaborolidine as Catalyst

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Supporting Information

Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm). Flash chromatography was performed using Baker silica gel (40 μ m particle size). NMR spectra were recorded on Varian Innova-500, or Mercury-400 instruments and calibrated using residual undeuterated solvent as an

internal reference. IR spectra were recorded on a Nicolet 5ZDX series or Avatar 360 FT-IR spectrometer. Low-resolution mass (CI) spectra were obtained by using a Platform II mass spectrometer. High-resolution mass spectral analyses were performed at the Harvard University Mass Spectrometry Center. Gas chromatography (GC) analyses were performed on Hewlett-Packard 6850 Series GC System equipped with flame-ionization detector using a J & W Scientific Cyclosil-B column (30 m x 0.25 mm). Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from phosphorus pentoxide. Toluene was distilled from sodium. Trifluoromethanesulfonimide was purchased from Aldrich. Boroxines was prepared according to literature procedure. The intramolecular precursors were stored in sealed round-bottom flask under argon at -50°C.

Preparation of Chiral Catalyst (1). A 100-mL, two-necked, round-bottom flask equipped with a stirring bar, a glass stopper and a 50-mL pressure-equalizing addition funnel (containing a cotton plug and *ca.* 10 g of 4A molecular sieves,¹ and functioning as a Soxhlet extractor) fitted on top with a reflux condenser and a nitrogen inlet adaptor was charged with (*S*)-(-)- α,α -diphenyl-2-pyrrolidinemethanol (41 mg, 0.16 mmol), tri-*o*-tolylboroxine (19 mg, 0.054 mmol) and 30 mL of toluene. The resulting solution was heated to reflux (bath temperature $\sim 145^\circ\text{C}$). After 4 h, the reaction mixture was cooled to *ca.* 60°C and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of *ca.* 10 mL. This distillation protocol was repeated three times with 10 mL of toluene. The solution was then allowed to cool to room temperature and the distillation head was quickly replaced with a nitrogen inlet adaptor. Concentration *in vacuum* (*ca.* 0.1 mmHg, 30 min) afforded the corresponding oxazaborolidine as a clear oil. To the neat wax-like oxazaborolidine precursor (0.16 mmol, theoretical) at -78°C was added dropwise a solution of trifluoromethanesulfonimide (0.200 M in toluene, freshly prepared, 667 μL , 0.133 mmol). After 10 to 15 min at 0°C , a colorless homogeneous solution of cationic catalyst was obtained.

¹ Molecular sieves (pellets) were dried in vacuum at *ca.* 300°C for 10 min prior to use.

(+)-(4*R*, 3*aR*, 7*aR*)- 4-Methyl-2, 3, 3*a*, 4, 5, 7*a*-hexahydro-1*H*-indene-4-carbaldehyde (3*b*). To a toluene solution of the freshly prepared catalyst **1**, neat 2-methyl-(*E*, *E*)-deca-2, 7, 9-trienal **2b** (109 mg, 0.665 mmol) was added at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 108 hours and then quenched by addition of 100 μL of Et_3N . After the mixture had warmed to room temperature, the residue was purified directly by silica gel chromatography (elution with hexanes then hexanes/ether 20 : 1) to afford the Diels-Alder adduct **3b** (101 mg, 93%) as a colorless oil.

R_f 0.30 (hexanes/ Et_2O , 4 : 1). $[\alpha]_{\text{D}}^{20} = +10$ ($c = 1.06$, CHCl_3 , 98% *d.e.*, 90% *e.e.*); *lit.*² $[\alpha]_{\text{D}}^{24} = -14.4$ ($c = 1.065$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 9.48 (s, 1H, CHO), 5.84 (d, $J = 10.3$ Hz, 1H, H7), 5.59 (dq, $J = 2.6, 10.2$ Hz, 1H, H6), 2.44 (dq, $J = 3.4, 18.1$ Hz, 1H), 1.90 (m, 2H), 1.78 (dq, $J = 2.0, 18.0$ Hz, 1H), 1.70 (m, 2H), 1.54 (m, 2H), 1.18 (m, 2H), 1.01 (s, 3H, Me); ^{13}C NMR (125 MHz, CDCl_3) : δ 205.8, 129.5, 124.5, 47.9, 46.6, 39.4, 33.6, 28.9, 23.8, 22.3, 12.6; MS: m/e 164.0 (M^+); FTIR (film) 3019, 2957, 2870, 1725, 1684, 1456, 1397, 1267cm^{-1} . The *exo/endo* ratio and the enantioselectivity were determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m $\times$ 0.25 mm, $100\text{ }^{\circ}\text{C}$, 25 psi); retention times: 32.60 min (*endo*, major), 31.95 min (*endo*, minor), 26.75 min (*exo* isomer), 23.35 min (*exo* isomer). The absolute configuration was determined by comparison of optical rotation with the known adduct.

(+)-(4*S*, 3*aR*, 7*aR*)-4-Bromo-2, 3, 3*a*, 4, 5, 7*a*-hexahydro-1*H*-indene-4-carbaldehyde (3*c*). To freshly prepared catalyst **1**, neat 2-bromo-(*Z*, *E*)-deca-2, 7, 9-trienal **2c** (152 mg, 0.665 mmol) was added at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 72 hours, then 100 μL of Et_3N was added and the mixture was brought to room temperature. The crude product was purified by silica gel

2 (a) Furuta, K.; Kanematsu, A.; Yamamoto, H. *Tetrahedron Lett.* **1989**, 30, 7231. (b) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, 118, 3049. (c) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, 120, 6920.

chromatography (hexanes/ether 20 : 1) to afford the Diels-Alder adduct **3c** (124 mg, 82%) as a pale yellow oil.

R_f 0.32 (hexanes/Et₂O, 5 : 1). $[\alpha]_D^{25} = +136$ ($c = 0.95$, CHCl₃, 98% *d.e.*, 94% *e.e.*); ¹H NMR (500 MHz, CDCl₃): δ 9.53 (s, 1H), 5.93 (br d, $J = 10.3$ Hz, 1H), 5.60 (dq, $J = 10.0, 2.4$ Hz, 1H), 3.15 (ddt, $J = 19.5, 4.9, 2.4$ Hz, 1H), 2.65 (ddt, $J = 19.5, 3.9, 2.0$ Hz, 1H), 2.36 (m, 1H), 1.95 (m, 1H), 1.80 (m, 3H), 1.44 (m, 1H), 1.33 (m, 1H), 1.25 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 193.9, 129.5, 122.5, 74.6, 48.5, 42.0, 36.2, 27.9, 24.8, 22.3; FTIR (neat) 3028, 2962, 2873, 1724, 909, 733, 698 cm⁻¹; MS: m/e 228 (M⁺). Enantioselectivity was determined by reduction with NaBH₄ to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 3.57 (s, MeO, 3H, minor), 3.55 (s, MeO, 3H, major); ¹⁹F NMR integration (376.2 MHz, CDCl₃): δ -71.79 (s, CF₃, major), -71.89 (s, CF₃, minor).

(+)-(4*S*, 3*aS*, 7*aS*)-2, 3, 3*a*, 4, 5, 7*a*-Hexahydro-1*H*-indene-4-carboxylic acid 2, 2, 2-trifluoro-ethyl Ester (5**).** To freshly prepared catalyst **1**, neat 2-methyl-(*E*, *E*)-deca-2, 7, 9-trienoic acid 2, 2, 2-trifluoro ethyl ester **4** (165 mg, 0.665 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 2h and then heated at 40 °C for 24 hours. Then 100 μ L of Et₃N was added to quench the reaction. The crude product was purified by silica gel chromatography (elution with hexanes/ether 50 : 1) to afford the Diels-Alder adduct **5** (124 mg, 75%) as a pale yellow oil and 33mg of starting material (20%).

R_f 0.75 (hexanes/Et₂O, 3 : 1). $[\alpha]_D^{22} = +33$ ($c = 1.0$, CHCl₃, 98% *d.e.*, 93% *e.e.*); ¹H NMR (500 MHz, CDCl₃): δ 5.85 (d, $J = 9.7$ Hz, 1H, H4), 5.59 (dq, $J = 3.4, 9.8$ Hz, 1H, H3), 4.49 (m, 2H), 2.62 (dt, $J = 4.0, 17.6$ Hz, 1H), 2.4 (m, 3H), 1.50-2.00 (m, 5H), 1.26 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 174.2, 130.1, 125.3, 123.2(q, 1C, $J = 275$ Hz), 60.3(q, 1C, $J = 36.5$ Hz), 45.9, 45.1, 44.4, 29.9, 29.1, 28.1, 22.0; FTIR (neat) 2977, 2870, 1754, 1283, 1162, 1137, 975 cm⁻¹. The relative configuration was determined by ¹H NMR NOE experiment. The *exo/endo* ratio was determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m $\times$ 0.25 mm, 100 °C, 25 psi); retention times: 18.4 min (*endo*, major), 23.2 min (*exo*, minor). Enantioselectivity was determined by reduction with NaBH₄ to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ¹H NMR integration (500 MHz, CDCl₃): δ 4.13 (dd, 1H, $J = 11.0, 4.5$ Hz, major), 4.38 (dd, 1H, $J = 11.0, 4.5$ Hz, minor). The

absolute configuration was determined by reduction with LiAlH_4 to the corresponding alcohol and measurement of optical rotation: $[\alpha]_{\text{D}}^{23} +38$ ($c = 1.00$, CHCl_3 , 98% *d.e.*, 93% *e.e.*), *lit.*³ $[\alpha]_{\text{D}}^{25} = +41$ ($c = 1.94$, CCl_4).

(+)-(1*S*, 4*aS*, 8*aS*)-1, 2, 4*a*, 5, 6, 7, 8, 8*a*-Octahydro-naphthalene-1-carboxylic Acid 2, 2, 2-Trifluoroethyl Ester (7). To freshly prepared catalyst **1**, neat undeca-2, 8, 10-(*E*, *E*)-trienoic acid **2**, 2, 2-trifluoro-ethyl ester **6** (173 mg, 0.665 mmol) was added at room temperature. The reaction mixture was stirred and heated at 40 °C for 24 hours. Then 100 μL of Et_3N was added to quench the reaction. The crude product was purified by silica gel chromatography (elution with hexanes/ether 50 : 1) to afford the Diels-Alder adduct **7** (70 mg, 41%) and recovered starting material (78 mg, 45%) as a pale yellow oil.

R_f 0.70 (hexanes/ Et_2O , 3 : 1). $[\alpha]_{\text{D}}^{25} = +24.8$ ($c = 0.9$, CHCl_3 , 90.5% *d.e.*, 92% *e.e.*); ^1H NMR (500 MHz, CDCl_3): δ 5.59 (m, 1H, H3), 5.46 (d, $J = 10.0$ Hz, 1H, H3), 4.49 (m, 2H), 2.52 (dt, $J = 6.0$, 11.5 Hz, 1H), 2.30 (m, 1H), 1.76 (d, $J = 9.0$ Hz, 2H), 1.62-1.04 (m, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 174.2, 132.4, 123.8, 122.3 (q, 1C, $J = 276$ Hz), 60.2 (q, 1C, $J = 36.6$ Hz), 46.2, 42.5, 41.6, 33.1, 30.4, 29.6, 26.7, 26.5; FTIR (neat) 2924, 2853, 1754, 1288, 1166, 1143 cm^{-1} . The relative configuration was determined by ^1H NMR NOE experiment. The *exo/endo* ratio was determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m $\times$ 0.25 mm, 120 °C, 25 psi); retention times: 16.1 min (*endo*, major), 17.2 min (*exo*, minor). Enantioselectivity was determined by reduction with NaBH_4 to the corresponding alcohol, conversion to the (*R*)-MTPA ester derivative and ^1H NMR integration (500 MHz, CDCl_3): δ 4.30 (dd, 1H, $J = 10.5$, 3.5 Hz, major), 4.24 (dd, 1H, $J = 10.5$, 3.5 Hz, minor). The absolute configuration was determined by conversion of the Diels-Alder adduct to their corresponding benzyl ester with lithium benzyl oxide and measurement of optical rotation: $[\alpha]_{\text{D}}^{23} +6.9$ ($c = 1.00$, CHCl_3 , 90.5% *d.e.*, 92% *e.e.*); *lit.*⁴ $[\alpha]_{\text{D}}^{25} = +5.5$ ($c = 0.77$, CHCl_3).

3 (a) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1980**, 45(21), 4264. (b) Roush, W. R.; Gillis, H. R.; KO, A. I. *J. Am. Chem. Soc.* **1982**, 104, 2269. (c) Roush, W. R.; Gillis, H. R. *J. Org. Chem.* **1982**, 47(25), 4825. (d) Kbusch, W. R.; Hall, S. E. *J. Am. Chem. Soc.* **1981**, 103, 5200. (f) H. O. House and T. H. Cronin, *J. Org. Chem.*, **1965**, 30, 1061.

4 Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, 110, 1238.

(+) - (1R, 4aR, 8aR)-Methyl-1, 2, 4a, 5, 6, 7, 8, 8a-octahydro-naphthalene-1-carbaldehyde (9). To a toluene solution of the freshly prepared catalyst **1**, neat 2-methyl-(*E, E*)-Undeca-2, 7, 9-trienal **8** (117 mg, 0.665 mmol) was added at -78°C . The reaction mixture was stirred at -45°C for 48 hours and then quenched by addition of 100 μL of Et_3N . The crude product was purified by silica gel chromatography with elution by hexanes/ether (20 : 1) to afford the Diels-Alder adduct **9** (108 mg, 90%) as a colorless oil.

R_f 0.75 (Hex / Et_2O 3 : 1); $[\alpha]_{\text{D}}^{23} = +5$ ($c = 0.6$, CHCl_3 , 2 : 1 *endo* : *exo*, 80 % *e.e.* for *endo*, 89 % *e.e.* for *exo*). ^1H NMR (500 MHz, CDCl_3): δ 1.01(s, 3H, Me), 1.09-1.90 (m, 11H), 2.36 (dq, $J = 2.0, 19.5$ Hz, 1H), 5.58 (dq, $J = 2.4, 10.0$ Hz, 1H, H3), 5.48 (d, $J = 10.0$ Hz, 1H, H4), 9.42 (s, 1H, CHO); FTIR (neat) 2922, 2853, 1724, 1446, 1189 cm^{-1} . The *exo/endo* ratio and the enantioselectivity were determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m $\times$ 0.25 mm, 120°C , 25 psi), retention times: 21.99min (*exo*, minor), 25.00 min (*exo*, major), 27.33min (*endo*, minor), 28.28 min (*endo*, major).

(-)-(8S, 4aS, 8aS)-1-Oxo-3, 4, 4a, 7, 8, 8a-hexahydro-1H-isochromene-8-carboxylic Acid Ethyl Ester (11). To freshly prepared catalyst **1**, neat (*E, E*)-but-2-enedioic acid ethyl ester hexa-3, 5-dienyl ester **10** (149 mg, 0.665 mmol) was added at 0°C . The reaction mixture was heated to 40°C and stirred for 24 hours, then quenched by addition of 100 μL of Et_3N . The crude product was purified directly by silica gel chromatography with elution by hexanes/ether (4 : 1) to afford the Diels-Alder adduct **11** (105 mg, 71%) as a colorless oil and 15 mg of starting material (10%).

R_f 0.15 (Hex / Et_2O 2 : 1); $[\alpha]_{\text{D}}^{23} = -50.3$ ($c = 0.6$, CHCl_3 , 90.4 % *e.e.*, pure *endo*). ^1H NMR (500 MHz, CDCl_3) : δ 5.85 (m, 1H), 5.51 (dq, $J = 3.0, 6.0$ Hz, 1H), 4.26 (m, 2H), 4.15 (q, $J = 8.5, 16.5$ Hz, 2H), 3.45 (m, 1H), 3.27 (m, 1H), 2.91 (brs, 1H), 2.26-2.55 (m, 2H), 2.12-2.18 (m, 1H), 1.69-1.74 (m, 1H),

1.25 (t, $J = 8.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.6, 172.1, 128.2, 127.8, 66.6, 61.1, 40.6, 39.3, 28.8, 28.5, 23.2, 14.4; FTIR (neat) 3023, 2931, 2922, 1729, 1274, 1155, 1093 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{12}\text{H}_{17}\text{O}_4]$ ($[\text{M}+\text{H}]^+$): 225.1127; found 225.1134. Diastereoselectivity⁵ was determined by ^1H NMR and enantioselectivity were determined by GC analysis of the following partly reduced product using a J & W Scientific Cyclosil-B column.

2, 2a, 3, 5a, 6, 7, 8a, 8b-Octahydro-1, 8-dioxa-acenaphthylene. The enantioselectivity of **11** was determined by analysis of 2, 2a, 3, 5a, 6, 7, 8a, 8b-octahydro-1, 8-dioxa-acenaphthylene (71% yield), which was obtained by partial reduction of **11** with LAH (0.3 eq) in anhydrous ether at 0 °C for 20 min (work up with 1N HCl).

R_f 0.17 (Hex-Et₂O 2 : 1). ^1H NMR integration (500 MHz, CDCl_3): δ 5.74 (m, 2H), 5.10 (d, $J = 4.0$ Hz, 1H), 4.30 (t, $J = 7.5$ Hz, 1H), 3.85 (ddd, $J = 11.5, 3.5, 1.5$ Hz, 1H), 3.49 (dd, $J = 9.0$ Hz, 1H), 3.39 (dt, $J = 12.0, 2.0$ Hz, 1H), 2.59(m, 1H), 2.40(m, 1H), 2.30(m, 1H), 1.85-1.91(m, 1H), 1.69-1.73(m, 1H), 1.42-1.62(m, 2H); ^{13}C NMR (125MHz, CDCl_3): δ 131.1, 126.9, 100.8, 73.8, 63.4, 44.4, 33.2, 31.5, 28.5, 28.2; FTIR (neat): 2921, 2859, 1505, 1274, 1110 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{10}\text{H}_{15}\text{O}_2]$ ($[\text{M}+\text{H}]^+$): 167.1072; found 167.1055. Enantioselectivity were determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m $\times$ 0.25 mm, 130 °C, 25 psi), retention times: 23.9 min (*endo*, major), 24.6 min (*endo*, minor).

4-(4-Bromo-benzoyloxy)-8-[2-(4-bromo-benzoyloxy)-ethyl]-1-methyl-7-oxo-6-oxa-bicycle [3.2.1] octane-2-carboxylic Acid Ethyl Ester (12). To a solution of the (-)-(8*S*,

⁵ Chen, C. Y.; Hart, D. J. *J. Org. Chem.* **1993**, 58(15), 3840.

4a*S*, 8a*S*)-1-oxo-3, 4, 4a, 7, 8, 8a-hexahydro-1*H*-isochromene-8-carboxylic acid ethyl ester (22 mg, 0.1 mmol) in acetone-H₂O (10 : 1, 3 mL) was added NMO (7.3 mg, 0.15 mmol) and OsO₄ (4 mg, 0.015 mmol) at –20 °C under nitrogen atmosphere. After being stirred for 2h at –20°C, the reaction mixture was treated with saturated aqueous Na₂SO₃ solution and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel (elution with ethyl acetate) to afford the dihydroxylation product. To the solution of diol (15 mg) in pyridine (2 mL) was added *p*-bromobenzoyl chloride (102 mg, 8 *eq*) and dimethylaminopyridine (57 mg, 8 *eq*) at room temperature. After being stirred at room temperature for 3h, the reaction mixture was quenched with 5% HCl at 0 °C and extracted with ether. The extract was washed with saturated aqueous NaHCO₃, brine and dried over MgSO₄. After concentration, the residue was purified by column chromatography (elution with hexanes/ether 10 : 1) to afford the 17 mg of product **12** as a white solid. Recrystallization from a mixture solvent (1 mL of benzene-hexanes 1 : 10) at 0 °C for 2 days provided the colorless crystal suitable for the X-ray structure determination.

¹H NMR (CDCl₃, 500 MHz): δ 7.90(t, *J* = 9.0 Hz, 4H), 7.60 (d, *J* = 8.5 Hz, 4H), 5.31 (dd, *J* = 7.0, 10.0Hz, 1H), 4.79 (s, 1H), 4.40 (m, 2H), 4.13 (m, 2H), 3.13 (dd, *J* = 3.5, 7.0Hz, 1H), 3.04 (d, *J* = 3.5 Hz, 1H), 2.70 (dd, *J* = 7.0, 9.0Hz, 1H), 2.30 (m, 1H), 2.00 (m, 2 H), 1.88 (m, 1H), 1.20 (t, *J* = 11.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 173.0, 172.1, 165.2, 165.0, 132.13(4C), 132.11(4C), 131.6(2C), 131.4(2C), 82.8, 70.5, 62.4, 45.3, 40.8, 39.2, 31.8, 29.9, 22.9, 14.4; FTIR (neat) 3335, 2923, 1792, 1717, 1268, 1011, 783, 756, 668 cm⁻¹.

(+)-(4*S*, 3a*S*, 7a*S*)-7-(tert-Butyl-dimethyl-silanyloxy)-2, 3, 3a, 4, 5, 7a-hexahydro-1*H*-indene-4-carboxylic Acid Methyl Ester (14a). To the precursor oxazaborolidine (0.16 mmol, theoretical) in 2 mL of toluene, a solution of trifluoromethanesulfonimide (0.200 M in toluene, freshly prepared, 571 μL, 0.114 mmol) was added dropwise at –78 °C to form **1**. After stirring for 10 min at –78 °C, (*E*, *Z*)-8-(*tert*-butyl-dimethyl-silanyloxy)-deca-2, 7, 9-trienoic acid methyl ester **13a** (206 mg, 0.665 mmol) was added by syringe at –78 °C. The reaction mixture was stirred at –50 °C for 24 hours and –20 °C for 24 hours until the reaction to complete the reaction. After addition of 100 μL of Et₃N, the crude

product was purified by silica gel chromatography (gradient elution with 5% ether-hexanes) to afford the Diels-Alder adduct **14a** (191 mg, 93%) as a colorless oil.

R_f 0.85 (Hex/Et₂O 2 : 1); $[\alpha]_D^{23} = +65$ ($c = 1.1$, CHCl₃, 96% *ee*, 99:1 *de*); ¹H NMR (500 MHz, CDCl₃): δ 4.64 (s, 1H), 3.68 (s, 3H), 2.38 (brs, 2H), 2.05-1.67 (m, 4H), 1.38-1.07 (m, 5H), 0.91 (s, 9H), 0.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 175.9, 153.1, 100.9, 47.4, 47.0, 45.2, 29.5, 28.7, 27.0, 25.9(3C), 22.6, 18.3, 14.3, -4.3(2C); FTIR (neat) 2953, 2929, 2858, 1737, 1167, 839 cm⁻¹; HRMS (EI) calcd for [C₁₇H₃₁O₃Si] ([M+H]⁺): 311.2042; found 311.2034. The relative configuration was determined by NOE experiment.

(+)-(4*S*, 3*aS*, 7*aS*)-7-Oxo-octahydro-indene-4-carboxylic Acid Methyl Ester (15). After treatment of **14a** with THF-aqueous HCl at room temperature for 1h, the reaction mixture was neutralized with aqueous NaHCO₃ solution at 0°C and extracted with ether. The extract was washed with water, brine and dried over MgSO₄. After concentration, the residue was purified by column chromatography (elution with hexanes-ether 3 : 1) to afford the product **15** as a colorless solid.

R_f 0.20 (Hex-Et₂O 2 : 1); mp = 56°C; $[\alpha]_D^{25} = +40$ ($c = 2.5$, CHCl₃, 96% *ee*, 98% *de*); ¹H NMR (400 MHz, CDCl₃): δ 3.67 (s, 3H), 2.55(dt, $J = 11.2, 4.0$ Hz, 1H), 2.38(m, 2H), 2.26 (m, 2H), 1.92 (m, 2H), 1.70 (m, 5H), 1.35(m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 209.9, 174.8, 56.2, 52.0, 50.2, 47.9, 40.6, 31.0, 30.8, 22.5, 21.3; FTIR (neat) 2953, 2925, 2872, 1735, 1716, 1174, 1086 cm⁻¹; HRMS (EI) calcd for [C₁₁H₁₇O₃] ([M+H]⁺): 197.1177; found 197.1183. The *exo/endo* ratio and the enantioselectivity were determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m × 0.25 mm, 150 °C, 25 psi), retention times: 16.29min (*exo*), 16.88 min (*exo*), 17.71min (*endo*, major), 18.63min (*endo*, minor). The absolute configuration was determined by three-step conversion of the **15** to the (+) - (octahydro-inden-4-yl)-methanol, $[\alpha]_D^{27} = +30$ ($c = 0.6$, CHCl₃), and comparison with the reference sample made as described below.

(+) - (Octahydro-inden-4-yl)-methanol. Catalyzed hydrogenation of **5** with 5% Pd/C in ethanol produced the dihydro **5** in quantitative yield, which was then reduced with LAH in ether to afford (+)-(octahydro-inden-4-yl)-methanol in 75% yield.

$[\alpha]_D^{23} = +28$ ($c = 0.5$, CHCl_3 , 90% *de*, 92% *ee*); ^1H NMR (500 MHz, CDCl_3): δ 3.67 (dd, $J = 4.5$, 10.5 Hz, 1H), 1.89–1.83 (m, 4H), 1.75 (m, 2H), 1.60 (m, 2H), 1.29 (m, 3H), 1.11 (m, 3H), 0.96 (dt, $J = 4.0$, 11.5 Hz, 1H), 0.83 (m, 1H); FTIR (neat) 2921, 2855, 758, 668 cm^{-1} .

(+)-(1*S*, 4*aS*, 8*aS*)- 4-Oxo-decahydro-naphthalene-1-carboxylic Acid Methyl Ester (18). To freshly prepared catalyst **1**, (*E*, *Z*)-9-(*tert*-butyl-dimethylsilanyloxy)-undeca-2, 8, 10-trienoic acid methyl ester **16** (214 mg, 0.665 mmol) was added at room temperature. The reaction mixture was heated at 40 °C and stirred for 24 hours. Then 100 μL of Et_3N was added to quench the reaction. The crude product was purified by silica gel chromatography (elution with hexanes-ether 20 : 1) to afford the Diels-Alder adduct **17** (111 mg, 52%) and recovered starting material (85 mg, 40%) as a pale yellow oil. After treatment with THF-aqueous HCl, *trans*-decalone **18** was obtained as colorless oil.

R_f 0.22 (Hex- Et_2O 2 : 1); $[\alpha]_D^{27} = +26$ ($c = 1.1$, CHCl_3 , 90% *ee*, 60% *de*); ^1H NMR (400 MHz, CDCl_3): δ 3.70 (s, 3H), 2.55 (dt, $J = 11.0$, 3.0 Hz, 1H), 2.43 (m, 2H), 2.35 (m, 1H), 2.22 (m, 2H), 1.98 (m, 2H), 1.80 (m, 1H), 1.72 (m, 2H), 1.25 (m, 2H), 1.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.6, 175.1, 53.2, 52.0, 49.4, 45.9, 40.4, 32.4, 29.8, 25.5, 25.3, 25.2; FTIR (neat) 2926, 2855, 1733, 1709, 1163, 732 cm^{-1} . The *exo/endo* ratio and the enantioselectivity were determined by GC analysis using a J & W Scientific Cyclosil-B column (30 m x 0.25 mm, 135 °C, 25 psi), retention times: 36.33 min (*exo*), 37.26 min (*exo*), 41.28 min (*endo*, major), 41.70 min (*endo*, minor). The absolute configuration was assigned by analogy with that of adduct (+)-(4*S*, 3*aS*, 7*aS*)-7-oxo-octahydro-indene-4-carboxylic acid methyl ester.

2-Methyl-(E, E)-deca-2, 7, 9-trienal (2b). To a solution of octa-5, 7-dienal (744 mg, 6 mmol) in 20 mL of benzene, 2.32 g (7.3 mmol) of 2-(triphenylphosphoranylidene)propionaldehyde was added. The reaction mixture was stirred at 80 °C for 48 h, and then solvent was removed *in vacuo*. Purification of the residue by chromatography over 100 g of silica gel using 5% ether-hexanes as eluant afforded 780 mg of **2b** (80%).

^1H NMR (CDCl_3 , 500 MHz): δ 9.40 (s, CHO), 6.48 (t, $J = 7.0$ Hz, H3), 6.30 (dt, $J = 17.0, 10.0$ Hz, H9), 6.07 (dd, $J = 15.0, 10.5$ Hz, H8), 5.68 (dt, $J = 15.5, 8.0$ Hz, H7), 5.11 (dd, $J = 17.0, 0.6$ Hz, H10_{syn}), 4.98 (dd, $J = 10.5, 0.6$ Hz, H10_{anti}), 2.37 (dq, $J = 0.5, 7.5$ Hz, 2H, H4), 2.15 (q, $J = 7.0$ Hz, 2H, H6), 1.74 (s, 3H), 1.62 (quin, $J = 7.5$ Hz, 2H, H5); ^{13}C NMR (125 MHz, CDCl_3): δ 195.5, 154.5, 139.8, 137.2, 134.1, 132.1, 115.6, 32.3, 28.6, 28.1, 22.6; FTIR (film) 2926, 1683, 1003 cm^{-1} .

2-Bromo-deca-2, 7, 9-trienoic Acid Ethyl Ester. To a solution of octa-5, 7-dienal (744 mg, 6 mmol) in 20 mL of CH_2Cl_2 , ethyl bromo-triphenylphosphoranylidene acetate (3.0 g, 7 mmol) was added and the reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (hexanes/ether, 100 : 1) to give the α -bromo ester shown above (784 mg, 72%) as a light yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 7.27 (t, $J = 7.32$ Hz, Z isomer, 1H), 6.65 (t, $J = 7.68$ Hz, E isomer, 1H), 6.30 (dt, $J = 16.8, 10.2$ Hz, 1H), 6.05 (dd, $J = 14.6, 15.4$ Hz, 1H), 5.68 (dt, $J = 15.4, 6.95$ Hz, 1H), 5.09 (d, $J = 17.2$ Hz, 1H), 4.96 (d, $J = 10.2$ Hz, 1H), 4.27 (q, $J = 7.32$ Hz, 2H), 2.50 (q, $J = 7.68$ Hz, E isomer, 2H), 2.34 (q, $J = 7.32$ Hz, Z isomer, 2H), 2.11 (br q, $J = 6.95$ Hz, 2H), 1.56–1.38 (m, 2H), 1.33 (t, $J = 7.32$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.7, 146.2, 137.4, 134.8, 131.6, 131.5, 115.2, 62.6, 32.4, 32.2, 28.9, 14.4. FTIR (film): 2931, 2855, 1712, 1251, 902, 726 cm^{-1} .

2-Bromo-(Z, E)-deca-2, 7, 9-trienal (2c). To a solution of 2-bromo-deca-2, 7, 9-trienoic acid ethyl ester (600 mg, 2.2 mmol) in dry ether (15 mL), DIBAL (4 mL, 1 M in hexanes, 4 mmol) was added

dropwise during 1h at $-78\text{ }^{\circ}\text{C}$. The resulting mixture was stirred for 2 hours at $-78\text{ }^{\circ}\text{C}$ and MeOH and H_2O were added to quench the reaction. Then the precipitate was filtered through a short pad of Celite and Na_2SO_4 and the combined solution was concentrated to afford the primary alcohol which was immediately subjected to Swern oxidation. To a solution of oxalyl chloride (304 mg, 2.4 mmol) in CH_2Cl_2 (8 mL), DMSO (376 mg, 4.8 mmol) in 1 mL of CH_2Cl_2 was added dropwise at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 30 min, a solution of the crude alcohol obtained above in 1 mL of CH_2Cl_2 was added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred for another 30min and Et_3N (720 mg, 3.6 mmol) was added. After another 30min at $-78\text{ }^{\circ}\text{C}$, the reaction mixture was allowed to warm up to room temperature in 1 hour. Water was added and the solution was extracted with CH_2Cl_2 ($3 \times 50\text{ mL}$). The combined organic phase was washed with 1N HCl ($2 \times 10\text{ mL}$), water, brine and dried over MgSO_4 . The concentrated crude product was purified by flash chromatography (hexanes/ether, 50 : 1) to give the desired bromoaldehyde **2c** as a light yellow oil (320 mg, 64% yield for two steps).

^1H NMR (CDCl_3 , 500 MHz) : δ 9.21 (s, CHO), 7.15 (t, $J = 7.3\text{ Hz}$, H3), 6.31 (dt, $J = 17.0, 10.3\text{ Hz}$, H9), 6.09 (dd, $J = 14.6, 9.8\text{ Hz}$, H8), 5.69 (dt, $J = 15.1, 7.3\text{ Hz}$, H7), 5.13 (d, $J = 17.0\text{ Hz}$, 1H, 10_{syn}), 5.00 (d, $J = 10.3$, 1H, 10_{anti}), 2.55 (q, $J = 7.3\text{ Hz}$, 2H, H4), 2.19 (q, $J = 7.3\text{ Hz}$, 2H, H6), 1.69 (quin, $J = 7.3\text{ Hz}$, 2H, H5); ^{13}C NMR (100MHz, CDCl_3): δ 186.3, 155.4, 137.1, 133.6, 132.4, 129.3, 115.9, 32.3, 31.7, 27.2; FTIR (film) 2928, 2859, 1698, 1616, 1003, 898 cm^{-1} .

2-Methyl-(E, E)-deca-2, 7, 9-trienoic Acid 2, 2, 2-Trifluoro Ethyl Ester (4). To a solution of the octa-5, 7-dienal (744 mg, 6 mmol) in 20 mL of CH_2Cl_2 , 2.93 g (7.3 mmol) of (carbotrifluoroethoxymethylene)triphenylphosphorane was added at $0\text{ }^{\circ}\text{C}$. The solution was stirred for 24 h at $23\text{ }^{\circ}\text{C}$, and then the solvent was removed *in vacuo*. Purification of the residue by flash chromatography using 2% ether-hexanes as eluant afforded 1.28 g of **4** as a colorless oil (85%, $E/Z = 15 : 1$).

^1H NMR (CDCl_3 , 500 MHz): δ 7.10 (dt, $J = 15.5, 7.0\text{ Hz}$, H5), 6.30 (dt, $J = 17.5, 10.0\text{ Hz}$, H11), 6.06 (dd, $J = 15.0, 10.0\text{ Hz}$, H10), 5.88 (d, $J = 15.5\text{ Hz}$, H4), 5.66 (dt, $J = 15.0, 7.0\text{ Hz}$, H9), 5.11 (dd, $J = 16.5, 0.6\text{ Hz}$, 12_{syn}), 4.98 (dd, $J = 10.5, 0.6\text{ Hz}$, 12_{anti}), 4.51 (q, $J = 7.5\text{ Hz}$, 2H, H2), 2.40 (dq, $J = 1.5, 7.0\text{ Hz}$, 2H, H6), 2.12 (q, $J = 7.0\text{ Hz}$, 2H, H8), 1.60 (quin, $J = 7.5\text{ Hz}$, 2H, H7); ^{13}C NMR (125 MHz, CDCl_3): δ 164.9, 152.2, 137.2, 134.1, 132.1, 123.3(q, 1C, $J = 276\text{ Hz}$), 119.8, 115.6, 60.4(q, 1C, $J = 37.5\text{ Hz}$), 32.1, 31.9, 27.5; FTIR (neat) 2952, 2869, 1748, 1270, 1167 cm^{-1} .

(E)-9,9-Dimethoxynona-1,3-diene. To a solution of diethyl allylphosphonate (2.1 g, 12.0 mmol) in anhydrous THF (15 mL) was added dropwise BuLi (6.0 mL, 2.0 M in hexanes, 12.0 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring at $-78\text{ }^{\circ}\text{C}$ for 20 min, a solution of the 6,6-dimethoxy-hexanal (1.6 g, 10.0 mmol) in HMPA (3.0 mL, 18 mmol) was added dropwise. The resulting solution was stirred for 2 h at $-78\text{ }^{\circ}\text{C}$, and then allowed to warm to r. t. Stirring was continued for an additional 8 h at r. t. before quenching with *aq.* NH_4Cl solution. The mixture was extracted with Et_2O ($3 \times 50\text{ mL}$). The combined organic phase was washed with brine (10 mL), dried over MgSO_4 and concentrated to afford the crude product. Purification by flash chromatography (hexanes- $\text{EtOAc} = 10 : 1$) gave the desired diene as a colorless oil in 75% yield (1.49 g, $E/Z = 20 : 1$, determined by integration of ^1H NMR signals of H-2).

R_f 0.36 ($\text{EtOAc-Hex } 1 : 9$); ^1H NMR (500 MHz, CDCl_3): δ 6.30 (ddd, $J = 17.0, 10.4, 10.4\text{ Hz}$, 1H), 6.05 (dd, $J = 15.3, 10.5\text{ Hz}$, 1H), 5.69 (dt, $J = 15.2, 7.0\text{ Hz}$, 1H), 5.08 (ddd, $J = 17.0, 1.1, 0.5\text{ Hz}$, 1H), 4.95 (ddd, $J = 10.1, 1.1, 0.5\text{ Hz}$, 1H), 4.36 (t, $J = 5.8\text{ Hz}$, 1H), 3.31 (s, 6H), 2.09 (br q, $J = 7.0\text{ Hz}$, 2H), 1.63–1.57 (m, 2H), 1.46–1.31 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ 137.4, 135.3, 131.3, 115.0, 104.6, 52.8(2C), 32.6, 32.5, 29.2, 24.4; FTIR (film): 3086, 2988, 2857, 1651, 1602 cm^{-1} ; HRMS: m/e calcd for $\text{C}_{10}\text{H}_{17}\text{O}$ ($\text{M}^+ - \text{OCH}_3$) 153.1280; found 153.1280.

(E)-Nona-6,8-dienal. To a solution of (E)-9,9-dimethoxynona-1,3-diene (1.0 g, 5.4 mmol) in THF (20 mL) was added 2N HCl (5 mL). After stirring for 8 h at r.t., the mixture was extracted with Et_2O ($3 \times 50\text{ mL}$). The organic phase was combined, washed with *aq.* NaHCO_3 solution ($3 \times 10\text{ mL}$), brine ($2 \times 10\text{ mL}$), and dried (MgSO_4). The solvent was removed *in vacuo* to give 0.7 g (93%) of aldehyde as a colorless oil.

R_f 0.33 ($\text{EtOAc/Hex } 1 : 9$). ^1H NMR (500 MHz, CDCl_3): δ 9.71 (t, $J = 1.8\text{ Hz}$, 1H), 6.25 (ddd, $J = 17.1, 10.2, 10.2\text{ Hz}$, 1H), 6.00 (dd, $J = 15.1, 10.3\text{ Hz}$, 1H), 5.62 (dt, $J = 15.1, 6.8\text{ Hz}$, 1H), 5.05 (br d, $J = 17.0\text{ Hz}$, 1H), 4.91 (br d, $J = 10.1\text{ Hz}$, 1H), 2.39 (td, $J = 7.2, 1.8\text{ Hz}$, 2H), 2.07 (br q, $J = 6.4\text{ Hz}$, 2H), 1.66–1.55 (m, 2H), 1.46–1.34 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 202.5, 137.2, 134.5, 131.5, 115.1, 43.7, 32.3, 28.6, 21.6; MS: m/e 152 (M^+).

Undeca-2, 8, 10-(*E, E*)-trienoic Acid 2, 2, 2-Trifluoro-ethyl Ester (6). To a solution of the (*E*)-nona-6, 8-dienal (816 mg, 6 mmol) in 20 mL of CH₂Cl₂, 2.93 g (7.3 mmol) of (carbotrifluoroethoxymethylene)triphenylphosphorane was added at 0 °C. The solution was stirred for 24 h at 23 °C, and then solvent was removed *in vacuo*. Purification of the residue by flash chromatography using 2% ether-hexanes as eluant afforded 1.26 g of **6** as a colorless oil (80%, *E* / *Z* = 14 : 1).

¹H NMR (CDCl₃, 500 MHz): δ 7.09 (dt, *J* = 15.5, 7.0 Hz, H5), 6.30 (dt, *J* = 17.5, 10.5 Hz, H12), 6.06 (dd, *J* = 15.5, 10.8 Hz, H11), 5.88 (dt, *J* = 15.5, 1.5 Hz, H4), 5.68 (dt, *J* = 15.5, 7.0 Hz, H10), 5.09 (d, *J* = 15.5 Hz, H13_{syn}), 4.97 (dd, *J* = 10.5 Hz, H13_{anti}), 4.51 (q, *J* = 8.3 Hz, 2H, H2), 2.25 (dq, *J* = 7.5, 1.5 Hz, 2H, H6), 2.11 (q, *J* = 7.0 Hz, 2H, H9), 1.46 (m, 4H, H7, H8); ¹³C NMR (125 MHz, CDCl₃): δ 164.9, 152.5, 137.3, 134.8, 131.6, 123.3 (q, 1C, *J* = 27.5 Hz), 119.7, 115.3, 60.3 (q, 1C, *J* = 37.5 Hz), 32.5, 32.4, 28.8, 27.5; FTIR (neat) 3734, 2930, 2859, 1736, 1653, 1159 cm⁻¹.

2-Methyl-(*E, E*)-Undeca-2, 7, 9-trienal (8). To a solution of the (*E*)-nona-6, 8-dienal (680 mg, 5 mmol) in 20 mL of benzene, 2.22 g (7.0 mmol) of 2-(triphenylphosphoranylidene)propionaldehyde was added at room temperature. The reaction mixture was refluxed for 48 h, and then solvent was removed *in vacuo*. Purification of the residue by flash chromatography using 5% ether-hexanes as eluant afforded 720 mg of **8** (81%).

¹H NMR (CDCl₃, 400 MHz): δ 9.39 (s, CHO), 6.47 (dt, *J* = 1.4, 7.5 Hz, H3), 6.30 (dt, *J* = 17.2, 7.1 Hz, H10), 6.05 (dd, *J* = 15.4, 10.1 Hz, H9), 5.68 (dt, *J* = 15.4, 6.6 Hz, H8), 5.11 (dd, *J* = 15.9, 1.5 Hz, H11_{syn}), 4.96 (dd, *J* = 10.2, 1.5 Hz, H11_{anti}), 2.35 (q, *J* = 6.9 Hz, 2H, H4), 2.11 (q, *J* = 6.6 Hz, 2H, H6), 1.73 (s, 3H), 1.49 (quin, *J* = 1.5, 3.1 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 195.6, 154.8, 139.7, 137.3, 134.8, 131.6, 115.3, 32.5, 29.05, 29.03, 28.1, 9.4; FTIR (neat) 3629, 2927, 1684, 1003 cm⁻¹.

(*E*)-Methyl 3, 5-Hexadienyl Alcohol. A solution of lithium aluminum hydride (7.9 mL, 1.0 M in THF) was added to a solution of (*E*)-methyl-3, 5-hexadienoate (1 g, 7.9 mmol) in THF at 0 °C. The reaction mixture was stirred for 1 h and then was quenched with aq. NaHCO₃ solution and water. The mixture was extracted with ether and the organic layers were combined, dried over anhydrous NaSO₄ and concentrated. The resulting oil was purified by silica gel chromatography to afford 542 mg of (*E*)-methyl 3, 5-hexadienyl alcohol (70%).

^1H NMR (CDCl_3 , 300 MHz): δ 6.29 (ddd, $J = 19, 10, 9$ Hz, 1H), 6.10 (m, 1H), 5.74 (m, 1H), 5.12 (d, $J = 17$ Hz, 1H), 5.02 (d, $J = 10$ Hz, 1H), 3.65 (s, 3H), 3.08 (d, $J = 7$ Hz, 2H); FTIR (neat) 3332, 2926, 1042, 1001, 896 cm^{-1} .

(*E, E, E*)-But-2-enedioic Acid Ethyl Ester Hexa-3, 5-dienyl Ester (10). To a solution of fumaric acid monoethyl ester (720 mg, 5 mmol) in 20 mL of CH_2Cl_2 oxalyl chloride (760 mg, 6.0 mmol) was added slowly at 0 °C. After being stirred for 30 min at room temperature, the solution was removed *in vacuo*. The residue was dissolved in anhydrous THF (20 mL) and (*E*)-methyl 3, 5-hexadienyl alcohol (490 mg, 5 mmol) and Et_3N (505 mg, 5 mmol) were added at -78 °C. After stirring at -78 °C for 1h, aqueous NH_4Cl solution (3 mL) was added and the reaction mixture warmed to room temperature. The solution was extracted with ether (3×50 mL) and the combined organic phase was washed with H_2O (3×10 mL) and brine and dried over MgSO_4 . After concentration on a rotavap, the residue was purified by chromatography on silica gel using hexanes-ether (10 : 1) as eluent to give the desired ester as a colorless oil (997 mg, 89%).

^1H NMR (CDCl_3 , 400 MHz): δ 6.83 (s, 2H), 6.29 (dt, $J = 16.8, 10.4$ Hz, 1H), 6.12 (dd, $J = 15.0, 10.5$ Hz, 1H), 5.65 (dt, $J = 15.0, 7.5$ Hz, 1H), 5.13 (dd, $J = 16.8$ Hz, 1H), 5.01 (d, $J = 10.0$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 4H), 2.46 (q, $J = 6.8$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 165.1(2C), 136.8, 134.0, 133.9, 133.6, 129.4, 116.6, 64.6, 61.6, 31.9, 14.3; FTIR (neat) 1717, 1293, 1256, 1151, 1029, 774 cm^{-1} ; HRMS (EI) calcd for $[\text{C}_{12}\text{H}_{17}\text{O}_4]$ ($[\text{M}+\text{H}]^+$): 225.1127; found 225.1129.

8-Oxo-oct-2-enoic Acid Methyl Ester. To a solution of acetal (2.16 g, 10.0 mmol) in THF (20 mL) was added 2N HCl (15 mL). After stirring for 8 h at r.t., the reaction mixture was extracted with Et_2O (3×50 mL). The organic phase was combined, washed with *aq.* NaHCO_3 solution (3×10 mL), brine (2×5 mL), and dried (MgSO_4). The solvent was removed in *vacuo* to give 1.48 g (87%) of 8-oxo-oct-2-enoic acid methyl ester as a colorless oil.

R_f 0.45 (EtOAc-Hex 1 : 3). ^1H NMR (300 MHz, CDCl_3): δ 9.73 (s, 1H), 6.91 (dt, $J = 15.3, 7.0$ Hz, 1H), 5.80 (dd, $J = 15.3, 1.8$ Hz, 1H), 3.68 (s, 3H), 2.42 (t, $J = 7.2, 1.8$ Hz, 2H), 2.19 (q, $J = 6.6$ Hz, 2H),

1.62(quin, $J = 6.6$ Hz, 2H), 1.47 (quin, $J = 7.2$ Hz, 2H); FTIR (neat) 2946, 2861, 1716, 1656, 1435, 1197, 1176, 1037, 851 cm^{-1} ; MS: m/e 170 (M^+).

9-Hydroxy-undeca-2, 10-dienoic Acid Methyl Ester. To a stirred solution of 8-oxo-oct-2-enoic acid methyl ester (850 mg, 5 mmol) in THF (20 mL) was added dropwise vinylmagnesium bromide (10 mL, 1.0 M in THF, 10 mmol) at -78°C and the reaction mixture was stirred at -78°C for 2h. After the aqueous NH_4Cl (10 mL) was added to the mixture, the resulting precipitate was removed from filtration. The filtrate was extracted by ether (3×50 mL) and dried over MgSO_4 . The concentrated crude product was purified by flash chromatography on silica gel using hexanes-ether (10 : 1) as eluent to give the alcohol as a colorless oil (841 mg, 85%).

R_f 0.43 (EtOAc–Hex 1 : 3). ^1H NMR (400 MHz, CDCl_3): δ 6.94 (dt, $J = 10.5, 6.8$ Hz, 1H), 5.79 (m, 2H), 5.18 (d, $J = 17.2$ Hz, 1H), 5.06 (d, $J = 10.0$ Hz, 1H), 4.09 (m, 1H), 3.70 (s, 3H), 2.19 (q, $J = 9.7$ Hz, 2H), 1.65 (m, 2H), 1.43 (m, 4H); FTIR (neat) 3391, 2932, 2858, 1720, 1654, 1436, 1313, 1198, 1176, 1048, 981 cm^{-1} ; MS: m/e 198 (M^+).

8-Oxo-deca-2, 9-dienoic Acid Methyl Ester. To a solution of 9-hydroxy-undeca-2, 10-dienoic acid methyl ester (792 mg, 4 mmol) in 20 mL of CH_2Cl_2 , Dess-Martin periodinane (1.7 g, 4 mmol) was added at 0°C . After stirring for 2 h at room temperature, the reaction mixture was diluted with ether (30 mL) and poured into 10 mL of saturated aqueous NaHCO_3 and 10 mL of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The resulting mixture was stirred for 30min, extracted with ether (3×50 mL) and the extract was washed with *aq.* NaHCO_3 (2×10 mL), brine and dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (hexanes / ether = 10 : 1) to give the ketone as a colorless oil (705 mg, 90%).

R_f 0.47 (1 : 3 EtOAc–Hex). ^1H NMR (300 MHz, CDCl_3): δ 6.94 (dt, $J = 15.6, 7.2$ Hz, 1H), 6.34 (dd, $J = 10.2$ Hz, 1H), 6.20 (d, $J = 18.0$ Hz, 1H), 5.84 (dd, $J = 15.3, 1.8$ Hz, 1H), 5.81 (q, $J = 1.8$ Hz, 1H), 3.71 (s, 3H), 2.59 (t, $J = 7.5$ Hz, 2H), 2.21 (dq, $J = 6.9, 1.2$ Hz, 2H), 1.65 (quin, $J = 7.5$ Hz, 2H), 1.47 (q, $J = 6.9$ Hz, 2H); FTIR (neat) 2946, 2860, 1720, 1697, 1532, 1489, 1397, 1308, 1198, 1176, 1072, 825 cm^{-1} ; MS: m/e 196 (M^+).

(*E, Z*)-8-(*tert*-Butyl-dimethyl-silanyloxy)-deca-2, 7, 9-trienoic Acid Methyl Ester (13a). To a solution of 8-oxo-deca-2, 9-dienoic acid methyl ester (588 mg, 3 mmol) and *tert*-butyldimethylsilyl triflate (1.0 mL, 4.5 mmol) in 20 mL of anhydrous THF, potassium hexamethyldisilazide (9 mL, 0.5 M in toluene, 4.5 mmol) was added dropwise at -78°C under nitrogen. The resulting solution was stirred at -78°C for 30 min and at room temperature for 1h. The solution was quenched with *aq.* NaHCO_3 solution and extracted with Et_2O (3×50 mL). The combined organic phase was washed with cold saturated NaHCO_3 solution (2×10 mL) and brine (5 mL). The solution was dried over MgSO_4 and the solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel (hexanes / ether = 30 : 1) to give the **13a** as a colorless oil (856 mg, 92%, *E* / *Z* = 15 : 1).

^1H NMR (CDCl_3 , 500 MHz): δ 6.95 (dt, J = 15.5, 7.5 Hz, 1H, H4), 6.15 (dd, J = 17.5, 10.5 Hz, 1H, H10), 5.82 (dt, J = 15.5, 1.5 Hz, 1H, H3), 5.29 (d, J = 17.5 Hz, 1H, H11*trans*), 4.97 (d, J = 10.5 Hz, 1H, H11*syn*), 4.76 (t, J = 7.0 Hz, 1H, H8), 3.72 (s, 3H), 2.22 (dq, J = 1.5, 7.5 Hz, 2H, H5), 2.13 (q, J = 7.0 Hz, 2H, H7), 1.53 (quin, J = 7.0 Hz, 2H, H6), 0.99 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 167.3, 149.5, 149.1, 135.7, 121.3, 114.9, 112.6, 51.6, 32.1, 28.1, 26.2(3C), 25.7, 18.6, -3.4(2C); HRMS (EI) calcd for $[\text{C}_{17}\text{H}_{31}\text{O}_3\text{Si}]$ ($[\text{M}+\text{H}]^+$): 311.2042; found 311.2034; FTIR (neat) 2951, 2929, 2857, 1727, 1251, 1048, 835 cm^{-1} .

(*E, Z*)-9-(*tert*-Butyl-dimethyl-silanyloxy)-undeca-2, 8, 10-trienoic Acid Methyl Ester (16). To a solution of 9-oxo-undeca-2, 10-dienoic acid methyl ester (420 mg, 2 mmol) and *tert*-butyldimethylsilyl triflate (6.9 mL, 3 mmol) in 20 mL of anhydrous THF, potassium hexamethyldisilazide (6 mL, 0.5 M in toluene, 3 mmol) was added dropwise at -78°C under nitrogen. The resulting solution was stirred at -78°C for 30 min and room temperature for 1h. The solution was quenched with *aq.* NaHCO_3 solution and extracted with Et_2O (3×50 mL). The organic phase was washed with cold saturated NaHCO_3 solution (2×10 mL) and brine (2×5 mL). The combined organic phase was dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexanes / ether = 20 : 1) to give the **16** as a colorless oil (583 mg, 90%, *E* / *Z* = 10 : 1).

^1H NMR (CDCl_3 , 500 MHz): δ 6.96 (dt, J = 15.5, 7.5 Hz, 1H, H4), 6.14 (dd, J = 17.1, 10.5 Hz, 1H, H11), 5.81 (dt, J = 15.5, 1.5 Hz, 1H, H3), 5.27 (d, J = 17.1 Hz, 1H, H12 *trans*), 4.95 (d, J = 10.5 Hz,

1H, H12 *syn*), 4.75(t, $J = 7.2$ Hz, 1H, H9), 3.72(s, 3H), 2.21 (q, $J = 7.2$ Hz, 2H), 2.10 (q, $J = 7.0$ Hz, 2H), 1.45(m, 4H), 0.99(s, 9H), 0.10(s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 167.4, 149.8, 148.8, 135.8, 121.2, 115.6, 112.3, 51.6, 32.3, 29.2, 28.0, 26.2(3C), 25.9, 18.7, -3.4(2C); FTIR (neat) 2929, 2857, 1725, 1653, 1252, 1045, 837 cm^{-1} .