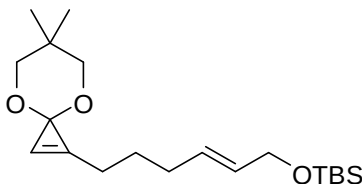


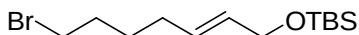
Supporting Information
Intramolecular Diels–Alder Reactions of Cyclopropenone Ketals

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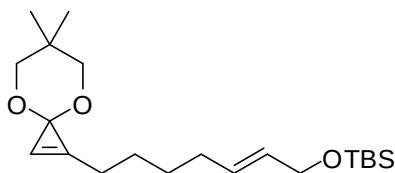
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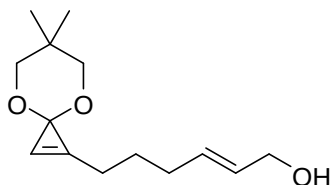
(S1). A solution of cyclopropenone ketal **10** (210 mg, 1.5 mmol) and HMPA (805 μ L, 4.5 mmol) in THF at -78 $^{\circ}$ C was slowly treated with *n*-BuLi (0.60 mL of 2.5 M solution in hexanes, 1.5 mmol) and the mixture was stirred for 30 min at this temperature. A solution of the TBS ether of (*E*)-6-bromohex-2-en-1-ol^{S1} (450 mg, 1.54 mmol) in THF was added dropwise and the mixture was warmed to -30 $^{\circ}$ C and stirred at this temperature for 12 h. Saturated aqueous NH_4Cl was added and the solution was extracted with EtOAc (3×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (SiO_2 , 10% EtOAc–hexane) afforded **S1** (430 mg, 81%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.46 (t, 1H, $J = 0.9$ Hz), 5.70–5.65 (m, 1H), 5.61–5.56 (m, 1H), 4.14 (m, 2H), 3.56 (d, 2H, $J = 10.2$ Hz), 3.53 (d, 2H, $J = 10.8$ Hz), 2.52 (td, 2H, $J = 0.6, 7.2$ Hz), 2.15 (m, 2H), 1.68 (quint, 2H, $J = 7.2$ Hz), 1.00 (s, 3H), 0.95 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.3, 132.2, 131.5, 117.5, 85.2, 78.2, 65.2, 32.9, 31.8, 28.6, 27.2, 25.8, 23.6, 23.3, 19.8, -3.9 ; IR (neat) ν_{max} 2929, 2853, 1468, 1253, 1072 cm^{-1} ; ESI-TOF HRMS m/z 353.2508 ($[\text{M} + \text{H}]^+$, $\text{C}_{20}\text{H}_{36}\text{O}_3\text{Si} + \text{H}^+$ requires 353.2506).



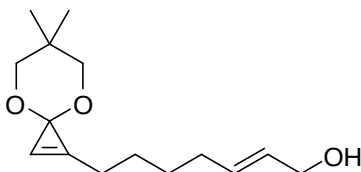
(S2). Prepared from 6-bromohex-1-ene (1.35 mL, 10 mmol) following the procedure detailed for (*E*)-6-bromohex-2-en-1-ol^{S1} to give **S2** (1.74 g, 5.7 mmol) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 5.66 (dt, 1H, $J = 1.5, 6.6, 15.0$ Hz), 5.57 (dt, 1H, $J = 1.2, 5.1, 15.0$ Hz), 4.13 (m, 2H), 3.50 (t, 2H, $J = 6.9$ Hz), 2.08 (m, 2H), 1.87 (m, 2H), 1.53 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 131.9, 131.6, 65.2, 35.5, 34.0, 32.8, 29.4, 27.2, 19.8, -4.0 ; IR (neat) ν_{max} 2929, 2891, 2855, 1462, 1253, 1106 cm^{-1} ; ESI-TOF HRMS m/z 329.0908 ($[\text{M} + \text{Na}]^+$, $\text{C}_{13}\text{H}_{27}\text{BrOSi} + \text{Na}^+$ requires 329.0907).



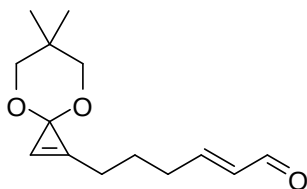
(S3). Prepared from cyclopropenone ketal **10** (360 mg, 2.6 mmol) and **S2** (870 mg, 2.8 mmol) following the procedure detailed for **S1** providing **S3** (750 mg, 80%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.43 (t, 1H, J = 0.9 Hz), 5.67 (m, 1H), 5.56 (m, 1H), 4.13 (dq, 2H, J = 1.2, 5.4 Hz), 3.55 (m, 4H), 2.51 (td, 2H, J = 1.2, 7.5 Hz), 2.07 (m, 2H), 1.62 (quint, 2H, J = 7.8 Hz), 1.49 (m, 2H), 1.00 (s, 3H), 0.95 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.5, 132.1, 131.6, 117.3, 85.2, 78.2, 65.3, 33.4, 31.8, 30.8, 28.4, 27.2, 26.2, 23.5, 23.3, 19.8, -3.9; IR (neat) ν_{max} 2951, 2931, 2855, 1468, 1255, 1074 cm^{-1} ; ESI-TOF HRMS m/z 367.2667 ($[\text{M} + \text{H}]^+$, $\text{C}_{21}\text{H}_{38}\text{O}_3\text{Si} + \text{H}^+$ requires 367.2663).



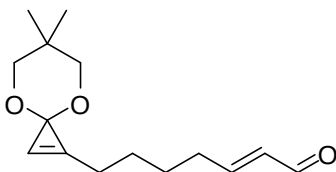
(S4). A solution of **S1** (430 mg, 1.22 mmol) in 5 mL of THF was buffered with acetic acid (115 μL) and then treated with 1 M Bu_4NF in THF (3.6 mL, 3.6 mmol) at 0 $^\circ\text{C}$. The mixture was allowed to warm to 25 $^\circ\text{C}$ and stirred for 16 h. Saturated aqueous NaHCO_3 was added and mixture was allowed to stir for 10 min. The solution was extracted with EtOAc (2×5 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (SiO_2 deactivated with 2% Et_3N , 40% EtOAc–hexane) afforded **S4** (288 mg, 98%) as a clear oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.47 (t, 1H, J = 0.9 Hz), 5.64 (m, 2H), 4.00 (m, 2H), 3.56 (d, 2H, J = 10.2 Hz), 3.53 (d, 2H, J = 10.2 Hz), 2.51 (td, 2H, J = 1.2, 7.2 Hz), 2.13 (m, 2H), 1.67 (quint, 2H, J = 7.2 Hz), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.3, 133.0, 131.5, 117.5, 85.2, 78.2, 64.1, 33.0, 31.8, 28.6, 25.8, 23.6, 23.3; IR (neat) ν_{max} 3409, 2945, 2846, 1468, 1267 cm^{-1} ; ESI-TOF HRMS m/z 239.1641 ($[\text{M} + \text{H}]^+$, $\text{C}_{14}\text{H}_{22}\text{O}_3 + \text{H}^+$ requires 239.1642).



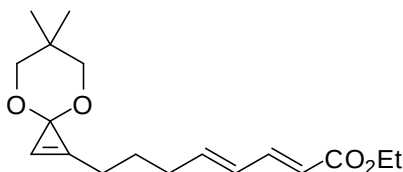
(S5). Prepared from **S3** (473 mg, 1.29 mmol) following the procedure detailed for **S4** providing **S5** (299 mg, 92%) as a clear oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.44 (t, 1H, J = 1.2 Hz), 5.62 (m, 2H), 3.99 (m, 2H), 3.55 (m, 5H), 2.51 (td, 2H, J = 1.2, 7.2 Hz), 2.07 (m, 2H), 1.62 (quint, 2H, J = 7.5 Hz), 1.48 (m, 2H), 1.00 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.5, 132.5, 132.0, 117.3, 85.2, 78.2, 64.2, 33.4, 31.8, 30.3, 28.4, 26.2, 23.5, 23.3; IR (neat) ν_{max} 3429, 2932, 2852, 1275, 1071, 1019 cm^{-1} ; ESI-TOF HRMS m/z 253.1794 ($[\text{M} + \text{H}]^+$, $\text{C}_{15}\text{H}_{24}\text{O}_3 + \text{H}^+$ requires 253.1798).



(S6). Molecular sieves and 4-methylmorpholine *N*-oxide (140 mg, 1.2 mmol) were added to a solution of alcohol **S4** (200 mg, 0.8 mmol) in CH₂Cl₂ (40 mL), and the mixture was stirred for 10 min. Tetrapropylammonium perruthenate (TPAP) (25 mg, 0.07 mmol) was added and the reaction mixture turned black. The reaction mixture was allowed to stir at 25 °C for 15 min. The reaction mixture was then filtered over Celite, concentrated, and purified by flash chromatography (SiO₂, 40% EtOAc–hexane) to give **19** (150 mg, 78%) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 9.53 (d, 1H, *J* = 7.8 Hz), 7.54 (t, 1H, *J* = 1.2 Hz), 7.01 (dt, 1H, *J* = 7.2, 15.6 Hz), 6.11 (ddt, 1H, *J* = 1.5, 7.8, 15.6 Hz), 3.57 (d, 2H, *J* = 10.2 Hz), 3.54 (d, 2H, *J* = 10.8 Hz), 2.58 (td, 2H, *J* = 1.2, 7.2 Hz), 2.49 (qd, 2H, *J* = 1.2, 7.2 Hz), 1.84 (quint, 2H, *J* = 7.2 Hz), 1.02 (s, 3H), 0.93 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 195.2, 159.5, 138.6, 135.1, 118.2, 85.1, 78.2, 33.3, 31.8, 27.2, 25.8, 23.6, 23.2; IR (neat) ν_{max} 2950, 2845, 1689, 1275 cm⁻¹; ESI-TOF HRMS *m/z* 237.1483 ([M + H]⁺, C₁₄H₂₀O₃ + H⁺ requires 237.1485).

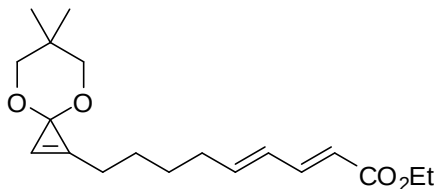


(S7). Prepared from **S5** (287 mg, 1.14 mmol) following the procedure detailed for **S6** providing **S7** (230 mg, 83%) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 9.52 (d, 1H, *J* = 7.8 Hz), 7.48 (s, 1H), 7.00 (dt, 1H, *J* = 6.6, 15.6 Hz), 6.10 (ddt, 1H, *J* = 1.5, 7.8, 15.6 Hz), 3.56 (d, 2H, *J* = 10.2 Hz), 3.53 (d, 2H, *J* = 10.8 Hz), 2.55 (t, 2H, *J* = 6.3 Hz), 2.41 (m, 2H), 1.66 (m, 4H), 1.01 (s, 3H), 0.94 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 195.2, 160.1, 139.1, 134.8, 117.7, 85.1, 78.2, 33.7, 31.8, 28.8, 28.4, 26.1, 23.5, 23.2; IR (neat) ν_{max} 2944, 2846, 1688, 1275, 1071 cm⁻¹; ESI-TOF HRMS *m/z* 251.1646 ([M + H]⁺, C₁₅H₂₂O₃ + H⁺ requires 251.1642).

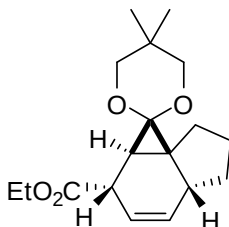


(4a). A solution of **S6** (34 mg, 0.14 mmol) and (carbethoxymethylene)triphenylphosphorane (98 mg, 0.28 mmol) was stirred in CH₂Cl₂ (2 mL) at 25 °C for 8 h. The reaction mixture was concentrated and purified by flash chromatography (SiO₂, 10–15% EtOAc–hexane gradient) to afford **4a** (21 mg, 50%) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 7.51 (t, 1H, *J* = 1.2 Hz), 7.25 (dd, 1H, *J* = 10.8, 15.6 Hz), 6.35–6.23 (m, 2H), 5.85 (d, 1H, *J* = 15.6 Hz), 4.13 (q, 2H, *J* = 7.2 Hz), 3.57 (d, 2H, *J* = 10.2 Hz), 3.54 (d, 2H, *J* = 10.2 Hz), 2.54 (td, 2H, *J* = 1.2, 7.2 Hz), 2.31 (q, 2H, *J* = 7.2 Hz), 1.75 (quint, 2H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.2 Hz), 1.01 (s, 3H),

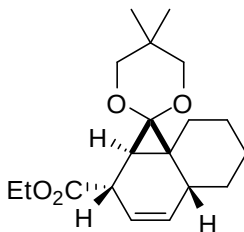
0.93 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 168.0, 146.5, 145.3, 138.8, 130.8, 121.3, 117.8, 85.0, 78.1, 61.4, 33.6, 31.7, 28.0, 25.7, 23.5, 23.2, 15.5; IR (neat) ν_{max} 2949, 2847, 1708, 1641, 1467, 1242 cm^{-1} ; ESI-TOF HRMS m/z 307.1909 ($[\text{M} + \text{H}]^+$, $\text{C}_{18}\text{H}_{26}\text{O}_4 + \text{H}^+$ requires 307.1904).



(5a). Prepared from **S7** (50 mg, 0.2 mmol) following the procedure detailed for **4a** providing **5a** (51 mg, 80%) as a clear oil: ^1H NMR (acetone- d_6 , 400 MHz) δ 7.46 (t, 1H, $J = 1.0$ Hz), 7.24 (dd, 1H, $J = 10.0, 15.2$ Hz), 6.27 (m, 2H), 5.83 (d, 1H, $J = 15.2$ Hz), 4.14 (q, 2H, $J = 7.0$ Hz), 3.54 (m, 4H), 2.53 (td, 2H, $J = 0.8, 6.8$ Hz), 2.24 (q, 2H, $J = 6.6$ Hz), 1.60 (m, 4H), 1.23 (t, 3H, $J = 7.2$ Hz), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 168.1, 146.5, 145.9, 139.3, 130.4, 121.2, 117.5, 85.2, 78.2, 61.4, 34.1, 31.8, 29.6, 28.4, 26.2, 23.5, 23.3, 15.5; IR (neat) ν_{max} 2940, 2847, 1712, 1642, 1261, 1024 cm^{-1} ; ESI-TOF HRMS m/z 321.2062 ($[\text{M} + \text{H}]^+$, $\text{C}_{19}\text{H}_{28}\text{O}_4 + \text{H}^+$ requires 321.2060).

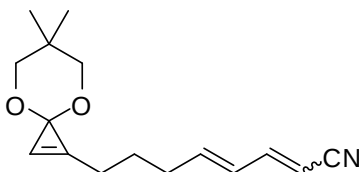


(4b). A solution of **4a** (15.8 mg, 0.05 mmol) in benzene (5.1 mL) was allowed to stir at 25 °C for 48 h. The mixture was purified by flash chromatography (SiO_2 , 10% EtOAc-hexane) to give **4b** (14.3 mg, 94%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 5.72 (dt, 1H, $J = 3.0, 10.2$ Hz), 5.67 (dt, 1H, $J = 3.0, 10.2$ Hz), 4.15 (q, 2H, $J = 7.2$ Hz), 3.61 (d, 1H, $J = 10.8$ Hz), 3.58 (d, 1H, $J = 10.8$ Hz), 3.51–3.55 (m, 2H), 3.04 (m, 1H), 2.38 (m, 1H), 2.00–2.11 (m, 2H), 1.60–1.75 (m, 2H), 1.41–1.51 (m, 2H), 1.29 (d, 1H, $J = 1.8$ Hz), 1.25 (t, 3H, $J = 7.2$ Hz), 1.00 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 173.9, 131.8, 121.5, 89.8, 76.1, 75.8, 60.9, 36.9, 34.9, 34.3, 32.7, 32.2, 30.8, 27.1, 25.9, 22.3, 22.0, 14.2; IR (neat) ν_{max} 2953, 2865, 1731, 1241 1096 cm^{-1} ; ESI-TOF HRMS m/z 307.1900 ($[\text{M} + \text{H}]^+$, $\text{C}_{18}\text{H}_{26}\text{O}_4 + \text{H}^+$ requires 307.1904).

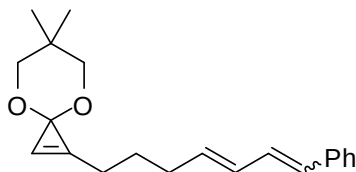


(5b). A solution of **5a** (28 mg, 0.09 mmol) in benzene (9 mL) was warmed at 60 °C for 64 h. The mixture was concentrated and purified by flash chromatography (SiO_2 , 10%

EtOAc–hexanes) to give **5b** (22 mg, 78%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 5.73 (qd, 1H, J = 1.8, 5.1 Hz), 5.43 (q, 1H, J = 5.2 Hz), 4.12 (q, 2H, J = 7.2 Hz), 3.55 (d, 1H, J = 10.8 Hz), 3.51 (d, 1H, J = 10.8 Hz), 3.48 (d, 1H, J = 10.8 Hz), 3.44 (d, 1H, J = 10.8 Hz), 3.40 (m, 1H), 2.27 (m, 1H), 1.80 (m, 1H), 1.66–1.74 (m, 2H), 1.61 (m, 1H), 1.44–1.50 (m, 2H), 1.22–1.32 (m, 2H), 1.23 (t, 3H, J = 6.9 Hz), 1.15–1.21 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 174.4, 136.5, 121.2, 92.5, 77.6, 77.4, 62.0, 41.1, 34.8, 34.6, 32.3, 32.2, 31.4, 31.3, 27.2, 25.5, 23.5, 23.3, 15.5; IR (neat) ν_{max} 2926, 2853, 1731, 1162 cm^{-1} ; ESI–TOF HRMS m/z 321.2069 ($[\text{M} + \text{H}]^+$, $\text{C}_{19}\text{H}_{28}\text{O}_4 + \text{H}^+$ requires 321.2060).

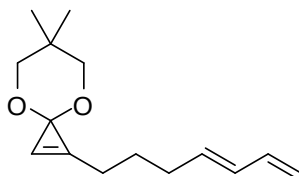


(6a). A solution of **S6** (34 mg, 0.14 mmol) and $\text{Ph}_3\text{P}=\text{CHCN}$ (126 mg, 0.42 mmol) was stirred in CH_2Cl_2 (2 mL) at 25 °C for 8 h. The reaction mixture was concentrated and purified by flash chromatography (SiO_2 , 10–15% EtOAc–hexane gradient) to afford **6a** (23 mg, 60%) as a clear oil of a mixture of isomers (2:1, *E:Z*). For the major *E* isomer: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.51 (t, 1H, J = 0.6 Hz), 7.13 (dd, 1H, J = 10.5, 15.9 Hz), 6.24–6.35 (m, 2H), 5.55 (d, 1H, J = 16.2 Hz), 3.52–3.58 (m, 4H), 2.54 (td, 2H, J = 1.2, 7.2 Hz), 2.32 (dd, 2H, J = 7.2, 14.4 Hz), 1.73–1.79 (m, 2H), 1.02 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 152.5, 146.3, 138.8, 130.7, 119.9, 118.0, 98.8, 85.1, 78.2, 33.5, 31.8, 27.8, 25.8, 23.6, 23.2. For the minor *Z* isomer: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.52 (t, 1H, J = 1.2 Hz), 7.01 (t, 1H, J = 10.8 Hz), 6.54–6.59 (m, 1H), 6.36 (m, 1H), 5.37 (d, 1H, J = 10.8 Hz), 3.57 (d, 2H, J = 10.8 Hz), 3.54 (d, 2H, J = 10.2 Hz), 2.56 (td, 2H, J = 1.2, 7.2 Hz), 2.36–2.41 (m, 2H), 1.77 (m, 2H), 1.02 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 151.3, 147.0, 138.8, 129.0, 118.1, 118.0, 97.1, 85.1, 78.2, 33.6, 31.8, 28.0, 25.8, 23.6, 23.2; IR (neat) ν_{max} 2950, 2847, 2213, 1727, 1640, 1469, 1272, 1071 cm^{-1} ; ESI–TOF HRMS m/z 260.1652 ($[\text{M} + \text{H}]^+$, $\text{C}_{16}\text{H}_{21}\text{NO}_2 + \text{H}^+$ requires 260.1645).

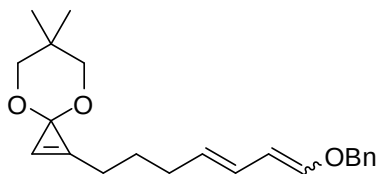


(7a). A solution of benzyltriphenylphosphonium bromide (170 mg, 0.39 mmol) in THF (10 mL) at –78 °C was slowly treated with *n*-BuLi (0.15 mL of 2.5 M solution in hexanes, 0.39 mmol) and allowed to stir for 10 min. The reaction mixture was warmed to 0 °C and stirred for 20 min before being cooled to –78 °C and a solution of aldehyde **S6** (30 mg, 0.13 mmol) in THF (1 mL) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for 2 h. The mixture was diluted with saturated aqueous NH_4Cl , extracted with EtOAc (2 $\times$ 10 mL), dried and concentrated under a reduced pressure. Flash chromatography (SiO_2 , 10% EtOAc–hexane) gave **7a** (59 mg,

98% yield) as a colorless oil as a mixture of isomers (1.4:1, *E:Z*). For the major *E* isomer: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.49 (t, 1H, J = 0.9 Hz), 7.44 (d, 2H, J = 7.2 Hz), 7.30 (t, 2H, J = 7.8 Hz), 7.20 (m, 1H), 6.87 (dd, 1H, J = 10.5, 15.9 Hz), 6.51 (d, 1H, J = 15.6 Hz), 6.31 (m, 1H), 5.86–5.91 (m, 1H), 3.58 (d, 2H, J = 10.2 Hz), 3.55 (d, 2H, J = 10.2 Hz), 2.55 (td, 2H, J = 0.6, 7.2 Hz), 2.25–2.29 (m, 2H), 1.71–1.76 (m, 2H), 1.02 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.5, 139.1, 138.9, 136.4, 133.2, 131.1, 130.4, 128.9, 127.9, 117.7, 85.2, 78.2, 33.6, 31.8, 28.6, 25.8, 23.6, 23.3. For the minor *Z* isomer: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.47 (t, 1H, J = 1.2 Hz), 7.35 (m, 4H), 7.24 (m, 1H), 6.66–6.71 (m, 1H), 6.33 (d, 1H, J = 12.0 Hz), 6.25 (t, 1H, J = 11.4 Hz), 5.93 (m, 1H), 3.56 (d, 2H, J = 10.2 Hz), 3.53 (d, 2H, J = 10.2 Hz), 2.53 (td, 2H, J = 1.2, 7.2 Hz), 2.27 (m, 2H), 1.72 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.5, 139.1, 138.9, 132.1, 130.6, 130.1, 129.5, 129.0, 128.5, 117.7, 85.1, 78.2, 33.5, 31.8, 28.5, 25.7, 23.6, 23.3; IR (neat) ν_{max} 2949, 2844, 1725, 1468, 1275, 1072 cm^{-1} ; ESI-TOF HRMS m/z 311.2001 ($[\text{M} + \text{H}]^+$, $\text{C}_{21}\text{H}_{26}\text{O}_2 + \text{H}^+$ requires 311.2005).

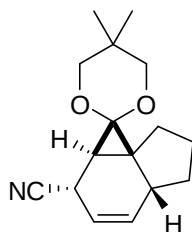


(8a). A solution of methyltriphenylphosphonium bromide (140 mg, 0.38 mmol) in THF (2 mL) at $-40\text{ }^{\circ}\text{C}$ was slowly treated with *n*-BuLi (0.16 mL of 2.5 M solution in hexanes, 0.39 mmol) and allowed to stir for 10 min. The reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 1 h before being cooled to $-40\text{ }^{\circ}\text{C}$ and a solution of aldehyde **S6** (30 mg, 0.13 mmol) in THF (1 mL) was added dropwise. The reaction mixture was allowed to warm to $25\text{ }^{\circ}\text{C}$ and stirred overnight. The mixture was diluted with water, extracted with EtOAc ($3 \times 20\text{ mL}$), dried and concentrated under a reduced pressure. Flash chromatography (SiO_2 , 15% EtOAc–hexane) gave **8a** (15 mg, 75% yield) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.47 (t, 1H, J = 0.6 Hz), 6.33 (dt, 1H, J = 10.2, 17.4 Hz), 6.11 (dd, 1H, J = 4.8, 10.5 Hz), 5.72–5.77 (m, 1H), 5.09 (d, 1H, J = 17.4 Hz), 4.95 (d, 1H, J = 10.2 Hz), 3.56 (d, 2H, J = 10.2 Hz), 3.53 (d, 2H, J = 10.2 Hz), 2.52 (td, 2H, J = 1.2, 7.2 Hz), 2.20 (q, 2H, J = 7.4 Hz), 1.70 (quint, 2H, J = 7.2 Hz), 1.01 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 139.25, 139.20, 136.1, 133.6, 117.7, 116.2, 85.2, 78.2, 33.3, 31.8, 28.5, 25.8, 23.6, 23.3; IR (neat) ν_{max} 2951, 2860, 1469, 1105 cm^{-1} ; ESI-TOF HRMS m/z 235.1686 ($[\text{M} + \text{H}]^+$, $\text{C}_{15}\text{H}_{22}\text{O}_2 + \text{H}^+$ requires 235.1692).

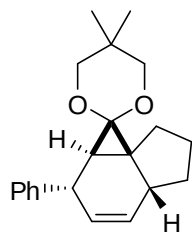


(9a). A solution of (benzyloxymethyl)triphenylphosphonium chloride (265 mg, 0.63 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ was treated with *t*-BuOK (0.63 mL of 1.0 M solution in THF) and allowed to stir for 10 min. The reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ and stirred for 20 min before being cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of aldehyde **S6** (75 mg,

0.31 mmol) in THF (1 mL) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for 2 h. The mixture was diluted with saturated aqueous NH₄Cl, extracted with EtOAc (2 × 10 mL), dried and concentrated under a reduced pressure. Flash chromatography (SiO₂, 10% EtOAc–hexane) gave **9a** (29 mg, 29% yield) as a colorless oil of a mixture of isomers (1:1.5, *E:Z*). For the major *Z* isomer: ¹H NMR (CD₃CN, 600 MHz) δ 7.31–7.40 (m, 6H), 6.35 (m, 1H), 6.04 (d, 1H, *J* = 6.0 Hz), 5.54 (m, 1H), 5.06 (dd, 1H, *J* = 6.0, 10.8 Hz), 4.85 (s, 2H), 3.56 (d, 2H, *J* = 10.8 Hz), 3.53 (d, 2H, *J* = 10.8 Hz), 2.48 (td, 2H, *J* = 0.6, 7.2 Hz), 2.15 (m, 2H), 1.62–1.67 (m, 2H), 0.97 (s, 3H), 0.94 (s, 3H); ¹³C NMR (CD₃CN, 150 MHz) δ 145.4, 138.66, 138.65, 130.8, 129.3, 128.8, 128.5, 124.4, 116.3, 107.7, 84.1, 77.2, 74.6, 32.5, 30.7, 27.7, 24.7, 22.3, 22.1. For the minor *E* isomer: ¹H NMR (CD₃CN, 600 MHz) δ 7.31–7.43 (m, 6H), 6.60 (d, 1H, *J* = 12.6 Hz), 5.94 (m, 1H), 5.63 (dd, 1H, *J* = 10.8, 12.6 Hz), 5.43–5.48 (m, 1H), 4.79 (s, 2H), 3.52–3.57 (m, 4H), 2.48 (t, 2H, *J* = 7.2 Hz), 2.09–2.13 (m, 2H), 1.61–1.67 (m, 2H), 0.98 (s, 3H), 0.95 (s, 3H); ¹³C NMR (CD₃CN, 150 MHz) δ 149.7, 138.7, 138.2, 129.3, 128.89, 128.82, 128.5, 127.7, 116.3, 108.3, 84.1, 77.3, 72.3, 32.4, 30.7, 27.8, 24.7, 22.3, 22.1; IR (neat) ν_{max} 2949, 2850, 1655, 1616, 1454, 1268, 1068 cm⁻¹; ESI–TOF HRMS *m/z* 341.2122 ([*M* + H]⁺, C₂₂H₂₈O₃ + H⁺ requires 341.2111).

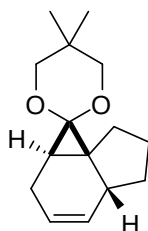


(6b). A solution of **6a** (22 mg, 0.085 mmol) in benzene (8.5 mL) was allowed to stir at room temperature for 36 h. The reaction mixture was concentrated and purified by flash chromatography (SiO₂, 15–20% EtOAc–hexane gradient) to give recovered *Z* isomer of **6a** (7.1 mg, 97% yield) and **6b** (12.6 mg, 86% yield based on *E* isomer) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 5.87 (dt, 1H, *J* = 3.0, 10.2 Hz), 5.53 (dt, 1H, *J* = 3.0, 10.2 Hz), 3.65 (d, 1H, *J* = 10.8 Hz), 3.58 (d, 1H, *J* = 10.8 Hz), 3.57–3.53 (m, 2H), 3.43 (m, 1H), 2.41 (m, 1H), 2.15 (m, 1H), 2.06 (m, 1H), 1.76 (m, 1H), 1.68 (m, 1H), 1.56 (m, 1H), 1.46 (m, 1H), 1.23 (d, 1H, *J* = 1.8 Hz), 1.00 (s, 3H), 0.96 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 134.4, 123.1, 120.2, 90.1, 77.4, 77.2, 36.4, 35.5, 34.1, 33.7, 32.3, 28.4, 27.5, 23.26, 23.21, 22.9; IR (neat) ν_{max} 2953, 2863, 2240, 1469, 1448, 1113 cm⁻¹; ESI–TOF HRMS *m/z* 282.1470 ([*M* + Na]⁺, C₁₆H₂₁NO₂ + Na⁺ requires 282.1464).

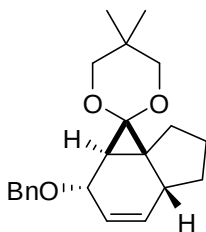


(7b). A solution of **7a** (29.5 mg, 0.095 mmol) in benzene (9.5 mL) was warmed at 60 °C for 20 h. The reaction mixture was concentrated and purified by flash chromatography

(SiO₂, 5–10% EtOAc–hexane gradient) to give recovered *Z* isomer of **7a** (10 mg, 85% yield) and **7b** (16.2 mg, 94% yield based on *E* isomer) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 7.29–7.34 (m, 2H), 7.25–7.27 (m, 2H), 7.17–7.21 (m, 1H), 5.68–5.71 (m, 1H), 5.45 (dt, 1H, *J* = 2.7, 10.2 Hz), 3.69 (d, 1H, *J* = 10.8 Hz), 3.60 (dd, 1H, *J* = 1.2, 10.8 Hz), 3.55 (dd, 1H, *J* = 0.6, 10.8 Hz), 3.52 (dd, 1H, *J* = 1.2, 10.2 Hz), 3.44 (m, 1H), 2.52 (m, 1H), 2.16 (m, 1H), 2.05 (m, 1H), 1.81 (m, 1H), 1.70 (m, 1H), 1.52 (m, 2H), 1.00 (s, 3H), 0.98 (s, 3H); 0.87 (s, 1H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 148.9, 130.4, 130.2, 129.5, 129.4, 128.7, 91.8, 77.5, 77.4, 38.4, 37.0, 36.1, 34.6, 34.4, 34.3, 32.3, 27.8, 23.4, 23.2; IR (neat) $\nu_{\max}$ 2950, 2857, 1449, 1098 cm⁻¹; ESI–TOF HRMS *m/z* 311.2005 ([*M* + *H*]⁺, C₂₁H₂₆O₂ + *H*⁺ requires 311.2005).

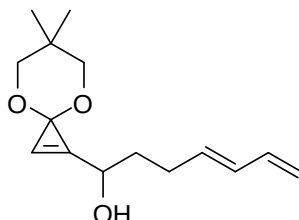


(8b). A solution of **8a** (2.5 mg, 0.01 mmol) in benzene (2 mL) was warmed at 45 °C for 12 h. The reaction mixture was concentrated and purified by flash chromatography (SiO₂, 6% EtOAc–hexane) to give **8b** (1.8 mg, 72% yield) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 5.54–5.57 (m, 1H), 5.46–5.50 (m, 1H), 3.48–3.56 (m, 4H), 2.34 (m, 1H), 2.22–2.28 (m, 1H), 1.98–2.10 (m, 3H), 1.72 (m, 1H), 1.62 (m, 1H), 1.44 (m, 1H), 1.35 (m, 1H), 0.97 (s, 3H), 0.96 (s, 3H), 0.89 (dd, 1H, *J* = 1.5, 8.7 Hz); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 130.5, 124.8, 92.1, 77.3, 77.1, 37.1, 35.5, 34.2, 33.6, 32.3, 27.8, 25.4, 23.4, 23.1, 20.2; IR (neat) $\nu_{\max}$ 2950, 2859, 1105 cm⁻¹; ESI–TOF HRMS *m/z* 235.1703 ([*M* + *H*]⁺, C₁₅H₂₂O₂ + *H*⁺ requires 235.1692).

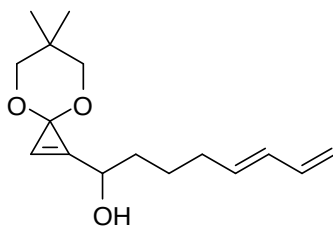


(9b). A solution of **9a** (17.2 mg, 0.05 mmol) in benzene (5.0 mL) was stirred at room temperature for 16 h. The reaction mixture was concentrated and purified by flash chromatography (SiO₂, 5–10% EtOAc–hexane gradient) to give recovered *Z* isomer of **9a** (8.7 mg, 85% yield) and **9b** (6.0 mg, 87% yield based on *E* isomer) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 7.41 (d, 2H, *J* = 7.8 Hz), 7.34 (t, 2H, *J* = 7.8 Hz), 7.27 (t, 1H, *J* = 7.5 Hz), 5.66–5.72 (m, 2H), 4.67 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 11.4 Hz), 4.00 (m, 1H), 3.61 (d, 1H, *J* = 10.2 Hz), 3.53 (dd, 1H, *J* = 1.2, 10.8 Hz), 3.43–3.47 (m, 2H), 2.37 (m, 1H), 1.99–2.10 (m, 2H), 1.72 (m, 1H), 1.65 (m, 1H), 1.49 (m, 2H), 1.11 (s, 1H), 1.00 (s, 3H), 0.93 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 141.2, 134.3, 130.0, 129.4, 129.0, 128.0, 90.4, 77.4, 77.2, 70.9, 69.2, 36.7, 36.1, 33.8, 33.7, 32.2, 31.8, 27.7,

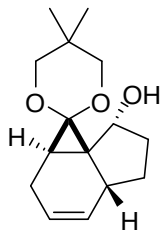
23.4, 23.1; IR (neat) $\nu_{\max}$ 2951, 2900, 2859, 1451, 1096, 1062 cm^{-1} ; ESI-TOF HRMS m/z 363.1931 ($[\text{M} + \text{H}]^+$, $\text{C}_{22}\text{H}_{28}\text{O}_3 + \text{H}^+$ requires 363.1936).



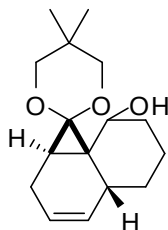
(13a). A solution of cyclopropenone ketal **10** (50 mg, 0.36 mmol) and HMPA (195 μL , 1.1 mmol) in THF (1.5 mL) at -78°C was slowly treated with *n*-BuLi (0.14 mL of 2.5 M solution in hexanes, 0.36 mmol) and the mixture was stirred for 30 min at this temperature. A solution of (*E*)-hepta-4,6-dienal^{S2} (33 mg, 0.3 mmol) in THF (0.5 mL) was added dropwise and the mixture was stirred at this temperature for 1 h. Saturated aqueous NH_4Cl was added and the solution was warmed to 25°C and extracted with EtOAc (3×10 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (SiO_2 , 35% EtOAc–hexane) afforded **13a** (185 mg, 44%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.49 (d, 1H, $J = 1.6$ Hz), 6.28–6.38 (m, 1H), 6.09–6.14 (m, 1H), 5.78 (m, 1H), 5.08 (m, 1H), 4.94 (m, 1H), 4.68 (m, 1H), 4.44 (d, 1H, $J = 5.6$ Hz), 3.53–3.63 (m, 4H), 2.27 (m, 2H), 1.79 (m, 2H), 1.00 (s, 3H), 0.95 (s, 3H). Due to rapid cyclization, further characterization could not be carried out without significant presence of Diels–Alder product **13b**.



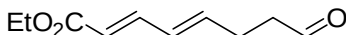
(14a). Prepared from cyclopropenone ketal **10** (30 mg, 0.19 mmol) and (*E*)-octa-5,7-dienal^{S2} (20 mg, 0.16 mmol) following the procedure detailed for **13a** providing **14a** (30 mg, 70%) as a colorless oil: ^1H NMR (acetone- d_6 , 600 MHz) δ 7.45 (d, 1H, $J = 1.2$ Hz), 6.32 (dt, 1H, $J = 10.2, 16.8$ Hz), 6.09 (dd, 1H, $J = 10.2, 15.6$ Hz), 5.73 (dt, 1H, $J = 6.6, 15.6$ Hz), 5.07 (d, 1H, $J = 17.4$ Hz), 4.93 (d, 1H, $J = 10.2$ Hz), 4.67 (t, 1H, $J = 6.0$ Hz), 4.39 (d, 1H, $J = 5.4$ Hz), 3.63 (d, 1H, $J = 6.0$ Hz), 3.61 (d, 1H, $J = 6.0$ Hz), 3.54 (d, 2H, $J = 10.2$ Hz), 2.14 (m, 2H), 1.71 (m, 2H), 1.59 (m, 2H), 1.01 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 143.6, 139.3, 136.7, 133.1, 116.9, 116.1, 85.8, 78.4, 68.1, 37.5, 33.8, 31.7, 26.3, 23.5, 23.3; IR (neat) $\nu_{\max}$ 3423, 2949, 2860, 1468, 1267, 1070 cm^{-1} ; ESI-TOF HRMS m/z 265.1799 ($[\text{M} + \text{H}]^+$, $\text{C}_{16}\text{H}_{24}\text{O}_3 + \text{H}^+$ requires 265.1798)



(13b). A solution of **13a** (23 mg, 0.1 mmol) in benzene (10 mL) was allowed to stir at room temperature for 14 h. The reaction mixture was concentrated and flash chromatography (SiO₂, 35% EtOAc–hexanes) gave **13b** (21 mg, 91% yield) as a colorless oil: ¹H NMR (C₆D₆, 600 MHz) δ 5.65–5.68 (m, 1H), 5.53–5.56 (m, 1H), 4.26 (t, 1H, *J* = 4.2 Hz), 3.28–3.35 (m, 3H), 3.23 (dd, 1H, *J* = 1.2 10.8 Hz), 2.53 (m, 1H), 2.10–2.21 (m, 2H), 1.71–1.84 (m, 3H), 1.61 (m, 1H), 1.45 (dd, 1H, *J* = 1.8, 8.4 Hz), 1.17 (s, 1H), 0.85 (s, 3H), 0.64 (s, 3H); ¹³C NMR (C₆D₆, 150 MHz) δ 129.0, 123.2, 90.7, 75.9, 75.8, 72.6, 38.3, 35.2, 33.4, 30.7, 30.6, 22.2, 21.8, 18.8, 18.6; IR (neat) ν_{max} 3444, 2951, 2862, 1110, 1087 cm⁻¹; ESI–TOF HRMS *m/z* 273.1474 ([M + Na]⁺, C₁₅H₂₂O₃ + Na⁺ requires 273.1461).

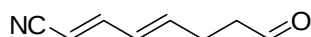


(14b). A solution of **14a** (13 mg, 0.05 mmol) in benzene (5.0 mL) was allowed to stir at 60 °C for 18 h. The reaction mixture was concentrated and flash chromatography (SiO₂, 20% EtOAc–hexanes) gave **14b** (10.4 mg, 80% yield; dr 2:1) as a colorless oil of a mixture of diastereomers: ¹H NMR (acetone-*d*₆, 600 MHz) δ 5.55 (m, 1H), 5.39 (m, 0.33H), 5.30 (m, 0.67H), 3.83 (m, 0.33H), 3.75 (dd, 0.67H, *J* = 1.2, 10.8 Hz), 3.44–3.64 (m, 4.67H), 3.21 (d, 0.33H, *J* = 1.8 Hz), 2.50 (m, 0.67H), 2.28–2.41 (m, 2H), 2.21 (m, 0.33H), 1.69–1.89 (m, 2.67H), 1.61 (dd, 0.33H, *J* = 2.4, 6.0 Hz), 1.37–1.49 (m, 2H), 1.17 (m, 1H), 1.07 (s, 2H), 1.02 (s, 1H), 0.93 (m, 1H), 0.91 (s, 1H), 0.82 (s, 2H); ¹³C NMR (CD₃CN, 150 MHz) δ 132.46, 132.44, 122.0, 121.1, 92.6, 92.2, 76.7, 76.6, 76.4, 76.2, 72.4, 68.8, 34.8, 34.5, 34.0, 32.9, 32.7, 32.1, 31.39, 31.34, 29.6, 27.0, 22.6, 22.3, 22.16, 22.14, 22.0, 21.9, 21.27, 21.22, 19.9; IR (neat) ν_{max} 3499, 2929, 2860, 1443, 1251, 1093, 1066 cm⁻¹; ESI–TOF HRMS *m/z* 287.1618 ([M + Na]⁺, C₁₆H₂₄O₃ + Na⁺ requires 287.1618).

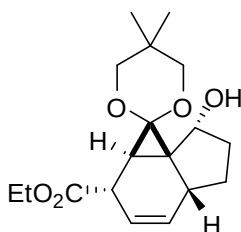


(15). Molecular sieves and 4-methylmorpholine *N*-oxide (43 mg, 0.36 mmol) were added to a solution of ethyl (2*E*,4*E*)-8-hydroxyocta-2,4-dienoate^{S3} (45 mg, 0.24 mmol) in CH₂Cl₂ (5 mL), and the mixture was stirred for 10 min. Tetrapropylammonium perruthenate (TPAP) (15 mg, 0.04 mmol) was added and the reaction mixture turned black. The reaction mixture was allowed to stir at 25 °C for 15 min. The reaction mixture was then filtered over Celite, concentrated, and purified by flash chromatography

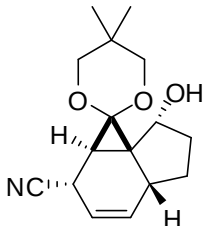
(SiO₂, 30% EtOAc–hexane) to give **15** (25 mg, 57% yield) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 9.75 (t, 1H, *J* = 1.2 Hz), 7.22 (dd, 1H, *J* = 10.8, 15.0 Hz), 6.32 (dd, 1H, *J* = 10.8, 15.0 Hz), 6.23 (dt, 1H, *J* = 6.6, 15.0 Hz), 5.86 (d, 1H, *J* = 15.6 Hz), 4.13 (q, 2H, *J* = 7.2 Hz), 2.63 (td, 2H, *J* = 1.2, 7.2 Hz), 2.48 (q, 2H, *J* = 6.8 Hz), 1.23 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 202.7, 168.0, 146.2, 144.1, 130.8, 121.7, 61.4, 43.9, 26.9, 15.5; IR (neat) ν_{max} 2982, 2900, 2829, 1710, 1642, 1252, 1136 cm⁻¹; ESI–TOF HRMS *m/z* 183.1009 ([*M* + *H*]⁺, C₁₀H₁₄O₃ + *H*⁺ requires 183.1016).



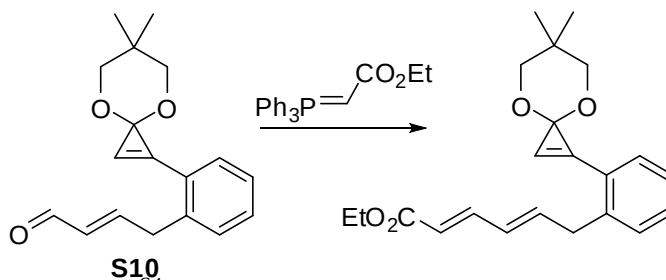
(16). Prepared from (2*E*)-6-*tert*-butyldimethylsilyloxyhex-2-enal^{S3} (80 mg, 0.35 mmol) and Ph₃P=CHCN (210 mg, 0.70 mmol) following the procedure detailed for ethyl (2*E*,4*E*)-8-hydroxyocta-2,4-dienoate.^{S3} Oxidation following the procedure detailed for **15** gave **16** (20 mg, 42% yield) as a colorless oil of a mixture of diastereomers (2:1, *E*:*Z*): For the major *E* isomer: ¹H NMR (acetone-*d*₆, 600 MHz) δ 9.74 (t, 1H, *J* = 1.2 Hz), 7.12 (dd, 1H, *J* = 10.2, 16.2 Hz), 6.35 (m, 1H), 6.26 (m, 1H), 5.57 (d, 1H, *J* = 15.6 Hz), 2.65 (m, 2H), 2.49 (m, 2H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 202.5, 152.3, 145.1, 130.7, 119.9, 99.2, 43.7, 26.8. For the minor *Z* isomer: ¹H NMR (acetone-*d*₆, 600 MHz) δ 9.77 (t, 1H, *J* = 1.2 Hz), 6.99 (t, 1H, *J* = 10.8 Hz), 6.54 (m, 1H), 6.35 (m, 1H), 5.38 (d, 1H, *J* = 10.8 Hz), 2.68 (m, 2H), 2.55 (m, 2H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 202.5, 151.1, 146.0, 129.0, 119.9, 97.5, 43.8, 26.9; IR (neat) ν_{max} 2897, 2832, 2726, 2213, 1720, 1640, 1390, 1157 cm⁻¹.



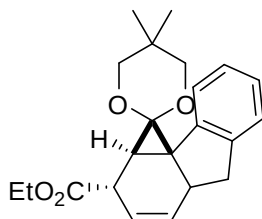
(17). Prepared from cyclopropenone ketal **10** (25 mg, 0.17 mmol) and **15** (23 mg, 0.12 mmol) following the procedure detailed for **13a** providing **17** (5.1 mg) as a colorless oil: ¹H NMR (C₆D₆, 600 MHz) δ 5.73–5.79 (m, 2H), 4.42 (s, 1H), 3.87 (q, 2H, *J* = 7.2 Hz), 3.38 (m, 1H), 3.32 (d, 1H, *J* = 10.2 Hz), 3.24–3.27 (m, 3H), 2.53 (m, 1H), 1.99 (m, 2H), 1.75 (m, 1H), 1.61–1.72 (m, 2H), 0.87–0.90 (m, 6H), 0.56 (s, 3H); ¹³C NMR (C₆D₆, 150 MHz) δ 173.9, 132.2, 121.0, 90.6, 76.2, 76.1, 72.1, 61.1, 39.8, 37.5, 35.8, 35.4, 30.7, 30.6, 23.8, 22.3, 21.7, 14.0; ESI–TOF HRMS *m/z* 345.1676 ([*M* + *Na*]⁺, C₁₈H₂₆O₅ + *Na*⁺ requires 345.1672).



(18). Prepared from cyclopropenone ketal **10** (30 mg, 0.21 mmol) and **16** (27 mg, 0.19 mmol) following the procedure detailed for **13a** providing **18** (3.5 mg) as a white solid: mp 104–105 °C; ^1H NMR (C_6D_6 , 600 MHz) δ 5.46 (dt, 1H, $J = 3.0, 10.2$ Hz), 5.30 (dt, 1H, $J = 3.0, 10.2$ Hz), 4.04 (d, 1H, $J = 4.8$ Hz), 3.07–3.10 (m, 3H), 2.98 (d, 1H, $J = 10.8$ Hz), 2.96 (m, 1H), 2.21 (m, 1H), 1.80 (d, 1H, $J = 2.4$ Hz), 1.52–1.59 (m, 3H), 1.37 (m, 1H), 1.01 (d, 1H, $J = 4.2$ Hz), 0.83 (s, 3H), 0.49 (s, 3H); ^{13}C NMR (C_6D_6 , 150 MHz) δ 132.9, 120.9, 119.0, 88.5, 75.8, 75.7, 71.6, 38.2, 34.7, 32.8, 30.4, 29.8, 22.0, 21.8, 21.5; IR (neat) ν_{max} 3494, 2920, 2852, 2244, 1737, 1461, 1242, 1118 cm^{-1} ; ESI–TOF HRMS m/z 298.1414 ($[\text{M} + \text{Na}]^+$, $\text{C}_{16}\text{H}_{21}\text{NO}_3 + \text{Na}^+$ requires 298.1414). The structure and stereochemistry of **18** (CCDC763497) were confirmed with a single-crystal X-ray structure determination conducted on a colorless white needle grown from EtOAc.

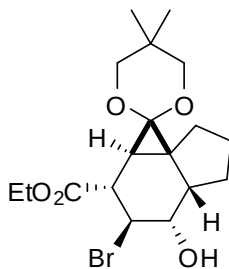


(19). A solution of enal **S10**^{S4} (17 mg, 0.06 mmol) in CH_2Cl_2 (3 mL) was treated with (carbethoxymethylene)triphenylphosphorane (42 mg, 0.12 mmol) for 8 h. The reaction mixture was concentrated and purified by flash chromatography (SiO_2 , 10–20% EtOAc–hexane gradient) to give **19** (15 mg, 70% yield) as a colorless oil of a mixture of rotamers (2:1): ^1H NMR (acetone- d_6 , 600 MHz) δ 8.17 (s, 0.66H), 8.16 (s, 0.33H), 7.72 (d, 0.33H, $J = 7.2$ Hz), 7.67 (m, 0.66H), 7.64 (dd, 0.33H, $J = 1.2, 7.2$ Hz), 7.41 (m, 1H), 7.34–7.38 (m, 1.66H), 7.26 (dd, 0.66H, $J = 10.8, 15.0$ Hz), 7.20 (d, 0.33H, $J = 16.2$ Hz), 7.05 (dt, 0.33H, $J = 6.6, 15.6$ Hz), 6.47 (m, 0.66H), 6.39 (m, 1H), 5.95 (dt, 0.33H, $J = 1.8, 15.6$ Hz), 5.85 (d, 0.66H, $J = 15.6$ Hz), 4.13 (m, 2H), 3.81 (m, 1.33H), 3.73 (d, 2H, $J = 10.8$ Hz), 3.64 (m, 2H), 3.23 (tt, 0.66H, $J = 1.5, 6.9$ Hz), 1.21–1.27 (m, 6H), 0.88 (s, 2H), 0.87 (s, 1H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 168.0, 167.4, 148.2, 146.2, 143.6, 141.5, 139.2, 133.58, 133.51, 132.5, 132.3, 132.2, 132.0, 131.7, 131.1, 130.3, 129.3, 128.7, 127.4, 126.8, 125.7, 123.9, 121.9, 119.8, 119.7, 84.1, 78.1, 78.0, 61.5, 61.4, 38.2, 37.1, 31.9, 24.0, 23.9, 22.9, 15.5; IR (neat) ν_{max} 2952, 2847, 1709, 1641, 1469, 1295, 1263 cm^{-1} ; ESI–TOF HRMS m/z 355.1908 ($[\text{M} + \text{H}]^+$, $\text{C}_{22}\text{H}_{26}\text{O}_4 + \text{H}^+$ requires 355.1904).

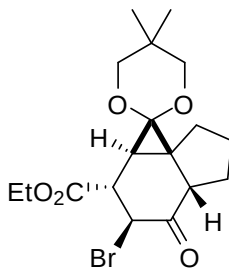


(20). A solution of **19** (15 mg, 0.04 mmol) in benzene (4.2 mL) was warmed at 80 °C for 12 h. The reaction mixture was concentrated and purified by flash chromatography

(SiO₂, 10% EtOAc–hexane) to give **20** (10.2 mg, 69% yield) as a clear oil: ¹H NMR (acetone-*d*₆, 600 MHz) δ 7.10–7.17 (m, 4H), 5.89 (dt, 1H, *J* = 3.0, 10.2 Hz), 5.77 (dt, 1H, *J* = 3.0, 10.2 Hz), 4.13 (q, 2H, *J* = 7.2 Hz), 3.56–3.65 (m, 3H), 3.50 (dd, 1H, *J* = 10.2, 16.2 Hz), 3.31 (d, 1H, *J* = 10.8 Hz), 3.21 (m, 1H), 3.01 (m, 1H), 2.77 (dd, 1H, *J* = 6.6, 16.2 Hz), 1.84 (d, 1H, *J* = 2.4 Hz), 1.22 (t, 3H, *J* = 7.2 Hz), 1.13 (s, 3H), 0.79 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 174.4, 145.2, 144.4, 133.9, 128.3, 127.9, 125.8, 124.0, 123.8, 91.9, 77.4, 77.2, 62.4, 40.1, 40.0, 37.9, 35.1, 32.4, 32.1, 23.4, 22.9, 15.4; IR (neat) $\nu_{\max}$ 2955, 2903, 2860, 1731, 1468, 1250, 1162 cm⁻¹; ESI–TOF HRMS *m/z* 355.1919 ([*M* + *H*]⁺, C₂₂H₂₆O₄ + *H*⁺ requires 355.1904).

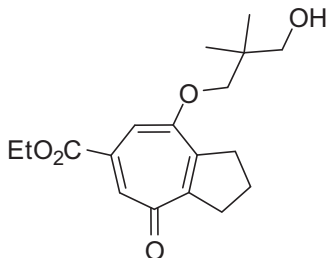


(21). A solution of cycloadduct **4b** (15 mg, 0.05 mmol) in THF:H₂O (9:1, 2 mL) was treated with *N*-bromosuccinimide (18 mg, 0.1 mmol) and the mixture was stirred at 25 °C for 14 h. Saturated Na₂S₂O₃ and NaHCO₃ were added and the mixture was allowed to stir for 5 min. The reaction mixture was extracted with EtOAc (2 × 2 mL), dried (Na₂SO₄), and concentrated under reduced pressure. Flash chromatography (SiO₂, 10–20% EtOAc–hexane gradient) gave **21** (16 mg, 80% yield) as a colorless oil: ¹H NMR (acetone-*d*₆, 500 MHz) δ 4.29 (dd, 1H, *J* = 4.0, 6.5 Hz), 4.26–4.13 (m, 3H), 4.02 (m, 1H), 3.63 (d, 1H, *J* = 10.5 Hz), 3.56 (s, 2H), 3.52 (d, 1H, *J* = 10.5 Hz), 3.11 (t, 1H, *J* = 4.0 Hz), 2.11 (m, 1H), 1.95 (m, 2H), 1.77 (m, 2H), 1.57 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz), 1.27 (s, 1H), 1.05 (s, 3H), 0.93 (s, 3H); ¹³C NMR (acetone-*d*₆, 150 MHz) δ 173.3, 91.1, 77.5, 77.4, 75.8, 62.4, 58.3, 44.2, 43.2, 36.3, 36.1, 33.5, 32.3, 29.8, 27.6, 23.4, 22.9, 15.5; IR (neat) $\nu_{\max}$ 3462, 2955, 2864, 1734, 1469, 1179 cm⁻¹; ESI–TOF HRMS *m/z* 425.0934 ([*M* + Na]⁺, C₁₈H₂₇BrO₅ + Na⁺ requires 425.0934).



(22). A solution of bromohydrin **21** (16 mg, 0.04 mmol) in CH₂Cl₂ (1.5 mL) was treated with pyridine (9.5 μL, 0.12 mmol) followed by Dess–Martin periodinane (51 mg, 0.12 mmol), and the mixture was allowed to stir at 25 °C for 16 h. Saturated Na₂S₂O₃ and saturated NaHCO₃ were added and the reaction mixture was allowed to stir until clear (15 min). The mixture was extracted with EtOAc (2 × 2 mL), dried (Na₂SO₄), and concentrated under reduced pressure. Flash chromatography (SiO₂, 20% EtOAc–hexane)

afforded **22** (13.5 mg, 85%) as a colorless oil: ^1H NMR (acetone- d_6 , 500 MHz) δ 4.57 (d, 1H, J = 3.0 Hz), 4.26 (m, 2H), 3.72 (d, 1H, J = 11.0 Hz), 3.61 (d, 1H, J = 10.5 Hz), 3.56 (s, 2H), 3.25 (dd, 1H, J = 2.7, 7.2 Hz), 2.62 (dd, 1H, J = 4.5, 9.0 Hz), 2.15 (m, 1H), 2.02 (m, 2H), 1.70 (m, 3H), 1.56 (d, 1H, J = 7.5 Hz), 1.31 (t, 3H, J = 7.2 Hz), 1.13 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (acetone- d_6 , 150 MHz) δ 205.8, 171.5, 92.1, 77.7, 77.5, 63.1, 51.2, 46.9, 44.1, 37.1, 32.7, 32.5, 32.3, 27.8, 27.7, 23.6, 22.9, 15.5; IR (neat) ν_{max} 2956, 2867, 1735, 1721, 1469, 1446, 1228 cm^{-1} ; ESI-TOF HRMS m/z 423.0777 ($[\text{M} + \text{Na}]^+$, $\text{C}_{18}\text{H}_{25}\text{BrO}_5 + \text{Na}^+$ requires 423.0777).



(**24**). A solution of **22** (12 mg, 0.03 mmol) in CH_2Cl_2 (2 mL) at 0 $^\circ\text{C}$ was treated with DBU (14 μL , 0.09 mmol) and the reaction mixture was stirred for 45 min at this temperature. The mixture was diluted with CH_2Cl_2 (1 mL), and organic layer was washed with saturated aqueous NaCl (1 mL), dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography (SiO_2 , 50% EtOAc–hexane) afforded **24** (8 mg, 83%) as a white solid: mp 81–82 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 600 MHz) δ 7.63 (s, 1H), 6.98 (s, 1H), 4.36 (q, 2H, J = 7.2 Hz), 3.82 (s, 2H), 3.55 (d, 2H, J = 6 Hz), 3.13 (t, 2H, J = 7.8 Hz), 3.08 (t, 2H, J = 7.8 Hz), 1.94 (quint, 2H, J = 7.8 Hz), 1.39 (t, 3H, J = 6.9 Hz), 1.05 (s, 6H). ^{13}C NMR (CDCl_3 , 150 MHz) δ 183.4, 176.6, 167.7, 160.7, 157.2, 155.2, 147.5, 135.6, 133.6, 106.7, 73.7, 68.8, 62.5, 36.6, 36.2, 36.1, 21.6, 20.1, 14.1; IR (neat) ν_{max} 3404, 2960, 2928, 2873, 1721, 1526, 1256 cm^{-1} ; ESI-TOF HRMS m/z 321.1697 ($[\text{M} + \text{H}]^+$, $\text{C}_{18}\text{H}_{24}\text{O}_5 + \text{H}^+$ requires 321.1696). The structure of **24** (CCDC763498) was confirmed with a single-crystal X-ray structure determination conducted on a colorless white needle grown from EtOAc.

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