SUPPORTING INFORMATION

Novel [2+2+2+1] Cycloaddition of Ene-diynes Catalyzed by Rhodium complexes

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General method and materials: Unless otherwise stated, all reactions were carried out under argon or carbon monoxide in oven-dried glassware using standard Schlenk techniques. Solvents were reagent grade and freshly distilled before use. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone under nitrogen. Toluene was distilled from sodium and dichloromethane from calcium hydride. Anhydrous *N,N*-dimethylformamide (DMF) was purchased from DrySolv[®] and used without further purification. Other solvents were used without purification. Carbon monoxide was purchased from Liquid Carbonic Specialty Gases, Oak Brook, Illinois and passed through Drierite[®] before use. All reactions were monitored by thin layer chromatography (TLC) using E. Merck 60F₂₅₄ precoated silica gel plates. Flash chromatography was performed with the indicated solvents and using Fisher silica gel (particle size 170-400 Mesh). Yields refer to chromatographically and spectroscopically pure compounds. Melting points were taken in a Thomas Hoover capillary melting point apparatus. Infrared spectra were recorded with Shimadzu FTIR-84005 spectrophotometer. ¹H-NMR spectra were recorded with a Varian Inova-400 (400 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform ($\delta = 7.26$ ppm). ¹³C-NMR spectra were recorded with a Varian Inova-400 (100 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform ($\delta = 77.0$ ppm). High and low resolution mass spectra were carried out by the Mass Spectroscopy Service at the University of Illinois. **Caution:** Since carbon monoxide is a toxic gas, all reactions should be carried out in a hood with sufficient ventilation.

4,4,9,9-Tetra(carbethoxy)tridec-1-ene-6,11-diyne (3): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.29); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (m, 12 H), 1.74 (t, 3 H, *J* = 3.2 Hz), 2.73-2.76 (m, 4 H), 2.86-2.88 (m, 2 H), 2.90-2.92 (m, 2 H), 4.19 (m, 8 H), 5.08-5.21 (m, 2 H), 5.53-5.67 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.3, 13.9, 13.9, 22.6, 22.6, 36.2, 56.6, 56.7, 61.4, 61.6, 73.1, 77.5, 77.6, 77.7, 119.4, 131.9, 168.9, 169.6; IR (neat, cm⁻¹) 2982 (s), 1738 (s), 1326 (m), 1290 (m), 1210 (m). HRMS (EI) *m/z* calcd for C₂₅H₃₄O₈ (M⁺) 462.2254, found 462.2252 (Δ = -0.4 ppm).

9,9-Bis(carbethoxy)-4-oxatridec-1-ene-6,11-diyne (6): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.45); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, 6 H, *J* = 7.2 Hz), 1.74 (t, 3 H, *J* = 2.6 Hz), 2.89 (m, 2 H), 3.00 (m, 2 H), 4.01 (dt, 2 H, *J* = 1.4 Hz / *J* = 5.6 Hz), 4.10 (t, 2 H, *J* = 2.2 Hz), 4.20 (q, 4 H, *J* = 7.2 Hz), 5.20 (m, 1 H), 5.31 (m, 1 H), 5.89 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.5, 14.0, 22.9, 23.0, 56.7, 57.4, 61.8, 70.2, 73.1, 79.0, 79.1, 81.2, 117.7, 134.1, 169.0; IR (neat, cm⁻¹) 2982 (w), 1738 (s), 1307(w), 1290 (m), 1209 (m), 1193 (m), 1151 (w), 1124 (w), 1070 (m), 1063 (m), 440 (s). HRMS (EI) *m/z* calcd for C₁₈H₂₅O₅ (M+H)⁺ 321.1702, found 321.1704 (Δ = 0.6 ppm).

4,9-Bis(4-methylbenzenesulfonyl)-4,9-diazatridec-1-ene-6,11-diyne (7): Yellow oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.41); ¹H NMR (400 MHz, CDCl₃) δ 1.61 (t, 3 H, *J* = 2.4 Hz), 2.42 (s, 3 H), 2.45 (s, 3 H), 3.71 (d, 2 H, *J* = 6.0 Hz), 3.83 (m, 2 H), 3.87 (s, 2 H), 3.97 (s, 2 H), 5.20 (m, 2 H), 5.67 (m, 1 H), 7.28 (d, 2 H, *J* = 8.0 Hz), 7.32 (d, 2 H, *J* = 8.0 Hz), 7.62 (d, 2 H, *J* = 8.0 Hz), 7.69 (d, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 3.3, 21.5, 21.6, 35.9, 36.1, 36.5, 49.1, 71.2, 78.2, 78.4, 81.8, 119.8, 127.6, 127.8, 129.4, 129.5, 132.0, 135.4, 136.0, 143.6, 143.7; IR (neat, cm⁻¹) 2920 (m), 2256 (w), 1597 (s), 1493 (m), 1439 (s), 1350 (s), 1331 (s), 1161 (s), 1092 (s), 903 (s), 802 (s), 748 (s), 663 (s), 450 (s). HRMS (EI) *m/z* calcd for C₂₅H₂₈N₂O₄S₂ (M)⁺ 484.1491, found 484.1492 (Δ = 0.2 ppm).

9,9-Bis(carbethoxy)-4-(carbo-*tert*-butoxy)-4-azatridec-1-ene-6,11-diyne (8): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.54); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, 6 H, *J* = 7.2 Hz), 1.45 (s, 9 H), 1.74 (t, 3 H, *J* = 2.6 Hz), 2.88 (m, 2 H), 2.95 (m, 2 H), 3.89 (m, 4 H), 4.20 (q, 4 H, *J* = 7.2 Hz), 5.14 (m, 2 H), 5.74 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.4, 14.0, 22.8, 22.9, 28.3, 28.4, 48.2, 56.7, 61.7, 73.1, 78.9, 79.0, 80.1, 115.7, 133.5, 154.8, 169.0; IR (neat, cm⁻¹) 2978 (s), 2932 (s), 1739 (s), 1697 (s), 1643

(w), 1506 (m), 1477 (m), 1456 (s), 1427 (m), 1406 (s), 1392 (m), 1365 (s), 1325 (m), 1288 (s), 1246 (s), 1209 (s), 1192 (s), 1173 (s), 1147 (s), 1095 (m), 1070 (s), 1053 (s), 997 (m), 916 (m), 882 (s), 439 (s). HRMS (EI) m/z calcd for $C_{23}H_{32}NO_6$ (M-H)⁻ 418.2229, found 418.2222 (Δ = -1.7 ppm).

4,4,9,9-Tetra(methoxymethyl)tridec-1-ene-6,11-diyne (9): Light yellow oil; TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.60); ¹H NMR (400 MHz, CDCl₃) δ 1.79 (t, 3 H, J = 2.4 Hz), 2.15 (m, 2 H), 2.16 (m, 2 H), 2.25 (q, 2 H, J = 2.4 Hz), 2.29 (t, 2 H, J = 2.4 Hz), 3.24 (m, 4 H), 3.32 (s, 6 H), 3.33 (m, 4 H), 3.34 (s, 6 H), 5.08 (m, 2 H), 5.81 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.6, 22.2, 22.3, 22.4, 36.3, 42.0, 42.2, 52.3, 59.4, 74.1, 74.5, 75.3, 77.4, 78.3, 78.6, 117.8, 134.0; IR (neat, cm⁻¹) 2980 (w), 2920 (m), 2887 (m), 2808 (m), 1448 (w), 1197 (m), 1109 (s), 968 (w), 916 (w), 445 (s). HRMS (EI) m/z calcd for $C_{21}H_{34}O_4$ (M)⁺ 350.2457, found 350.2460 (Δ = 0.8 ppm).

4,4,9,9-Tetra(benzyloxymethyl)tridec-1-ene-6,11-diyne (10): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.54); ¹H NMR (400 MHz, CDCl₃) δ 1.74 (t, 3 H, J = 2.4 Hz), 2.20 (m, 2 H), 2.23 (m, 2 H), 2.32 (q, 2 H, J = 2.4 Hz), 2.36 (t, 2 H, J = 2.4 Hz), 3.36 (s, 2 H), 3.37 (s, 2 H), 3.47 (s, 4 H), 4.47 (s, 4 H), 4.48 (s, 4 H), 5.03 (m, 2 H), 5.77 (m, 1 H), 7.30 (m, 20 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.5, 22.4, 22.5, 36.4, 42.3, 42.5, 71.7, 72.1, 73.2, 73.3, 75.4, 77.4, 78.5, 78.7, 117.9, 127.3, 128.21, 128.23, 134.1, 138.8, 138.9; IR (neat, cm⁻¹) 3063 (w), 2905 (m), 2858 (s), 1497 (m), 1452 (s), 1363 (s), 1205 (m), 1097 (s), 1027 (m), 914 (w), 735 (s), 696 (s), 445 (s). HRMS (EI) m/z calcd for $C_{45}H_{50}O_4$ (M)⁺ 654.3709, found 654.3708 (Δ = -0.1 ppm).

4,4,9,9-Tetra(acetoxymethyl)tridec-1-ene-6,11-diyne (11): Colorless oil; TLC (SiO₂, EtOAc:hexanes 1:4, R_f = 0.18); ¹H NMR (400 MHz, CDCl₃) δ 1.77 (t, 3 H, J = 2.4 Hz), 2.06 (s, 12 H), 2.19 (m, 2 H), 2.23 (m, 2 H), 2.30 (q, 2 H, J = 2.4 Hz), 2.35 (t, 2 H, J = 2.4 Hz), 3.98 (s, 4 H), 4.06 (s, 4 H), 5.12 (m, 2 H), 5.75 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.5, 20.8, 22.4, 22.5, 36.1, 40.2, 40.3, 65.3, 65.5, 73.4, 77.3, 77.9, 78.1, 78.8, 119.4, 132.1, 170.6, 170.7; IR (neat, cm⁻¹) 3076 (w), 2955 (m), 2920 (m), 2850 (w), 2359 (w), 2341 (w), 1740 (s), 1640 (w), 1468 (m), 1433 (m), 1383 (s), 1365 (s), 1234 (s), 1041 (s), 1000 (w), 985 (w), 445 (s). HRMS (EI) m/z calcd for $C_{25}H_{35}O_8$ (M+H)⁺ 463.2331, found 463.2327 (Δ = -0.8 ppm).

4,9-Bis(4,4-dimethyl-3,5-dioxanyl)tridec-1-ene-6,11-diyne (12): Light yellow oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.18); ¹H NMR (400 MHz, CDCl₃) δ 1.40 (s, 6 H), 1.41 (s, 6 H), 1.79 (t, 3 H, *J* = 2.4 Hz), 2.17 (m, 2 H), 2.35 (m, 4 H), 2.36 (m, 2 H), 3.64 (s, 4 H), 3.73 (s, 4 H), 5.13 (m, 2 H), 5.75 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.5, 22.0, 22.7, 23.2, 23.4, 24.1, 25.5, 35.5, 35.6, 37.1, 66.2, 66.8, 74.5, 78.3, 78.5, 79.1, 98.0, 98.1, 118.8, 132.5; IR (neat, cm⁻¹) 3074 (w), 2991 (m), 2939 (m), 2860 (m), 1639 (w), 1477 (w), 1452 (s), 1371 (s), 1257 (m), 1226 (m), 1198 (s), 1155 (m), 1117 (m), 1068 (s), 1037 (m), 919 (w), 829 (s), 445 (s). HRMS (EI) *m/z* calcd for C₂₃H₃₄O₄ (M)⁺ 374.2457, found 374.2461 (Δ = 1.0 ppm).

4,4,9,9-Tetra(carbethoxy)-1-trimethylsilyl-dodec-11-ene-1,6-diyne (13): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.62); ¹H NMR (400 MHz, CDCl₃) δ 0.11 (s, 9 H), 1.24 (t, 6 H, *J* = 7.2 Hz), 1.25 (t, 6 H, *J* = 7.2 Hz), 2.73 (m, 4 H), 2.91 (m, 2 H), 2.95 (s, 2 H), 4.19 (m, 8 H), 5.10 (m, 1 H), 5.17 (m, 1 H), 5.60 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ -0.1, 14.0, 14.1, 22.7, 22.8, 23.8, 36.3, 56.6, 56.8, 61.5, 61.8, 77.6, 77.9, 88.1, 101.1, 119.6, 132.0, 168.7, 169.8; IR (neat, cm⁻¹) 2982 (w), 2963 (w), 1738 (s), 1444 (w), 1425 (w), 1367 (m), 1325 (w), 1288 (m), 1249 (m), 1209 (s), 1192 (s), 1138 (w), 1070 (w), 1055 (w), 1032 (m), 845 (s), 759 (w), 425 (s). HRMS (EI) *m/z* calcd for C₂₇H₄₀O₈Si (M)⁺ 520.2492, found 520.2498 (Δ = 1.1 ppm).

General procedure for the [2+2+2+1] cycloaddition reaction: A typical procedure is described for the reaction of enediyne **3**. All other reactions are run following the same procedure unless otherwise noted. Enediyne **3** (100 mg, 0.216 mmol) was introduced to a Schlenck tube, followed by Cl(CH₂)₂Cl (2.16 mL) under argon, and then CO was bubbled into the solution at room temperature. After 15 min, [Rh(COD)Cl]₂ (5.3 mg, 0.0108 mmol, 5 mol%) was added under CO and the resulting mixture was stirred at room temperature for an additional 5 min. Then, the reaction mixture was heated to 50 °C with stirring and kept for 16 h under CO (ambient pressure, bubbled into the solution). All volatiles were removed from the reaction mixture under reduced pressure and the crude product purified by flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 3:7) affording **3a** as a light yellow oil in 92.5% yield by ¹H-NMR (93 mg, 88 % isolated yield) and **3b** as a colorless oil in 5.5% yield by ¹H-NMR (< 4 mg, <4 % isolated yield).

6-Methyl-2,2,8,8-tetra(carbethoxy)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (3a): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.30); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (m, 12 H), 1.90 (s, 3 H), 1.96 (m, 1 H), 2.61-3.20 (m, 10 H), 4.22 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 15.8, 37.4, 39.9, 40.3, 40.9, 42.4, 45.7, 56.9, 59.1, 61.7, 129.7, 130.8, 147.3, 149.5, 170.7, 170.8, 170.9, 171.0, 197.3; IR (neat, cm⁻¹) 2910 (s), 1731 (s), 1644 (s), 1367 (m), 1289 (m), 1068 (m). HRMS (EI) m/z calcd for C₂₆H₃₄O₉ (M⁺) 490.2203, found 490.2205 (Δ = 0.4 ppm).

5-Methyl-2,2,7,7-tetra(carbethoxy)-1,3,3a,4,6,8-hexahydro-*as*-indacene (3b): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.56); ¹H NMR (400 MHz, CDCl₃) δ 1.22 (m, 12 H), 1.70 (s, 3 H), 1.82 (m, 1 H), 1.84 (m, 1 H), 2.13 (m, 1 H), 2.60-3.07 (m, 8 H), 4.18 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 19.4, 35.9, 36.1, 36.7, 36.8, 39.7, 41.3, 59.4, 59.7, 61.4, 123.5, 128.2, 128.9, 131.1, 171.6, 171.7, 171.9. HRMS (EI) m/z calcd for C₂₅H₃₅O₈ (MH⁺) 463.2332, found 463.2325 (Δ = -1.5 ppm).

8,8-Bis(carbethoxy)-6-methyl-5-oxo-1,3a,4,5,7,9-hexahydro-3H-2-oxacyclopenta[*e*]azulene (6a): Light yellow oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.15); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (m, 6 H), 1.93 (s, 3 H), 2.55-2.68 (m, 2 H), 2.91-3.02 (m, 3 H), 3.21 (m, 2 H), 3.45 (t, 1 H, *J* = 9.2 Hz), 4.21 (m, 4 H), 4.27 (t, 1 H, *J* = 8.2 Hz), 4.40 (d, 1 H, *J* = 15.6 Hz), 4.52 (d, 1 H, *J* = 15.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 16.1, 38.6, 39.4, 42.0, 42.4, 57.2, 61.9, 62.0, 71.4, 74.6, 127.1, 131.6, 146.9, 149.2, 170.7, 170.8, 196.7; IR (CDCl₃, cm⁻¹) 2983 (m), 1728 (s), 1643 (s), 1367 (m), 1300 (m), 1261 (s), 1194 (s), 1165 (m), 1117 (w), 1097 (w), 1053 (s), 738 (s). HRMS (ESI) m/z calcd for C₁₉H₂₄O₆Na (M+Na)⁺ 371.1471, found 371.1471; m/z calcd for C₁₉H₂₅O₆ (M+H)⁺ 349.1651, found 349.1650 (Δ = -0.2 ppm).

2,8-Bis(4-methylbenzenesulfonyl)-6-methyl-2,8-diaza-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (7a): White solid; m. p. 168-170 °C; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.13); ¹H NMR (400 MHz, CDCl₃) δ 1.80 (s, 3 H), 2.44 (s, 3 H), 2.45 (m, 1 H), 2.46 (s, 3 H), 2.50 (m, 1 H), 2.61 (t, 1 H, *J* = 9.8 Hz), 2.96 (br, 1 H), 3.55 (d, 1 H, *J* = 16.4 Hz), 3.80-4.04 (m, 5 H), 4.16 (d, 1 H, *J* = 16.0 Hz), 7.34 (d, 2 H, *J* = 8.0 Hz), 7.38 (d, 2 H, *J* = 8.0 Hz), 7.71 (d, 4 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 15.6, 21.5, 21.6, 37.9, 42.5, 51.9, 52.1, 53.8, 54.1, 126.5, 127.8, 127.9, 130.0,

131.6, 131.8, 132.3, 142.4, 143.8, 144.4, 195.3; IR (CDCl₃, cm⁻¹) 2910 (w), 1662 (s), 1649 (m), 1598 (w), 1345 (s), 1165 (s), 1335 (w), 1100 (w), 1038 (w), 910 (w), 825 (m), 815 (m), 732 (w), 450 (s). HRMS (EI) m/z calcd for C₂₆H₂₈N₂O₅S₂ (M)⁺ 512.1440, found 512.1438 (Δ = -0.4 ppm).

2,7-Bis(4-methylbenzenesulfonyl)-5-methyl-2,7-diaza-1,3a,4,5,7,9-hexahydro-*as*-indacene (7b): White solid; m. p. 248-250 °C; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.30); ¹H NMR (400 MHz, CDCl₃) δ 1.63 (s, 3 H), 1.78 (t, 1 H, *J* = 17.2 Hz), 2.10 (dd, 1 H, *J* = 8.8 Hz / 16.8 Hz), 2.41 (s, 3 H), 2.44 (s, 3 H), 2.59 (t, 1 H, *J* = 9.8 Hz), 2.88 (br, 1 H), 3.58 (d, 1 H, *J* = 15.6 Hz), 3.72-4.01 (m, 6 H), 7.29 (d, 2 H, *J* = 8.0 Hz), 7.33 (d, 2 H, *J* = 8.0 Hz), 7.68 (d, 2 H, *J* = 8.0 Hz), 7.69 (d, 2 H, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.4, 21.5, 32.8, 39.3, 48.8, 49.7, 49.9, 54.6, 124.6, 124.7, 125.4, 127.6, 127.7, 129.7, 129.8, 132.8, 132.9, 143.7, 143.8; IR (CDCl₃, cm⁻¹) 2900 (w), 1660 (w), 1345 (m), 1165 (s), 1100 (m), 1038 (w), 910 (w), 825 (m), 815 (m), 732 (w), 450 (s). HRMS (EI) m/z calcd for C₂₅H₂₈N₂O₄S₂ (M)⁺ 484.1490, found 484.1487 (Δ = -0.6 ppm).

8,8-Bis(carbethoxy)-6-methyl-2-(carbo-*tert*-butoxy)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-azuleno[4,5-*c*]pyrrole (8a): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.12); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (m, 6 H), 1.47 (s, 9 H), 1.92 (s, 3 H), 2.60 (m, 1 H), 2.74 (m, 1 H), 2.95-3.22 (m, 6 H), 4.05-4.24 (m, 7 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 16.0, 28.4, 39.8, 42.4, 44.2, 51.0, 57.0, 62.0, 80.0, 129.2, 131.5, 144.7, 148.7, 154.0, 170.7, 170.9, 197.0; IR (CDCl₃, cm⁻¹) 2982 (s), 1728 (s), 1693 (s), 1643 (s), 1412 (s), 1369 (s), 1261 (s), 1199 (s), 1165 (s), 895 (m), 451 (s). HRMS (ESI) m/z calcd for C₂₄H₃₃NO₇Na (M+Na)⁺ 470.2155, found 470.2150 (Δ = -1.1 ppm).

6-Methyl-2,2,8,8-tetra(methoxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (9a): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.20); ¹H NMR (400 MHz, CDCl₃) δ 1.38 (dd, 1 H, *J* = 11.2 Hz / *J* = 12.8 Hz), 1.86 (s, 3 H), 2.00 (m, 1 H), 2.22-2.64 (m, 8 H), 2.81 (m, 1 H), 3.16 (m, 1 H), 3.24 (m, 3 H), 3.30-3.36 (m, 16 H); ¹³C NMR (100 MHz, CDCl₃) δ 15.9, 37.2, 38.5, 39.0, 39.2, 41.6, 44.5, 46.8, 47.0, 59.3, 74.8, 75.6, 75.8, 76.8, 130.2, 131.6, 150.9, 153.3, 198.6; IR (neat, cm⁻¹) 3302 (m), 2978 (s), 2924 (s), 2877 (s), 2823 (s), 2804 (s), 2742 (w), 2361 (w), 1643 (s), 1581 (m), 1477 (s), 1458 (s), 1423 (m), 1389 (m), 1335 (m), 1308 (m), 1199 (s), 1165 (s), 1103 (s), 960 (s), 470 (s). HRMS (ESI) m/z calcd for C₂₂H₃₄O₅Na (M+Na)⁺ 401.2304, found 401.2305 (Δ = 0.2 ppm).

6-Methyl-2,2,8,8-tetra(benzyloxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (10a): Light yellow oil; TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.16); ¹H NMR (400 MHz, CDCl₃) δ 1.37 (dd, 1 H, *J* = 11.2 Hz / *J* = 12.8 Hz), 1.86 (s, 3 H), 2.08 (dd, 1 H, *J* = 7.6 Hz / *J* = 12.8 Hz), 2.26-2.61 (m, 8 H), 2.78 (br, 1 H), 3.26 (d, 1 H, *J* = 8.8 Hz), 3.32 (d, 1 H, *J* = 8.8 Hz), 3.37 (s, 2 H), 3.38 (s, 2 H), 3.42 (d, 1 H, *J* = 8.8 Hz), 3.49 (d, 1 H, *J* = 8.8 Hz), 4.44 (m, 2 H), 4.48 (s, 2 H), 4.50 (s, 2 H), 4.51 (s, 2 H), 7.24-7.34 (m, 20 H); ¹³C NMR (100 MHz, CDCl₃) δ 15.9, 31.1, 38.8, 39.2, 39.6, 41.8, 44.7, 46.7, 47.1, 72.1, 73.0, 73.2, 73.24, 73.3, 73.33, 74.4, 127.3, 127.4, 127.5, 128.3, 130.1, 131.5, 138.5, 138.6, 138.7, 150.9, 153.4, 198.6; IR (neat, cm⁻¹) 3086 (w), 3028 (m), 2854 (s), 2789 (w), 2361 (w), 2341 (w), 1635 (s), 1581 (m), 1497 (s), 1457 (s), 1423 (m), 1362 (s), 1308 (m), 1242 (m), 1203 (m), 1099 (s), 1072 (s), 1026 (w), 737 (s), 698 (s), 463 (s). HRMS (ESI) *m/z* calcd for C₄₆H₅₁O₅ (M+H)⁺ 683.3737, found 683.3743 (Δ = 0.8 ppm).

6-Methyl-2,2,8,8-tetra(acetoxymethyl)- 5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (11a): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 2:3, R_f = 0.20); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (m, 1 H), 1.39-1.45 (m, 1 H), 1.61 (br, 1 H), 1.88 (s, 3 H), 2.04-2.09 (m, 13 H), 2.59 (m, 3 H), 2.27-2.44 (m, 3 H), 2.88 (br, 1 H), 3.89-4.14 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 16.1, 20.7, 20.8, 36.8, 38.6, 38.8, 39.2, 41.2, 42.7, 45.2, 46.4, 64.3, 66.3, 66.5, 67.4, 131.1, 131.4, 149.1, 150.6, 170.7, 170.8, 170.9, 171.0, 197.6; IR (neat, cm⁻¹) 3456 (w), 2951 (m), 2893 (m), 2361 (w), 1740 (s), 1643 (s), 1585 (m), 1466 (m), 1427 (m), 1365 (s), 1242 (s), 1041 (s), 984 (w), 910 (w), 845 (w), 478 (s). HRMS (ESI) *m/z* calcd for C₂₆H₃₄O₉Na (M+Na)⁺ 513.2101, found 513.2100 (Δ = -0.2 ppm).

6-Methyl-2,2,8,8-tetra(4,4-dimethyl-3,5-dioxanyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (12a): Colorless gum; TLC (SiO₂, EtOAc:hexanes = 2:3, R_f = 0.38); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (dd, 1 H, *J* = 11.2 Hz / *J* = 12.8 Hz), 1.42 (s, 3 H), 1.43 (s, 3 H), 1.44 (s, 6 H), 1.89 (s, 3 H), 2.10 (ddd, 1 H, *J* = 1.6 Hz / *J* = 7.6 Hz / *J* = 12.8 Hz), 2.30-2.63 (m, 8 H), 2.77 (br, 1 H), 3.50 (dd, 1 H, *J* = 0.8 Hz / *J* = 11.6 Hz), 3.64 (m, 6 H), 3.74 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 16.0, 22.6, 23.7, 23.8, 24.9, 36.8, 38.3, 39.9, 40.2, 40.6, 41.1, 42.7, 46.6, 67.3, 68.4, 68.5, 69.2, 98.0, 98.1, 131.0, 131.4, 149.8, 151.6, 198.1; IR (neat, cm⁻¹) 2989 (s), 2939 (s), 2858 (s), 1643 (s), 1581 (s), 1454 (s), 1423 (s), 1385 (s), 1369 (s), 1315 (s), 1242 (s), 1199 (s), 1157 (s), 1095 (s), 1064 (s), 1034 (s), 933 (s), 833 (s), 733 (s), 451 (s). HRMS (ESI) *m/z* calcd for C₂₄H₃₅O₅ (M+H)⁺ 403.2484, found 403.2488 (Δ = 1.0 ppm).

2,2,8,8-Tetra(carbethoxy)-6-trimethylsilanyl-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (13a): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.23); ¹H NMR (400 MHz, CDCl₃) δ 0.21 (s, 9 H), 1.25 (m, 12 H), 1.91 (m, 1 H), 2.53-2.72 (m, 3 H), 2.96-3.17 (m, 7 H), 4.20 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 1.1, 13.96, 14.0, 39.1, 39.2, 40.5, 40.9, 43.4, 46.6, 57.6, 59.2, 61.79, 61.8, 61.9, 130.9, 138.7, 147.6, 155.5, 170.7, 170.88, 170.9, 171.0, 203.8; IR (neat, cm⁻¹) 2984 (m), 1728 (s), 1649 (m), 1445 (m), 1367 (s), 1250 (s), 1192 (s), 1163 (m), 1097 (w), 1067 (w), 1021 (w), 847 (s). HRMS (EI) m/z calcd for C₂₈H₄₀O₉Si (M)⁺ 548.2442, found 548.2446 (Δ = 0.7 ppm).