SUPPORTING INFORMATION

Silicon-Initiated Carbonylative Carbotricyclization and [2+2+2+1] Cycloaddition of Enediynes 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. 4,9-Dioxa-dodeca-1-ene-6,11-diyne (**5a**) was synthesized according to the literature procedure.¹ Rh(acac)(CO)₂, was provided by Mitsubishi Chemical Corporation and used as received. [Rh(COD)Cl]₂ was prepared by the literature method.² 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

¹ Griggs, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. I* **1988**, 1365-1369.

² Giordano, G.; Grabtree, R. H. *Inorganic Synthesis* **1990**, 28, 88-90.

(particle size 170-400 Mesh). Yields refer to chromatographically and spectroscopically pure compounds. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded with Shimadzu FTIR-84005 spectrophotometer. ^1H NMR spectra were recorded with a Varian Inova-400 (400 MHz) or a Gemini-300 (300 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform ($\delta = 7.26$ ppm). ^{13}C NMR spectra were recorded with a Varian Inova-400 (100 MHz) or a Gemini-300 (75 MHz) at ambient temperature using an internal deuterium lock. Chemical shifts are referenced to residual chloroform ($\delta = 77.0$ ppm). High-resolution mass spectrometry (HRMS) was carried out at the Mass Spectrometry 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.

CO-SiCaT Substrates:

4,4,9,9-Tetra(carbethoxy)dodec-11-ene-1,6-diyne (**5a**):

Diethyl propargylmalonate³ (**27**, 16.62 g, 83.9 mmol) in THF (50 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 3.86 g, 96.5 mmol) in THF (100 mL) under N₂, and the mixture was stirred at room temperature for 1 h. The reaction mixture was cannulated into a solution of 1,4-dibromo-2-butyne⁴ (53.3 g, 251.6 mmol) in THF (200 mL), and the resulting mixture was stirred at room temperature for 2 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with Et₂O. The combined organic extracts were washed

³ Khan, A. M. *J. Chem. Res. Miniprint* **1991**, 3, 601.

⁴ Johnson, A. W. *J. Chem. Soc.* **1946**, 1009-1014.

with water and brine, dried over Na_2SO_4 , filtered and concentrated. Excess 1,4-dibromo-2-butyne was recovered by distillation in *vacuo*. The remaining dark oil was purified by flash chromatography on silica gel using hexanes:EtOAc (11:1) as eluent to give 5,5-bis(carbethoxy)-1-bromoocta-2,7-diyne (**28**, 20.78 g, 79%) as a viscous colorless oil⁵: TLC (SiO_2 , hexanes:EtOAc = 5:1, R_f = 0.43); ^1H NMR (300 MHz, CDCl_3) δ 1.27 (t, 6 H, J = 7.1 Hz), 2.03 (t, 1 H, J = 2.7 Hz), 2.97 (d, 2 H, J = 2.7 Hz), 3.05 (t, 2 H, J = 2.2 Hz), 3.87 (t, 2 H, J = 2.5 Hz), 4.24 (q, 4 H, J = 7.1 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 14.6, 22.7, 23.0, 56.4, 62.2, 71.9, 78.5, 78.6, 82.00, 168.8.

Diethyl allylmalonate (**29**, 10.54 g, 50.0 mmol) in THF (50 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 2.4 g, 60.0 mmol, 1.2 eq.) in THF (100 mL) under N_2 , and the mixture was stirred at room temperature for 1 h. Bromooctadiyne **28** (15.76 g, 50.0 mmol) in THF (25 mL) was added dropwise *via* an addition funnel, and the mixture was stirred at room temperature for 3 h. Water was added to quench the reaction, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexanes:EtOAc (10:1) as eluent to give **5a** (19.12 g, 85%) as a viscous colorless oil: TLC (SiO_2 , hexanes:EtOAc = 5:1, R_f = 0.30); ^1H NMR (300 MHz, CDCl_3) δ 1.24 (t, 6 H, J = 7.2 Hz), 1.25 (t, 6 H, J = 7.2 Hz), 1.99 (t, 1 H, J = 2.4 Hz), 2.74 (d, 2 H, J = 2.4 Hz), 2.75 (d, 2 H, J = 7.8 Hz), 2.93 (d, 2 H, J = 2.4 Hz), 2.94 (d, 2 H, J = 2.4 Hz), 4.21 (q, 4 H, J = 7.2 Hz), 4.23 (q, 4 H, J = 7.2 Hz), 5.12 (dd, 1 H, J = 2.1 Hz / J = 15.9 Hz), 5.12 (dd, 1 H, J = 2.1 Hz / J = 22.8 Hz), 5.60 (ddt, 1 H, J = 15.9 Hz / J = 22.8 Hz / J = 7.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9 (2C), 13.93 (2C), 22.3, 22.6 (2C), 36.2, 56.3, 56.7, 61.5 (2C), 61.9 (2C), 71.4, 78.1 (2C), 78.7, 119.7, 132.0, 168.9 (2C), 169.9 (2C); IR (neat, cm^{-1}) 3282 (m), 2983 (m), 2937 (w), 2908 (w), 1737 (s), 1465 (m), 1446 (m), 1429 (m), 1390 (w), 1367 (m), 1325 (m), 1290 (s), 1244 (m), 1211 (s), 1194 (s), 1139 (m), 1096 (m), 1071 (m), 1055 (m), 1014 (m), 926 (w), 858 (w), 648 (w). HRMS (DCI) m/z calcd for $\text{C}_{24}\text{H}_{33}\text{O}_8$ ($M + 1$)⁺ 449.2175, found 449.2180 (Δ = 1.1 ppm).

⁵ Grigg, R.; Loganathan, V.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakun, T. *Tetrahedron* **1996**, *52*, 11479-11502.

9,9-Bis(carbethoxy)-4-oxadodec-11-ene-1,6-diyne (5c):

Allylmalonate **29** (0.63 mL, 3.21 mmol) in THF (3 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 147 mg, 3.69 mmol) in THF (6 mL) at room temperature under N₂, and the mixture was stirred at room temperature for 1 h. 1-Bromo-5-oxaocta-2,7-diyne¹ (**30**, 600 mg, 3.21 mmol) in THF (2 mL) was added dropwise, and the mixture was stirred at room temperature for 2 h. Water was added to quench the reaction, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexane:EtOAc (8:1) as eluent to give **5c** (860 mg, 88%) as a colorless oil: TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.37); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, 6 H, *J* = 7.2 Hz), 2.42 (t, 1 H, *J* = 2.2 Hz), 2.70-2.90 (m, 4 H), 4.15-4.30 (m, 8 H), 5.05-5.23 (m, 2 H), 5.50-5.74 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.8, 36.4, 55.9, 56.5, 61.5, 61.6, 74.7, 78.0, 78.8, 81.9, 119.6, 131.6, 169.5; IR (neat, cm⁻¹) 3282 (w), 3080 (w), 2985 (m), 1733 (s), 1639 (w), 1465 (w), 1445 (m), 1366 (m), 1245 (s), 1195 (s), 1130 (m), 1074 (s), 447 (s). HRMS (EI) *m/z* calcd for C₁₇H₂₂O₅ (M)⁺ 306.1466, found 306.1467 (Δ = 0.3 ppm).

4,9-Bis(4-methylbenzenesulfonyl)-4,9-diazadodec-11-ene-1,6-diyne (5d):

¹ Griggs, R.; Scott, R.; Stevenson, P. J. *Chem. Soc., Perkin Trans. I* **1988**, 1365-1369.

N-Propargyl-4-methylbenzenesulfonamide⁶ (**31**, 8.6 g, 41.0 mmol) in DMF (50 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 2.30 g, 57.4 mmol) in DMF (200 mL) under N₂ and the mixture was stirred at room temperature for 1 h. The reaction mixture was added to a solution of 1,4-dibromo-2-butyne⁴ (26.10g, 123.0 mmol) in DMF (20 mL) via cannula, and the resulting mixture was stirred at room temperature for 1 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with EtOAc (500 mL). The combined organic extracts were washed with water, brine, dried over Na₂SO₄, filtered and concentrated. Excess 1,4-dibromo-2-butyne was recovered by distillation in *vacuo*. The remaining dark oil was purified by flash chromatography on silica gel using hexanes:EtOAc (10:1) as eluent to give 5-(4-methylbenzenesulfonyl)-1-bromo-5-azaocta-2,7-diyne (**32**) as a viscous yellow oil (8.01g, 57%): ¹H NMR (300 MHz, CDCl₃) δ 2.16 (t, 1 H, *J* = 2.4 Hz), 2.43 (s, 3 H), 3.70 (t, 2 H, *J* = 2.4 Hz), 4.11 (s, 1 H), 4.12 (s, 1 H), 4.22 (s, 2 H), 7.31 (d, 2 H, *J* = 9.0 Hz), 7.71 (d, 2 H, *J* = 9.0 Hz).

N-Allyl-4-methylbenzenesulfonamide⁷ (**33**, 2.13 g, 10.0 mmol) in DMF (10 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 0.56 g, 14.0 mmol) in DMF (25 mL) under N₂, and the mixture was stirred at room temperature for 1 h. Bromodiyne **32** (3.41 g, 10.0 mmol) in DMF (5 mL) was added dropwise and the mixture was stirred at room temperature for 2 h. Water was added to quench the reaction, and the reaction mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexanes:EtOAc (10:1) as eluent to give **5d** (2.98 g, 64%) as a white solid: m. p. 119-120 °C; TLC (SiO₂, hexanes:EtOAc = 1:2, R_f = 0.62); ¹H NMR (300 MHz, CDCl₃) δ 2.08 (t, 1 H, *J* = 2.4 Hz), 2.43 (s, 3 H), 2.44 (s, 3 H), 3.71 (d, 2 H, *J* = 6.6 Hz), 3.89 (d, 2 H, *J* = 2.4 Hz), 3.90 (d, 1 H, *J* = 2.4 Hz), 3.91 (d, 1 H, *J* = 2.4 Hz), 3.96 (d, 1 H, *J* = 2.4 Hz), 3.97 (d, 1 H, *J* = 2.4 Hz), 5.18 (dd, 1 H, *J* = 1.5 Hz / *J* = 11.4 Hz), 5.20 (dd, 1 H, *J* = 1.5 Hz / *J* = 17.7 Hz), 5.68 (ddt, 1 H, *J* = 11.4 Hz / *J* = 17.7 Hz / *J* = 6.6 Hz), 7.26 (d, 2 H, *J* = 12.6 Hz), 7.30 (d, 2 H, *J* = 16.8 Hz), 7.64 (d, 2 H, *J* = 13.5 Hz), 7.68 (d, 2 H, *J* = 13.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 21.4, 21.6, 35.8, 36.1, 49.0, 74.0, 76.0, 78.0, 78.5, 119.9, 127.7 (2C), 127.8 (2C), 129.6 (2C), 129.5, 131.4, 135.2, 136.0,

⁶ Masquelin, T.; Obrecht, D. *Synthesis* **1995**, 276-284.

⁴ Johnson, A. W. *J. Chem. Soc.* **1946**, 1009-1014.

⁷ Hubert, A. J.; Feron, A.; Goebbels, G.; Warin, R.; Teyssie, P. *J. Chem. Soc. Perkin Trans II* **1977**, 11-14.

143.9, 144.2; IR (neat, cm^{-1}) 3274 (m), 2980 (w), 2923 (w), 2855 (w), 1597 (m), 1494 (w), 1431 (m), 1349 (s), 1333 (s), 1163 (s), 1093 (s), 899 (s), 816 (m), 752 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_4\text{S}_2$ C, 61.25; H, 5.57; N, 5.95, found C, 61.12; H, 5.70; N, 5.88.

4,4-Bis(carbethoxy)-9-(4-methylbenzenesulfonyl)-9-azadodec-11-ene-1,6-diyne (5e):

N-Allylsulfonamide **33**⁷ (617 mg, 2.92 mmol) in DMF (3 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 140 mg, 3.50 mmol) in DMF (7 mL) under N_2 , and the mixture was stirred at room temperature for 1 h. Bromooctadiyne **28** (960 mg, 2.92 mmol) in DMF (2 mL) was added dropwise, and the mixture was stirred at room temperature for 1 h. Water was added to quench the reaction, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexane:EtOAc (5:1) as eluent to give product **5e** (1.22 g, 91%) as a colorless oil: Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 1:4, R_f = 0.47); ^1H NMR (300 MHz, CDCl_3) δ 1.23 (t, 6 H, J = 7.2 Hz), 2.00 (t, 1 H, J = 2.7 Hz), 2.41 (s, 3 H), 2.70 (d, 2 H, J = 3.3 Hz), 2.72-2.75 (m, 2 H), 3.78 (d, 2 H, J = 6.6 Hz), 4.05-4.08 (m, 2 H), 4.10-4.23 (m, 4 H), 5.22 (dd, 1 H, J = 1.8 Hz / J = 11.7 Hz), 5.29 (bd, 1 H, J = 7.8 Hz), 5.61-5.79 (m, 1 H), 7.32 (d, 2 H, J = 7.8 Hz), 7.71 (d, 2 H, J = 7.8 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 21.6, 22.6, 36.0, 48.8, 56.0, 62.0, 71.6, 76.1, 78.4, 80.0, 119.8, 127.6, 129.5, 132.0, 136.1, 143.4, 168.9; IR (neat, cm^{-1}) 3392 (s), 2983 (m), 1736 (s), 1349 (s), 1335 (m), 1294 (m), 1210 (m), 1163 (s), 574 (m), 425 (s). HRMS (EI) m/z calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_6\text{S}$ ($\text{M}+\text{H}$)⁺ 460.1794, found 460.1796 (Δ = 0.4 ppm).

⁷ Hubert, A. J.; Feron, A.; Goebbels, G.; Warin, R.; Teyssie, P. *J. Chem. Soc. Perkin Trans II* **1977**, 11-14.

9,9-Bis(carbethoxy)-4-(4-methylbenzenesulfonyl)-4-azadodec-11-ene-1,6-diyne (5f):

Allylmalonate **29** (0.57 ml, 2.88 mmol) in THF (3 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 138 mg, 3.45 mmol) in THF (7 mL) under N₂, and the mixture was stirred at room temperature for 1 h. Bromodiyne **32** (980 mg, 2.88 mmol) in THF (2 mL) was added dropwise, and the mixture was stirred at room temperature for 1 h. Water was added to quench the reaction, and the reaction mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexane:EtOAc = 8:1 as eluent to give **5f** (992 mg, 85%) as a colorless oil: TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.44); ¹H NMR (300 MHz, CDCl₃) δ 1.20 (t, 6 H, *J* = 7.2 Hz), 2.09 (t, 1 H, *J* = 2.4 Hz), 2.39 (s, 3 H), 2.56-22.67 (m, 4 H), 4.08-4.23 (m, 8 H), 5.06 (bd, 1 H, *J* = 12.0 Hz), 5.06 (bd, 1 H, *J* = 12.0 Hz), 5.40-5.60 (m, 1 H), 7.27 (d, 2 H, *J* = 8.1 Hz), 7.67 (d, 2 H, *J* = 8.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 21.5, 22.7, 35.9, 36.4, 56.4, 61.5, 73.8, 75.3, 76.2, 80.9, 119.6, 127.7, 129.5, 131.6, 135.2, 143.8, 169.5; IR (neat, cm⁻¹) 3277(s), 3078 (w), 2983 (m), 2924 (w), 1732 (s), 1443 (m), 1354 (s), 1330 (s), 1290 (s), 1245 (m), 1214 (s), 1194 (s), 1163 (s), 1137 (m), 1093 (s), 904 (s), 745 (s), 656 (s), 569 (s), 544 (s). HRMS (EI) *m/z* calcd for C₂₄H₃₀NO₆S (M+H)⁺ 460.1794, found 460.1795 (Δ = 0.2 ppm).

9,9-Bis(carbethoxy)-4-(carbo-*tert*-butoxy)-4-azadodec-11-ene-1,6-diyne (5g):

A solution of N-*tert*-butoxycarbonyl-1-amino-3-propyne⁸ (**34**, 234 mg, 1.51 mmol) in DMF (2 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 84.6 mg, 2.11 mmol) in DMF (7.5 mL) under argon and the resulting mixture was stirred for 1 h at room temperature. A

⁸ Moloney, G. P.; Martin, G. R.; Mathews, N.; Hobbs, H.; Dodsworth, S.; Sang, P. Y.; Knight, C.; Maxwell, M.; Glen, R. C. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2713-2723.

solution of diethyl(4-bromo-2-butynyl)-2-propenylmalonate⁹ (**35**, 500 mg, 1.51 mmol) in DMF (1 mL) was then added dropwise and the reaction mixture was stirred at room temperature for an additional 9 h. Water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexane = 1:9) afforded **5g** as a colorless oil (430 mg, 70%): 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), 1.47 (s, 9 H), 2.19 (t, 1 H, *J* = 2.4 Hz), 2.79 (m, 4 H), 4.12 (m, 4 H), 4.19 (q, 4 H, *J* = 7.2 Hz), 5.14 (m, 2 H), 5.61 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 22.8, 28.3, 36.5, 56.8, 61.6, 78.0, 79.0, 80.9, 119.7, 131.8, 154.2, 169.8; IR (neat, cm⁻¹) 3284 (m), 2979 (s), 2933 (m), 1736 (s), 1701 (s), 1641 (w), 1477 (m), 1444 (s), 1406 (s), 1394 (m), 1367 (s), 1338 (w), 1286 (m), 1246 (s), 1215 (s), 1190 (s), 1167 (s), 1117 (m), 1097 (m), 1068 (m), 1036 (m), 928 (m), 862 (s), 432 (s). HRMS (EI) *m/z* calcd for C₂₂H₃₂NO₆ (M+H)⁺ 406.2229, found 406.2224 (Δ = -1.2 ppm).

4,4,9,9-Tetra(hydroxymethyl)dodec-11-ene-1,6-diyne (5k):

A solution of enediyne **5a** (6.4 g, 14.3 mmol) in Et₂O (25 mL) was added dropwise to a suspension of LiAlH₄ (4.4 g, 85.8 mmol) in Et₂O (100 mL) at 0 °C. After stirring for 20 h at room temperature, the reaction mixture was treated with aqueous 1 N NaOH. The resultant white suspension was dried over MgSO₄ and filtered through a short pad of Celite[®] topped with a thin layer of MgSO₄. The combined filtrate and washings were concentrated to give crude 4,4,9,9-tetra(hydroxymethyl)dodec-11-ene-1,6-diyne (**5k**, 3.83 g, 95%). The product was crystallized from minimum amount of EtOAc at room temperature overnight to give pure **5k** as a white solid: m. p. 88-89 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.81 (t, 1 H, *J* = 2.4 Hz), 1.90 (d, 2 H, *J* = 7.2 Hz), 1.93 (d, 1 H, *J* = 2.1 Hz), 1.94 (d, 1 H, *J* = 2.1 Hz), 2.07 (d, 1 H, *J* = 2.1 Hz), 2.08 (d, 1 H, *J* = 2.1 Hz), 2.10 (d, 2 H, *J* = 2.4 Hz), 3.30 (d, 4 H, *J* = 6.0 Hz), 3.37 (d, 4 H, *J* = 6.0 Hz), 3.66 (t, 2 H, *J* = 6.0 Hz), 3.72 (t, 2 H, *J* = 6.0 Hz), 4.84 (dd, 1 H, *J* = 2.1 Hz / *J* = 10.2 Hz), 4.89 (dd, 1 H, *J* = 2.1

⁹ Steinig, A. G.; De Meijere, A. *Eur. J. Org. Chem.* **1999**, 1333-1344.

Hz / J = 17.7 Hz), 5.60 (ddt, 1 H, J = 10.2 Hz / J = 17.7 Hz / J = 7.2 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 21.0, 21.1, 21.3, 35.4, 41.9 (2C), 65.0 (2C), 65.9 (2C), 70.1, 77.7, 78.5, 80.6, 117.5, 133.4; IR (neat, cm^{-1}) 3584 (m), 3367 (s), 3358 (s), 3338 (s), 3295 (s), 3077 (m), 3003 (w), 2929 (s), 2884 (s), 1637 (m), 1464 (m), 1433 (s), 1376 (m), 1364 (w), 1338 (m), 1285 (w), 1258 (w), 1234 (w), 1100 (m), 1031 (s), 920 (m), 861 (w). HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{25}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 281.1753, found 281.1754 (Δ = 0.3 ppm).

4,4,9,9-Tetra(methoxymethyl)dodec-11-ene-1,6-diyne (5h):

4,4,9,9-Tetra(benzyloxymethyl)dodec-11-ene-1,6-diyne (5i):

Enediyne **5k** (1.4 g, 5.0 mmol) in DMF (10 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 1.2 g, 30 mmol) in DMF (50 mL) under N₂, and the mixture was stirred at room temperature for 1 h. Benzyl bromide (4.1 g, 24.0 mmol) in DMF (10 mL) was added slowly *via* an addition funnel, and the resulting mixture was stirred at room temperature for 3 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried (MgSO₄), filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexanes:EtOAc (20:1) as eluent to give **5i** (2.23 g, 70%) as a viscous colorless oil: TLC (SiO₂, hexanes:EtOAc = 5:1, R_f = 0.51); ¹H NMR (300 MHz, CDCl₃) δ 1.92 (t, 1 H, *J* = 2.6 Hz), 2.18 (d, 2 H, *J* = 7.5 Hz), 2.21 (d, 1 H, *J* = 1.8 Hz), 2.22 (d, 1 H, *J* = 1.8 Hz), 2.37 (d, 2 H, *J* = 2.6 Hz), 2.38 (s, 2 H), 3.34 (s, 2 H), 3.35 (s, 2 H), 3.46 (s, 4 H), 4.45 (s, 4 H), 4.47 (s, 4 H), 5.01 (dd, 1 H, *J* = 2.4 Hz / *J* = 9.9 Hz), 5.04 (dd, 1 H, *J* = 2.4 Hz / *J* = 16.8 Hz), 5.75 (ddt, 1 H, *J* = 9.9 Hz / *J* = 16.8 Hz / *J* = 7.5 Hz), 7.20-7.32 (m, 20 H); ¹³C NMR (75 MHz, CDCl₃) δ 22.1, 22.4, 22.5, 36.4, 42.3, 42.3, 70.3, 71.5 (2C), 72.1 (2C), 73.2 (2C), 73.3 (2C), 78.1, 78.9, 81.0, 117.9, 127.3 (8C), 127.4 (4C), 128.2 (8C), 134.0, 138.7 (2C), 138.8 (2C); IR (neat, cm⁻¹) 3405 (m), 3417 (m), 3294 (s), 3382 (m), 3065 (m), 3087 (m), 3007 (w), 3032 (m), 2907 (s), 2864 (s), 1721 (s), 1496 (w), 1475 (w), 1453 (s), 1431 (w), 1365 (m), 1315 (m), 1274 (s), 1204 (w), 1177 (w), 1097 (s), 1074 (s), 1028 (m), 1002 (w), 918 (w), 805 (w), 750 (s), 698 (m). HRMS (EI) *m/z* calcd for C₄₄H₄₈O₄ (M)⁺ 640.3553, found 640.3560 (Δ = 1.1 ppm).

4,4,9,9-Tetra(acetoxymethyl)dodec-11-ene-1,6-diyne (5j):

To a solution of enediyne **5k** (1.37 g, 4.9 mmol) and DMAP (50 mg, 0.4 mmol) in DMF (20 mL) was added acetic anhydride (2.8 mL, 2.99 g, 29.3 mmol) in DMF (20 mL) under N₂, and the mixture was stirred at room temperature for 16 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO₄, filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexanes:EtOAc (20:1) as eluent to give enediyne **5j** (1.41 g, 65%) as a viscous colorless oil: TLC (SiO₂, EtOAc:hexanes = 1:5, R_f = 0.41); ¹H NMR (300 MHz, CDCl₃) δ 2.01 (t, 1 H, *J* = 2.7 Hz), 2.04 (s, 6 H), 2.05 (s, 6 H), 2.16 (d, 2 H, *J* = 7.8 Hz), 2.20 (d, 1 H, *J* = 1.8 Hz), 2.21 (d, 1 H, *J* = 1.8 Hz), 2.34 (d, 2 H, *J* = 2.7 Hz), 2.35 (bs, 2 H), 3.96 (s, 4 H), 4.06 (s, 4 H), 5.08 (d, 1 H, *J* = 18.3 Hz), 5.12 (d, 1 H, *J* = 10.2 Hz), 5.71 (ddt, 1 H, *J* = 10.2 Hz / *J* = 18.3 Hz / *J* = 7.8 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 20.7 (2C), 20.8 (2C), 22.2, 22.3 (2C), 36.1, 40.1, 40.2, 65.0 (2C), 65.5 (2C), 71.6, 77.5, 78.4, 78.9, 119.4, 132.0, 170.6 (2C), 170.7 (2C); IR (neat, cm⁻¹) 3275 (m), 2956 (m), 2912 (m), 2361 (m), 2341 (m), 1745 (s), 1684 (m), 1670 (w), 1651 (w), 1642 (m), 1469 (m), 1434 (m), 1383 (m), 1367 (s), 1232 (s), 1041 (s), 922 (m), 821 (w), 733 (w). HRMS (FAB) *m/z* calcd for C₂₄H₃₃O₈ (M+H)⁺ 449.2175, found 449.2174 (Δ = -0.2 ppm).

4,9-Bis(4,4-dimethyl-3,5-dioxanyl)dodec-11-ene-1,6-diyne (5l**):**

2,2-Dimethoxypropane (1.6 mL, 13.5 mmol) and *p*-toluenesulfonic acid monohydrate (21 mg, 0.108 mmol, 2 mol%) were added to a solution of enediyne **5k** (1.56 g, 5.4 mmol) in acetone (25 mL) and the mixture was stirred at room temperature for 12 h. A small amount of NaHCO₃ was added to neutralize the acid, followed by addition of water, and the resulting mixture was extracted with Et₂O. The combined ether extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude oil was purified by flash chromatography on silica gel using hexanes:EtOAc = 20:1 as eluent to give enediyne **5l** (1.40 g, 80%) as a viscous colorless oil: TLC (SiO₂, hexanes:EtOAc = 5:1, R_f = 0.45); ¹H NMR (300 MHz, CDCl₃) δ 1.38 (s, 6 H), 1.41 (s, 6 H), 2.01 (t, 1 H, *J* = 2.7 Hz), 2.13 (d, 2 H, *J* = 7.2 Hz), 2.33 (d, 1 H, *J* = 1.8 Hz), 2.34 (d, 1 H, *J* = 1.8 Hz), 2.36 (d, 1 H, *J* = 1.8 Hz), 2.37 (d, 1 H, *J* = 1.8 Hz), 2.41 (d, 2 H, *J* = 2.7 Hz), 3.61 (s, 4 H),

3.73 (s, 4 H), 5.09 (d, 1 H, $J = 9.6$ Hz), 5.10 (d, 1 H, $J = 18.3$ Hz), 5.73 (ddt, 1 H, $J = 9.6$ Hz / $J = 18.3$ Hz / $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 21.9 (2C), 22.7, 22.8, 23.1, 24.3, 25.6, 35.3, 35.6, 37.1, 66.1 (2C), 66.8 (2C), 71.2, 77.8, 79.3, 79.8, 98.1, 98.2, 118.8, 132.4; IR (neat, cm^{-1}) 3290 (m), 3076 (w), 2992 (s), 2941 (s), 2909 (s), 2865 (s), 1639 (w), 1477 (w), 1453 (m), 1431 (m), 1372 (s), 1350 (w), 1336 (w), 1288 (w), 1259 (s), 1227 (s), 1198 (s), 1156 (s), 1116 (s), 1087 (s), 1071 (s), 1037 (s), 998 (w), 924 (m), 883 (w), 867 (m), 827 (s), 730 (w), 697 (w), 687 (w). HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{33}\text{O}_4$ ($\text{M}+\text{H}$) $^+$ 361.2379, found 361.2378 ($\Delta = -0.3$ ppm).

CO-SiCaT Products (Continued from the Main Text):

2,8-Dioxa-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (6b): White solid; m. p. 179-180 °C; TLC (SiO_2 , hexanes:EtOAc = 5:1, $R_f = 0.15$); ^1H NMR (300 MHz, CDCl_3) δ 2.52 (dt, 1 H, $J = 2.4$ Hz / $J = 14.4$ Hz), 2.66 (t, 1 H, $J = 14.4$ Hz), 3.15 (m, 1 H), 3.45 (dd, 1 H, $J = 9.0$ Hz / $J = 10.2$ Hz), 4.30 (t, 1 H, $J = 8.4$ Hz), 4.36-4.58 (m, 6 H), 6.01 (s, 1 H); ^{13}C -NMR (75 MHz, CDCl_3) δ 39.3, 40.9, 70.9, 71.4, 73.6, 74.1, 121.0, 126.7, 147.6, 152.8, 196.3; IR (neat, cm^{-1}) 2956 (w), 2925 (m), 2842 (m), 1634 (s), 1608 (s), 1373 (w), 1318 (w), 1274 (m), 1191 (w), 1136 (m), 1116 (m), 1075 (s), 1051 (s), 920 (s), 867 (w), 756 (w), 726 (w), 684 (w). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$ C, 68.74; H, 6.29, found C, 68.81; H, 6.15.

8,8-Bis(carbethoxy)-5-oxo-1,5,6,6a,7,9-hexahydro-3H-2-oxa-cyclopenta[*e*]azulene (6c): Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 1:4, $R_f = 0.26$); ^1H NMR (400 MHz, CDCl_3) δ 1.15-1.30 (m, 6 H), 1.96 (t, 1 H, $J = 11.8$ Hz), 2.50-2.80 (m, 3 H), 2.80-3.20 (m, 3 H), 4.10-4.30 (m, 4 H), 4.40-4.65 (m, 4 H), 5.95 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.0, 38.2, 39.9, 40.8, 44.3, 59.0, 61.9, 72.2, 74.1, 120.4, 129.3, 148.2, 152.7, 170.5, 170.7, 197.2; IR (neat, cm^{-1}) 2982 (s), 2939 (s), 2908 (s), 2835 (s), 1732 (s), 1651 (s), 1600 (s), 1446 (s), 1427 (m), 1365 (s), 1288

(s), 1242 (s), 1191 (s), 1122 (s), 937 (s), 860 (m), 440 (s). HRMS (EI) m/z calcd for $C_{18}H_{22}O_6$ (M)⁺ 334.1416, found 334.1414 (Δ = -0.6 ppm).

2,8-Bis(4-methylbenzenesulfonyl)-2,8-diaza-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta-

[e]azulene (6d): White solid; m. p. 196 °C (decomp); TLC (SiO₂, hexanes:EtOAc = 1:2, R_f = 0.27); ¹H NMR (300 MHz, CDCl₃) δ 2.44 (s, 3 H), 2.46 (s, 3 H), 2.61 (t, 1 H, J = 10.2 Hz), 3.04 (m, 1 H), 3.57 (d, 1 H, J = 16.5 Hz), 3.83 (d, 1 H, J = 10.2 Hz), 3.81 (bd, 1 H), 3.99 (bd, 5 H), 4.12 (d, 1 H, J = 16.5 Hz), 5.95 (s, 1 H), 7.35 (d, 2 H, J = 7.5 Hz), 7.37 (d, 2 H, J = 8.1 Hz), 7.70 (d, 4 H, J = 8.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 21.5, 21.5, 37.9, 41.9, 51.8, 52.0, 53.7, 54.4, 124.0, 126.6, 128.0 (2C), 128.1 (2C), 130.1 (4C), 131.6, 132.1, 144.7 (2C), 145.5, 148.5, 195.5; IR (neat, cm⁻¹) 2925 (w), 1658 (s), 1651 (m), 1597 (w), 1345 (s), 1161 (s), 1132 (w), 1092 (w), 1037 (w), 911(w), 865 (w), 840 (w), 823 (m), 816 (m), 732 (w). HRMS (FAB) m/z calcd for $C_{25}H_{27}N_2O_5S_2$ ($M + 1$)⁺ 499.1361, found 499.1354 (Δ = - 1.4 ppm).

8,8-Bis(carbethoxy)-2-(4-methylbenzenesulfonyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-

azuleno[4,5-c]pyrrole (6e): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.23); ¹H NMR (400 MHz, CDCl₃) δ 1.23 (t, 3 H, J = 7.2 Hz), 1.26 (t, 3 H, J = 7.2 Hz), 2.05 (s, 1 H), 2.46-2.68 (m, 6 H), 2.84-3.28 (m, 5 H), 3.67 (bd, 1 H, J = 16.5 Hz), 3.85 (dd, 1 H, J = 8.1 Hz / J = 8.1 Hz), 4.08-4.25 (m, 4 H), 6.04 (s, 1 H), 7.37 (bd, 2 H, J = 8.7 Hz), 7.72 (bd, 2 H, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 21.5, 37.7, 39.2, 42.5, 43.2, 52.4, 53.9, 57.4, 62.0, 62.0, 124.8, 127.9, 129.5, 129.9, 131.7, 144.2, 144.9, 153.3, 170.1, 170.4, 196.2; IR (neat, cm⁻¹) 2983 (s), 1728 (s), 1642 (s), 1351 (s), 1196 (s). HRMS (EI) m/z calcd for $C_{25}H_{30}NO_7S$ ($M+H$)⁺ 488.1743, found 488.1743 (Δ = 0.0 ppm).

8,8-Bis(carbethoxy)-2-(4-methylbenzenesulfonyl)-5-oxo-2,3,5,6a,7,9-hexahydro-1H,6H-azuleno

[4,5-c]pyrrole (6f): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.28); ¹H NMR (400 MHz, CDCl₃) δ 1.61-1.81 (m, 6 H), 1.92 (t, 1 H, *J* = 12.2 Hz), 2.35-2.57 (m, 5 H), 2.59-2.71 (m, 1 H), 2.78-3.06 (m, 3 H), 3.82-4.26 (m, 8 H), 5.89 (s, 1 H), 7.32 (d, 2 H, *J* = 8.2 Hz), 7.69 (d, 2 H, *J* = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 21.5, 37.8, 40.3, 40.8, 44.0, 52.4, 54.7, 58.8, 62.0, 62.0, 123.0, 126.4, 127.8, 130.0, 132.2, 144.2, 149.0, 150.7, 170.3, 170.5, 196.5; IR (neat, cm⁻¹) 2982 (m), 2350 (w), 1729 (s), 1649 (s), 1643 (s), 1349 (m), 1257 (s), 1196 (s), 1163 (m), 1095 (s), 1068 (m), 667 (s), 609 (s), 471 (s). HRMS (EI) *m/z* calcd for C₂₅H₂₉NO₇S (M)⁺ 487.1665, found 487.1662 (Δ = - 0.6 ppm).

8,8-Bis(carbethoxy)-2-(carbo-*tert*-butoxy)-5-oxo-1,5,6,6a,7,9-hexahydro-3H-azuleno[4,5-

c]pyrrole (6g): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.12); ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, 3 H, *J* = 6.4 Hz), 1.22 (t, 3 H, *J* = 6.4 Hz), 1.42 (s, 9 H), 1.94 (t, 1 H, *J* = 12.2 Hz), 2.40-3.20 (m, 6 H), 4.40-4.30 (m, 8 H), 5.95 (d, 1 H, *J* = 9.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.87, 13.90, 28.3, 37.7, 40.3, 40.9, 44.3, 50.9, 51.0, 53.0, 53.2, 58.8, 61.9, 80.1, 122.8, 123.0, 127.2, 127.8, 149.9, 150.2, 150.3, 151.0, 153.8, 170.4, 170.6, 196.9; IR (neat, cm⁻¹) 2980 (m), 1730 (s), 1703 (s), 1650 (s), 1415 (s), 1201 (s), 1165 (s). HRMS (EI) *m/z* calcd for C₂₃H₃₁NO₇ (M)⁺ 433.2101, found: 433.2100 (Δ = -0.2 ppm).

2,2,8,8-Tetra(methoxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (6h):

Colorless oil; TLC (SiO₂, hexanes:EtOAc = 5:1, R_f = 0.15); ¹H NMR (300 MHz, CDCl₃) δ 1.40

(dd, 1 H, $J = 11.7$ Hz / $J = 12.6$ Hz), 1.98 (dd, 1 H, $J = 8.1$ Hz / $J = 12.6$ Hz), 2.23-2.49 (m, 6 H), 2.56 (dd, 1 H, $J = 1.8$ Hz / $J = 17.1$ Hz), 2.56 (d, 1 H, $J = 14.7$ Hz), 2.89 (m, 1 H), 3.14 (s, 2 H), 3.19 (s, 2 H), 3.22 (s, 2 H), 3.26 (s, 3 H), 3.29 (s, 2 H), 3.30 (s, 3 H), 3.31 (s, 3 H), 3.32 (s, 3 H), 5.96 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 37.5, 38.0, 39.1, 39.3, 42.6, 45.3, 45.7, 46.7, 59.3 (4C), 74.7, 75.2, 75.5, 76.6, 123.8, 131.2, 153.7, 158.1, 198.9; IR (neat, cm^{-1}) 2977 (s), 2923 (s), 2882 (s), 2825 (s), 2745 (w), 1641 (s), 1593 (m), 1478 (w), 1460 (w), 1451 (w), 1202 (m), 1110 (s). HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{O}_5$ (M^+) 364.2250, found 364.2252 ($\Delta = 0.5$ ppm).

2,2,8,8-Tetra(benzyloxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[e]azulene (6i):

Colorless oil; TLC (SiO_2 , hexanes:EtOAc = 5:1, $R_f = 0.20$); ^1H NMR (300 MHz, CDCl_3) δ 1.41 (dd, 1 H, $J = 11.4$ Hz / $J = 12.9$ Hz), 2.09 (dd, 1 H, $J = 8.1$ Hz / $J = 12.9$ Hz), 2.28-2.53 (m, 7 H), 2.64 (dd, 1 H, $J = 1.5$ Hz / $J = 17.1$ Hz), 2.86 (m, 1 H), 3.25 (d, 1 H, $J = 9.0$ Hz), 3.31 (d, 1 H, $J = 9.0$ Hz), 3.36 (s, 2 H), 3.39 (s, 2 H), 3.42 (d, 1 H, $J = 9.0$ Hz), 3.49 (d, 1 H, $J = 9.0$ Hz), 4.45 (s, 2 H), 4.48 (s, 4 H), 4.51 (s, 2 H), 5.96 (s, 1 H), 7.29 (m, 20 H); ^{13}C NMR (75 MHz, CDCl_3) δ 37.4, 38.3, 39.3, 39.7, 42.84, 45.5, 45.6, 46.9, 72.0, 72.4, 73.1, 73.1, 73.2, 73.3, 73.3, 74.2, 123.7, 127.2 (4C), 127.4 (4C), 127.5 (4C), 128.2 (4C), 128.3 (4C), 131.1, 138.4, 138.5 (2C), 138.5, 153.6, 158.1, 198.8; IR (neat, cm^{-1}) 3087 (w), 3063 (m), 3029 (m), 3007 (m), 2918 (s), 2854 (s), 2790 (w), 1638 (s), 1596 (m), 1453 (m), 1362 (w), 1341 (w), 1332 (w), 1307 (w), 1099 (s), 750 (m), 738 (m), 697 (m). HRMS (EI) m/z calcd for $\text{C}_{45}\text{H}_{48}\text{O}_5$ (M^+) 668.3502, found 668.3514 ($\Delta = 1.8$ ppm).

2,2,8,8-Tetra(acetoxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[e]azulene (6j):

White solid; m. p. 96-97 $^\circ\text{C}$; TLC (SiO_2 , hexanes:EtOAc = 1:1, $R_f = 0.20$); ^1H NMR (300 MHz,

CDCl₃) δ 1.43 (t, 1 H, J = 12.2 Hz), 2.03 (s, 3 H), 2.04 (s, 3 H), 2.04 (s, 3 H), 2.06 (s, 3 H), 2.36 (d, 1 H, J = 12.9 Hz), 2.25 - 2.38 (m, 3 H), 2.45 - 2.53 (m, 3 H), 2.57 (d, 1 H, J = 14.9 Hz), 2.62 (dd, 1 H, J = 1.7 Hz / J = 17.3 Hz), 2.93 (m, 1 H), 3.98 (m, 8 H), 5.99 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 20.8 (2C), 20.8 (2C), 37.1, 38.2, 38.8, 39.3, 42.3, 43.6, 44.9, 45.3, 64.8, 65.9, 66.2, 67.3, 124.7, 130.7, 151.8, 155.3, 170.7 (2C), 170.8 (2C), 197.8; IR (neat, cm⁻¹) 2951 (w) 2894 (w), 1739 (s) 1640 (s), 1596 (w), 1428 (w), 1380 (m), 1364 (m), 1237 (s), 1040 (s), 842 (w), 782 (w), 760 (w), 603 (w). HRMS (FAB) m/z calcd for C₂₅H₃₃O₉ (M + 1)⁺ 477.2125, found 477.2129 (Δ = 0.8 ppm).

2,2,8,8-Tetra(hydroxymethyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (6k):

White solid; m. p. 163-164 °C; TLC (SiO₂, CH₃Cl:CH₃OH = 5:1, R_f = 0.20); ¹H NMR (300 MHz, CD₃OD) δ 1.39 (dd, 1 H, J = 11.4 Hz / J = 12.9 Hz), 1.95 (dd, 1 H, J = 7.2 Hz / J = 12.9 Hz), 2.28 (d, 1 H, J = 18 Hz), 2.35-2.42 (m, 5 H), 2.48 (d, 1 H, J = 7.8 Hz), 2.57 (d, 1 H, J = 15.0 Hz), 2.89 (m, 1 H), 3.37 (s, 2 H), 3.42 (s, 2 H), 3.43 (s, 2 H), 3.51 (s, 2 H), 4.80 (s, 4 H), 5.93 (s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 38.2, 38.7, 39.4, 39.4, 43.0, 46.6, 48.1, 49.4, 65.1, 65.7, 65.8, 67.1, 124.0, 132.8, 156.3, 161.7, 201.5; IR (neat, cm⁻¹) 3389 (s), 3374 (s), 3364 (s), 2926 (m), 2875 (m), 1660 (w), 1621 (s), 1591 (s), 1033 (s), 601 (w). Anal. Calcd for C₁₇H₂₄O₅ C, 66.21; H, 7.84 found C, 66.12; H, 7.70.

2,2,8,8-Tetra(4,4-dimethyl-3,5-dioxanyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-

cyclopenta[*e*]azulene (6l): White solid; m. p. 147-148 °C; TLC (SiO₂, hexanes:EtOAc = 5:1, R_f = 0.20); ¹H NMR (300 MHz, CDCl₃) δ 1.25 (dd, 1 H, J = 11.1 Hz / J = 12.6 Hz), 1.42 (s, 12 H), 2.09

(dd, 1 H, $J = 6.6$ Hz / $J = 11.1$ Hz), 2.29-2.54 (m, 6 H), 2.37 (dd, 1 H, $J = 3.0$ Hz / $J = 14.4$ Hz), 2.62 (d, 1 H, $J = 18.9$ Hz), 2.85 (m, 1 H), 3.48 (d, 1 H, $J = 11.4$ Hz), 3.61-3.66 (m, 6 H), 3.74 (d, 1 H, $J = 12.6$ Hz), 6.01 (s, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.4, 23.5, 23.9, 25.0, 37.0, 39.2, 39.4, 40.2, 40.7, 40.8, 43.6, 45.5, 67.1, 67.8, 68.3, 69.1, 98.0, 98.1, 124.5, 131.0, 152.6, 156.3, 198.2; IR (neat, cm^{-1}) 2990 (m), 2936 (s), 2925 (s), 2855 (s), 1643 (s), 1596 (w), 1384 (m), 1370 (m), 1280 (w), 1251 (m), 1198 (s), 1155 (w), 1104 (w), 1096 (m), 1060 (s), 1033 (w), 933 (w), 847 (w), 831 (m), 847 (w), 757 (m), 778 (w), 730 (w), 576 (m). HRMS (EI) m/z calcd for $\text{C}_{23}\text{H}_{32}\text{O}_5$ (M^+) 388.2250, found 388.2245 ($\Delta = -1.3$ ppm).

CO-SiCaT Reactions; Other Products:

3,3,3',3'-Tetra(carbethoxy)-5-(*E*)-(dimethylphenylsilyl)methylene-5'-methyl-

bis(cyclopentylidene) (**9**): Colorless oil; TLC (SiO_2 , hexanes:EtOAc = 5:1, $R_f = 0.50$); ^1H NMR (300 MHz, CDCl_3) δ 0.39 (s, 3 H), 0.40 (s, 3 H), 1.07 (d, 3 H, $J = 7.0$ Hz), 1.19 (t, 3 H, $J = 7.1$ Hz), 1.20 (t, 3 H, $J = 7.1$ Hz), 1.21 (t, 3 H, $J = 7.1$ Hz), 1.23 (t, 3 H, $J = 7.1$ Hz), 2.09 (dd, 1 H, $J = 4.1$ Hz / $J = 13.5$ Hz), 2.65 (dd, 1 H, $J = 8.2$ Hz / $J = 13.5$ Hz), 2.82 - 2.93 (m, 5 H), 3.15 (d, 1 H, $J = 15.9$ Hz), 3.28 (m, 1 H), 4.12 - 4.23 (m, 8 H), 5.77 (s, 1 H), 7.32 - 7.58 (m, 5 H); ^{13}C NMR (75 MHz, CDCl_3) δ -1.43, -1.4, 13.9 (4C), 18.00, 28.3, 32.2, 39.9, 40.1, 42.2, 42.3, 57.3, 58.1, 61.4 (2C), 61.5 (2C), 121.6, 127.9 (2C), 128.9, 130.0, 133.8 (2C), 138.9, 143.0, 153.8, 171.5, 172.0 (2C), 172.3; IR (neat, cm^{-1}) 3070 (w), 2980 (m), 2961 (m), 2936 (m), 2907 (m), 2874 (w), 1732 (s), 1464 (m), 1446 (m), 1428 (m), 1390 (w), 1367 (m), 1299 (m), 1255 (s), 1228 (m), 1191 (m), 1163 (m), 1116 (m), 1097 (m), 1070 (m), 861 (m), 833 (s), 784 (m). HRMS (FAB) m/z calcd for

$C_{32}H_{45}O_8Si$ ($M + 1$)⁺ 585.2865, found 585.2884 ($\Delta = 3.2$ ppm).

3,3,3',3'-Tetra(carbethoxy)-5-(*E*)-(dimethylphenylsilyl)methylene-5'-(2-formylmethyl)bis

(cyclopentylidene) (10): Colorless oil; TLC (SiO₂, hexanes:EtOAc = 5:1, $R_f = 0.20$); ¹H NMR (300 MHz, CDCl₃) δ 0.35 (s, 3 H), 0.37 (s, 3 H), 1.17 (t, 3 H, $J = 7.1$ Hz), 1.81 (t, 3 H, $J = 7.1$ Hz), 1.21 (t, 3 H, $J = 7.1$ Hz), 1.23 (t, 3 H, $J = 7.1$ Hz), 2.10 (dd, 1 H, $J = 4.4$ Hz / $J = 13.7$ Hz), 2.36 (ddd, 1 H, $J = 1.6$ Hz / $J = 10.4$ Hz / $J = 18.1$ Hz), 2.68 (dd, 1 H, $J = 9.5$ Hz / $J = 13.7$ Hz), 2.79 - 2.98 (m, 6 H), 3.05 (d, 1 H, $J = 17.3$ Hz), 3.70 (m, 1 H), 4.05 - 4.21 (m, 8 H), 5.58 (m, 1 H), 7.29 - 7.47 (m, 5 H), 9.62 (d, 1 H, $J = 0.8$ Hz); ¹³C NMR (75 MHz, CDCl₃) δ -1.5, -1.4, 14.0 (4C), 34.5, 40.1, 40.2, 41.5, 42.2, 46.1, 57.2, 58.3, 61.5 (2C), 61.7, 61.8, 122.9, 127.9 (2C), 129.0, 131.0, 133.6 (2C), 138.7, 140.1, 153.2, 171.1 (2C), 171.2, 171.9, 200.7; IR (neat, cm⁻¹) 2981 (m), 2938 (m), 2905 (m), 1731 (s), 1367 (m), 1296 (m), 1257 (s), 1190 (m), 1162 (m), 1112 (m), 1096 (m), 1069 (m), 1023 (w), 859 (w), 838 (m), 733 (w). HRMS (FAB) m/z calcd for $C_{33}H_{43}O_9Si$ ($M-H$)⁻ 611.2673, found 611.2676 ($\Delta = 0.5$ ppm).

4,9-Bis(4-methylbenzenesulfonyl)-9-cyclohexyl-4,9-diazanona-1,6-diyne (11):

N-cyclohexenyl-4-methylbenzenesulfonamide¹¹ (**36**, 1.05 g, 4.20 mmol) in DMF (3 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 202 mg, 5.04 mmol) in DMF (6 mL) under N₂, and the mixture was stirred at room temperature for 1 h. Bromodiyne **32** (1.43 g,

¹¹ O'Brien, P.; Childs, A. C.; Ensor, G. J.; Hill, C. L.; Kirby, J. P.; Dearden, M. J.; Oxenford, S. J.; Rosser, C. M. *Org. Lett.* **2003**, 5, 4955-4957.

4.20 mmol) in DMF (3 mL) was added dropwise, and the mixture was stirred at room temperature for 1 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude was purified by flash chromatography on silica gel using hexane:EtOAc (5:1) as eluent to give product **11** (1.40 g, 65%) as a colorless oil: TLC (SiO₂, hexanes:EtOAc = 4:1, R_f = 0.29); ¹H NMR (300 MHz, CDCl₃) δ 1.50-1.65 (m, 2 H), 1.65-1.83 (m, 2 H), 1.90-1.97 (m, 2 H), 2.08 (s, 1 H), 2.42 (s, 6 H), 3.81 (d, 1 H, *J* = 17.0 Hz), 3.97 (d, 1 H, *J* = 17.0 Hz), 4.02 (bs, 4 H), 4.40-4.51 (m, 1 H), 5.20-5.30 (m, 1 H), 5.79-5.89 (m, 1 H), 7.21-7.36 (m, 4 H), 7.62-7.88 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃) δ 21.3, 21.5, 21.5, 21.5, 24.3, 27.9, 32.6, 36.0, 36.4, 54.9, 73.9, 73.9, 76.2, 82.5, 127.1, 127.3, 127.8, 129.5, 129.5, 133.0, 135.2, 138.0, 143.3, 143.9. HRMS (EI) *m/z* calcd for C₂₇H₃₀N₂O₄S₂ (M⁺) 510.1647, found 510.1644 (Δ = - 0.6 ppm).

3-[4-[(Dimethylphenylsilyl)methylene]-1-(4-methylbenzenesulfonyl)pyrrolidin-3-ylidene]-1-(4-methylbenzenesulfonyl)-2,3,3a,6,7,7a-hexahydro-1H-indole (16): Colorless oil; TLC (SiO₂, hexanes:EtOAc = 4:1, R_f = 0.35); ¹H NMR (300 MHz, CDCl₃) δ 0.36 (s, 6 H), 1.55-1.75 (m, 2 H), 1.85-2.00 (bs, 1 H), 2.41 (s, 3 H), 2.44 (s, 3 H), 2.30-2.60 (m, 2 H), 3.33 (bs, 1 H), 3.40-3.80 (m, 5 H), 3.90-4.05 (m, 1 H), 5.29 (bd, 1 H, *J* = 9.9 Hz), 5.78 (s, 1 H), 5.83-5.93 (m, 1 H), 7.15-7.50 (m, 11 H); 7.68 (d, 2 H, *J* = 8.2 Hz); ¹³C NMR (75 MHz, CDCl₃) δ -2.0, -1.8, 19.5, 21.5, 24.0, 29.6, 42.3, 51.6, 53.6, 53.7, 58.9, 120.8, 122.6, 126.6, 127.8, 127.9, 128.1, 129.4, 129.7, 129.8, 130.2, 131.8, 132.0, 133.7, 134.1, 137.4, 143.8, 144.0, 148.7; IR (neat, cm⁻¹) 2955 (s), 2925 (s), 1739 (s), 1340 (s), 1251 (s), 1118 (s). HRMS (EI) *m/z* calcd for C₃₅H₄₀N₂O₄S₂Si (M)⁺ 644.2199, found 644.2200 (Δ = 0.1 ppm).

[2+2+2+1] cycloaddition Substrates:**4,4,9,9-Tetra(carbethoxy)tridec-1-ene-6,11-diyne (7a):**

To a solution of triethyl methanetricarboxylate (1.95 g, 7.52 mmol) in a mixture 1:1 toluene-DMF (20 mL) was added 1-bromo-2-butyne¹² (1.0 g, 7.52 mmol) dropwise. The resultant slurry was heated to 80°C and kept at this temperature overnight. After 14 h, the mixture was filtrated off and the white solid was washed with toluene. The solution was diluted with water and extracted with Et_2O . The combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtrated and concentrated under reduced pressure affording yellow oil that was used in the next step without any further purification. The obtained crude product (2.14 g, 7.52 mmol) in solution of THF (4 mL) was added to a suspension of NaOEt (646 mg, 9.4 mmol) in THF (20 mL) via cannula under N_2 . The resultant dark orange solution was stirred at room temperature overnight. The reaction mixture was then acidified to pH 1 with 2 *N* HCl and extracted with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 , filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc :hexanes = 1:9) afforded 2-(but-2-ynyl)malonate **37** as a colorless oil (1.3 g, 82% for two steps): TLC (SiO_2 , hexanes: EtOAc = 9:1, R_f = 0.48); ^1H NMR (400 MHz, CDCl_3) δ 1.25 (t, 6 H, J = 7.2 Hz), 1.73 (m, 3 H), 2.69 (m, 2 H), 3.48 (t, 1 H, J = 7.8 Hz), 4.20 (q, 4 H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 3.4, 14.0, 18.8, 51.7, 61.5, 74.9, 77.7, 168.2.

¹² Marson, C. M.; Grabowska, U.; Walsgrove, T.; Eggleston, D. S.; Baures, P. W. *J. Org. Chem.* **1994**, 59, 284-290.

To a suspension of NaH (60% dispersion in mineral oil, 226 mg, 5.65 mmol) in THF (5.8 mL) under N₂, was added a solution of **37** (1.0 g, 4.74 mmol) in THF (2.8 mL) dropwise. After 2 h at room temperature, the mixture was added to a solution of 1,4-dibromo-2-butyne⁴ (3.0 g, 14.13 mmol) in THF (11.2 mL) via cannula at room temperature and the resultant brown reaction mixture was stirred overnight. After 16 h, the dark red solution was quenched with water and extracted with Et₂O. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. The excess of 1,4-dibromo-2-butyne was distilled off (P = 0.5 mmHg, bp 59-60 °C) and the dark residue purified by flash chromatography on silica gel (EtOAc:hexanes = 1:9) affording bromodiyne **38** as pale yellow oil (1.18 g, 73%): TLC (SiO₂, hexanes:EtOAc = 9:1, R_f = 0.48); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (t, 6 H, *J* = 7.2 Hz), 1.75 (t, 3 H, *J* = 2.5 Hz), 2.88 (q, 2 H, *J* = 2.5 Hz), 3.02 (t, 2 H, *J* = 2.5 Hz), 3.86 (t, 2 H, *J* = 2.4 Hz), 4.22 (q, 4 H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 3.3, 3.4, 14.0, 14.7, 23.0, 56.7, 61.8, 72.9, 78.2, 79.1, 82.2, 168.8.

Allylmalonate **29** (0.35 ml, 1.75 mmol) in THF (2 mL) was added slowly to a suspension of NaH (60% dispersion in mineral oil, 80.5 mg, 2.01 mmol) in THF (4 mL) under N₂, and the mixture was stirred at room temperature for 1 h. Bromodiyne **38** (600 mg, 1.75 mmol) in THF (1 mL) was added dropwise, and the mixture was stirred at room temperature overnight. Water was added slowly to quench the reaction, and the reaction mixture was extracted with Et₂O. The combined organic extracts were washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed on silica gel using hexanes:EtOAc (9:1) as eluent to give product **7a** (702 mg, 87%) as a 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).

⁴ Johnson, A. W. *J. Chem. Soc.* **1946**, 1009-1014.

4,9-Dioxatridec-1-ene-6,11-diyne (7b):

This enediyne was prepared following the same procedure as that for the preparation of **5b** using 1-bromo-2-butyne instead of propargyl bromide. Enediyne **7b** was obtained as a colorless oil in 79% isolated yield: TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.68); ¹H NMR (400 MHz, CDCl₃) δ 1.86 (t, 3 H, *J* = 2.2 Hz), 4.05 (dt, 2 H, *J* = 1.2 Hz / *J* = 6.0 Hz), 4.20 (m, 4 H), 4.28 (t, 2 H, *J* = 1.6 Hz), 5.21 (m, 1 H), 5.31 (m, 1 H), 5.9 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.6, 56.6, 57.2, 57.4, 70.6, 74.3, 81.8, 82.6, 83.1, 117.9, 133.9; IR (neat, cm⁻¹) 2945 (w), 2920 (w), 2896 (w), 2854 (w), 1443 (m), 1425 (w), 1383 (w), 1346 (s), 1138 (s), 1119 (s), 1074 (s), 1022 (w), 993 (w), 926 (m), 440 (s). HRMS (EI) *m/z* calcd for C₁₁H₁₄O₂ (M)⁺ 178.0993, found 178.0990 (Δ = - 1.7 ppm).

4,4-Bis(carbethoxy)-9-oxatridec-1-ene-6,11-diyne (7c):

To a solution of **5c** (410 mg, 1.34 mmol) in THF (10 mL) at -78 °C under Argon was added LiHMDS (1.0 M in THF, 1.61 mL, 1.61 mmol) dropwise. The resulting solution was stirred for 3 h at this temperature before MeI (334.4 μL, 5.36 mmol) was added. The reaction mixture was stirred for an additional 5 h at -78 °C before being allowed to warm up to room temperature over night. After 15 h, water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 5:95 to 1:9) afforded enediyne **7c** as a colorless oil (245 mg, 53 %): TLC (SiO₂, EtOAc:hexanes = 1:9, R_f = 0.37); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, 6 H, *J* = 7.2 Hz), 1.85 (t, 3 H, *J* = 2.4 Hz), 2.79 (m, 2 H), 2.83 (m, 2 H), 4.15-4.23 (m, 8 H), 5.14 (m, 2 H), 5.63 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.6, 14.1, 23.0, 36.5, 56.1, 56.6, 56.8, 61.6, 74.4, 78.5, 81.7, 82.9, 119.7, 131.8, 169.8; IR (neat, cm⁻¹) 3277 (w), 3078 (w), 2982 (m), 2904 (w), 1732 (s), 1641 (w), 1465 (w), 1445 (m), 1367 (m), 1288 (m), 1215 (s), 1192 (s),

1130 (m), 1074 (s), 1036 (m), 926 (m), 858 (w), 447 (s). HRMS (EI) m/z calcd for $C_{18}H_{25}O_5$ (M+H)⁺ 321.1702, found 321.1704 (Δ = 0.6 ppm).

9,9-Bis(carbethoxy)-4-oxatridec-1-ene-6,11-diyne (7d):

To a solution of KOH (11.2 g, 200 mmol) and 2-butyne-1,4-diol (**39**, 8.7 g, 100 mmol) in DMSO (100 mL) was added allyl bromide (8.7 mL, 100 mmol) and the mixture was stirred at room temperature for 3 h under argon. The crude solution was diluted with CH₂Cl₂, washed with 2N HCl, with NaHCO₃ (sat.), brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 3:7) afforded hydroxyenyne **40** as a light yellow oil (5.2 g, 41 %): ¹H NMR (400 MHz, CDCl₃) δ 1.79 (s, 1 H), 4.05 (dt, 2 H, J = 1.2 Hz / J = 5.6 Hz), 4.19 (t, 2 H, J = 1.2 Hz), 4.31 (t, 2 H, J = 2.0 Hz), 5.90 (m, 1 H), 5.25 (m, 2 H).

To a solution of **40** (1.5 g, 11.89 mmol) and pyridine (210 μ L) in Et₂O (10 mL) at 0 °C, was added dropwise a solution of PBr₃ (491 μ L, 5.15 mmol) in Et₂O (2.5 mL). The resultant reaction mixture was stirred under argon for 19 h at room temperature. Water was then added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9) afforded bromoenyne **41** as a colorless oil (1.4 g, 62%): ¹H NMR (400 MHz, CDCl₃) δ 3.95 (t, 2 H, J = 2.0 Hz), 4.05 (dt, 2 H, J = 1.2 Hz / J = 6.0 Hz), 4.21 (t, 2 H, J = 2.0 Hz), 5.21-5.34 (m, 2 H), 5.85-5.95 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 57.3, 70.8, 81.3, 82.9, 118.0, 133.8. HRMS (EI) m/z calcd for C₇H₈BrO (M-H)⁻ 186.9758, found 186.9761 (Δ = 1.6 ppm).

A solution of butynylmalonate **37** (670 mg, 3.16 mmol) in THF (3.5 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 152 mg, 3.79 mmol) in THF (6.5 mL) under argon and the resulting mixture was stirred for 2.5 h at room temperature. A solution of bromoenyne **41** (600 mg, 3.16 mmol) in THF (2 mL) was then added dropwise and the reaction

mixture was stirred at room temperature for an additional 21 h. Water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9) afforded **7d** as a colorless oil (785 mg, 78%). 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).

4,4-Bis(carbethoxy)-9-(4-methylbenzenesulfonyl)-9-azatridec-1-ene-6,11-diyne (7e):

N-tert.-Butoxycarbonyl-*p*-toluenesulfonamide (3.4 g, 12.56 mmol) was added to a solution of 2-butyne-1-ol (800 mg, 11.41 mmol) and PPh₃ (3.3 g, 12.56 mmol) in THF (40 mL) at room temperature under argon. After 10 minutes, diisopropyl azodicarboxylate (DIAD, 2.6 mL, 12.56 mmol) was added and the resulting reaction mixture was stirred for 9 h. Water was then added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure affording butynylamide **42** that was used without purification in the next step. Trifluoroacetic acid (10 mL) was added to a solution of **42** in CH₂Cl₂ (10 mL) and the mixture was stirred for 1 h at room temperature before saturated solution of NaHCO₃ (10 mL) was added. The aqueous phase was extracted with CH₂Cl₂ and the combined organic layers dried over Na₂SO₄. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded butylsulfonamide **43** as a white solid (1.95 g, 76 % for 2 steps): m. p. 68-70 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.60 (t, 3 H, *J* = 2.4 Hz), 2.43 (s, 3 H), 3.76 (m, 2 H), 4.52 (t, 1 H, *J* =

4.8 Hz), 7.31 (m, 2 H), 7.77 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.3, 21.5, 33.4, 73.2, 81.08, 127.5, 129.5, 136.8, 143.6.

A solution of **43** (337 mg, 1.51 mmol) in DMF (2 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 84.6 mg, 2.11 mmol) in DMF (7.5 mL) under argon and the resulting mixture was stirred for 2 h at room temperature. A solution of bromomalonate **35** (500 mg, 1.51 mmol) in DMF (1 mL) was then added dropwise and the reaction mixture was stirred at room temperature for an additional 8 h. Water was added followed by extraction with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded **7e** as a colorless oil (560 mg, 78 %): TLC (SiO_2 , EtOAc:hexanes = 1:4, R_f = 0.44); ^1H NMR (400 MHz, CDCl_3) δ 1.23 (t, 6 H, J = 7.2 Hz), 1.62 (t, 3 H, J = 2.4 Hz), 2.41 (s, 3 H), 2.65 (m, 4 H), 4.05 (q, 2 H, J = 2.4 Hz), 4.08 (t, 2 H, J = 2.4 Hz), 4.17 (q, 4 H, J = 7.2 Hz), 5.09 (m, 2 H), 5.53 (m, 1 H), 7.28 (m, 2 H), 7.69 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.3, 14.0, 21.5, 22.8, 36.4, 36.45, 36.5, 56.6, 61.6, 71.4, 75.8, 80.5, 81.7, 119.6, 127.9, 129.4, 131.8, 135.5, 143.5, 169.6; IR (neat, cm^{-1}) 3078 (w), 2979 (m), 2922 (w), 2237 (w), 1728 (s), 1641 (w), 1597 (w), 1494 (w), 1464 (w), 1441 (m), 1352 (s), 1331 (s), 1288 (s), 1248 (m), 1215 (s), 1194 (s), 1163 (s), 1138 (m), 1093 (s), 1068 (m), 1036 (m), 1018 (w), 904 (s), 746 (s), 659 (s), 569 (s), 540 (s). HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{32}\text{NO}_6\text{S}$ ($\text{M}+\text{H}$) $^+$ 474.1950, found 474.1947 (Δ = -0.6 ppm).

4,9-Bis(4-methylbenzenesulfonyl)-4,9-diazatridec-1-ene-6,11-diyne (7f):

To a suspension of NaH (60% dispersion in mineral oil, 170 mg, 4.26 mmol) in DMF (11.2 mL) under argon, was added a solution of *N*-allylsulfonamide **33** (750 mg, 3.55 mmol) in DMF (5.6 mL) dropwise. After 1 h at room temperature, the mixture was added to a solution of 1,4-dibromo-2-butyne (2.26 g, 10.65 mmol) in DMF (22.5 mL) via cannula at room temperature and the

resultant reaction mixture was stirred for an additional 4 h. Water was then added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 5:95 to 1:9) afforded bromoenyne **44** as a white solid (980 mg, 81 %): m. p. 58-60 °C; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.48); ¹H NMR (400 MHz, CDCl₃) δ 2.44 (s, 3 H), 3.61 (t, 2 H, *J* = 2.2 Hz), 3.80 (d, 2 H, *J* = 6.4 Hz), 4.13 (t, 2 H, *J* = 2.0 Hz), 5.23-5.32 (m, 2 H), 5.68-5.78 (m, 1 H), 7.32 (dm, 2 H, *J* = 8.4 Hz), 7.73 (dm, 2 H, *J* = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 21.5, 36.1, 49.2, 79.7, 80.5, 120.1, 127.7, 129.5, 131.8, 135.8, 143.6; IR (neat, cm⁻¹) 2900 (w), 1350 (m), 1165 (s). HRMS (EI) *m/z* calcd for C₁₄H₁₇BrNO₂S (M+H)⁺ 342.0163, found 342.0161 (Δ = -0.6 ppm).

To a suspension of NaH (60% dispersion in mineral oil, 57 mg, 1.40 mmol) in DMF (4 mL) under argon, was added a solution of butynylsulfonamide **43** (261 mg, 1.17 mmol) in DMF (2 mL) dropwise. After 1 h at room temperature, bromoenyne **44** in DMF (1 mL) was added and the resultant reaction mixture was stirred for an additional 2 h. Water was then added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:4 to 3:7) afforded **7f** as a viscous yellow oil (535 mg, 94%): 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-(4-methylbenzenesulfonyl)-4-azatridec-1-ene-6,11-diyne (7g):

A solution of *N*-allylsulfonamide **33** (308 mg, 1.46 mmol) in DMF (1.5 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 81.6 mg, 2.04 mmol) in DMF (3.5 mL) under argon and the resulting mixture was stirred for 2 h at room temperature. A solution of bromodiyne **38** (500 mg, 1.46 mmol) in DMF (1 mL) was then added dropwise and the reaction mixture was stirred at room temperature for an additional 8 h. Water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded **7g** as a colorless oil (392 mg, 57 %): TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.47); ¹H NMR (400 MHz, CDCl₃) δ 1.22 (t, 6 H, *J* = 7.2 Hz), 1.75 (t, 3 H, *J* = 2.6 Hz), 2.44 (s, 3 H), 2.65 (m, 2 H), 2.73 (m, 2 H), 3.77 (d, 2 H, *J* = 6.4 Hz), 4.05 (m, 2 H), 4.16 (q, 4 H, *J* = 7.2 Hz), 5.21 (dm, 1 H), 5.29 (dm, 1 H), 5.70 (m, 1 H), 7.31 (d, 2 H, *J* = 8.0 Hz), 7.71 (d, 2 H, *J* = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 3.5, 14.0, 21.5, 22.6, 22.8, 36.1, 48.7, 56.4, 61.8, 73.0, 75.9, 78.9, 80.4, 119.8, 127.6, 129.5, 132.1, 136.2, 143.4, 168.9; IR (neat, cm⁻¹) 2982 (m), 1736 (s), 1445 (w), 1429 (w), 1417 (w), 1350 (s), 1331 (m), 1329 (w), 1290 (m), 1240 (w), 1209 (m), 1196 (m), 1163 (s), 1118 (w), 1093 (m), 1070 (w), 1053 (m), 900 (w), 756 (w), 663 (m), 573 (m), 424 (s). HRMS (EI) *m/z* calcd for C₂₅H₃₂NO₆S (M+H)⁺ 474.1950, found 474.1945 (Δ = -1.0 ppm).

9,9-Bis(carbethoxy)-4-(carbo-*tert*-butoxy)-4-azatridec-1-ene-6,11-diyne (7h):

A solution of *N*-allyl-*t*-butylcarbamate (**45**, 230 mg, 1.46 mmol) in DMF (1.5 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 81.6 mg, 2.04 mmol) in DMF (3.5 mL) under Argon and the resulting mixture was stirred for 2 h at room temperature. A solution of bromodiyne **38** (500 mg, 1.46 mmol) in DMF (1 mL) was then added dropwise and the reaction mixture was stirred at room temperature for an additional 9 h. Water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded **7h** as a colorless oil (373 mg, 61 %). 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{23}\text{H}_{32}\text{NO}_6$ ($\text{M}-\text{H}$) $^-$ 418.2229, found 418.2222 ($\Delta = -1.7$ ppm).

4,4,9,9-Tetra(hydroxymethyl)tridec-1-ene-6,11-diyne (7p):

This enediynes was prepared following the same procedure as that for the preparation of **5k** except for using enyne **7a**. Tetrahydroxyenediyne **7p** was obtained as a colorless viscous oil in 85% isolated yield: TLC (SiO_2 , EtOAc :hexanes = 7:1, $R_f = 0.1$); ^1H NMR (400 MHz, CDCl_3) δ 1.79 (t, 3 H, $J = 2.4$ Hz), 2.12 (m, 2 H), 2.21 (br, 4 H), 2.24 (m, 4 H), 2.32 (t, 2 H, $J = 2.4$ Hz), 3.63 (s, 2 H), 3.64 (s, 2 H), 3.70 (s, 4 H), 5.13 (m, 2 H), 5.80 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.5, 22.0, 22.4, 22.5, 36.6, 42.3, 42.4, 67.1, 67.7, 74.8, 78.5, 78.7, 79.1, 118.6, 133.4; IR (neat, cm^{-1}) 3350 (s), 2918 (s), 2881 (s), 1724 (w), 1462 (m), 1435 (s), 1375 (m), 1336 (m), 1256 (m), 1097 (m), 1032 (s), 918 (m), 445 (s). HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{O}_4$ (M) $^+$ 294.1831, found 294.1836 ($\Delta = 1.7$ ppm).

4,4,9,9-Tetra(methoxymethyl)tridec-1-ene-6,11-diyne (7i):

This enediynes was prepared following the same procedure as for the preparation of **5h** except for using **7p**. Tetramethoxyenediyne **7i** was obtained as a light yellow oil in 77% isolated yield: TLC (SiO_2 , EtOAc :hexanes = 1:9, $R_f = 0.60$); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{21}\text{H}_{34}\text{O}_4$ (M) $^+$ 350.2457, found 350.2460 ($\Delta = 0.8$ ppm).

4,4,9,9-Tetra(benzyloxymethyl)tridec-1-ene-6,11-diyne (7j):

To a solution of **5i** (500 mg, 0.78 mmol) in THF (6.5 mL) at $-78\text{ }^{\circ}\text{C}$ under argon was added LiHMDS (1.0 M in THF, 0.94 mL, 0.94 mmol) dropwise. The resulting solution was stirred for 3 h at this temperature before MeI (196.7 μL , 3.12 mmol) was added. The reaction mixture was stirred for an additional 5 h at $-78\text{ }^{\circ}\text{C}$ before being allowed to warm up to room temperature overnight. After 15 h, water was added followed by extraction with Et_2O . The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc :hexanes = 5:95 to 1:9) afforded enediyne **7j** as a colorless oil (487 mg, 95 %): TLC (SiO_2 , EtOAc :hexanes = 1:9, $R_f = 0.54$); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{45}\text{H}_{50}\text{O}_4$ (M) $^+$ 654.3709, found 654.3708 ($\Delta = -0.1$ ppm).

4,4,9,9-Tetra(acetoxymethyl)tridec-1-ene-6,11-diyne (7k):

This enediyne was prepared following the same procedure as for the preparation of **5j** except for using **7p**. Tetraacetoxyenediyne **7k** was obtained as a colorless oil in 69% isolated yield: 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 C₂₅H₃₅O₈ (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 (7l):

This enediyne was prepared following the same procedure as for the preparation of **5l** except for using **7p**. Enediyne **7l** was obtained as a light yellow oil in 86% isolated yield: 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).

1-Phenyl-4,4,9,9-tetra(carbethoxy)dodec-11-ene-1,6-diyne (7m):

To a solution of **7a** (800 mg, 1.78 mmol) and PhI (408 mg, 1.96 mmol) in CH₂Cl₂ (12 mL) were successively added TEA (4 mL), PdCl₂(PPh₃)₂ (125 mg, 178 μmol) and CuI (31.1 mg, 160 μmol) under argon. The resulting reaction mixture was stirred for 22 h at room temperature and directly subjected to flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) for purification. **7m** was obtained as an orange oil (659 mg, 71 %): TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.59); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (m, 12 H), 2.75 (m, 4 H), 2.98 (t, 2 H, *J* = 2.4 Hz), 3.15 (s, 2 H), 4.20 (m, 8 H), 5.13 (m, 2 H), 5.60 (m, 1 H), 7.25 (m, 3 H), 7.35 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.7, 22.9, 23.4, 36.3, 56.8, 61.5, 61.8, 77.5, 78.1, 83.5, 84.1, 119.6, 123.2, 127.9, 128.1, 131.6, 131.9, 168.8, 169.7; IR (neat, cm⁻¹) 2982 (w), 1736 (s), 1288 (m), 1209 (s), 1194 (s), 1159 (w), 1138 (w), 1095 (w), 1070 (w), 858 (w), 758 (w), 692 (w), 450 (s). HRMS (EI) *m/z* calcd for C₃₀H₃₆O₈ (M)⁺ 524.2410, found 524.2407 (Δ = -0.5 ppm).

4,4,9,9-Tetra(carbethoxy)-1-trimethylsilyl-dodec-11-ene-1,6-diyne (7n):

To a solution of **7a** (800 mg, 1.78 mmol) in THF (18 mL) at -78 °C under argon was added LiHMDS (1.0 M in THF, 2.14 mL, 2.14 mmol) dropwise. The resulting solution was stirred for 2 h at this temperature before TMSCl (773 mg, 7.12 mmol) in THF (4 mL) was added. The reaction mixture was stirred for an additional 3 h at -78 °C before being allowed to warm up to 0 °C. Water was then added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9) afforded enediyne **7n** as a colorless oil (881 mg, 95%): 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{27}\text{H}_{40}\text{O}_8\text{Si}$ (M) $^+$ 520.2492, found 520.2498 (Δ = 1.1 ppm).

1-(3-Pyridyl)-4,4,9,9-tetra(carbethoxy)dodec-11-ene-1,6-diyne (7o):

To a solution of **7a** (800 mg, 1.78 mmol) and 3-iodopyridine (410 mg, 1.96 mmol) in CH_2Cl_2 (12 mL) were successively added triethylamine (4 mL), $\text{PdCl}_2(\text{PPh}_3)_2$ (125 mg, 178 μmol) and CuI (31.1 mg, 160 μmol) under argon. The resulting reaction mixture was stirred for 22 h at room temperature and directly subjected to flash chromatography on silica gel (EtOAc:hexanes = 1:4 to 3:7) for purification. **7o** was obtained as a yellow oil (720 mg, 77 %): TLC (SiO_2 , EtOAc:hexanes = 1:4, R_f = 0.62); ^1H NMR (400 MHz, CDCl_3) δ 1.22 (m, 12 H), 2.73 (m, 4 H), 2.96 (t, 2 H, J = 2.4 Hz), 3.16 (s, 2 H), 4.20 (m, 8 H), 5.12 (m, 2 H), 5.58 (m, 1 H), 7.19 (m, 1 H), 7.62 (dt, 1 H, J = 8.0 Hz / J = 2.0 Hz), 8.47 (d, 1 H, J = 3.6 Hz), 8.56 (br, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.7, 22.9, 23.4, 36.3, 56.6, 56.7, 61.5, 61.9, 77.3, 78.2, 80.2, 87.9, 119.6, 122.8, 131.9, 138.5, 148.3, 152.3, 168.7, 169.7; IR (neat, cm^{-1}) 2982 (m), 2935 (w), 1736 (s), 1475 (w), 1466 (w), 1445 (w), 1427 (w), 1408 (w), 1388 (w), 1367 (w), 1327 (w), 1290 (m), 1267 (w), 1211 (s), 1194 (s), 1070 (m), 1053 (m), 1041 (w), 858 (m), 806 (w), 706 (w), 450 (s). HRMS (EI) m/z calcd for $\text{C}_{29}\text{H}_{35}\text{NO}_8$ (M) $^+$: 525.2363 found 525.2371 (Δ = 1.6 ppm).

1-Bis[4,4,9,9-tetra(carbethoxy)dodec-11-ene-1,6-diyne] (7q):

Dienetetrayne **7q** is the dimer of **7a**. This compound was formed as side product during the Sonogashira coupling for the synthesis of **7m** and **7o** and isolated. Yellow oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.35); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (t, 24 H, *J* = 7.2 Hz), 2.73 (m, 8 H), 2.90 (m, 4 H), 3.00 (s, 4 H), 4.20 (q, 16 H, *J* = 7.2 Hz), 5.13 (m, 4 H), 5.59 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 22.7, 23.0, 23.3, 36.3, 56.5, 56.7, 61.6, 62.0, 67.8, 72.3, 77.2, 78.3, 119.6, 131.9, 169.7, 168.5; IR (neat, cm⁻¹) 2982 (s), 2937 (m), 1738 (s), 1466 (m), 1444 (m), 1427 (m), 1389 (w), 1367 (m), 1323 (m), 1288 (s), 1248 (s), 1195 (s), 1139 (m), 1095 (m), 1070 (m), 1053 (m), 1015 (m), 926 (m), 856 (s), 680 (w), 652 (w), 450 (s). HRMS (EI) *m/z* calcd for C₄₈H₆₂O₁₆ (M)⁺ 894.4038, found 894.4039 (Δ = 0.1 ppm).

[2+2+2+1] Cycloaddition Products (Continued from the Main Text):

6-Methyl-1,3a,4,9-tetrahydro-3H,7H-2,8-dioxacyclopenta[*e*]azulen-5-one (8b): White solid; m.p. 138-140 °C; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.15); ¹H NMR (400 MHz, CDCl₃) δ 1.83 (s, 3 H), 2.67 (m, 2 H), 3.11 (br, 1 H), 3.46 (dd, 1 H, *J* = 8.4 Hz / *J* = 10 Hz), 4.32 (m, 2 H), 4.47 (m, 3 H), 4.65 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 15.1, 39.2, 41.4, 70.6, 71.9, 73.5, 74.3, 126.6, 128.8, 144.7, 148.0, 196.2; IR (CDCl₃, cm⁻¹) 2843 (m), 2251 (m), 1651 (s), 1605 (m), 1346 (m), 1309 (m), 1107 (m), 1055 (s), 916 (s), 906 (s), 897 (s), 754 (s), 714 (s), 648 (s). HRMS (EI) *m/z* calcd for C₁₂H₁₄O₃ (M)⁺ 206.0943, found 206.0949 (Δ = 2.9 ppm).

5-Methyl-1,3,3a,4,6,8-hexahydro-2,7-dioxa-*as*-indacene (17b): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.42); ¹H NMR (400 MHz, CDCl₃) δ 1.73 (s, 3 H), 2.01 (m, 1 H), 2.22 (m, 1 H), 3.00 (br, 1 H), 3.39 (dd, 1 H, *J* = 8.4 Hz / *J* = 10.0 Hz), 4.27-4.51 (m, 6.5 H), 5.05 (m, 0.5 H); ¹³C NMR (100 MHz, CDCl₃) δ 19.6, 32.4, 41.2, 67.8, 69.3, 69.5, 74.6, 121.6, 126.0, 126.1, 131.5; IR (neat, cm⁻¹) 2927 (m), 2906 (m), 2849 (s), 2380 (w), 2360 (w), 2125 (w), 1350 (w), 1045

(s), 1032 (s). HRMS (EI) m/z calcd for $C_{11}H_{14}O_2$ (M)⁺ 178.0994, found 178.0992 (Δ = -1.1 ppm).

8,8-Bis(carbethoxy)-4-methyl-5-oxo-1,5,6,6a,7,9-hexahydro-3H-2-oxa-cyclopenta[*e*]azulene

(8c): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.26); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (m, 6 H), 1.80 (s, 3 H), 1.96 (dd, 1 H, J = 12.0 Hz / J = 12.8 Hz), 2.65-2.73 (m, 3 H), 2.92-3.06 (m, 3 H), 4.20 (m, 4 H), 4.50-4.65 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 14.9, 38.1, 39.6, 40.9, 44.8, 59.3, 61.9, 72.7, 74.0, 128.1, 129.2, 145.2, 148.1, 170.7, 170.8, 196.9; IR (neat, cm⁻¹) 2982 (s), 2939 (s), 2908 (s), 2835 (s), 1732 (s), 1651 (s), 1600 (s), 1446 (s), 1427 (m), 1365 (s), 1288 (s), 1242 (s), 1191 (s), 1122 (s), 937 (s), 860 (m), 440 (s). HRMS (EI) m/z calcd for $C_{19}H_{24}O_6$ (M)⁺ 348.1573, found 348.1572 (Δ = -0.3 ppm).

7,7-Bis(carbethoxy)-4-methyl-1,3,5,5a,6,8-hexahydroindeno[4,5-*c*]furan (17c): Light yellow

oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.52); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (m, 6 H), 1.68 (s, 3 H), 1.81-2.04 (m, 2 H), 2.16-2.26 (m, 1 H), 2.66-3.05 (m, 4 H), 4.19 (m, 4 H), 4.35-4.47 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 19.5, 35.8, 36.0, 40.0, 41.1, 59.8, 61.6, 69.4, 69.6, 121.5, 126.5, 128.3, 131.4, 171.7, 171.8; IR (neat, cm⁻¹) 2978 (s), 2908 (s), 2847 (s), 2361 (w), 1724 (s), 1446 (m), 1365 (m), 1281 (s), 1250 (s), 1188 (s), 1142 (s), 1095 (s), 1064 (s), 902 (m), 860 (m), 451 (s). HRMS (ESI) m/z calcd for $C_{18}H_{24}O_5Na$ ($M+Na$)⁺ 343.1521, found 343.1513 (Δ = -2.3 ppm).

8,8-Bis(carbethoxy)-6-methyl-5-oxo-1,3a,4,5,7,9-hexahydro-3H-2-oxacyclopenta[*e*]azulene

(8d): 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); ^{13}C NMR (100 MHz, CDCl_3) 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 (neat, 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 $\text{C}_{19}\text{H}_{24}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 371.1471, found 371.1471 (Δ = -1.5 ppm); m/z calcd for $\text{C}_{19}\text{H}_{25}\text{O}_6$ ($\text{M}+\text{H}$) $^{+}$ 349.1651, found 349.1650 (Δ = -0.3 ppm).

8,8-Bis(carbethoxy)-4-methyl-2-(4-methylbenzenesulfonyl)-5-oxo-2,3,5,6a,7,9-hexahydro-

1H,6H-azuleno[4,5-c]pyrrole (8e): White solid; m.p. 150-152 °C; TLC (SiO_2 , EtOAc:hexanes = 3:7, R_f = 0.28); ^1H NMR (400 MHz, CDCl_3) δ 1.25 (m, 6 H), 1.80 (s, 3 H), 1.92 (m, 1 H), 2.43 (s, 3 H), 2.56 (m, 2 H), 2.65 (m, 1 H), 2.81-2.94 (m, 2 H), 3.02 (d, 1 H, J = 19.0 Hz), 3.99-4.23 (m, 8 H), 7.35 (d, 2 H, J = 8.0 Hz), 7.73 (d, 2 H, J = 8.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.0, 15.4, 21.5, 37.7, 40.0, 40.9, 44.7, 52.6, 54.3, 59.1, 62.0, 126.4, 127.8, 129.9, 130.4, 132.6, 144.1, 144.6, 147.7, 170.5, 170.7, 196.4; IR (CDCl_3 , cm^{-1}) 2982 (w), 2350 (w), 1724 (s), 1651 (s), 1597 (m), 1350 (s), 1257 (s), 1196 (s), 1165 (s), 1095 (s), 1068 (m), 667 (s), 609 (s), 471 (s). HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{32}\text{NO}_7\text{S}$ ($\text{M}+\text{H}$) $^{+}$ 502.1899, found 502.1897 (Δ = -0.4 ppm).

7,7-Bis(carbethoxy)-4-methyl-2-(4-methylbenzenesulfonyl)-2,3,5,5a,6,8-hexahydro-1H-2-aza-

as-indacene (17e): Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 3:7, R_f = 0.52); ^1H NMR (400 MHz, CDCl_3) δ 1.24 (m, 6 H), 1.65 (s, 3 H), 1.78 (m, 2 H), 2.14 (m, 1 H), 2.43 (s, 3 H), 2.60-2.65 (m, 2 H), 2.77 (d, 1 H, J = 19.0 Hz), 2.98 (d, 1 H, J = 19.0 Hz), 3.73-4.00 (m, 4 H), 4.17 (q, 4 H, J = 7.2 Hz), 7.32 (d, 2 H, J = 8.4 Hz), 7.71 (d, 2 H, J = 8.4 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.0, 19.4, 21.5, 35.4, 35.9, 39.6, 41.0, 49.9, 50.1, 59.6, 61.6, 124.1, 125.1, 127.8, 128.1, 129.3,

129.7, 129.8, 143.6, 171.5, 171.6; IR (neat, cm^{-1}) 3456 (w), 3294 (w), 2982 (s), 2924 (s), 2854 (m), 1724 (s), 1597 (m), 1446 (s), 1346 (s), 1250 (s), 1165 (s), 1095 (s), 1057 (s), 860 (m), 814 (s), 710 (s), 667 (s), 463 (s). HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_6\text{SNa}$ ($\text{M}+\text{Na}$)⁺ 496.1770, found 496.1766 ($\Delta = -0.8$ ppm).

2,8-Bis(4-methylbenzenesulfonyl)-6-methyl-2,8-diaza-5-oxo-1,3a,4,5,7,9-hexahydro-3H-

cyclopenta[*e*]azulene (8f): White solid; m.p. 168-170 °C; TLC (SiO_2 , EtOAc:hexanes = 3:7, R_f = 0.13); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 (CDCl_3 , 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 $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_5\text{S}_2$ (M)⁺ 512.1440, found 512.1438 ($\Delta = -0.4$ ppm).

2,7-Bis(4-methylbenzenesulfonyl)-5-methyl-2,7-diaza-1,3a,4,5,7,9-hexahydro-*as*-indacene

(17f): White solid; m.p. 248-250 °C; TLC (SiO_2 , EtOAc:hexanes = 3:7, R_f = 0.30); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 (CDCl_3 , 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 $C_{25}H_{28}N_2O_4S_2$ (M)⁺ 484.1490, found 484.1487 (Δ = -0.6 ppm).

8,8-Bis(carbethoxy)-6-methyl-2-(4-methylbenzenesulfonyl)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-azuleno[4,5-c]pyrrole (8g): White soft needles; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.23); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (q, 6 H, J = 7.2 Hz), 1.89 (s, 3 H), 2.45 (s, 3 H), 2.49-2.68 (m, 3 H), 2.93-3.25 (m, 5 H), 3.69 (m, 1 H), 3.82 (dd, 1 H, J = 9.2 Hz / J = 8.4 Hz), 4.13-4.24 (m, 5 H), 7.36 (m, 2 H), 7.71 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 16.1, 21.6, 37.5, 39.6, 42.2, 43.5, 54.1, 52.4, 56.9, 62.0, 62.1, 127.9, 129.9, 132.0, 132.1, 142.3, 144.1, 148.5, 170.5, 170.7, 196.2; IR (neat, cm⁻¹) 2983 (m), 2930 (m), 2905 (m), 1728 (s), 1643 (s), 1346 (s), 1304 (m), 1265 (s), 1196 (s), 1165 (s), 1095 (m), 1057 (m), 471 (s). HRMS (ESI) m/z calcd for $C_{26}H_{32}NO_7S$ ($M+H$)⁺ 502.1899, found 502.1906 (Δ = 1.4 ppm).

7,7-Bis(carbethoxy)-5-methyl-2-(4-methylbenzenesulfonyl)-2,3,3a,4,6,8-hexahydro-1H-2-aza-as-indacene (17g): White soft needles; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.49); ¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, 3 H, J = 7.2 Hz), 1.23 (t, 3 H, J = 7.2 Hz), 1.69 (s, 3 H), 1.85 (m, 1 H), 2.04-2.12 (m, 1 H), 2.43 (s, 3 H), 2.64 (dd, 1 H, J = 9.2 Hz / J = 10.2 Hz), 2.75-2.95 (m, 5 H), 3.68 (m, 1 H), 3.86 (dd, 1 H, J = 9.2 Hz / J = 7.6 Hz), 4.05 (m, 1 H), 4.17 (m, 4 H), 7.32 (m, 2 H), 7.71 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 19.4, 21.5, 33.3, 36.6, 36.7, 39.4, 49.1, 54.7, 59.2, 61.6, 61.7, 124.1, 124.5, 127.7, 128.7, 129.7, 130.9, 133.2, 143.6, 171.3, 171.4; IR (CDCl₃, cm⁻¹) 2991 (m), 2935 (m), 2905 (m), 2874 (w), 1724 (s), 1342 (m), 1250 (m), 1192 (m), 1161 (s), 1095 (m), 918 (s), 895 (s), 756 (s), 710 (s), 652 (s), 463 (s). HRMS (ESI) m/z calcd for $C_{25}H_{31}NO_6SNa$ ($M+Na$)⁺ 496.1770, found 496.1764 (Δ = -1.2 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 (8h): 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 (8i): 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 (8j): 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{46}\text{H}_{51}\text{O}_5$ ($\text{M}+\text{H}$) $^+$ 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

(8k): Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 2:3, R_f = 0.20); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{26}\text{H}_{34}\text{O}_9\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 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 (8l): Colorless gum; TLC (SiO_2 , EtOAc:hexanes = 2:3, R_f = 0.38); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{24}\text{H}_{35}\text{O}_5$ ($\text{M}+\text{H}$) $^+$ 403.2484, found 403.2488 ($\Delta = 1.0$ ppm).

6-Phenyl-2,2,8,8-tetra(carbethoxy)-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[e]azulene

(8m): Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 1:4, $R_f = 0.17$); ^1H NMR (400 MHz, CDCl_3) δ 1.20 (dt, 6 H, $J = 2.4$ Hz / $J = 7.2$ Hz), 2.01 (dd, 1 H, $J = 11.2$ Hz / $J = 12.8$ Hz), 2.27 (dt, 6 H, $J = 4.0$ Hz / $J = 7.2$ Hz), 2.68-3.13 (m, 10 H), 4.12-4.25 (m, 8 H), 7.03-7.05 (m, 2 H), 7.27-7.38 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.94, 13.96, 13.98, 14.0, 38.0, 39.9, 40.6, 41.1, 43.7, 45.8, 57.3, 59.1, 61.8, 61.9, 127.1, 128.3, 129.1, 129.5, 136.6, 139.0, 149.5, 151.0, 170.5, 170.7, 170.8, 170.9, 196.6; IR (neat, cm^{-1}) 3460 (w), 2982 (s), 2939 (s), 2905 (s), 2874 (m), 2361 (w), 2337 (w), 1724 (s), 1651 (s), 1581 (s), 1443 (s), 1423 (m), 1388 (m), 1365 (s), 1257 (s), 1234 (s), 1188 (s), 1161 (s), 1099 (s), 1072 (s), 1057 (s), 1018 (s), 860 (s), 756 (m), 702 (s), 459 (s). HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{37}\text{O}_9$ ($\text{M}+\text{H}$) $^+$ 553.2438, found 553.2432 ($\Delta = -1.1$ ppm).

5-Phenyl-2,2,7,7-tetra(carbethoxy)-1,3,3a,4,6,8-hexahydro-as-indacene (17m): Colorless oil; white solid upon standing; TLC (SiO_2 , EtOAc:hexanes = 1:4, $R_f = 0.41$); ^1H NMR (400 MHz, CDCl_3) δ 1.22 (t, 3 H, $J = 7.2$ Hz), 1.25 (m, 9 H), 1.93 (t, 1 H, $J = 12.4$ Hz), 2.44-3.20 (m, 10 H), 4.08 (q, 2 H, $J = 7.2$ Hz), 4.21 (m, 6 H), 7.17-7.33 (m, 5 H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9,

14.0, 14.1, 35.0, 36.1, 36.3, 38.9, 40.2, 41.2, 59.6, 59.8, 61.4, 61.6, 126.2, 126.9, 127.1, 128.0, 129.4, 132.3, 134.5, 141.7, 171.3, 171.5, 171.7, 171.8; IR (neat, cm^{-1}) 3433 (m), 2981 (s), 2935 (s), 2905 (s), 2874 (m), 1716 (s), 1597 (m), 1446 (s), 1388 (m), 1365 (s), 1234 (s), 1180 (s), 1095 (s), 1064 (s), 1018 (s), 860 (s), 764 (s), 702 (s), 444 (s). HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{36}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}$)⁺ 547.2308, found 547.2304 ($\Delta = -0.7$ ppm).

2,2,8,8-Tetra(carbethoxy)-6-trimethylsilanyl-5-oxo-1,3a,4,5,7,9-hexahydro-3H-cyclopenta[*e*]azulene (8n): Colorless oil; TLC (SiO_2 , EtOAc:hexanes = 1:4, $R_f = 0.23$); ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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 $\text{C}_{28}\text{H}_{40}\text{O}_9\text{Si}$ (M)⁺ 548.2442, found 548.2446 ($\Delta = 0.7$ ppm).

5-(3-Pyridyl)-2,2,7,7-tetra(carbethoxy)-1,3,3a,4,6,8-hexahydro-*as*-indacene (17o): A 10 mL reaction vessel equipped with a stirring bar and a CO inlet, was charged with $\text{Rh}(\text{acac})(\text{CO})_2$ (2.4 mg, 5 mol%). After purging the reaction vessel with CO, toluene (1 mL) was added to dissolve the catalyst. PhMe_2SiH (30 mL, 1 equiv.) was then added and the mixture was stirred at room temperature. After 5 min., a solution of enediyne **7o** (100 mg, 0.190 mmol) in toluene (0.9 mL) was added and the reaction mixture stirred under CO (1 atm) for 14 h at 60 °C. All volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel using hexanes:EtOAc (9:1 to 7:3) as eluant, affording **17o** as an orange oil (88.2 mg,

88%): TLC (SiO₂, EtOAc:hexanes = 2:3, R_f = 0.29); ¹H NMR (400 MHz, CDCl₃) δ 1.29 (t, 3 H, *J* = 7.2 Hz), 1.22-1.28 (m, 9 H), 1.93 (t, 1 H, *J* = 12.2 Hz), 2.41-3.15 (m, 10 H), 4.09 (qd, 2 H, *J* = 7.2 Hz / *J* = 0.8 Hz), 4.16-4.24 (m, 6 H), 7.23 (ddd, 1 H, *J* = 0.8 Hz / *J* = 4.8 Hz / *J* = 8.0 Hz), 7.55 (dt, 1 H, *J* = 2.0 Hz / *J* = 8.0 Hz), 8.42 (dd, 1 H, *J* = 1.6 Hz / *J* = 4.8 Hz), 8.54 (d, 1 H, *J* = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 14.0, 14.1, 34.4, 35.9, 36.3, 38.8, 40.1, 41.1, 59.5, 59.7, 61.5, 61.6, 61.7, 123.0, 123.5, 129.1, 133.7, 133.8, 136.5, 137.2, 147.3, 148.3, 171.1, 171.2, 171.6, 171.7; IR (neat, cm⁻¹) 2978 (m), 2946 (w), 1736 (s), 1374 (w), 1291 (s), 1242 (s), 1192 (s), 1157 (m), 1099 (w), 1064 (m), 1018 (w), 434 (s). HRMS (EI) *m/z* calcd for C₂₉H₃₅NO₈ (M)⁺: 525.2363, found 525.2372 (Δ = 1.7 ppm).

SiCaT Reaction of Allenyldiynes:

5,5,10,10-Tetra(carbethoxy)-1,2-diene-7,12-diyne (19):

To a solution of propargyl chloride (4.0 g, 52.58 mmol) in Et₂O (100 mL) at -78 °C was added *n*-BuLi (32.86 mL, 52.58 mmol) dropwise. After addition, the resulting reaction mixture was stirred for an additional 2 h at this temperature and added to a suspension of (HCHO)_n (1.66 g) in Et₂O (11 mL) via cannula at 0 °C. The reaction was allowed to warm up to room temperature overnight. After 19 h at room temperature, water was added and the mixture was extracted with

Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:4) afforded 4-chlorobut-2-yn-1-ol¹³ (**46**) as colorless oil (4.05 g, 74 %): ¹H NMR (400 MHz, CDCl₃) δ 1.80 (br, 1 H), 4.17 (t, 2 H, *J* = 2.0 Hz), 4.32 (t, 2 H, *J* = 2.0 Hz).

A solution of **46** (615 mg, 5.88 mmol) in Et₂O (4 mL) was added to a suspension of LiAlH₄ (258 mg, 6.47 mmol) in Et₂O (8 mL) at 0 °C. The resultant reaction mixture was warmed up to room temperature and stirred for 1 h before water and was added. The aqueous layer was extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:4 to 3:7) afforded but-3,4-dien-1-ol¹⁴ (**47**) as colorless oil (335 mg, 80 %): ¹H NMR (400 MHz, CDCl₃) δ 1.75 (br, 1 H), 4.16 (m, 2 H), 4.87 (m, 2 H), 5.35 (m, 1 H).

To a solution of **47** (331 mg, 4.66 mmol) and pyridine (173 μL) in Et₂O (5 mL) at -40 °C, was added PBr₃ (192 μL, 2.02 mmol) over a 15 minutes period. The resulting reaction mixture was stirred for 2 h at -40 °C, warmed to room temperature over a period of 3 h before being heated to 40 °C and stirred for an additional 30 minutes. The obtained orange solution was then poured onto a solution of brine and extracted with Et₂O. The organic layers were dried over Na₂SO₄, filtrated and concentrated under reduced pressure affording 4-bromobut-1,2-diene¹⁵ (**48**), which was used without purification in the next step.

To a suspension of NaH (60% dispersion in mineral oil, 373 mg, 9.32 mmol) in THF (6.6 mL) at 0 °C under argon was added diethyl malonate (1.4 mL, 9.32 mmol). The reaction mixture was warmed up to room temperature and stirred for 1 h. A solution of bromomethylallene **48** (620 mg, 4.66 mmol) in THF (2.2 mL) was then added dropwise and the resultant mixture stirred for an additional 18 h at room temperature. Water was then added and the organic phase was extracted with Et₂O. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded but-3,4-dienylmalonate¹⁵ (**49**) as a colorless oil (712 mg, 72 % for 2 steps): ¹H NMR (400 MHz, CDCl₃) δ 1.27 (t, 6 H, *J* = 7.2 Hz), 2.59 (m, 2 H), 3.47 (t, 1 H, *J* = 7.6 Hz), 4.20 (m, 4 H), 4.72 (m, 2 H), 5.14 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 27.4, 51.6, 61.4, 76.2, 86.8, 168.9, 210.1; IR (neat, cm⁻¹) 2984 (m), 2937 (w), 2906 (w), 1958 (m), 1751 (s), 1732 (s),

¹³ Gerson, F.; Hopf, H.; Merstetter, P.; Mlynek, C.; Fisher, D. *J. Am. Chem. Soc.* **1998**, *120*, 4815-4824.

¹⁴ Bailey, W. J.; Pfeifer, C. R. *J. Org. Chem.* **1955**, *20*, 1337-1341.

¹⁵ Meguro, M.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 694-695.

1466 (s), 1445 (w), 1369 (m), 1334 (m), 1267 (m), 1230 (m), 1155 (m), 1095 (m), 1041 (m), 852 (m), 737 (m), 424 (s). HRMS (EI) m/z calcd for $C_{11}H_{16}O_4$ (M)⁺ 212.1049, found 212.1045 (Δ = -1.9 ppm).

A solution of allenylmethylmalonate **49** (309 mg, 1.46 mmol) in THF (2 mL) was added to a suspension of NaH (60% dispersion in mineral oil, 71 mg, 1.75 mmol) in THF (3 mL) under argon and the resulting mixture was stirred for 2 h at room temperature. A solution of bromodiyne **38** (500 mg, 1.46 mmol) in THF (1 mL) was then added dropwise and the reaction mixture was stirred at room temperature for an additional 3 h. Water was added followed by extraction with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. Flash chromatography on silica gel (EtOAc:hexanes = 1:9) afforded allenyldiyne **19** as a light yellow oil (561 mg, 81%): 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), 1.24 (t, 6 H, J = 7.2 Hz), 1.73 (t, 3 H, J = 2.4 Hz), 2.71 (dt, 2 H, J = 8.0 Hz / J = 2.4 Hz), 2.79 (t, 2 H, J = 2.4 Hz), 2.85 (q, 2 H, J = 2.4 Hz), 2.90 (t, 2 H, J = 2.4 Hz), 4.19 (m, 8 H), 4.66 (dt, 2 H, J = 6.4 Hz / J = 2.4 Hz), 4.93 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 3.4, 14.0, 22.7, 22.8, 31.5, 56.7, 57.2, 61.5, 61.7, 73.2, 74.6, 77.2, 77.6, 77.7, 78.7, 84.0, 169.0, 169.6, 210.1; IR (neat, cm⁻¹) 2932 (m), 2935 (w), 1950 (w), 1736 (s), 1429 (w), 1367 (m), 1325 (w), 1288 (s), 1244 (m), 1207 (s), 1153 (w), 1095 (m), 1070 (m), 1053 (m), 1016 (w), 858 (m), 450 (s). HRMS (EI) m/z calcd for $C_{26}H_{34}O_8$ (M)⁺ 474.2254, found 474.2253 (Δ = -0.2 ppm).

4-Methyl-2,2,8,8-tetra(carbethoxy)-1,6,7,9-tetrahydro-3H-cyclopenta[a]naphthalene (20):

Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.41); ¹H NMR (400 MHz, CDCl₃) δ 1.23 (t, 6 H, J = 7.2 Hz), 1.26 (t, 6 H, J = 7.2 Hz), 2.17 (s, 3 H), 2.28 (t, 2 H, J = 6.6 Hz), 2.74 (t, 2 H, J = 6.6 Hz), 3.08 (s, 2 H), 3.49 (s, 2 H), 3.52 (s, 2 H), 4.20 (m, 8 H), 6.71 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 18.6, 25.7, 28.0, 31.9, 39.2, 39.3, 53.6, 59.7, 61.4, 61.7, 126.7, 128.4, 131.0, 133.3, 136.4, 138.2, 171.4, 171.9; IR (neat, cm⁻¹) 3464 (w), 2982 (s), 2935 (s), 2904 (s), 2365 (w), 1724 (s), 1443 (s), 1388 (m), 1365 (s), 1296 (s), 1242 (s), 1180 (s), 1165 (s), 1053 (s), 1029 (s), 860 (s), 771 (m), 702 (m), 459 (s). HRMS (ESI) m/z calcd for $C_{26}H_{34}O_8Li$ (M+Li)⁺ 481.2414,

found 481.2413 ($\Delta = -0.2$ ppm).

Reactions of Diynals Under CO-SiCaT and [2+2+2+1] Cycloaddition Conditions:

4,4,9,9-Tetra(carbethoxy)undeca-6,11-diyn-1-al (**21a**):

To a suspension of NaH (60% dispersion in mineral oil, 1.64 g, 40.9 mmol) in THF (100 mL) was added dropwise a solution of diethyl (1,1-diethoxyethyl)malonate¹⁶ (**50**, 7.55 g, 27.3 mmol) in THF (25 mL) under N₂. The reaction mixture was stirred for 2 h at room temperature. A solution of bromodiyne **28** (8.61 g, 27.3 mmol) in THF (10 mL) was then added dropwise and the resultant mixture stirred for an additional 3 h at room temperature. Water was added and the organic phase was extracted with Et₂O. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded diyneketal **51** as a colorless oil (14.1 g, 95%): TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.38); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, 6 H, *J* = 6.9 Hz), 1.25 (t, 6 H, *J* = 6.9 Hz), 1.27 (t, 6 H, *J* = 6.9 Hz), 1.99 (t, 1 H, *J* = 2.4 Hz), 2.35 (d, 2 H, *J* = 6.0 Hz), 2.83 (m, 2 H), 2.93 (m, 4 H), 3.46 (q, 1 H, *J* = 7.2 Hz), 3.47 (q, 1 H, *J* = 7.2 Hz), 3.63 (q, 1 H, *J* = 7.2 Hz), 3.64 (q, 1 H, *J* = 7.2 Hz), 4.19 (q, 4 H, *J* = 6.9 Hz), 4.20 (q, 4 H, *J* = 6.9 Hz), 4.51 (t, 1 H, *J* = 6.0 Hz).

¹⁶ Wermuth, C. G.; Bourguignon, J. -J.; Schlewer, G.; Gies, J. -P.; Schoenfelder, A.; Melikian, A.; Bouchet, M. - J.; Chantreux, D.; Molimard, J. - C.; Heaulme, M.; Chambon, J. -P.; Biziere, K. *J. Med. Chem.* **1987**, *30*, 239-249.

p-Toluenesulfonic acid (96 mg, 0.38 mmol) was added to a solution of diyneketal **51** (2.0 g, 3.81 mmol) in a mixture of acetone/water (10:1, 50 mL). The reaction mixture was refluxed for 10 h, concentrated under reduced pressure, diluted with Et₂O and washed with water and brine successively. The organic layer was dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:4) afforded diynal **21a** as a colorless oil (1.37 g, 80%): TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.4); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, 6 H, *J* = 7.1 Hz), 1.25 (t, 6 H, *J* = 7.1 Hz), 1.99 (t, 1 H, *J* = 2.4 Hz), 2.83 (s, 6 H), 3.08 (d, 2 H, *J* = 1.2 Hz), 4.13 (q, 4 H, *J* = 7.1 Hz), 4.14 (q, 4 H, *J* = 7.1 Hz), 9.64 (t, 1 H, *J* = 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.4, 13.7, 22.1, 22.3, 23.6, 45.5, 53.8, 55.9, 61.6, 61.7, 70.9, 71.9, 77.8, 78.2, 168.5, 168.7, 198.6; IR (neat, cm⁻¹) 3282 (m), 2982 (m), 2926 (m), 2853 (m), 1737 (s), 1465 (m), 1447 (m), 1368 (m), 1324 (m), 1291 (s), 1209 (s), 1197 (s), 1094 (m), 1077 (m), 1054 (m), 1015 (m), 440 (s). HRMS (EI) *m/z* calcd for C₂₃H₃₀O₉ (M)⁺ 450.1888, found 450.1890 (Δ = 0.4 ppm).

4,4,9,9-Tetra(carbethoxy)dodeca-6,11-diyn-1-al (**21b**):

To a suspension of NaH (60% dispersion in mineral oil, 90.9 mg, 2.3 mmol) in THF (5.6 mL) was added a solution of malonateketal **50** (419 mg, 1.5 mmol) in THF (1.4 mL) under N₂. The reaction mixture was stirred for 2 h at room temperature. A solution of bromodiyne **38** (520 mg, 1.5 mmol) in THF (0.6 mL) was then added dropwise and the resultant mixture stirred for an additional 3 h at room temperature. Water was then added and the organic phase was extracted with Et₂O. The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc:hexanes = 1:9 to 1:4) afforded diyneketal **52** as pale yellow oil (772 mg, 95%): TLC (SiO₂, EtOAc:hexanes = 1:4, R_f =

0.38); ^1H NMR (400 MHz, CDCl_3) δ 1.18 (m, 6 H), 1.22 (m, 12 H), 1.72 (t, 3 H, $J = 2.6$ Hz), 2.36 (d, 2 H, $J = 5.7$ Hz), 2.81 (m, 2 H), 2.84 (m, 2 H), 2.89 (m, 2 H), 3.45 (m, 2 H), 3.63 (m, 2 H), 4.18 (m, 8 H), 4.52 (t, 1 H, $J = 5.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 3.4, 13.9, 14.0, 15.1, 22.7, 22.8, 23.3, 35.7, 54.7, 56.7, 61.4, 61.7, 62.1, 73.2, 77.7, 77.9, 78.7, 100.3, 169.0, 169.9. HRMS (EI) m/z calcd for $\text{C}_{28}\text{H}_{43}\text{O}_{10}$ ($\text{M}+\text{H}$) $^+$: 539.2856 found 539.2842 ($\Delta = -2.6$ ppm).

p-Toluenesulfonic acid (67.6 mg, 0.26 mmol) was added to a solution of diyneketal **52** (1.42 g, 2.64 mmol) in a mixture of acetone/water (10:1, 35 mL). The reaction mixture was refluxed for 13 h, concentrated under reduced pressure, diluted with Et_2O and washed with water and brine successively. The organic layer was dried over Na_2SO_4 , filtrated and concentrated under vacuum. Flash chromatography on silica gel (EtOAc :hexanes = 1:4) afforded **21b** as a colorless oil (1.17 g, 96%): TLC (SiO_2 , EtOAc :hexanes = 1:4, $R_f = 0.4$); ^1H NMR (400 MHz, CDCl_3) δ 1.24 (m, 12 H), 1.73 (t, 3 H, $J = 2.6$ Hz), 2.83 (m, 2 H), 2.90 (m, 4 H), 3.17 (d, 2 H, $J = 1.2$ Hz), 4.20 (m, 8 H), 9.74 (t, 1 H, $J = 1.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 3.4, 13.9, 14.0, 22.7, 22.8, 24.1, 45.9, 54.2, 56.6, 61.7, 62.1, 73.0, 77.6, 78.5, 78.9, 168.9, 169.0, 198.9; IR (neat, cm^{-1}) 2982 (w), 1736 (s), 1448 (w), 1429 (w), 1367 (w), 1325 (w), 1288 (m), 1209 (s), 1197 (s), 1093 (w), 1070 (w), 1053 (w), 1016 (w), 860 (m), 440 (s). HRMS (EI) m/z calcd for $\text{C}_{24}\text{H}_{32}\text{O}_9$ (M) $^+$ 464.2046, found 464.2047 ($\Delta = 0.2$ ppm).

Reaction of undeca-5,10-diyn-1-al (21a): A 10mL reaction vessel equipped with stirring bar and a CO inlet, was charged with $\text{Rh}(\text{acac})(\text{CO})_2$ (1.4 mg, 5 mol%). After purging the reaction vessel with CO, toluene (1.1 mL) was added to dissolve the catalyst. Dimethylphenylsilane (17.6 μL , 0.11 mmol, 1 eq.) was then added and the mixture was stirred at ambient temperature. After 5 min, a solution of diynal **21a** (50 mg, 0.11 mmol) was added and the reaction mixture stirred at 50 $^\circ\text{C}$ under CO (1 atm) for 24h. All volatiles were removed under reduced pressure. The crude was purified by column chromatography on silica gel using hexanes/ EtOAc 5:1 as eluent to give **22** as a colorless oil (52 mg, 81%).

3,3,3',3'-Tetra(carbethoxy)-5-(*E*)-(dimethylphenylsilyl)methylene-5'-hydroxybicyclopentylidene (22): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.28); ¹H NMR (300 MHz, CDCl₃) δ 0.40 (s, 3 H), 0.42 (s, 3 H), 1.19 (t, 3 H, *J* = 6.9 Hz), 1.20 (t, 3 H, *J* = 6.9 Hz), 1.25 (t, 3 H, *J* = 6.9 Hz), 1.26 (t, 3 H, *J* = 6.9 Hz), 2.42 (dd, 1 H, *J* = 6.0 Hz / *J* = 14.4 Hz), 2.57 (bs, 1 H), 2.79 (d, 1 H, *J* = 18.9 Hz), 2.94 (dd, 2 H, *J* = 9.0 Hz / *J* = 2.4 Hz), 3.09 (d, 2 H, *J* = 6.9 Hz); 3.18 (d, 1 H, *J* = 18.9 Hz); 4.15 (m, 9 H); 4.89 (t, 1 H, *J* = 5.4 Hz); 6.30 (s, 1 H); 7.32 (m, 3 H); 7.54 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ -1.6, -1.4, 13.9, 13.9, 39.3, 39.8, 41.8, 43.6, 57.5, 58.3, 61.6, 61.7, 62.0, 71.4, 123.9, 127.9, 129.0, 133.9, 136.3, 138.1, 153.1, 171.4, 171.4; IR (neat, cm⁻¹) 3519 (W), 3464 (w), 3069 (w), 3050 (w), 2981 (m), 2957 (w), 2907 (w), 1730 (s), 1632 (w), 1465 (w), 1446 (w), 1445 (w), 1427 (m), 1390 (w), 1367 (m), 1282 (s), 1248 (s), 1247 (s), 1192 (s), 1161 (m), 1113 (m), 1097 (m), 1069 (m). HRMS (EI) *m/z* calcd for C₃₁H₄₂O₉Si (M)⁺ 586.2598, found 586.2596 (Δ = - 0.3 ppm).

3,3,3',3'-Tetra(carbethoxy)-5-(dimethylphenylsilyl)methylbicyclopentyl-5,5'-diene (23): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 1:4, R_f = 0.25); ¹H NMR (300 MHz, CDCl₃) δ 0.33 (m, 6 H), 0.39 (m, 2 H), 1.25 (m, 12 H), 2.94 (d, 4 H, *J* = 14.9 Hz), 3.18 (d, 4 H, *J* = 14.9 Hz), 4.15 (m, 8 H), 5.37 (s, 1 H), 7.32 (m, 3 H), 7.54 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ -1.6, -1.4, 13.9, 13.9, 20.2, 39.8, 42.0, 43.3, 47.2, 65.7, 59.2, 61.4, 61.5, 124.0, 125.2, 129.0, 136.7, 171.2, 172.3.

[2+2+2+1] cycloaddition reaction of dodeca-5,10-diyn-1-al (21b): Diynal **21b** (50 mg, 0.108 mmol) was introduced to a Schlenck tube, followed by toluene (1.08 mL) under argon, and then CO was bubbled into the solution at room temperature. After 15 min, [Rh(COD)Cl]₂ (2.7 mg, 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 24 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 **24b** (12.8 mg, 24%), **25b** (21.8 mg, 41%) and **26b** (16.5 mg, 33%).

6-Methyl-2,2,8,8-tetra(carbethoxy)-5-oxo-1,3,3a,5,7,9-hexahydro-4-oxa-cyclopenta[e]azulene

(24b): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.30); ¹H NMR (400 MHz, CDCl₃) δ 1.26 (m, 12 H), 2.05 (s, 3 H), 2.43 (dd, 1 H, *J* = 7.2 Hz / *J* = 14.0 Hz), 2.90-3.26 (m, 7 H), 4.21 (m, 8 H), 4.93 (t, 1 H, *J* = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.92, 13.95, 14.0, 18.2, 37.3, 38.2, 39.1, 39.8, 57.6, 59.0, 61.9, 62.0, 62.1, 76.3, 125.8, 135.9, 140.1, 148.1, 168.3, 169.8, 170.4, 170.5, 170.7; IR (neat, cm⁻¹) 2982 (s), 2939 (m), 1732 (s), 1639 (s), 1446 (m), 1365 (m), 1281 (s), 1238 (s), 1196 (s), 1161 (s), 1068 (s), 1057 (s), 860 (m), 470 (s). HRMS (EI) *m/z* calcd for C₂₅H₃₂O₁₀ (M)⁺ 492.1995, found 492.1992 (Δ = - 0.6 ppm).

6-Methyl-2,2,8,8-tetra(carbethoxy)-5-oxo-1,3,5,6,7,9-hexahydro-4-oxa-cyclopenta[e]azulene

(25b): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.43); ¹H NMR (400 MHz, CDCl₃) δ 1.25 (m, 12 H), 1.44 (d, 3 H, *J* = 7.2 Hz), 2.87 (m, 1 H), 2.94-3.28 (m, 8 H), 4.22 (m, 8 H); ¹³C NMR (100 MHz, CDCl₃) δ 12.4, 13.97, 14.0, 37.7, 39.3, 39.7, 40.1, 40.2, 55.4, 58.4, 61.9, 62.1, 114.6, 130.8, 131.1, 144.8, 165.8, 170.7, 171.0, 171.1, 171.6; IR (neat, cm⁻¹) 2982 (s), 2939 (s), 1724 (s), 1655 (m), 1446 (s), 1385 (s), 1365 (s), 1249 (s), 1188 (s), 1157 (s), 1072 (s), 860 (s), 463 (s). HRMS (EI) *m/z* calcd for C₂₅H₃₂O₁₀ (M)⁺ 492.1995, found 492.1994 (Δ = - 0.2 ppm).

3,3,3',3'-Tetra(carbethoxy)-5-acetyl-bicyclopentyl-5,5'-diene (26b): Colorless oil; TLC (SiO₂, EtOAc:hexanes = 3:7, R_f = 0.37); ¹H NMR (400 MHz, CDCl₃) δ 1.24 (t, 6 H, *J* = 7.2 Hz), 1.25 (t, 6 H, *J* = 7.2 Hz), 2.24 (s, 3 H), 3.09 (s, 2 H), 3.11 (t, 2 H, *J* = 1.6 Hz), 3.29 (d, 2 H, *J* = 1.6 Hz), 3.35 (s, 2 H), 4.20 (m, 8 H), 5.79 (t, 1 H, *J* = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 29.6, 40.7, 41.7, 42.5, 44.5, 56.7, 59.1, 61.7, 61.9, 131.0, 135.2, 135.9, 140.7, 171.1, 171.6, 198.7; IR (neat, cm⁻¹) 2982 (s), 2939 (m), 2908 (m), 1732 (s), 1686 (s), 1659 (m), 1431 (m), 1365 (s), 1257 (s), 1184 (s), 1161 (s), 1076 (s), 1057 (s), 1015 (s), 860 (m), 470 (s). HRMS (EI) *m/z* calcd for C₂₄H₃₂O₉ (M)⁺ 464.2046, found 464.2042 (Δ = - 0.9 ppm).