Cyclization/Hydrosilylation of Functionalized Diynes Catalyzed by a Cationic Platinum Phenanthroline Complex

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Supporting Information

Experimental procedures and analytical and spectroscopic data for new compounds (12 pages).

Experimental

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained at 300 MHz for ^{1}H and at 75 MHz for ^{13}C in $CDCl_3$ unless otherwise specified. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). CH_2Cl_2 and 1,2-dichloroethane (DCE) were distilled from CaH_2 under nitrogen. Toluene (Aldrich, anhydrous) and silanes (Aldrich) were used as received. The synthesis of dimethyl dipropargylmalonate (**1**), 4,4-bis(hydroxymethyl)-1,6-heptadiyne, and 2,2-dimethyl-5,5-di-prop-2-ynyl-[1,3] dioxane (Table 1, entry 7) have been reported.[1]

Diynes

4,4-Bis(trimethylacetoxymethyl)-1,6-heptadiyne (Table 1, entry 4). A solution of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (1.15 g, 7.6 mmol), trimethylacetylchloride (2.68 g, 22 mmol, NEt_3 (2.2 g, 22 mmol), and DMAP (125 mg, 1 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 12 h. Aqueous work-up and chromatography (SiO_2; EtOAc–hexane = 24:1) gave 4,4-bis(trimethylacetoxymethyl)-1,6-heptadiyne (1.05 g, 41%) as a colorless oil. ^{1}H NMR: δ 4.07 (s, 4 H), 2.40 (d, J = 2.7 Hz, 4 H), 2.02 (t, J = 2.7 Hz, 2 H), 1.19 (s, 18 H). $^{13}C\{^{1}H\}$ NMR: δ 177.8, 78.9, 71.8, 40.6, 39.0, 27.2, 22.4. Anal. calcd. (found) for $C_{19}H_{28}O_4$: C, 71.22 (71.29); H, 8.81 (8.99).

4,4-Dibenzyloxymethyl-1,6-heptadiyne (Table 1, entry 5). A solution of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (1.25 g, 8.2 mmol) in THF (5 mL) and benzyl bromide (4.0 g, 23 mmol) were added sequentially to a suspension of NaH (60% in oil, 1.0 g, 25 mmol) in THF (15 mL) and the resulting solution was stirred at room temperature for 12 h. Aqueous work up and chromatography (SiO_2; EtOAc–hexane = 24:1) gave 4,4-dibenzyloxymethyl-hepta-1,6-diyne (1.1 g, 38%) as a colorless oil. ^{1}H NMR: δ 7.30 (s, 10 H), 4.51 (s, 4 H), 3.50

(s, 4 H), 2.42 (d, J = 2.7 Hz, 4 H), 1.94 (t, J = 2.7 Hz, 2 H). $^{13}C\{^1H\}$ NMR: δ 138.7, 128.4, 127.7, 127.6, 80.9, 73.5, 71.3, 70.8, 42.2, 22.2. Anal. calcd. (found) for $C_{23}H_{24}O_2$: C, 83.10 (83.16); H, 7.28 (7.23).

4,4-Bis-(*t*-butyldimethylsilyloxymethyl)-1,6-heptadiyne (Table 1, entry 6). A solution of TBDMSCl (2.2 g, 14.7 mmol) in CH_2Cl_2 (10 mL) was added slowly to a solution of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (1.0 g, 6.6 mmol) and triethylamine (1.6 g, 15.8 mmol) in CH_2Cl_2 (20 mL) and the resulting solution was stirred at room temperature for 4 h. Aqueous work up and chromatography (SiO_2; hexane–ether = 50:1 → 5:1) gave 4-hydroxymethyl-(*t*-butyldimethylsilyloxymethyl)-1,6-heptadiyne (**S1**) (1.7 g, 6.4 mmol, 97%) as a colorless oil. **S1** (1.0 g, 3.8 mmol) and a solution of TBDMSCl (1.0 g, 6.7 mmol) in THF (5 mL) were added sequentially to a slurry of NaH (0.20 g, 5.0 mmol) in THF (15 mL) and the resulting suspension was refluxed for 10 h. Aqueous work up and chromatography (SiO_2; hexane–ether = 50:1) gave 4,4-bis-(*t*-butyldimethylsilyloxymethyl)-1,6-heptadiyne (0.81 g, 2.13 mmol, 57%) as a colorless oil.

For S1: ^1H NMR (400 MHz): δ 3.69 (d, J = 6.0 Hz, 2 H), 3.67 (s, 2 H), 2.58 (t, J = 6.0 Hz, 1 H), 2.34 (dd, J = 2.8, 4.8 Hz, 4 H), 2.01 (t, J = 2.8 Hz, 2 H), 0.90 (br s, 9 H), 0.08 (br s, 6 H). $^{13}C\{^1H\}$ NMR (100 MHz): δ 80.6, 71.1, 67.2, 67.0, 42.2, 26.0, 25.8, 21.7, 18.3, –5.5.

For 4,4-Bis-(*t*-butyldimethylsilyloxymethyl)-1,6-heptadiyne: ^1H NMR (400 MHz): δ 3.53 (s, 3 H), 2.28 (d, J = 2.8 Hz, 4 H), 1.95 (t, J = 2.8 Hz, 2 H), 0.89 (s, 18 H), 0.05 (s, 12 H). $^{13}C\{^1H\}$ NMR (100 MHz): δ 81.3, 71.3, 63.4, 43.5, 26.0, 21.1, 18.5, –5.4. IR (neat, cm^{-1}): 3312, 2954, 2929, 2857, 1459, 1463, 1255. Anal. calcd (found) for $C_{21}H_{40}O_2Si_2$: H, 10.69 (10.84); C, 66.25 (66.40).

4-Carbomethoxy-4-phenyl-1,6-heptadiyne (Table 1, entry 8). Methyl phenyl acetate (2.0 g, 13.3 mmol) and propargyl bromide (6.0 g, 40.3 mmol) were added sequentially to a slurry of NaH (1.2 g, 30 mmol) in THF (50 mL) at 0 °C and the resulting suspension was stirred at room temperature for 60 h. Aqueous work up and chromatography (SiO_2; hexanes–ether = 10:1) gave 4-carbomethoxy-4-phenyl-1,6-heptadiyne (1.5 g, 50%) as a white

solid. ^{1}H NMR: δ 7.24-7.37 (m, 5 H), 3.69 (s, 3 H), 3.12 (dq, *J* = 2.6, 7.0 Hz, 4 H), 1.97 (d, *J* = 2.6 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 172.8, 138.5, 127.8, 127.0, 125.3, 79.2, 70.7, 52.4, 52.0, 24.8. IR (neat, cm^{-1}): 3296, 3286, 1729, 1290, 1218. Anal. calcd (found) for $C_{15}H_{14}O_2$: H, 6.24 (6.29); C, 79.62 (79.39).

1-Carbomethoxy-1-methanesulfonyl-1,6-heptadiyne (Table 1, entry 9). Methyl methanesulfonyl acetate (2.02 g, 13.3 mmol) and propargyl bromide (6.0 g, 40.3 mmol) were added sequentially to a slurry of NaH (1.2 g, 30 mmol) in THF (50 mL) at 0 ºC and the resulting suspension was stirred at room temperature for 3 h. Aqueous work up and chromatography (SiO_2; hexanes–EtOAc = 4:1 → 2:1) gave 1-carbomethoxy-1-methanesulfonyl-1,6-heptadiyne (2.0 g, 66%) as a slightly yellowish solid. ^{1}H NMR (400 MHz): δ 3.88 (s, 3 H), 3.20 (d, *J* = 2.0 Hz, 4 H), 3.13 (s, 3 H), 2.18 (t, *J* = 2.4 Hz, 2 H). ^{13}C{^{1}H} NMR: δ 166.9, 77.2, 73.2, 72.2, 54.2, 39.5, 21.5. IR (neat, cm^{-1}): 3297, 3282, 3012, 2963, 2932, 1780, 1438, 1328, 1301, 1217, 1225. Anal. calcd (found) for $C_{10}H_{12}O_4S$: H, 5.30 (5.43); C, 52.62 (52.64).

4-Carbomethoxy-4-dimethylcarbamoyl-1,6-heptadiyne (Table 1, entry 10). Malonamic acid methyl ester (2.0 g, 17.1 mmol) and propargyl bromide (7.6 g, 51.0 mmol) were added sequentially to a slurry of NaH (1.5 g, 37.5 mmol) in THF (50 mL) at 0 ºC and the resulting suspension was stirred at room temperature for 1.2 h. Aqueous work up and chromatography (SiO_2; hexanes then acetone) gave 4-carbomethoxy-4-carbamoyl-1,6-heptadiyne (**S2**) (1.5 g, 6.7 mmol, 50%) as a white solid. A solution of **S2** (1.0 g, 5.2 mmol) in THF (5 mL) and methyl iodide (3 mL, 47 mmol) were added sequentially to a slurry of NaH (0.6 g, 15 mmol) in THF (15 mL) and the resulting suspension was stirred at room temperature for 30 minutes. Aqueous work up and chromatography (hexane–EtOAc = 4:1 → 2:1) gave 4-carbomethoxy-4-dimethylcarbamoyl-1,6-heptadiyne (260 mg, 23%) as a white solid.

For S2: ^{1}H NMR (400 MHz, DMSO): δ 3.79 (s, 3 H), 3.03 (d, *J* = 2.8 Hz, 4 H), 2.95 (s, 6 H), 2.04 (t, *J* = 2.4 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz, DMSO): δ 171.6, 167.3, 78.7, 72.1, 55.7, 533, 37.3, 24.1.

For 4-carbomethoxy-4-dimethylcarbamoyl-1,6-heptadiyne: ^{1}H NMR (400 MHz): δ 3.79 (s, 3 H), 3.03 (d, *J* = 2.8 Hz, 4 H), 2.95 (s, 6 H), 2.04 (t, *J* = 2.4 Hz, 2 H). ^{13}C{^{1}H} NMR (100 MHz): δ 171.6, 78.7, 72.1, 55.7, 53.3, 37.3, 24.1. IR (neat, cm^{-1}): 3283, 3237, 1735, 1653, 1638, 1302. Anal. calcd (found) for $C_{12}H_{15}NO_3$: H, 6.83 (6.73); C 65.14 (65.27); N 6.33 (6.32)

4,4-Dicarbomethoxy-3-methyl-1,6-heptadiyne (Table 1, entry 11). Dimethyl propargylmalonate (2.0 g, 11.8 mmol) and 3-bromo-3-methyl-1-butyne (1.9 g, 14.3 mmol) were added sequentially to a slurry of NaH (0.8 g, 20.0 mmol) in THF (30 mL) at 0 ºC and the resulting suspension was refluxed for 6 h. Aqueous work up and chromatography (SiO_2; hexane–ether = 50:1 → 12:1) gave 4,4-dicarbomethoxy-3-methyl-1,6-heptadiyne (360 mg, 1.62 mmol, 14%) as a colorless oil. ^{1}H NMR (400 MHz): δ 3.71 (s, 3 H), 3.46 (dq, *J* = 2.8, 7.2 Hz, 1 H), 3.11 (dd, *J* = 2.8, 7.2 Hz, 1 H), 2.89 (dd, *J* = 2.8, 7.2 Hz, 1 H), 2.15 (d, *J* = 2.8 Hz, 1 H), 2.04 (t, *J* = 2.8 Hz, 1 H), 1.38 (d, *J* = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR (100 MHz): δ 169.4, 169.1, 83.9, 79.1, 71.8, 71.5, 59.9, 53.0, 52.8, 30.3, 23.7, 17.5. IR (neat, cm^{-1}): 3289, 2954, 1738, 1731, 1434, 1230. Anal. calcd (found) for $C_{12}H_{14}O_4$: H, 6.35 (6.35); C, 64.85 (64.63).

4,4,5,5-Tetracarboethoxy-1,7-octadiyne (Table 1, entry 12). A suspension of 1,1,2,2-tetracarboethoxyethane (10 g, 31 mmol), NaH (60% in oil, 3.7 g, 92 mmol), and propargyl bromide (80% by weight in toluene, 25 g, 170 mmol) in THF (100 mL) was refluxed overnight . Aqueous work up and chromatography (SiO_2; EtOAc–hexane = 3:1) gave 4,4,5,5-tetracarboethoxy-1,7-octadiyne (9.52 g, 77%) as a tan solid. ^{1}H NMR: δ 4.17 (m, 8 H), 3.06 (d, *J* = 2.6 Hz, 4 H), 1.97 (t, *J* = 2.6 Hz, 2 H), 1.22 (t, *J* = 7.2 Hz, 12 H). ^{13}C{^{1}H} NMR: δ 168.4, 79.9, 71.1, 62.2, 61.5, 22.7, 13.9. Anal. calcd. (found) for $C_{20}H_{26}O_8$: C, 60.90 (61.23); H, 6.64 (6.80).

1,2-Dialkylidenecycloalkanes

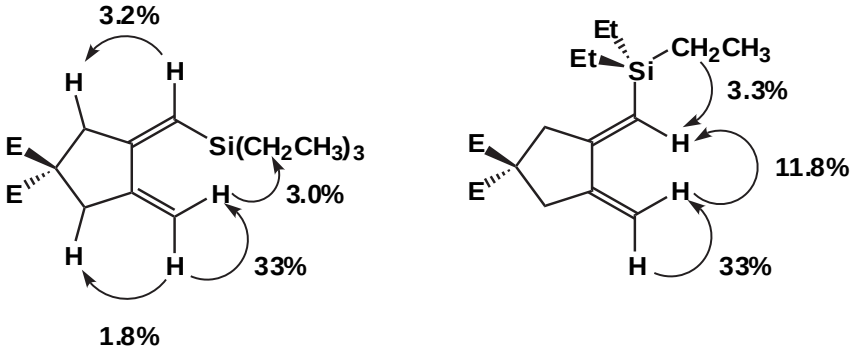
General Procedure for Cyclization/Hydrosilylation. Toluene (20 mL) was added to a mixture of (phen)Pt(Me)$_2$ (9 mg, 0.023 mmol), B(C_6F_5)$_3$ (12 mg, 0.023 mmol), and diyne (0.5 mmol) at 0 °C. The resulting orange solution was heated at 110 °C for 1-3 h, cooled to

room temperature and concentrated under vacuum. Evaporation of solvent and chromatography of the residue on neutral grade III alumina gave the 1,2-dialkylidenecyclopentane as a colorless oil or solid.

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-(triethylsilylmethylene) cyclopentane (*Z*-2). ^{1}H NMR: δ 5.41 (t, *J* = 1.9 Hz, 1 H), 5.31 (t, *J* = 2.0 Hz, 1 H), 5.00 (t, *J* = 1.6 Hz, 1 H), 3.70 (s, 6 H), 3.07 (d, *J* = 1.87 Hz, 2 H), 3.03 (t, *J* = 1.9 Hz, 2 H), 0.89 (t, *J* = 7.9 Hz, 9 H), 0.64 (q, *J* = 7.9 Hz, 6 H). IR (neat, cm^{-1}): 2954, 2912, 2876, 1754, 1745, 1738, 1731, 1681, 1651, 1455, 1434, 1257, 1201, 1164, 1073, 1015. ^{13}C{^{1}H} NMR: δ 171.1, 153.4, 146.0, 119.9, 109.2, 56.3, 52.1, 44.8, 41.2, 6.9, 3.5. Anal. calcd. (found) for $C_{17}H_{28}SiO_4$: C, 62.93 (62.79); H, 8.70 (8.68).

(*E*)-1,1-Dicarbomethoxy-3-methylene-4-(triethylsilylmethylene) cyclopentane (*E*-2). ^{1}H NMR: δ 5.97 (t, *J* = 2.4 Hz, 1 H), 5.40 (t, *J* = 2.4 Hz, 1 H), 4.94 (t, *J* = 2.0 Hz, 1 H), 3.73 (s, 6 H), 3.04 (d, *J* = 2.2 Hz, 2 H), 3.03 (t, *J* = 2.1 Hz, 2 H), 0.95 (t, *J* = 8.0 Hz, 9 H), 0.65 (q, *J* = 8.0 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 171.9, 162.7, 145.9, 116.6, 105.7, 57.9, 53.0, 41.5, 40.7, 7.7, 4.3. MS calcd. (found) for $C_{17}H_{29}SiO_4$ (MH^+): 325 (325).

Figure S1. ^{1}H NMR NOE analysis of *E*-**2** and *Z*-**2**.



(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-(dimethyl-*t*-butylsilylmethylene) cyclopentane (Table 1, entry 1). ^{1}H NMR: δ 5.51 (br s, 1 H), 5.31 (t, *J* = 1.9 Hz, 1 H), 5.02 (s, 1 H), 3.70 (s, 6 H), 3.08 (d, *J* = 1.8 Hz, 2 H), 3.02 (br s, 1 H), 0.87 (s, 9 H), 0.08 (s, 6 H).

$^{13}C\{^{1}H\}$ NMR: δ 171.1, 153.3, 144.2, 120.4, 110.1, 56.1, 52.1, 44.7, 41.4, 25.6, 16.4, –5.9. HRMS(EI) calcd. (found) for $C_{17}H_{29}SiO_4$ (MH+): 325.1835 (523.1843).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-(dimethylbenzylsilylmethylene) cyclopentane (Table 1, entry 2). ^{1}H NMR: δ 7.25 - 6.95 (m, 5 H), 5.49 (s, 1 H), 5.29 (s, 1 H), 5.08 (s, 1 H), 3.71 (s, 6 H), 3.06 (m, 4 H), 2.20 (s, 2 H), 0.90 (s, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 171.9, 154.2, 145.3, 140.2, 128.5, 128.3, 124.2, 122.2, 111.2, 57.1, 53.0, 45.5, 42.3, 26.0, –2.1. Anal. calcd. (found) for $C_{20}H_{26}SiO_4$: C, 67.01 (67.12); H, 7.31 (7.10).

(*Z*)-1,1-Dicarbomethoxy-3-methylene-4-(tributylsilylmethylene) cyclopentane (Table 1, entry 3). ^{1}H NMR: δ 5.42 (t, *J* = 1.8 Hz, 1 H), 5.30 (t, *J* = 2.2 Hz, 1 H), 5.00 (t, *J* = 2.0 Hz, 1 H), 3.70 (s, 6 H), 3.06 (d, *J* = 1.8 Hz, 2 H), 3.03 (t, *J* = 2.1 Hz, 2 H), 1.35 - 1.15 (m, 12 H), 0.85 (t, *J* = 6.8 Hz, 9 H), 0.61 (m, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 172.0, 153.8, 145.5, 121.8, 110.2, 57.2, 52.9, 45.8, 42.2, 26.9, 26.5, 14.0, 13.1. Anal. calcd. (found) for $C_{23}H_{40}SiO_4$: C, 67.60 (67.24); H, 9.87 (9.73).

(*Z*)-1,1-Bis(trimethylacetoxymethyl)-3-methylene-4-(triethylsilylmethylene)cyclopentane (Table 1, entry 4). ^{1}H NMR: δ 5.38 (s, 1 H), 5.32 (br s, 1 H), 4.97 (br s, 1 H), 3.94 (s, 4 H), 2.45 (d, *J* = 1.7 Hz, 2 H), 2.40 (br s, 2 H), 1.18 (s, 18 H), 0.90 (t, *J* = 7.9 Hz, 9 H), 0.63 (q, *J* = 7.9 Hz, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 178.5, 155.9, 146.7, 121.1, 110.6, 66.5, 44.4, 42.9, 40.6, 39.2, 27.4, 7.9, 4.5. Anal. calcd. (found) for $C_{25}H_{44}SiO_4$: C, 68.76 (69.17); H, 10.16 (10.39).

(*Z*)-4,4-Dibenzyloxymethyl-1,6-heptadiyne-3-methylene-4-(triethylsilyl methylene)cyclopentane (Table 1, entry 5). ^{1}H NMR: δ 7.29 (m, 10 H), 5.33 (t, *J* = 1.7 Hz, 1 H), 5.27 (br s, 1 H), 4.91 (br s, 1 H), 4.49 (s, 4 H), 3.37 (s, 4 H), 2.44 (br s, 1 H), 2.44 (d, *J* = 1.9 Hz, 2 H), 2.40 (t, *J* = 1.7 Hz, 2 H), 0.90 (t, *J* = 7.83 Hz, 9 H), 0.62 (q, *J* = 7.8 Hz, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 157.9, 148.2, 139.1, 128.5, 127.6, 119.7, 109.7, 73.4, 73.2, 44.9, 44.5, 40.7, 8.0, 4.6. Anal. calcd. (found) for $C_{29}H_{40}SiO_2$: C, 77.62 (77.35); H, 8.99 (8.84).

(*Z*)-(8,8-Dimethyl-3-methylene-7,9-dioxa-spiro[4.5]dec-2-ylidenemethyl)-triethylsilane (Table 1, entry 7). ^{1}H NMR (400 MHz): δ 5.38 (s, 1 H), 5.31 (s, 1 H), 4.96 (s,

1 H), 3.60 (s, 4 H), 2.41 (d, *J* = 1.6 Hz, 2 H), 2.39 (s, 2 H), 1.40 (s, 6 H), 0.90 (t, *J* = 8.0 Hz, 9 H), 0.60-0.66 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 156.6, 147.2, 120.6, 110.2, 98.0, 68.4, 45.6, 41.5, 38.2, 24.2, 23.8, 7.8, 4.5. IR (neat, cm^{-1}): 2990, 2950, 2871, 1454. Anal. calcd (found) for $C_{18}H_{32}O_2Si$: H, 10.45 (10.42); C, 70.07 (69.83).

(*Z*)-1-Carbomethoxy-3-methylene-1-phenyl-4-(tributylsilylmethylene)-cyclopentane (Table 1, entry 8). ^{1}H NMR: δ 7.20-7.34 (m, 5 H), 5.51 (s, 1 H), 5.34 (s, 1 H), 5.05 (s, 1 H), 3.60 (s, 3 H), 3.45 (dd, *J* = 1.3, 15.2 Hz, 1 H), 3.42 (td, *J* = 1.6, 13.9 Hz, 1 H), 1.20-1.33 (m, 12 H), 0.86 (t, *J* = 7.0 Hz, 9 H), 0.60-0.64 (m, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 174.7, 154.1, 145.1, 141.5, 127.7, 126.3, 125.9, 120.5, 109.0, 54.1, 51.7, 47.8, 44.1, 26.0, 25.6, 25.5, 13.2, 12.2. IR (cm^{-1}, neat): 3030, 2954, 2920, 1733, 1463, 1446. Anal. calcd (found) for $C_{27}H_{42}O_2Si$: H, 9.92 (10.32); C, 76.60 (76.21).

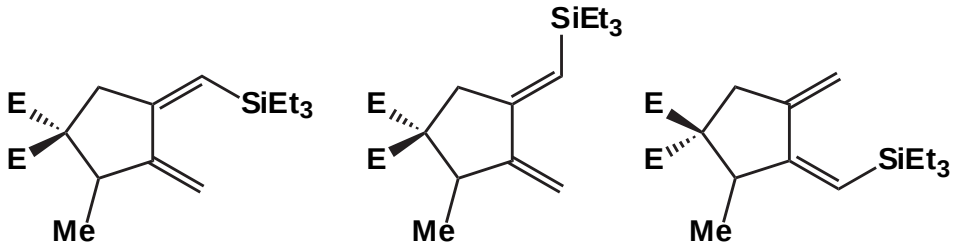
(*Z*)-1-Carbomethoxy-1-methanesulfonyl-3-methylene-4-(triethylsilylmethylene)-cyclopentane (Table 1, entry 9). ^{1}H NMR (400 MHz): δ 5.49 (t, *J* = 2.0 Hz, 1 H), 5.38 (t, *J* = 2.0 Hz, 1 H), 3.79 (s, 2 H), 3.24 (dq, *J* = 2.8, 16.0 Hz, 2 H), 3.22 (d, *J* = 2.4 Hz, 2 H), 3.02 (s, 3 H), 0.90 (t, *J* = 6.8 Hz, 9 H), 0.61-0.67 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 169.3, 152.0, 143.7, 122.6, 111.2, 73.8, 53.9, 42.6, 38.7, 38.4, 7.7, 4.3. IR (neat, cm^{-1}). Anal. calcd (found) for $C_{16}H_{28}O_4SSi$: H, 8.19 (8.45); C, 55.78 (56.01).

(*Z*)-1-Carbomethoxy-1-dimethylcarbamoyl-3-methylene-4-(triethylsilylmethylene)-cyclopentane (Table 1, entry 10). ^{1}H NMR (400 MHz): δ 5.35 (s, 1 H), 5.26 (t, *J* = 2.0 Hz, 1 H), 4.95 (s, 1 H), 3.69 (s, 3 H), 3.15 (td, *J* = 2.0, 15.6 Hz, 1 H), 3.09 (dq, *J* = 2.0, 16.8 Hz, 2 H), 2.94 (d, *J* = 16.4 Hz, 2 H), 2.92 (s, 3H), 2.82 (s, 3 H), 0.88 (t, *J* = 8.0 Hz, 9 H), 0.58-0.64 (m, 6 H). $^{13}C\{^{1}H\}$ NMR (100 MHz): δ 174.1, 170.1, 154.9, 146.1, 119.9, 109.6, 56.1, 52.9, 46.0, 43.0, 37.0, 7.8, 4.7, 4.4. IR (neat, cm^{-1}). Anal. calcd (found) for $C_{18}H_{31}NO_3Si$: H, 9.26 (9.58); C, 64.05 (63.94); N, 4.15 (4.38).

(*Z*)-1,1-Dicarbomethoxy-2-methyl-3-methylene-4-(triethylsilylmethylene)cyclopentane (Table 1, entry 11). The sample employed for spectroscopy consisted of a 1:1 mixture of E/Z isomers. ^{1}H NMR: δ 5.40 (t, *J* = 2.0 Hz, 1 H),

5.35 (d, *J* = 2.4 Hz, 1 H), 5.34 (d, *J* = 2.0 Hz, 1 H), 5.33 (d, *J* = 2.0 Hz, 1 H), 4.99 (t, *J* = 2.4 Hz, 1 H), 4.93 (d, *J* = 2.0 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.67 (s, 3 H),3.30 - 3.15 (m, 4 H), 2.85 - 2.75 (m, 2 H), 1.11 (d, *J* = 7.2 Hz, 3 H), 1.07 (d, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.6 Hz, 9 H), 0.90 (t, *J* = 7.6 Hz, 9 H), 0.68 - 0.62 (m, 12 H). $^{13}C\{^{1}H\}$ NMR: δ 172.1, 170.8, 160.1, 154.1, 151.3, 145.3, 120.2, 118.8, 109.9, 108.8, 61.2, 60.9, 52.8, 52.3, 48.4, 45.7, 43.6, 39.7, 16.4, 15.7, 7.76, 4.44. IR (neat, cm^{-1}). Anal. calcd (found) for $C_{18}H_{30}O_4Si$: H, 8.93 (8.90); C, 63.87 (63.82).

Chart S1. Potentialtial isomers formed in the cyclization/hydrosilylation of 4,4-dicarbomethoxy-3-methyl-1,6-heptadiyne.



Assignment of the isomerics as mixture of E/Z stereoisomers (*Z*-**S3** and *E*-**S3**, Chart S1) rather than a mixture of the 2-methyl/3-methyl regioisomers (*Z*-**S3** and *Z*-**S4**, Chart S1) was based on two spectroscopic features. First, the ^{1}H NMR spectrum of a 1:1 mixture of the isomers displayed four one proton doublets and two one proton triplets in the olefinic region. This pattern is consistent with a 1:1 mixture of *Z*-**S3** and *E*-**S3**, but is inconsistent with a 1:1 mixture of *Z*-**S3** and *Z*-**S4**, which should display three one proton doublets and three one proton triplets in the olefinic region. Secondly, the ^{13}C NMR spectrum of the isomeric mixture displayed an olefinic resonance at δ 160.1. Of all the 1,2-dialkylidenecyclopentanes synthesized in the study, the only other example of an olefinic peak with a chemical shift δ >160 was in the case of *E*-**2** (δ 162.7).

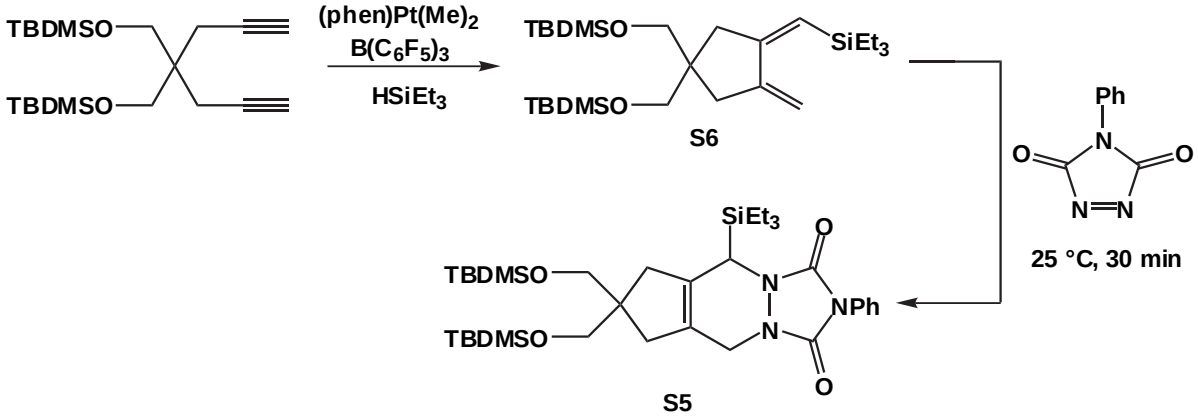
(*Z*)-1,1,2,2-Tetracarboethoxy-4-methylene-5-(triethylsilylmethylene) cyclohexane (Table 1, entry 12). ^{1}H NMR: δ 5.35 (s, 1 H), 5.14 (t, *J* = 2.1 Hz, 1 H), 4.94 (t, *J* = 2.2 Hz, 1 H), 4.31 (q, *J* = 7.0 Hz, 4 H), 4.28 (q, *J* = 7.0 Hz, 4 H), 3.23 (br s, 2 H), 3.09 (br s, 2 H), 1.37 (t, *J* = 7.0 Hz, 6 H), 1.36 (t, *J* = 7.0 Hz, 6 H), 1.01 (t, *J* = 7.7 Hz, 9 H), 0.68 (q, *J* = 7.7 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 168.6, 168.5, 151.7, 143.1, 124.0, 113.0, 60.8, 60.7, 60.6, 58.4, 42.7, 38.1, 13.0, 6.7, 4.0. Anal. calcd. (found) for $C_{26}H_{42}SiO_8$: C, 61.15 (61.05); H, 8.29 (8.37).

Diels–Alder Adducts

Adduct of Diene 2 and N-Phenylmaleimide (3). A solution of **2** (19:1 mixture of E/Z isomers) (88 mg, 0.27 mmol) and N-phenylmaleimide (50 mg, 0.29 mmol) in toluene (4 mL) and stirred at 80 for 20 h. Toluene was evaporated under vacuum and the residue was chromatographed (SiO_2; hexane–EtOAc = 10:1 → 3:1) to give **3** (138 mg, 102%) viscous colorless oil. ^{1}H NMR (400 MHz): δ 7.39 (t, *J* = 7.6 Hz, 2 H), 7.31 (t, *J* = 10.8 Hz, 1 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 3.68 (s, 3 H), 3.60 (s, 3 H), 3.28 (t, *J* = 8.4 Hz, 1 H), 3.17 (d, *J* = 8.4 Hz, 1 H), 3.02 (bd, *J* = 15.6 Hz, 1 H), 2.97 (bd, *J* = 16.4 Hz, 1 H), 2.93 (bd, *J* = 20.0 Hz, 1 H), 2.89 (bd, *J* = 11.6 Hz, 1 H), 2.85 (bd, *J* = 15.2 Hz, 1 H), 2.59 (bd, *J* = 16.8 Hz, 1 H), 2.54 (s, 1 H), 2.30-2.34 (m, 1 H), 0.97 (t, *J* = 7.6 Hz, 9 H), 0.61 (q, *J* = 7.6 Hz, 6 H). ^{13}C{^{1}H} NMR (100 MHz): δ 180.0, 179.4, 172.6, 172.3, 134.3, 132.4, 129.2, 128.7, 127.8, 126.7, 58.2, 53.0, 44.8, 44.0, 40.8, 40.1, 25.0, 24.8, 7.6, 3.5. IR (neat, cm^{-1}): 2953, 2911, 2876, 1737, 1730, 1712, 1598, 1257, 1197. HRMS cacld (found) for $C_{27}H_{35}NO_6Si$ (M^+): 497.2234 (497.2220).

Adduct of 3-Methylene-4-(triethylsilylmethylene)-1,1-bis-(*t*-butyldimethylsilyloxymethyl)cyclopentane (S6) with 4-Phenyl-[1,2,4]triazole-3,5-dione (S5) (Table 1, entry 6). Toluene (20 mL) was added to a mixture of (phen)$PtMe_2$ (19 mg, 0.22 mmol), $B(C_6F_5)_3$ (12 mg, 0.23 mmol), 4,4-bis(*t*-butyldimethylsiloxymethyl)-1,6-heptadiyne (135 mg, 0.36 mmol) at 0 °C and heated at 110 °C for 2 h to form 3-methylene-4-(triethylsilylmethylene)-1,1-bis-(*t*-butyldimethylsilyloxymethyl)-cyclopentane (**S6**) as an 8:1 mixture of E/Z isomers (Scheme S1). (Chromatographic separation of **S6** from disilylated

impurites was unsuccessful due to the low polarity of **S6**). The solution was cooled to 0 °C and treated with 4-phenyl-[1,2,4]triazole-3,5-dione (70 mg, 0.40 mmol) and stirred at room temperature for 30 min. The solvent was evaporated and the residue was chromatographed (SiO_2; hexane–EtOAc = 50:1 → 12:1) to give **S5** (171 mg, 72%) as a white solid. ^{1}H NMR (400 MHz): δ 7.53-7.51 (m, 2 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 4.35 (s, 1 H), 4.18 (bd, *J* = 15.6 Hz, 1 H), 3.95 (bd, *J* = 15.6 Hz, 1 H), 3.44-3.59 (m, 4 H), 2.43 (bd, *J* = 15.6 Hz, 1 H), 2.17 (s, 2 H), 2.12 (t, *J* = 16.4 Hz, 1 H), 0.97 (t, *J* = 7.6 Hz, 9 H), 0.90 (s, 9 H), 0.88 (s, 9 H), 0.57-0.75 (m, 6 H), 0.05 (s, 6 H), 0.03 (s, 6 H). ^{13}C{^{1}H} NMR: δ 154.3, 149.3, 131.8, 131.7, 129.3, 128.1, 125.5, 124.1, 66.0, 65.6, 49.6, 46.8, 46.7, 39.7, 38.7, 26.1, 18.5, 7.3, 3.1, –5.3. IR (neat, cm^{-1}): 2953, 2929, 2880, 2855, 1775, 1720, 1713, 1415, 1254. Anal. calcd (found) for $C_{35}H_{61}N_3O_4Si$: H, 9.15 (9.38); C, 62.54 (62.59); N, 6.25 (6.28).



Scheme S1

References

1) Lautens, M.; Smith, N. D.; Ostrovsky, D. *J. Org. Chem*. **1997**, *62*, 8970.