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Supporting Information

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Highly Stereoselective Synthesis of TMS-, Alkyl-, or Aryl Substituted *cis*-[3]cumulenols *via* α-Alkynylated Zirconacyclopentenes

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Experimental section

All reactions were carried out using standard Schlenk techniques under nitrogen. THF was distilled from sodium, benzophenone. Zirconocene dichloride and EtMgBr (1.0M solution in THF) were purchased from Aldrich Chemical Company. Aldehydes such as butyraldehyde or Pyridine-2-carboxaldehyde were purchased from Acros Co. Ltd. 1,3-Butadiynes were prepared according to the published method.

^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ (containing 0.03% TMS) solutions on Varian XL-300 MHz spectrometer. GC analysis was performed on SHIMADZU GC-14B equipped with fused silica capillary column SHIMADZU CBP1-M25-O25 and SHIMADZU CR8A-Chromatopac integrator. High-resolution mass spectra was obtained by using IonSpec 4.7 Tesla FTMS, Concept 1H Series and APEXIII 7.0 Tesla FTMS mass spectrometers. Single crystal X-ray diffraction data were collected on Bruker SMART APEX diffractiometers with molybdenum anodes.

(*Z*)-5,8-Bis(trimethylsilyl)-deca-5,6,7-trien-4-ol (3a). Column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afford 198 mg (67%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.16 (s, 9H), 0.19 (s, 9H), 0.92 (t, *J*=7.2Hz, 3H), 1.12 (t, *J*=7.2Hz, 3H), 1.41–1.50 (m, 4H), 2.36 (q, *J*=7.2Hz, 2H), 4.36 (m, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.44, -0.64, 13.28, 13.97, 18.746, 28.78, 40.08, 73.47, 131.02, 133.538, 170.62, 170.63. HRMS (MALDI/DHB) for $C_{16}H_{32}OSi_2Na$ $[M+Na]^+$: calcd 319.1889, found 319.1893.

(*Z*)-1-(4-Dimethylaminophenyl)-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (3c). Column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afford

216 mg (58%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 0.37 (s, 9H), 1.30 (t, *J*=7.2Hz, 3H), 2.55 (q, *J*=7.2Hz, 2H), 3.02 (bs, 1H), 3.10 (s, 6H), 5.50 (s, 1H), 6.86 (m, 2H), 7.38 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.39, -0.82, 13.34, 28.74, 40.61, 75.78, 112.44, 128.42, 130.60, 130.67, 132.96, 150.33, 169.00, 170.77. HRMS (EI) for $C_{21}H_{33}NSi_2$ $[M-H_2O]^+$: calcd 355.2152, found 355.2150.

(*Z*)-1-(4-Nitrophenyl)-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (3d). Column chromatography on silica gel (petroleum ether/ethyl acetate=10:1) afford 247 mg (66%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 0.30 (s, 9H), 1.11 (t, *J*=7.2Hz, 3H), 2.44 (q, *J*=7.2Hz, 2H), 3.14 (bs, 1H), 5.61 (s, 1H), 7.66 (d, *J*=8.1Hz, 2H), 8.29 (d, *J*= 8.4Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.49, -0.64, 13.12, 29.02, 75.33, 123.42, 127.20, 127.75, 137.17, 147.15, 150.48, 169.42, 173.41. HRMS (EI) calcd for $C_{19}H_{29}NO_3Si_2$ 375.1686, found 375.1700.

(*Z*)-1-(4-Phenylethynylphenyl)-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (3e). Column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afford 301 mg (70%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 0.32 (s, 9H), 1.21 (t, *J*= 7.2Hz, 3H), 2.47 (q, *J*= 7.2Hz, 2H), 3.19 (bs, 1H), 5.50 (s, 1H), 7.41–7.48 (m, 5H), 7.61–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.49, -0.72, 13.16, 28.83, 75.89, 89.30, 89.34, 122.34, 123.19, 127.14, 128.03, 128.15, 129.14, 131.41, 134.71, 143.09, 170.21, 171.43. HRMS (EI) for $C_{27}H_{32}Si_2$ $[M-H_2O]^+$: calcd 412.2043, found 412.2024.

(*E*)-5-Ethyl-2-propyl-1-(pyridin-2-yl)-octa-2,3,4-trien-1-ol (3f). Column chromatography on silica gel (petroleum ether/ethyl acetate=5:1) afford 165 mg (61%)

product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85–1.00 (m, 9H), 1.45–1.62 (m, 4H), 1.93–2.23 (m, 6H), 4.80 (bs, 1H), 5.32 (s, 1H), 7.18–7.22 (m, 1H), 7.33 (d, *J*= 8.1 Hz, 1H),7.64–7.70 (m, 1H), 8.53 (dd, *J*= 4.2, 0.6Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.13, 13.85, 13.87, 20.82, 20.94, 29.26, 32.68, 38.26, 75.76, 117.74, 121.28, 122.39, 123.85, 136.56, 147.69, 155.14, 158.03, 160.04. HRMS (EI) calcd for $C_{18}H_{25}NO$ 271.1936, found 271.1947.

(*E*)-8-Ethyl-5-propylundeca-5,6,7-trien-4-ol (3g). Column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afford 151 mg (64%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.88–0.97 (m, 9H), 1.11 (t, *J*= 6.9 Hz, 3H), 1.41–1.62 (m, 8H), 1.95 (bs, 1H), 2.13–2.18 (m, 6H), 4.10–4.12 (m,1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.28, 13.86, 13.94, 13.98, 18.65, 20.88, 21.08, 29.19, 33.98, 38.10, 38.27, 73.63, 119.64, 122.38, 154.77, 156.07. HRMS (MALDI/DHB) for $C_{16}H_{28}ONa$ $[M+Na]^+$: calcd 259.2038, found 259.2021.

(*E*)-5-Ethyl-1-phenyl-2-propylocta-2,3,4-trien-1-ol (3h). Column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afford 185 mg (71%) product as a yellow oil. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.86–0.98 (m, 6H), 1.11 (t, *J*= 7.2 Hz, 3H), 1.49–1.63 (m, 4H), 1.98–2.03 (m, 2H), 2.16–2.20 (m, 4H), 2.66 (s, 1H), 5.14 (s, 1H), 7.26–7.41(m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.29, 13.84, 13.90, 20.86, 20.93, 29.24, 33.90, 38.25, 76.10, 119.23, 123.36, 126.81, 127.64, 128.31, 142.37, 154.41, 156.51. HRMS (MALDI/DHB) for $C_{19}H_{26}ONa$ $[M+Na]^+$: calcd 293.1881, found 293.1882.

(*E*)-1,2,5-Triphenylhepta-2,3,4-trien-1-ol (3i). Column chromatography on silica gel

(petroleum ether : ethyl acetate: triethyl amine = 100 : 10 : 2) afforded 220 mg (65%) product as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.08 (t, *J* = 7.4Hz, 3H), 2.50 (q, *J* = 7.4Hz, 2H), 2.93 (bs,1H), 5.87 (s, 1H), 7.14–7.33 (m, 9H), 7.45–7.48 (m, 2H), 7.30–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.74, 26.12, 73.53, 120.98, 124.85, 126.68, 126.78, 127.23, 127.29, 127.57, 127.73, 128.29, 128.36, 136.95, 138.15, 142.27, 154.24, 154.71. HRMS (MALDI/DHB) for $C_{25}H_{22}ONa$ $[M+Na]^+$: calcd 361.1568, found 361.1561.

(*E*)-2,5-Diphenyl-1-(thien-2-yl)-hepta-2,3,4-trien-1-ol (3j). Column chromatography on silica gel (petroleum ether : ethyl acetate: triethyl amine = 100 : 10 : 2) afforded 210 mg (62%) product as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.23 (t, *J* = 7.2Hz, 3H), 2.66 (q, *J* = 7.4Hz, 2H), 2.74 (bs, 1H), 6.11 (s, 1H), 6.90–6.92 (m, 1H), 7.06 (d, *J* = 3.6Hz, 1H), 7.18–7.39 (m, 7H), 7.58–7.64 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.80, 26.19, 69.43, 120.58, 125.20, 125.30, 125.32, 126.69, 126.79, 127.13, 127.48, 127.95, 128.47, 128.49, 136.63, 138.13, 146.57, 153.84, 154.36. HRMS (MALDI/DHB) for $C_{23}H_{21}OS$ $[M+H]^+$: calcd 345.1313, found 345.1313.

(*E*)-1-Furan-2-yl-2,5-diphenylhepta-2,3,4-trien-1-ol (3k). Column chromatography on silica gel (petroleum ether : ethyl acetate: triethyl amine = 100 : 10 : 2) afforded 180 mg (55%) product as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.22 (t, *J* = 7.2 Hz, 3H), 2.67 (q, *J* = 7.2 Hz, 2H), 2.74 (bs, 1H), 5.92 (s, 1H), 6.28–6.33 (m, 2H), 7.18–7.39 (m, 7H), 7.56-7.64 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.85, 26.21, 67.41, 107.62, 110.32, 118.37, 125.29, 126.83, 126.96, 127.46, 127.94, 128.45, 136.72, 138.12, 142.36, 154.00, 154.76. HRMS (EI) for $C_{23}H_{18}O$ $[M-H_2O]^+$: calcd 310.1358, found 310.1362.

(*E*)-2,5-Bis(4-methoxyphenyl)-1-phenylhepta-2,3,4-trien-1-ol (3l). Column chromatography on silica gel (petroleum ether : ethyl acetate: triethyl amine = 50 : 10 : 2) afforded 206 mg (52%) product as an unstable yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.02 (t, *J* = 7.2Hz, 3H), 2.43 (q, *J* = 7.3Hz, 2H), 3.66 (s, 3H), 3.70 (s, 3H), 5.78 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 7.13–7.25 (m, 4H), 7.39–7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.96, 26.21, 55.28, 55.33, 73.76, 113.98, 114.03, 119.08, 122.93, 126.91, 127.73, 128.02, 128.47, 128.50, 129.93, 131.26, 142.57, 152.10, 152.28, 158.92, 159.34. HRMS (MALDI/DHB) for $C_{27}H_{27}O_3$ $[M+H]^+$: calcd 399.1960, found 399.1946.

(*Z*)-1-Phenyl-2,5-di-(thien-2-yl)-hepta-2,3,4-trien-1-ol (3m). Column chromatography on silica gel (petroleum ether : ethyl acetate: triethyl amine = 100 : 10 : 2) afforded 124 mg (35%) product as an unstable yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.04 (t, *J* = 7.4Hz, 3H), 2.48 (q, *J* = 7.3Hz, 2H), 5.73 (s, 1H), 6.87–6.94 (m, 2H), 7.08–7.29 (m, 7H), 7.44 (d, *J* = 7.2Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.62, 27.05, 74.48, 115.17, 118.54, 124.94, 125.16, 126.64, 126.79, 127.19, 127.84, 127.91, 127.93, 128.43, 141.88, 142.69, 144.88, 148.65, 148.70. HRMS (MALDI/DHB) for $C_{21}H_{19}OS_2$ $[M+H]^+$: calcd 351.0877, found 351.0868.

(*Z*)-7-Deuterio-1-phenyl-2,5-bis(trimethylsilyl)hepta-2,3,4-trien-1-ol (3n-*D*) Column chromatography on silica gel (petroleum ether : ethyl acetate: triethyl amine = 100 : 10 : 2) afforded 200 mg (60%) product as a yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 0.37 (s, 9H), 1.23–1.30 (m, 2H), 2.52 (t, *J* = 7.2Hz, 2H), 3.12 (bs, 1H), 5.54 (s, 1H), 7.41–7.55 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.39, -0.78,

13.00 (t), 13.29, 28.78, 76.15, 127.38, 127.72, 128.31, 129.73, 134.28, 142.80, 170.19, 170.41. HRMS (MALDI/DHB) for $C_{19}H_{29}DOSi_2Na$ $[M+Na]^+$: calcd 354.1796, found 354.1801.

A *cis-trans* isomerization of 3d: Treatment of **3d** in $CDCl_3$ with 0.3% (mol/mol) I_2 at room temperature for 0.5 h, an isomerization occurred to afford a mixture of *cis*/*trans* isomers with a ratio of 1 : 2.8 (trans/cis). ^1H NMR ($CDCl_3$, Me_4Si) δ (two isomers) 0.20 (s), 0.23 (s), 0.28 (s), 0.33 (s), 1.14 (t, *J*= 7.2 Hz), 1.30 (t, *J*= 7.2 Hz), 2.47 (q, *J*=7.2 Hz), 2.58 (q, *J*=7.2 Hz), 3.01 (d, *J*= 4.8 Hz), 3.13 (d, *J*= 4.8 Hz), 5.64 (d, *J*= 4.8Hz), 5.68 (d, *J*= 4.8 Hz), 7.67-7.73 (m), 8.33 (d, *J*= 8.1 Hz); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.76, -1.49, -0.75, -0.64, 13.12, 13.67, 28.60, 29.03, 75.32, 75.53, 123.44, 123.51, 127.69, 127.73, 127.77, 128.74, 137.20, 138.37, 147.17, 150.46, 169.42, 169.90, 173.36, 173.90.

3,8-dimethyl-4,7-bis-trimethylsilyl-deca-4,5,6-triene-3,8-diol (4b). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford 187 mg (55%) product as a white oil. The product was obtained as a mixture of diastereoisomers with a ratio of 1.2 : 1. ^1H NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.21 (s, 18H), 0.82-0.88 (m, 6H), 1.35 (d, *J*= 4.8Hz, 6H), 1.61–1.73 (m, 4H), 2.50 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.77, 0.78, 8.25, 8.28, 29.10, 29.14, 35.56, 35.64, 78.95, 79.01, 136.52, 136.82, 170.88, 171.10. HRMS (MALDI/DHB) for $C_{18}H_{36}O_2Si_2Na$ $[M+Na]^+$: calcd 363.2152, found 363.2146.

7,12-dimethyl-8,11-bis-trimethylsilyl-octadeca-8,9,10-triene-7,12-diol (4c). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford

totally 190 mg (42%) product as a white solid. The product was obtained as a mixture of diastereoisomers with a ratio of 1.1 : 1. Isomer 1: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.21 (s, 18H), 0.82–0.86 (m, 6H), 1.24–1.34 (m, 16H), 1.34 (s, 6H), 1.59–1.68 (m, 4H), 2.23 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -0.84, 14.04, 22.63, 23.89, 29.64, 29.70, 31.83, 43.20, 78.95, 137.21, 170.50. Isomer 2: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.21 (s, 18H), 0.82–0.86 (m, 6H), 1.23 (bs, 16H), 1.36 (s, 6H), 1.59-1.62 (m, 4H), 2.38 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -0.82, 14.05, 22.66, 23.90, 29.60, 29.72, 31.87, 43.29, 78.88, 136.87, 170.85. HRMS (MALDI/DHB) for $C_{26}H_{52}O_2Si_2Na$ $[M+Na]^+$: calcd 475.3404, found 475.3399.

2,3,8,9-tetramethyl-4,7-bis-trimethylsilyl-deca-4,5,6-triene-3,8-diol (4d). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford 202 mg (55%) product as a light-yellow oil. The product was obtained as a mixture of diastereoisomers with a ratio of 1.1 : 1. ^{1}H NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.17 (s, 18H), 0.81 (d, *J*= 6.6 Hz), 0.82 (d, *J*= 6.6 Hz), 0.90 (d, *J*= 6.6 Hz), 1.27–1.30 (m), 1.85–1.97 (m), 2.31 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.87, 0.88, 16.84, 16.87, 17.34, 17.38, 26.85, 26.90, 36.95, 80.79, 80.88, 137.36, 137.64, 170.27, 170.54. HRMS (MALDI/DHB) for $C_{20}H_{40}O_2Si_2Na$ $[M+Na]^+$: calcd 391.2465, found 391.2460.

2,4,9,11-tetramethyl-5,8-bis-trimethylsilyl-dodeca-,5,6,7-triene-4,9-diol (4e). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford totally 178 mg (55%) product as a light-yellow oil. The product was obtained as a mixture of diastereoisomers with a ratio of 1.1 : 1. Isomer 1: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.21 (s, 18H), 0.89 (d, *J*= 6.9 Hz, 6H), 0.93 (d, *J*= 6.9 Hz, 6H), 1.37 (s, 6H),

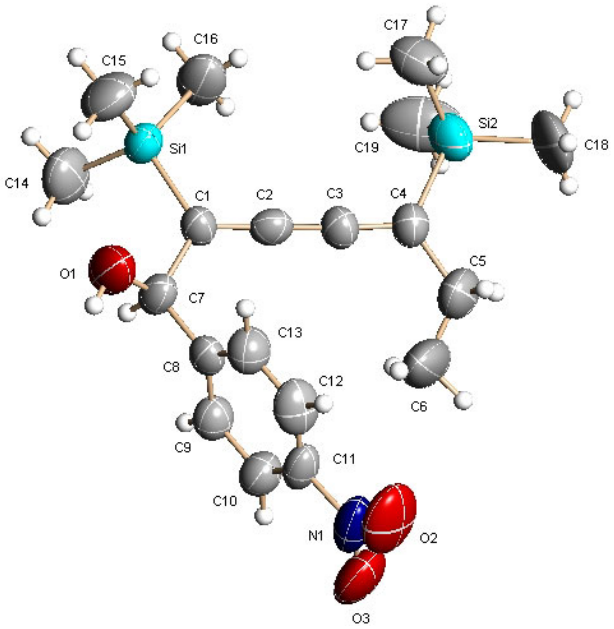
1.49–1.66 (m, 4H), 1.72–1.80 (m, 2H), 2.17 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.92, 24.52, 24.61, 24.64, 30.37, 51.38, 79.45, 137.58, 170.18; Isomer 2: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.211 (s, 18H), 0.87 (d, *J*= 6.9 Hz, 6H), 0.93 (d, *J*= 6.9 Hz, 6H), 1.37 (s, 6H), 1.48–1.64 (m, 4H), 1.70-1.79 (m, 2H), 2.32 (bs, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.88, 24.57, 24.59, 24.62, 30.24, 51.44, 79.29, 137.13, 170.49. HRMS (MALDI/DHB) for $C_{22}H_{44}O_2Si_2Na$ $[M+Na]^+$: calcd 419.2778, found 419.2776.

4,9-dimethyl-5,8-bis-trimethylsilyl-dodeca-5,6,7-triene-4,9-diol (4f). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford 162 mg (44%) product as a light-yellow oil. The diastereomeric ratio is 1.2 : 1. ^{1}H NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.22 (s, 18H), 0.88 (t, *J*= 7.5 Hz, 6H), 1.24–1.46 (m, 4H), 1.35 (s), 1.37 (s), 1.53–1.73 (m, 4H), 2.36 (bs), 2.44 (bs); ^{13}C NMR ($CDCl_3$, Me_4Si) δ(2 isomers) 0.80, 14.41, 17.22, 29.68, 29.74, 45.52, 45.62, 78.95, 136.89, 137.08, 170.55, 170.83; HRMS (MALDI/DHB) for $C_{20}H_{40}O_2Si_2Na$ $[M+Na]^+$: calcd 391.2465, found 391.2461.

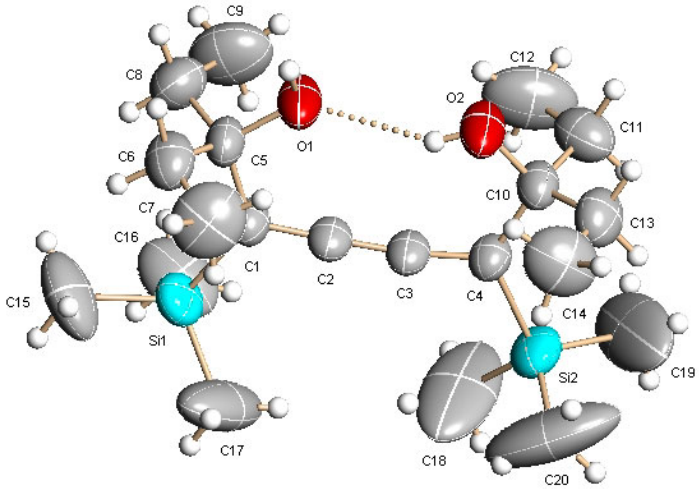
2,5,10,13-tetramethyl-6,9-bis-trimethylsilyl-tetradeca-6,7,8-triene-5,10-diol (4g). Column chromatography on alumina (petroleum ether/ethyl acetate=20:1) afford 195 mg (46%) product as a white solid. The product was obtained as a mixture of diastereoisomers with a ratio of 1.2 : 1. ^{1}H NMR ($CDCl_3$, Me_4Si) δ (2 isomers) 0.20 (s), 0.83 (d, *J*= 6.9Hz), 1.14–1.22 (m), 1.33 (d, *J*= 5.4Hz), 1.42–1.47 (m), 1.59–1.64 (m), 2.31 (bs), 2.46 (bs); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.83, 0.86, 22.57, 22.62, 22.66, 22.69, 28.37, 28.41, 29.46, 29.57, 32.79, 32.83, 40.97, 78.69, 78.86, 136.86, 137.29, 170.49, 170.87. HRMS (MALDI/DHB) for $C_{24}H_{48}O_2Si_2Na$ $[M+Na]^+$: calcd 447.3091, found 447.3084.

Determination of Intermediate 6b. To a solution of Cp_2ZrCl_2 (0.365 g, 1.25 mmol) in THF (5 ml) was added EtMgBr (1.0 M THF solution, 2.5 mmol) at -50°C. After stirring for 1h at the same temperature, 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.19 g, 1 mmol) was added and the reaction mixture was warmed up to room temperature and stirred for 2 h. *p*-Methoxybenzaldehyde (0.12 mL, 1 mmol) was added and the mixture was stirred for 6 h. The solvent was partially evaporated *in vacuo* and 1 mmol mesitylene was added as internal standard. NMR yield is 75%. ^{1}H NMR (benzene-d_6, Me_4Si) δ -0.04 (s, 9H, TMS), 0.22 (s, 9H, TMS), 0.90–0.99 (m, 2H, CH_2), 1.14–1.31 (m, 2H, CH_2), 3.34 (s, 3H, OCH_3), 5.41 (s, 1H, CHAr), 5.60 (s, 5H, Cp), 5.81(s, 5H, Cp), 6.68 (d, *J*= 8.4 Hz, Ar), 7.09 (d, *J*= 8.7 Hz, Ar); ^{13}C NMR (benzene-d_6, Me_4Si) δ -1.48 (TMS), -0.62 (TMS), 38.06 (CH_2), 41.76 (CH_2), 54.75 (OCH_3), 88.00 (CHAr), 110.46 (Cp), 111.07 (Cp), 113.79 (Ar), 129.04 (Ar), 133.83 (C*TMS*), 136.60 (C*TMS*), 159.66 (Ar), 173.70 (=C=), 175.44 (=C=).

The NMR data of **6b** in $CDCl_3$: ^{1}H NMR ($CDCl_3$, Me_4Si) δ -0.38 (s, 9H, TMS), -0.09 (s, 9H, TMS), 0.52–0.64 (m, 2H, CH_2), 0.72–0.83 (m, 2H, CH_2), 3.46 (s, 3H, OCH_3), 5.03 (s, 1H, CHAr), 5.37 (s, 5H, Cp), 5.62 (s, 5H, Cp), 6.68 (d, *J*= 8.7 Hz, Ar), 7.09 (d, *J*= 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.58 (TMS), -1.81 (TMS), 36.67 (CH_2), 40.31 (CH_2), 53.98 (OCH_3), 86.60 (CHAr), 109.18 (Cp), 109.76 (Cp), 112.41 (Ar), 126.54 (Ar), 127.70 (Ar), 132.52 (C*TMS*), 135.35 (C*TMS*), 158.19 (Ar), 172.09 (=C=), 173.74 (=C=).



X-ray single-crystal structure of **3d**



X-ray single-crystal structure of **4a**