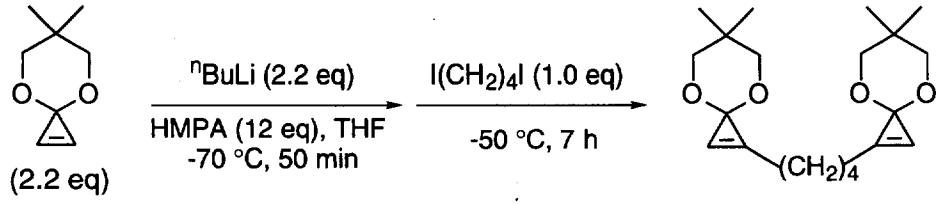
Experiments:

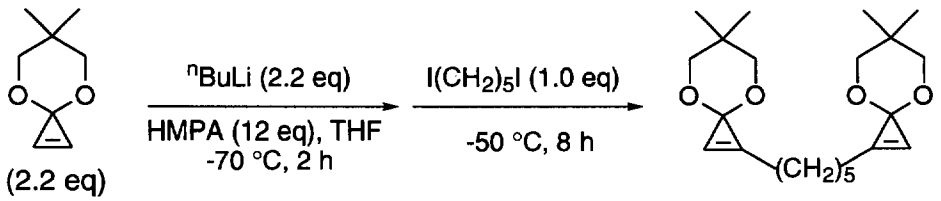
General. All reactions were carried out in oven-dried or flame-dried glassware under a nitrogen atmosphere. All solvents were reagent grade. Tetrahydrofuran (THF) was freshly distilled from sodium /benzophenone under nitrogen and stored over 4 Å sieves to the level of less than 20 ppm of water content. Hexmethylphosphoramide (HMPA) was freshly distilled from calcium hydride under nitrogen and stored over 4 A sieves. Methanol was distilled from magnesium /magnesium oxide under nitrogen and stored over 3 Å sieves. Butyllithiun (BuLi) was purchased from Aldrich and standardized by titration with *l*-menthol. IR spectra were recorded on a JASCO IR-800 spectrometer. ^{1}H NMR spectra were taken at 400 MHz and ^{13}C NMR spectra were taken at 100 MHz, using a JEOL EX-400 instrument. High-resolution mass (FAB) spectra were recorded on a JEOL JMS-SX102L mass spectrometer. Reaction of cyclization gave only one single isomer of the carbocycle in each case as determined by the ^{1}H NMR analysis of the crude reaction mixture. Routine flash column chromatography was performed with the indicated solvents using silica gel-60 (Merck, 230–400 mesh). Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC–908 machine equipped with JAIGEL–1H (20 mm I. D. x 600 nm) and -2H (20 mm I. D. x 600 nm) GPC columns using $CHCl_3$ as eluent. All reaction mixtures were magnetically stirred and monitored by thin-layer chromatography using a Merck precoated silica gel plate. The percentage of water inclusion in the solvents was analyzed by a Karl-Fischer Moisture Titration MKC-210 Aquamicron A & C.

Synthesis of tetramethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (5.6 g, 40 mmol) and HMPA (17 mL, 100 mmol) in anhydrous THF (50 mL) at -70 °C was added BuLi (24 mL of a 1.67 M solution in hexane, 40 mmol) over 10 min. After stirring for 50 min, 1,4-diiodobutane (5.6 g, 18 mmol) was added at -70 °C with a syringe over 10 min. The solution was stirred at -70 °C for 1 h, and then stirred at -50 °C for 7 h. NH_4Cl powder (0.3 g) was added, the reaction mixture was stirred at 25 °C for 10 min, poured into H_2O (100 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 23% EtOAc/hexane) afforded the title compound (4.6 g, 77% yield) as a white solid: mp 98-99 °C; R_f = 0.30 (EtOAc/hexane = 1/2); IR (KBr) ν 2958, 2858, 1728, 1468, 1361, 1284, 1088, 1014, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 6H), 1.07 (s, 6H), 1.74 (t, J = 6.8 Hz, 4 H), 2.57 (t, J = 6.8 Hz, 4 H), 3.58 (d, J = 10.4 Hz, 4 H), 3.63 (d, J = 10.4 Hz, 4 H), 7.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.4, 24.5, 26.5, 30.3, 77.1, 83.4, 115.8, 137.3. Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.74; H, 9.03.

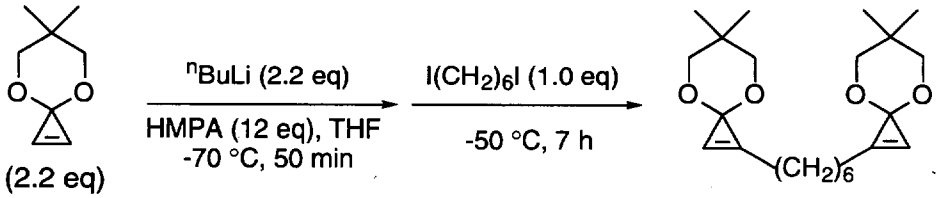
Synthesis of pentamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (5.6 g, 40 mmol) and HMPA (17 mL, 100 mmol) in anhydrous THF (50 mL) at -70 °C was added BuLi (26.5 mL of a 1.51 M solution in hexane, 40 mmol) over 10 min. After stirring for 2 h, 1,5-

diiodopentane (5.9 g, 18 mmol) was added at -70 °C by syringe over 10 min. The solution was stirred at -70 °C for 1 h, and then stirred at -50 °C for 8 h. NH_4Cl power (0.3 g) was added, the reaction mixture was stirred at 25 °C for 10 min, poured into H_2O (100 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 23% EtOAc/hexane) afforded the title compound (4.8 g, 76% yield) as a white solid: mp: 49 -50 °C; R_f = 0.21 (EtOAc/hexane = 3/10); IR (KBr) ν 2949, 2846, 1728, 1471, 1279, 1074, 1022, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 6H), 1.07 (s, 6H), 1.51 (m, 2 H), 1.66 (m, 4 H), 2.54 (t, J = 6.8 Hz, 4 H), 3.59 (d, J = 10.5 Hz, 4 H), 3.63 (d, J = 10.5 Hz, 4 H), 7.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.4, 24.7, 26.8, 28.4, 30.3, 77.0, 83.4, 115.5, 137.5. Anal. Calcd for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.54; H, 9.29.

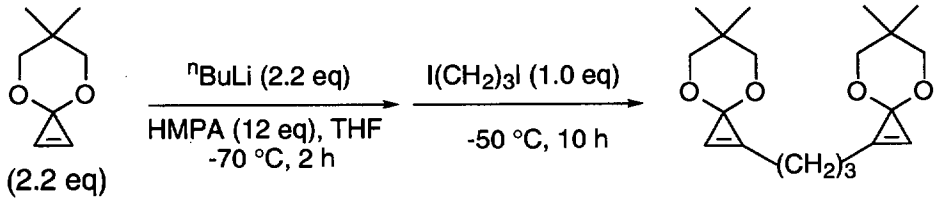
Synthesis of hexamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (5.6 g, 40 mmol) and HMPA (17 mL, 100 mmol) in anhydrous THF (50 mL) at -70 °C was added BuLi (24 mL of a 1.67 M solution in hexane, 40 mmol) over 10 min. After stirring for 50 min, 1,6-diiodohexane (6.1 g, 18 mmol) was added at -70 °C by syringe over 10 min. The solution was stirred at -70 °C for 1 h, and then stirred at -50 °C for 7 h. NH_4Cl power (0.3 g) was added, the reaction mixture was stirred at 25 °C for 10 min, poured into H_2O (100 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 23% EtOAc/hexane) afforded the title compound (4.6 g, 71% yield) as a white solid: mp 78-79 °C; R_f = 0.45 (EtOAc/hexane = 1/2); IR (KBr) ν 2927, 2858, 1730,

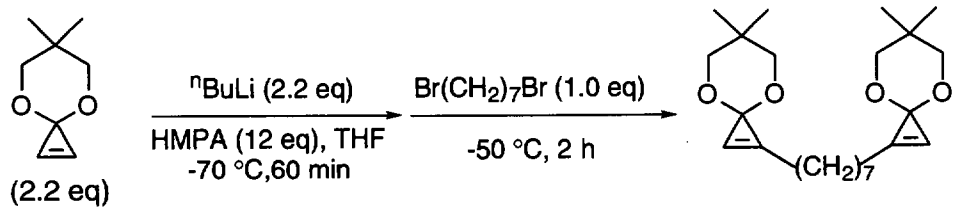
1466, 1273, 1016, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 6H), 1.06 (s, 6H), 1.43 (m, 4 H), 1.64 (m, 4 H), 2.53 (t, J = 7.1 Hz, 4 H), 3.58 (d, J = 10.5 Hz, 4 H), 3.63 (d, J = 10.5 Hz, 4 H), 7.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.4, 24.8, 27.0, 28.6, 30.3, 77.0, 83.5, 115.3, 137.7. Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.14; H, 9.46.

Synthesis of trimethylene-tethered bis(cyclopropenone acetal)



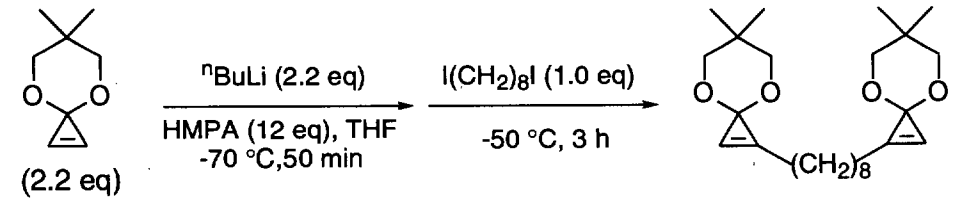
To a solution of cyclopropenone acetal (5.6 g, 40 mmol) and HMPA (17 mL, 100 mmol) in anhydrous THF (50 mL) at -70 °C was added BuLi (24 mL of a 1.67 M solution in hexane, 40 mmol) over 10 min. After stirring for 2 h, 1,3-diiodopropane (5.3 g, 18 mmol) was added at -70 °C with a syringe over 10 min. The solution was stirred at -70 °C for 1 h, and then stirred at -50 °C for 10 h. NH_4Cl powder (0.3 g) was added, the reaction mixture was stirred at 25 °C for 10 min, poured into H_2O (100 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 23% EtOAc/hexane) afforded the title compound (2.6 g, 45% yield) as a white solid: mp 68-69 °C; R_f = 0.31 (EtOAc/hexane = 1/2); IR (KBr) ν 2956, 2850, 1728, 1471, 1284, 1066, 1014, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (s, 6H), 1.06 (s, 6H), 1.96 (t, J = 7.3 Hz, 2 H), 2.65 (t, J = 7.3 Hz, 4 H), 3.59 (d, J = 10.5 Hz, 4 H), 3.63 (d, J = 10.5 Hz, 4 H), 7.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.4, 24.3, 24.8, 30.3, 77.0, 83.3, 116.1, 137.0. Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.25; H, 9.86.

Synthesis of heptamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (3.0 g, 21.4 mmol) and HMPA (9.3 mL, 53.6 mmol) in anhydrous THF (30 mL) at -70 °C was added BuLi (13.4 mL of a 1.60 M solution in hexane, 21.4 mmol) over 6 min. After stirring for 60 min, 1,7-dibromoheptane (2.5 g, 9.6 mmol) was added at -70 °C with a syringe over 5 min. The solution was stirred at -50 °C for 2 h, and then the reaction mixture was slowly raised to -10 °C (2 h), poured into H_2O (80 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 17% EtOAc/hexane) afforded compound (2.6 g, 71% yield) as a white solid: mp 73-74 °C; R_f = 0.43 (EtOAc/hexane = 1/2); IR (KBr) ν 2924, 2848, 1728, 1468, 1265, 1014, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 1.07 (s, 6H), 1.38 (m, 6 H), 1.63 (m, 4 H), 2.53 (t, J = 7.2 Hz, 4 H), 3.60 (d, J = 10.4 Hz, 4 H), 3.64 (d, J = 10.4 Hz, 4 H), 7.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.5, 24.9, 27.2, 29.0, 29.0, 30.4, 77.1, 83.5, 115.2, 137.7. Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.37; H, 9.64. Found: C, 73.56; H, 9.67.

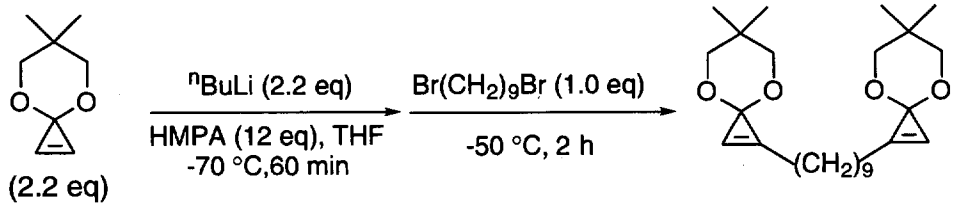
Synthesis of octamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (5.6 g, 40 mmol) and HMPA (17 mL, 100 mmol) in anhydrous THF (50 mL) at -70 °C was added BuLi (26.5 mL of a 1.51 M solution in hexane, 40 mmol) over 10 min. After stirring for 50 min, 1,8-diiodooctane (6.6 g, 18 mmol) was added at -70 °C with a syringe over 10

min. The solution was stirred at -70 °C for 30 min, and then stirred at -50 °C for 3 h. NH_4Cl powder (0.3 g) was added, the reaction mixture was stirred at 25 °C for 10 min, poured into H_2O (100 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 23% EtOAc/hexane) afforded the title compound (5.4 g, 77% yield) as a white solid: mp 56-57 °C; R_f = 0.48 (EtOAc/hexane = 1/2); IR (KBr) ν 2925, 2848, 1728, 1466, 1265, 1016, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 1.06 (s, 6H), 1.32 (m, 4 H), 1.38 (m, 4 H), 1.61 (m, 4 H), 2.52 (t, J = 6.8 Hz, 4 H), 3.59 (d, J = 10.2 Hz, 4 H), 3.63 (d, J = 10.2 Hz, 4 H), 7.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.4, 24.9, 27.2, 29.0, 29.1, 30.4, 77.1, 83.6, 115.3, 137.9. Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 73.91; H, 9.77.

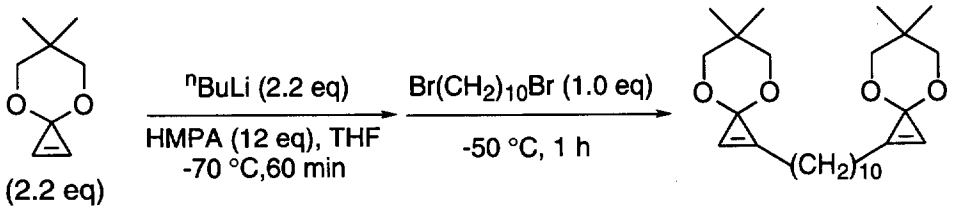
Synthesis of nonamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (3.0 g, 21.4 mmol) and HMPA (9.3 mL, 53.6 mmol) in anhydrous THF (30 mL) at -70 °C was added BuLi (13.5 mL of a 1.58 M solution in hexane, 21.4 mmol) over 6 min. After stirring for 60 min, 1,9-dibromononane (2.7 g, 9.6 mmol) was added at -70 °C with a syringe over 5 min. The solution was stirred at -50 °C for 2 h, and then the reaction mixture was slowly raised to -10 °C (2 h), poured into H_2O (80 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 17% EtOAc/hexane) afforded compound (2.8 g, 72% yield) as a white solid: mp 58-59 °C; R_f = 0.51 (EtOAc/hexane = 1/2); IR (KBr) ν 2920, 2850, 1728, 1469, 1276, 1018, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 6H), 1.07

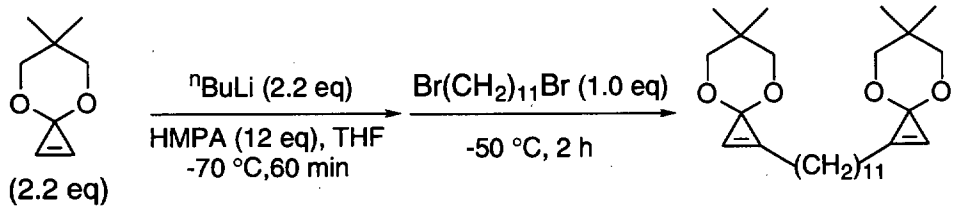
(s, 6H), 1.31 (m, 6 H), 1.39 (m, 4 H), 1.63 (m, 4 H), 2.53 (t, J = 7.2 Hz, 4 H), 3.60 (d, J = 10.4 Hz, 4 H), 3.64 (d, J = 10.4 Hz, 4 H), 7.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.5, 25.0, 27.3, 29.1, 29.3, 29.4, 30.4, 77.1, 83.5, 115.1, 137.8. Anal. Calcd for $C_{23}H_{36}O_4$: C, 74.22; H, 9.97. Found: C, 73.92; H, 9.95.

Synthesis of decamethylene-tethered bis(cyclopropenone acetal)



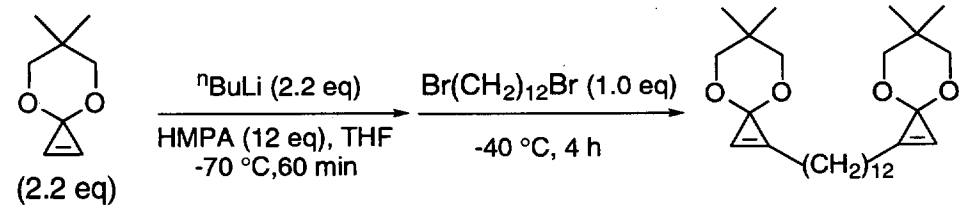
To a solution of cyclopropenone acetal (3.0 g, 21.4 mmol) and HMPA (9.3 mL, 53.6 mmol) in anhydrous THF (30 mL) at -70 °C was added BuLi (13.4 mL of a 1.60 M solution in hexane, 21.4 mmol) over 6 min. After stirring for 60 min, 1,10-dibromodecane (3.2 g, 9.6 mmol) in THF (8 mL) was added at -70 °C with a syringe over 10 min. The solution was stirred at -50 °C for 1 h, and then the reaction mixture was slowly raised to 0 °C (3 h), poured into H_2O (80 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 17% EtOAc/hexane) afforded the title compound (2.7 g, 67% yield) as a white solid: mp 65-66 °C; R_f = 0.53 (EtOAc/hexane = 1/2); IR (KBr) ν 2915, 2848, 1726, 1469, 1284, 1014, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 1.07 (s, 6H), 1.29 (m, 8 H), 1.39 (m, 4 H), 1.63 (m, 4 H), 2.53 (t, J = 7.4 Hz, 4 H), 3.60 (d, J = 10.4 Hz, 4 H), 3.64 (d, J = 10.4 Hz, 4 H), 7.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.5, 25.0, 27.3, 29.2, 29.3, 29.5, 30.5, 77.1, 83.5, 115.1, 137.8. Anal. Calcd for $C_{28}H_{46}O_4$: C, 74.60; H, 10.11. Found: C, 75.71; H, 10.12.

Synthesis of undecamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (3.0 g, 21.4 mmol) and HMPA (9.3 mL, 53.6 mmol) in anhydrous THF (30 mL) at -70 °C was added BuLi (13.4 mL of a 1.60 M solution in hexane, 21.4 mmol) over 6 min. After stirring for 60 min, 1,11-dibromoundecane (3.0 g, 9.6 mmol) was added at -70 °C with a syringe over 5 min. The solution was stirred at -50 °C for 2 h, and then the reaction mixture was slowly raised to -10 °C (2 h), poured into H_2O (80 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 17% EtOAc/hexane) afforded the title compound (3.5 g, 85% yield) as a white solid: mp 67-68 °C; R_f = 0.55 (EtOAc/hexane = 1/2); IR (KBr) ν 2918, 2850, 1728, 1469, 1284, 1018, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 6H), 1.07 (s, 6H), 1.28 (m, 10 H), 1.37 (m, 4 H), 1.63 (m, 4 H), 2.53 (t, J = 7.4 Hz, 4 H), 3.60 (d, J = 10.4 Hz, 4 H), 3.64 (d, J = 10.4 Hz, 4 H), 7.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 22.5, 25.0, 27.3, 29.2, 29.3, 29.5, 29.6, 30.4, 77.1, 83.5, 115.1, 137.8. Anal. Calcd for $C_{28}H_{46}O_4$: C, 74.86; H, 10.25. Found: C, 74.88; H, 10.21.

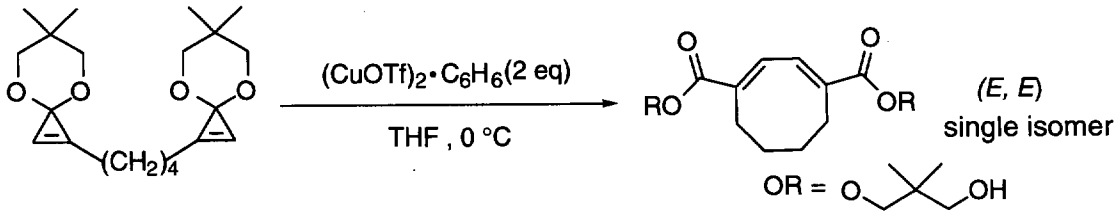
Synthesis of dodecamethylene-tethered bis(cyclopropenone acetal)



To a solution of cyclopropenone acetal (3.0 g, 21.4 mmol) and HMPA (9.3 mL, 53.6 mmol) in anhydrous THF (30 mL) at -70 °C was added BuLi (13.4 mL of a 1.60 M solution in hexane, 21.4 mmol) over 6 min. After stirring for 60 min,

1,12-dibromododecane (3.2 g, 9.6 mmol) in THF (8 mL) was added at -70 °C with a syringe over 10 min. The solution was stirred at -40 °C for 4 h, and then the reaction mixture was slowly raised to 0 °C (1.5 h), poured into H_2O (80 mL), and extracted with EtOAc, the organic extracts were washed with water and brine, and then dried over Na_2SO_4. Removal of solvent followed by flash chromatography on silica gel (eluent: 17% EtOAc/hexane) afforded the title compound (3.2 g, 75% yield) as a white solid: mp 67-68 °C; R_f = 0.58 (EtOAc/hexane = 1/2); IR (KBr) ν 2917, 2850, 1728, 1471, 1278, 1018, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 1.06 (s, 6H), 1.27 (m, 12 H), 1.37 (m, 4 H), 1.60 (m, 4 H), 2.52 (t, J = 7.2 Hz, 4 H), 3.59 (d, J = 10.4 Hz, 4 H), 3.63 (d, J = 10.4 Hz, 4 H), 7.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 22.4, 24.9, 27.2, 29.1, 29.3, 29.5, 29.6, 30.4, 77.1, 83.5, 115.0, 137.8. Anal. Calcd for $C_{28}H_{46}O_4$: C, 75.29; H, 10.38. Found: C, 75.35; H, 10.36.

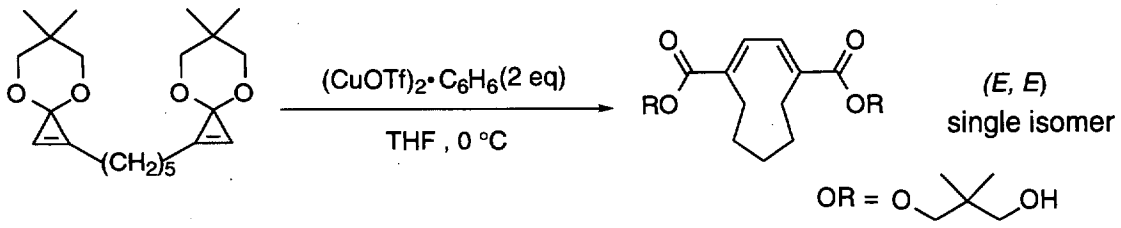
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclooctadiene by Cu(I)-mediated cyclization



A solution of tetramethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.30 mmol) in anhydrous THF (50 mL) was added to a solution of $(CuOTf)_2 \cdot C_6H_6$ (302 mg, 0.60 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (33 mg, 30% yield) as a white solid (a single isomer shown

by HPLC analysis): mp 87-88 °C; R_f = 0.31 (EtOAc/hexane = 1/1); IR (KBr) ν 3420, 2961, 2874, 1710, 1624, 1473, 1288, 1243, 1165, 1053, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.55 (m, 4 H, CH_2CH_2), 2.12 (t, J = 6.4 Hz, 2 H, OH), 2.39 (m, 4 H, CH_2CH_2), 3.34 (d, J = 6.4 Hz, 4H, $HOCH_2$) , 4.05 (s, 4H, CH_2O), 7.24 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 22.7 (CH_2CH_2), 27.4 (CH_2CH_2), 36.7 ($C(CH_3)_2$), 68.3 (OCH_3), 69.9 ($HOCH_2$), 134.4 (C=CH), 135.6 (C=CH), 167.5(C=O) ; high-resolution mass spectrum (FAB) m/z 369.2269 [(M + H)$^+$; calcd for $C_{20}H_{33}O_6$: 369.2277]. Anal. Calcd for $C_{20}H_{32}O_6$: C, 65.19; H, 8.75. Found: C, 65.05; H, 8.79.

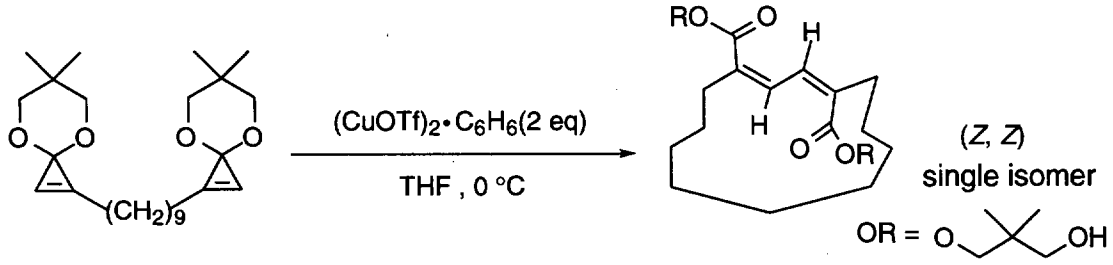
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclononadiene by Cu(I)-mediated cyclization



A solution of pentamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.29 mmol) in anhydrous THF (50 mL) was added to a solution of $(CuOTf)_2 \cdot C_6H_6$ (292 mg, 0.58 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (21 mg, 19% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1); IR (KBr) ν 3421, 2956, 2873, 1714, 1623, 1473, 1264, 1230, 1192, 1119, 1054, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.60 (m, 6 H, CH_2CH_2), 2.17 (t, J = 6.8 Hz, 2 H, OH), 2.35 (m, 4 H, CH_2CH_2), 3.33

(d, J = 6.8 Hz, 4H, HOCH_2) , 4.06 (s, 4H, CH_2O), 7.20 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (C(CH_3)$_2$), 26.1 (CH_2CH_2), 29.5 (CH_2CH_2), 29.8 (CH_2CH_2), 36.7 (C(CH_3)$_2$), 68.2 (OCH_3), 69.7 (HOCH_2), 136.6 (C=CH), 137.0 (C=CH), 167.4(C=O) ; high-resolution mass spectrum (FAB) m /z 383.2423 [(M + H)$^+$; calcd for $C_{21}H_{35}O_6$: 383.2434].

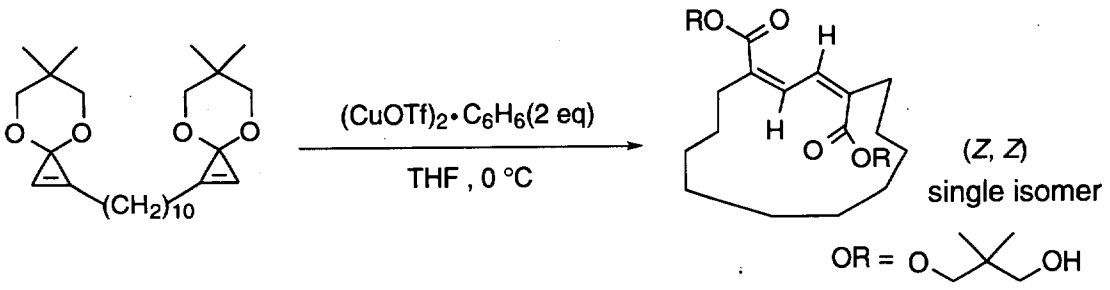
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclotridecadiene by Cu(I)-mediated cyclization



A solution of nonamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.25 mmol) in anhydrous THF (50 mL) was added to a solution of (CuOTf)$_2$•C_6H_6 (252 mg, 0.50 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (21 mg, 19% yield) as a colorless oil: R_f = 0.32 (EtOAc/hexane = 1/1); IR (KBr) ν 3447, 2933, 2861, 1711, 1590, 1473, 1228, 1203, 1053, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 12H, C(CH_3)$_2$), 1.03-1.30 (m, 10 H, CH_2CH_2), 1.79 (m, 4 H, CH_2CH_2), 2.36 (t, J = 6.4 Hz, 2 H, OH), 2.59 (m, 4 H, CH_2CH_2), 3.33 (d, J = 6.4 Hz, 4H, HOCH_2) , 4.10 (s, 4H, CH_2O), 7.62 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (C(CH_3)$_2$), 26.1 (CH_2CH_2), 26.3 (CH_2CH_2), 26.5 (CH_2CH_2), 27.3 (CH_2CH_2), 27.6 (CH_2CH_2), 36.9 (C(CH_3)$_2$), 68.1 (OCH_3), 69.7 (HOCH_2), 133.9 (C=CH), 137.5 (C=CH), 168.0(C=O); high-

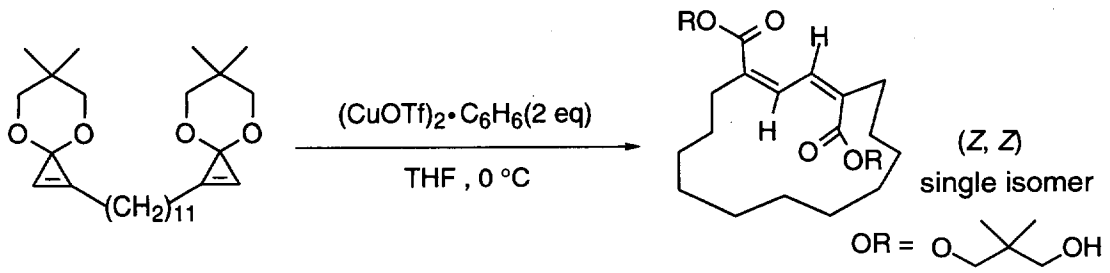
resolution mass spectrum (FAB) *m* /z 439.3037 [(M + H)$^+$; calcd for $C_{25}H_{43}O_6$: 439.3060]. Anal. Calcd for $C_{25}H_{42}O_6$: C, 68.46; H, 9.65. Found: C, 68.36; H, 9.66.

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclotetradecadiene by Cu(I)-mediated cyclization



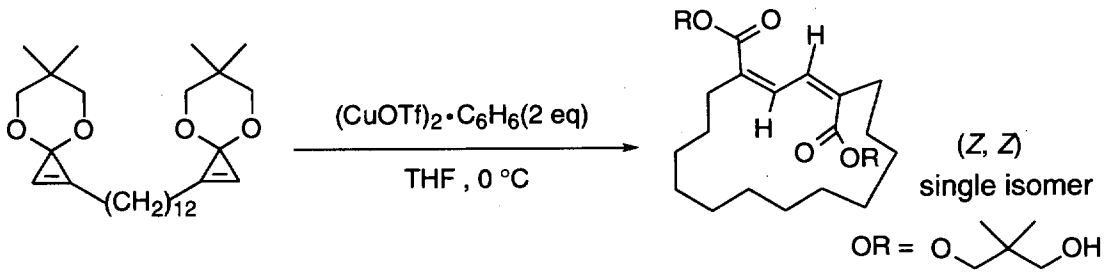
A solution of decamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.24 mmol) in anhydrous THF (50 mL) was added to a solution of $(CuOTf)_2 \cdot C_6H_6$ (242 mg, 0.48 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (47 mg, 43% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1); IR (KBr) ν 3447, 2929, 2860, 1710, 1592, 1473, 1242, 1189, 1055, 751 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.06-1.23 (m, 12 H, CH_2CH_2), 1.65 (m, 4 H, CH_2CH_2), 2.26 (t, J = 6.4 Hz, 2 H, OH), 2.62 (t, J = 6.0 Hz, 4 H, CH_2CH_2), 3.33 (d, J = 6.4 Hz, 4H, $HOCH_2$) , 4.00-4.15 (m, 4H, CH_2O), 7.56 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 25.5 (CH_2CH_2), 25.8 (CH_2CH_2), 26.1 (CH_2CH_2), 26.3 (CH_2CH_2), 26.8 (CH_2CH_2), 36.9 ($C(CH_3)_2$), 68.2 (OCH_3), 69.7 ($HOCH_2$), 133.4 (C=CH), 137.8 (C=CH), 168.1(C=O); high-resolution mass spectrum (FAB) *m* /z 453.3216 [(M + H)$^+$; calcd for $C_{26}H_{45}O_6$: 453.3216].

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclopentadecadiene by Cu(I)-mediated cyclization



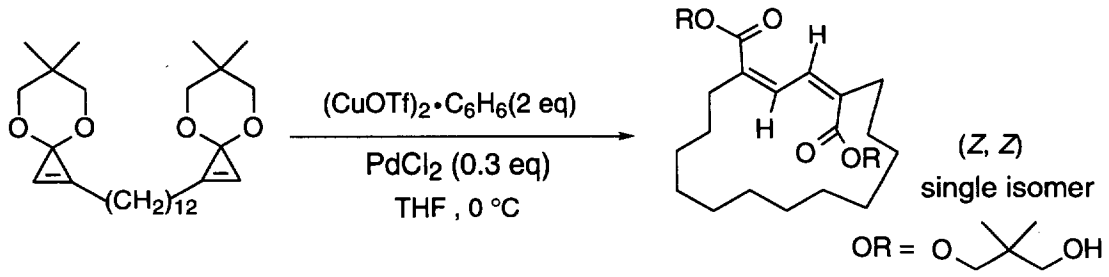
A solution of undecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.23 mmol) in anhydrous THF (50 mL) was added to a solution of $(CuOTf)_2 \cdot C_6H_6$ (232 mg, 0.46 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (42 mg, 39% yield) as a colorless oil: R_f = 0.35 (EtOAc/hexane = 1/1); IR (KBr) ν 3451, 2932, 2860, 1710, 1587, 1457, 1239, 1203, 1054, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 12H, $C(CH_3)_2$), 1.03-1.40 (m, 14 H, CH_2CH_2), 2.23 (t, J = 6.4 Hz, 2 H, OH), 2.50 (m, 4 H, CH_2CH_2), 2.66 (m, 4 H, CH_2CH_2), 3.33 (d, J = 6.4 Hz, 4H, $HOCH_2$) , 3.97-4.18 (m, 4H, CH_2O), 7.57 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 24.7 (CH_2CH_2), 25.8 (CH_2CH_2), 25.9 (CH_2CH_2), 26.8 (CH_2CH_2), 27.2 (CH_2CH_2), 28.7 (CH_2CH_2), 36.8 ($C(CH_3)_2$), 68.2 (OCH_3), 69.8 ($HOCH_2$), 133.5 (C=CH), 138.2 (C=CH), 168.1 (C=O); high-resolution mass spectrum (FAB) m/z 467.3358 [$(M + H)^+$; calcd for $C_{27}H_{47}O_6$: 467.3373]. Anal. Calcd for $C_{27}H_{46}O_6$: C, 69.49; H, 9.94. Found: C, 69.64; H, 9.91.

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclohexadecadiene by Cu(I)-mediated cyclization



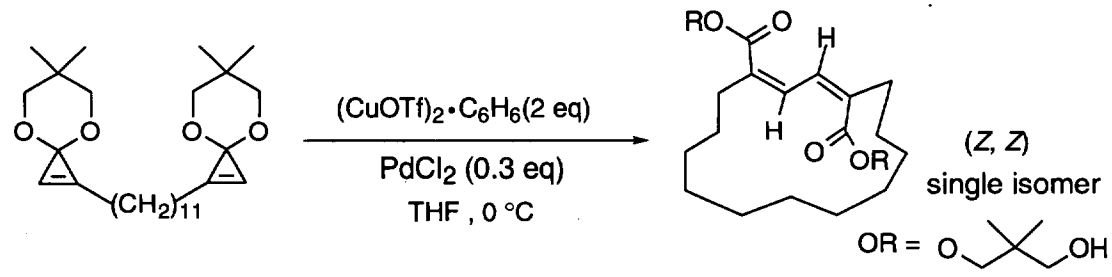
A solution of dodecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.22 mmol) in anhydrous THF (50 mL) was added to a solution of $(CuOTf)_2 \cdot C_6H_6$ (221 mg, 0.44 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (71 mg, 66% yield) as a colorless oil: R_f = 0.38 (EtOAc/hexane = 1/1); IR (KBr) ν 3438, 2930, 2859, 1710, 1589, 1472, 1240, 1054, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.04-1.48 (m, 16 H, CH_2CH_2), 2.22 (t, J = 6.8 Hz, 2 H, OH), 2.50 (m, 4 H, CH_2CH_2), 2.67 (m, 4 H, CH_2CH_2),3.34 (d, J = 6.8 Hz, 4H, $HOCH_2$) , 3.97-4.18 (m, 4H, CH_2O), 7.59 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 25.7 (CH_2CH_2), 25.8 (CH_2CH_2), 26.6 (CH_2CH_2), 26.9 (CH_2CH_2), 27.3 (CH_2CH_2), 28.5 (CH_2CH_2), 36.8 ($C(CH_3)_2$), 68.2 (OCH_3), 69.7 ($HOCH_2$), 133.3 (C=CH), 137.8 (C=CH), 168.1(C=O); high-resolution mass spectrum (FAB) m/z 481.3504 [$(M + H)^+$; calcd for $C_{28}H_{49}O_6$: 481.3529]. Anal. Calcd for $C_{28}H_{48}O_6$: C, 69.96; H, 10.07. Found: C, 70.23; H, 10.13.

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclohexadecadiene by Cu(I)/ Pd(II)-mediated cyclization



A solution of dodecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.22 mmol) in anhydrous THF (50 mL) was added to a suspension of $(CuOTf)_2 \cdot C_6H_6$ (221 mg, 0.44 mmol) and $PdCl_2$ (11.7 mg, 0.066 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (84 mg, 78% yield) as a colorless oil: R_f = 0.38 (EtOAc/hexane = 1/1).

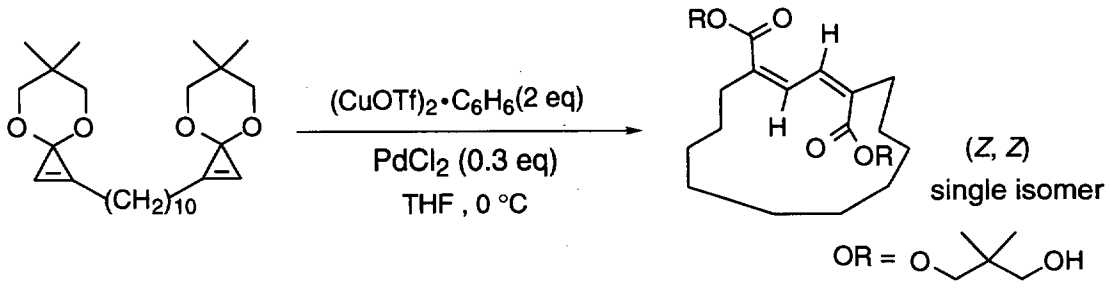
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclopentadecadiene by Cu(I)/ Pd(II)-mediated cyclization



A solution of undecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.23 mmol) in anhydrous THF (50 mL) was added to a suspension of $(CuOTf)_2 \cdot C_6H_6$ (232 mg, 0.46 mmol) and $PdCl_2$ (12.2 mg, 0.069 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was

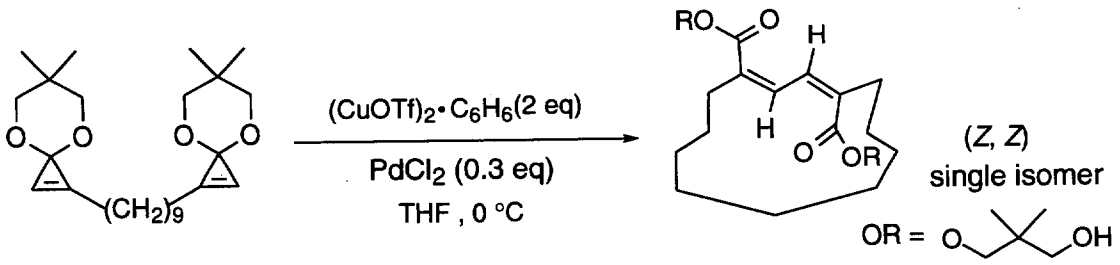
added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (61 mg, 56% yield) as a colorless oil: R_f = 0.35 (EtOAc/hexane = 1/1).

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclotetradecadiene by Cu(I)/ Pd(II)-mediated cyclization



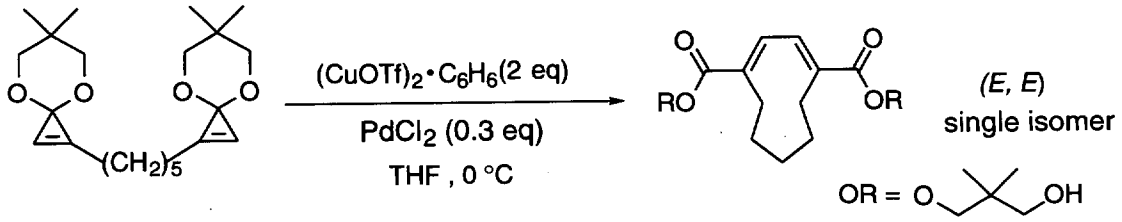
A solution of decamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.24 mmol) in anhydrous THF (50 mL) was added to a suspension of $(CuOTf)_2 \cdot C_6H_6$ (242 mg, 0.48 mmol) and $PdCl_2$ (13.0 mg, 0.072 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered a pad of though Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (73 mg, 67% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1).

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclotridecadiene by Cu(I)/ Pd(II)-mediated cyclization



A solution of nonamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.25 mmol) in anhydrous THF (50 mL) was added to a suspension of $(CuOTf)_2 \cdot C_6H_6$ (252 mg, 0.50 mmol) and $PdCl_2$ (13.3 mg, 0.075 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (36 mg, 33% yield) as a colorless oil: R_f = 0.32 (EtOAc/hexane = 1/1).

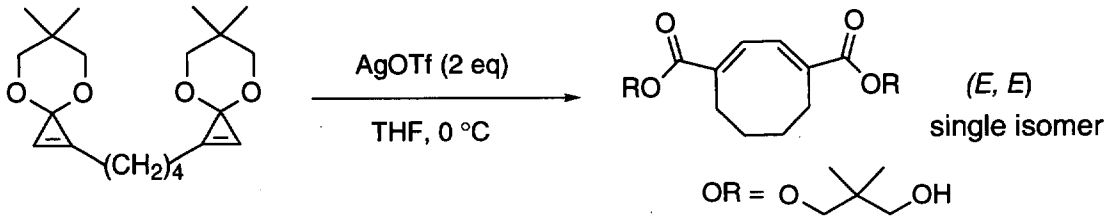
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclononadecadiene by Cu(I)/ Pd(II)-mediated cyclization



A solution of pentamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.29 mmol) in anhydrous THF (50 mL) was added to a suspension of $(CuOTf)_2 \cdot C_6H_6$ (293 mg, 0.58 mmol) and $PdCl_2$ (15.4 mg, 0.087 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 2 h. The resulting mixture was filtered though a pad of Celite. The filtrate was concentrated, H_2O (10 mL) was added, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts

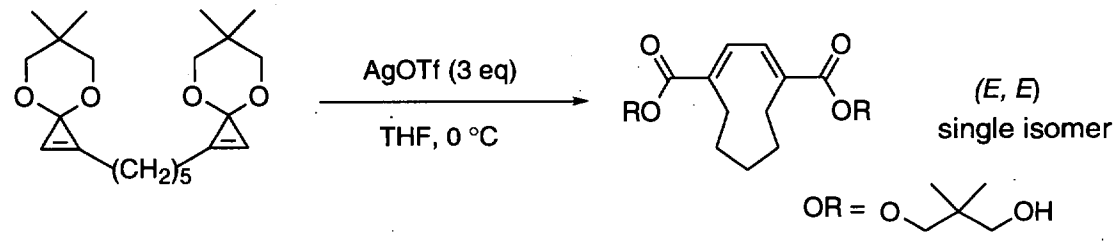
were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (22 mg, 20% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1).

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclooctadiene by AgOTf-mediated cyclization



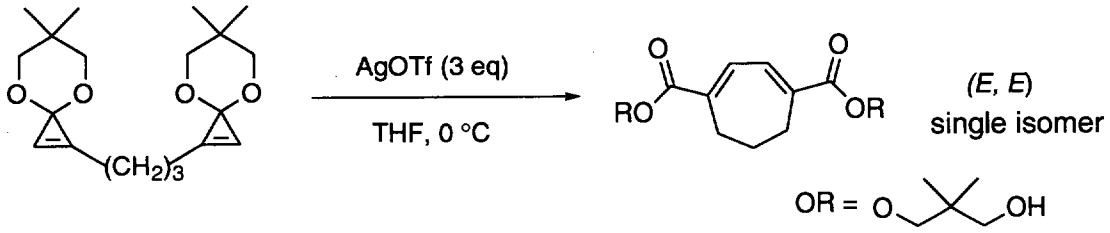
A solution of tetramethylene-tethered bis(cyclopropenone acetal) (300 mg, 0.90 mmol) in anhydrous THF (3 mL) was added to a solution of AgOTf (462 mg, 1.80 mmol) in THF (3 mL) at 0 °C the aid of a syringe pump at a rate of 0.66 mL/h. After addition, the reaction was stirred at 0 °C for 1 h. K_2CO_3 (0.3 g) and sat. NaCl (5 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound as a white (290 mg, 88% yield) solid (a single isomer shown by HPLC analysis): mp 87-88 °C; R_f = 0.31 (EtOAc/hexane = 1/1).

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclononadiene by AgOTf-mediated cyclization



A solution of pentamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.29 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (221 mg, 0.86 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g) and sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (19 mg, 17% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1).

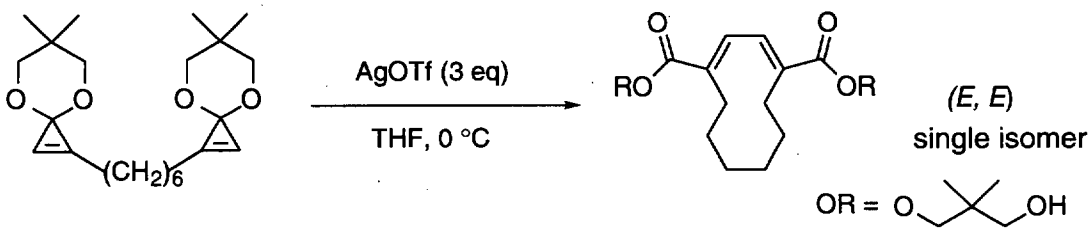
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cycloheptadiene by AgOTf-mediated cyclization



A solution of trimethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.31 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (239 mg, 0.93 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g) and sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (8 mg, 7% yield) as a colorless oil: R_f = 0.38 (EtOAc/hexane = 1/1); IR (KBr) ν 3447, 2961, 2866, 1700, 1635, 1473, 1268, 1215, 1159, 1052, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.94 (m, 2 H, CH_2CH_2), 2.12 (t, J = 6.0 Hz, 2

H, OH), 2.70 (t, J = 5.6 Hz, 4 H, CH_2CH_2), 3.34 (d, J = 6.0 Hz, 4H, $HOCH_2$) , 4.04 (s, 4H, CH_2O), 7.14 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 24.8 (CH_2CH_2), 30.6 (CH_2CH_2), 36.7 ($C(CH_3)_2$), 68.2 (OCH_3), 70.0 ($HOCH_2$), 131.7 (C=CH), 139.9 (C=CH), 167.8(C=O); high-resolution mass spectrum (FAB) *m* /z 355.2124 [(M + H)$^+$; calcd for $C_{19}H_{31}O_6$: 355.2121]. Anal. Calcd for $C_{19}H_{30}O_6$: C, 64.39; H, 8.53. Found: C, 64.34; H, 8.49.

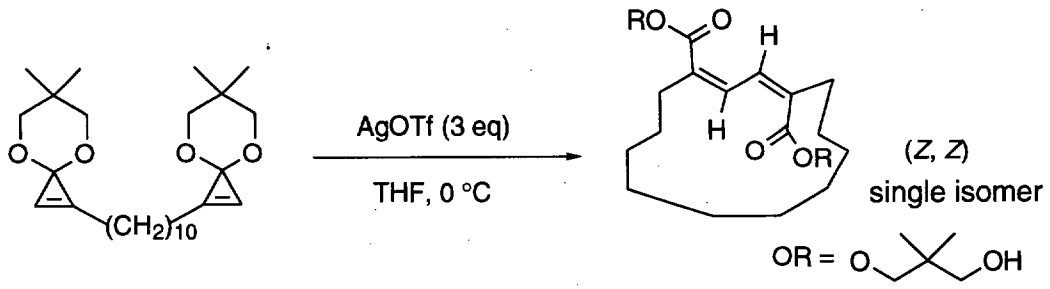
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(*E*)-1,(*E*)-3-cyclodecadiene by AgOTf-mediated cyclization



A solution of hexamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.28 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (213 mg, 0.83 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g), sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (6 mg, 6% yield) as a colorless oil: R_f = 0.29 (EtOAc/hexane = 1/1); IR (KBr) ν 3423, 2959, 2872, 1713, 1615, 1462, 1253, 1218, 1170, 1053, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 12H, $C(CH_3)_2$), 1.23 (m, 4 H, CH_2CH_2), 1.55 (m, 4 H, CH_2CH_2), 2.33 (t, J = 6.4 Hz, 2 H, OH), 2.40 (t, J = 6.4 Hz, 4 H, CH_2CH_2), 3.32 (d, J = 6.4 Hz, 4H, $HOCH_2$) , 4.05 (s, 4H, CH_2O), 7.23 (s, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 24.8 (CH_2CH_2), 25.6 (CH_2CH_2), 26.0 (CH_2CH_2),

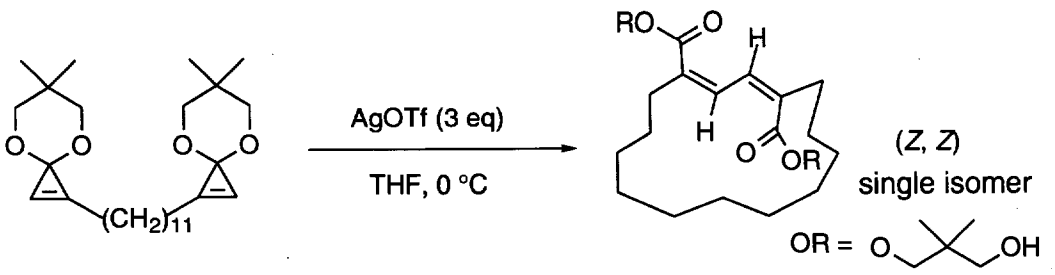
36.7 ($C(CH_3)_2$), 68.1 (OCH_3), 69.6 ($HOCH_2$), 134.5 (C=CH), 137.2 (C=CH), 167.1(C=O) ; high-resolution mass spectrum (FAB) *m /z* 397.2571 [$(M + H)^+$; calcd for $C_{22}H_{37}O_6$: 397.2590]. Anal. Calcd for $C_{22}H_{36}O_6$: C, 66.64; H, 9.15. Found: C, 66.55; H, 9.11.

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclotetradecadiene by AgOTf-mediated cyclization



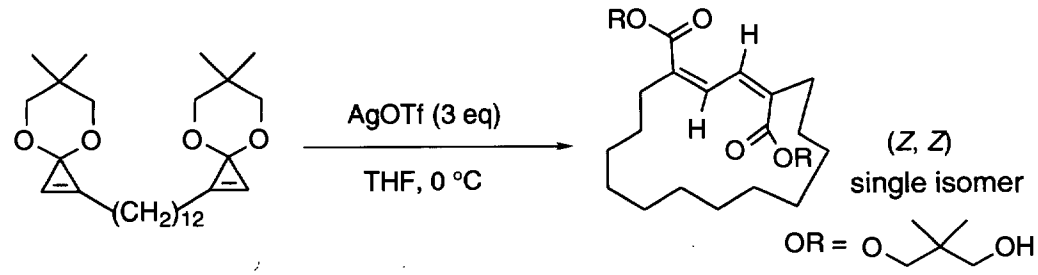
A solution of decamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.24 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (185 mg, 0.72 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g), sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (hexane/EtOAc, 10/7) gave the title compound (12 mg, 11% yield) as a colorless oil: R_f = 0.33 (EtOAc/hexane = 1/1).

Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclopentadecadiene by AgOTf-mediated cyclization



A solution of undecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.23 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (177 mg, 0.69 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g), sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (Hexane/EtOAc, 10/7) gave the title compound (16 mg, 15% yield) as a colorless oil: R_f = 0.35 (EtOAc/hexane = 1/1).

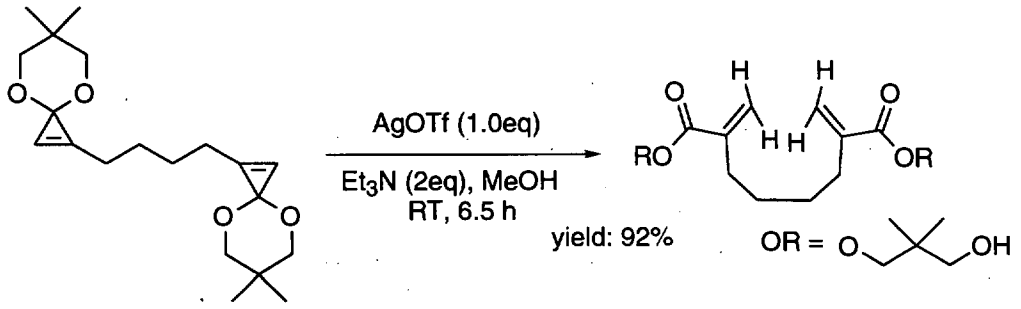
Synthesis of 1,4-bis(2,2-dimethyl-3-hydroxypropoxycarbonyl)-(Z)-1,(Z)-3-cyclohexadecadiene by AgOTf-mediated cyclization



A solution of dodecamethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.22 mmol) in anhydrous THF (50 mL) was added to a solution of AgOTf (170 mg, 0.66 mmol) in THF (50 mL) at 0 °C with the aid of a syringe pump at a rate of 50 mL/h. After addition, the reaction was stirred at 0 °C for 30 min. K_2CO_3 (0.1 g), sat. NaCl (3 mL) were added, and the resulting mixture was stirred at 0 °C for 15 min, and then filtered though a pad of Celite. The filtrate was

concentrated, extracted with EtOAc (3 x 20 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (Hexane/EtOAc, 5/3) gave the title compound (37 mg, 34% yield) as a colorless oil: R_f = 0.38 (EtOAc/hexane = 1/1).

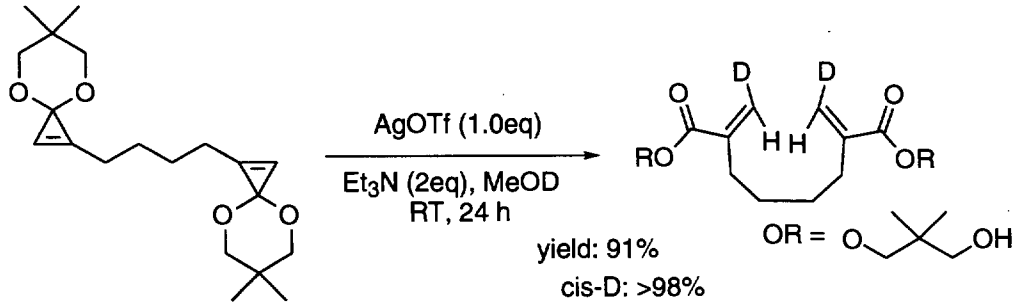
In situ trapping of the vinyl silver intermediate with MeOH (giving tetramethylene-tethered bis(2,2-dimethyl-3-hydroxypropyl propenoate)



AgOTf (77 mg, 0.30 mmol) was added to a solution of tetramethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.30 mmol) and Et_3N (61 mg, 0.60 mmol) in anhydrous MeOH (2 mL) at -70 °C. After addition, the reaction was stirred at -70 °C for 30 min, and then stirred at 25 °C for 8 h. The resulting mixture was passed though short SiO_2 column, then HCl (3 mL, 0.3 M) were added, and the resulting mixture was stirred for 10 min. Saturated aqueous $NaHCO_3$ was added and adjusted pH to 7, extracted with EtOAc (3 x 15 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (Hexane/EtOAc, 5/3) gave compound **2** as a white solid (103 mg, 93% yield): mp 52 -53 °C; R_f = 0.10 (EtOAc/hexane = 1/2); IR (KBr) ν 3419, 2958, 2873, 1714, 1630, 1473, 1304, 1180, 1051, 817 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 12H, $C(CH_3)_2$), 1.51 (m, 4 H, CH_2CH_2), 2.24 (t, J = 5.2 Hz, 2 H, OH), 2.33 (t, J = 7.6 Hz, 4 H, CH_2CH_2), 3.33 (d, J = 5.2 Hz, 4H, $HOCH_2$) , 4.01 (s, 4H, CH_2O), 5.56 (d, J = 1.2 Hz, 2 H, C=CH), 6.16 (d, J = 1.2 Hz, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 ($C(CH_3)_2$), 28.0

(CH_2CH_2), 31.7 (CH_2CH_2), 36.6 ($C(CH_3)_2$), 68.2 (OCH_3), 69.5 ($HOCH_2$), 125.2 (C=CH), 140.4 (C=CH), 167.7 (C=O); MS-FAB *m /z* 371.2 [$(M + H)^+$; calcd for $C_{25}H_{43}O_6$: 371.2]. Anal. Calcd for $C_{20}H_{34}O_6$: C, 64.84; H, 9.25. Found: C, 64.55; H, 9.04.

In situ trapping of the vinyl silver intermediate with MeOD (giving tetramethylene-tethered bis(2,2-dimethyl-3-hydroxypropyl-(Z)-3-deuterium propenoate)



AgOTf (77 mg, 0.30 mmol) was added to a solution of tetramethylene-tethered bis(cyclopropenone acetal) (100 mg, 0.30 mmol) and Et_3N (61 mg, 0.60 mmol) in anhydrous MeOD (2 mL) at -70 °C. After addition, the reaction was stirred at -70 °C for 30 min, and then stirred at 25 °C for 24 h. The resulting mixture was passed though short SiO_2 column, then HCl (3 mL, 0.3 M) were added, and the resulting mixture was stirred for 10 min. Saturated aqueous $NaHCO_3$ was added and adjusted pH to 7, extracted with EtOAc (3 x 15 mL), and the combined EtOAc extracts were dried over Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (Hexane/EtOAc, 5/3) gave compound **2** as a white solid (102 mg, 91% yield, cis-D > 99%): mp 53-54 °C; R_f = 0.10 (EtOAc/hexane = 1/2); IR (KBr) ν 3440, 2958, 2873, 1716, 1608, 1475, 1248, 1172, 1053, 879 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 12H, $C(CH_3)_2$), 1.51 (m, 4 H, CH_2CH_2), 2.28 (s, 2 H, OH), 2.33 (t, J = 7.6 Hz, 4 H, CH_2CH_2), 3.32 (d, J = 5.2 Hz, 4H, $HOCH_2$) , 4.01 (s, 4H, CH_2O), 5.54 (t, J = 1.2 Hz, 2 H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 ($C(CH_3)_2$), 28.1 (CH_2CH_2), 31.7 (CH_2CH_2), 36.7 ($C(CH_3)_2$), 68.2 (OCH_3), 69.5 ($HOCH_2$), 125.2 (C=CH), 140.1 (C=CH), 167.6 (C=O);

MS-FAB *m* /z 373.3 [(M + H)$^+$; calcd for $C_{20}H_{33}D_2O_6$: 373.3]. Anal. Calcd for $C_{20}D_2H_{32}O_6$: C, 64.49; H, 9.74. Found: C, 64.55; H, 9.67.

Cartesian Coordinate of representative stationary points
(B3LYP/631A//B3LYP/631A)

Cationic vinylcopper(I) complex **A**

SCF Done: E(RB+HF-LYP) = -1905.74475372 a.u.

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.440271	-.587672	.000000
2	6	1.251901	.809443	.000000
3	6	.000000	1.363347	.000000
4	1	2.159011	1.409620	.000000
5	29	-1.606689	.366813	.000000
6	1	-.022618	2.455166	.000000
7	8	2.613800	-1.200526	.000000
8	8	.410381	-1.426319	.000000
9	1	3.418150	-.611479	.000000
10	1	.692960	-2.386847	.000000

Cationic copper vinylcarbene complex **B**

SCF Done: E(RB+HF-LYP) = -1756.71940620 a.u.

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1	1.927838	-.858815	.000000
2	6	2.277287	.171512	.000000
3	6	1.390767	1.215228	.000000
4	1	3.353527	.329509	.000000
5	6	.000000	.985230	.000000
6	1	1.776282	2.234239	.000000
7	1	-.592870	1.906508	.000000
8	29	-.981831	-.615285	.000000