Supporting Information

Thermal and Palladium-Catalyzed [3 + 2] Synthesis of Cyclopentadienone Acetals from Cyclopropenone Acetals and Acetylenes

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1. General

IR spectra were obtained on an ASI Applied Systems REACT IR1000 equipped with an attenuated total reflection (ATR) instrument. NMR spectra were obtained on JEOL FX-200, EX-270, ECX-400, ECA-500 and Bruker AV-500 spectrometers. ¹H NMR spectra in CDCl₃ were referenced internally to tetramethylsilane as a standard. ¹³C NMR spectra in CDCl₃ were referenced to the solvent resonance, and methyl, methylene, and methyne signals were assigned by DEPT spectra. Nuclear Overhauser effects were measured by DPGSE-NOE method¹ or differential NOE method. *Endo* selectivity in Diels-Alder reaction between cyclopentadienone acetal (CPDA) and olefin was determined by three-bond coupling constant (³J_{CH}) measurement.² X-ray diffraction study was carried out on a MacScience DIP2030 Imaging Plate diffractometer. Space group determination, structural

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(1) Stott, K.; Keeler, J.; Van, Q. N.; Shaka, A. *J. Magn. Reson.* **1997**, *125*, 302-324.

(2) Hansen, P. E. *Prog. NMR Spectrosc.* **1981**, *14*, 175-296; Matsumori, N.; Kaneno, D. Murata, M. Nakamura, H.; Tachibana, K. *J. Org. Chem.* **1999**, *64*, 866-876.

solution, and refinement were performed using a maXus program.

2. Materials

Substituted cyclopropenone acetals (CPA) were synthesized as previously reported.³ Acetylenes and olefins were purchased and purified by distillation or recrystallization before reactions. Phenyl(trifluoromethanesulfonyl)acetylene **10** was synthesized as reported.⁴ Palladium(II) acetate was purchased and purified by recrystallization. THF (dehydrated, stabilizer-free) was purchased from WAKO Chemical Industry, Ltd. and dried on molecular sieves 4Å. All other solvents were purified by distillation and dried on molecular sieves 4Å.

3. Synthetic Procedure and Physical Properties

Thermal synthesis of 4-ethyl-8,8-dimethyl-2-phenyl-1-trifluoromethanesulfonyl-6,10-dioxo-spiro[4.5]deca-1,3-diene 14a: Ethyl-CPA **2** (525 μ L, 3.00 mmol) and phenyl(trifluoromethanesulfonyl)acetylene **10** (606 mg, 2.59 mmol) were dissolved in 1.5 mL of toluene in a sealed tube. The reaction vessel was heated at 150 °C for 23 h. The solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 3% ethyl acetate/hexane) afforded the title compound **14a** as a yellow solid (698 mg, 1.74 mmol, 67%). A single crystal was obtained by recrystallization from ethyl acetate/hexane, and the structure was determined by X-ray diffraction study (Figure S11). IR (powder) 2972, 2949, 2903, 2876, 1621, 1548, 1490, 1471, 1451, 1424, 1397, 1355, 1320, 1270, 1197, 1177, 1158, 1131, 1081, 1027, 992, 973, 934, 888, 861, 807, 768, 699, 656 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 1.00 (s, 3H), 1.20 (t, J = 7.3 Hz, 3H), 1.21 (s, 3H), 2.55 (dq, J = 2.4, 7.3 Hz, 2H), 3.70 (d, J = 11 Hz, 2H), 4.34 (d, J = 11 Hz, 2H), 5.90 (t, J = 2.4 Hz, 1H), 7.39 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 10.56 (CH_3), 22.00 (CH_2), 22.81 (CH_3), 23.93

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- (3) Nakamura, M.; Wang, X. -Q.; Isaka, M.; Yamago, S.; Nakamura, E. *Org. Synth.* **2003**, *80*, 144-159; Isaka, M.; Matsuzawa, S.; Yamago, S.; Ejiri, S.; Miyachi, Y.; Nakamura, E. *J. Org. Chem.* **1989**, *54*, 4727-4729; Isaka, M.; Ando, R.; Morinaka, Y.; Nakamura, E. *Tetrahedron Lett.* **1991**, *32*, 1339-1342.
- (4) Xiang, J. S.; Mahadevan, A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4284-4290.

(CH₃), 29.49, 72.00 (CH₂), 107.92, 120.06 (q, $J = 325$ Hz, CF₃), 126.62 (CH), 127.45 (CH), 127.90 (CH), 128.51, 129.73 (CH), 132.89, 164.50, 168.84; Anal. Calcd for C₁₈H₂₁O₄SF₃: C, 56.71; H, 5.26; S, 7.97; F, 14.16. Found: C, 56.85; H, 5.35; S, 7.90; F, 14.39.

Thermal synthesis of 8,8-dimethyl-4-phenyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14b: Phenyl-CPA **3** (324 mg, 1.50 mmol) and dimethyl acetylenedicarboxylate **11** (184 μ L, 1.50 mmol) were dissolved in 0.38 mL of toluene and heated at 100 °C for 1 h. The solvent was removed *in vacuo* to give crude materials. Yield was determined to be 40% by ¹H NMR analysis of the crude materials using tetrachloroethane as an internal standard.

Thermal synthesis of 8,8-dimethyl-3-naphthalen-1-yl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14c: 1-Naphthyl-CPA **4** (266 mg, 1.00 mmol) and dimethyl acetylenedicarboxylate **11** (123 μ L, 1.00 mmol) were dissolved in 0.50 mL of toluene and heated at 100 °C for 1 h. The solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 15% ethyl acetate/hexane) afforded the title compound **14c** in 42% yield (173 mg, 0.424 mmol) and regioisomer **14e** (eluent: 15% ethyl acetate/hexane) in 3% yield (11.2 mg, 0.027 mmol). **14c**: IR (powder) 2954, 2871, 1727, 1710, 1644, 1588, 1436, 1397, 1345, 1304, 1268, 1248, 1227, 1204, 1173, 1142, 1094, 1073, 1054, 1019, 994, 940, 805, 782, 741, 708, 668 cm⁻¹; ¹H NMR (500

MHz, CDCl₃) δ 0.83 (s, 3H), 1.47 (s, 3H), 3.48 (s, 3H), 3.79 (m, 4H), 3.85 (s, 3H), 7.13 (s, 1H), 7.45 (m, 4H), 7.84 (m, 2H), 7.94 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 22.09 (CH₃), 22.79 (CH₃), 30.60, 52.01 (CH₃), 52.10 (CH₃), 75.29 (CH₂), 106.97, 125.04 (CH), 125.27 (CH), 126.06 (CH), 126.11 (CH), 126.28 (CH), 128.30 (CH), 129.01 (CH), 130.83, 131.11, 132.27 (CH), 133.44, 134.71, 141.46, 147.32, 161.42, 164.71; Anal. Calcd for C₂₄H₂₄O₆: C, 70.57; H, 5.92. Found: C, 70.45; H, 6.11. Position of the naphthyl substituent on cyclopentadiene ring was determined by NOE measurement (Figure S1).

14e: IR (powder) 2954, 2875, 1721, 1642, 1603, 1586, 1573, 1509, 1434, 1333, 1461, 1397, 1256, 1239, 1167, 1140, 1108, 1092, 1061, 1028, 984, 801, 776, 739, 699, 666, 938, 911, 897, 868 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.63 (s, 3H), 0.80 (s, 3H), 3.47 (d, *J* = 11.6 Hz, 2H), 3.82 (d, *J* = 11.6 Hz, 2H), 3.84 (s, 3H), 3.93 (s, 3H), 6.36 (s, 1H), 7.46 (m, 3H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.83 (m, 2H), 8.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 22.40 (CH₃), 22.48 (CH₃), 29.72, 52.35 (CH₃), 52.71 (CH₃), 72.55 (CH₂), 109.43, 124.77 (CH), 125.75 (CH), 126.12 (CH), 126.15 (CH), 126.72 (CH), 127.25 (CH), 128.01 (CH), 128.38 (CH), 132.10, 132.43, 133.49, 136.42, 142.18, 147.37, 163.43, 167.06; Anal. Calcd for C₂₄H₂₄O₆: C, 70.57; H, 5.92. Found: C, 70.35; H, 6.01. Position of the naphthyl substituent on cyclopentadiene ring was determined by NOE measurement (Figure S2).

Thermal synthesis of 8,8-dimethyl-1,3-diphenyl-4-trifluoromethanesulfonyl-6,10-dioxaspiro[4.5]deca-1,3-diene-2-carboxylic acid isopropyl ester 14d: Disubstituted CPA 5 was

synthesized *in situ* as previously reported.⁵ To a solution of phenyl-CPA **3** (64.9 mg, 0.300 mmol) and *N,N,N',N',N'',N''*-hexamethylphosphorimidic triamide (HMPA) (104 μ L, 0.300 mmol) in 0.60 mL of THF was added 183 μ L of BuLi (1.64 M in hexane, 0.300 mmol), and the reaction mixture was stirred at -78 °C for 2 h. The solution was transferred into a solution of isopropyl chloroformate (36.4 μ L, 0.320 mmol) in 0.30 mL of THF at -78 °C, and the reaction mixture was stirred for 2 h. Phenyl(trifluoromethanesulfonyl)acetylene **10** (70.2 mg, 0.300 mmol) was then added, and the reaction mixture was warmed to ambient temperature and stirred for 24 h. The mixture was diluted with ether, washed with water and saturated brine, and dried over Na₂SO₄. The solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 35% ethyl acetate/hexane) afforded the title compound **14d** as a solid (63.5 mg, 0.120 mmol, 40%). IR (CHCl₃) 3010, 2400, 1720, 1350, 1210, 1100, 760 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.57 (s, 3H), 0.73 (d, *J* = 6.0 Hz, 6H), 1.05 (s, 3H), 3.63 (d, *J* = 11.0 Hz, 2H), 3.91 (d, *J* = 11.0 Hz, 2H), 4.63 (dq, *J* = 6.0, 6.0 Hz, 1H), 7.5 (m, 10H); Anal. Calcd for C₂₆H₂₇O₆SF₃: C, 59.53; H, 5.19; S, 6.11. Found: C, 59.80; H, 5.40, S, 6.30.

Palladium-catalyzed synthesis of 4-ethyl-8,8-dimethyl-2-phenyl-1-trifluoromethanesulfonyl-6,10-dioxaspiro[4.5]deca-1,3-diene 14a: To a solution of palladium(II) acetate (0.22 mg, 0.0010 mmol) and phenyl(trifluoromethanesulfonyl)acetylene **10** (23.4 mg, 0.100 mmol) in THF (20 μ L) was added a solution of ethyl-CPA **2** (35.0 μ L, 0.200 mmol) in THF (180 μ L) during the period of 20 min. The reaction mixture was stirred for 4 h at room temperature and the solvent was removed *in vacuo* to give crude materials. The spectra of the major product were

(5) Tokuyama, H.; Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 5523-5530.

identical to those of CPDA **14a** (see above). Yield was determined to be 28% by ^1H NMR using tetrachloroethane as an internal standard.

Palladium-catalyzed synthesis of 8,8-dimethyl-4-phenyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester **14b:** To a solution of palladium(II) acetate (11.2 mg, 0.0500 mmol) and dimethyl acetylenedicarboxylate **11** (615 μL , 5.00 mmol) in THF (1.0 mL) was added a solution of phenyl-CPA **3** (2.16 g, 10.0 mmol) in THF (9.0 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 3 h, diluted with ether, and filtrated to give crude materials as a viscous liquid and 484 mg of diene **15** as a white precipitate (1.12 mmol, 22%). Purification of the filtrate by silica gel column chromatography (eluent: 25% ethyl acetate/hexane) afforded the title compound **14b** as a white solid (1.56 g, 4.36 mmol, 87%). A single crystal of **14b** was obtained by recrystallization from ethyl acetate/hexane, and the structure was determined by X-ray diffraction study (Figure S12). A single crystal of **15** was also obtained by recrystallization from methylene chloride, and the structure was determined by X-ray diffraction study (Figure S19). IR (powder) 2963, 2955, 2895, 1723, 1713, 1588, 1448, 1433, 1366, 1268, 1241, 1164, 1131, 1103, 1058, 1025, 1008, 995, 969, 934, 909, 863, 791, 771, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.78 (s, 3H), 1.29 (s, 3H), 3.64 (dd, $J = 1.4, 11$ Hz, 2H), 3.80 (s, 3H), 3.89 (s, 3H), 4.15 (d, $J = 11$ Hz, 2H), 6.52 (s, 1H), 7.34 (m, 3H), 7.76 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.78 (CH_3), 24.07 (CH_3), 29.42, 52.32 (CH_3), 52.82 (CH_3), 73.04 (CH_2), 109.84, 123.23 (CH), 127.35 (CH), 127.96 (CH), 128.41 (CH), 132.95, 136.37, 142.43, 147.99, 162.98, 168.27; Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_6$: C, 67.03; H, 6.19. Found: C, 66.96; H, 6.24.

2,5-Diphenyl-hexa-2,4-dienedioic acid bis-(3-hydroxy-2,2-dimethyl-propyl)ester 15: IR (powder) 3309, 2960, 2935, 2875, 1733, 1710, 1636, 1509, 1492, 1476, 1443, 1418, 1401, 1374, 1364, 1355, 1339, 1314, 1287, 1233, 1183, 1154, 1059, 1036, 1019, 974, 946, 913, 780, 764, 729, 700, 666, 617 cm^{-1} ; ^1H NMR (500 MHz, CD_2Cl_2) 0.78 (s, 12H), 1.96 (bs, 2H), 3.15 (s, 4H), 3.92 (s, 4H), 7.31 (m, 4H), 7.40 (s, 2H), 7.40 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) 21.63 (CH_3), 36.76, 68.70 (CH_2), 70.76 (CH_2), 128.55 (CH), 129.00 (CH), 130.68 (CH), 135.53 (CH), 139.71, 167.26; Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{O}_6$: C, 72.08; H, 7.35. Found: C, 71.82; H, 7.27.

Palladium-catalyzed synthesis of 8,8-dimethyl-4-naphthalen-1-yl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14e: To a solution of palladium(II) acetate (2.2 mg, 0.010 mmol) and dimethyl acetylenedicarboxylate **11** (123 μL , 1.00 mmol) in THF (0.2 mL) was added a solution of 1-naphthyl-CPA **4** (533 mg, 2.00 mmol) in THF (1.8 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 23 h, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 20% ethyl acetate/hexane) afforded the title compound **14e** as a white solid (287 mg, 0.71 mmol, 71%). The spectra of the major product were identical to those of CPDA **14e** (see above).

Palladium-catalyzed synthesis of 4-(4-methoxy-phenyl)-8,8-dimethyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14f: To a solution of palladium(II) acetate (2.2 mg, 0.010 mmol) and dimethyl acetylenedicarboxylate **11** (123 μ L, 1.00 mmol) in THF (0.2 mL) was added a solution of 4-methoxyphenyl-CPA **6** (493 mg, 2.00 mmol) in THF (1.8 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 2 h, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 15% ethyl acetate/hexane) afforded the title compound **14f** as a white solid (356 mg, 0.91 mmol, 91%). A single crystal was obtained by recrystallization from ethyl acetate/hexane, and the structure was determined by X-ray diffraction study (Figure S13). IR (powder) 2958, 1738, 1723, 1605, 1511, 1463, 1430, 1347, 1287, 1252, 1237, 1177, 1144, 1102, 1057, 1027, 984, 940, 895, 828, 785, 766, 695, 660 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.79 (s, 3H), 1.32 (s, 3H), 3.65 (d, $J = 12$ Hz, 2H), 3.82 (s, 3H + 3H), 3.89 (s, 3H), 4.18 (d, $J = 12$ Hz, 2H), 6.44 (s, 1H), 6.89 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.76 (CH_3), 24.21 (CH_3), 29.35, 52.34 (CH_3), 52.85 (CH_3), 55.23 (CH_3), 73.13 (CH_2), 109.95, 113.69 (CH), 121.56 (CH), 125.75, 128.92 (CH), 137.13, 141.76, 147.95, 159.99, 163.5, 168.74; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_7$: C, 64.94; H, 6.23. Found: C, 64.85; H, 6.32.

Palladium-catalyzed synthesis of 4-(4-chloro-phenyl)-8,8-dimethyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14g: To a solution of palladium(II) acetate (4.5 mg, 0.020 mmol) and dimethyl acetylenedicarboxylate **11** (246 μ L, 2.00 mmol) in THF (0.4 mL) was added a solution of 4-chlorophenyl-CPA **7** (1.00 g, 4.00 mmol) in THF (3.6 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 2 h, and the solvent was removed *in vacuo* to give crude materials.

Purification by silica gel column chromatography (eluent: 10% ethyl acetate/hexane) afforded the title compound **14g** as a white solid (584 mg, 1.49 mmol, 74%). IR (powder) 3089, 2995, 2962, 2950, 2927, 2904, 2867, 2854, 1725, 1254, 1241, 1135, 828, 785 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.78 (s, 3H), 1.28 (s, 3H), 3.64 (d, J = 11.6 Hz, 2H), 3.83 (s, 3H), 3.90 (s, 3H), 4.15 (d, J = 11.6 Hz, 2H), 6.52 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 22.71 (CH_3), 24.02 (CH_3), 29.38, 52.44 (CH_3), 52.95 (CH_3), 73.19 (CH_2), 109.91, 123.89 (CH), 128.47 (CH), 128.87 (CH), 131.57, 134.57, 136.42, 142.89, 147.00, 163.17, 168.55; Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{ClO}_6$: C, 61.15; H, 5.39. Found: C, 61.20; H, 5.54.

Palladium-catalyzed synthesis of 4-ethyl-8,8-dimethyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14h: To a solution of palladium(II) acetate (2.2 mg, 0.010 mmol) and dimethyl acetylenedicarboxylate **11** (123 μL , 1.00 mmol) in THF (0.2 mL) was added a solution of ethyl-CPA **2** (350 μL , 2.00 mmol) in THF (1.8 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 2 h, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 15% ethyl acetate/hexane) afforded the title compound **14h** as white solid (235 mg, 0.76 mmol, 76%). A single crystal was obtained by recrystallization from chloroform, and the structure was determined by X-ray diffraction study (Figure S14). IR (powder) 2973, 2952, 2903, 2880, 2873, 1728, 1715, 1605, 1471, 1437, 1431, 1396, 1363, 1334, 1262, 1224, 1150, 1117, 1095, 1069, 1056, 1027, 1020, 988, 945, 903, 851, 804, 791, 768, 712 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.77 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H), 1.26 (s, 3H), 2.28 (dq, J = 2.4, 7.2 Hz, 2H), 3.55 (dd, J = 11 Hz, 2H), 3.79 (s, 3H), 3.86 (s, 3H), 4.06 (d, J = 11 Hz, 2H), 5.94 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 10.65 (CH_3), 19.30 (CH_2), 22.36 (CH_3), 22.90 (CH_3), 29.64, 52.24 (CH_3), 52.68 (CH_3), 72.78 (CH_2), 107.70, 119.19 (CH), 137.58,

141.31, 154.72, 163.63, 167.94; Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.82; H, 7.19.

Palladium-catalyzed synthesis of 4-(1-hydroxy-cyclohexyl)-8,8-dimethyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14i: To a solution of palladium(II) acetate (9.0 mg, 0.040 mmol) and dimethyl acetylenedicarboxylate **11** (492 μ L, 4.00 mmol) in THF (0.4 mL) was added a solution of 1-hydroxycyclohexyl-CPA **8** (953 mg, 4.00 mmol) in THF (3.6 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 2 days, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 10% ethyl acetate/hexane) afforded the title compound **14i** as a white solid (1.07 g, 2.8 mmol, 71%). A single crystal was obtained, and the structure was determined by X-ray diffraction study (Figure S15). IR (powder) 3460, 3440, 2964, 2931, 2852, 1740, 1723, 1640, 1600, 1470, 1438, 1414, 1391, 1329, 1293, 1252, 1223, 1208, 1189, 1158, 1146, 1096, 1056, 1017, 986, 976, 955, 836, 789 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.77 (s, 3H), 1.26 (m, 1H), 1.36 (s, 3H), 1.51 (m, 2H), 1.60 (m, 1H), 1.70 (m, 2H), 1.70 (m, 2H), 1.96 (m, 2H), 3.63 (d, $J = 12$ Hz, 2H), 3.80 (s, 3H), 3.81 (s, 1H), 3.87 (s, 3H), 4.85 (d, $J = 12$ Hz, 2H), 6.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.79 (CH_2), 22.49 (CH_3), 23.83 (CH_3), 25.63 (CH_2), 29.29, 37.36 (CH_2), 52.39 (CH_3), 52.96 (CH_3), 72.18, 73.23 (CH_2), 111.12, 123.34 (CH), 135.88, 142.36, 152.42, 163.15, 168.56; Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 62.91; H, 7.48.

Palladium-catalyzed synthesis of 8,8-dimethyl-4-trimethylsilylanyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1,2-dicarboxylic acid dimethyl ester 14j: To a solution of palladium(II) acetate (2.2 mg, 0.010 mmol) and dimethyl acetylenedicarboxylate **11** (123 μ L, 1.00 mmol) in THF (0.2 mL) was added a solution of trimethylsilyl-CPA **9** (456 μ L, 2.00 mmol) in THF (1.8 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 1 h, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 5% ethyl acetate/hexane) afforded the title compound **14j** as a white solid (353 mg, 1.0 mmol, 100%). A single crystal was obtained, and the structure was determined by X-ray diffraction study (Figure S16). IR (powder) 2975, 2959, 2951, 2945, 2906, 2883, 1732, 1717, 1625, 1484, 1436, 1425, 1320, 1313, 1267, 1257, 1245, 1221, 1202, 1141, 1106, 1065, 1026, 1016, 994, 982, 857, 839, 826, 802, 787, 768, 751, 694 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.22 (s, 9H), 0.76 (s, 3H), 1.30 (s, 3H), 3.57 (dd, $J = 1.2, 11$ Hz, 2H), 3.78 (s, 3H), 3.87 (s, 3H), 4.01 (d, $J = 11$ Hz, 2H), 6.53 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -0.56 (CH_3), 23.32 (CH_3), 24.31 (CH_3), 30.03, 52.89 (CH_3), 53.43 (CH_3), 73.64 (CH_2), 114.41, 137.28 (CH), 136.22, 147.45, 153.97, 163.59, 169.52; Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_6\text{Si}$: C, 57.60; H, 7.39. Found: C, 57.54; H, 7.34.

Palladium-catalyzed synthesis of 8,8-dimethyl-4-trimethylsilylanyl-6,10-dioxaspiro[4.5]deca-1,3-diene-1-carboxylic acid methyl ester 14k: To a solution of palladium(II) acetate (2.2 mg, 0.010 mmol) in THF (0.1 mL) was added methyl propiolate **12** (178 μ L, 2.00 mmol) and trimethylsilyl-CPA **9** (228 μ L, 1.00 mmol). The reaction mixture was stirred at ambient temperature for 6 days, and the solvent was removed *in vacuo* to give crude materials. Purification on silica gel column chromatography (eluent: 10% ethyl

acetate/hexane) afforded the title compound **14k** as a white solid (113 mg, 0.38 mmol, 38%). A single crystal was obtained by recrystallization from pentane, and the structure was determined by X-ray diffraction study (Figure S17). IR (powder) 2962, 2951, 2897, 1705, 1600, 1545, 1472, 1437, 1399, 1364, 1309, 1275, 1246, 1238, 1192, 1180, 1130, 1079, 1050, 1022, 993, 939, 867, 831, 756, 699, 640, 621, 611 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.24 (s, 9H), 0.89 (s, 3H), 1.31 (s, 3H), 3.46 (d, $J = 10.9$ Hz, 2H), 3.75 (s, 3H), 4.54 (d, $J = 10.9$ Hz, 2H), 6.40 (d, $J = 2.3$ Hz, 1H), 7.17 (d, $J = 2.3$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -1.31 (CH_3), 22.32 (CH_3), 24.57 (CH_3), 29.42, 51.80 (CH_3), 71.82 (CH_2), 111.26, 137.91 (CH), 141.68, 145.37 (CH), 160.12, 165.14; Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_4\text{Si}$: C, 60.78; H, 8.16. Found: C, 60.57; H, 8.13.

Palladium-catalyzed synthesis of 8,8-dimethyl-1-phenyl-4-trimethylsilanyl-6,10-dioxaspiro[4.5]deca-1,3-diene-2-carboxylic acid methyl ester 14l: To a solution of palladium(II) acetate (1.1 mg, 0.0050 mmol) and methyl phenylpropiolate **13** (73.3 μL , 0.500 mmol) in THF (0.1 mL) was added a solution of trimethylsilyl-CPA **9** (228 μL , 1.00 mmol) in THF (0.9 mL) during the period of 20 min. The reaction mixture was stirred at ambient temperature for 1 day, and the solvent was removed *in vacuo* to give a crude material. Purification by silica gel column chromatography (eluent: 10% ethyl acetate/hexane) afforded the title compound **14l** as a white solid (179 mg, 0.48 mmol, 96%). A single crystal was obtained by recrystallization from methylene chloride/pentane, and the structure was determined by X-ray diffraction study (Figure S18). IR (powder) 2958, 2889, 2870, 1722, 1648, 1634, 1599, 1553, 1494, 1466, 1444, 1436, 1366, 1321, 1264, 1229, 1169, 1153, 1137, 1096, 1060, 1038, 1033, 1016, 1003, 997, 964, 838, 788, 759, 712, 701, 689, 628 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.28 (s, 9H), 0.54 (s, 3H), 1.09 (s, 3H), 3.42 (d, $J = 11.5$ Hz, 2H), 3.55 (s, 3H), 3.69 (d, $J = 11.5$ Hz, 2H), 6.76 (s, 1H), 7.4 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ -0.65 (CH_3),

23.08 (CH₃), 23.73 (CH₃), 30.56, 51.36 (CH₃), 72.03 (CH₂), 113.26, 127.66 (CH), 127.78 (CH), 128.36 (CH), 130.72, 137.12, 140.91 (CH), 149.67, 159.29, 164.17; Anal. Calcd for C₂₁H₂₈O₄Si: C, 67.71; H, 7.58. Found: C, 67.46; H, 7.52.

Synthesis of Diels-Alder adduct with maleic anhydride 16: CPDA **14b** (179 mg, 0.500 mmol) and maleic anhydride (88.3 mg, 0.900 mmol) were dissolved in 1.0 mL of toluene and stirred for 4 h at 65 °C. The solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 30% ethyl acetate/hexane) afforded the title compound **16** as a white solid (228 mg, 0.50 mmol, 100%). A single crystal was obtained by recrystallization from methylene chloride/pentane, and the structure was determined by X-ray diffraction study (Figure S20). IR (powder) 2983, 2952, 2894, 1858, 1783, 1727, 1598, 1436, 1347, 1302, 1229, 1206, 1164, 1119, 1106, 1084, 1048, 1032, 1009, 942, 919, 834, 787, 753, 727, 697, 660 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.41 (s, 3H), 0.69 (s, 3H), 3.09 (dd, *J* = 0.9, 11.0 Hz, 1H), 3.28 (dd, *J* = 0.9, 11.0 Hz, 1H), 3.35 (d, *J* = 11.0 Hz, 1H), 3.46 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 3.90 (s, 3H), 4.54 (m, 2H), 7.23 (s, 1H), 7.43 (m, 3H), 7.54 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.10 (CH₃), 22.57 (CH₃), 29.76 (CH₃), 46.84 (CH), 47.19 (CH), 52.35 (CH₃), 52.91 (CH₃), 65.90, 66.86, 72.85 (CH₂), 72.90 (CH₂), 119.96, 128.49 (CH), 128.68 (CH), 128.74 (CH), 131.96, 136.93, 144.56 (CH), 161.88, 167.73, 168.20, 169.27; Anal. Calcd for C₂₄H₂₄O₉: C, 63.15; H, 5.30. Found: C, 62.96; H, 5.26.

Synthesis of Diels-Alder adduct with acrylonitrile 17: CPDA **14b** (143 mg, 0.400 mmol) was dissolved in 1.6 mL of acrylonitrile and stirred at ambient temperature for 14 h, and acrylonitrile was removed *in vacuo* to give the title compound **17** as a white solid (162 mg, 0.394 mmol, 98%). IR (powder) 2956, 2902, 2875, 2240, 1737, 1706, 1605, 1465, 1438, 1341, 1295, 1283, 1260, 1248, 1225, 1169, 1131, 1106, 1059, 1030, 988, 976, 951, 882, 832, 803, 793, 772, 754, 731, 700, 658, 625 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.42 (s, 3H), 0.68 (s, 3H), 1.79 (dd, J = 5, 16 Hz, 1H), 3.04 (dd, J = 2, 14 Hz, 1H), 3.15 (dd, J = 12, 16 Hz, 1H), 3.28 (dd, J = 2, 11 Hz, 1H), 3.32 (d, J = 11 Hz, 1H), 3.45 (d, J = 14 Hz, 1H), 3.81 (s, 3H), 3.82 (s, 3H), 4.05 (dd, J = 5, 12 Hz, 1H), 7.18 (s, 1H), 7.40 (m, 3H), 7.80 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.21 (CH₃), 22.54 (CH₃), 29.88, 30.32 (CH), 34.00 (CH₂), 52.06 (CH₃), 52.41 (CH₃), 62.91, 66.78, 72.56 (CH₂), 72.67 (CH₂), 114.96, 120.33, 128.49 (br, CH + CH), 128.52 (CH), 132.72, 140.13, 143.27 (CH), 162.88, 167.00; Anal. Calcd for C₂₃H₂₅NO₆: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.00; H, 6.22; N, 3.24. The position of cyanyl substituent on bicyclo[2.2.1]heptene skeleton was determined by NOE measurement (Figure S3). *Endo* selectivity was determined by three-bond coupling constant (³ J_{CH}) measurement (Figure S4). The value of ³ J_{CH} = 6.0 Hz shows that the dihedral angle is 180°.

Synthesis of Diels-Alder adduct with ethylene 18: Method A; CPDA **14b** (89.6 mg, 0.250 mmol) was dissolved in 1.0 mL of toluene and stirred for at 100 °C for 8 days under atmospheric pressure ethylene (balloon), and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 20% ethyl acetate/hexane) afforded the title compound **18** as a white solid (96 mg, 0.25 mmol, 100%). Method B; CPDA **14b** (89.6 mg, 0.250 mmol) was dissolved in 1.0 mL of toluene and stirred

at 100 °C for 8 days under 2 MPa pressure ethylene, and the solvent was removed *in vacuo* to give crude materials. Purification by silica gel column chromatography (eluent: 20% ethyl acetate/hexane) afforded of the title compound **18** as a white solid (97 mg, 0.25 mmol, 100%). IR (powder) 2964, 2952, 2875, 1725, 1713, 1603, 1466, 1441, 1428, 1328, 1268, 1254, 1227, 1192, 1169, 1127, 1110, 1083, 1065, 1019, 1003, 976, 967, 949, 934, 882, 864, 807, 793, 772, 754, 720, 695, 631 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.44 (s, 3H), 0.69 (s, 3H), 1.30 (ddd, *J* = 4, 10, 11Hz, 1H), 1.43 (ddd, *J* = 4, 10, 11Hz, 1H), 2.71 (ddd, *J* = 4, 10, 10Hz, 1H), 2.85 (ddd, *J* = 4, 10, 10Hz, 1H), 3.02 (dd, *J* = 1, 11 Hz, 1H), 3.28 (dd, *J* = 1, 11 Hz, 1H), 3.33 (d, *J* = 11 Hz, 1H), 3.41 (d, *J* = 11 Hz, 1H), 3.76 (s, 3H), 3.81 (s, 3H), 7.13 (s, 1H), 7.33 (m, 3H), 7.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.44 (CH₃), 22.76 (CH₃), 26.93 (CH₂), 28.14 (CH₂), 30.08, 51.63 (CH₃), 52.01 (CH₃), 63.15, 63.78, 72.34 (CH₂), 72.44 (CH₂), 115.81, 127.45 (CH), 128.00 (CH), 128.79 (CH), 136.62, 137.11, 146.89 (CH), 163.73, 171.72; Anal. Calcd for C₂₂H₂₆O₆: C, 68.38; H, 6.78. Found: C, 68.26; H, 6.87.

Synthesis of Diels-Alder adduct with 2,5-norbornadiene 19: CPDA **14b** (143 mg, 0.400 mmol) was dissolved in 0.80 mL of 2,5-norbornadiene and stirred at 80 °C for 7 h, and the solvent was removed *in vacuo* to give the title compound **19** as a white solid (176 mg, 0.392 mmol, 98%). A single crystal was obtained by recrystallization from methylene chloride/pentane, and the structure was determined by X-ray diffraction study (Figure S21). IR (powder) 2962, 2946, 1740, 1717, 1600, 1465, 1447, 1434, 1362, 1312, 1299, 1275, 1264, 1250, 1233, 1221, 1210, 1191, 1177, 1158, 1127, 1113, 1094, 1073, 1059, 1032, 1003, 974, 965, 942, 924, 909, 895, 868, 853, 814, 801, 785, 770, 747, 720, 702, 687, 656, 621 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.43 (s, 3H), 0.70 (s, 3H), 0.99 (d, *J* = 10 Hz, 1H), 1.84 (d, *J* = 10 Hz, 1H), 2.61

(d, $J = 2$ Hz, 1H), 2.82 (d, $J = 2$ Hz, 1H), 3.00 (d, $J = 11$ Hz, 1H), 3.04 (d, $J = 7$ Hz, 1H), 3.16 (d, $J = 11$ Hz, 1H), 3.17 (d, $J = 7$ Hz, 1H), 3.23 (d, $J = 11$ Hz, 1H), 3.37 (d, $J = 11$ Hz, 1H), 3.78 (s, 3H), 3.79 (s, 3H), 6.30 (dd, $J = 3, 3$ Hz, 1H), 6.38 (dd, $J = 3, 3$ Hz, 1H), 7.06 (s, 1H), 7.35 (m, 3H), 7.54 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 22.83 (CH_3), 23.09 (CH_3), 30.54, 41.44 (CH), 42.08 (CH_2), 42.44 (CH), 46.59 (CH), 47.25 (CH), 51.89 (CH_3), 51.96 (CH_3), 64.64, 65.11, 72.27 (CH_2), 72.36 (CH_2), 121.05, 127.43 (CH), 128.12 (CH), 128.76 (CH), 135.62, 136.99, 140.19 (CH), 141.49 (CH), 147.80 (CH), 164.13, 171.55; Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{O}_6$: C, 71.98; H, 6.71. Found: C, 71.80; H, 6.75.

Synthesis of Diels-Alder adduct with ethyl vinyl ether 20: CPDA **14b** (179 mg, 0.500 mmol) was dissolved in 2.0 mL of ethyl vinyl ether and stirred at 30 °C for 26 h, and the solvent was removed *in vacuo* to give the title compound **20** as a white solid (215 mg, 0.50 mmol, 100%). IR (powder) 2954, 2933, 2890, 2875, 1731, 1702, 1605, 1434, 1355, 1337, 1295, 1260, 1245, 1225, 1171, 1084, 963, 928, 878, 853, 797, 758, 702 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.44 (s, 3H), 0.67 (s, 3H), 1.02 (t, $J = 7$ Hz, 3H), 1.47 (dd, $J = 2, 12$ Hz, 1H), 2.91 (d, $J = 11$ Hz, 1H), 3.07 (dd, $J = 7, 12$ Hz, 1H), 3.29 (m, 2H), 3.2-3.4 (m, 2H), 3.38 (d, $J = 11$ Hz, 1H), 3.77 (s, 3H), 3.79 (s, 3H), 4.99 (dd, $J = 2, 7$ Hz, 1H), 7.11 (s, 1H), 7.31 (m, 1H), 7.36 (m, 2H), 7.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.12 (CH_3), 22.43 (CH_3), 22.72 (CH_3), 30.14, 37.32 (CH_2), 51.54 (CH_3), 51.96 (CH_3), 63.10, 65.06 (CH_2), 68.66, 72.12 (CH_2), 72.25 (CH_2), 80.05 (CH), 116.49, 127.35 (CH), 127.95 (CH), 128.59 (CH), 135.27, 137.66, 144.26 (CH), 163.51, 171.24; Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{O}_7$: C, 66.96; H, 7.02. Found: C, 66.86; H, 7.07. The position of ethoxy substituent on bicyclo[2.2.1]heptene skeleton was determined by NOE measurement (Figure S5). *Endo* selectivity was determined by three-bond coupling

constant ($^3J_{\text{CH}}$) measurement (Figure S6). The value of $^3J_{\text{CH}} = 5.0$ Hz shows that the dihedral angle is 180° .

Synthesis of Diels-Alder adduct with furan 21: CPDA **14b** (179 mg, 0.500 mmol) was dissolved in 1.0 mL of furan and refluxed for 2 days, and the solvent was removed *in vacuo* to give crude materials. Purification on silica gel column chromatography (eluent: 25% ethyl acetate/hexane) afforded the title compound **21** as a white solid (200 mg, 0.47 mmol, 94%). IR (powder) 2960, 2902, 2875, 1737, 1706, 1605, 1465, 1438, 1341, 1295, 1283, 1260, 1248, 1225, 1169, 1131, 1106, 1059, 1030, 988, 976, 951, 882, 832, 803, 793, 772, 754, 731, 700, 658, 625 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.44 (s, 3H), 0.71 (s, 3H), 3.04 (dd, $J = 0.8, 11$ Hz, 1H), 3.26 (dd, $J = 0.8, 11$ Hz, 1H), 3.30 (d, $J = 11$ Hz, 1H), 3.52 (d, $J = 11$ Hz, 1H), 3.76 (s, 3H), 3.88 (s, 3H), 4.44 (ddd, $J = 2, 2, 9$ Hz, 1H), 4.68 (dd, $J = 2, 3$ Hz, 1H), 5.78 (d, $J = 9$ Hz, 1H), 6.15 (dd, $J = 2, 3$ Hz, 1H), 7.13 (s, 1H), 7.36 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.32 (CH_3), 22.61 (CH_3), 30.01, 50.41 (CH), 51.59 (CH_3), 52.12 (CH_3), 66.87, 67.02, 72.21 (CH_2), 72.37 (CH_2), 84.65 (CH), 98.83 (CH), 118.46, 127.57 (CH), 128.07 (CH), 128.46 (CH), 131.97, 135.30, 148.33 (CH), 149.27 (CH), 163.10, 170.15; Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_7$: C, 67.59; H, 6.15. Found: C, 67.52; H, 6.26. The position of substituents on bicyclo[2.2.1]heptene skeleton was determined by HMBC and NOE measurement (Figure S7-9). *Endo* selectivity was determined by three-bond coupling constant ($^3J_{\text{CH}}$) measurement (Figure S10). The value of $^3J_{\text{CH}} = 5.5$ Hz shows that the dihedral angle is 180° .

Synthesis of Dimethyl 4-phenylphthalate 22: Diels-Alder adduct with **19** (113 mg, 0.250 mmol) was dissolved in 2.0 mL of tetralin in a sealed tube. The reaction vessel was heated at 230 °C for 5 days. Purification by silica gel column chromatography (eluent: 5% ethyl acetate/toluene) afforded the title compound **22** in 86% yield (58.4 mg, 0.216 mmol) and tetraalkoxyethylene **23**^[6] (eluent: 40% ethyl acetate/hexane) in 52 % yield (14.6 mg, 0.0644 mmol). IR (powder) 3014, 2956, 1725, 1605, 1582, 1566, 1508, 1436, 1395, 1298, 1285, 1272, 1248, 1194, 1160, 1129, 1077, 1046, 1025, 1000, 959, 922, 897, 863, 824, 793, 780, 766, 746, 699, 675 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.93 (s, 3H), 3.94 (s, 3H), 7.46 (m, 3H), 7.62 (m, 2H), 7.74 (dd, *J* = 2, 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.91 (d, *J* = 2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 52.56 (CH₃), 52.66 (CH₃), 127.12 (CH), 127.25 (CH), 128.38 (CH), 128.94 (CH), 129.21 (CH), 129.63 (CH), 129.78, 132.99, 138.86, 144.24, 167.55, 168.25; Anal. Calcd for C₂₃H₂₅NO₆: C, 71.10; H, 5.22. Found: C, 70.96; H, 5.16.

5,5,5',5'-Tetramethyl-[2,2']bi[[1,3]dioxanylidene] 23: IR (powder) 2956, 2925, 2873, 2856, 1725, 1602, 1472, 1447, 1436, 1401, 1376, 1260, 1233, 1169, 1115, 1094, 1073, 1061, 1034, 762, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.13 (s, 12H), 4.08 (s, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 21.12 (CH₃), 28.44, 77.47 (CH₂), 148.09; Anal. Calcd for C₁₂H₂₀O₄: C, 63.14; H, 8.83. Found: C, 63.34; H, 8.73.

(6) Merkley, N.; Warkentin, J. *Can. J. Chem.* **2002**, *80*, 1187-1195.

4. Selected NMR Spectra

Figure S1. 1D DPGFSE-NOESY spectrum of CPDA **14c** measured at 400 MHz in CDCl_3 .

Figure S2.1D differential NOE spectrum of CPDA **14e** measured at 400 MHz in CDCl_3 .

Figure S3. 2D NOESY spectrum of Diels-Alder adduct **17**.

Figure S4. Carbon long-range J-resolved spectrum of Diels-Alder adduct **17**.

Figure S5. 1D DPFGE-NOESY spectrum of Diels-Alder adduct **20**.

Figure S6. Carbon long-range J-resolved spectrum of Diels-Alder adduct **20**.

Figure S7. HMQC spectrum of Diels-Alder adduct **21**.

Figure S8. HMBC spectrum of Diels-Alder adduct **21**.

Figure S9. 2D NOESY spectrum of Diels-Alder adduct **21**.

Figure S10. Carbon long-range J-resolved spectrum of Diels-Alder adduct **21**.

4. X-ray Structures

Figure S11. ORTEP drawing of CPDA **14a**. Color codes of atoms (other than C and H): O = red, F = green, S = purple.

Table S1. Crystal data for CPDA **14a** and collection parameters.

crystal system	monoclinic	formula	$\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_4\text{S}$
space group	$P2_1/n$	Z	4
a , Å	11.6920(8)	V , Å ³	1896.8(2)
b , Å	8.7560(3)	D_{calcd} , g•cm ⁻³	1.409
c , Å	18.7450 (12)	R , R_w	0.056, 0.123
α , deg.	90	GOF on F	0.456
β , deg.	98.724(3)	no. of observation	2930
γ , deg.	90	no. of variables	266

Figure S12. ORTEP drawing of CPDA **14b**. Color codes of atoms (other than C and H): O = red.

Table S2. Crystal data for CPDA **14b** and collection parameters.

crystal system	orthorhombic	formula	C ₂₀ H ₂₂ O ₆
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Z</i>	4
<i>a</i> , Å	8.1340(2)	<i>V</i> , Å ³	1881.2(2)
<i>b</i> , Å	12.2180(7)	<i>D</i> _{calcd} , g•cm ⁻³	1.265
<i>c</i> , Å	18.9290(9)	<i>R</i> , <i>R</i> _w	0.039, 0.091
<i>α</i> , deg.	90	GOF on <i>F</i>	0.234
<i>β</i> , deg.	90	no. of observation	1950
<i>γ</i> , deg.	90	no. of variables	236

Figure S13. ORTEP drawing of CPDA **14f**. Color codes of atoms (other than C and H): O = red.

Table S3. Crystal data for CPDA **14f** and collection parameters.

crystal system	orthorhombic	formula	C ₂₁ H ₂₄ O ₇
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Z</i>	4
<i>a</i> , Å	6.3680(3)	<i>V</i> , Å ³	2022.10(13)
<i>b</i> , Å	8.1790(3)	<i>D</i> _{calcd} , g•cm ⁻³	1.276
<i>c</i> , Å	38.8240(9)	<i>R</i> , <i>R</i> _w	0.042, 0.094
<i>α</i> , deg.	90	GOF on <i>F</i>	0.294
<i>β</i> , deg.	90	no. of observation	2080
<i>γ</i> , deg.	90	no. of variables	254

Figure S14. ORTEP drawing of CPDA **14h**. Color codes of atoms (other than C and H): O = red.

Table S4. Crystal data for CPDA **14h** and collection parameters.

crystal system	monoclinic	formula	C ₁₆ H ₂₂ O ₆
space group	<i>P</i> 2 ₁ /n	<i>Z</i>	4
<i>a</i> , Å	10.1380(5)	<i>V</i> , Å ³	1724.1(2)
<i>b</i> , Å	10.8380(8)	<i>D</i> _{calcd} , g•cm ⁻³	1.196
<i>c</i> , Å	16.0890(9)	<i>R</i> , <i>R</i> _w	0.049, 0.099
<i>α</i> , deg.	90	GOF on <i>F</i>	0.391
<i>β</i> , deg.	102.771(4)	no. of observation	3380
<i>γ</i> , deg.	90	no. of variables	200

Figure S15. ORTEP drawing of CPDA **14i**. Two conformers were found in a unit cell. Color codes of atoms (other than C and H): O = red.

Table S5. Crystal data for CPDA **14i** and collection parameters.

crystal system	monoclinic	formula	$\text{C}_{20}\text{H}_{28}\text{O}_7$
space group	$P2_1/c$	Z	8
a , Å	15.5630(9)	V , Å ³	4029.1(3)
b , Å	20.8620(11)	D_{calcd} , g•cm ⁻³	1.254
c , Å	12.5750(4)	R , R_w	0.073, 0.184
α , deg.	90	GOF on F	0.552
β , deg.	99.303(3)	no. of observation	7422
γ , deg.	90	no. of variables	550

Figure S16. ORTEP drawing of CPDA **14j**. Color codes of atoms (other than C and H): O = red, Si = blue.

Table S6. Crystal data for CPDA **14j** and collection parameters.

crystal system	triclinic	formula	C ₁₇ H ₂₆ O ₆ Si
space group	<i>P</i> -1	<i>Z</i>	2
<i>a</i> , Å	8.6610(4)	<i>V</i> , Å ³	970.81(11)
<i>b</i> , Å	9.2980(7)	<i>D</i> _{calcd} , g•cm ⁻³	1.213
<i>c</i> , Å	12.9150(10)	<i>R</i> , <i>R</i> _w	0.050, 0.103
<i>α</i> , deg.	90.589(4)	GOF on <i>F</i>	0.347
<i>β</i> , deg.	99.965(5)	no. of observation	3129
<i>γ</i> , deg.	108.200(5)	no. of variables	218

Figure S17. ORTEP drawing of CPDA **14k**. Color codes of atoms (other than C and H): O = red, Si = blue.

Table S7. Crystal data for CPDA **14k** and collection parameters.

crystal system	triclinic	formula	$C_{15}H_{24}O_4Si$
space group	<i>P</i> -1	<i>Z</i>	2
<i>a</i> , Å	6.4240(14)	<i>V</i> , Å ³	873.9(5)
<i>b</i> , Å	12.052(4)	<i>D</i> _{calcd} , g•cm ⁻³	1.127
<i>c</i> , Å	12.936(5)	<i>R</i> , <i>R</i> _w	0.079, 0.197
α , deg.	106.8200	GOF on <i>F</i>	0.598
β , deg.	103.22(2)	no. of observation	3187
γ , deg.	105.12(2)	no. of variables	182

Figure S18. ORTEP drawing of CPDA **14I**. Color codes of atoms (other than C and H): O = red, Si = blue.

Table S8. Crystal data for CPDA **14I** and collection parameters.

crystal system	monoclinic	formula	C ₂₁ H ₂₈ O ₄ Si
space group	<i>P</i> 2 ₁	<i>Z</i>	2
<i>a</i> , Å	10.3190(11)	<i>V</i> , Å ³	1037.9(2)
<i>b</i> , Å	10.5730(6)	<i>D</i> _{calcd} , g•cm ⁻³	1.192
<i>c</i> , Å	10.4460(10)	<i>R</i> , <i>R</i> _w	0.091, 0.326
<i>α</i> , deg.	90	GOF on <i>F</i>	0.819
<i>β</i> , deg.	114.405(5)	no. of observation	2132
<i>γ</i> , deg.	90	no. of variables	236

Figure S19. ORTEP drawing of diene **15**. Color codes of atoms (other than C and H): O = red.

Table S9. Crystal data for diene **15** and collection parameters.

crystal system	monoclinic	formula	C ₂₈ H ₃₄ O ₆
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Z</i>	2
<i>a</i> , Å	14.929(2)	<i>V</i> , Å ³	1335.8(2)
<i>b</i> , Å	5.8210(3)	<i>D</i> _{calcd} , g•cm ⁻³	1.160
<i>c</i> , Å	21.044(2)	<i>R</i> , <i>R</i> _w	0.141, 0.315
<i>α</i> , deg.	90	GOF on <i>F</i>	1.128
<i>β</i> , deg.	133.076(10)	no. of observation	2543
<i>γ</i> , deg.	90	no. of variables	155

Figure S20. ORTEP drawing of Diels-Alder adduct **16**. Color codes of atoms (other than C and H): O = red.

Table S10. Crystal data for Diels-Alder adduct **16** and collection parameters.

crystal system	monoclinic	formula	C ₂₄ H ₂₄ O ₉
space group	<i>P</i> 2 ₁ /n	<i>Z</i>	4
<i>a</i> , Å	12.038(2)	<i>V</i> , Å ³	2224.6(4)
<i>b</i> , Å	10.3700(6)	<i>D</i> _{calcd} , g•cm ⁻³	1.363
<i>c</i> , Å	18.678(2)	<i>R</i> , <i>R</i> _w	0.095, 0.176
<i>α</i> , deg.	90	GOF on <i>F</i>	1.355
<i>β</i> , deg.	107.431(5)	no. of observation	4036
<i>γ</i> , deg.	90	no. of variables	299

Figure S21. ORTEP drawing of Diels-Alder adduct **19**. Color codes of atoms (other than C and H): O = red.

Table S11. Crystal data for Diels-Alder adduct **19** and collection parameters.

crystal system	triclinic	formula	C ₂₇ H ₃₀ O ₆
space group	<i>P</i> -1	<i>Z</i>	2
<i>a</i> , Å	9.9730(5)	<i>V</i> , Å ³	1166.7(2)
<i>b</i> , Å	11.3770(10)	<i>D</i> _{calcd} , g•cm ⁻³	1.282
<i>c</i> , Å	10.8700(10)	<i>R</i> , <i>R</i> _w	0.167, 0.486
<i>α</i> , deg.	94.578(4)	GOF on <i>F</i>	1.242
<i>β</i> , deg.	99.652(5)	no. of observation	3947
<i>γ</i> , deg.	104.643(5)	no. of variables	303