

## Supporting Information

# Mechanochemical Synthesis of Extended Iptycenes

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**General Methods and Material:**

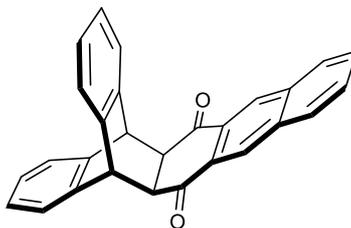
**Material:** All reactions were carried out under argon using standard Schlenk techniques unless otherwise noted. All solvents were of ACS reagent grade or better unless otherwise noted. Silica gel (40  $\mu\text{m}$ ) was purchased from SiliCycle Inc. All reagent grade materials were purchased from Alfa Aesar or Sigma-Aldrich and used without further purification. Mechanochemical syntheses were carried out in a conventional ball mill (Retsch, Mixer Mill 400).

**NMR Spectroscopy:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all compounds were acquired in  $\text{CDCl}_3$  on a Bruker Avance Spectrometer operating at 400 and 100 MHz for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, respectively). Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and referenced with TMS for  $^1\text{H}$  NMR and  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR.

**Infrared Spectroscopy:** Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 Fourier Transform Infrared Spectrometer (FT-IR) using the attenuated total reflectance (ATR) technique on a Ge crystal.

**Mass Spectrometry:** High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility employing electrospray (ESI) as the ionization technique.

**Quartz crystal microbalance (QCM) measurements:** QCM measurements were performed on a Q-Sense E1 single-sensor micro-balance system, which was connected to a KIN-TEK gas generator system that was calibrated for each volatile organic analyte and was used to deliver the gaseous analyte diluted in nitrogen gas. The absorbing materials (10-13) were dissolved in benzene and were deposited on QCM sensor by dropcasting. The residue solvent was removed by putting the sensor under vacuum. The sensor was exposed to each analyte for 1 min with 2 min of nitrogen flow in between exposures to analyte.

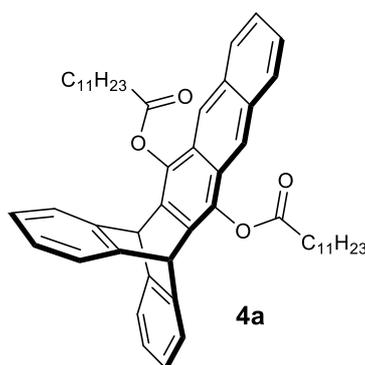
**Mechanochemical synthesis of cycloadduct (1) of anthracene and 1,4-anthraquinone.****1**

To a stainless steel vial (25 mL volume) was added anthracene (1.03 g, 5.76 mmol), 1,4-anthraquinone (1.2 g, 1.0 equiv, 5.76 mmol) and ZnCl<sub>2</sub> (3.93 g, 5.0 equiv, 28.82 mmol) followed by one stainless milling ball (10 mm diameter). The tightly sealed vial was subjected to milling for 4.5 h at 30 Hz. After washing out the milling vial using H<sub>2</sub>O (40 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and the combined organic phase was collected and washed with 3N HCl and brine. After dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated to give the crude product, which was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and precipitated from cold MeOH. Vacuum filtration followed by washing with cold MeOH and drying gave cycloadduct **1** as a off-white solid (1.95 g, 5.04 mmol, yield: 87%). IR (ATR): 1619, 1458, 1291, 1266, 1192, 1039, 921, 829, 759, 747, 666, 641 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 2H), 7.97 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.64 (dt, *J* = 6.3, 3.3 Hz, 2H), 7.49 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.23 (dd, *J* = 16.77, 5.4, 3.2 Hz, 2H), 7.16 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.81 (dd, *J* = 5.4, 3.2 Hz, 2H), 5.12 (t, *J* = 1.3 Hz, 2H), 3.49 – 3.46 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 196.7, 142.3, 140.2, 135.0, 130.7, 129.9, 129.3, 128.7, 126.5, 126.3, 124.7, 123.9, 50.4, 49.2.<sup>1</sup> The characterization data is consistent with that described in reference 1.

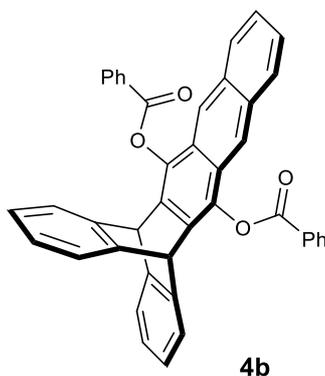
**General procedure for mechanochemical aromatization of 1, 5, or 7 with various anhydrides, triphenylsilyl chloride, and tosyl chloride.**

To a stainless steel vial (25 mL volume) was added **1** (0.300 g, 0.78 mmol), lauric anhydride (0.743 mg, 2.5 equiv, 1.94 mmol), and 4-dimethylaminopyridine (0.474 mg, 3.88 mmol, 5.0 equiv) followed by one stainless milling ball (10 mm diameter). The

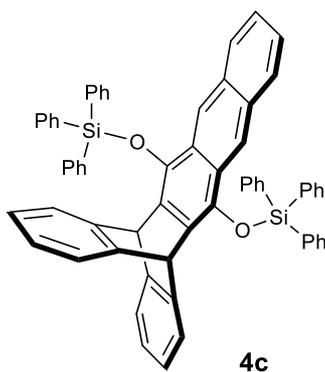
tightly sealed vial was subjected to milling for 1.5 h with a frequency of 30 Hz. After washing out the milling vial using  $\text{CH}_2\text{Cl}_2$  (20 mL), the resulting  $\text{CH}_2\text{Cl}_2$  solution was filtered through a short pad of silica gel and washed with  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated to give the crude product, which was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and precipitated from cold MeOH. Vacuum filtration followed by washing with cold MeOH and drying gave **4a** as a white solid (516 mg, 0.69 mmol, yield: 88%).



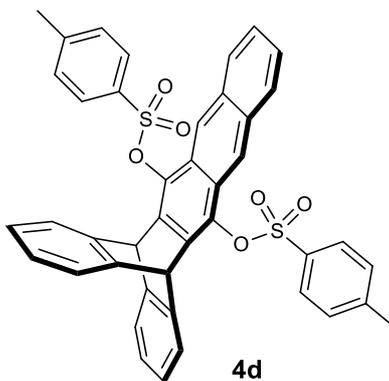
M.P.: 89–92 °C. IR (ATR): 2926, 2852, 1761, 1461, 1317, 1215, 1187, 1138, 1106, 998, 906, 876, 759, 751, 722, 640  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.29 (s, 2H), 7.96 (dt,  $J = 6.4, 3.3$  Hz, 2H), 7.46 (ddd,  $J = 7.2, 5.9, 3.2$  Hz, 6H), 7.11 (dd,  $J = 5.4, 3.1$  Hz, 4H), 5.54 (s, 2H), 3.02 (t,  $J = 7.5$  Hz, 4H), 2.12 (p,  $J = 7.5$  Hz, 4H), 1.79 – 1.66 (m, 4H), 1.64 – 1.25 (m, 28H), 1.01 – 0.87 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  171.8, 143.1, 137.9, 131.7, 131.6, 128.3, 126.0, 125.9, 125.3, 124.3, 120.4, 48.6, 34.5, 32.0, 29.8, 29.72, 29.70, 29.6, 29.5, 29.4, 25.6, 22.7, 14.2. HRMS (ESI): calc for  $\text{C}_{52}\text{H}_{63}\text{O}_4$   $[\text{M}+\text{NH}_4]^+$  768.4986, found 768.4974.



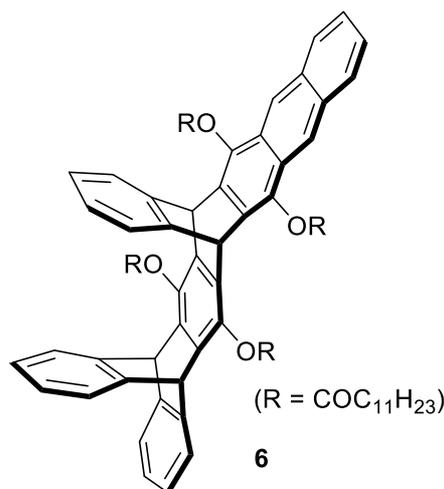
**4b.** Yield: 86%. White solid. M.P.: 340–345 °C. IR (ATR): 1741, 1463, 1450, 1252, 1239, 1204, 1176, 1139, 1114, 1096, 1075, 1050, 1025, 1002, 881, 855, 738, 707, 684, 640  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.52 – 8.46 (m, 4H), 8.27 (s, 2H), 7.83 – 7.73 (m, 4H), 7.66 (dd,  $J = 8.3, 7.1$  Hz, 4H), 7.37 – 7.28 (m, 6H), 7.00 (dd,  $J = 5.4, 3.1$  Hz, 4H), 5.53 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.7, 143.2, 138.3, 134.2, 132.0, 131.9, 130.7, 129.3, 129.1, 128.3, 126.1, 125.9, 125.5, 124.4, 120.5, 48.5. HRMS (ESI): calc for  $\text{C}_{42}\text{H}_{30}\text{NO}_4$   $[\text{M}+\text{NH}_4]^+$  612.2169, found 612.2172.



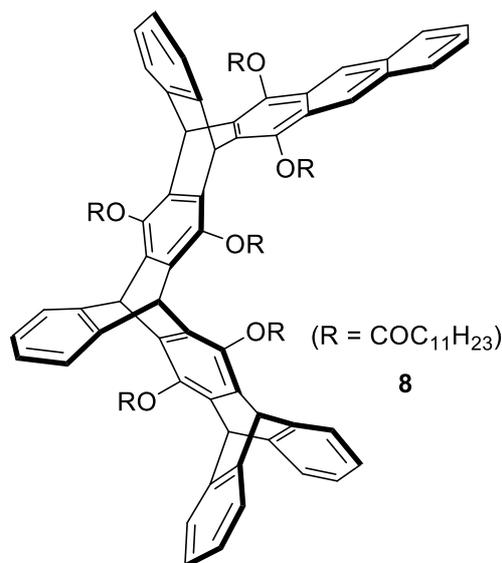
**4c:** Yield: 97%. White solid. M.P.: 279–282 °C. IR (ATR): 1429, 1351, 1327, 1143, 1118, 1023, 880, 839, 820, 748, 739, 711, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 (s, 2H), 7.71 – 7.63 (m, 12H), 7.45 – 7.35 (m, 6H), 7.29 (t,  $J = 7.4$  Hz, 12H), 7.15 (dt,  $J = 6.4, 3.3$  Hz, 2H), 7.10 (dt,  $J = 6.6, 3.2$  Hz, 2H), 6.68 (dd,  $J = 5.4, 3.2$  Hz, 4H), 6.58 (dd,  $J = 5.4, 3.2$  Hz, 4H), 5.65 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  144.0, 139.8, 135.8, 133.9, 130.8, 130.5, 128.1, 128.0, 127.7, 126.5, 124.9, 124.8, 123.5, 122.2, 47.8. HRMS (ESI): calc for  $\text{C}_{64}\text{H}_{47}\text{O}_2\text{Si}_2$   $[\text{M}+\text{H}]^+$  903.3109, found 903.3118.



**4d**: Yield: 77%. Light yellow solid. M.P.: 253–256 °C. IR (ATR): 1385, 1366, 1303, 1190, 1173, 1087, 975, 891, 820, 810, 761, 749, 731, 706, 677, 668, 656, 642  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.85 – 7.81 (m, 4H), 7.64 – 7.59 (m, 6H), 7.39 (dt,  $J = 6.4, 3.2$  Hz, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.23 (m, 4H), 7.14 (dd,  $J = 5.5, 3.2$  Hz, 4H), 6.22 (s, 2H), 2.39 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  145.7, 143.3, 138.3, 135.1, 133.5, 131.2, 129.9, 128.6, 127.9, 126.0, 125.9, 125.0, 124.9, 48.7, 21.6. HRMS (ESI): calc for  $\text{C}_{42}\text{H}_{34}\text{NO}_6\text{S}_2$   $[\text{M}+\text{NH}_4]^+$  712.1822, found 712.1831.



**6**: Light yellow solid. Yield: 85%. M.P.: 180–183 °C. IR (ATR): 2923, 2853, 1765, 1464, 1316, 1199, 1133, 1106, 875, 751  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (s, 2H), 7.80 (dd,  $J = 6.4, 3.3$  Hz, 2H), 7.33 (dt,  $J = 6.4, 3.2$  Hz, 2H), 7.20 – 7.12 (m, 6H), 6.91 (dd,  $J = 5.4, 3.1$  Hz, 2H), 6.83 (ddd,  $J = 14.4, 5.4, 3.1$  Hz, 4H), 5.41 (s, 2H), 5.21 (s, 2H), 2.87 – 2.74 (m, 8H), 1.97 (h,  $J = 7.4$  Hz, 8H), 1.65 – 1.12 (m, 64H), 0.88 – 0.75 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  171.3, 171.1, 144.3, 144.15, 142.18, 138.8, 138.1, 137.1, 134.1, 131.7, 130.5, 128.3, 126.2, 125.9, 125.38, 125.35, 125.3, 124.5, 123.93, 123.86, 120.5, 49.1, 42.9, 34.4, 34.4, 32.0, 29.79, 29.76, 29.65, 29.58, 29.55, 29.4, 25.7, 25.6, 22.7, 14.2 (the signals from some of the aliphatic carbons are overlapped in  $^{13}\text{C}$  NMR). HRMS (ESI): calc for  $\text{C}_{90}\text{H}_{114}\text{NaO}_8$   $[\text{M}+\text{Na}]^+$  1345.8406, found 1345.8428.

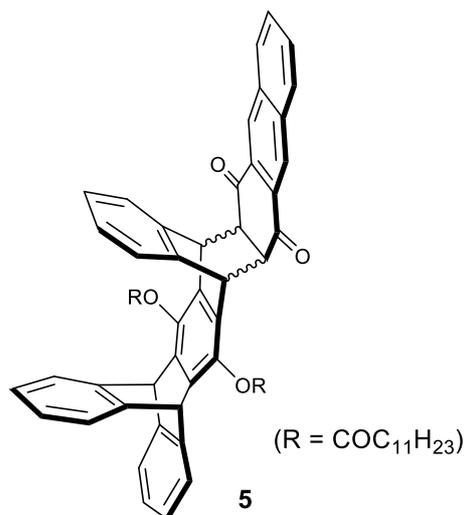


**8:** Light yellow solid. Yield: 74%. IR (ATR): 2923, 2852, 1765, 1463, 1377, 1316, 1187, 1135, 1105, 873, 752, 721, 667, 655, 648  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.15 (s, 1H), 7.87 (dd,  $J = 6.4, 3.3$  Hz, 1H), 7.42 (dt,  $J = 6.6, 3.2$  Hz, 1H), 7.17 (dddd,  $J = 30.7, 13.8, 5.4, 3.2$  Hz, 4H), 7.03 – 6.95 (m, 1H), 6.88 (ddd,  $J = 10.5, 5.4, 3.1$  Hz, 2H), 6.75 (dd,  $J = 5.4, 3.1$  Hz, 1H), 5.42 (s, 1H), 5.32 (s, 1H), 5.21 (s, 1H), 2.98 – 2.72 (m, 6H), 2.02 (tt,  $J = 12.0, 6.5$  Hz, 7H), 1.71 – 1.24 (m, 34H), 0.92 (dq,  $J = 7.0, 3.1$  Hz, 10H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  171.3, 171.0, 170.8, 144.2, 144.22, 143.3, 141.9, 138.8, 138.7, 138.2, 136.6, 136.5, 135.3, 134.6, 131.7, 130.3, 128.2, 126.2, 125.8, 125.6, 125.3, 125.3, 125.2, 124.5, 124.1, 123.8, 123.7, 120.5, 48.9, 43.4, 43.0, 34.4, 34.3, 32.04, 32.01, 29.82, 29.77, 29.66, 29.63, 29.58, 29.48, 29.46, 25.7, 25.6, 22.8, 14.2. (the signals from some of the aliphatic carbons are overlapped in  $^{13}\text{C}$  NMR). HRMS (ESI): calc for  $\text{C}_{104}\text{H}_{126}\text{NO}_{10}$   $[\text{M}+\text{NH}_4]^+$  1914.2751, found 1914.2764.

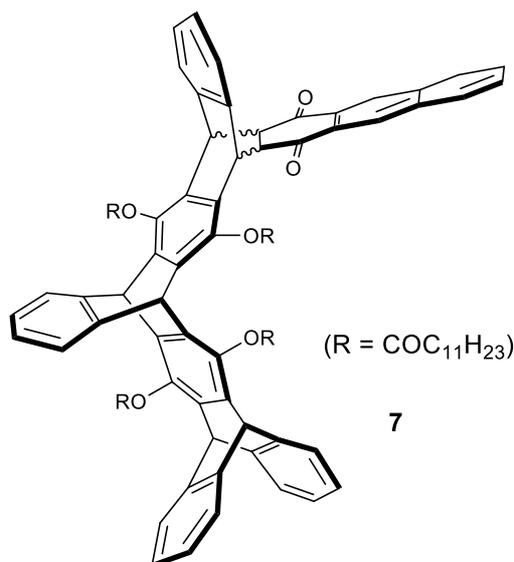
**Procedure for mechanochemical promoted Diels-Alder reaction between 4a or 6 and 1,4-anthraquinone.**

To a stainless steel vial (25 mL volume) was added **4a** (0.200 g, 0.26 mmol), 1,4-anthraquinone (67 mg, 1.2 equiv, 0.32 mmol),  $\text{ZnCl}_2$  (0.301 mg, 2.21 mmol, 8.3 equiv) and perfluorononanoic acid (156 mg, 0.985 mmol, 3.7 equiv) followed by one stainless milling ball (10 mm diameter). The tightly sealed vial was subjected to milling for 4.5 h (7.5 h in the reaction with **6**) with a frequency of 30 Hz. After washing out the milling

vial using  $\text{CH}_2\text{Cl}_2$  (20 mL), the resulting  $\text{CH}_2\text{Cl}_2$  solution was filtered through a short pad of silica gel and washed with  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated to give the crude product, which was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and precipitated from cold MeOH. Vacuum filtration followed by washing with cold MeOH and drying gave **5** as a light yellow solid (240 mg, 0.25 mmol, yield: 94%). The product contains a mixture of two stereoisomers (exo/endo = 86:14).



M.P.: 169–172 °C. IR (ATR): 2926, 2854, 1760, 1681, 1620, 1459, 1299, 1265, 1191, 1135, 1102, 1036, 918, 758, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (The major isomer, 400 MHz, Chloroform-*d*)  $\delta$  8.31 (s, 2H), 7.85 (dd,  $J = 6.2, 3.3$  Hz, 2H), 7.52 (dt,  $J = 6.4, 3.3$  Hz, 2H), 7.24 (ddd,  $J = 17.0, 5.4, 3.2$  Hz, 4H), 7.05 – 6.95 (m, 2H), 6.94 (dd,  $J = 5.4, 3.1$  Hz, 2H), 6.86 (dd,  $J = 5.4, 3.1$  Hz, 2H), 6.71 (dd,  $J = 5.5, 3.2$  Hz, 2H), 5.35 (s, 2H), 4.98 (d,  $J = 1.2$  Hz, 2H), 3.29 (t,  $J = 1.2$  Hz, 2H), 2.92 – 2.84 (m, 4H), 2.00 (h,  $J = 7.8$  Hz, 4H), 1.63 (p,  $J = 7.2$  Hz, 4H), 1.55 – 1.15 (m, 28H), 0.88 – 0.76 (m, 6H).  $^{13}\text{C}$  NMR (The major isomer, 101 MHz, Chloroform-*d*)  $\delta$  195.9, 171.9, 144.4, 144.4, 139.7, 138.4, 137.1, 135.0, 132.8, 130.8, 129.8, 129.3, 128.7, 126.4, 125.5, 125.4, 124.9, 123.91, 123.87, 49.2, 48.8, 43.1, 34.4, 32.0, 29.78, 29.75, 29.69, 29.52, 29.50, 29.4, 25.7, 22.7, 14.2. HRMS (ESI): calc for  $\text{C}_{66}\text{H}_{70}\text{NaO}_6$   $[\text{M}+\text{Na}]^+$  981.5065, found 981.5066.

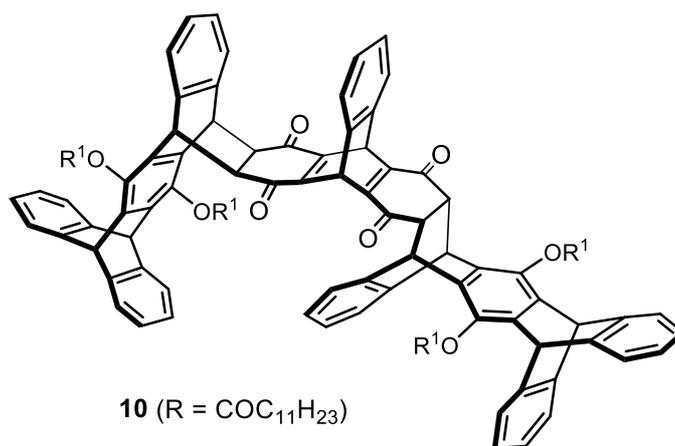


**7:** Light yellow solid. Yield: 82%. M.P.: 69–72 °C. IR (ATR): 2925, 2854, 1766, 1682, 1460, 1262, 1190, 1135, 1104, 752 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 2H), 7.93 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.60 (dt, *J* = 6.4, 3.3 Hz, 2H), 7.28 (s, 2H), 7.16 (dd, *J* = 5.4, 3.2 Hz, 2H), 7.04 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.93 (dd, *J* = 5.4, 3.1 Hz, 4H), 6.87 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.45 (s, 2H), 5.30 (s, 2H), 4.98 (t, *J* = 1.2 Hz, 2H), 3.42 (t, *J* = 1.2 Hz, 2H), 2.94 – 2.82 (m, 8H), 2.08 (p, *J* = 7.5 Hz, 8H), 1.68 (q, *J* = 7.4 Hz, 8H), 1.64 – 1.21 (m, 56H), 0.91 (h, *J* = 5.1, 4.4 Hz, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 184.7, 171.3, 171.1, 144.3, 144.2, 142.2, 140.1, 138.8, 138.1, 137.1, 134.1, 131.7, 130.5, 130.2, 129.6, 128.9, 128.3, 126.2, 125.9, 125.4, 125.3, 125.2, 124.5, 123.9, 123.8, 120.5, 49.1, 42.9, 34.4, 34.3, 32.0, 29.79, 29.75, 29.65, 29.58, 29.55, 29.43, 25.7, 25.6, 22.7, 14.2. (the signals from some of the aliphatic carbons are overlapped in <sup>13</sup>C NMR). HRMS (ESI): calc for C<sub>104</sub>H<sub>126</sub>NO<sub>10</sub> [M+NH<sub>4</sub>]<sup>+</sup> 1549.9376, found 1549.9342.

**Procedure for mechanochemical promoted double Diels-Alder reaction between **4a** and **9**.**

To a ZrO<sub>2</sub> vial (10 mL volume) was added **9** (0.040 g, 0.126 mmol), **4a** (237 mg, 2.5 equiv, 0.316 mmol), ZnCl<sub>2</sub> (0.172 mg, 1.26 mmol, 10 equiv) and perfluorononanoic acid (235 mg, 0.505 mmol, 4.0 equiv) followed by one ZrO<sub>2</sub> milling ball (10 mm diameter). The tightly sealed vial was subjected to milling for 6 h with a frequency of 30 Hz. After washing out the milling vial using CH<sub>2</sub>Cl<sub>2</sub> (20 mL), the resulting CH<sub>2</sub>Cl<sub>2</sub>

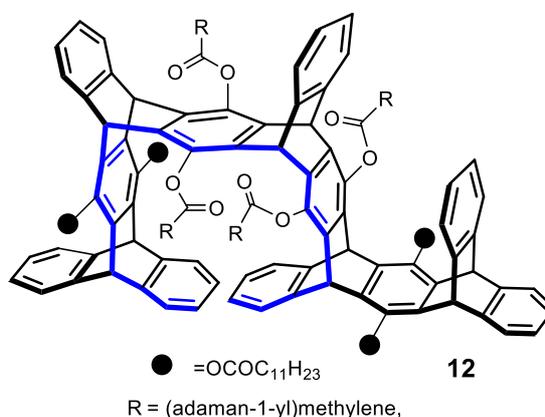
solution was filtered through a short pad of silica gel and washed with  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated to give the crude product, which was purified by silica gel column chromatography by using a mixture of hexane and ethyl acetate as the eluent to give **10** as an off-white solid, which was washed with cold methanol to give pure product (177 mg, 0.097 mmol, yield: 77%).



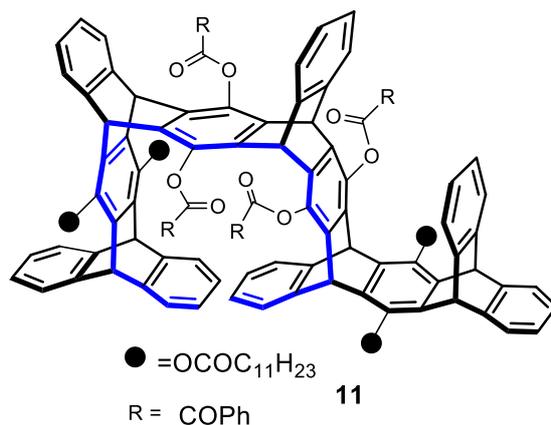
**10**: M.P.: 217-220 °C. IR (ATR): 2925, 2854, 1768, 1671, 1560, 1459, 1366, 1298, 1253, 1191, 1136, 1107, 996, 968, 781, 759, 748  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 – 7.12 (m, 8H), 6.99 – 6.87 (m, 6H), 6.82 (td,  $J$  = 5.3, 3.0 Hz, 4H), 6.79 – 6.74 (m, 2H), 6.67 (dd,  $J$  = 5.3, 3.2 Hz, 2H), 6.49 (dt,  $J$  = 6.0, 3.2 Hz, 4H), 6.10 (dd,  $J$  = 5.5, 3.1 Hz, 2H), 5.34 (s, 2H), 5.28 (s, 2H), 5.25 (s, 2H), 4.40 (d,  $J$  = 1.3 Hz, 2H), 4.36 (d,  $J$  = 1.3 Hz, 2H), 2.87 – 2.74 (m, 12H), 2.02 – 1.87 (m, 8H), 1.64 – 1.15 (m, 60H), 0.83 (td,  $J$  = 6.9, 2.3 Hz, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  192.6, 192.4, 171.8, 171.7, 155.1, 144.3, 144.2, 144.1, 140.8, 138.44, 138.38, 138.3, 137.42, 137.36, 137.2, 131.7, 131.4, 126.5, 125.6, 125.5, 125.5, 125.4, 124.8, 124.5, 123.93, 123.86, 123.7, 49.7, 49.2, 48.8, 44.9, 44.6, 42.3, 34.32, 34.25, 32.02, 29.80, 29.77, 29.76, 29.72, 29.67, 29.53, 29.47, 25.7, 25.6, 22.8, 14.2 (the signals from some of the carbons are overlapped in <sup>13</sup>C NMR). HRMS (ESI): calc for C<sub>124</sub>H<sub>138</sub>NO<sub>12</sub> [M+NH<sub>4</sub>]<sup>+</sup> 1834.0247, found 1834.0222.

### General procedure for mechanochemical aromatization of **10** with various anhydrides.

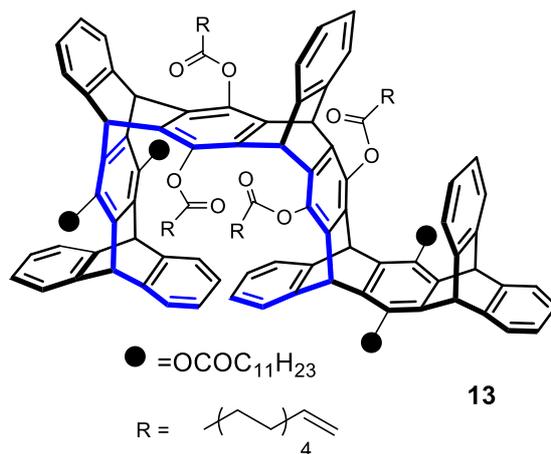
To a stainless steel vial (5 mL volume) was added **10** (0.070 g, 0.0385 mmol), 1-adamantaneacetic anhydride (0.074 mg, 5.0 equiv, 0.192 mmol), and 4-dimethylaminopyridine (0.047 mg, 0.385 mmol, 10 equiv) followed by two stainless milling ball (6 mm diameter). The tightly sealed vial was subjected to milling for 3 h with a frequency of 30 Hz. After washing out the milling vial using CH<sub>2</sub>Cl<sub>2</sub> (20 mL), the resulting CH<sub>2</sub>Cl<sub>2</sub> solution was filtered through a short pad of silica gel and washed with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was evaporated to gave **12** as a white solid (82 mg, 0.0325 mmol, yield: 85%).



M.P.: 157–160 °C. IR (ATR): 2923, 2851, 1766, 1461, 1242, 1112, 1095, 748 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.09 (ddd, *J* = 17.7, 5.4, 3.2 Hz, 8H), 6.88 (ddt, *J* = 12.7, 5.3, 3.2 Hz, 6H), 6.82 – 6.64 (m, 14H), 5.22 (s, 2H), 5.17 (s, 2H), 5.16 (s, 2H), 5.11 (s, 2H), 5.08 (s, 2H), 2.67 (ddt, *J* = 12.2, 8.3, 5.1 Hz, 8H), 2.55 – 2.36 (m, 8H), 2.08 (d, *J* = 13.0 Hz, 12H), 2.01 – 1.14 (m, 120H), 0.83 (dt, *J* = 7.1, 3.9 Hz, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.9, 168.2, 168.2, 144.5, 144.4, 144.2, 144.2, 143.7, 143.6, 143.5, 138.7, 138.6, 136.4, 136.3, 135.8, 135.74, 135.73, 135.6, 135.5, 135.3, 125.34, 125.28, 125.22, 125.19, 123.9, 123.8, 123.7, 49.1, 48.9, 48.1, 47.9, 43.63, 43.60, 43.5, 42.7, 42.5, 36.9, 36.8, 34.4, 34.3, 33.1, 32.9, 32.0, 29.8, 29.73, 29.64, 29.60, 29.56, 29.50, 29.43, 29.42, 28.65, 28.61, 25.7, 25.6, 22.8, 14.2. (some of the signals are overlapped in <sup>13</sup>C NMR). HRMS (ESI): calc *m/z* for C<sub>172</sub>H<sub>206</sub>N<sub>2</sub>O<sub>162</sub> [M+2NH<sub>4</sub>]<sup>2+</sup> 1278.2695, found 1278.2680.

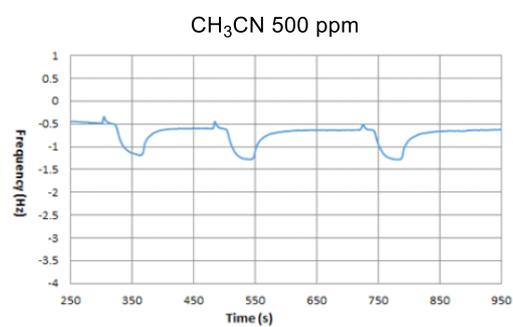
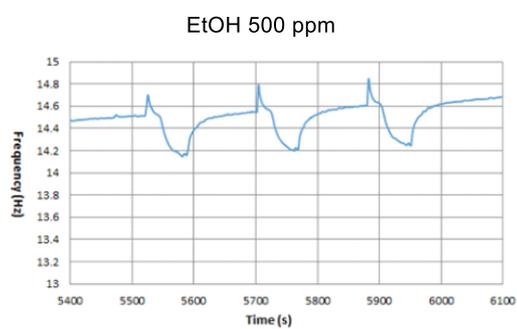
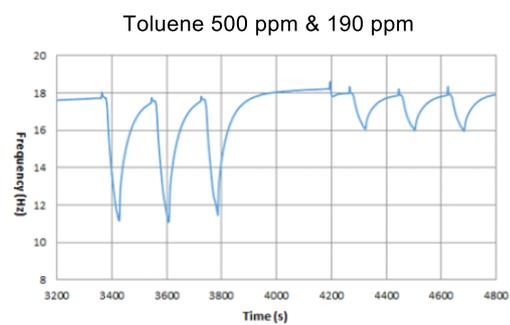
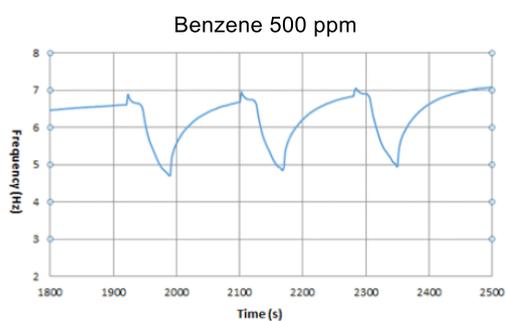
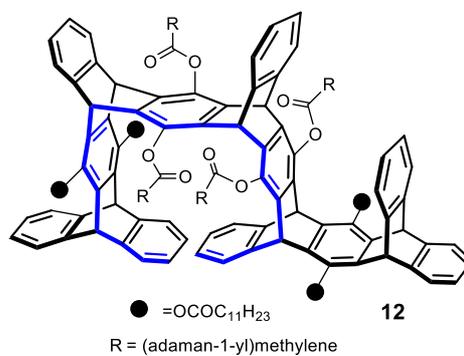


**11**: Off-white solid. Yield: 52%. M.P.: 155–158 °C. IR (ATR): 2926, 2853, 1748, 1461, 1269, 1231, 1216, 1177, 1135, 1103, 1082, 1063, 1026, 750, 706, cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.23 – 8.14 (m, 4H), 8.08 (d, *J* = 7.6 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 4H), 7.26 (t, *J* = 7.6 Hz, 4H), 7.15 – 6.88 (m, 14H), 6.87 – 6.63 (m, 14H), 5.30 (s, 2H), 5.15 (s, 2H), 5.11 (s, 2H), 5.06 (s, 2H), 5.03 (s, 2H), 2.32 – 2.06 (m, 8H), 1.53 (d, *J* = 12.0 Hz, 12H), 1.36 – 1.01 (m, 60H), 0.84 (dd, *J* = 6.9, 3.5 Hz, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 170.95, 170.90, 163.7, 163.5, 144.4, 144.22, 144.21, 143.6, 143.5, 143.4, 139.0, 138.9, 138.6, 138.5, 136.3, 136.2, 136.1, 136.0, 135.5, 135.2, 133.5, 130.3, 130.2, 129.2, 128.9, 128.7, 128.6, 125.4, 125.4, 125.2, 124.3, 124.2, 124.0, 123.9, 123.8, 123.7, 48.8, 43.7, 43.6, 33.91, 33.86, 32.0, 29.8, 29.7, 29.5, 29.34, 29.31, 22.8, 14.2 (some of the signals are overlapped in <sup>13</sup>C NMR). HRMS (ESI): calc *m/z* for C<sub>152</sub>H<sub>158</sub>N<sub>2</sub>O<sub>16</sub> [M+2NH<sub>4</sub>]<sup>2+</sup> 1134.0817, found 1134.0837.



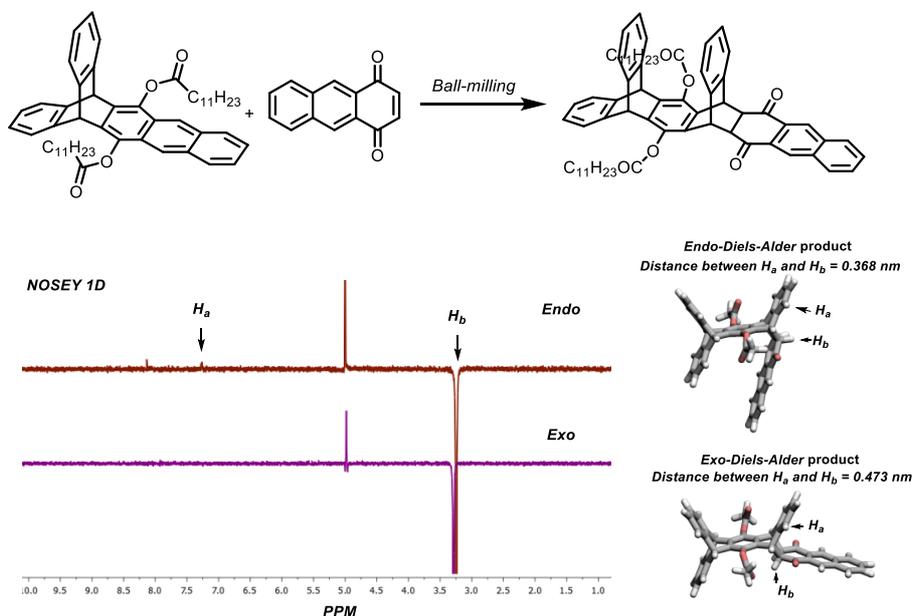
**13:** Light yellow solid. Yield: 73%. M.P.: 115–118 °C. IR (ATR): 2926, 2854, 1767, 1462, 1300, 1242, 1190, 1133, 1103, 1013, 908, 750  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.18 (td,  $J = 8.4, 3.5$  Hz, 8H), 7.02 (td,  $J = 6.3, 5.6, 3.8$  Hz, 6H), 6.94 – 6.73 (m, 14H), 5.89 (dddd,  $J = 16.8, 12.5, 10.2, 6.6$  Hz, 4H), 5.22 (s, 2H), 5.20 (s, 2H), 5.18 (s, 2H), 5.18 (s, 2H), 5.16 (s, 2H), 5.11 – 4.97 (m, 8H), 2.75 (t,  $J = 7.5$  Hz, 8H), 2.73 – 2.62 (m, 8H), 2.14 (p,  $J = 6.8$  Hz, 8H), 2.10 – 1.93 (m, 16H), 1.69 – 1.24 (m, 104H), 0.98 – 0.89 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  171.0, 170.6, 170.5, 144.4, 144.2, 143.5, 143.4, 143.3, 139.1, 138.68, 138.66, 138.61, 136.5, 135.8, 135.7, 135.6, 135.4, 135.2, 125.5, 125.4, 125.3, 124.0, 123.9, 123.8, 114.41, 114.40, 49.0, 48.9, 43.42, 43.3, 34.32, 34.29, 33.92, 33.89, 32.0, 29.81, 29.80, 29.76, 29.69, 29.66, 29.63, 29.58, 29.46, 29.32, 29.28, 29.09, 29.07, 25.64, 25.58, 25.51, 22.8, 14.2 (some of the signals are overlapped in  $^{13}\text{C}$  NMR). HRMS (ESI): calc  $m/z$  for  $\text{C}_{168}\text{H}_{214}\text{N}_2\text{O}_{16} [\text{M}+2\text{NH}_4]^{2+}$  1258.3008, found 1258.3015.

## Representative QCM measurement result of the gas absorption property of absorptive materials.



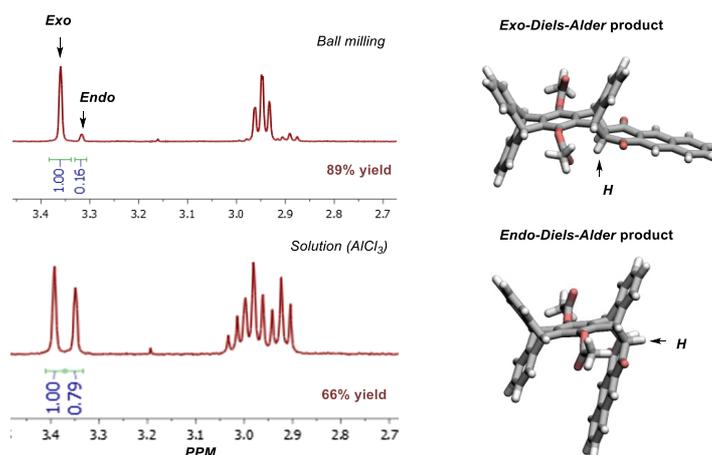
### Determination of the configuration of the Diels-Alder product **5**

The stereochemistry of Diels-Alder product **5** was determined by 1D NOESY experiment. A signal enhancement was observed in the *endo* isomer as a result of the short distance between  $H_a$  and  $H_b$ .



**Figure S1.** The NOESY 1D experiment to determine the configuration of Diels-Alder product **5**.

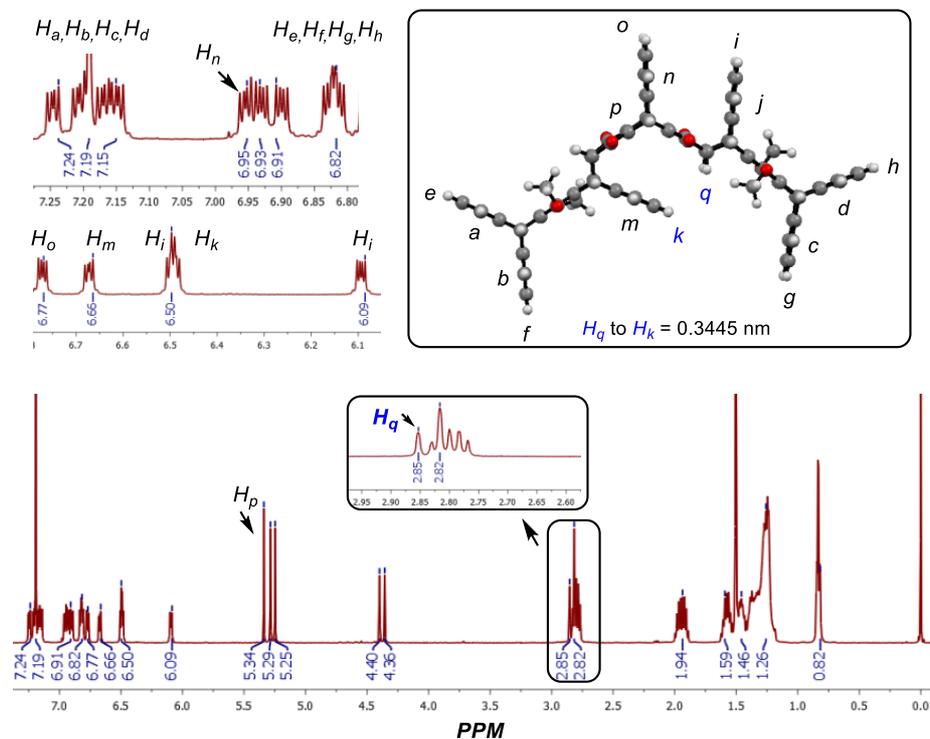
### A comparison of the stereoselectivity and yield of Diels-Alder reaction for the preparation of **5**.



**Figure S2.** A comparison of the stereoselectivity and yield of Diels-Alder reaction for the preparation of **5**.

**The assignment of the  $^1\text{H}$  NMR signal of Diels-Alder product 10.**

An NOE effect was observed between  $\text{H}_q$  and  $\text{H}_k$  as a result of the short distance between these two proton.



**Figure S3.** The assignment of the  $^1\text{H}$  NMR signal of Diels-Alder product 10.

**Reference:**

1. Patney, H. K. *Synthesis* **1991**, 694.

**$^1\text{H}$ , and  $^{13}\text{C}$  NMR spectrum of all new products:**