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Supporting Online Material for

Diels-Alder in Aqueous Molecular Hosts: Unusual Regioselectivity and Efficient Catalysis

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Supporting Information

Diels-Alder in Aqueous Molecular Hosts: Unusual Regioselectivity and Efficient Catalysis

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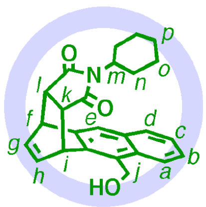
Contents:

Materials and Methods: ^{1}H, ^{13}C NMR, and 2D NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. TMS ($CDCl_3$ solution) in a capillary served as external standard (δ = 0 ppm). IR measurements were carried out using a DIGILAB FTS2000S instrument. Melting points were determined on a Yanaco MF-500V micro melting point apparatus. Diffraction measurements were made using a Bruker SMART CCD diffractometer. Reagents and solvents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries, Ltd., and Sigma-Aldrich Co. Deuterated H_2O was acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements.

Diels-Alder reaction of 9-hydroxymethylanthracene and *N*-cyclohexylphthalimide within cage **1** (typical procedure): 9-hydroxymethylanthracene (**3a**) and *N*-cyclohexylphthalimide (**4a**) (6.0 μmol each) were suspended in a D_2O solution (1.0 mL) of **1** (5.0 μmol) and stirred at room temperature for 5 min to give a **1**⊃(**3a•4a**) complex, quantitatively (Fig. S1a). When the solution was stirred at 80 ºC for 5 h, the color changed from orange to pale yellow. ^{1}H NMR analysis of the solution revealed the formation of **1**⊃**5** complex in >98% yield based on **1** (Fig. S1a). After filtration, extraction with $CDCl_3$, and removal of solvent under vacuum, *syn*-1,4-Diels-Alder adduct **5** was isolated as a white solid (Fig. S4). Isolated yield of **5** was estimated to be 93% by the large-scale reaction (10-times). The structure of **1**⊃**5** was characterized by X-ray crystallographic analysis. A pale-yellow single crystal of **1**⊃**5** was obtained by the slow evaporation of water from an aqueous solution **1**⊃**5** at room temperature over 5 days. It was attached to a loop of nylon fiber with antifreeze reagent (poly(vinylalcohol)) and transferred to a Bruker SMART/CCD diffractometer. Non-hydrogen atoms except for counter ions and water molecules were refined anisotropically and hydrogen atoms were fixed at calculated positions (Table S2 and Fig. S15, S16). These data (CCDC-293777) can be obtained free of charge from the Cambridge Crystallographic Data Center.

Physical data of **1**⊃(**3a•4a**): ^{1}H NMR (500 MHz, D_2O, 27 ºC, TMS as external standard): *δ* 9.39 (d, *J* = 5.0 Hz, 24H, PyH_α, **1**), 8.74 (br, 24H, PyH_β, **1**), 6.60 (d, *J* = 8.0 Hz, 2H, **3a**), 6.24 (t, *J* = 7.0 Hz, 2H, **3a**), 6.01 (br, 2H, **3a**), 5.94 (br, 2H, **3a**), 5.65 (s, 1H, **3a**), 5.61 (br, 2H, **4a**), 3.24(s, 24H, CH_2, **1**), 3.08 (s, 2H, **3a**), 2.78 (s, 72H, CH_3, **1**), 1.12 (br, 1H, **4a**), 0.46 (br, 2H, **4a**), –0.03~–0.83 (br, 8H, **4a**) (Fig. S1(a)).



Physical data of **1**⊃**5**: ^{1}H NMR (500 MHz, $CDCl_3$, 27 ºC, TMS as external standard): *δ* 9.67 (d, *J* = 5.5 Hz, 3H, **1**), 9.62 (d, *J* = 5.5 Hz, 3H, **1**), 9.42-9.37 (m, 12H, **1**), 9.32 (d, *J* = 4.5 Hz, free **1**), 9.30 (s, 3H, **1**), 9.18 (d, *J* = 5.0 Hz, 3H, **1**), 9.12 (d, *J* = 5.0 Hz, 3H, **1**), 8.86 (t, *J* = 7.0 Hz, 6H, **1**), 8.77 (d, *J* = 4.5 Hz, free **1**), 8.72 (d, *J* = 5.5 Hz, 6H, **1**), 8.48 (d, *J* = 5.0 Hz, 3H, **1**), 8.43 (d, *J* = 5.5 Hz, 3H, **1**), 6.68 (d, *J* = 8.5 Hz, 1H, C*H*, **5**), 6.54-6.51 (m, 2H, C*H*, **5**), 6.48 (d, *J* = 8.5 Hz, 1H, C*H*, **5**), 5.23 (t, *J* = 7.5 Hz, 1H, C*H*, **5**), 5.14 (s, 1H, C*H*, **5**), 4.78 (1H, C*H*, **5**), 3.18 (s, 24H, **1**), 3.00 (2H, **5**), 2.85-2.75 (m, 72H, **1**), 2.60 (m, 1H, **5**), 2.31 (s, 2H, **5**), 1.93 (d, *J* = 5.0 Hz, 1H, **5**), 1.83 (d, *J* = 12.0 Hz, 1H, **5**), 1.32 (br, 1H, **5**), 0.97 (br, 1H, **5**), 0.51 (d, *J* = 12.0 Hz, 1H, **5**), 0.19 (d, *J* = 10.5 Hz, 1H, **5**), –0.53~–0.62 (m, 3H, **5**), –0.90 (q, *J* = 12.5 Hz, 1H, **5**), –1.10 (q, *J* = 11.0 Hz, 1H, **5**), –1.23 (q, *J* = 12.5 Hz, 1H, **5**), –1.51 (d, *J* = 12.0 Hz, 1H, **5**), –2.16 (d, *J* = 12.0 Hz, 1H, **5**) (Fig. S1(b)); ^{13}C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 178.7 (*C*O), 175.4 (*C*O), 169.6 (C_q, **1**), 169.2 (C_q, **1**), 169.1 (C_q, **1**), 167.4 (C_q, **1**), 152.7 (*C*H, **1**), 152.6 (*C*H, **1**), 152.3 (*C*H, **1**), 152.1 (*C*H, **1**), 146.2 (C_q, **1**), 145.4 (C_q, **1**), 145.3 (C_q, **1**), 145.1 (C_q, **1**), 134.1, 133.9 (*C* × 2), 133.0, 130.1, 128.7, 127.3, 127.1, 126.5 (*C*H, **1**), 126.0 (*C*H, **1**), 125.9 (*C*H, **1**), 125.7 (*C*H, **1**), 125.6, 124.64, 123.1, 122.3, 62.9 (*C*H, **1**), 54.2, 50.5 (*C*H, **1**), 49.4, 44.8, 44.2, 41.3, 37.0, 26.2, 25.4, 24.0, 23.9, 23.8; IR (KBr, cm^{-1}): 3461 (br), 3101, 3062, 3027, 2934, 2855, 1686, 1618, 1576, 1522, 1470, 1331, 1315, 1238, 1205, 1062, 1041, 1008, 955, 876, 812, 673; m.p.: > 200 ºC (decomposed).

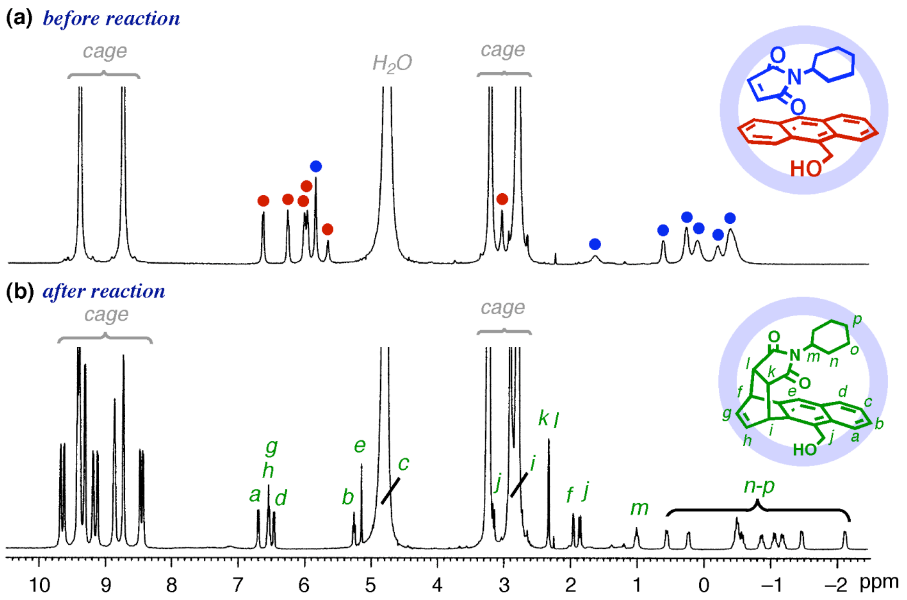


Fig. S1. ^{1}H-NMR spectra (500 MHz, D_2O, r.t.) of (**a**) **1**⊃(**3a•4a**) and (**b**) **1**⊃**5**.

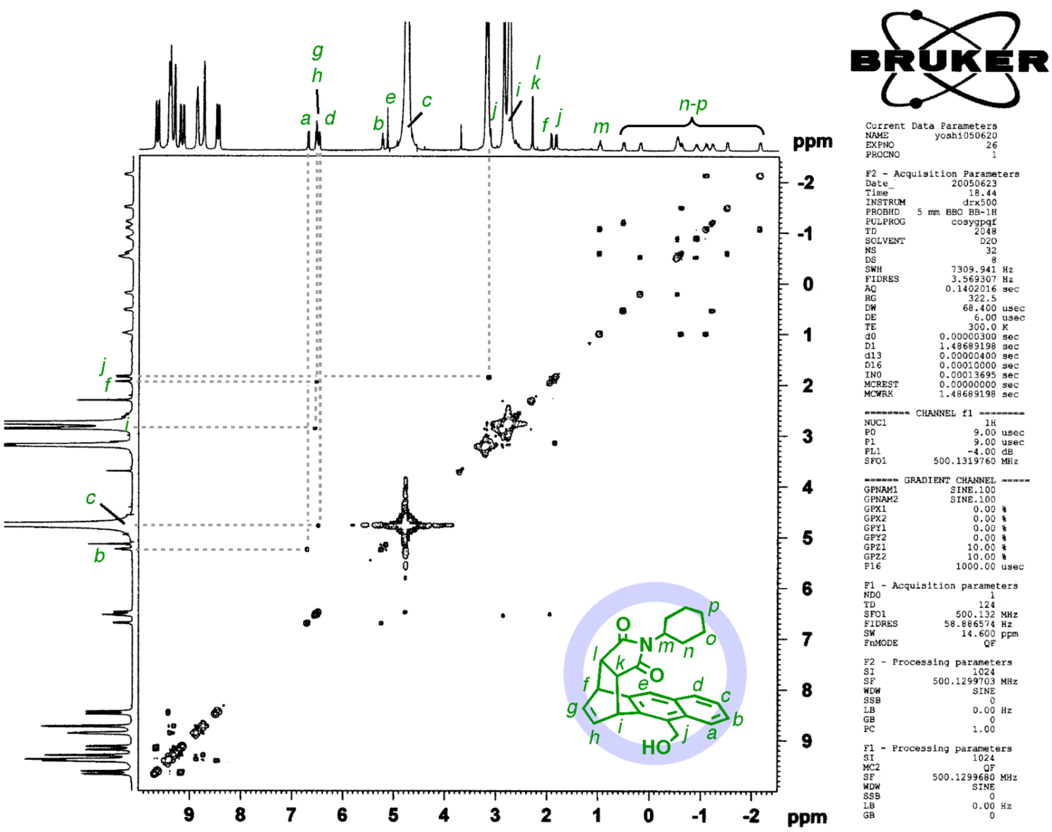


Fig. S2. HH-COSY spectrum (500 MHz, D_2O, r.t.) of **1**⊃**5**.

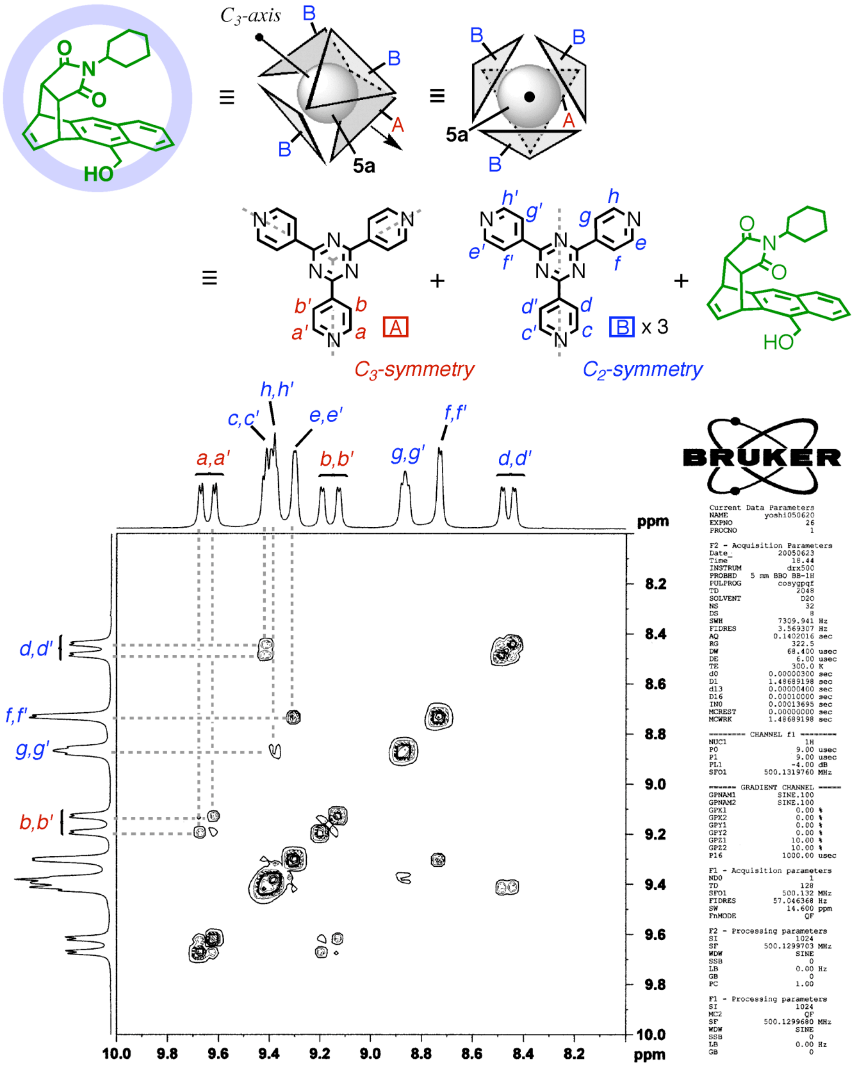
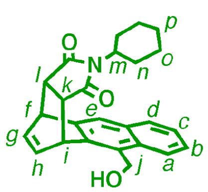


Fig. S3. HH-COSY spectrum (500 MHz, D_2O, r.t.) of $\mathbf{1}\supset\mathbf{5}$ around aromatic region.



Physical data of **5**: ^{1}H NMR (500 MHz, $CDCl_3$, 27 ºC, TMS as external standard): δ 8.20 (d, J = 8.5 Hz, 1H, H_a), 7.74 (d, J = 7.5 Hz, 1H, H_d), 7.58 (s, 1H, H_e), 7.51 (dd, J = 7.5, 8.5 Hz, 1H, H_b), 7.45 (dd, J = 7.5, 7.5 Hz, 1H, H_c), 6.77 (dd, J = 6.0, 7.0, 1H, H_g), 6.70 (dd, J = 6.0, 7.0 Hz, 1H, H_h), 5.19 (dd, J = 2.5, 12.5 Hz, 1H, H_j), 5.11 (t, J = 12.5 Hz, 1H, H_j), 4.95 (s, 1H, H_i), 4.46 (s, 1H, H_f), 3.30 (t, J = 8.5, 1H, H_m), 3.18 (d, J = 8.0, 1H, H_k), 3.10 (d, J = 8.0, 1H, H_l), 2.66 (dd, J = 2.5, 10.5, 1H, OH), 1.44-1.28 (m, 5H, H_{cyclo}), 0.86 (m, 3H, H_{cyclo}), 0.26 (d, J = 12.0, 1H, H_{cyclo}), 0.12 (d, J = 12.0, 1H, H_{cyclo}) (Fig. S4); ^{13}C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 179.5 (CO), 177.1 (CO), 136.1 (C_gH), 135.5 (C_q), 135.3 (C_q), 134.9 (C_hH), 132.2 (C_q), 131.1 (C_q), 130.8 (C_q), 128.1 (C_dH), 126.4 (C_bH), 125.8 (C_cH), 124.6 (C_aH), 123.8 (C_eH), 57.2 (C_jH_2), 51.2 (C_mH), 46.2 (C_kH), 46.1 (C_lH), 42.2 (C_fH), 37.8 (C_iH), 27.7 ($C_nH_2 \times 2$), 25.4 ($C_oH_2 \times 2$), 24.6 (C_pH_2) (Fig. S5); IR (ATR, cm^{-1}): 2931 (br), 2856, 1765, 1681, 1453, 1398, 1375, 1348, 1261, 1198, 1148, 1053, 988, 892, 756, 729; m.p. 164-165 ºC; E.A. Calcd. for $C_{25}H_{25}NO_3$•H_2O: C, 74.05; H, 6.71; N, 3.45. Found: C, 74.24; H, 6.43; N, 3.25.

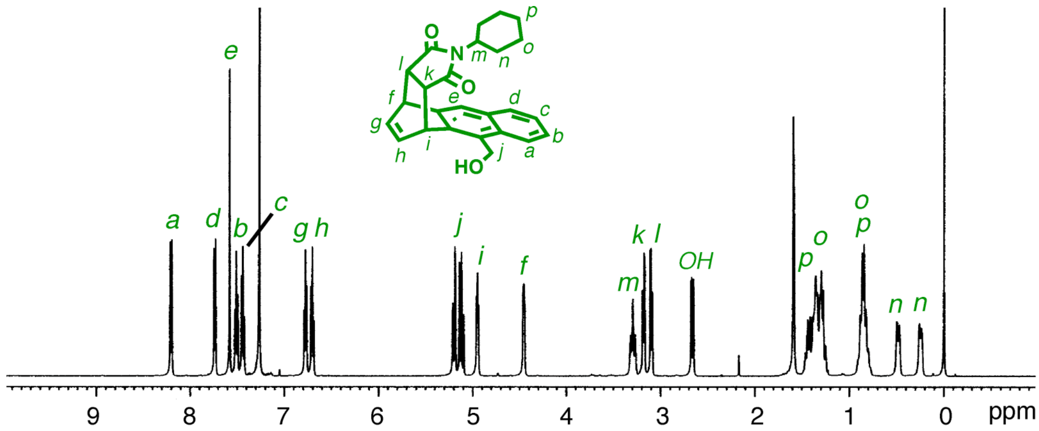


Fig. S4. ^{1}H-NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **5** after the purification.

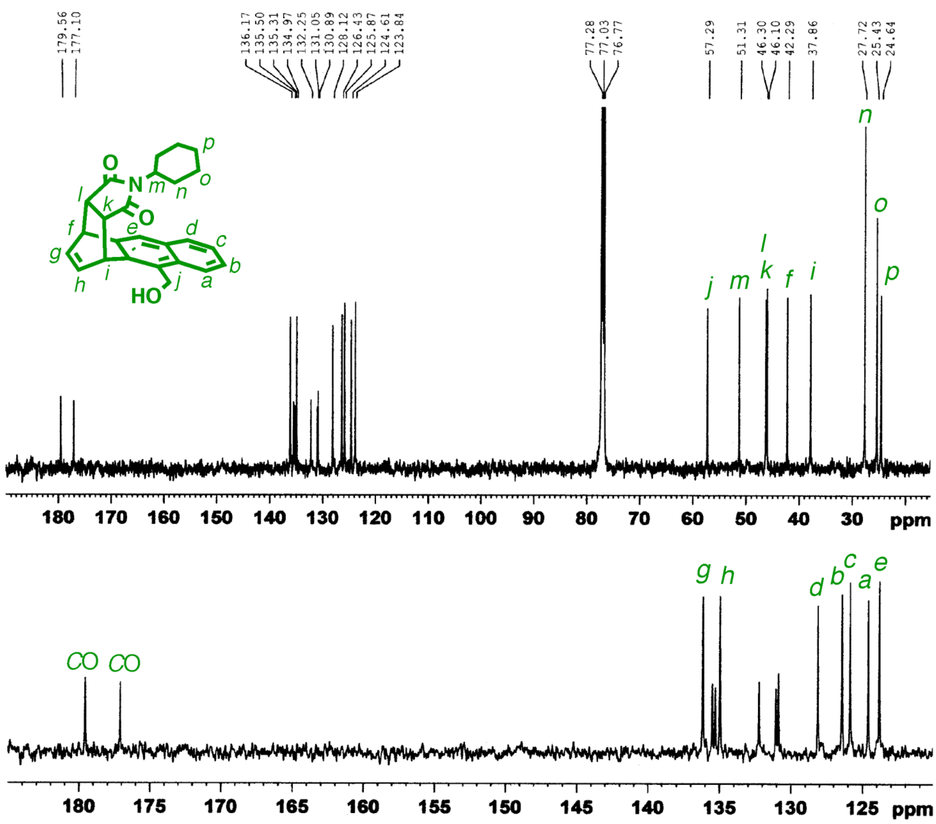


Fig. S5. ^{13}C-NMR spectra (500 MHz, $CDCl_3$, r.t.) of **5**.

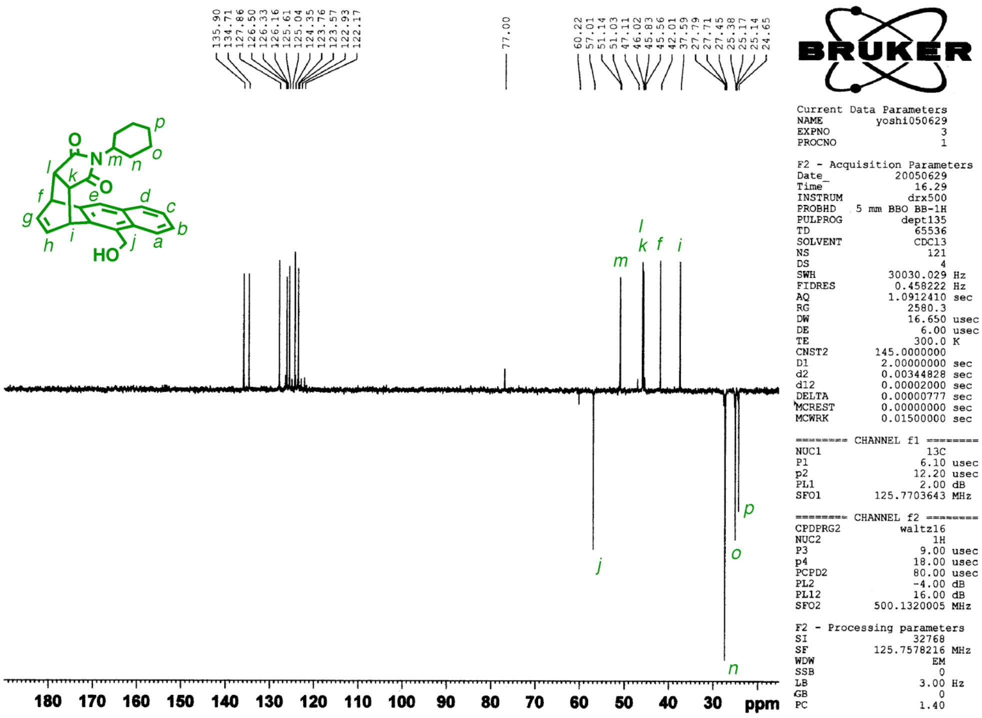


Fig. S6. DEPT spectrum (500 MHz, $CDCl_3$, r.t.) of **5**.

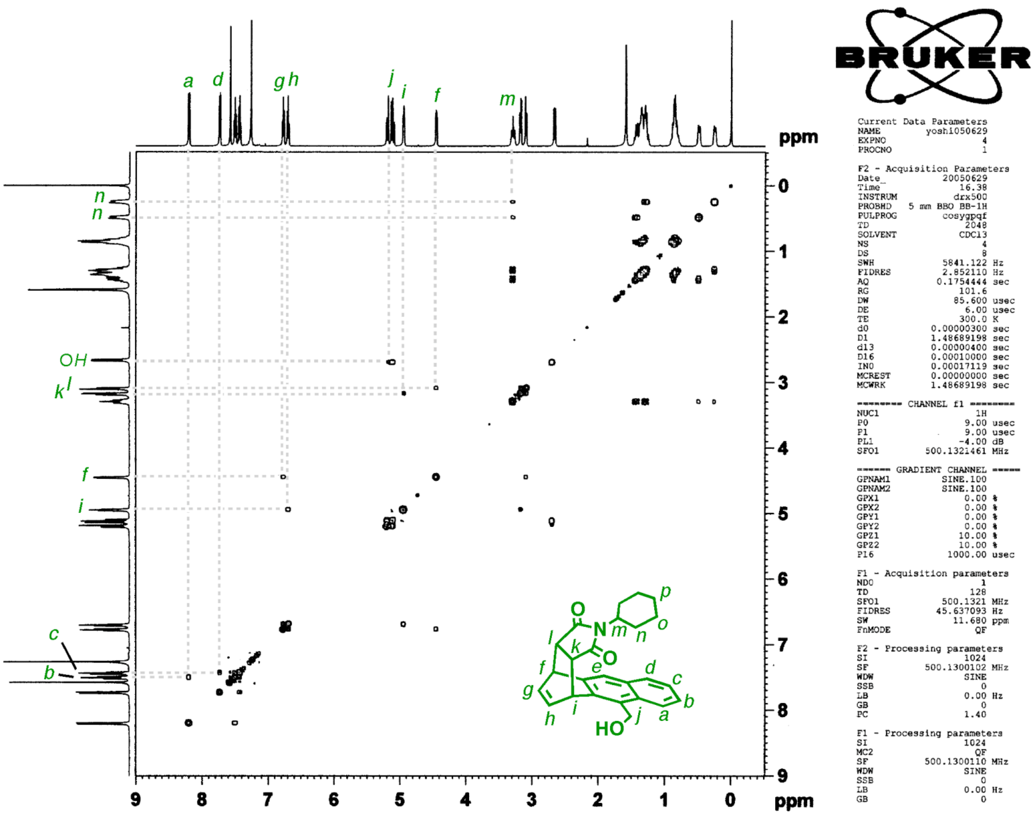


Fig. S7. HH-COSY spectrum (500 MHz, $CDCl_3$, r.t.) of **5**.

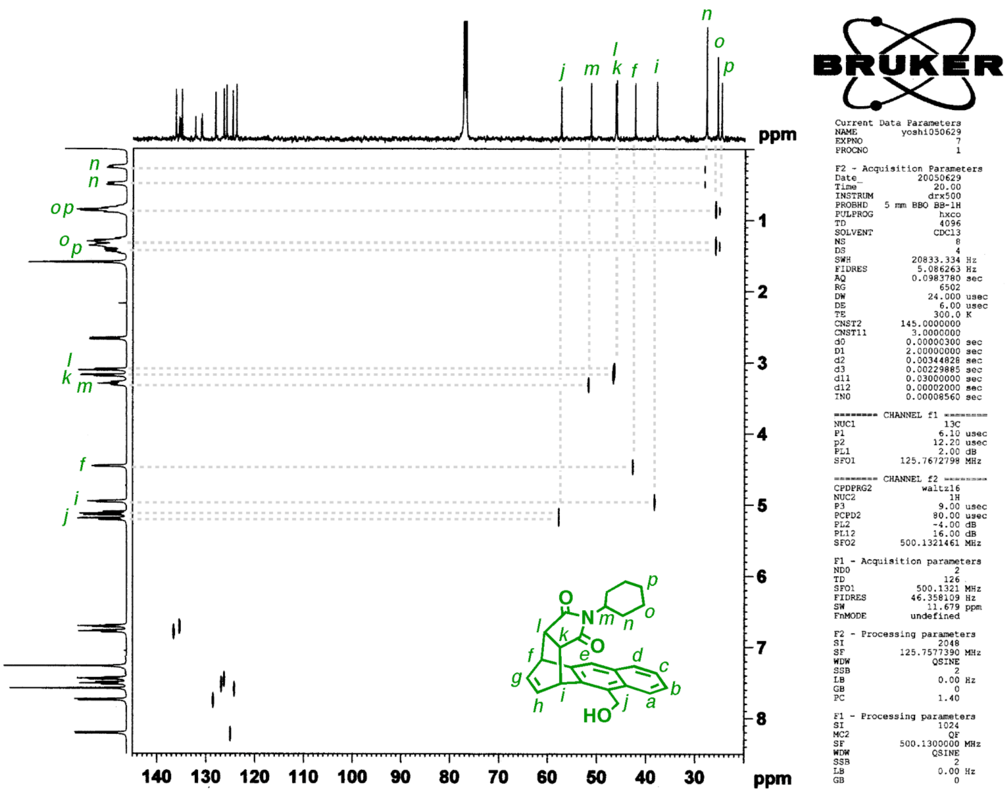


Fig. S8. CH-COSY spectrum (500 MHz, $CDCl_3$, r.t.) of **5**.

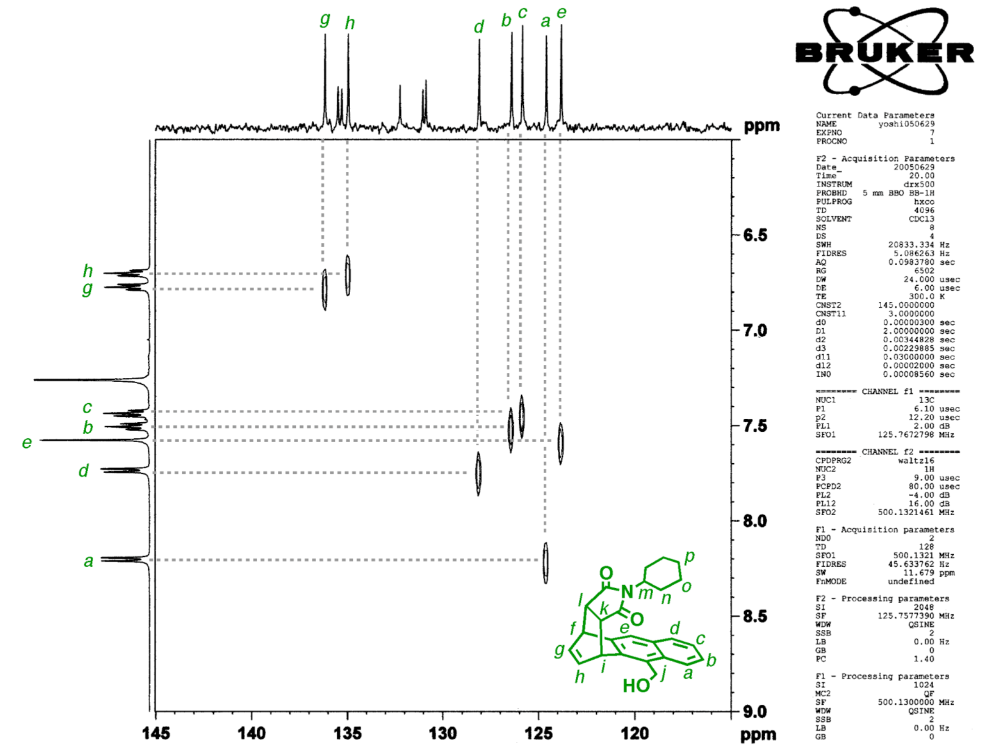
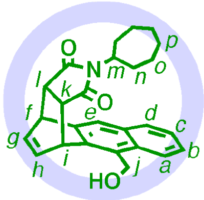
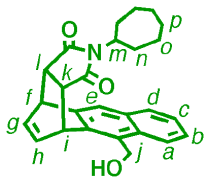


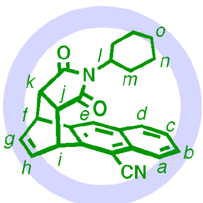
Fig. S9. CH-COSY spectrum (500 MHz, $CDCl_3$, r.t.) of **5** around aromatic region.



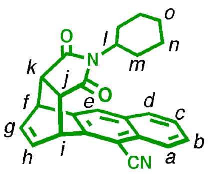
Physical data of **1⊃5b** (9-hydroxymethyl, *N*-cycloheptyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS as external standard): δ 9.68 (d, J = 5.7 Hz, 3H, **1**), 9.63 (d, J = 5.7 Hz, 3H, **1**), 9.44-9.39 (m, 12H, **1** (and free **1**)), 9.32 (s, 6H, **1**), 9.20 (d, J = 5.0 Hz, 3H, **1**), 9.14 (d, J = 5.0 Hz, 3H, **1**), 8.89 (d, J = 6.5 Hz, 6H, **1**), 8.76 (d, J = 6.5 Hz, 6H, **1**), 8.75 (s, free **1**), 8.50 (d, J = 4.5 Hz, 3H, **1**), 8.46 (d, J = 4.5 Hz, 3H, **1**), 6.69 (d, J = 8.0 Hz, 1H, H_a), 6.57 (br, 2H, H_g and H_h), 6.52 (d, J = 7.5 Hz, 1H, H_d), 5.23 (t, J = 7.5 Hz, 1H, H_b), 5.12 (s, 1H, H_e), 4.77 (d, 1H, H_c), 3.19 (s, 25H, **1** and H_j (and free **1**)), 2.88-2.77 (m, 73H, **1** and H_i (and free **1**)), 2.43 (s, 2H, H_k and H_l), 1.93 (s, 1H, H_f), 1.85 (d, J = 11.5 Hz, 1H, H_j), 1.14 (br, 1H, H_m), 0.48 (br, 1H, H_{cyclo}), 0.26 (br, 2H, H_{cyclo}), 0.17 (br, 1H, H_{cyclo}), –0.11 (br, 1H, H_{cyclo}), –0.28 (br, 1H, H_{cyclo}), –0.56 (br, 2H, H_{cyclo}), –0.85 (br, 1H, H_{cyclo}), –1.05 (br, 1H, H_{cyclo}), –1.53 (br, 1H, H_{cyclo}), –2.10 (br, 1H, H_{cyclo}); Yield: 83% (based on **1**).



Physical data of **5b** (9-hydroxymethyl, *N*-cycloheptyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS as external standard): δ 8.21 (d, J = 8.0 Hz, 1H, H_a), 7.74 (d, J = 8.0 Hz, 1H, H_d), 7.58 (s, 1H, H_e), 7.51 (dd, J = 7.5, 7.5 Hz, 1H, H_b), 7.44 (dd, J = 7.5, 7.5 Hz, 1H, H_c), 6.78 (dd, J = 6.5, 7.0, 1H, H_g), 6.71 (dd, J = 6.5, 7.0 Hz, 1H, H_h), 5.19 (d, J = 12.5 Hz, 1H, H_j), 5.11 (d, J = 12.5 Hz, 1H, H_j), 4.95 (t, J = 10.0 Hz, 1H, H_i), 4.45 (s, J = 10.0 Hz, 1H, H_f), 3.40 (m, 1H, H_m), 3.18 (dd, J = 3.7, 8.5, 1H, H_k), 3.10 (dd, J = 3.3, 8.8, 1H, H_l), 1.38-1.15 (m, 7H, H_{cyclo}), 0.90 (m, 3H, H_{cyclo}), 0.55 (br, 1H, H_{cyclo}), 0.33 (br, 1H, H_{cyclo}); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C): δ 179.5 (CO), 177.1 (CO), 136.1 (C_gH), 135.5 (C_q), 135.3 (C_q), 135.0 (C_hH), 132.2 (C_q), 131.1 (C_q), 130.9 (C_q), 128.1 (C_dH), 126.4 (C_bH), 125.9 (C_cH), 124.6 (C_aH), 123.9 (C_eH), 57.3 ($C_j H_2$), 53.1 (C_mH), 46.3 (C_kH), 46.1 (C_lH), 42.3 (C_fH), 37.9 (C_iH), 30.7 ($C_n H_2$), 30.6 ($C_n H_2$), 27.4 ($C_o H_2$), 27.2 ($C_o H_2$), 25.2 ($C_p H_2$), 25.1 ($C_p H_2$); IR (ATR, cm^{-1}): 2928 (br), 2853, 1766, 1680, 1452, 1394, 1374, 1346, 1256, 1196, 1148, 1052, 993, 747; m.p. 173-175 °C; E.A. Calcd. for $C_{26}H_{27}NO_3{\bullet}(H_2O)_{0.33}$: C, 76.07; H, 6.88; N, 3.41. Found: C, 76.28; H, 6.75; N, 3.27.



Physical data of **1⊃5c** (9-CN, *N*-cyclohexyl): ^{1}H NMR (500 MHz, D_2O, 27 °C, TMS as external standard): δ 9.64 (br, 3H, **1**), 9.59 (br, 3H, **1**), 9.45 (br, 3H, **1**), 9.39 (br, 9H, **1** (and free **1**)), 9.30 (br, 6H, **1**), 9.13 (d, J = 11.0 Hz, 6H, **1**), 8.87 (br, 6H, **1**), 8.79 (br, free **1**), 8.74 (br, 6H, **1**), 6.67 (d, J = 8.0 Hz, 1H, H_a), 6.55 (br, 2H, H_g and H_h), 6.53 (d, J = 8.0 Hz, 1H, H_d), 5.53 (br, 1H, H_b), 5.35 (s, 1H, H_e), 5.09 (br, 1H, H_c), 3.19 (s, 24H, **1** (and free **1**)), 2.92 (s, 1H, C*H* of **5c**), 2.87-2.76 (br, 72H, **1** (and free **1**)), 2.37 (m, 1H, C*H* of **5c**), 2.30 (s, 1H, C*H* of **5c**), 2.27 (d, J = 9.5 Hz, 1H, C*H* of **5c**), 1.02 (d, J = 10.0 Hz, 1H, H_{cyclo}), 0.42 (d, J = 10.0 Hz, 1H, H_{cyclo}), –0.07 (d, J = 10.0 Hz, 1H, H_{cyclo}), –0.25 (d, J = 10.0 Hz, 1H, H_{cyclo}), –0.58 (d, J = 12.5 Hz, 1H, H_{cyclo}), –0.73 (t, J = 12.0 Hz, 2H, H_{cyclo}), –0.83 (d, J = 11.5 Hz, 1H, H_{cyclo}), –1.17 (d, J = 11.0 Hz, 1H, H_{cyclo}), –1.79 (d, J = 10.0 Hz, 1H, H_{cyclo}), –1.96 (d, J = 10.0 Hz, 1H, H_{cyclo}); Yield: 88% (based on **1**).



Physical data of **5c** (9-CN, *N*-cyclohexyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS as external standard): δ 8.17 (d, J = 8.5 Hz, 1H, H_a), 7.82 (d, J = 8.0 Hz, 1H, H_d), 7.81 (s, 1H, H_e), 7.64 (dd, J = 7.0, 8.5 Hz, 1H, H_b), 7.56 (dd, J = 7.0, 8.0 Hz, 1H, H_c), 6.79 (dd, J = 6.0, 7.0, 1H, H_g), 6.75 (dd, J = 6.0, 7.0 Hz, 1H, H_h), 5.00 (t, J = 4.5 Hz, 1H, H_i), 4.55 (q, J = 2.0 Hz, 1H, H_f), 3.34 (tt, J = 3.8, 12.5, 1H, H_l), 3.21 (dd, J = 3.8, 8.8, 1H, H_j), 3.13 (dd, J = 3.8, 8.8, 1H, H_k), 1.46 (dq, J = 3.0, 12.0, 2H, H_{cyclo}), 1.36 (br, 3H, H_{cyclo}), 0.87 (m, 3H, H_{cyclo}), 0.42 (d, J = 12.3, 1H, H_{cyclo}), 0.34 (d, J = 12.3, 1H, H_{cyclo}) (Fig. S10); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C): δ 176.6 (*C*O), 175.8 (*C*O), 143.5 (C_q), 136.5 (C_q), 136.3 (*C*H), 134.6 (*C*H), 131.4 (C_q), 130.8 (C_q), 128.4 (*C*H × 2), 127.6 (*C*H), 127.4 (*C*H), 125.3 (*C*H), 115.7 (*C*N), 106.1 (C_q), 51.1 (*C*H), 45.7 (*C*H), 45.5 (*C*H), 41.8 (*C*H), 40.7 (*C*H), 27.8 (CH_2), 27.7 (CH_2), 25.4 (CH_2 × 2), 24.6 (CH_2); IR (ATR, cm^{-1}): 2934 (br), 2858 (br), 2224 (CN), 1769, 1692, 1451, 1394, 1369, 1345, 1257, 1198, 1186, 1146, 897, 830, 817, 751, 732, 651; m.p. 196-198 °C; E.A. Calcd. for $C_{25}H_{22}N_2O_2$•$(H_2O)_{0.25}$: C, 77.60; H, 5.86; N, 7.24. Found: C, 77.72; H, 5.89; N, 7.03.

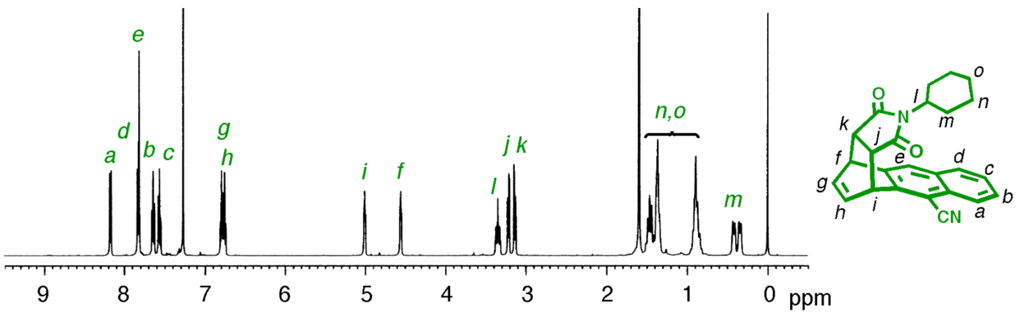
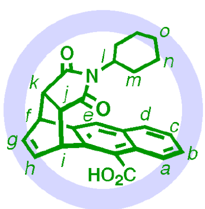
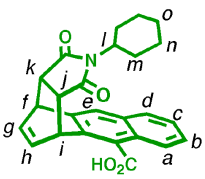


Fig. S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **5c**.



Physical data of **1⊃5d** (9-COOH, *N*-cyclohexyl): ^{1}H NMR (500 MHz, D_2O, 27 °C, TMS as external standard): δ 9.62 (d, J = 6.0 Hz, 3H, **1**), 9.58 (br, J = 6.0 Hz, 3H, **1**), 9.40-9.35 (m, 12H, **1** (and free **1**)), 9.28 (d, J = 5.0 Hz, 6H, **1**), 9.15 (d, J = 5.0 Hz, 3H, **1**), 9.07 (d, J = 5.0 Hz, 3H, **1**), 8.86 (d, J = 6.0 Hz, 3H, **1**), 8.83 (d, J = 6.0 Hz, **1**), 8.72 (d, J = 6.0 Hz, 6H, **1** (and free **1**)), 8.43 (d, J = 5.0 Hz, 3H, **1**), 8.36 (d, J = 5.0 Hz, 3H, **1**), 6.65 (t, J = 6.5 Hz, 1H, **5d**), 6.51 (br, 1H, **5d**), 6.43 (d, J = 7.5 Hz, 1H, **5d**), 6.01 (d, J = 8.5 Hz, 1H, **5d**), 5.48 (d, J = 7.0 Hz, 1H, **5d**), 5.27 (br, 1H, **5d**), 4.64 (s, 1H, **5d**), 3.20 (m, 24H, **1** (and free **1**)), 2.86-2.76 (m, 72H, **1** (and free **1**)), 2.56 (d, J = 5.5 Hz, 1H, **5d**), 2.23 (dd, J = 3.5, 8.5 Hz, 1H, **5d**), 1.87 (dd, J = 3.5, 8.5 Hz, 1H, **5d**), 0.99 (br, 1H, H_{cyclo}), 0.41 (br, 1H, H_{cyclo}), –0.14 (br, 2H, H_{cyclo}), –0.47 (br, 1H, H_{cyclo}), –0.58~–0.75 (br, 4H, H_{cyclo}), –1.73 (br, 1H, H_{cyclo}), –1.79 (br, 1H, H_{cyclo}); Yield: 92% (based on **1**).



Physical data of **5d** (9-COOH, *N*-cyclohexyl): [1]H NMR (500 MHz, $CDCl_3$, 27 ºC, TMS as external standard): δ 8.18 (d, J = 8.0 Hz, 1H, H_a), 7.76 (d, J = 8.0 Hz, 1H, H_d), 7.71 (s, 1H, H_e), 7.52 (dd, J = 7.0, 8.0 Hz, 1H, H_b), 7.48 (dd, J = 7.0, 8.0 Hz, 1H, H_c), 6.79 (dd, J = 6.0, 7.0, 1H, H_g), 6.75 (dd, J = 6.0, 7.0 Hz, 1H, H_h), 5.11 (s, 1H, H_i), 4.52 (t, J = 3.8 Hz, 1H, H_f), 3.40 (tt, J = 3.5, 12.5, 1H, H_m), 3.29 (dd, J = 3.5, 8.5, 1H, H_j), 3.16 (dd, J = 3.5, 8.5, 1H, H_k), 1.46 (dq, J = 3.5, 12.5, 1H, H_{cyclo}), 1.47-1.3 (m, 4H, H_{cyclo}), 0.91 (m, 3H, H_{cyclo}), 0.58 (d, J = 12.0, 1H, H_{cyclo}), 0.38 (d, J = 12.0, 1H, H_{cyclo}) (Fig. S11); [13]C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 179.8 (*C*O), 176.8 (*C*O × 2), 136.2 (*C*H), 135.5 (C_q × 2), 134.8 (*C*H), 131.9 (C_q), 128.7 (C_q), 127.9 (*C*H), 127.3 (*C*H), 126.5 (*C*H, C_q), 125.9 (*C*H), 125.6 (*C*H), 51.5 (*C*H), 46.1 (*C*H), 45.9 (*C*H), 42.0 (*C*H), 39.0 (*C*H), 27.7 (CH_2), 27.6 (CH_2), 25.4 (CH_2 × 2), 24.6 (CH_2); IR (ATR, cm^{-1}): 2930 (br), 2853, 1772, 1678, 1388, 1222, 1205, 1189, 1161, 1148, 755; m.p. 260-262 ºC; E.A. Calcd. for $C_{25}H_{23}NO_4{\bullet}(H_2O)_{0.33}$: C, 73.69; H, 5.85; N, 3.44. Found: C, 73.66; H, 5.80; N, 3.25.

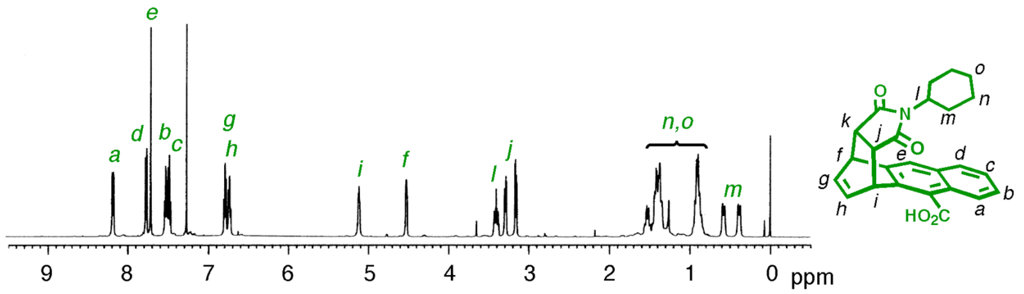
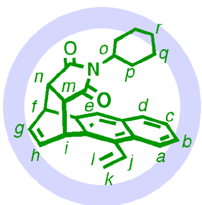
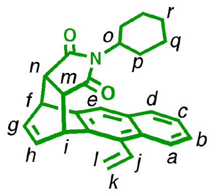


Fig. S11. [1]H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **5d**.



Physical data of **1⊃5e** (9-CH=CH_2, *N*-cyclohexyl): [1]H NMR (500 MHz, D_2O, 27 ºC, TMS as external standard): δ 9.53 (br, 6H, **1**), 9.29 (br, 12H, **1** (and free **1**)), 9.22 (br, 6H, **1**), 9.05 (br, 6H, **1**), 8.77 (br, 6H, **1**), 8.66 (br, 6H, **1** (and free **1**)), 8.37 (br, 6H, **1**), 8.36 (d, J = 5.0 Hz, 3H, **1**), 6.44 (t, J = 6.0 Hz, 1H, **5e**), 6.39 (br, J = 8.0 Hz, 1H, **5d**), 6.26 (br, 1H, **5e**), 5.82 (t, J = 6.5 Hz, 1H, **5e**), 5.46 (br, 1H, **5e**), 3.74 (d, J = 17.5 Hz, 1H, **5e**), 3.11 (s, 24H, **1** (and free **1**)), 2.77-2.58 (m, 72H, **1** (and free **1**)), 2.18 (s, 1H, **5e**), 2.11 (d, J = 5.0 Hz, 1H, **5e**), 1.77 (d, J = 5.0 Hz, 1H, **5e**), 0.89 (br, 1H, H_{cyclo}), 0.44 (br, 1H, H_{cyclo}), 0.22 (br, 1H, H_{cyclo}), –0.48 (d, J = 8.5 Hz, 2H, H_{cyclo}), –0.60 (br, 1H, H_{cyclo}), –1.02 (br, J = 7.5 Hz, 3H, H_{cyclo}), –1.47 (br, 1H, H_{cyclo}), –2.25 (br, 1H, H_{cyclo}); Yield: 70% (based on **1**).



Physical data of **5e** (9-CH=CH_2, *N*-cyclohexyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 ºC, TMS as external standard): δ 7.98 (d, J = 10.0 Hz, 1H, H_a), 7.72 (d, J = 10.0 Hz, 1H, H_d), 7.54 (s, 1H, H_e), 7.42-7.39 (m, J = 7.5, 2H, H_b and H_c), 7.06 (dd, J = 11.5, 18.0, 1H, H_j), 6.74 (dt, J = 1.0, 7.0 Hz, 1H, H_g), 6.69 (dt, J = 1.0, 7.0 Hz, 1H, H_h), 5.82 (dd, J = 1.8, 11.5, 1H, H_k), 5.53 (dd, J = 1.8, 18.0, 1H, H_l), 4.95 (t, J = 4.3 Hz, 1H, H_i), 4.45 (m, 1H, H_f), 3.32 (tt, J = 4.0, 12.5, 1H, H_o), 3.09 (dd, J = 3.2, 8.5, 1H, H_m), 3.06 (dd, J = 3.2, 8.5, 1H, H_n), 1.52-1.30 (m, 5H, H_{cyclo}), 0.88 (br, 3H, H_{cyclo}), 0.51 (d, J = 12.0, 1H, H_{cyclo}), 0.34 (d, J = 12.0, 1H, H_{cyclo}) (Fig. S12); ^{13}C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 177.4 (*C*O), 177.1 (*C*O), 136.2 (C_q), 136.0 (*C*H), 135.9 (*C*H), 133.7 (C_q), 132.6 (C_{vinyl}H), 132.1 (C_q), 131.8 (C_q), 130.4 (C_q), 127.9 (*C*H), 125.7 (*C*H), 125.6 (*C*H), 125.4 (*C*H), 122.5 (C_{vinyl}H), 121.9 (*C*H), 50.9 (*C*H), 46.0 (*C*H), 45.8 (*C*H), 42.2 (*C*H), 38.4 (*C*H), 27.8 (CH_2), 27.6 (CH_2), 25.4 (CH_2), 24.7 (CH_2); IR (ATR, cm^{-1}): 2931 (br), 2856, 1768, 1692, 1452, 1395, 1371, 1347, 1258, 1198, 1190, 1147, 893, 748, 645; m.p. 199-200 ºC; E.A. Calcd. for $C_{26}H_{25}NO_2$•$(H_2O)_{0.5}$: C, 79.56; H, 6.68; N, 3.57. Found: C, 79.32; H, 6.68; N, 3.35.

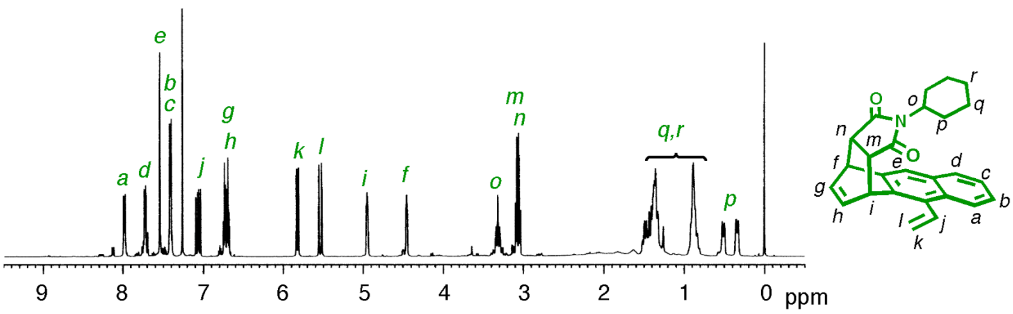
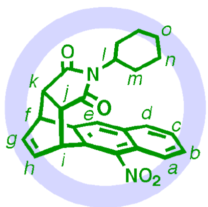
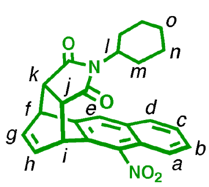


Fig. S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **5e**.



Physical data of **1⊃5f** (9-NO_2, *N*-cyclohexyl): ^{1}H NMR (500 MHz, D_2O, 27 ºC, TMS as external standard): δ 9.62 (br, 3H, **1**), 9.58 (br, 3H, **1**), 9.39 (br, 12H, **1** (and free **1**)), 9.12 (br, 3H, **1**), 9.10 (br, 3H, **1**), 8.86 (br, 6H, **1**), 8.80 (br, free **1**), 8.73 (br, 6H, **1**), 8.47 (br, 3H, **1**), 8.43 (br, 3H, **1**), 6.58 (t, J = 6.5 Hz, 1H, H_h), 6.49 (br, J = 8.0 Hz, 1H, H_d), 6.46 (d, J = 8.0 Hz, 1H, H_a), 6.40 (t, J = 6.5 Hz, 1H, H_g), 5.99 (t, J = 8.0 Hz, 1H, H_b), 5.58 (s, 1H, H_e), 4.30 (t, J = 8.0 Hz, 1H, H_c), 3.18 (s, 25H, **1** (and free **1**) and **5f**), 2.90-2.75 (m, 72H, **1** (and free **1**)), 2.34 (m, 1H, **5f**), 2.11 (m, 1H, **5f**), 1.65 (d, J = 13.0 Hz, 1H, **5f**), 1.03 (br, 1H, H_l), 0.61 (d, J = 13.0 Hz, 2H, H_{cyclo}), –0.27 (br, 2H, H_{cyclo}), –0.81 (d, 1H, H_{cyclo}), –0.99 (d, 4H, H_{cyclo}), –2.45 (br, 1H, H_{cyclo}); Yield: 92% (based on **1**).



Physical data of **5f** (9-NO_2, *N*-cyclohexyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 ºC, TMS as external standard): δ 7.82 and 7.81 (d, J = 7.5 Hz, 2H, H_a and H_d), 7.77 (s, 1H, H_e), 7.59 and 7.55 (t, 2H, H_b and H_c), 6.81 and 6.75 (dd, J = 6.5, 6.5 Hz, 1H, H_h and H_g), 4.79 (t, J = 4.2 Hz, 1H, H_i), 4.57 (m, 1H, *H*f), 3.30 (tt, *J* = 3.5, 12.3, 1H, *H*l), 3.14 (td, *J* = 1.5, 8.5, 1H, *H*j), 3.10 (dd, *J* = 3.7, 8.0, 1H, *H*k), 1.52 (q, *J* = 12.5, 2H, H_{cyclo}), 1.38 (br, 3H, H_{cyclo}), 0.97-0.82 (m, 3H, H_{cyclo}), 0.61 (d, *J* = 12.3, 1H, H_{cyclo}), 0.33 (d, *J* = 12.3, 1H, H_{cyclo}) (Fig. S13); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C): δ 176.5 (*C*O), 175.7 (*C*O), 144.2 (C_q), 136.7 (C_q), 136.3 (*C*H), 134.6 (*C*H), 132.1 (C_q), 130.1 (C_q), 128.4 (*C*H), 127.9 (*C*H), 127.4 (*C*H), 126.0 (*C*H), 123.1 (C_q), 122.1 (*C*H), 51.1 (*C*H), 45.7 (*C*H), 45.2 (*C*H), 41.6 (*C*H), 37.9 (*C*H), 27.8 (CH_2), 27.7 (CH_2), 25.4 (CH_2 × 2), 24.6 (CH_2); IR (ATR, cm^{-1}): 2948-2928 (br), 2858, 1771, 1694, 1611, 1519, 1447, 1394, 1370, 1345, 1288, 1256, 1198, 1185, 1145, 1096, 1033, 979, 889, 872, 826, 776, 756, 733, 686; m.p. 210-211 °C; E.A. Calcd. for $C_{25}H_{25}N_2O_4$•$(H_2O)_{0.5}$: C, 70.91; H, 5.47; N, 6.62. Found: C, 70.82; H, 5.55; N, 6.68.

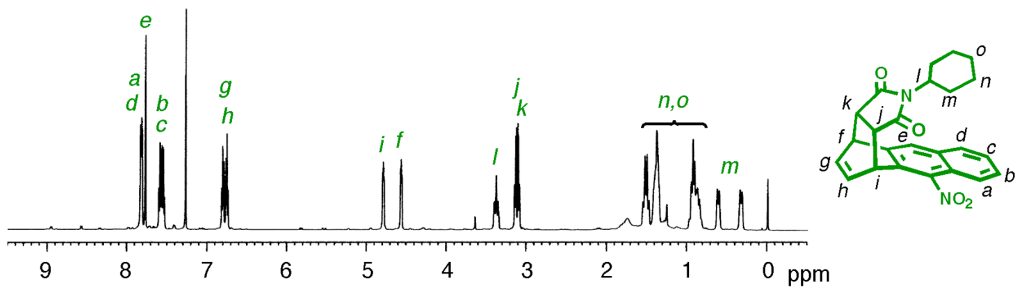
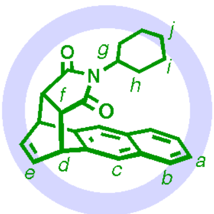
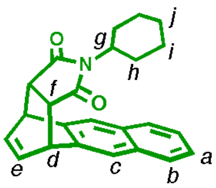


Fig. S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, r.t.) of **5f**.



Physical data of **1⊃5g** (9-H, *N*-cyclohexyl): ^{1}H NMR (500 MHz, D_2O, 27 °C, TMS as external standard): δ 9.43-9.39 (m, 24H, **1** (and free **1**)), 8.80-8.77 (m, 24H, **1** (and free **1**)), 6.42 (s, 2H, *H*e), 6.18 (d, 2H, *H*b), 5.64 (d, 2H, *H*a), 4.98 (s, 2H, *H*c), 3.20 (s, 24H, **1** (and free **1**)), 2.80 (s, 72H, **1** (and free **1**)), 2.27 (br, 2H, *H*d), 2.14 (s, 2H, *H*f), –0.87 (br, 1H, *H*g), –0.18 (br, 2H, H_{cyclo}), –0.78 (br, 2H, H_{cyclo}), –0.83 (br, 4H, H_{cyclo}), –1.77 (br, 2H, H_{cyclo}); Yield: 55% (based on **1**).



Physical data of **5g** (9-H, *N*-cyclohexyl): ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS as external standard): δ 7.73 (dd, *J* = 3.0, 6.3 Hz, 2H, *H*b), 7.59 (s, 2H, *H*c), 7.40 (dd, *J* = 3.0, 6.3 Hz, 2H, *H*a), 6.72 (dd, *J* = 3.5, 4.0 Hz, 2H, *H*e), 4.47 (s, 2H, *H*d), 3.30 (tt, *J* = 4.0, 13.0, 1H, *H*g), 3.09 (s, 2H, *H*f), 1.44 (q, *J* = 13.0, 2H, H_{cyclo}), 1.35 (d, *J* = 6.5, 2H, H_{cyclo}), 0.90-0.81 (m, 4H, H_{cyclo}), 0.39 (d, *J* = 13.0, 2H, H_{cyclo}); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C): δ 177.3 (*C*O), 136.5 (C_q), 135.7 (*C*H), 132.2 (C_q), 127.6 (*C*H), 125.7 (*C*H), 122.9 (*C*H), 51.0 (*C*H), 46.1 (*C*H), 41.9 (*C*H), 27.7 (CH_2), 25.4 (CH_2), 24.7 (CH_2).

Catalytic Diels-Alder reaction of 9-hydroxymethylanthracene and *N*-phenylphthalimide within cage **2** (typical procedure): When 9-hydroxymethylanthracene (**3a**) and *N*-phenylphthalimide (**4c**) (10.0 μmol each) were suspended in a H_2O (or D_2O) solution (1.0 mL) of **2** (1.0 μmol) (Fig. S14a) and stirred at room temperature for 5 h, the solution color changed from cloudy and yellow to cloudy and colorless (Fig. S14b). The solid product was dissolved in $CDCl_3$ and ^1H NMR analysis confirmed the formation of 9,10-Diels-Alder adduct **6** in >99% yield based on **3a** (Fig. S14c). After purification with a preparative HPLC instrument (Japan Analytical Industry, Co., Ltd. LC-918) equipped with JAIGEL 1H+2H gel permeation chromatography columns and removal of solvent under vacuum, **6** was isolated in 95% yield as a colorless solid.

Physical data of $\mathbf{2}\supset(\mathbf{3a}_n\cdot\mathbf{4c}_m)$ (n = 0.8, m = 1.5): ^1H NMR (500 MHz, D_2O, 27 ºC): δ 10.55 (br, 8H, **2**), 9.77 (br, 4H, **2**), 9.39 (br, 8H, **2**), 9.27 (br, 4H, **2**), 8.81 (br, 12H, **2**), 7.94 (br, 12H, **2**), 7.12 (br, **4c**), 6.80 (br, **4c**), 6.57 (br, **4c**), 6.48 (br, **3a**), 6.14 (br, **3a**), 5.98 (br, **3a**), 5.78 (br, **3a**), 3.59 (br, **3a**), 3.04-2.96 (m, 24H, **2**).

Physical data of $\mathbf{2}\supset\mathbf{6}_n$ (n = 0.8): ^1H NMR (500 MHz, D_2O, 27 ºC): δ 10.47 (br, 8H, **2**), 9.55 (br, 4H, **2**), 9.22 (br, 12H, **2**), 8.82 (br, 4H, **2**), 8.63 (br, 8H, **2**), 7.85 (br, 12H, **2**), 7.35 (br, **6**), 7.05 (br, **6**), 6.95 (br, **6**), 6.82 (br, **6**), 6.62 (br, **6**), 5.53 (br, **6**), 4.98 (br, **6**), 4.75 (br, **6**), 4.35 (br, **6**), 3.04-2.96 (m, 24H, **2**), 2.91 (br, **6**), 2.48 (br, **6**), 2.12 (br, **6**), 1.66 (br, **6**).

Physical data of **6**: ^1H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 7.66 (d, J = 7.5 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H), 7.37 (dd, J = 3.0, 4.5 Hz, 1H), 7.30-7.22 (m, 9H), 6.52 (dd, J = 3.0, 4.5 Hz, 1H), 5.17 (dd, J = 4.0, 11.5 Hz, 1H, H_b), 5.01 (dd, J = 5.0, 11.6 Hz, 1H, H_b), 4.86 (d, J = 3.0 Hz, 1H, H_c), 3.54 (d, J = 8.5 Hz, 1H, H_e), 3.46 (dd, J = 3.0, 8.5 Hz, 1H, H_d), 2.78 (br, 1H, H_a).

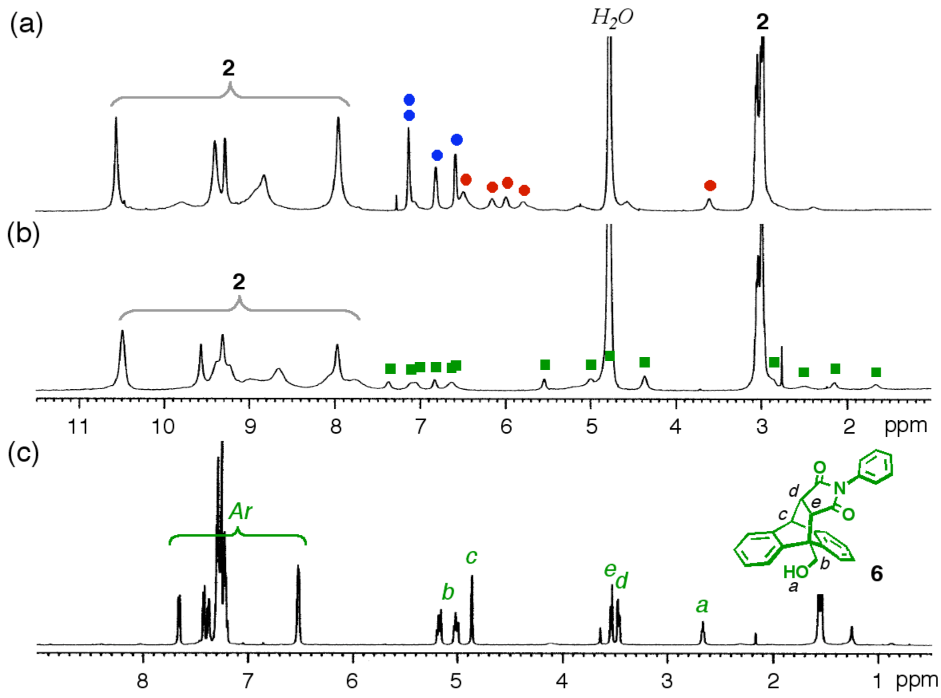
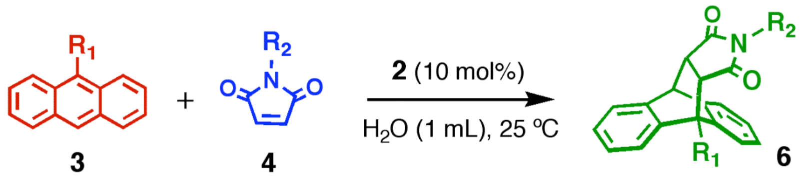


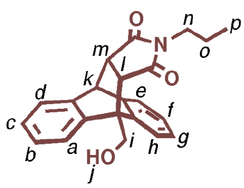
Fig. S14. [1]H NMR spectra (500 MHz, r.t.) of catalytic Diels-Alder reaction of hydroxymethylanthracene (**3a**) and *N*-phenylphthalimide (**4c**) in the aqueous solution of **2**. (a) Before and (b) after the reaction at r.t. for 5 h (red circle: **3a**, blue circle: **4c**, green square: **6**). (**c**) Diels-Alder product **6** was extracted with $CDCl_3$.

Table S1. Catalytic Diels-Alder reaction of **3** and **4** in the presence of **2** (10 mol%) in H_2O (1 mL) and control experiments in H_2O or $CDCl_3$ (1 mL) without **2**.

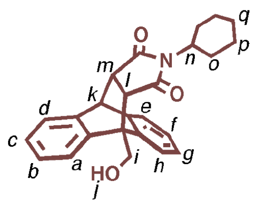


Entry	Substrate		Time	Yield(%) of **6**		
	3 (R_1)	**4** (R_2)		with **2**	without **2**	in $CHCl_3$ †
1	$-CH_2OH$	propyl	5 h	>99	8	0
2	$-CH_2OH$	cyclohexyl	15 h	98	0	6
3	$-CH_2OH$	phenyl	5 h	>99 *,†	3	9
4	$-CH_2OH$	phenyl	15 h	6	7	21
5	$-CH_2OH$	benzyl	5 h	>99	trace	0
6	$-CH_2OH$	xylyl	15 h	94	0	17
7	$-CH_3$	cyclohexyl	7 h	>99	0	5
8	$-CH_3$	phenyl	3 h	>99	5	17
9	$-CH=CH_2$	phenyl	1 d	88	0	trace
10	$-CH=CH_2$	benzyl	1 d	97	5	4
11	$-CO_2H$	benzyl	1 d	12	0	0
12	$-CH_2OH$	phenyl	1 d	>99 ‡	—	—

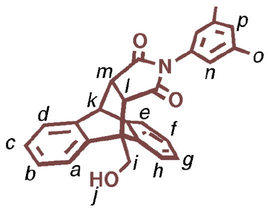
* $(en)Pd(NO_3)_2$: 10 mol% † without **2** ‡ **2** : 1 mol%, hexane (1 mL)



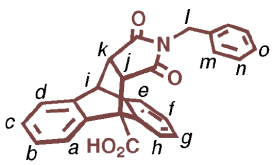
Physical data: [1]H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 7.58 (d, J = 7.5 Hz, 1H, H_a), 7.37 (d, J = 7.0 Hz, 1H, H_d), 7.29 (d, J = 7.5 Hz, 1H, H_e), 7.26 (d, J = 7.0 Hz, 1H, H_h), 7.22 (dd, J = 7.0 Hz, 1H, H_b), 7.17 (dd, J = 7.0 Hz, 1H, H_c), 7.13 (m, 1H × 2, H_f ,H_g), 5.14 (dd, J = 6.3, 11.6 Hz, 1H, H_i), 4.99 (dd, J = 5.0, 11.6 Hz, 1H, H_i), 4.75 (d, J = 3.0 Hz, 1H, H_k), 3.33 (d, J = 8.5 Hz, 1H, H_l), 3.27 (dd, J = 3.5, 8.5 Hz, 1H, H_m), 3.09 (t, J = 7.5 Hz, 2H, H_n), 2.83 (br, 1H, H_j), 0.87 (m, 3H, H_o), 0.48 (t, J = 7.5 Hz, 3H, H_p); [13]C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 177.1, 176.7, 142.2, 142.1, 139.3, 139.0, 126.9, 126.8, 126.6, 126.5, 125.3, 124.0, 123.1, 122.5, 60.7, 49.3, 47.8, 46.4, 45.6, 40.1, 20.4, 10.9; IR (KBr, cm^{-1}): 3487 (br), 3071, 3021, 2954 (br), 2876, 1768, 1686, 1458, 1403, 1350, 1323, 1204, 1135, 1060, 1018, 979, 878, 750; m.p.: 192-193 ºC; E.A. Calcd. for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.46; H, 6.34; N, 3.80.



Physical data: [1]H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 7.58 (d, J = 7.5 Hz, 1H, H_a), 7.37 (d, J = 7.0 Hz, 1H, H_d), 7.29 (d, J = 7.0 Hz, 1H, H_e), 7.26 (d, J = 7.0 Hz, 1H, H_h), 7.22 (dd, J = 7.5 Hz, 1H, H_b), 7.17 (dd, J = 7.5 Hz, 1H, H_c), 7.14 (m, 1H × 2, H_f ,H_g), 5.14 (dd, J = 6.6, 11.8 Hz, 1H, H_i), 4.97 (dd, J = 5.8, 11.6 Hz, 1H, H_i), 4.73 (d, J = 3.1 Hz, 1H, H_k), 3.52 (m, 1H, H_n), 3.26 (d, J = 8.5 Hz, 1H, H_l), 3.20 (dd, J = 3.0, 8.5 Hz, 1H, H_m), 2.77 (t, 1H, J = 5.8 Hz, H_j), 1.69 (q, J = 12.5 Hz, 2H, H_{cyclo}), 1.64 (d, J = 13.0 Hz, 2H, H_{cyclo}), 1.54 (s, 1H, H_{cyclo}), 1.07 (m, 3H, H_{cyclo}), 0.85 (m, 2H, H_{cyclo}); [13]C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 177.2, 176.9, 142.1 (C × 2), 139.3, 138.9, 126.8 (C × 2), 126.6, 126.5, 125.3, 124.0, 123.1, 122.4, 60.6, 51.4, 49.4, 47.3, 45.7, 28.0, 27.9, 25.6, 24.8; IR (KBr, cm^{-1}): 3511 (br), 2936 (br), 2858, 1767, 1689, 1458, 1398, 1373, 1346, 1256, 1197, 1146, 1054, 978, 893, 761; m.p. 228-230 ºC; E.A. Calcd. for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.27; H, 6.65; N, 3.41.



Physical data: [1]H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 7.65 (d, J = 7.5 Hz, 1H, H_a), 7.42 (d, J = 7.5 Hz, 1H, H_d), 7.38 (m, 1H, ArH), 7.29 (m, 1H, ArH), 7.25-7.19 (m, 4H, ArH), 6.91 (s, 1H, H_p), 6.06 (s, 2H × 2, H_n), 5.17 (dd, J = 5.5, 11.5 Hz, 1H, H_i), 5.01 (dd, J = 5.5, 12.0 Hz, 1H, H_i), 4.86 (d, J = 3.0 Hz, 1H, H_k), 3.51 (d, J = 8.5 Hz, 1H, H_l), 3.45 (dd, J = 3.0, 8.5 Hz, 1H, H_m), 2.65 (br, 1H, H_j), 2.21 (s, 6H, H_o); [13]C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 176.3, 176.2, 141.9 (C × 2), 139.4, 138.9 (C × 2), 131.0, 130.7, 127.0, 127.0, 126.7, 126.6, 125.5, 124.2, 124.1, 123.3, 122.5, 60.3, 49.7, 48.0, 46.3, 45.9, 21.1; IR (KBr, cm^{-1}): 3507 (br), 3019, 2955, 1771, 1692, 1598, 1462, 1394, 1280, 1205, 1141, 1037, 975, 849, 771, 741; m.p.: 228-229 ºC; E.A. Calcd. for $C_{27}H_{23}NO_3$•$(H_2O)_{0.25}$: C, 78.33; H, 5.72; N, 3.38. Found: C, 78.10; H, 5.97; N, 3.12.



Physical data: [1]H NMR (500 MHz, $CDCl_3$, 27 ºC): δ 7.86 (d, J = 7.5 Hz, 1H, ArH), 7.40 (br, 1H, ArH), 7.23 (br, 2H, ArH), 7.17 (br, 2H, ArH), 7.14 (t, J = 7.0 Hz, 2H, H_n), 7.06 (t, J = 7.5 Hz, 1H, H_o), 6.99 (t, J = 7.5 Hz, 1H, ArH), 6.79 (d, J = 7.5 Hz, 2H, H_m), 4.76 (d, J = 7.5 Hz, 1H, H_i), 4.27 (d, J = 5.0 Hz, 2H, H_l), 3.91 (dd, J = 2.8, 3.0 Hz, 1H, H_k); [13]C NMR (125 MHz, $CDCl_3$, 27 ºC): δ 176.2, 175.6, 163.3 140.9, 139.6, 137.3, 136.1, 134.6, 128.5, 127.6, 127.3, 127.0, 124.9, 124.1, 123.5, 56.6, 48.5, 47.6, 45.9, 42.4; IR (KBr, cm^{-1}): 3039 (br), 1770, 1730, 1686, 1457, 1435, 1403, 1343, 1201, 1170, 1080, 929, 886, 852; m.p. 251-253 ºC; E.A. Calcd. for $C_{26}H_{19}NO_4$•$(H_2O)_{0.25}$: C, 75.44; H, 4.75; N, 3.38. Found: C, 75.18; H, 4.84; N, 3.42.

Table S2. Crystal data and structure refinement for **1⊃5**.

Identification code	tamura3	
Empirical formula	C133 H169 N54 O122 Pd6	
Formula weight	5114.62	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I4(1)/a	
Unit cell dimensions	a = 26.2963(11) Å	α = 90°
	b = 26.2963(11) Å	β = 90°
	c = 31.951(3) Å	γ = 90°
Volume	22094(2) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	0.594 mm^{-1}	
F(000)	10388	
Crystal size	0.20 x 0.15 x 0.15 mm^3	
Theta range for data collection	2.41 to 27.57°	
Index ranges	–34<=h<=34, –34<=k<=34, –41<=l<=41	
Reflections collected	147512	
Independent reflections	12743 [R(int) = 0.0660]	
Completeness to theta = 27.57°	99.8 %	
Absorption correction	None	
Max. and min. transmission	0.9162 and 0.8904	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12743 / 348 / 801	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R_1 = 0.0826, wR_2 = 0.2149	
R indices (all data)	R_1 = 0.1162, wR_2 = 0.2468	
Largest diff. peak and hole	1.139 and –0.822 e.$Å^{-3}$	

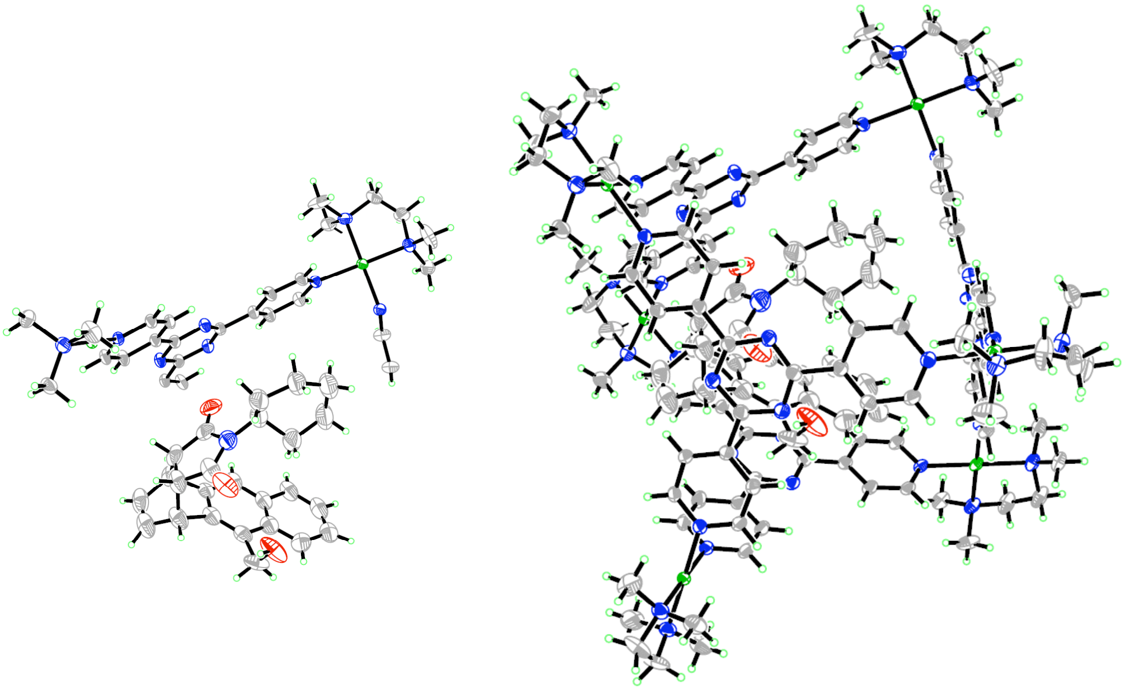


Fig. S15. ORTEP drawing (30% probability ellipsoid) of **1**⊃**5** after removing NO_3^- ions and solvents.

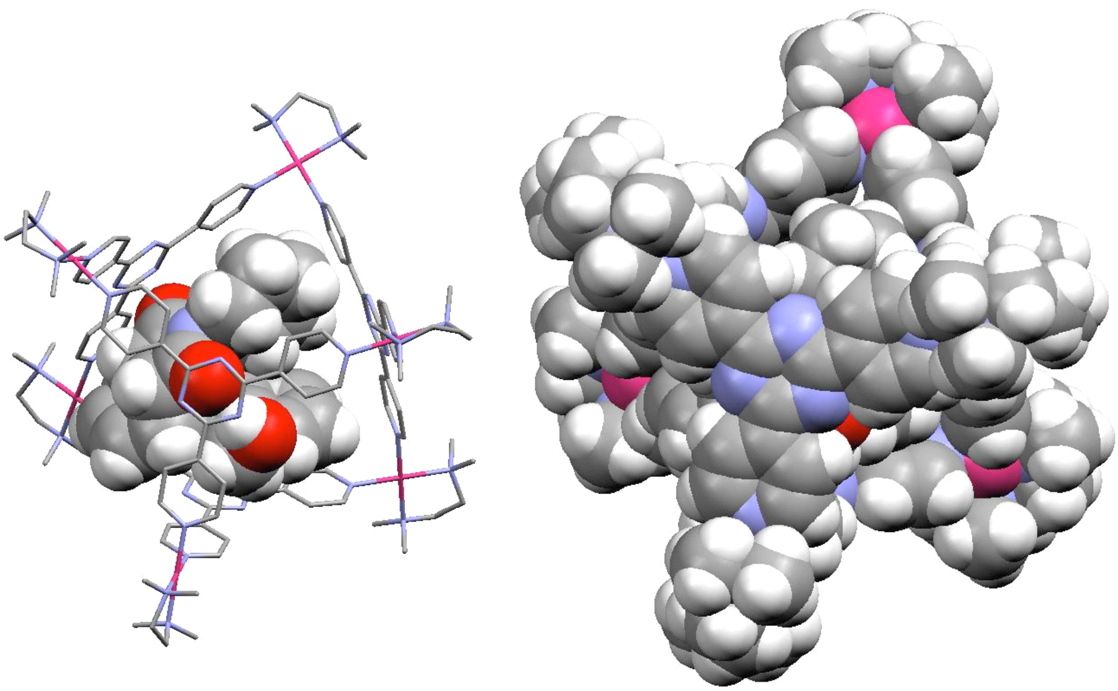


Fig. S16. Cylinder and/or Space-filling drawing of **1**⊃**5**.

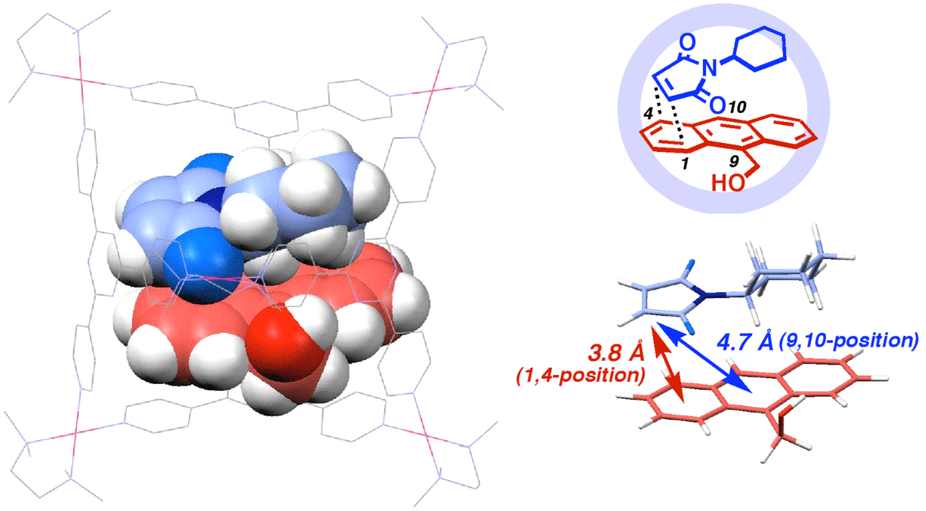


Fig. S17. Optimized structure of **1**⊃(**3a•4a**) by a force-field calculation and the distance between the C=C bond of **4a** and the 1,4-position or 9,10-position of **3a**.

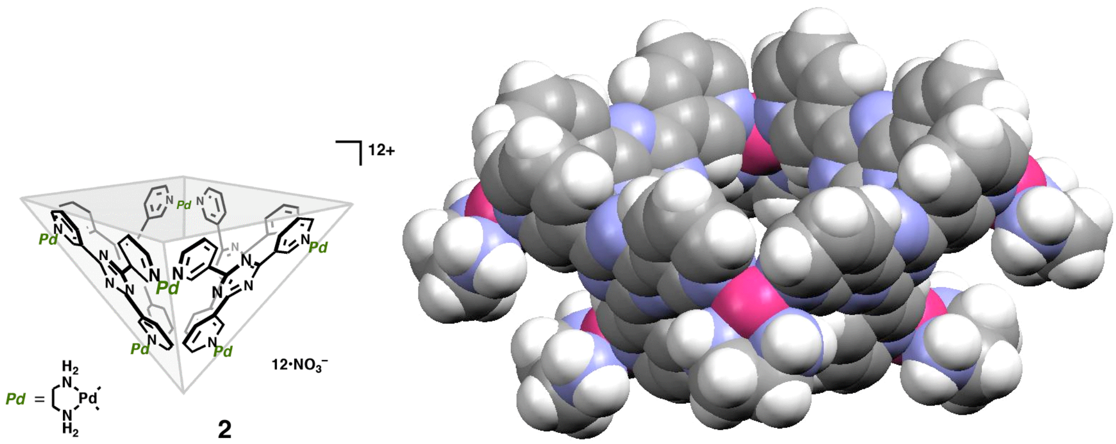


Fig. S18. Chemical structure of **2** and the Space-filling drawing.