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Supporting Information

Synthesis of Open-[70]Fullerenes Bearing a Huge Orifice

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1. General

The ^{1}H and ^{13}C NMR measurements were carried out at room temperature unless otherwise noted with a JEOL JNM ECA500, Bruker Avance III 600US Plus, and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of acetone-d_6 (δ 2.05 ppm in ^{1}H NMR, δ 29.92 ppm in ^{13}C NMR) and $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.00 ppm in ^{13}C NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3150 spectrometer. Cyclic voltammetry was conducted on a BAS Electrochemical Analyzer ALS620C using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out under N_2 atmosphere using ODCB solutions of 1.0 mM samples and 0.10 M tetrabutylammonium tetrafluoroborate (n-$Bu_4N{\cdot}BF_4$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene used as an internal standard which was added after each measurement. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia).

Fullerene C_{60} was purchased from SES Research Co. *o*-Dichlorobenzene (ODCB) was purchased from Sigma-Aldrich Co. LLC. Elemental sulfur and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Inc. Tetrakis(dimethylamino)ethylene (TDAE) and 4,5-dimethyl-1,2-phenylenediamine were purchased from Tokyo Chemical Industry Co. Ltd. Benzene and toluene were purchased from Nakalai Tesque, Inc. Carbon tetrachloride, *N*-methylmorpholine *N*-oxide (NMO), carbon disulfide, acetone, and ethyl acetate were purchased from FUJIFILM Wako Pure Chemical Corporation.

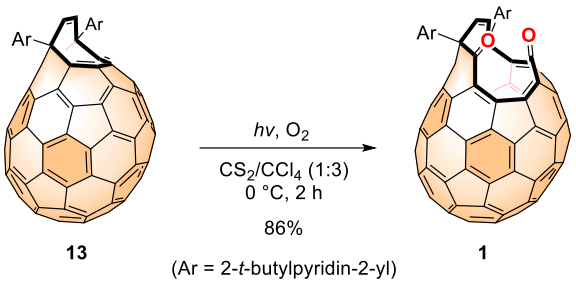
All reactions were carried out under Ar atmosphere except for cases showing specific notation. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. Compounds **13**[1] and **9**[2] were synthesized according to literature procedures.

2. Computational Methods

All calculations were conducted using the Gaussian 09 program. All structures at the stationary and transition states were optimized at the B3LYP/6-31G(d) or B3LYP-D3/6-31G(d) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory. Using the geometries optimized at the B3LYP-D3/6-31G(d) level of theory, GIAO (gauge-independent atomic orbital) calculations were performed at the B3LYP-D3/6-311G(d,p) level of theory.

3. Synthesis

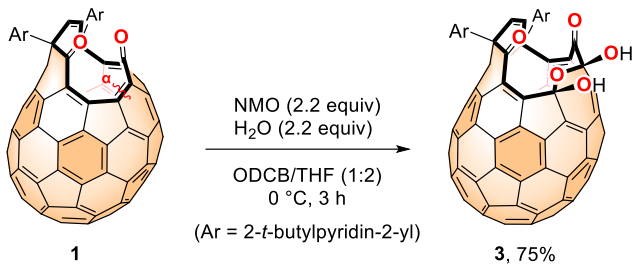
3.1. Synthesis of 1



Powdery **13** (280 mg, 242 μmol) dissolved in CS_2/CCl_4 (80 mL/240 mL) was placed into a circular glass tank with an inner diameter of 17.5 cm. The solution was bubbled with O_2 at 0 °C (water/ice bath) for 8 min and then irradiated by four white LED lamps (16 W × 4) for 2 h. The resulting crude mixture was evaporated and purified by column chromatography using silica gel (CS_2 to toluene) to give unreacted **13** (19.1 mg, 16.5 μmol, 7%) and **1** (248 mg, 208 μmol, 86%) as black powders.

1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, 1H, J = 8.0 Hz), 7.52 (t, 1H, J = 8.0 Hz), 7.27 (d, 1H, J = 8.0 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.19 (d, 1H, J = 8.0 Hz), 7.11 (d, 1H, J = 8.0 Hz), 6.70 (d, 1H, J = 10.3 Hz), 6.54 (d, 1H, J = 10.3 Hz), 1.24 (s, 9H), 1.09 (s, 9H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{92}H_{26}N_2O_2$ (**1**) 1190.2000; Found 1190.1988. (These data matched well with the reported ones.[1])

3.2. Synthesis of 3

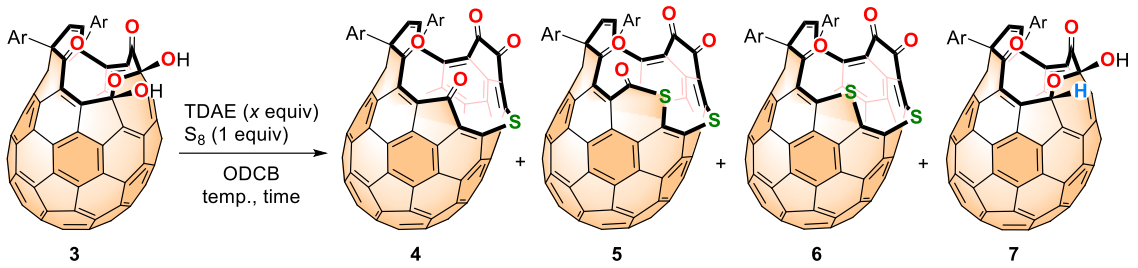


1 **3**, 75%

Powdery **1** (100 mg, 83.9 μmol) was placed into a Schlenk tube and degassed through three vacuum–Ar cycles. ODCB (10.0 mL) and then distilled water (degassed, 3.34 μL, ρ = 0.997 g/mL, 185 μmol, 2.20 equiv) were added to the tube. NMO (21.9 mg, 187 μmol, 2.23 equiv) dissolved in THF (20.0 mL) was transferred from a 50-mL two-neck flask to the Schlenk tube via a cannular. The resulting solution was cooled down to 0 °C (water/ice bath) and stirred for 3 h. The crude mixture was evaporated for removal of THF and then purified by column chromatography using silica gel (toluene/ethyl acetate (3:1)) to give **3** (78.1 mg, 62.9 μmol, 75%) as a black powder.

3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (t, 1H, J = 7.9 Hz), 7.53 (d, 1H, J = 7.9 Hz), 7.51 (t, 1H, J = 7.9 Hz), 7.34 (d, 1H, J = 7.9 Hz), 7.25 (d, 1H, J = 7.9 Hz), 7.10 (d, 1H, J = 7.9 Hz), 6.96 (d, 1H, J = 10.3 Hz), 6.49 (d, 1H, J = 10.3 Hz), 5.69 (br s, 1H), 5.15 (br s, 1H), 1.25 (s, 9H), 1.06 (s, 9H); HRMS (APCI) m/z: $[M–H_2O]^{\bullet-}$ Calcd for $C_{92}H_{26}N_2O_4$ (**3**–H_2O) 1222.1898; Found 1222.1896. (These data matched well with the reported ones.[1])

3.3. Synthesis of 4–7



[x = 0.5 (150 °C, 15 min)]

Powdery **3** (10.0 mg, 8.06 μmol) and S_8 (2.13 mg, 8.30 μmol, 1.03 equiv) were placed into a Schlenk tube and degassed through three vacuum–N_2 cycles. ODCB (0.500 mL) and then TDAE (0.93 μL, ρ = 0.868 g/mL, 4.0 μmol, 0.50 equiv) were added and the resulting solution was heated at 150 °C for 15 min (aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (100:1) to (50:1)) to give **7** (1.34 mg, 1.09 μmol, 14%) and **4** (2.47 mg, 1.97 μmol, 24%) as black powders.

[x = 1.0 (180 °C, 30 min)]

Powdery **3** (10.0 mg, 8.06 μmol) and S_8 (2.14 mg, 8.34 μmol, 1.04 equiv) were placed into a Schlenk tube and degassed through three vacuum–N_2 cycles. ODCB (0.500 mL) and then TDAE (1.86 μL, ρ = 0.868 g/mL, 8.06 μmol, 1.00 equiv) were added and the resulting solution was heated at 180 °C for 30 min (aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1) to (100:1), then (50:1)) to give **6** (5.93 mg, 4.71 μmol, 58%), **5** (0.96 mg, 0.75 μmol, 9%), and **4** (0.77 mg, 0.61 μmol, 8%) as black powders.

4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (t, 1H, J = 7.7 Hz), 7.54 (d, 1H, J = 7.7 Hz), 7.52 (t, 1H, J = 7.7 Hz), 7.30 (d, 1H, J = 7.7 Hz), 7.25 (d, 1H, J = 7.7 Hz), 7.20 (d, 1H, J = 10.3 Hz), 7.09 (d, 1H, J = 7.7 Hz), 6.52 (d, 1H, J = 10.3 Hz), 1.22 (s, 9H), 1.04 (s, 9H), –16.87 (s, 1.20H for entrapped H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.21, 184.88, 179.87, 179.45, 168.56, 168.31, 163.17, 161.15, 155.45, 151.01, 149.72, 149.60, 149.59, 149.53, 149.28, 149.12, 149.04, 148.78, 148.68, 148.61, 148.51, 147.96, 147.89, 147.29, 147.27, 147.21, 146.69, 146.08, 145.31, 144.34, 144.10, 144.07, 143.80, 143.77, 141.74, 141.28, 141.09, 141.01, 140.48, 139.88, 139.84, 139.41, 137.94, 137.91, 137.49, 137.33, 137.16, 136.27, 135.83, 135.72, 135.70, 135.22, 134.75, 134.21, 133.67, 133.33, 133.22,

133.20, 132.87, 132.81, 132.58, 132.53, 132.33, 130.89, 130.60, 129.04, 128.17, 126.94, 126.06, 126.01, 125.54, 125.11, 120.01, 119.65, 117.50, 117.27, 58.58, 53.89, 37.71, 37.56, 29.94, 29.81 (The sum of carbon signals must be 88 in theory. Observed 82. The 6 sp^2 carbon signals are overlapped.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{92}H_{26}N_2O_4S$ (**4**) 1254.1613; Found 1254.1607.

5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, 1H, J = 7.9 Hz), 7.57 (t, 1H, J = 7.9 Hz), 7.51 (t, 1H, J = 7.9 Hz), 7.24 (d, 1H, J = 7.9 Hz), 7.21 (d, 1H, J = 7.9 Hz), 7.15 (d, 1H, J = 7.9 Hz), 7.10 (d, 1H, J = 10.3 Hz), 6.36 (d, 1H, J = 10.3 Hz), 1.22 (s, 9H), 1.18 (s, 9H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 192.56 (2C), 168.47, 168.30, 163.92, 162.19, 157.26, 153.12, 152.26, 151.66, 151.29, 151.10, 151.04, 150.94, 150.87, 149.99, 149.94, 149.89, 149.72, 149.23, 149.12, 148.93, 148.90, 148.87, 148.79, 148.69, 148.68, 148.61, 148.52, 148.45, 148.23, 147.74, 147.50, 146.73, 146.57, 146.25, 144.96, 144.65, 144.49, 144.42, 143.54, 143.44, 143.15, 142.35, 141.64, 140.86, 140.43, 139.83, 139.78, 138.84, 137.76, 137.00, 136.94, 136.67, 136.07, 135.98, 135.13, 134.47, 134.15, 132.62, 132.46, 132.27, 132.17, 130.59, 130.55, 130.46, 130.39, 129.67, 129.27, 128.48, 126.73, 126.01, 125.99, 125.96, 125.75, 125.73, 119.88, 119.77, 117.28, 116.97, 91.84, 79.55, 57.45, 53.48, 37.68, 37.54, 29.94, 29.84 (The sum of carbon signals must be 88 in theory. Observed 88); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{92}H_{26}N_2O_4S_2$ (**5**) 1286.1339; Found 1286.1367.

6: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (t, 1H, J = 7.7 Hz), 7.58 (t, 1H, J = 7.7 Hz), 7.48 (d, 1H, J = 7.7 Hz), 7.26 (d, 1H, J = 7.7 Hz), 7.20 (d, 1H, J = 7.7 Hz), 7.16 (d, 1H, J = 7.7 Hz), 7.06 (d, 1H, J = 10.3 Hz), 6.45 (d, 1H, J = 10.3 Hz), 1.20 (s, 9H), 1.15 (s, 9H), –18.20 (s, 1.20H for entrapped H_2O); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.75, 184.84, 181.01, 168.53, 168.11, 163.49, 162.67, 161.27, 156.61, 152.90, 152.69, 152.08, 152.05, 151.97, 151.26, 151.14, 150.96, 150.62, 150.27, 150.08, 150.05, 149.00, 148.97, 148.92, 148.80, 148.65, 148.57, 148.45, 148.03, 147.86, 146.91, 145.45, 145.28, 145.22, 145.05, 143.51, 143.45, 143.18, 142.94, 142.31, 142.01, 141.23, 141.08, 140.94, 140.86, 139.70, 138.62, 138.47, 137.41, 137.03, 136.69, 136.64, 135.24, 134.33, 134.27, 134.07, 133.84, 133.49, 133.18, 132.65, 132.52, 131.82, 131.54, 131.00, 130.64, 130.18, 130.01, 129.12, 126.68, 126.64, 126.47, 126.26, 126.00, 125.77, 125.71, 125.11, 124.21, 119.82, 119.60, 117.48, 117.07, 58.10, 53.42, 37.64, 37.61, 29.90, 29.85 (The sum of carbon signals must be 87 in theory. Observed 87.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{91}H_{26}N_2O_3S_2$ (**6**) 1258.1390; Found 1258.1338.

7: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, 1H, J = 7.7 Hz), 7.53 (d, 1H, J = 7.7 Hz), 7.50 (t, 1H, J = 7.7 Hz), 7.29 (d, 1H, J = 7.7 Hz), 7.24 (d, 1H, J = 7.7 Hz), 7.10 (d, 1H, J = 7.7 Hz), 6.88 (d, 1H, J = 10.3 Hz), 6.67 (s, 1H), 6.38 (d, 1H, J = 10.3 Hz), 5.56 (br s, 1H), 1.24 (s, 9H), 1.07 (s, 9H), –19.62 (s, 0.28H for encapsulated H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.43, 184.37, 184.30, 180.67, 169.00, 168.27, 163.47, 161.18, 154.94, 152.31, 152.28, 151.86, 151.75, 151.63, 151.59, 151.34, 151.31, 151.18, 150.18, 149.52, 149.47, 149.25, 148.87, 148.73, 148.70, 148.66, 148.52, 147.97, 147.87, 147.42, 145.71, 145.22, 144.85, 143.47, 143.14, 142.57, 142.43, 141.22, 140.77, 140.13, 139.61, 139.42, 139.19, 139.16, 139.10, 138.59, 137.88, 137.64, 137.14, 135.55, 134.33, 134.14, 133.95, 133.87, 133.64, 133.28, 133.04, 132.99, 132.77, 132.66, 132.57, 131.31, 131.18, 130.58, 130.37, 130.31, 128.70, 127.78, 127.49, 126.41, 126.11, 125.90, 125.74, 123.79, 123.55, 122.48, 119.92, 119.53, 119.50, 119.19, 117.60, 117.19, 59.23, 53.59, 37.70, 37.45, 29.93, 29.83 (The sum of carbon signals must be 88 in theory. Observed 88.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{92}H_{28}N_2O_4$ (**7**) 1224.2055; Found 1224.2007.

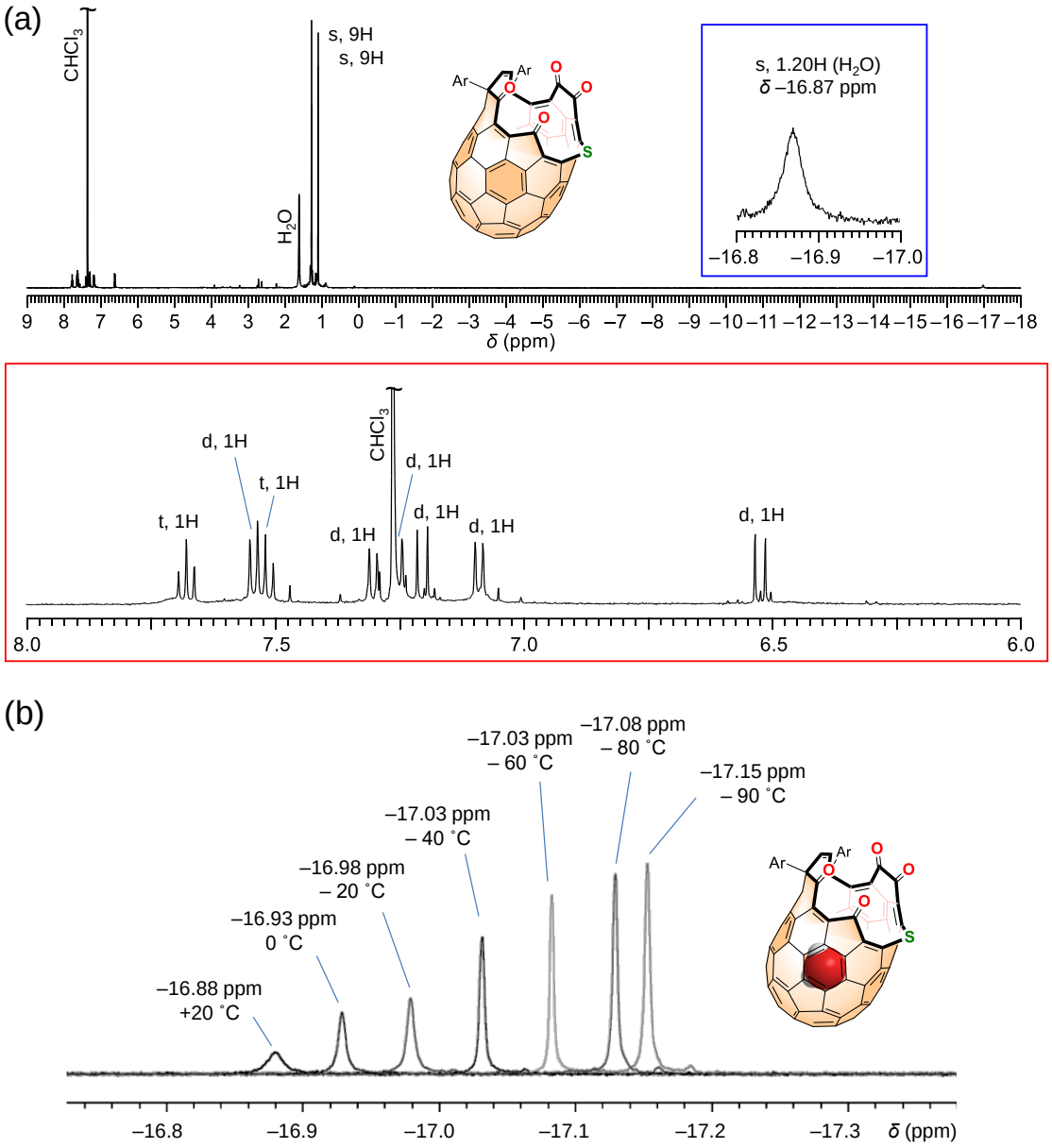


Figure S1. (a) ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **4** at room temperature. (b) ^{1}H NMR spectra (600 MHz, CS_2/CD_2Cl_2(1:1)) of H_2O@**4** at variable temperatures.

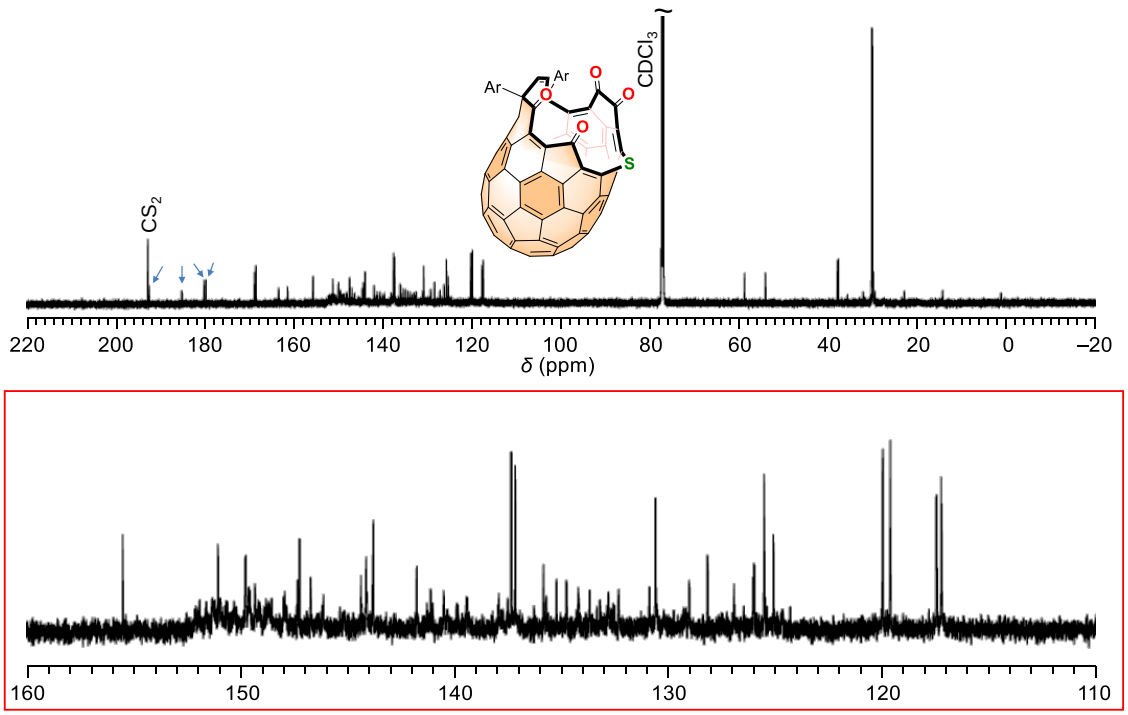


Figure S2. ^{13}C NMR spectra (151 MHz, $CDCl_3$) of **4**.

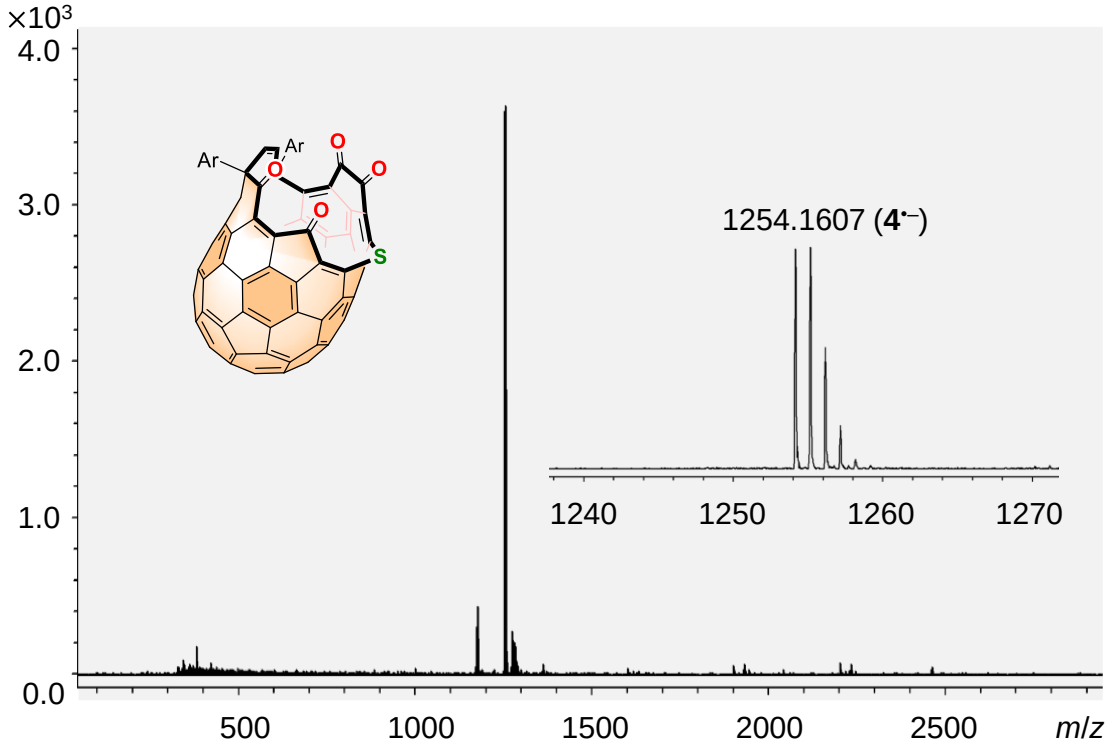


Figure S3. APCI mass spectra (negative ion mode) of **4**.

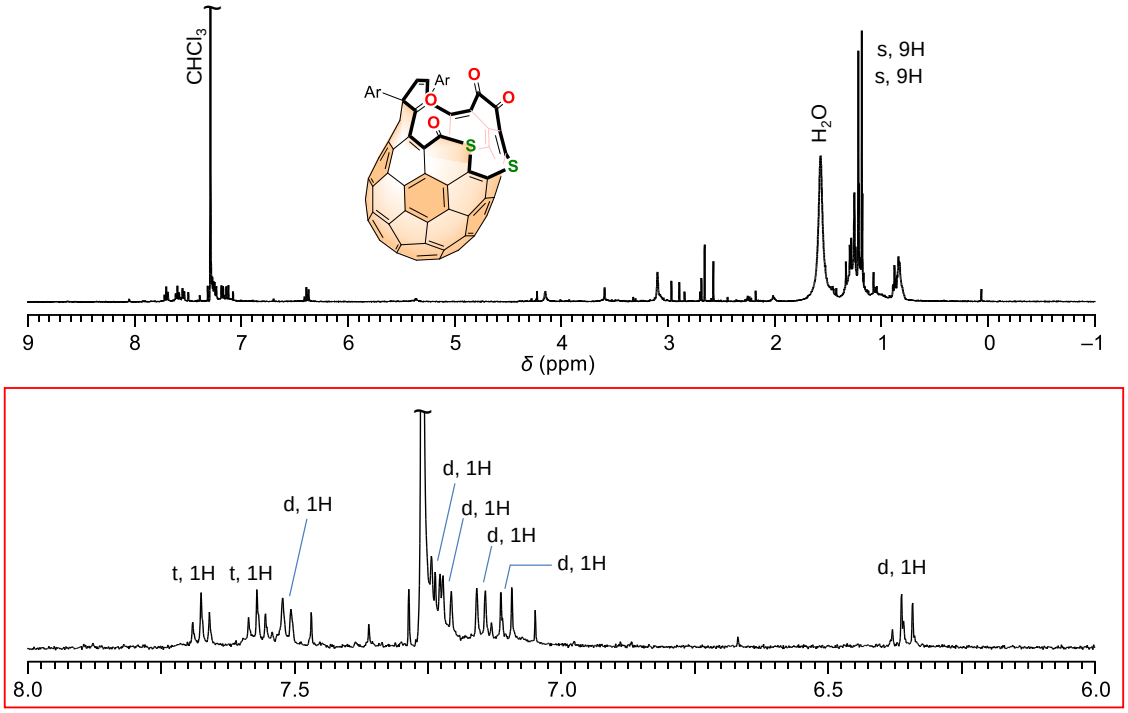


Figure S4. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **5**.

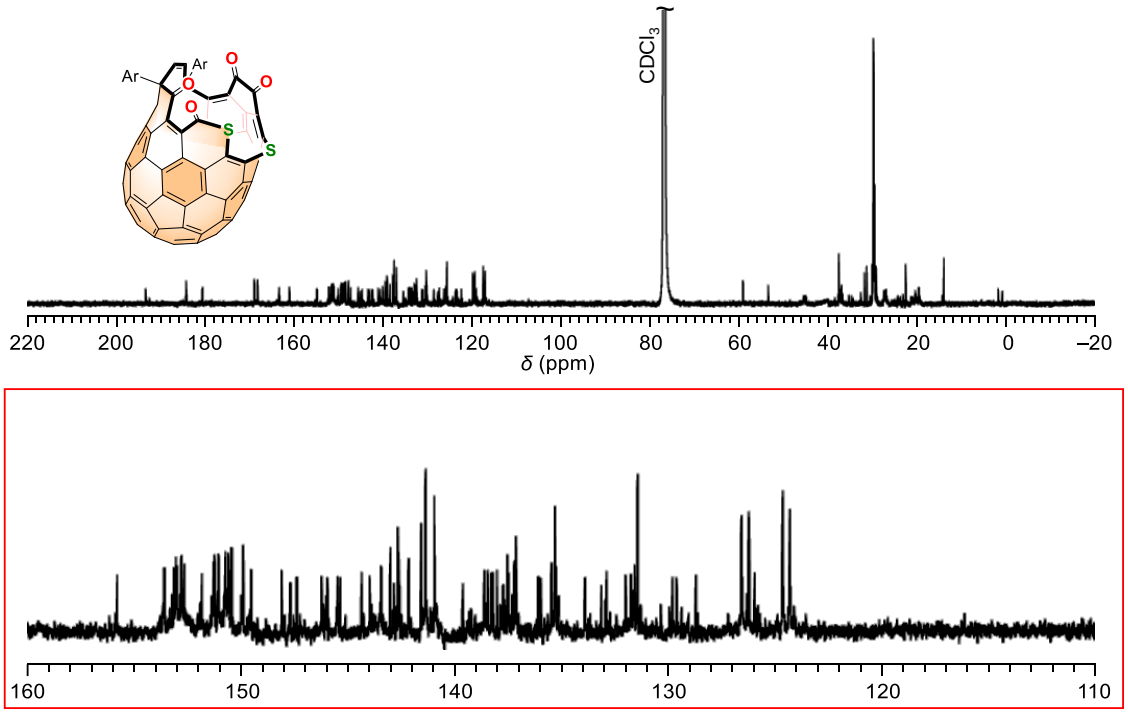


Figure S5. ^{13}C NMR spectra (201 MHz, $CDCl_3$) of **5**.

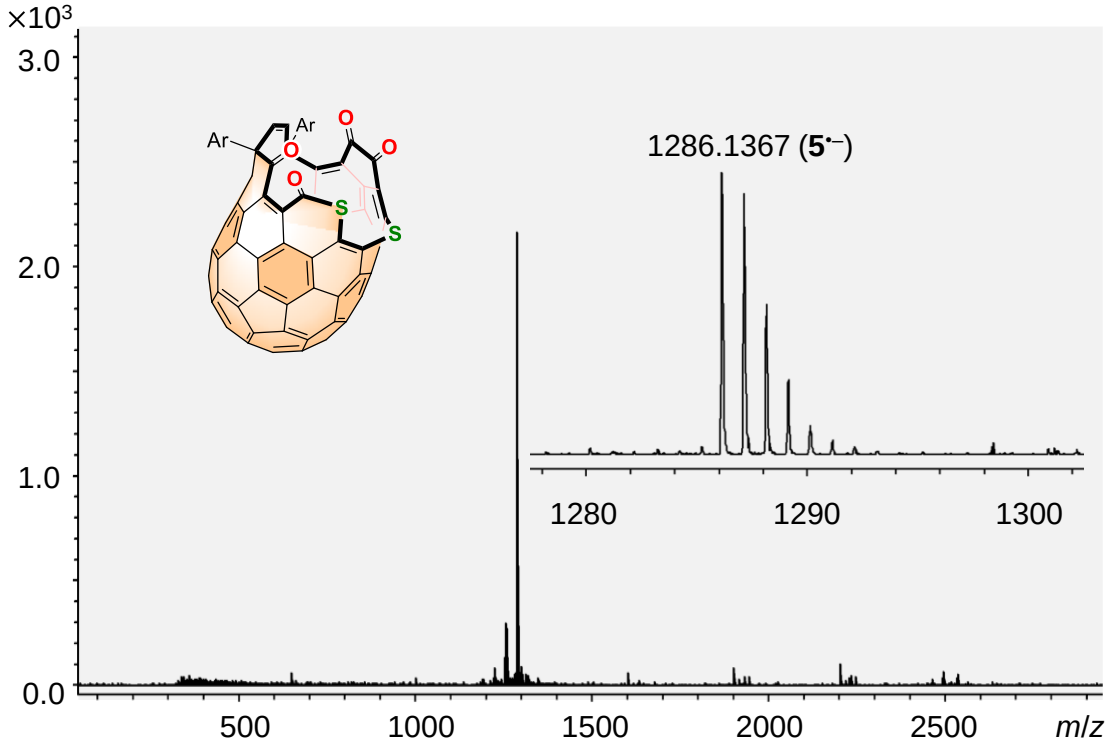


Figure S6. APCI mass spectra (negative ion mode) of **5**.

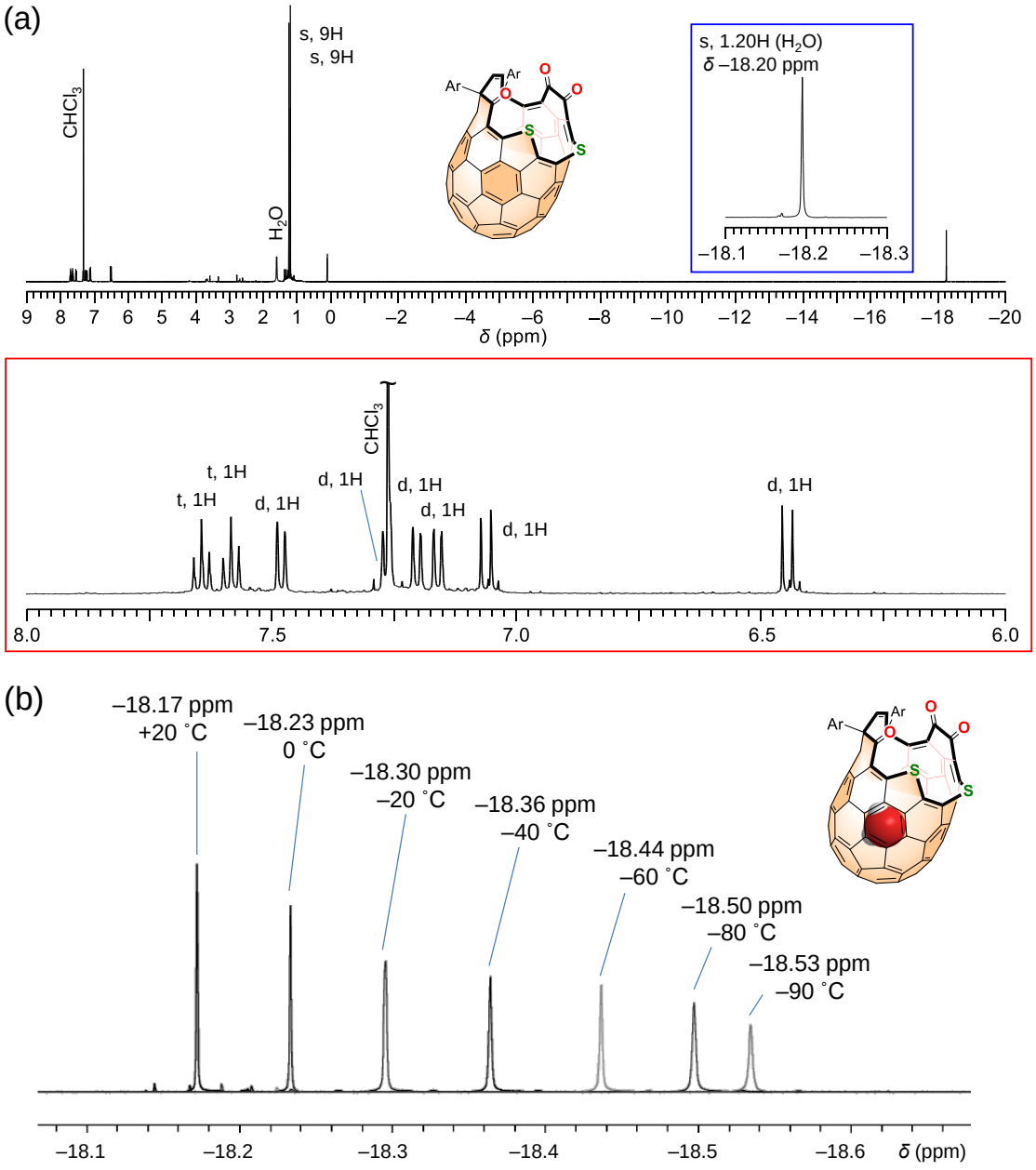


Figure S7. (a) ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **6** at room temperature. (b) ^{1}H NMR spectra (600 MHz, CS_2/CD_2Cl_2(1:1)) of H_2O@**6** at variable temperatures.

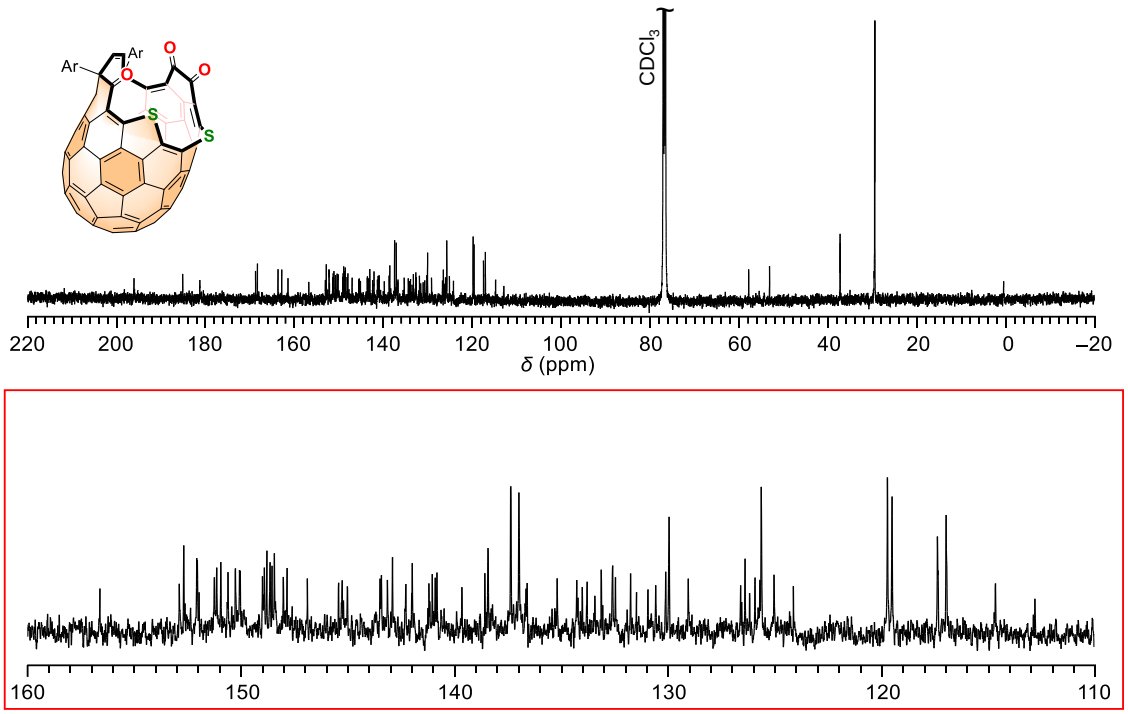


Figure S8. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of **6**.

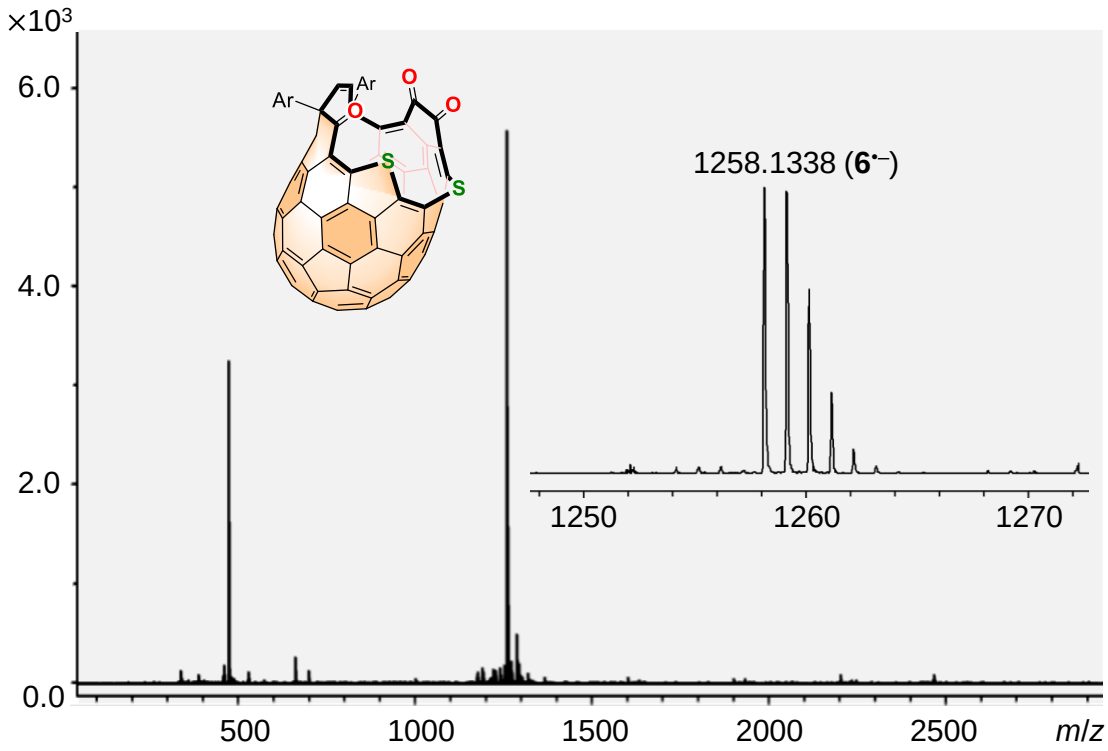


Figure S9. APCI mass spectra (negative ion mode) of **6**.

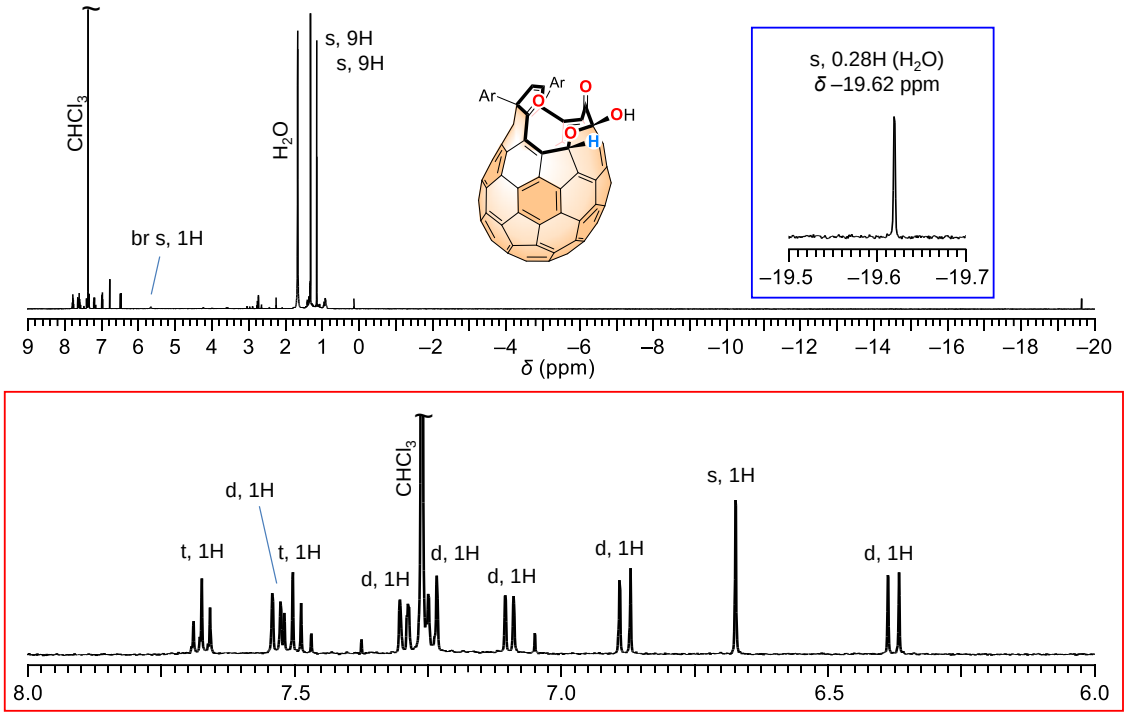


Figure S10. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **7**.

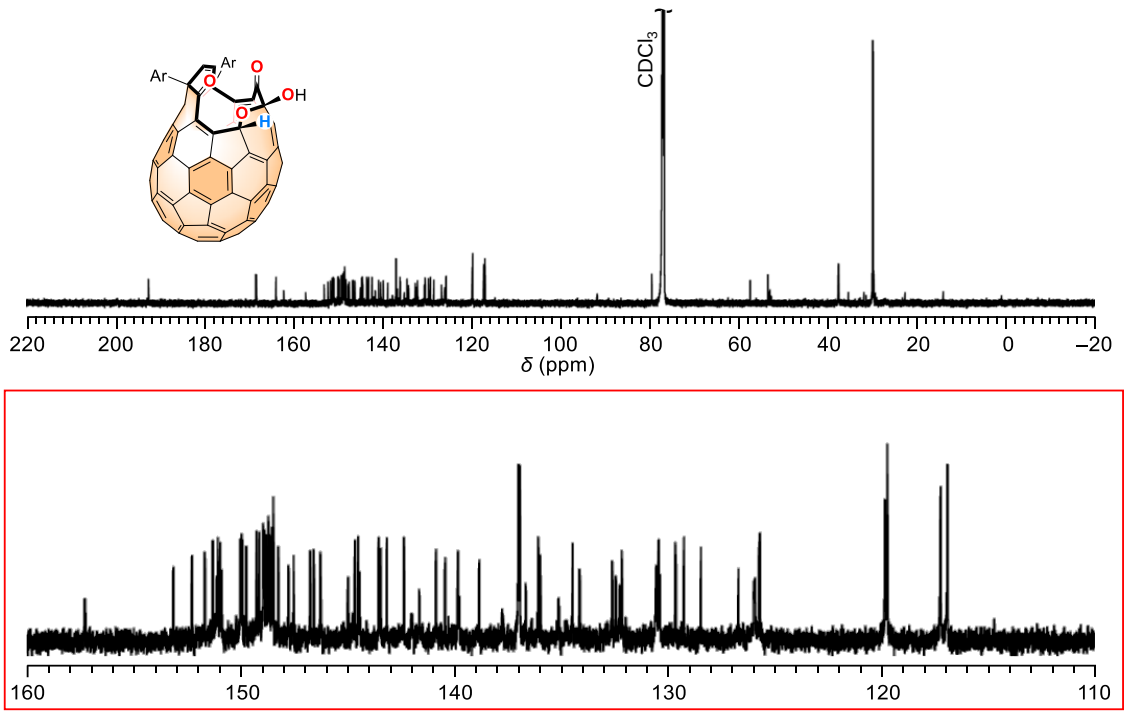


Figure S11. ^{13}C NMR spectra (151 MHz, $CDCl_3$) of **7**.

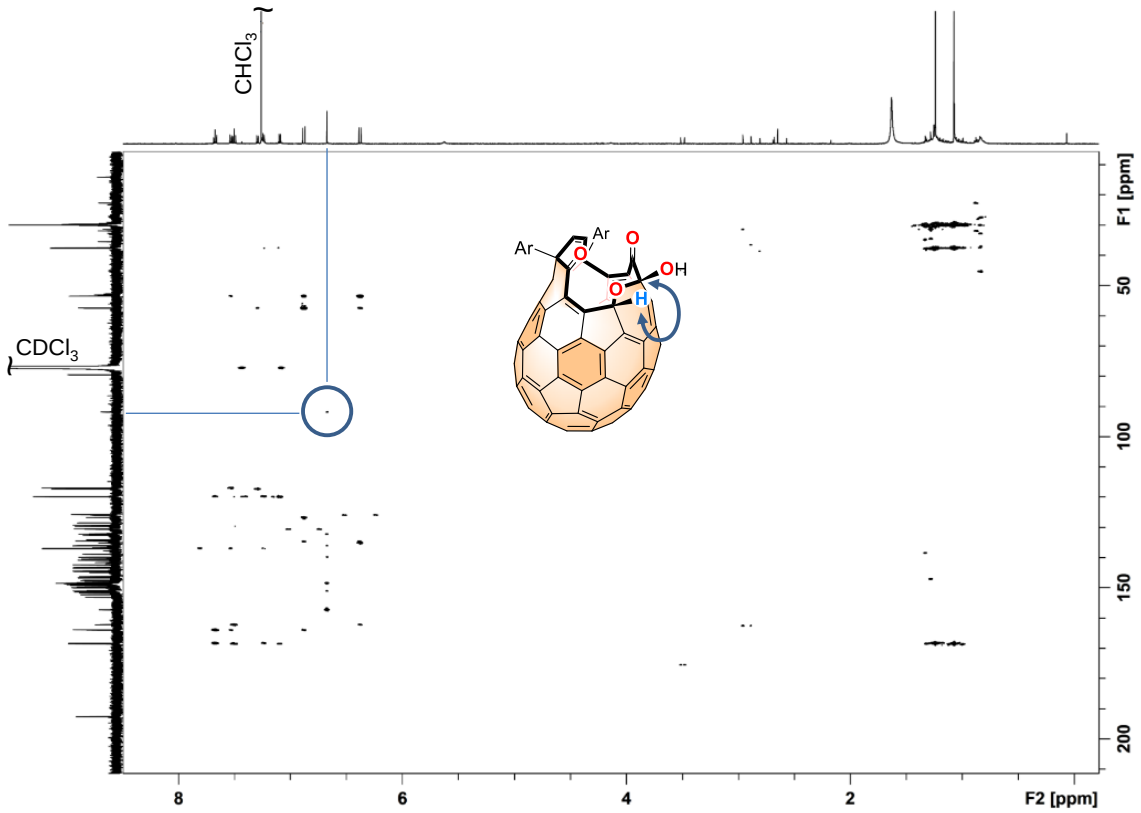


Figure S12. HMBC spectrum (600 MHz, $CDCl_3$) of **7**.

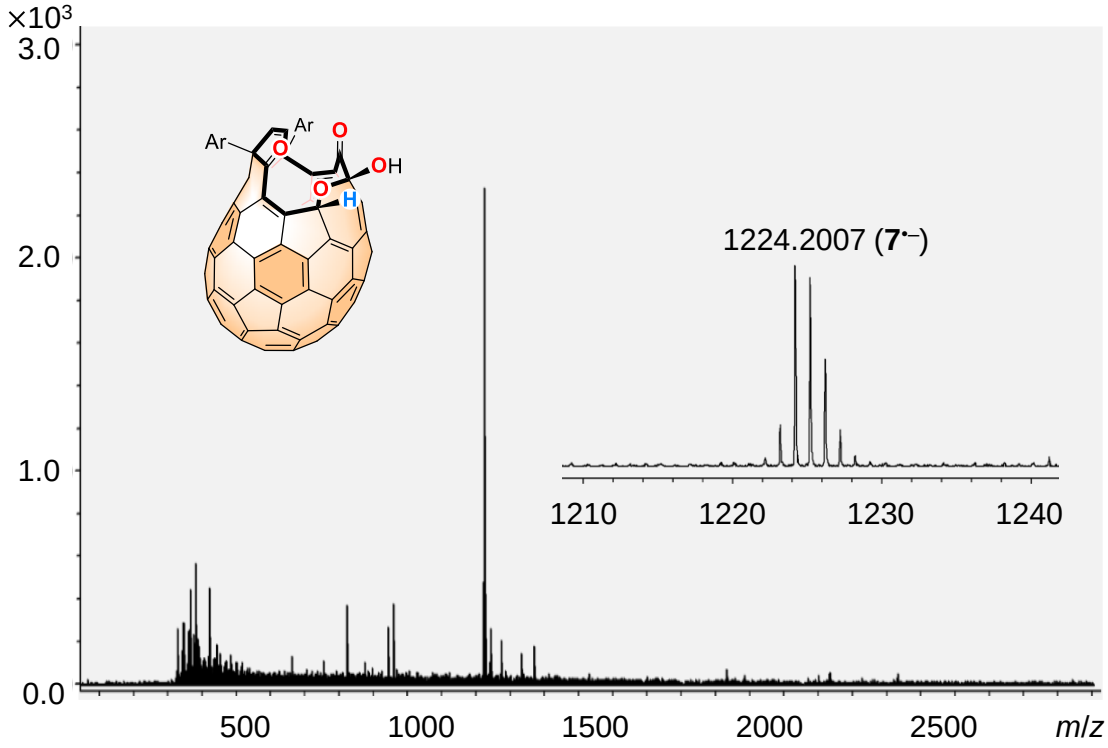
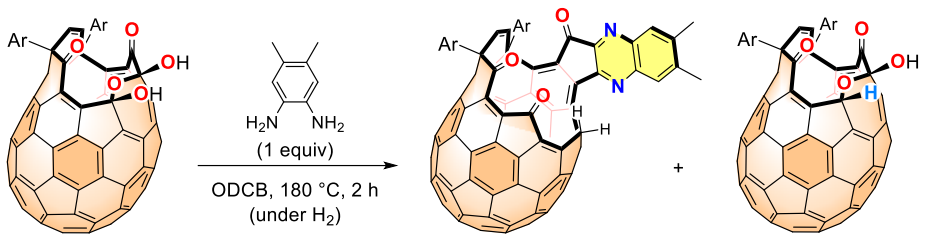


Figure S13. APCI mass spectra (negative ion mode) of **7**.

3.4. Synthesis of 8



3 **8**, 74% **7**, trace

Powdery **3** (10.0 mg, 8.06 μmol) and 4,5-dimethyl-1,2-phenylenediamine (1.15 mg, 8.44 μmol, 1.05 equiv) were placed into a Schlenk tube. ODCB (0.500 mL) was added and degassed through three vacuum–H_2 cycles. The resulting solution was heated at 180 °C for 2 h (aluminum block heater). The crude mixture was purified by column chromatography using silica gel (toluene to toluene/ethyl acetate (50:1)) to give **7** (trace) and **8** (7.94 mg, 5.92 μmol, 73%) as brown powders.

8: ^{1}H NMR (500 MHz, acetone-d_6/CS_2 (1:5)) δ 8.09 (s, 1H), 8.06 (s, 1H), 7.71 (t, 1H, J = 7.9 Hz), 7.65 (d, 1H, J = 7.9 Hz), 7.61 (d, 1H, J = 10.7 Hz), 7.55 (d, 1H, J = 7.9 Hz), 7.37 (d, 1H, J = 7.9 Hz), 7.26 (d, 1H, J = 7.9 Hz), 7.12 (d, 1H, J = 7.9 Hz), 6.38 (d, 1H, J = 10.7 Hz), 4.52 (d, 1H, J = 20.2 Hz), 2.67 (s, 6H), 2.53 (d, 1H, J = 20.2 Hz), 1.20 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (126 MHz, acetone-d_6/CS_2 (1:5)) δ 190.77, 188.34, 180.70, 168.41, 168.30, 163.40, 162.80, 155.64, 155.03, 154.00, 152.92, 152.73, 152.59, 151.89, 151.67, 151.56, 151.53, 151.38, 151.35, 151.09, 150.67, 150.64, 150.49, 149.80, 149.62, 149.51, 149.43, 149.33, 149.29, 149.07, 148.90, 148.31, 147.78, 147.69, 147.55, 147.26, 146.54, 146.39, 145.18, 144.22, 143.40, 143.32, 142.80, 142.74, 142.06, 141.87, 141.38, 141.33, 140.53, 139.45, 138.68, 138.50, 137.84, 137.78, 137.68, 137.22, 137.10, 135.78, 135.59, 135.43, 135.20, 134.81, 134.29, 134.03, 133.37, 133.28, 132.23, 131.87, 131.63, 131.27, 130.15, 130.10, 129.88, 128.03, 126.66, 123.86, 120.94, 120.41, 117.94, 117.92, 57.35, 52.68, 40.95, 37.91, 37.83, 30.54, 30.40, 21.37, 20.99 (The sum of carbon signals must be 96 in theory. Observed 89. The 7 sp^2 carbon signals are overlapped.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{100}H_{36}N_4O_3$ (**8**) 1340.2793; Found 1340.2812.

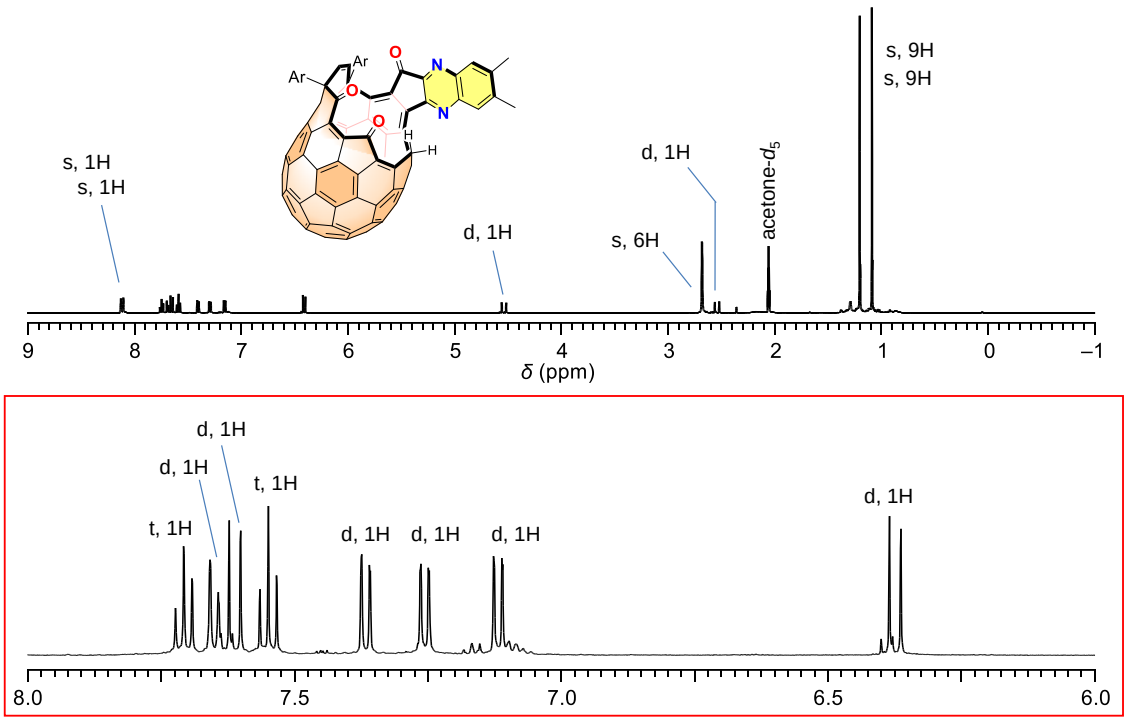


Figure S14. ^{1}H NMR spectra (500 MHz, acetone-d_6/CS_2 (1:5)) of **8**.

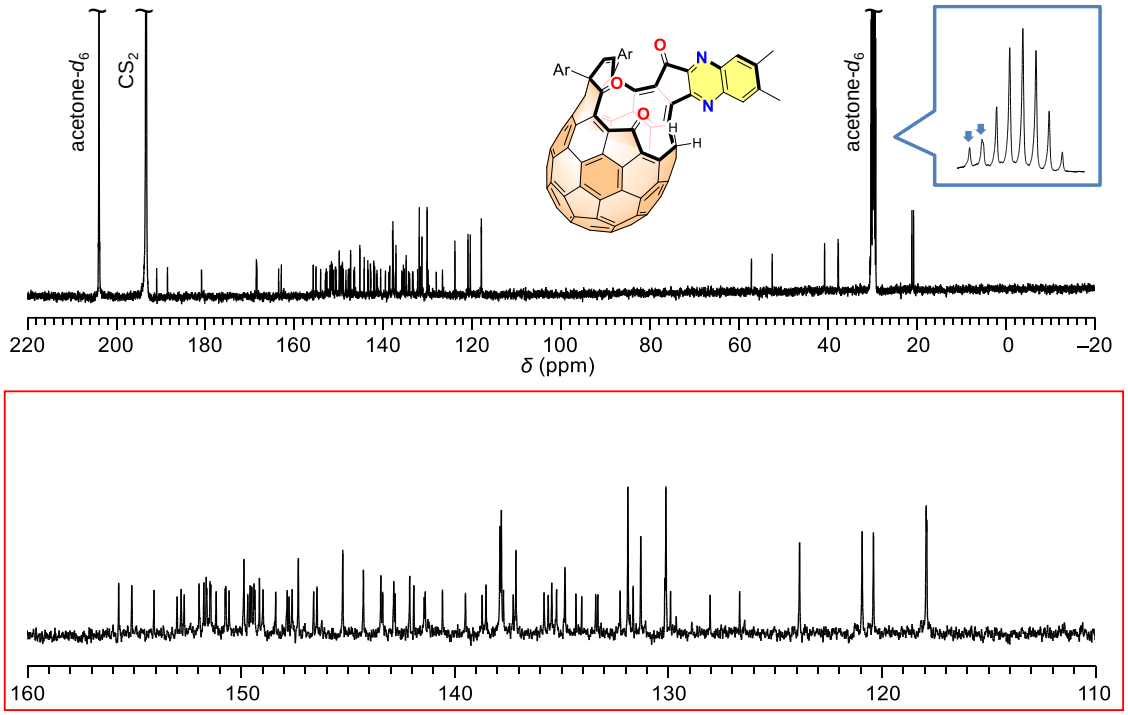


Figure S15. ^{13}C NMR spectra (126 MHz, acetone-d_6/CS_2 (1:5)) of **8**.

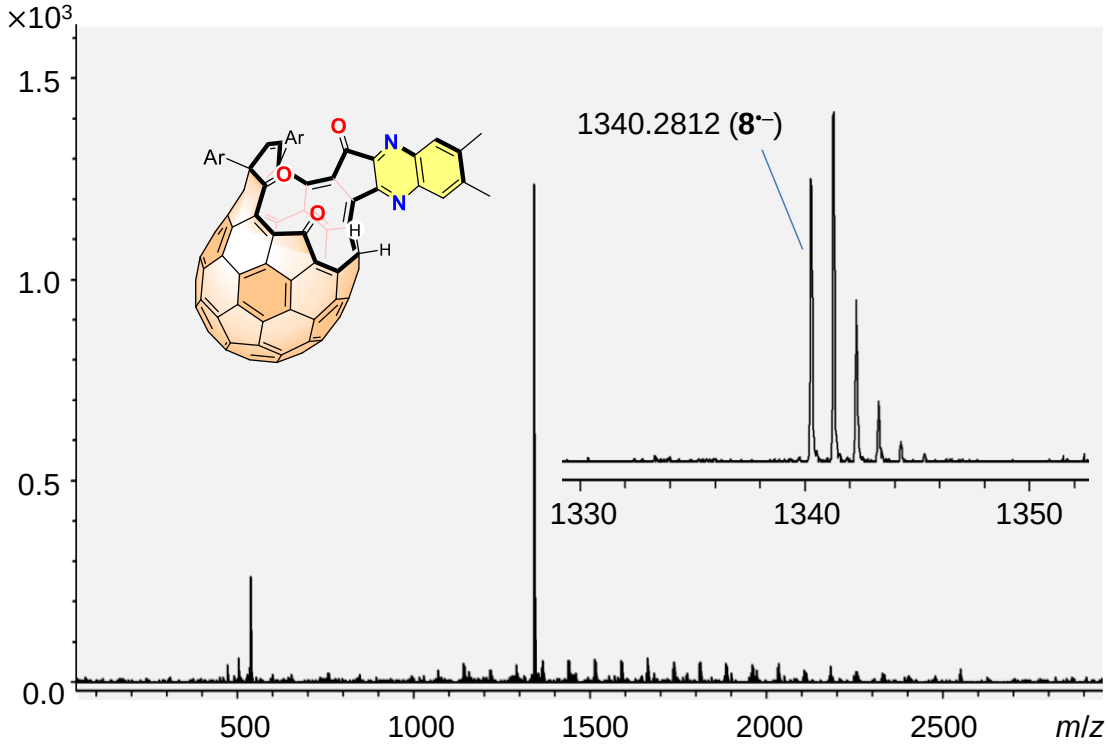
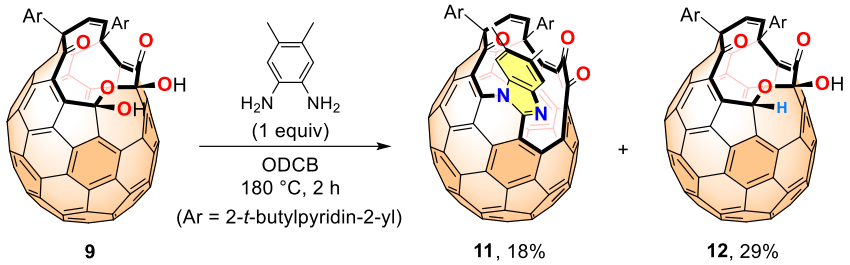


Figure S16. APCI mass spectra (negative ion mode) of **8**.

3.5. Synthesis of 11 and 12



9 **11**, 18% **12**, 29%

Powdery **9** (10.0 mg, 8.06 μmol) and 4,5-dimethyl-1,2-phenylenediamine (1.10 mg, 8.08 μmol, 1.00 equiv) were placed into a Schlenk tube and degassed through three vacuum–Ar cycles. ODCB (0.500 mL) was added. The resulting solution was heated at 180 °C for 2 h (aluminum block heater). The crude mixture was purified by column chromatography using silica gel (toluene/ethyl acetate (200:1) to (3:1)) to give **12** (2.84 mg, 2.32 μmol, 29%) and **11** (1.98 mg, 1.48 μmol, 18%) as brown powders.

11: ^{1}H NMR (500 MHz, acetone-d_6/CS_2 (1:5)) δ 7.91 (t, 1H, J = 7.7 Hz), 7.73 (t, 1H, J = 7.7 Hz), 7.63 (s, 1H), 7.52 (d, 1H, J = 7.7 Hz), 7.51 (d, 1H, J = 7.7 Hz), 7.48 (d, 1H, J = 7.7 Hz), 7.34 (s, 1H), 7.26 (d, 1H, J = 7.7 Hz), 6.63 (d, 1H, J = 10.3 Hz), 6.38 (d, 1H, J = 10.3 Hz), 2.51 (s, 3H), 2.50 (s, 3H), 1.60 (s, 9H), 1.21 (s, 9H), –17.22 (s, 0.26H); ^{13}C NMR (201 MHz, acetone-d_6/CS_2 (1:5)) δ 189.54, 180.45, 175.00, 168.90, 168.64, 164.38, 164.00, 156.09, 154.14, 153.15, 153.14, 152.24, 150.70, 150.45, 150.22, 150.00, 149.61, 149.57, 149.06, 148.69, 148.56, 147.99, 147.55, 147.45, 147.19, 147.07, 146.94, 146.85, 146.81, 146.42, 146.17, 146.01, 145.81, 145.80, 145.41, 145.39, 145.14, 144.29, 143.74, 143.12, 142.83, 142.45, 142.37, 141.03, 140.80, 140.60, 140.18, 140.13, 140.05, 139.63, 139.52, 139.34, 138.91, 138.51, 138.34, 137.82, 136.99, 136.79, 136.71, 136.02, 135.94, 135.51, 134.81, 134.51, 133.39, 133.13, 130.38, 130.32, 129.57, 128.63, 128.44, 128.15, 127.82, 127.31, 126.78, 125.03, 124.23, 122.63, 121.38, 121.31, 120.75, 118.95, 118.31, 117.80, 116.78, 58.60, 54.58, 38.40, 37.96, 31.05, 30.48, 21.57, 21.11 (The sum of carbon signals must be 96 in theory. Observed 93. The 3 sp^2 carbon signals are overlapped.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{100}H_{34}N_4O_3$ (**11**) 1338.2636; Found 1338.2652.

12: ^{1}H NMR (500 MHz, acetone-d_6/CS_2 (1:5)) δ 7.80 (t, 1H, J = 7.9 Hz), 7.72 (t, 1H, J = 7.9 Hz), 7.59 (dd, 1H, J = 7.9, 0.9 Hz), 7.56 (dd, 1H, J = 7.9, 0.9 Hz), 7.37 (dd, 1H, J = 7.9, 0.9 Hz), 7.28 (dd, 1H, J = 7.9, 0.9 Hz), 7.16 (s, 1H), 6.82 (d, 1H, J = 9.9 Hz), 6.59 (s, 1H), 6.50 (d, 1H, J = 9.9 Hz), 1.44 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (151 MHz, acetone-

d_6/CS_2 (1:5)) δ 195.10, 191.70, 169.33, 168.61, 164.10, 163.57, 156.44, 153.98, 152.16, 152.14, 152.12, 151.11, 151.01, 150.40, 150.17, 149.92, 149.66, 149.29, 149.14, 149.06, 148.93, 148.88, 148.60, 148.45, 148.23, 148.13, 147.87, 147.56, 147.36, 146.82, 146.77, 146.60, 146.54, 146.42, 146.32, 145.76, 145.26, 145.15, 144.80, 144.53, 144.49, 144.24, 143.50, 142.60, 142.51, 142.19, 142.06, 141.52, 141.34, 141.27, 140.16, 139.96, 139.89, 138.01, 137.87, 137.63, 137.40, 137.12, 136.72, 136.61, 136.42, 135.76, 134.53, 132.16, 131.68, 131.38, 131.25, 130.72, 130.07, 129.87, 129.74, 127.48, 127.14, 125.31, 124.39, 120.74, 120.43, 117.97, 117.73, 94.99, 80.26, 59.11, 54.54, 38.33, 37.98, 30.79, 30.53 (The sum of carbon signals must be 88 in theory. Observed 87. One sp^2 carbon signal is overlapped.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{92}H_{28}N_2O_4$ (**12**) 1224.2055; Found 1224.2040.

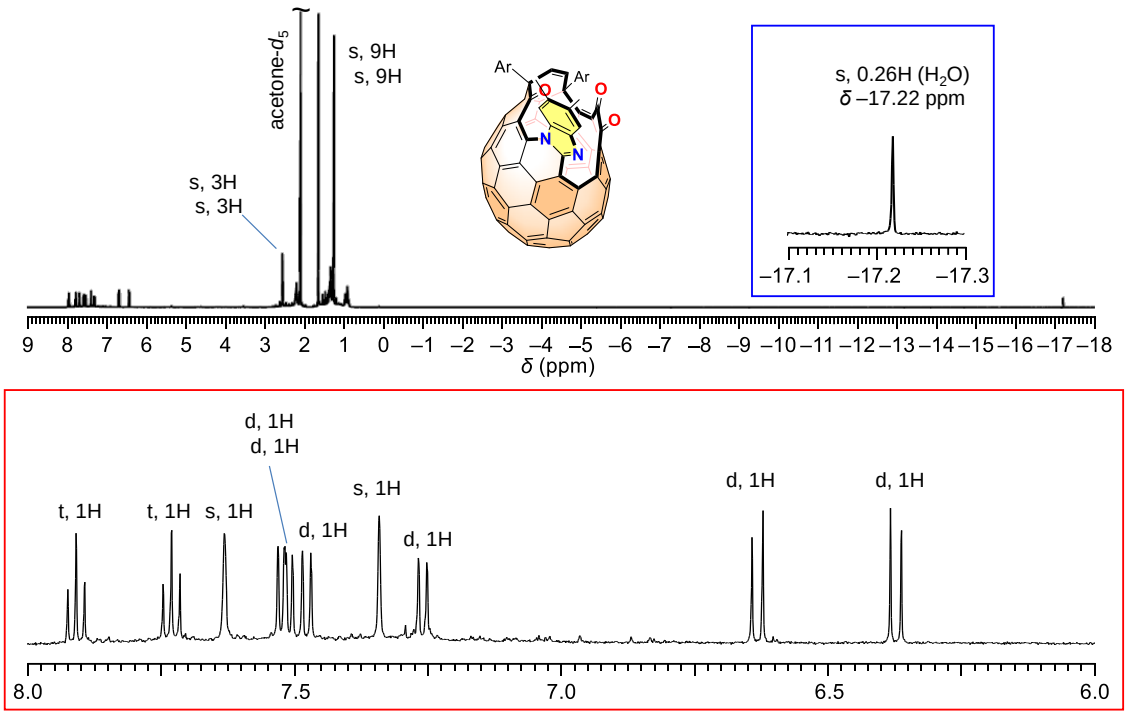


Figure S17. ^{1}H NMR spectra (500 MHz, acetone-d_6/CS_2 (1:5)) of **11**.

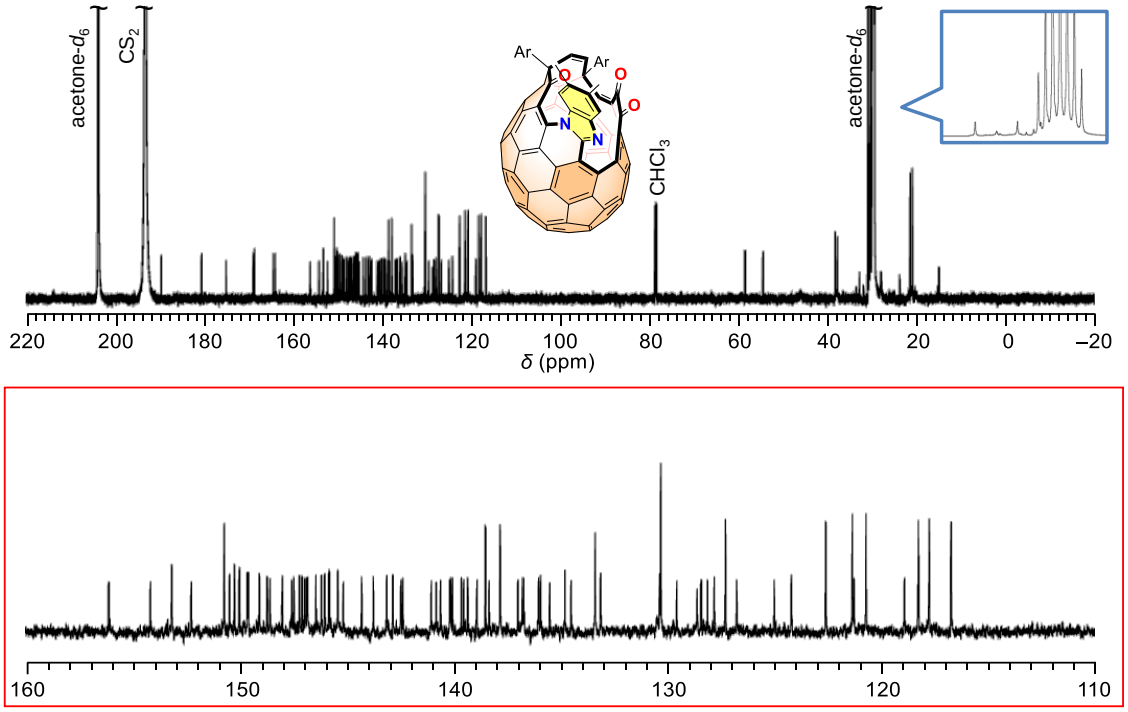


Figure S18. ^{13}C NMR spectra (201 MHz, acetone-d_6/CS_2 (1:5)) of **11**.

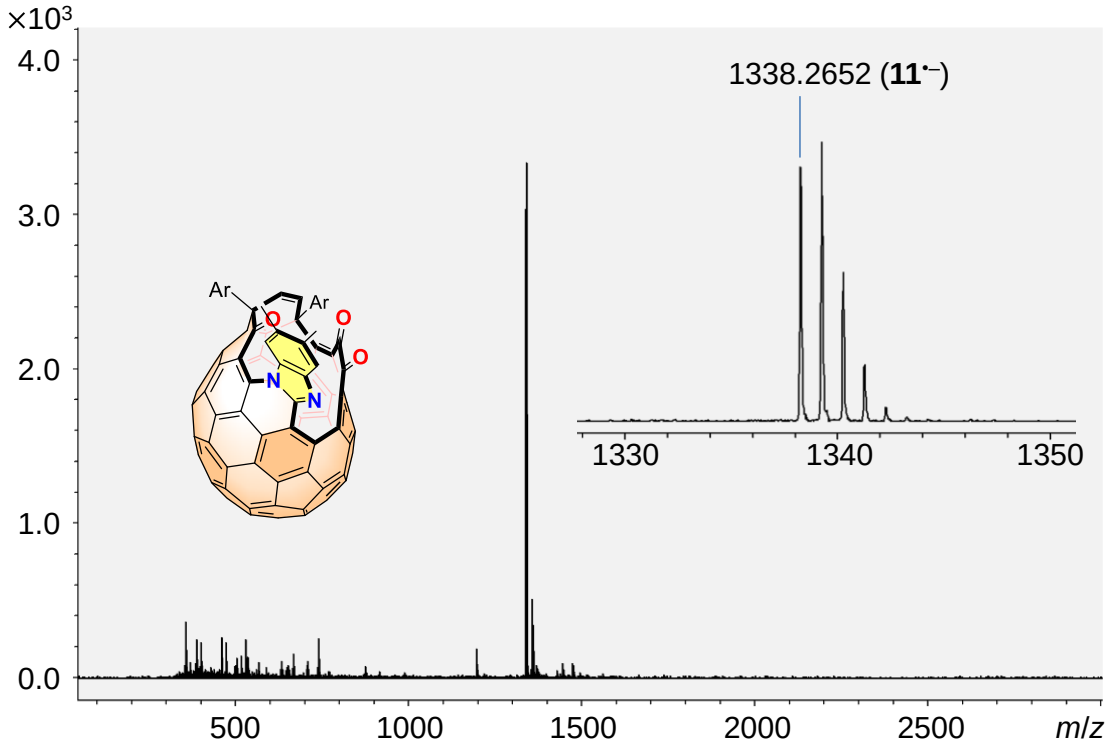


Figure S19. APCI mass spectra (negative ion mode) of **11**.

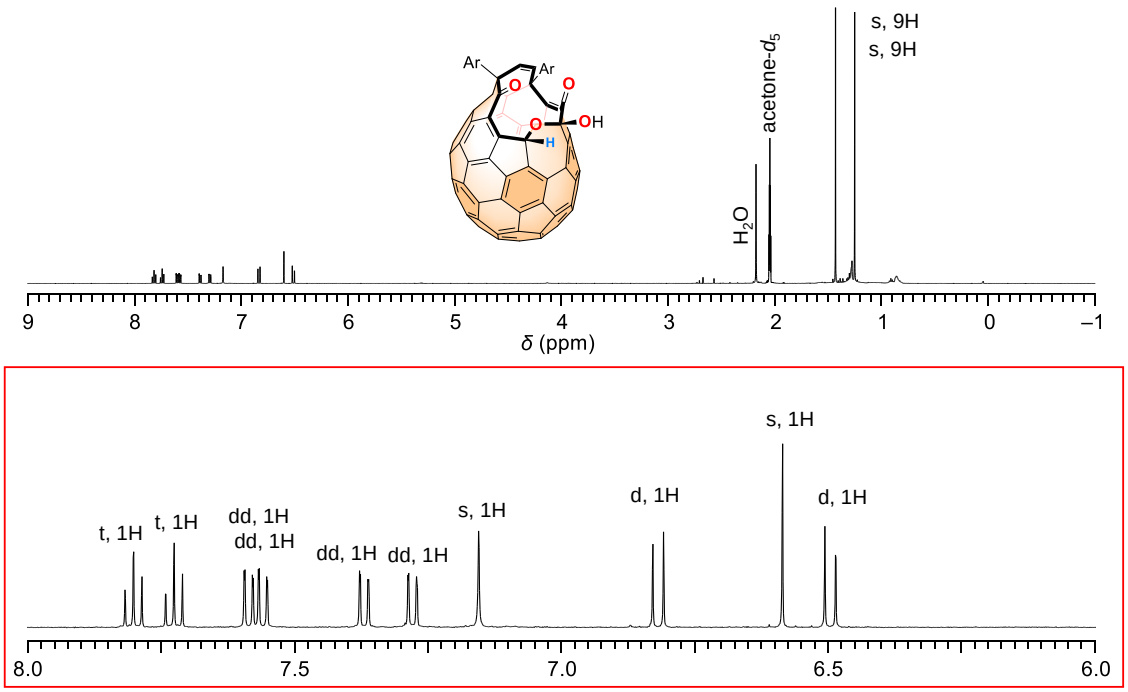


Figure S20. ^{1}H NMR spectra (500 MHz, acetone-d_6/CS_2 (1:5)) of **12**.

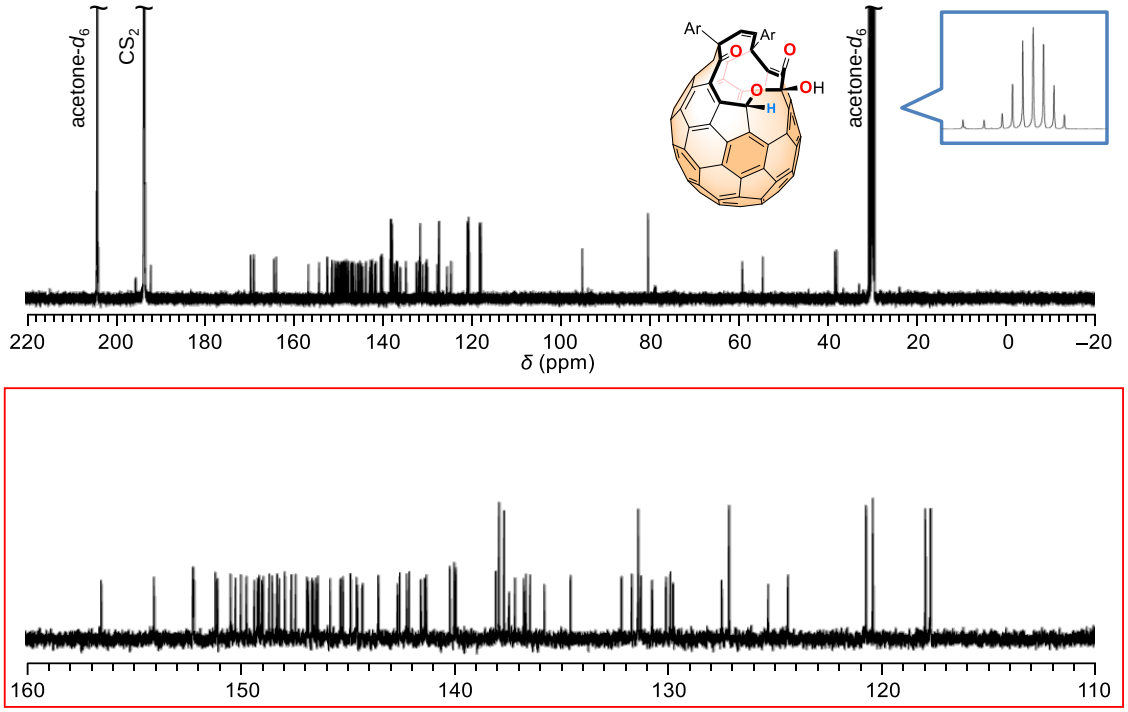


Figure S21. ^{13}C NMR spectra (151 MHz, acetone-d_6/CS_2 (1:5)) of **12**.

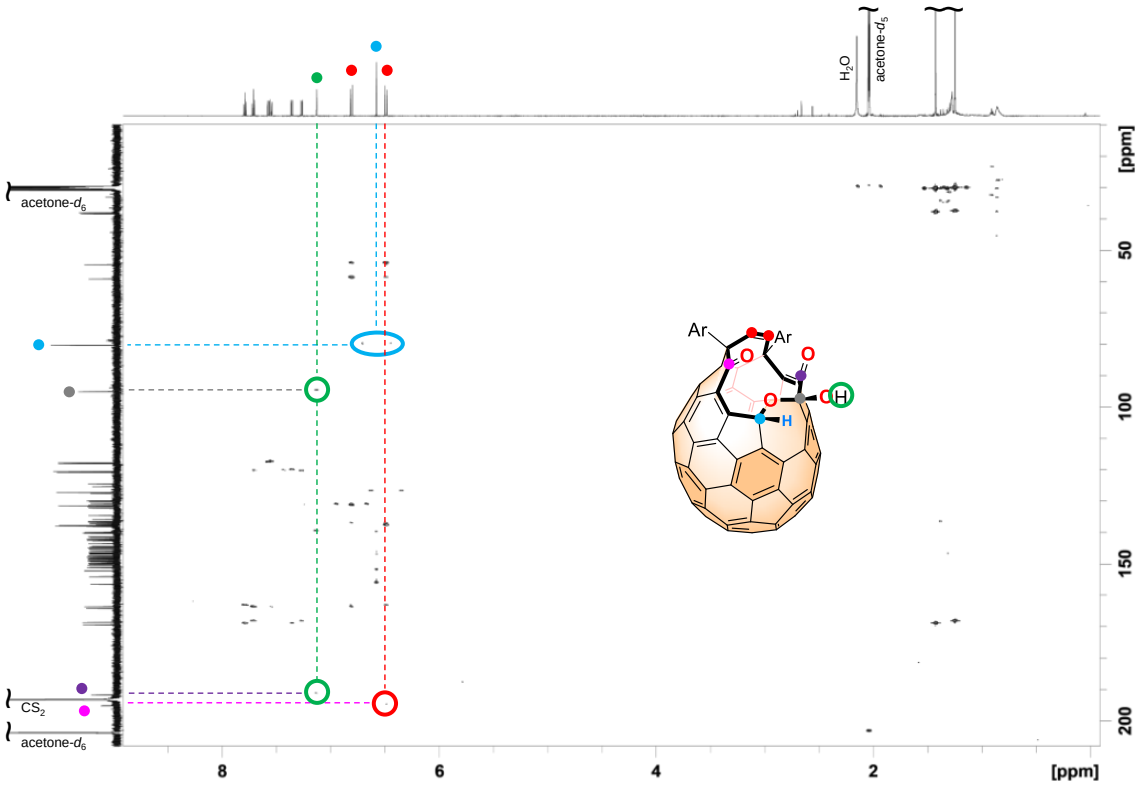


Figure S22. HMBC spectrum (600 MHz, acetone-d_6/CS_2 (1:5)) of **12**.

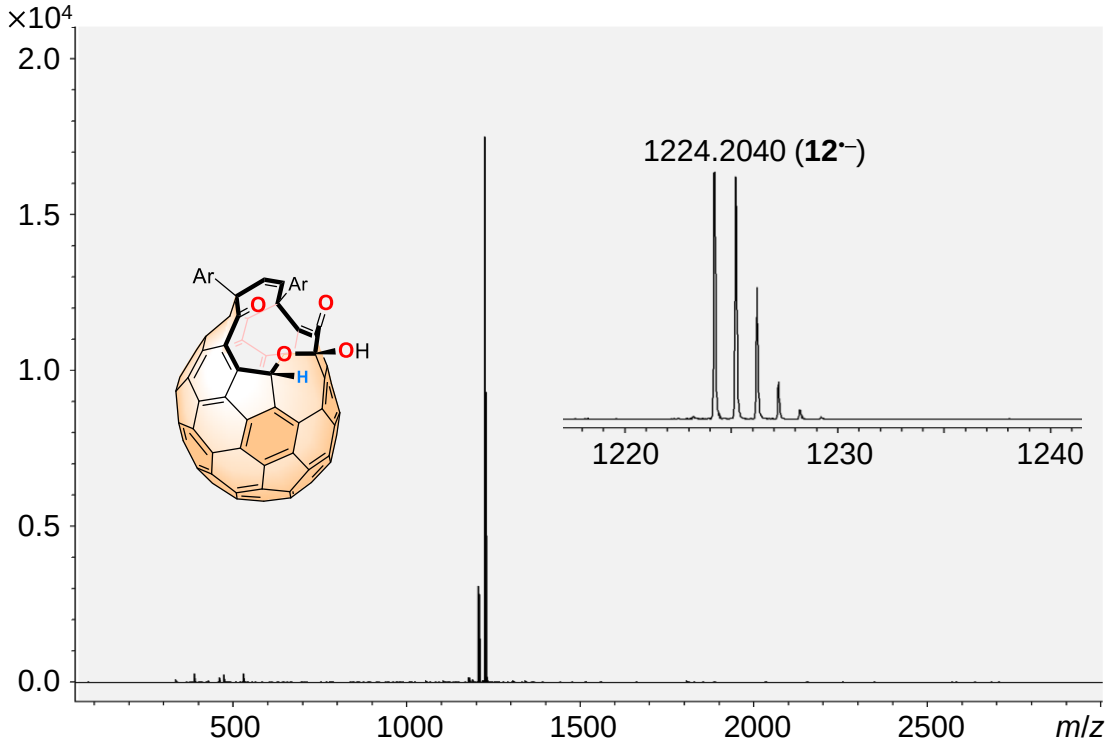


Figure S23. APCI mass spectra (negative ion mode) of **12**.

4. Single Crystal X-Ray Structure of 3•$(CS_2)_{2.5}$

Single crystals of **3** were obtained from a CS_2 solution by slow evaporation at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 12557 reflections were measured at the maximum 2θ angle of 49.5°, of which 9554 were independent reflections (R_{int} = 0.0505). The structure was solved by direct methods (SHELXT-97[3]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[3]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. Part of carbon atoms (C12, C62, and C74) was refined using ISOR instructions. The crystal data are as follows: $C_{94.5}H_{28}N_2O_5S_5$; FW = 1431.49, crystal size 0.17 × 0.08 × 0.04 mm^3, triclinic, *P*-1, a = 13.25(2) Å, b = 13.47(2) Å, c = 17.15(3) Å, α = 82.98(5)°, β = 80.57(6)°, γ = 80.95(4)°, V = 2969(9) Å^3, Z = 2, D_c = 1.601 g cm^{-3}. The refinement converged to R_1 = 0.0949, wR_2 = 0.2425 ($I > 2\sigma(I)$), GOF = 1.078. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2249119).

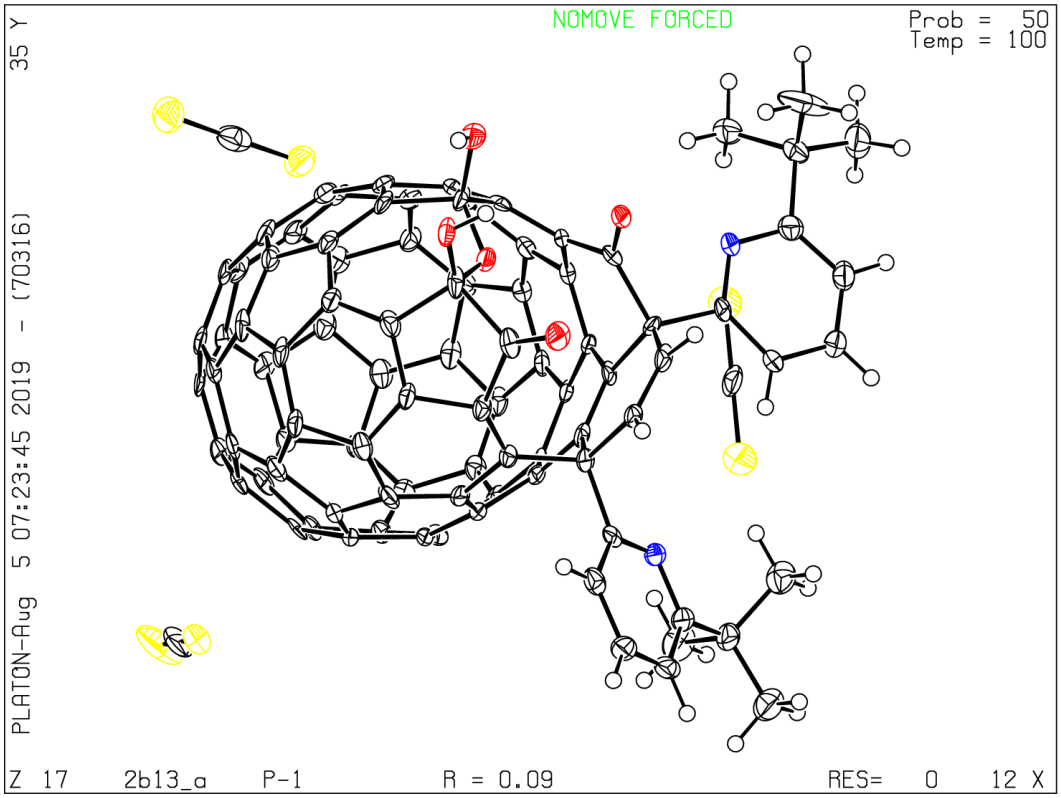


Figure S24. Single crystal X-ray structure of **3**•$(CS_2)_{2.5}$. Thermal ellipsoids are shown at 50% probability.

5. DFT Calculations

5.1. Orientation of H_2O inside 4'

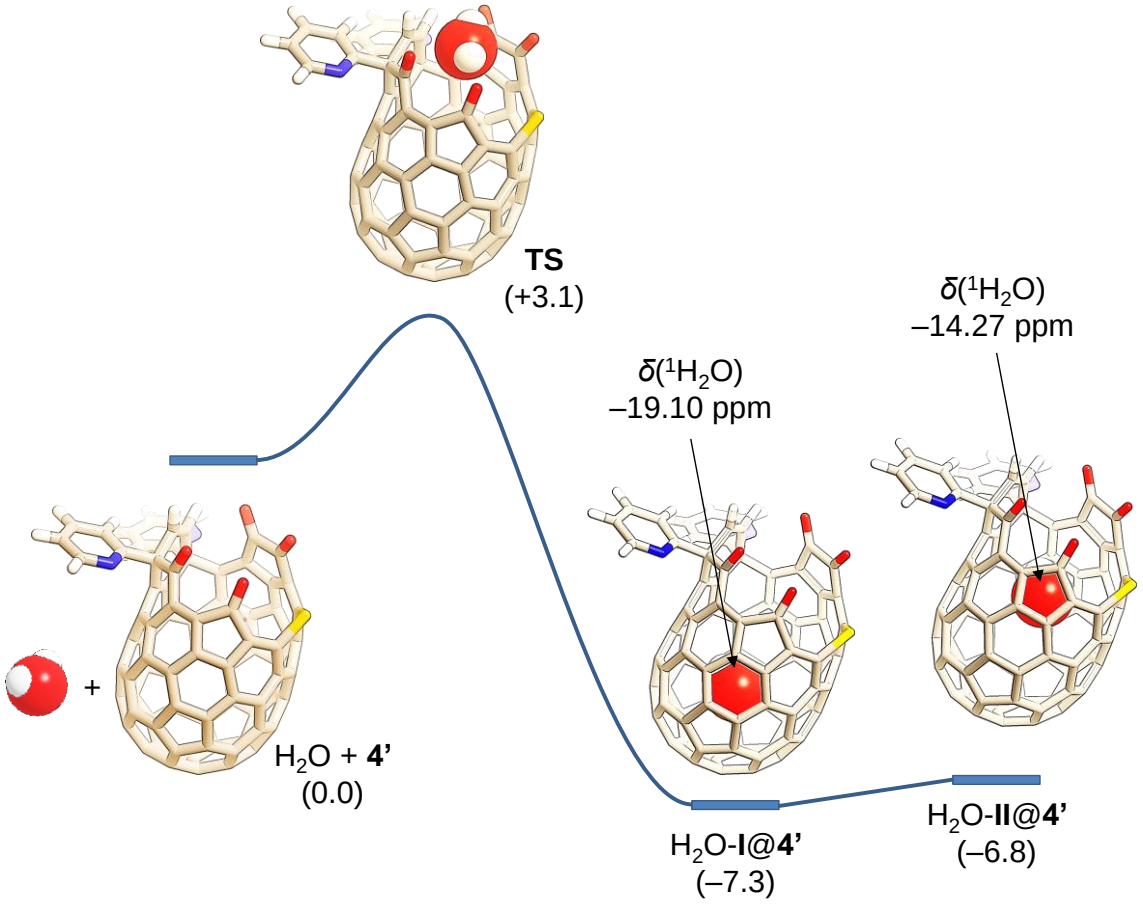


Figure S25. H_2O-insertion into **4'** and two water orientation for H_2O@**4'** with simulated ^1H NMR chemical shifts of the encapsulated H_2O molecules (Ar = 2-pyridyl, GIAO-B3LYP-D3/6-311G(d,p)//B3LYP-D3/6-31G(d)). The ΔG values were shown with units in kcal/mol at 298 K.

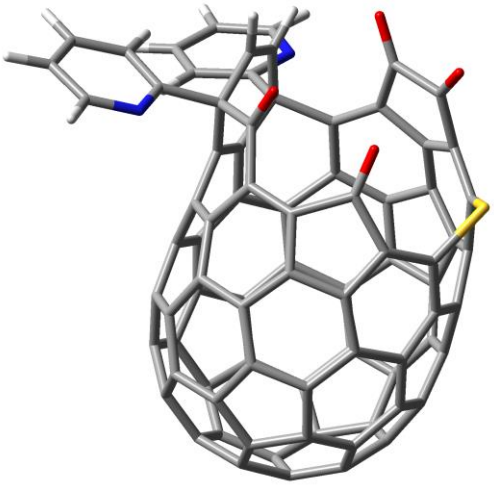
Table S1. Optimized structure of H_2O (B3LYP-D3/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.000000	0.119800	0.000000
2	1	0	0.761330	-0.479202	-0.000000
3	1	0	-0.761330	-0.479202	-0.000000

The total electronic energy was calculated to be –76.4089616 Hartree.

Table S2. Optimized structure of **4'** (B3LYP-D3/6-31G(d))



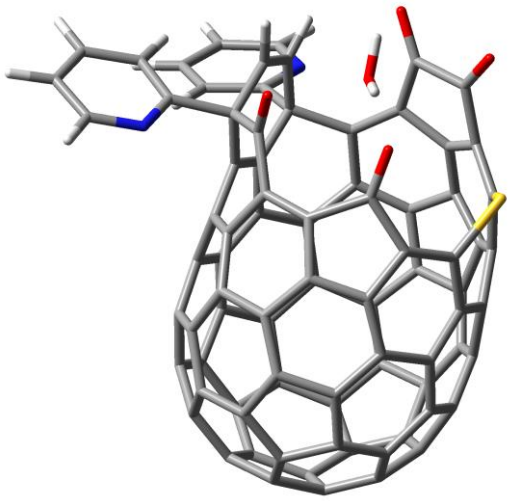
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.347873	1.015761	-3.317871
2	8	0	1.340081	2.988624	-3.376959
3	8	0	2.670785	5.082766	-1.303317
4	8	0	4.581299	3.351418	0.044857
5	6	0	3.537947	-0.623282	-1.549665
6	6	0	4.547655	0.278372	-0.893678
7	6	0	4.554649	0.567893	0.405078
8	6	0	3.506789	0.113842	1.391010
9	6	0	2.580020	1.262190	1.837484
10	6	0	2.593873	2.553352	1.303749
11	6	0	3.399642	3.337336	0.291550
12	6	0	2.381304	4.344655	-0.393481
13	6	0	1.102963	4.179434	0.345083
14	6	0	-0.232301	4.334296	-0.019836
15	6	0	-1.513446	3.395296	-2.043868
16	6	0	-1.045430	2.515070	-2.995704
17	6	0	0.417722	2.215133	-3.340895
18	6	0	0.429622	0.674945	-3.425865
19	6	0	1.356188	-0.215100	-2.911201
20	6	0	2.782342	0.159800	-2.673541
21	6	0	2.534544	-1.177903	-0.565479
22	6	0	2.549181	-0.898247	0.773798
23	6	0	1.483500	-1.397361	1.622226
24	6	0	0.980813	-0.563250	2.669417
25	6	0	1.444804	0.837005	2.657525
26	6	0	0.504935	1.792278	3.056962
27	6	0	0.442504	3.039037	2.366764
28	6	0	1.417111	3.362627	1.468949
29	6	0	-0.928121	3.317104	2.065883
30	6	0	-1.298992	3.768482	0.789409
31	6	0	-2.560807	3.232003	0.233147
32	6	0	-2.629213	2.987824	-1.187645
33	6	0	-3.532729	1.987525	-1.704505
34	6	0	-3.108308	1.144868	-2.815579
35	6	0	-1.800515	1.345509	-3.287987
36	6	0	-0.930303	0.258478	-3.557963
37	6	0	-1.361946	-1.072947	-3.390934
38	6	0	-0.426372	-1.981570	-2.753055
39	6	0	0.866611	-1.483474	-2.371055
40	6	0	1.435821	-1.928269	-1.135301
41	6	0	0.703770	-2.792269	-0.273818
42	6	0	0.734265	-2.522757	1.158112
43	6	0	-0.337953	-2.986407	1.947772
44	6	0	-0.849158	-2.182671	3.005772
45	6	0	-0.283989	-0.914360	3.287497
46	6	0	-1.227721	0.135719	3.673957
47	6	0	-0.834157	1.460153	3.444889
48	6	0	-1.716209	2.402191	2.831346
49	6	0	-3.013022	2.051785	2.436928
50	6	0	-3.457351	2.488202	1.108555
51	6	0	-4.503469	1.724250	0.535288
52	6	0	-4.541280	1.475913	-0.863998
53	6	0	-5.151036	0.172690	-1.086998
54	6	0	-4.691021	-0.645734	-2.107048
55	6	0	-3.627056	-0.167645	-2.957116

56	6	0	-2.759762	-1.271507	-3.247329
57	6	0	-3.284615	-2.438850	-2.571850
58	6	0	-2.399953	-3.336484	-1.991264
59	6	0	-0.967738	-3.082804	-2.049827
60	6	0	-0.401141	-3.489381	-0.809238
61	6	0	-1.460507	-4.009305	0.027204
62	6	0	-1.427270	-3.764599	1.388966
63	6	0	-2.640482	-3.428429	2.098499
64	6	0	-2.282062	-2.445323	3.101050
65	6	0	-3.162853	-1.414387	3.390974
66	6	0	-2.627224	-0.095498	3.627516
67	6	0	-3.514251	0.857660	3.018995
68	6	0	-4.601405	0.128445	2.416293
69	6	0	-5.101406	0.571014	1.202491
70	6	0	-5.490418	-0.394239	0.197038
71	6	0	-5.318487	-1.766456	0.427871
72	6	0	-4.797509	-2.615157	-0.629769
73	6	0	-4.501433	-2.064939	-1.877644
74	6	0	-3.884100	-3.573044	-0.029502
75	6	0	-2.708591	-3.920950	-0.702274
76	6	0	-3.850267	-3.324631	1.401354
77	6	0	-4.749677	-2.218944	1.683252
78	6	0	-4.410467	-1.286901	2.664445
79	6	0	4.256923	-1.819761	-2.213439
80	6	0	5.318281	-2.459757	-1.563171
81	6	0	5.907441	-3.562022	-2.178044
82	6	0	5.420267	-3.986345	-3.414795
83	6	0	4.356947	-3.282528	-3.979481
84	7	0	3.781129	-2.224258	-3.396484
85	6	0	4.252910	-0.476567	2.602231
86	6	0	4.671328	-1.812575	2.608164
87	6	0	5.400998	-2.278488	3.698752
88	6	0	5.692653	-1.396629	4.740278
89	6	0	5.240200	-0.081606	4.634173
90	7	0	4.536039	0.377360	3.591776
91	16	0	-0.599600	4.875341	-1.675417
92	1	0	5.298970	0.699018	-1.553733
93	1	0	5.311519	1.228447	0.810127
94	1	0	5.670595	-2.091847	-0.605093
95	1	0	6.734968	-4.079560	-1.700332
96	1	0	5.851670	-4.838358	-3.930980
97	1	0	3.944976	-3.576426	-4.942894
98	1	0	4.421595	-2.466103	1.778016
99	1	0	5.734364	-3.312086	3.736159
100	1	0	6.256613	-1.716278	5.611115
101	1	0	5.449862	0.641310	5.420448

The total electronic energy was calculated to be –4015.5613515 Hartree.

Table S3. Optimized structure of **TS** (B3LYP-D3/6-31G(d))



Standard orientation:

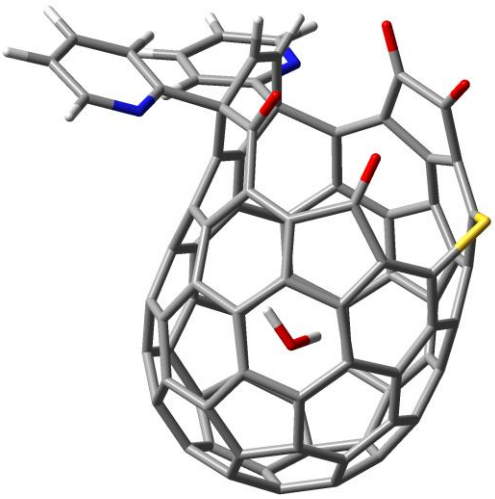
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.420978	0.423727	-3.608160
2	8	0	1.373680	2.841746	-3.715990
3	8	0	2.984472	5.246904	-0.854150
4	8	0	4.756236	3.308270	0.478736
5	6	0	3.430889	-0.827088	-1.525661
6	6	0	4.429613	0.097647	-0.884819
7	6	0	4.444238	0.405873	0.410004
8	6	0	3.400056	-0.025353	1.413905
9	6	0	2.544540	1.154453	1.926904
10	6	0	2.651462	2.472766	1.476451
11	6	0	3.552243	3.302614	0.596196
12	6	0	2.609203	4.378813	-0.102370
13	6	0	1.261247	4.146513	0.480879
14	6	0	-0.049095	4.285243	0.026822
15	6	0	-1.332195	3.345311	-2.054570
16	6	0	-0.952310	2.459400	-3.043144
17	6	0	0.453856	2.087046	-3.489159
18	6	0	0.412982	0.551232	-3.493272
19	6	0	1.289159	-0.371646	-2.947597
20	6	0	2.762703	-0.160083	-2.776582
21	6	0	2.376136	-1.288879	-0.543946
22	6	0	2.389853	-0.987361	0.791800
23	6	0	1.307992	-1.451252	1.642719
24	6	0	0.842994	-0.609273	2.700656
25	6	0	1.375414	0.765629	2.718225
26	6	0	0.475641	1.755302	3.131941
27	6	0	0.478451	3.012180	2.460058
28	6	0	1.498646	3.319595	1.614854
29	6	0	-0.866700	3.334268	2.103015
30	6	0	-1.167126	3.768259	0.800106
31	6	0	-2.431583	3.272257	0.212692
32	6	0	-2.484025	3.013059	-1.205878
33	6	0	-3.454100	2.075701	-1.729896
34	6	0	-3.087953	1.207943	-2.841719
35	6	0	-1.779515	1.334863	-3.326606
36	6	0	-0.971598	0.202852	-3.599223
37	6	0	-1.470309	-1.099813	-3.411730
38	6	0	-0.583011	-2.039148	-2.752565
39	6	0	0.725644	-1.589366	-2.367503
40	6	0	1.258887	-2.015743	-1.110485
41	6	0	0.486785	-2.837668	-0.243860
42	6	0	0.519191	-2.552950	1.183954
43	6	0	-0.571079	-2.976476	1.972572
44	6	0	-1.054828	-2.153282	3.027644
45	6	0	-0.437239	-0.912049	3.315777
46	6	0	-1.338762	0.173839	3.702622
47	6	0	-0.884181	1.479576	3.486844
48	6	0	-1.710553	2.456654	2.850360
49	6	0	-3.008605	2.159463	2.425146
50	6	0	-3.393004	2.596854	1.079128
51	6	0	-4.469613	1.886340	0.496820
52	6	0	-4.502975	1.630705	-0.900273
53	6	0	-5.187560	0.363151	-1.121285

54	6	0	-4.770417	-0.488046	-2.132275
55	6	0	-3.681073	-0.074062	-2.981532
56	6	0	-2.875918	-1.224540	-3.264859
57	6	0	-3.459804	-2.356600	-2.577328
58	6	0	-2.620569	-3.287419	-1.980486
59	6	0	-1.177445	-3.099959	-2.033292
60	6	0	-0.637663	-3.504085	-0.780305
61	6	0	-1.722864	-3.971257	0.053508
62	6	0	-1.687526	-3.714596	1.412323
63	6	0	-2.891046	-3.325034	2.111564
64	6	0	-2.498611	-2.355362	3.114075
65	6	0	-3.337360	-1.286988	3.393992
66	6	0	-2.746167	0.006339	3.636091
67	6	0	-3.577645	0.996801	3.008105
68	6	0	-4.686439	0.316787	2.390676
69	6	0	-5.143000	0.775417	1.165805
70	6	0	-5.570362	-0.175139	0.162856
71	6	0	-5.472734	-1.553378	0.405653
72	6	0	-4.987463	-2.436699	-0.640160
73	6	0	-4.658000	-1.913970	-1.891489
74	6	0	-4.124783	-3.431471	-0.024880
75	6	0	-2.961778	-3.839140	-0.685612
76	6	0	-4.089539	-3.172504	1.403868
77	6	0	-4.939566	-2.024241	1.669891
78	6	0	-4.568042	-1.104554	2.649982
79	6	0	4.148693	-2.103491	-2.036877
80	6	0	5.253081	-2.633071	-1.360473
81	6	0	5.819776	-3.815009	-1.834777
82	6	0	5.268853	-4.425683	-2.960917
83	6	0	4.164733	-3.820454	-3.561889
84	7	0	3.610933	-2.688765	-3.113783
85	6	0	4.147537	-0.693612	2.584957
86	6	0	4.544975	-2.034767	2.508800
87	6	0	5.273665	-2.575993	3.564090
88	6	0	5.585910	-1.762386	4.654594
89	6	0	5.152398	-0.437364	4.630686
90	7	0	4.448316	0.093949	3.622693
91	16	0	-0.304757	4.747902	-1.675888
92	1	0	5.190772	0.486990	-1.552400
93	1	0	5.212367	1.061817	0.801857
94	1	0	5.654119	-2.124375	-0.490922
95	1	0	6.680127	-4.249255	-1.332603
96	1	0	5.680779	-5.344884	-3.365800
97	1	0	3.700751	-4.260553	-4.442568
98	1	0	4.282854	-2.632924	1.641656
99	1	0	5.590900	-3.615047	3.537313
100	1	0	6.150547	-2.141981	5.500604
101	1	0	5.377391	0.233956	5.457495
102	8	0	3.262046	2.525077	-1.813878
103	1	0	4.120884	2.974506	-1.820761
104	1	0	2.858307	2.728595	-2.676386

The total electronic energy was calculated to be –4091.9878154 Hartree.

An imaginary frequency was found at –91.23 cm^{-1}.

Table S4. Optimized structure of H_2O-**I**@**4'** (B3LYP-D3/6-31G(d))



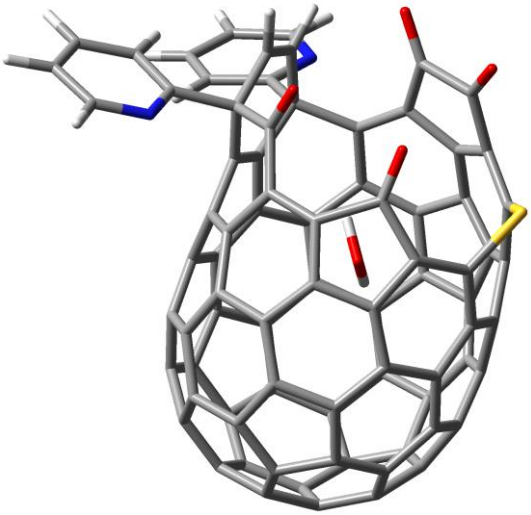
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.392544	1.024872	-3.310658
2	8	0	1.393188	3.006076	-3.366881
3	8	0	2.732106	5.085217	-1.285328
4	8	0	4.632268	3.338777	0.058174
5	6	0	3.572041	-0.623734	-1.550574
6	6	0	4.585719	0.269832	-0.889735
7	6	0	4.592890	0.554275	0.410167
8	6	0	3.541580	0.101989	1.393302
9	6	0	2.619598	1.253389	1.842153
10	6	0	2.639609	2.546320	1.312246
11	6	0	3.450324	3.330044	0.303365
12	6	0	2.437731	4.345021	-0.378875
13	6	0	1.157706	4.183190	0.357714
14	6	0	-0.176388	4.345857	-0.008134
15	6	0	-1.460198	3.420379	-2.035341
16	6	0	-0.994583	2.541613	-2.989293
17	6	0	0.466657	2.237333	-3.334522
18	6	0	0.471727	0.696903	-3.425024
19	6	0	1.394346	-0.198575	-2.912964
20	6	0	2.821325	0.168345	-2.672030
21	6	0	2.565099	-1.176975	-0.569518
22	6	0	2.580086	-0.903112	0.770923
23	6	0	1.510232	-1.399839	1.615667
24	6	0	1.010329	-0.566775	2.665135
25	6	0	1.481562	0.831225	2.659251
26	6	0	0.545111	1.789522	3.060144
27	6	0	0.489424	3.039030	2.374557
28	6	0	1.466958	3.360829	1.478986
29	6	0	-0.879482	3.325436	2.073432
30	6	0	-1.246960	3.781552	0.797762
31	6	0	-2.510345	3.252973	0.238331
32	6	0	-2.577841	3.013383	-1.182385
33	6	0	-3.484068	2.018482	-1.702372
34	6	0	-3.062876	1.179486	-2.815010
35	6	0	-1.754798	1.376675	-3.285932
36	6	0	-0.889603	0.287269	-3.560288
37	6	0	-1.328538	-1.041903	-3.397964
38	6	0	-0.398347	-1.956977	-2.762433
39	6	0	0.896876	-1.466107	-2.377497
40	6	0	1.462932	-1.919287	-1.143276
41	6	0	0.726491	-2.785411	-0.286266
42	6	0	0.755706	-2.520664	1.147441
43	6	0	-0.320963	-2.982146	1.932737
44	6	0	-0.829754	-2.179072	2.992281
45	6	0	-0.257603	-0.914905	3.279409
46	6	0	-1.196365	0.138724	3.669948
47	6	0	-0.796019	1.462350	3.445128

48	6	0	-1.673093	2.411082	2.833933
49	6	0	-2.971395	2.067879	2.435878
50	6	0	-3.412293	2.510808	1.108693
51	6	0	-4.461042	1.753644	0.531840
52	6	0	-4.496979	1.509817	-0.867370
53	6	0	-5.112703	0.211616	-1.096068
54	6	0	-4.655631	-0.604432	-2.117295
55	6	0	-3.587861	-0.128572	-2.961959
56	6	0	-2.726231	-1.234639	-3.255278
57	6	0	-3.257567	-2.401326	-2.585766
58	6	0	-2.379546	-3.306541	-2.008937
59	6	0	-0.946448	-3.058499	-2.064553
60	6	0	-0.382802	-3.474681	-0.825329
61	6	0	-1.446207	-3.991098	0.007625
62	6	0	-1.413227	-3.752996	1.370167
63	6	0	-2.624819	-3.413359	2.078843
64	6	0	-2.263652	-2.435742	3.084066
65	6	0	-3.139892	-1.401935	3.377366
66	6	0	-2.597469	-0.086874	3.619818
67	6	0	-3.479878	0.873556	3.012915
68	6	0	-4.570490	0.151730	2.407186
69	6	0	-5.064455	0.600771	1.193424
70	6	0	-5.457242	-0.358302	0.184435
71	6	0	-5.290765	-1.730626	0.410505
72	6	0	-4.772368	-2.577345	-0.648970
73	6	0	-4.473434	-2.024656	-1.893142
74	6	0	-3.864986	-3.540800	-0.051240
75	6	0	-2.691948	-3.893746	-0.723358
76	6	0	-3.831336	-3.297553	1.379131
77	6	0	-4.725519	-2.190139	1.663793
78	6	0	-4.385261	-1.264464	2.649776
79	6	0	4.284869	-1.821707	-2.218405
80	6	0	5.344257	-2.468169	-1.571405
81	6	0	5.927614	-3.571382	-2.190200
82	6	0	5.436693	-3.990178	-3.427317
83	6	0	4.375594	-3.280151	-3.988489
84	7	0	3.805436	-2.220925	-3.401740
85	6	0	4.282480	-0.496882	2.603550
86	6	0	4.696070	-1.834387	2.603680
87	6	0	5.420744	-2.308608	3.694021
88	6	0	5.712484	-1.433175	4.740928
89	6	0	5.265194	-0.115948	4.640313
90	7	0	4.565684	0.350924	3.598261
91	16	0	-0.540760	4.895876	-1.660893
92	1	0	5.339816	0.689260	-1.547360
93	1	0	5.352643	1.209446	0.818548
94	1	0	5.699780	-2.104544	-0.612867
95	1	0	6.753557	-4.093864	-1.715150
96	1	0	5.863503	-4.842706	-3.946444
97	1	0	3.960805	-3.569631	-4.952037
98	1	0	4.446727	-2.482666	1.769292
99	1	0	5.750254	-3.343581	3.727076
100	1	0	6.272669	-1.759397	5.611752
101	1	0	5.475219	0.602142	5.430907
102	8	0	-2.107736	-0.625815	0.118606
103	1	0	-1.220833	-0.938759	-0.113880
104	1	0	-1.979500	-0.150321	0.952790

The total electronic energy was calculated to be –4091.9991903 Hartree.

Table S5. Optimized structure of H_2O-**II**@**4'** (B3LYP-D3/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	3.355202	1.055078	-3.299157
2	8	0	1.340071	3.021592	-3.279938
3	8	0	2.653320	5.101298	-1.249911
4	8	0	4.566719	3.341479	0.055352
5	6	0	3.549612	-0.609756	-1.556588
6	6	0	4.558684	0.284563	-0.890051
7	6	0	4.566244	0.558326	0.412093
8	6	0	3.519704	0.089951	1.392591
9	6	0	2.584565	1.229238	1.843644
10	6	0	2.585530	2.523181	1.311834
11	6	0	3.386247	3.323748	0.305676
12	6	0	2.364125	4.342147	-0.357850
13	6	0	1.088292	4.160602	0.380631
14	6	0	-0.248109	4.322458	0.027049
15	6	0	-1.531478	3.412231	-1.999524
16	6	0	-1.051947	2.542584	-2.953323
17	6	0	0.415276	2.249659	-3.279692
18	6	0	0.432652	0.712791	-3.397340
19	6	0	1.364443	-0.182711	-2.903830
20	6	0	2.789502	0.189886	-2.667074
21	6	0	2.547910	-1.178724	-0.579339
22	6	0	2.565451	-0.918514	0.764974
23	6	0	1.501646	-1.432408	1.608164
24	6	0	0.997067	-0.611363	2.665572
25	6	0	1.454621	0.792353	2.665529
26	6	0	0.508845	1.741056	3.069367
27	6	0	0.439467	2.993719	2.391078
28	6	0	1.407904	3.326489	1.490028
29	6	0	-0.932508	3.275481	2.100668
30	6	0	-1.309592	3.741335	0.832284
31	6	0	-2.572165	3.212667	0.273759
32	6	0	-2.641870	2.987162	-1.148878
33	6	0	-3.537196	1.986320	-1.675978
34	6	0	-3.106219	1.159590	-2.794834
35	6	0	-1.798252	1.372493	-3.259697
36	6	0	-0.923345	0.293486	-3.539831
37	6	0	-1.349590	-1.041428	-3.394565
38	6	0	-0.411696	-1.955515	-2.771018
39	6	0	0.879429	-1.460303	-2.383982

40	6	0	1.451040	-1.923962	-1.157844	74	6	0	-3.862600	-3.598948	-0.073150
41	6	0	0.723429	-2.801272	-0.307609	75	6	0	-2.686065	-3.933403	-0.750519
42	6	0	0.753662	-2.551429	1.127510	76	6	0	-3.829429	-3.368855	1.360673
43	6	0	-0.317772	-3.027887	1.910968	77	6	0	-4.732419	-2.270424	1.656973
44	6	0	-0.831508	-2.238457	2.978577	78	6	0	-4.396828	-1.349551	2.650364
45	6	0	-0.269162	-0.972150	3.276359	79	6	0	4.268867	-1.796216	-2.237576
46	6	0	-1.217211	0.071195	3.672371	80	6	0	5.332811	-2.442423	-1.597851
47	6	0	-0.828400	1.399760	3.455759	81	6	0	5.923454	-3.534982	-2.228595
48	6	0	-1.714952	2.346605	2.854796	82	6	0	5.435044	-3.943559	-3.470057
49	6	0	-3.012039	1.996790	2.459925	83	6	0	4.368954	-3.234606	-4.023231
50	6	0	-3.462242	2.451654	1.139948	84	7	0	3.791723	-2.185822	-3.424895
51	6	0	-4.506014	1.689773	0.559624	85	6	0	4.264678	-0.505023	2.601343
52	6	0	-4.542929	1.458763	-0.842353	86	6	0	4.685195	-1.840241	2.602061
53	6	0	-5.146159	0.155735	-1.081884	87	6	0	5.413408	-2.309574	3.692234
54	6	0	-4.681164	-0.646834	-2.111731	88	6	0	5.701414	-1.431681	4.738080
55	6	0	-3.618516	-0.152880	-2.954189	89	6	0	5.247092	-0.116871	4.636871
56	6	0	-2.746174	-1.248708	-3.257927	90	7	0	4.544218	0.345277	3.595037
57	6	0	-3.266239	-2.427199	-2.599028	91	16	0	-0.628565	4.894680	-1.612966
58	6	0	-2.379230	-3.330076	-2.031120	92	1	0	5.307347	0.716217	-1.545909
59	6	0	-0.948413	-3.069113	-2.084605	93	1	0	5.320543	1.217167	0.824722
60	6	0	-0.379833	-3.493750	-0.851434	94	1	0	5.686367	-2.086702	-0.635605
61	6	0	-1.437537	-4.027073	-0.022193	95	1	0	6.752974	-4.057029	-1.759333
62	6	0	-1.404952	-3.802540	1.343045	96	1	0	5.867440	-4.787492	-3.998526
63	6	0	-2.618878	-3.478404	2.056454	97	1	0	3.955839	-3.516483	-4.989750
64	6	0	-2.263646	-2.506558	3.070571	98	1	0	4.438326	-2.490705	1.768644
65	6	0	-3.147768	-1.481833	3.373328	99	1	0	5.748419	-3.342743	3.725970
66	6	0	-2.616184	-0.164232	3.625001	100	1	0	6.264111	-1.754204	5.608656
67	6	0	-3.507221	0.793221	3.028357	101	1	0	5.454004	0.602988	5.426659
68	6	0	-4.593687	0.067828	2.420062	102	8	0	-0.425271	0.751508	-0.173542
69	6	0	-5.095733	0.524324	1.212168	103	1	0	0.523392	0.745086	0.022931
70	6	0	-5.482002	-0.429765	0.194755	104	1	0	-0.836606	0.578793	0.686327
71	6	0	-5.303838	-1.803749	0.407988						
72	6	0	-4.779724	-2.636590	-0.661017						
73	6	0	-4.485333	-2.068224	-1.900594						

The total electronic energy was calculated to be –4091.9965452 Hartree.

5.2. Molecular Orbitals of 8 and 11

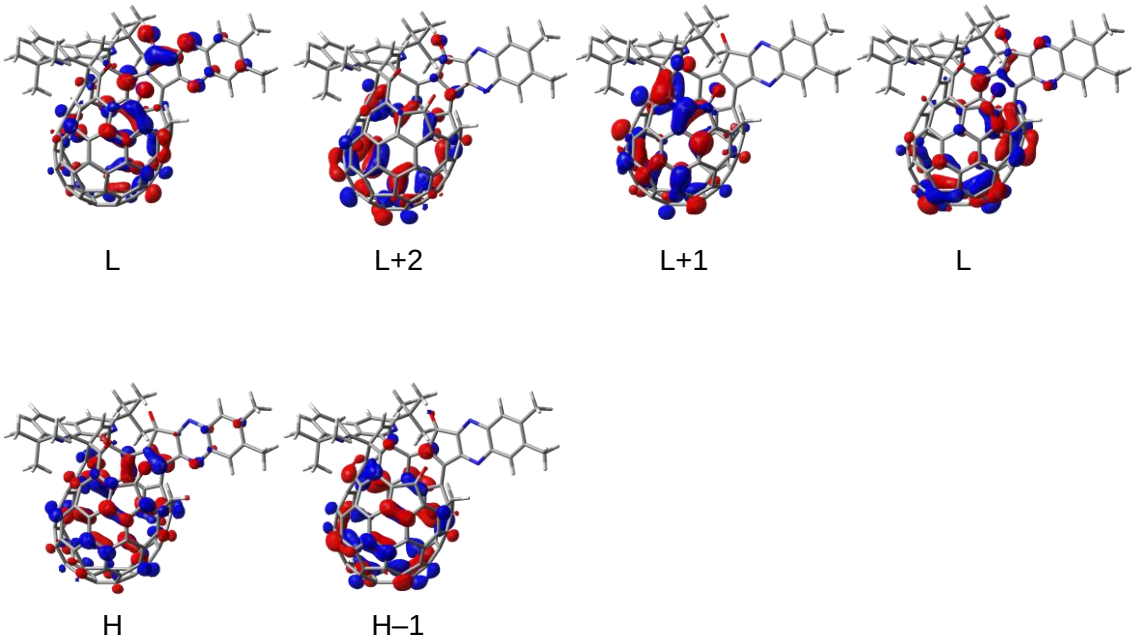


Figure S26. Molecular orbitals of **8** (B3LYP/6-31G(d)).

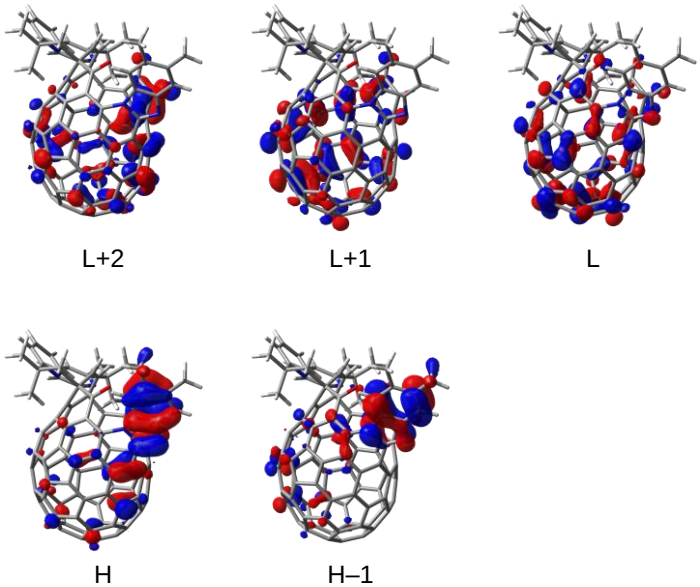
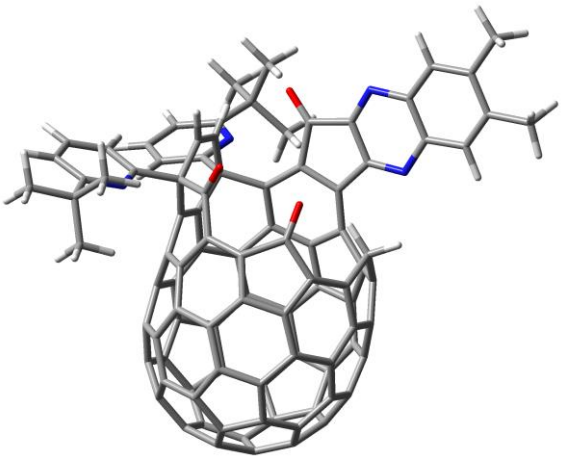


Figure S27. Molecular orbitals of **11** (B3LYP/6-31G(d)).

Table S6. Optimized structure of **8** (B3LYP/6-31G(d))



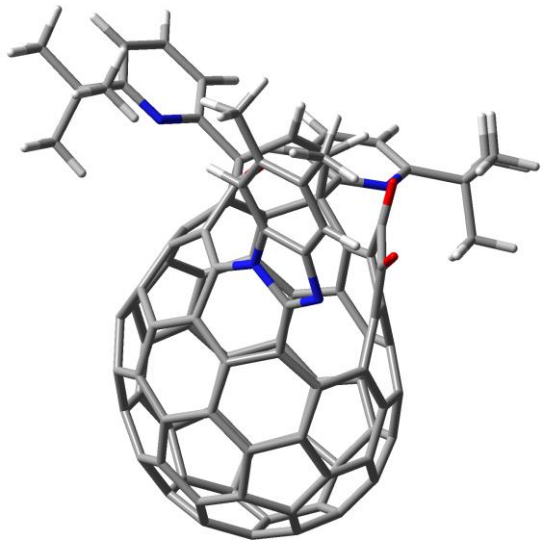
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.122242	-2.817385	2.559142
2	6	0	5.507804	-3.315331	1.252315
3	6	0	6.050566	-2.203031	0.492801
4	6	0	6.002101	-1.018531	1.331179
5	6	0	5.423732	-1.397921	2.607884
6	6	0	4.713880	-4.273577	0.613221
7	6	0	4.425591	-4.152664	-0.799965
8	6	0	4.944372	-3.088091	-1.526019
9	6	0	5.777973	-2.098042	-0.873432
10	6	0	5.433456	-0.813829	-1.449177
11	6	0	5.381709	0.318229	-0.649519
12	6	0	5.680074	0.218801	0.763858
13	6	0	4.773152	1.116244	1.447534
14	6	0	4.216167	0.751058	2.662711
15	6	0	4.545673	-0.524506	3.259787
16	6	0	3.334284	-1.027868	3.870768
17	6	0	3.060311	-2.387094	3.838152
18	6	0	3.963744	-3.301878	3.172193
19	6	0	3.141869	-4.290646	2.501600
20	6	0	3.509314	-4.768600	1.249928
21	6	0	1.704173	-2.823218	3.595353
22	6	0	1.747932	-3.999038	2.776265
23	6	0	3.058499	-4.587045	-1.028269
24	6	0	2.495705	-4.968024	0.230568
25	6	0	2.269115	-0.058613	3.651335
26	6	0	2.818775	1.034550	2.919210
27	6	0	3.941538	1.770774	0.460697
28	6	0	4.306732	1.280839	-0.825887
29	6	0	4.411821	-1.017793	-2.454077
30	6	0	4.113657	-2.415652	-2.504580
31	6	0	2.800490	-2.875007	-2.791730
32	6	0	2.254362	-3.989589	-2.030402
33	6	0	1.118004	-4.766621	0.506528
34	6	0	0.733759	-4.275818	1.819196
35	6	0	0.652297	-1.887054	3.445792
36	6	0	0.923512	-0.447642	3.450611
37	6	0	2.603649	2.136983	0.728554
38	6	0	2.018187	1.751823	2.005900
39	6	0	3.394788	-0.050991	-2.674573
40	6	0	3.324829	1.134007	-1.833712
41	6	0	1.880239	-1.913278	-3.268053
42	6	0	2.176400	-0.520608	-3.213176
43	6	0	0.276514	-4.409108	-0.585678
44	6	0	0.843824	-4.025503	-1.837892
45	6	0	-0.446546	-3.495330	1.895943
46	6	0	-0.448789	-2.323676	2.691399
47	6	0	2.057703	1.790015	-1.658177
48	6	0	1.724082	2.331133	-0.373884
49	6	0	0.601104	1.577380	2.066092
50	6	0	0.047861	0.454992	2.745238
51	6	0	-1.242612	-0.015159	2.218980
52	6	0	-1.385020	-1.406874	2.129867
53	6	0	-1.396619	-3.300488	0.801003
54	6	0	-1.010540	-3.753608	-0.443760
55	6	0	-0.071204	-3.124575	-2.501117
56	6	0	0.452825	-2.079375	-3.222872
57	6	0	0.973022	0.255969	-3.214798
58	6	0	0.940351	1.464842	-2.539562
59	6	0	-0.227412	2.267333	1.092026
60	6	0	0.336076	2.655176	-0.095238
61	6	0	-0.187213	-0.723735	-3.427497
62	6	0	-0.281070	2.325834	-2.495738
63	6	0	-2.135051	0.805626	1.470837
64	6	0	-2.126995	-2.041343	1.098089
65	6	0	-1.419694	-3.210234	-1.807436
66	6	0	-3.112360	-1.264693	0.506729
67	6	0	-4.229028	-1.644024	-0.368709
68	6	0	-5.059228	-0.501068	-0.556766
69	6	0	-3.168355	0.150542	0.773253
70	6	0	-4.469236	0.660829	0.196513
71	6	0	-1.735210	2.302659	1.359351
72	6	0	-2.071409	3.043884	2.674304
73	6	0	-2.457670	3.025230	0.240868
74	6	0	-0.444169	3.250662	-1.246174
75	6	0	-1.903063	3.408203	-0.908656
76	6	0	0.150131	4.637188	-1.606325
77	6	0	-0.130578	5.756098	-0.813373
78	6	0	0.432056	6.971905	-1.184420
79	7	0	0.931432	4.698452	-2.684893
80	7	0	-3.156400	2.613844	3.317645
81	6	0	-1.327435	4.147737	3.107413
82	6	0	-3.574772	3.243752	4.430541
83	6	0	-1.742623	4.799164	4.263912
84	6	0	1.473664	5.873052	-3.059793
85	6	0	-2.877532	4.347051	4.937795
86	6	0	1.240354	7.037988	-2.320072
87	6	0	2.338360	5.822739	-4.327313
88	6	0	-4.851582	2.672215	5.063154
89	8	0	-1.102228	2.327139	-3.387686
90	8	0	-5.028401	1.726467	0.373051
91	6	0	3.531265	4.873174	-4.071715
92	6	0	1.479889	5.265873	-5.486285
93	6	0	2.878987	7.208136	-4.722995
94	6	0	-5.241087	3.402367	6.360128
95	6	0	-6.000735	2.810483	4.036748
96	6	0	-4.621100	1.176085	5.375174
97	7	0	-6.169515	-0.504091	-1.248142

98	7	0	-4.497092	-2.826476	-0.877377
99	6	0	-6.477628	-1.715258	-1.810768
100	6	0	-5.646281	-2.869981	-1.625111
101	6	0	-6.034906	-4.086292	-2.230021
102	6	0	-8.014586	-3.031142	-3.177655
103	6	0	-7.650392	-1.834744	-2.590801
104	6	0	-7.184686	-4.186420	-2.991261
105	6	0	-9.272948	-3.120127	-4.005969
106	6	0	-7.562784	-5.504074	-3.621732
107	8	0	-1.373108	-0.507451	-3.553747
108	1	0	-2.111201	-3.892599	-2.319935
109	1	0	-1.920092	-2.242639	-1.762905
110	1	0	-3.511048	3.198790	0.414965
111	1	0	-2.511119	3.888962	-1.668928
112	1	0	-0.779440	5.671309	0.051738
113	1	0	0.238934	7.867098	-0.598757
114	1	0	-0.450329	4.477589	2.560283
115	1	0	-1.187994	5.654909	4.640621
116	1	0	-3.209434	4.848879	5.838720
117	1	0	1.674790	7.983967	-2.620173
118	1	0	4.143707	4.783535	-4.976945
119	1	0	4.172394	5.250566	-3.265799
120	1	0	3.181446	3.876665	-3.789770
121	1	0	2.091615	5.155561	-6.389682
122	1	0	1.059066	4.291227	-5.226088
123	1	0	0.649046	5.942009	-5.720537
124	1	0	3.479614	7.120288	-5.635107
125	1	0	2.070496	7.919480	-4.928970
126	1	0	3.524355	7.635370	-3.946247
127	1	0	-6.151935	2.956312	6.774853
128	1	0	-4.458953	3.324940	7.125016
129	1	0	-5.447947	4.464957	6.186228
130	1	0	-6.913675	2.342957	4.425254
131	1	0	-6.222020	3.865697	3.835340
132	1	0	-5.737731	2.334098	3.088460
133	1	0	-5.538049	0.727282	5.775344
134	1	0	-4.332156	0.634477	4.470899
135	1	0	-3.826842	1.045174	6.120343
136	1	0	-5.394879	-4.950371	-2.074392
137	1	0	-8.258981	-0.943350	-2.713483
138	1	0	-9.972813	-3.862487	-3.601382
139	1	0	-9.788401	-2.156397	-4.039255
140	1	0	-9.056480	-3.420716	-5.039142
141	1	0	-7.626337	-5.425121	-4.714572
142	1	0	-6.829028	-6.279080	-3.383533
143	1	0	-8.544063	-5.851534	-3.273879

The total electronic energy was calculated to be –4276.9278389 Hartree.

Table S7. Optimized structure of **11** (B3LYP/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.225220	-0.558649	0.300923
2	6	0	6.238082	-1.331397	-0.928017
3	6	0	5.880715	-2.700696	-0.604487
4	6	0	5.640027	-2.775345	0.824426
5	6	0	5.868419	-1.456146	1.388064
6	6	0	5.772086	-0.756139	-2.113176
7	6	0	4.946953	-1.518983	-3.026837
8	6	0	4.606065	-2.830870	-2.719032
9	6	0	5.073761	-3.428351	-1.483484
10	6	0	3.986528	-4.231409	-0.966894
11	6	0	3.737085	-4.278663	0.398442
12	6	0	4.588120	-3.556995	1.313598
13	6	0	3.734647	-3.061840	2.373718
14	6	0	3.963971	-1.818690	2.926022
15	6	0	5.054530	-0.999218	2.425036
16	6	0	4.576752	0.361234	2.415207
17	6	0	4.887504	1.214883	1.361926
18	6	0	5.735901	0.752819	0.288624
19	6	0	5.219342	1.330233	-0.936635
20	6	0	5.249362	0.594903	-2.108486
21	6	0	3.866218	2.076048	0.794978
22	6	0	4.050122	2.136193	-0.615032
23	6	0	3.951570	-0.633051	-3.603320
24	6	0	4.125756	0.664011	-3.014551
25	6	0	3.235988	0.366012	2.937049
26	6	0	2.830479	-0.982209	3.255619
27	6	0	2.369973	-3.469428	2.125632
28	6	0	2.375636	-4.218884	0.898082
29	6	0	2.876234	-4.145398	-1.886649
30	6	0	3.256562	-3.298936	-2.980227
31	6	0	2.300707	-2.488760	-3.647143
32	6	0	2.664384	-1.102817	-3.974398
33	6	0	3.011033	1.508969	-2.748563
34	6	0	2.931546	2.239683	-1.477203
35	6	0	2.572030	2.144607	1.343370
36	6	0	2.293184	1.279375	2.463793
37	6	0	1.231036	-2.750176	2.570211
38	6	0	1.470363	-1.409615	3.201378
39	6	0	1.538768	-4.165042	-1.415054
40	6	0	1.281274	-4.155858	0.020773
41	6	0	0.933979	-2.771719	-3.366922
42	6	0	0.570392	-3.582488	-2.254726
43	6	0	1.804876	1.145863	-3.380231
44	6	0	1.631063	-0.129431	-3.998970
45	6	0	1.638217	2.558601	-0.898975
46	6	0	1.468073	2.554173	0.526546
47	6	0	0.060531	-3.610813	0.546296
48	6	0	0.011866	-3.092778	1.871404
49	6	0	0.527211	-0.303532	3.222217
50	6	0	0.954075	0.948123	2.722729
51	6	0	-0.116101	1.795257	2.232987

52	6	0	0.115449	2.565855	1.112880	98	6	0	2.198061	6.603833	2.335778
53	6	0	0.426041	2.311623	-1.679197	99	6	0	-3.136728	-3.153192	3.471537
54	6	0	0.534337	1.587754	-2.863007	100	6	0	-4.092219	-3.479863	4.444454
55	6	0	0.239066	-0.483819	-3.836138	101	6	0	-3.555071	-2.772291	2.176046
56	6	0	-0.107818	-1.780267	-3.517529	102	6	0	-4.902668	-2.764787	1.818612
57	6	0	-0.683194	-3.102045	-1.724554	103	6	0	-5.845062	-3.105584	2.786491
58	6	0	-0.985742	-3.156306	-0.367888	104	6	0	-5.440291	-3.453310	4.113351
59	6	0	-0.877236	-0.043481	3.663554	105	6	0	-7.310949	-3.100079	2.422171
60	6	0	-1.330442	-2.882336	2.368236	106	6	0	-6.477579	-3.799586	5.156133
61	6	0	-1.137389	-2.009680	-2.530906	107	8	0	-1.565323	-0.617153	4.473632
62	6	0	-2.062851	-2.317231	0.111823	108	1	0	-4.201638	3.660407	-1.738526
63	6	0	-1.283952	1.357584	3.063487	109	1	0	-4.282045	2.336946	0.928926
64	6	0	-0.869982	2.356962	-1.044253	110	1	0	-1.498165	4.772253	-2.021174
65	6	0	-0.454098	0.592383	-3.180609	111	1	0	-1.056928	7.227242	-2.235898
66	6	0	-1.847556	1.445022	-1.395983	112	1	0	0.020276	8.434256	-0.353363
67	6	0	-1.537470	0.388833	-2.323470	113	1	0	-2.525975	3.819162	1.657405
68	6	0	-1.884067	-0.976155	-1.944945	114	1	0	-6.029686	3.861061	-3.443119
69	6	0	-3.308083	-0.115138	-0.059664	115	1	0	-7.113620	1.800082	-4.300694
70	6	0	-2.500160	-1.217965	-0.655516	116	1	0	-5.752155	-2.673030	-4.519917
71	6	0	-3.178912	1.321384	-0.691277	117	1	0	-4.530549	-1.842586	-3.531027
72	6	0	-4.690681	2.781937	-2.146067	118	1	0	-4.979387	-1.192732	-5.118296
73	6	0	-0.653064	4.692676	-0.028851	119	1	0	-8.029611	-1.650174	-4.853387
74	6	0	-3.325686	2.333423	0.417135	120	1	0	-7.299545	-0.169613	-5.480568
75	6	0	-1.031143	5.329690	-1.215788	121	1	0	-8.461919	-0.093111	-4.138156
76	6	0	-0.783078	6.693346	-1.329473	122	1	0	-7.396113	-2.597262	-2.609180
77	6	0	-0.178035	7.372372	-0.271525	123	1	0	-7.839398	-1.058552	-1.844084
78	6	0	-2.354814	3.149991	0.821489	124	1	0	-6.226327	-1.742738	-1.576272
79	7	0	-0.082834	5.343268	0.986294	125	1	0	0.417617	7.449358	4.249388
80	6	0	0.163170	6.663061	0.886610	126	1	0	-0.257446	5.992193	3.485152
81	6	0	-0.969886	3.202220	0.221726	127	1	0	-1.032183	7.567429	3.234336
82	6	0	-4.318575	1.500636	-1.723090	128	1	0	1.539100	9.214800	2.839503
83	6	0	-5.707779	2.885610	-3.087542	129	1	0	0.120535	9.352033	1.795237
84	6	0	-6.316721	1.726980	-3.570777	130	1	0	1.721304	9.031052	1.092114
85	6	0	-5.887274	0.481773	-3.097712	131	1	0	2.678676	6.995652	3.240085
86	7	0	-4.897342	0.392360	-2.187767	132	1	0	2.873739	6.779414	1.489900
87	8	0	-3.997642	-0.251541	0.931401	133	1	0	2.068033	5.524173	2.449256
88	7	0	-2.370449	-2.561325	1.464515	134	1	0	-3.764034	-3.758552	5.441197
89	8	0	-2.296167	1.932268	3.385123	135	1	0	-5.219624	-2.488583	0.820330
90	7	0	-1.762236	-3.211073	3.561166	136	1	0	-7.773354	-4.083859	2.576607
91	6	0	0.834415	7.297955	2.112813	137	1	0	-7.455388	-2.823028	1.373687
92	6	0	-6.483902	-0.856239	-3.557649	138	1	0	-7.877218	-2.386999	3.035476
93	6	0	-5.364896	-1.691642	-4.221038	139	1	0	-7.094595	-4.655893	4.853245
94	6	0	-7.633162	-0.670707	-4.564149	140	1	0	-7.166040	-2.964015	5.338504
95	6	0	-7.018536	-1.609861	-2.318111	141	1	0	-6.003201	-4.051486	6.109134
96	6	0	-0.066604	7.059550	3.346153	---					
97	6	0	1.062362	8.809707	1.940104	The total electronic energy was calculated to be –4275.6743344 Hartree.					

6. References

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