Supporting Information

Phosphorus ylides of cage-opened sulphide [60]fullerene derivatives

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1. General

The ^{1}H, ^{13}C, and ^{31}P NMR measurements were carried out at room temperature unless otherwise noted with a JEOL JNM ECA500 and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of benzene-d_6 (δ 7.15 ppm in ^{1}H NMR, δ 128.00 ppm in ^{13}C NMR), $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.00 ppm in ^{13}C NMR), and *o*-dichlorobenzene-d_4 (ODCB-d_4, δ 7.20 ppm in ^{1}H NMR, δ 132.35 ppm in ^{13}C NMR). The ^{31}P NMR chemical shifts were reported in ppm with reference to the chemical shift of H_3PO_4 (δ 0.00 ppm) in a glass sealed capillary which was inserted inside the NMR tube filled with benzene-d_6. APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. UV-vis 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 a $Ag/AgNO_3$ 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. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (250 mm in length, 20 mm in inner diameter) for preparative purpose. 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. Triphenylphosphine and hexane were purchased from Nakalai Tesque, Inc. Elemental sulfur was purchased from Kanto Chemical Co., Inc. Carbon disulfide, ethyl acetate, and acetone were purchased from FUJIFILM Wako Pure Chemical Corporation. *o*-Dichlorobenzene (ODCB) was purchased from Sigma-Aldroch Co. LLC. Tetrakis(dimethylamino)ethylene (TDAE) trimethylphosphite, and trimethylphosphine (1.0 M in toluene) were purchased from Tokyo Chemical Industry Co. Ltd.

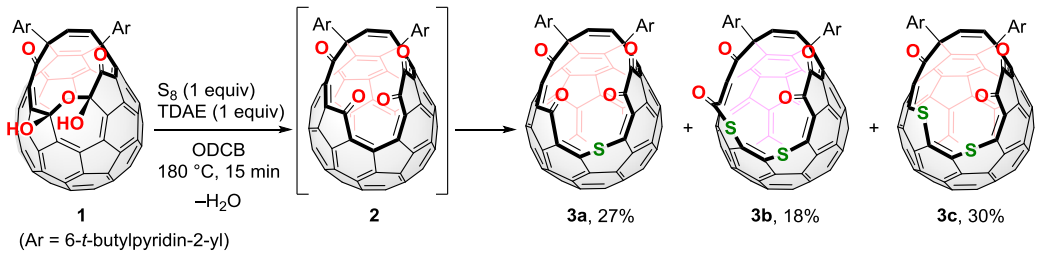
All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. Compounds **1**[1], **5a**,[2] and **4a**-**Me**[2] were synthesized according to literature procedures.

2. Computational Methods

All calculations were conducted using the Gaussian 09 program.[3] All structures at the stationary and transition states were optimized at the B3LYP/6-31G(d) or M06-2X/6-31G(d,p) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory. Mulliken atomic charges were calculated at the B3LYP/6-31G(d,p) level of theory using the structures optimized at the B3LYP/6-31G(d) level of theory. TD DFT calculations were performed at the CAM-B3LYP/6-31G(d) level of theory using the structures optimized at the B3LYP/6-31G(d) level of theory.

3. Synthesis

3.1. Synthesis of 3a–c from 1



Powdery **1** (10.0 mg, 8.92 μmol) and S_8 (2.3 mg, 9.0 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.500 mL) and TDAE (2.06 μL, ρ = 0.8695 g/mL, 8.94 μmol, 1.00 equiv) were added and the resulting solution was heated at 180 °C for 15 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1) to (50:1)) to give **3c** (3.07 mg, 2.69 μmol, 30%), **3b** (1.88 mg, 1.61 μmol, 18%), and **3a** (2.76 mg, 2.43 μmol, 27%) as brown powders.

3a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, 1H, J = 8.0 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.223 (d, 1H, J = 8.0 Hz), 7.219 (d, 1H, J = 8.0 Hz), 7.12 (d, 1H, J = 8.0 Hz), 7.10 (d, 1H, J = 8.0 Hz), 7.04 (d, 1H, J = 10.3 Hz), 6.50 (d, 1H, J = 10.3 Hz), 1.21 (s, 9H), 1.08 (s, 9H), –11.43 (br s, 1H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{82}H_{26}N_2O_4S$ (**3a**) 1134.1619; Found 1134.1634. (These data were matched well with the reported one.[4])

3b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 6.99 (d, 1H, J = 8.0 Hz), 6.97 (d, 1H, J = 10.3 Hz), 6.38 (d, 0.50H, J = 10.3 Hz), 6.36 (d, 0.50H, J = 10.3 Hz), 1.214 (s, 4.5H), 1.209 (s, 4.5H), 1.208 (s, 4.5H), 1.202 (s, 4.5H) (A part of the proton signals for the empty and encapsulated ones was separately observed.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{82}H_{26}N_2O_4S_2$ (**3b**) 1166.1339; Found 1166.1328. (These data were matched well with the reported one.[4])

3c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 8.0 Hz), 7.25 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.12 (d, 1H, J = 8.0 Hz), 7.03 (d, 0.44H, J = 10.3 Hz), 7.02 (d, 0.56H, J = 10.3 Hz), 6.57 (d, 0.44H, J = 10.3 Hz), 6.56 (d, 0.56H, J = 10.3 Hz), 1.21 (s, 9H), 1.15 (s, 9H), –10.96 (s, 0.72H) (A

part of the proton signals for the empty and encapsulated ones was separately observed.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{81}H_{26}N_2O_3S_2$ (**3c**) 1138.1390; Found 1138.1440. (These data were matched well with the reported one.[4])

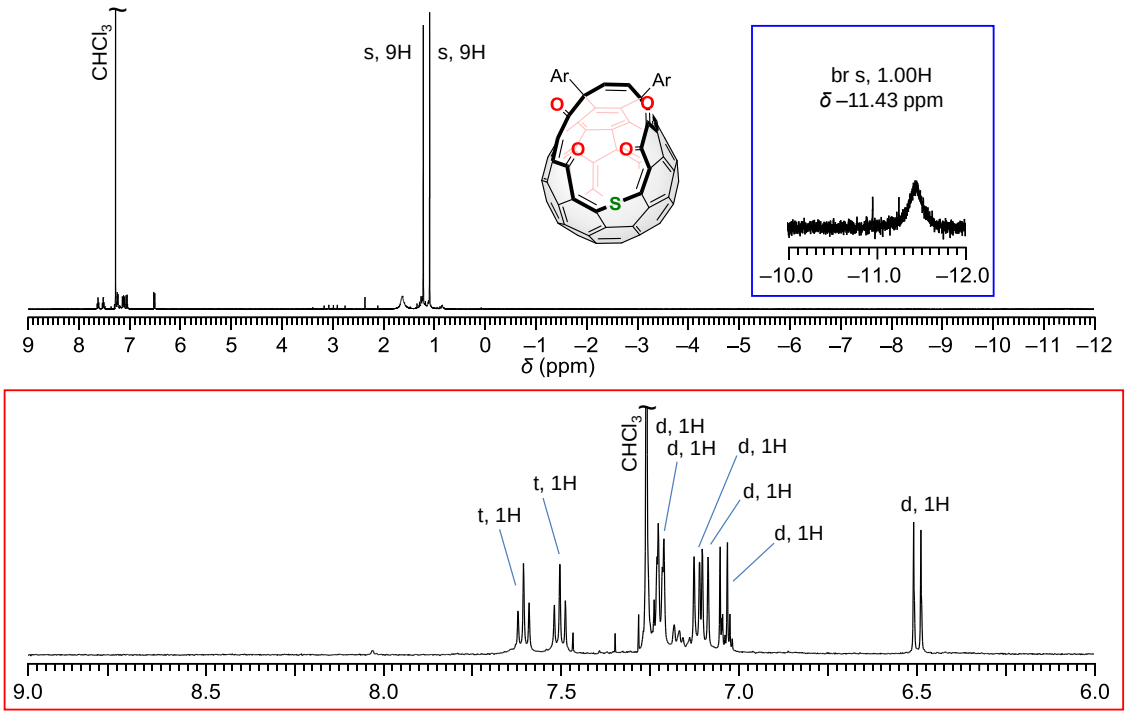


Figure S1. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3a**.

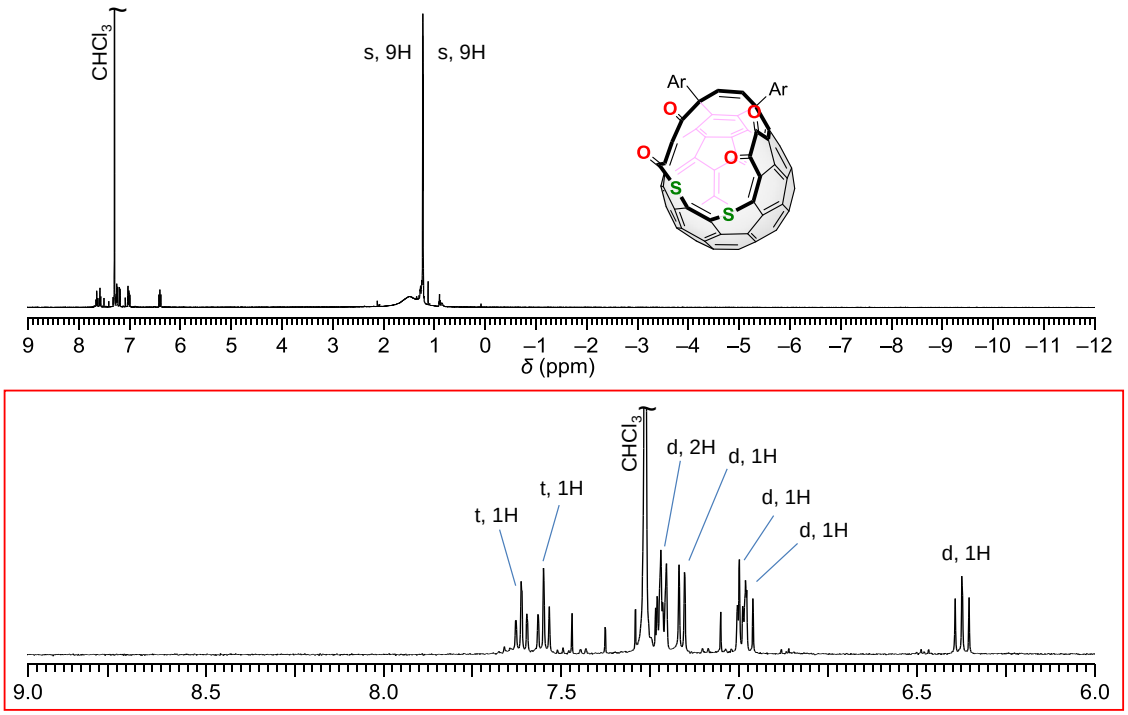


Figure S2. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3b**.

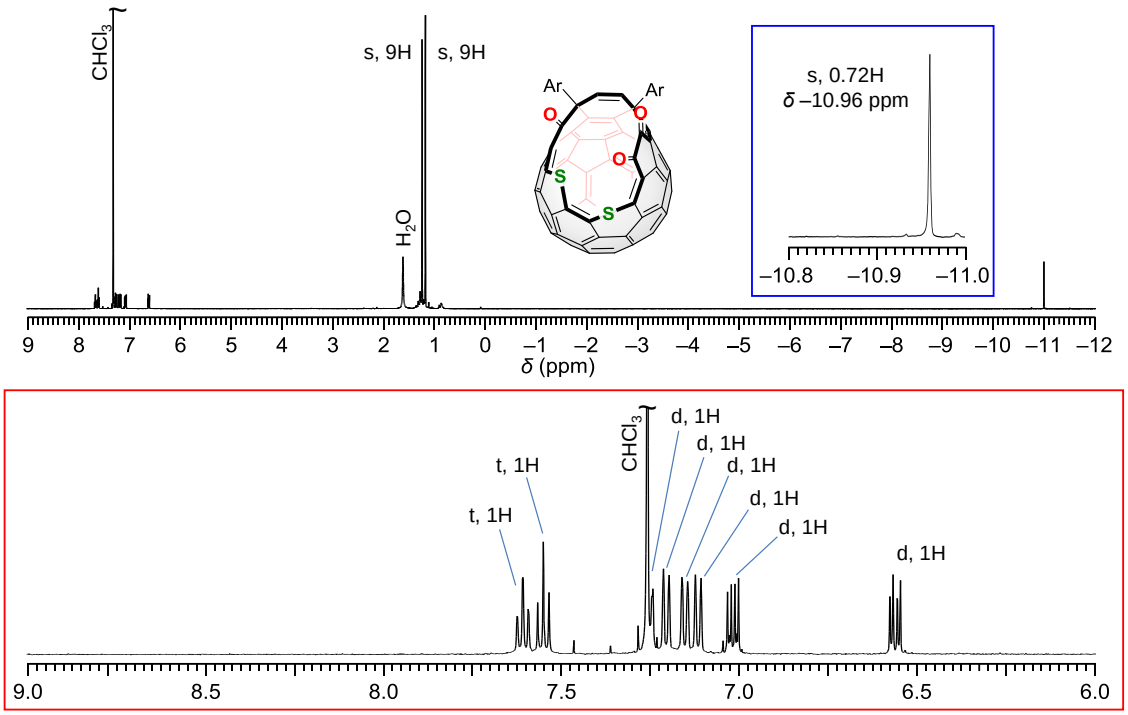
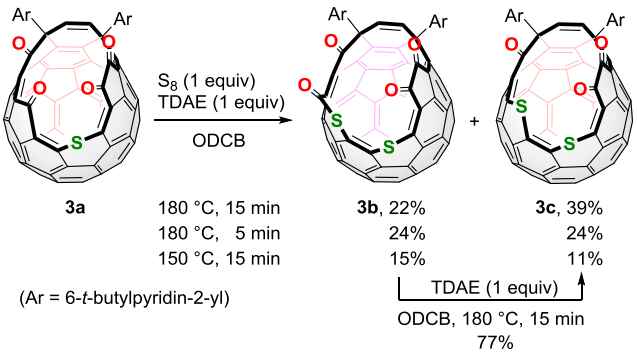


Figure S3. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3c**.

3.2. Synthesis of 3b and 3c from 3a



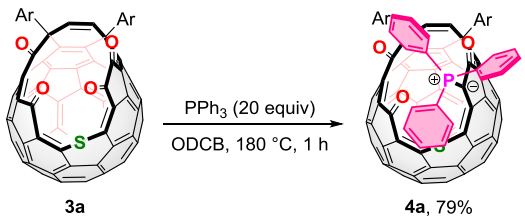
[Synthesis of **3b** and **3c** from **3a**]

Powdery **3a** (10.0 mg, 8.81 μmol) and S_8 (2.3 mg, 9.0 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.500 mL) and TDAE (2.03 μL, ρ = 0.8695 g/mL, 8.81 μmol, 1.00 equiv) were added and the resulting solution was heated at 180 °C for 15 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1) to (50:1)) to give **3c** (3.87 mg, 3.40 μmol, 39%), **3b** (2.28 mg, 1.95 μmol, 22%), and unreacted **3a** (2.06 mg, 1.81 μmol, 21%) as brown powders.

[Conversion of **3b** into **3c**]

Powdery **3b** (5.00 mg, 4.28 μmol) was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.250 mL) and TDAE (1.00 μL, ρ = 0.8695 g/mL, 4.34 μmol, 1.01 equiv) were added and the resulting solution was heated at 180 °C for 15 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1)) to give **3c** (3.77 mg, 3.23 μmol, 77%) as a brown powder.

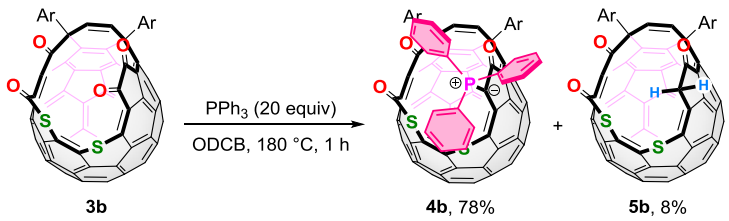
3.3. Reaction of 3a with PPh_3



Powdery **3a** (10.0 mg, 8.81 μmol) and PPh_3 (46.3 mg, 177 μmol, 20.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.301 mL) was added and the resulting solution was heated at 180 °C for 1 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (100:1) to (50:1)) to give **4a** (9.65 mg, 6.99 μmol, 79%) and unreacted **3a** (1.78 mg, 1.57 μmol, 18%) as brown powders.

4a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (br s, 6H), 7.77 (br s, 6H), 7.77–7.68 (br m, 3H), 7.54 (t, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.36–7.41 (m, 2H), 7.21 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.50 (d, J = 10.4 Hz, 1H) 1.12 (m, 18H), –11.14 (s, 1.29H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{88}H_{44}N_5O_3PS$ (**4a**) 1381.2614; Found 1381.2600. (These data were matched well with the reported one.[2])

3.4. Reaction of 3b with PPh_3



3b **4b**, 78% **5b**, 8%

Powdery **3b** (10.0 mg, 8.56 μmol) and PPh_3 (45.0 mg, 172 μmol, 20.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.292 mL) was added and the resulting solution was heated at 180 °C for 1 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (toluene to toluene/EtOAc (100:1)) to give **5b** (0.80 mg, 0.69 μmol, 8%) and **4b** (9.46 mg, 6.69 μmol, 78%) as brown powders.

4b: ^{1}H NMR (500 MHz, benzene-d_6) δ 8.00 (br s, 6H), 7.75 (d, 0.25H, J = 10.3 Hz), 7.73 (d, 0.75H, J = 10.3 Hz), 7.40 (br s, 6H), 7.30 (d, 0.25H, J = 8.0 Hz), 7.27 (d, 0.75H, J = 8.0 Hz), 7.23 (br s, 3H), 7.211 (d, 0.25H, J = 8.0 Hz), 7.205 (d, 0.75H, J = 8.0 Hz), 7.06 (d, 0.25H, J = 8.0 Hz), 7.05 (d, 0.75H, J = 8.0 Hz), 6.99 (d, 0.5H, J = 8.0 Hz), 6.97 (d, 0.5H, J = 8.0 Hz), 6.87 (d, 0.5H, J = 10.3 Hz), 6.86 (d, 0.25H, J = 10.3 Hz), 6.85 (d, 0.25H, J = 10.3 Hz), 6.743 (d, 1H, J = 8.0 Hz), 6.735 (d, 1H, J = 8.0 Hz), 1.244 (s, 4.5H), 1.239 (s, 4.5H), 1.11 (s, 4.5H), 1.10 (s, 4.5H), –10.11 (s, 0.76H) (The proton signals of the empty and encapsulated ones were separately observed.); ^{13}C NMR (126 MHz, benzene-d_6) δ 195.55, 195.50, 195.41, 183.85, 183.81, 168.34, 168.31, 167.91, 165.24, 165.01, 164.65, 164.51, 153.79, 153.68, 153.58, 153.31, 153.22, 153.12, 152.79, 152.76, 152.58, 152.43, 152.35, 151.98, 151.87, 151.79, 151.72, 151.684, 151.680, 151.61, 151.58, 151.48, 151.44, 151.40, 151.20, 151.18, 151.09, 151.05, 151.00, 150.75, 150.58, 150.55, 150.51, 150.37, 149.61, 149.57, 149.56, 149.43, 149.37, 149.33, 149.16, 148.38, 148.36, 148.32, 148.18, 148.14, 148.05, 147.87, 147.68, 146.34, 146.26, 146.19, 146.02, 145.98, 145.96, 145.90, 145.73, 145.61, 145.53, 145.51, 145.48, 145.46, 145.44, 145.37, 145.29, 145.26, 145.23, 145.21, 145.18, 145.06, 144.83, 144.80, 144.14, 144.12, 144.07, 144.05, 144.03, 143.87, 143.84, 143.82, 143.80, 143.61, 143.57, 142.08, 142.05, 141.94, 141.92, 141.88, 141.85, 141.79, 141.76, 141.66, 141.62, 141.57, 141.49, 141.24, 141.09, 141.02, 140.32, 140.28, 139.84, 139.82, 139.67, 139.55, 139.44, 139.42, 138.74, 138.65, 138.12, 138.08, 138.05, 137.96, 137.88, 137.81, 137.73, 137.69, 137.61, 137.57, 137.44, 137.31, 137.26, 137.17, 137.15, 137.11, 136.84, 136.82, 136.75, 136.70, 136.23, 136.12, 136.08, 135.96, 135.21, 135.13, 135.05, 135.03, 135.00, 134.99, 134.94, 134.84, 134.67,

134.63, 134.37, 133.42, 133.26, 133.16, 133.12, 132.90, 132.08, 132.00, 131.92, 131.74, 131.00, 130.31, 130.23, 130.15, 129.78, 129.66, 129.59, 129.57, 129.45, 129.22, 128.98, 127.18, 127.08, 126.96, 126.88, 126.74, 126.67, 125.24, 124.15, 124.07, 123.56, 123.50, 123.47, 120.65, 120.59, 120.52, 120.21, 118.51, 117.31, 116.69, 116.66, 70.76 (J_{CP} = 122 Hz), 70.64 (J_{CP} = 122 Hz), 59.28, 55.04, 55.01, 54.97, 37.81, 37.58, 30.08, 29.96, 29.94 (The carbon signals of the empty and encapsulated ones were separately observed. The sum of carbon signal of each cage must be 82 in theory. Observed 204 (for three components, probably **4b**, H_2O@**4b**, and N_2@**4b**). One carbonyl, 32 sp^2, and 9 sp^3 carbon signals are overlapped.); ^{31}P (202 MHz, benzene-d_6) 13.50, 13.44, 13.42 (The ^{31}P signal of the empty and encapsulated ones was separately observed.); HRMS (APCI) *m*/*z*: $[M+H]^+$ Calcd for $C_{100}H_{42}N_2O_3PS_2$ (**4b**+H) 1413.242369; Found 1413.2314.

5b: ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, 1H, *J* = 8.0 Hz), 7.53 (t, 1H, *J* = 8.0 Hz), 7.24 (d, 1H, *J* = 8.0 Hz), 7.18 (d, 1H, *J* = 8.0 Hz), 7.16 (d, 1H, *J* = 8.0 Hz), 6.98 (d, 0.36H, *J* = 8.0 Hz), 6.97 (d, 0.64H, *J* = 8.0 Hz), 6.90 (d, 0.64H, *J* = 10.3 Hz), 6.88 (d, 0.36H, *J* = 10.3 Hz), 6.28 (d, 0.64H, *J* = 10.3 Hz), 6.26 (d, 0.36H, *J* = 10.3 Hz), 4.45 (d, 0.64H, *J* = 21.8 Hz), 4.37 (d, 0.36H, *J* = 21.8 Hz), 4.19 (d, 0.64H, *J* = 21.8 Hz), 4.16 (d, 0.36H, *J* = 21.8 Hz), 1.243 (s, 3.24H), 1.240 (s, 5.76H), 1.192 (s, 3.24H), 1.187 (s, 5.76H), –10.83 (s, 0.86H) (The proton signals of the empty and encapsulated ones were separately observed.); ^{13}C NMR (201 MHz, $CDCl_3$) δ 196.50, 194.79, 194.55, 184.89, 168.75, 168.21, 164.37, 162.51, 154.39, 152.67, 151.63, 150.88, 150.73, 150.47, 150.25, 149.71, 149.38, 149.27, 149.05, 148.93, 148.73, 148.71, 148.61, 148.55, 148.45, 148.34, 148.32, 148.22, 148.19, 146.56, 146.49, 146.48, 146.30, 146.21, 145.94, 145.27, 144.90, 144.86, 144.75, 144.69, 144.23, 144.13, 143.95, 143.87, 143.85, 143.82, 143.62, 143.57, 143.36, 143.17, 143.12, 143.00, 142.88, 142.86, 142.72, 142.70, 142.50, 141.36, 141.17, 140.95, 139.34, 138.80, 138.76, 138.73, 138.58, 138.53, 138.51, 138.48, 138.34, 138.07, 138.02, 137.97, 137.53, 137.44, 137.36, 137.08, 136.94, 136.90, 136.51, 134.99, 134.42, 134.22, 134.12, 134.06, 133.93, 133.75, 133.70, 133.51, 131.12, 131.04, 130.38, 130.29, 130.02, 129.85, 129.82, 129.41, 129.36, 129.30, 129.12, 129.03, 128.93, 128.80, 128.05, 127.91, 127.78, 127.67, 126.96, 126.84, 126.76, 126.54, 126.44, 125.05, 124.98, 124.95, 124.45, 123.96, 123.93, 123.88, 121.80, 121.76, 121.55, 121.49, 119.91, 119.86, 119.62, 119.57, 119.10, 118.16, 117.41, 117.38, 116.90, 116.88, 59.95, 54.20, 54.15, 43.46, 43.41, 37.73, 37.63, 29.87, 29.70 (The sum of carbon signals must be 78 in theory. Observed 139 (for two components, **5b** and H_2O@**5b**).Two carbonyl, 10 sp^2, and five sp^3 carbon signals are overlapped.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{82}H_{28}N_2O_3S_2$ (**5b**) 1152.1547; Found 1152.1521.

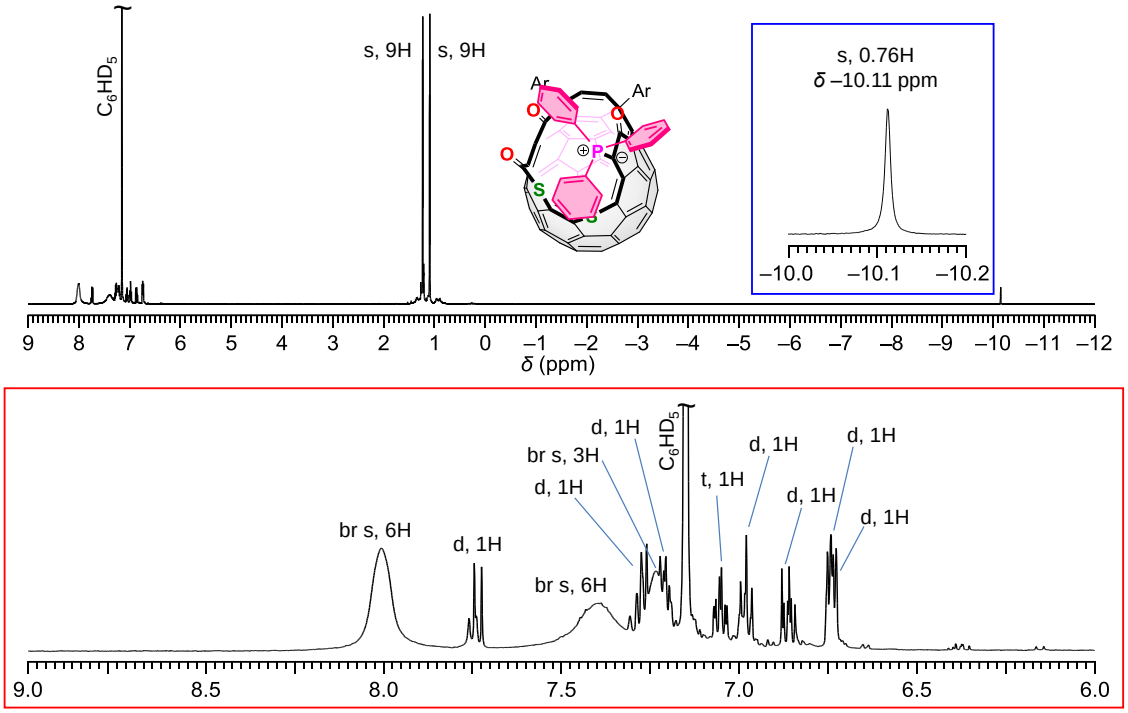


Figure S4. ^{1}H NMR spectra (500 MHz, benzene-d_6) of **4b**.

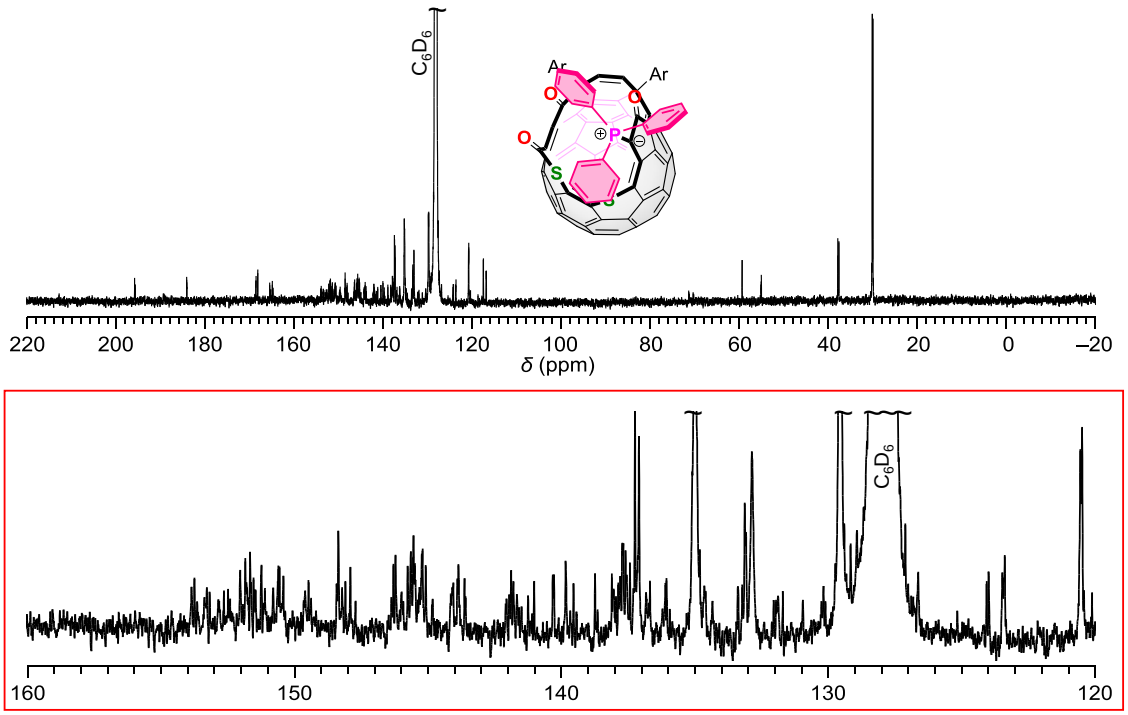


Figure S5. ^{13}C NMR spectra (126 MHz, benzene-d_6) of **4b**.

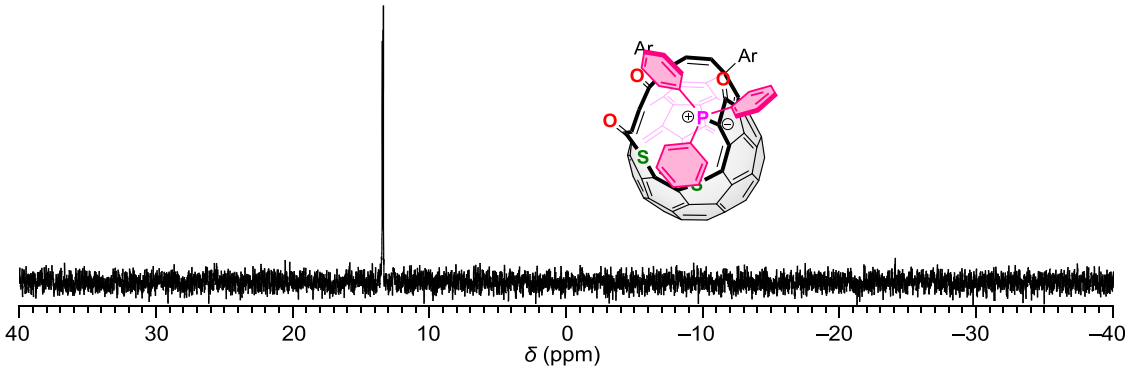


Figure S6. ^{31}P NMR spectrum (202 MHz, benzene-d_6) of **4b**.

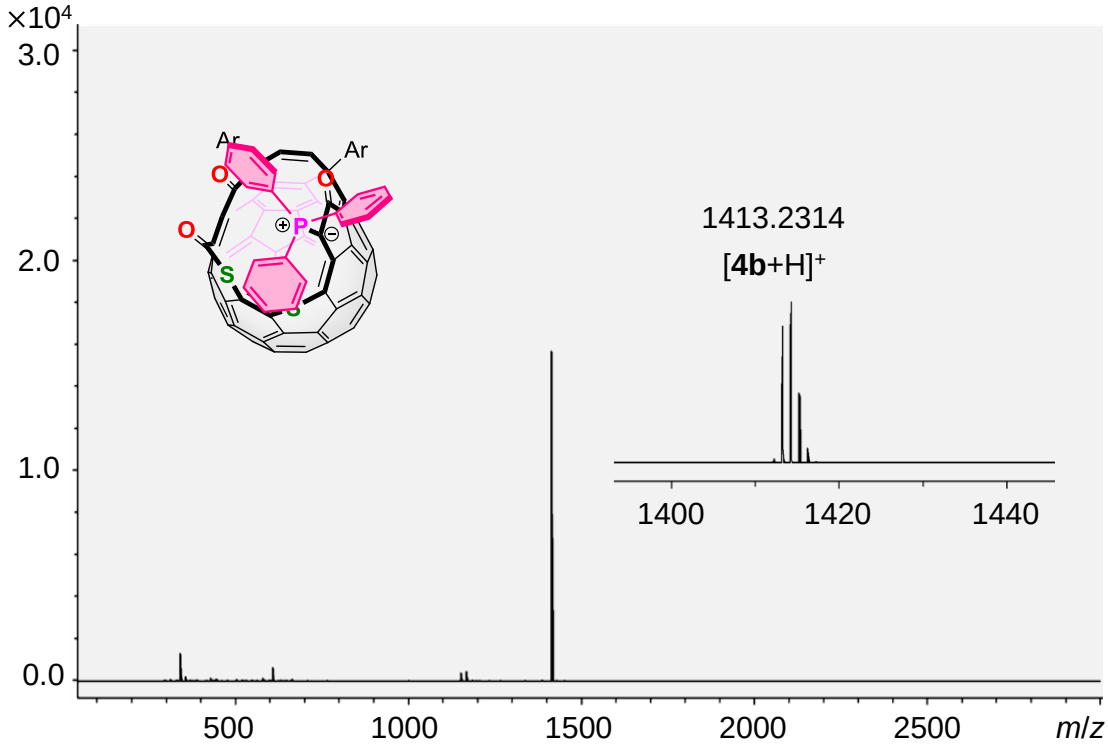


Figure S7. APCI mass spectra (positive ion mode) of **4b**.

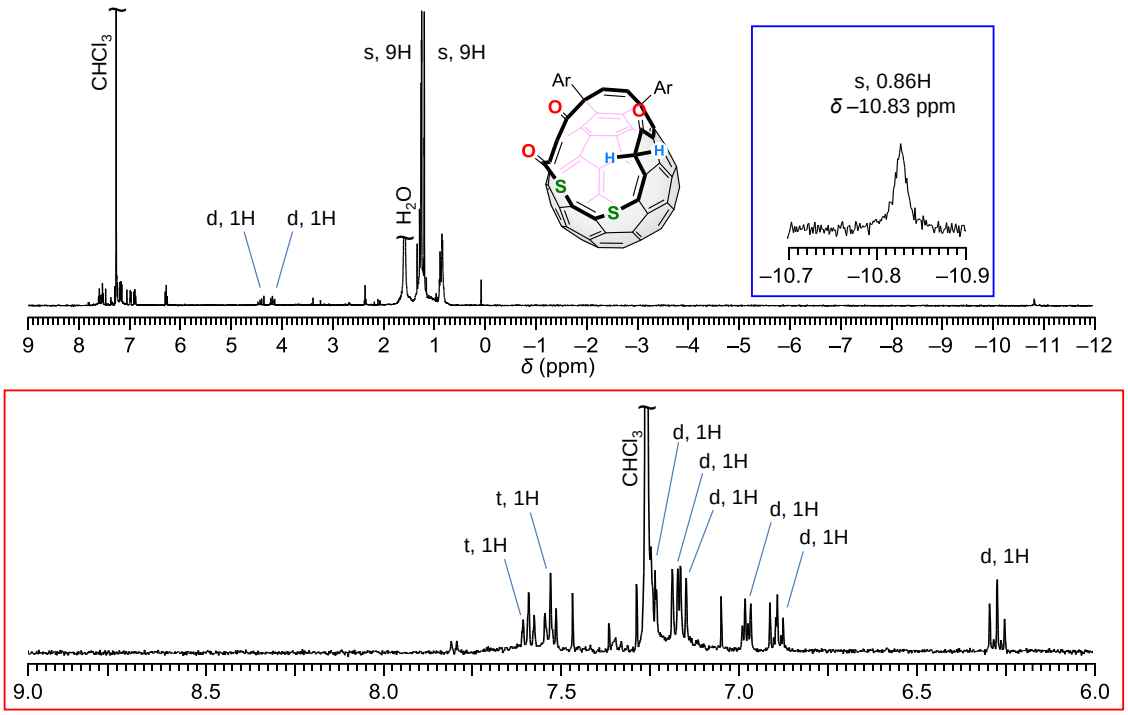


Figure S8. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **5b**.

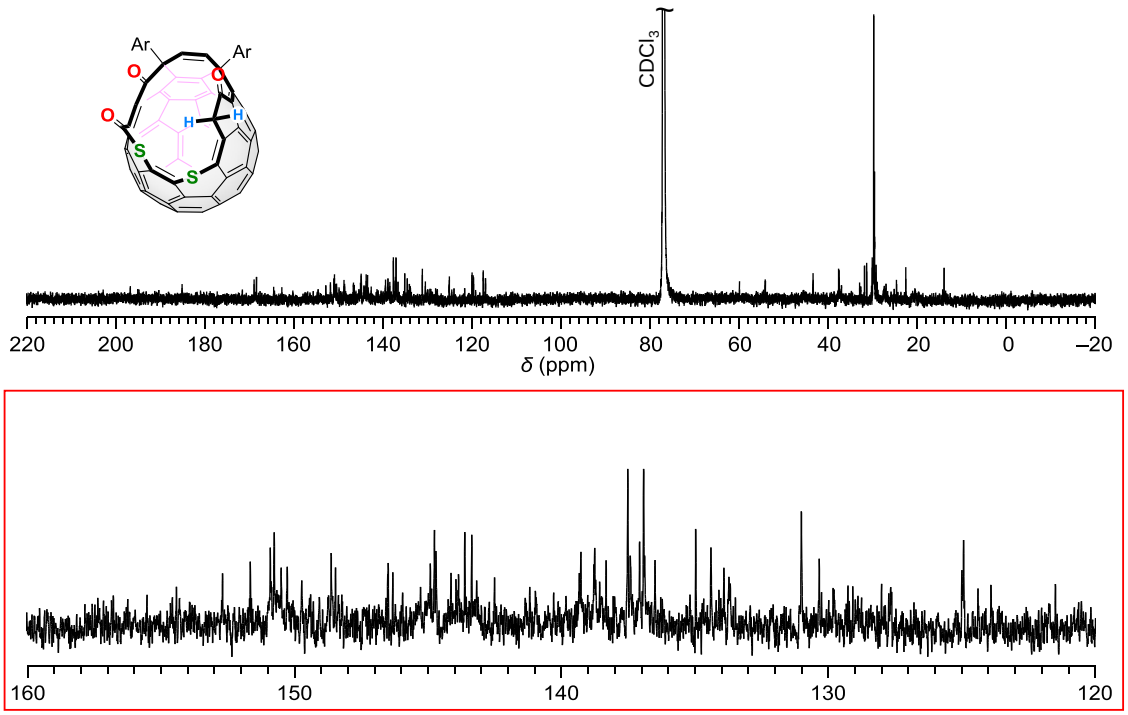


Figure S9. ^{13}C NMR spectra (201 MHz, $CDCl_3$) of **5b**.

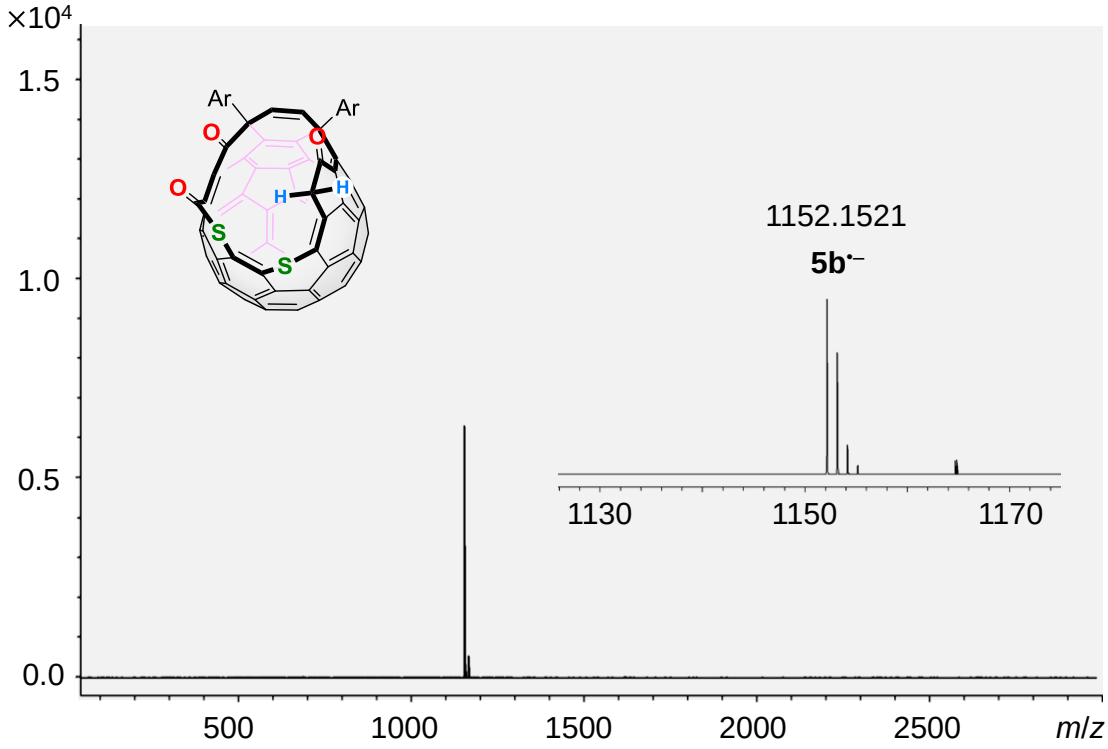
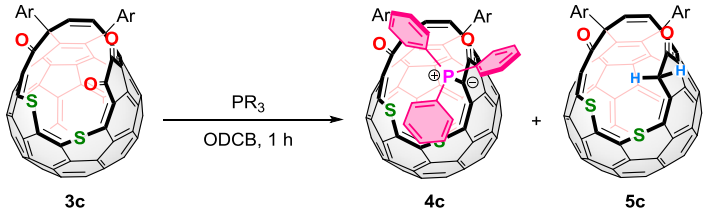


Figure S10. APCI mass spectrum (negative ion mode) of **5b**.

3.5. Reaction of 3b with PR_3



3c **4c** **5c**

PPh_3 (20 equiv), 180 °C	40%	18%
$P(OMe)_3$ (10 equiv), 180 °C	–	30%
PMe_3 (20 equiv), 60 °C	–	62%

[Reaction with PPh_3]

Powdery **3c** (20.0 mg, 17.6 μmol) and PPh_3 (92.0 mg, 351 μmol, 20.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.600 mL) was added and the resulting solution was heated at 180 °C for 1 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (toluene/hexane (1:1) to (3:1)) to give **5c** (3.59 mg, 3.19 μmol, 18%), unreacted **3c** (5.42 mg, 2.70 μmol, 15%), and **4c** (9.69 mg, 6.99 μmol, 40%) as brown powders.

[Reaction with $P(OMe)_3$]

Powdery **3c** (10.0 mg, 8.78 μmol) was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.600 mL) and $P(OMe)_3$ (10.4 μL, ρ = 1.052 g/mL, 88.2 μmol, 10.0 equiv) were added and the resulting solution was heated at 180 °C for 1 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (toluene/hexane (1:1)) to give **5c** (2.95 mg, 2.62 μmol, 30%) as a brown powder.

[Reaction with PMe_3]

Powdery **3c** (10.0 mg, 8.78 μmol) was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.300 mL) and PMe_3 (1.0 M in toluene, 176 μL, 176 μmol, 20.0 equiv) were added and the resulting solution was heated at 60 °C for 1 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/EtOAc (100:1)) to give **5c** (6.10 mg, 5.42 μmol, 62%) as a brown powder.

4c: ^{1}H NMR (500 MHz, benzene-d_6) δ 8.17 (dd, 6H, J = 8.0 Hz, J_{HP} = 12.6 Hz), 7.75 (d, 0.65H, J = 10.3 Hz), 7.74 (d, 0.35H, J = 10.3 Hz), 7.42 (d, 0.35H, J = 8.0 Hz), 7.41 (d, 0.65H, J = 8.0 Hz), 7.43–7.33 (m, 6H), 7.282 (d, 0.35H, J = 8.0 Hz), 7.275 (d, 0.65H, J = 8.0 Hz), 7.22 (br t, 3H, J = 8.0 Hz), 7.12 (t, 1H, J = 8.0 Hz), 7.01 (t, 1H, J = 8.0 Hz), 6.96 (d, 0.65H, J = 10.3 Hz), 6.95 (d, 0.35H, J = 10.3 Hz), 6.77 (d, 1H, J = 8.0 Hz), 6.76 (d, 1H, J = 8.0 Hz), 1.24 (s, 3.15H), 1.23 (s, 5.85H), 1.133 (s, 3.15H), 1.126 (s, 5.85H), –10.45 (s, 1.30H) (The proton signals of the empty and encapsulated ones were separately observed.); ^{13}C NMR (126 MHz, benzene-d_6) δ 198.89, 188.91, 188.83, 168.04, 167.99, 167.96, 167.83, 165.29, 164.47, 157.71, 154.14, 154.11, 153.91, 153.23, 152.22, 151.85, 151.34, 151.06, 150.89, 150.71, 150.68, 150.23, 149.94, 149.90, 149.74, 148.62, 148.60, 148.35, 148.18, 147.72, 146.02, 145.91, 145.85, 145.82, 145.68, 145.62, 145.38, 145.30, 145.28, 145.21, 145.18, 145.12, 144.98, 144.75, 144.68, 143.93, 143.83, 143.60, 143.57, 142.55, 142.51, 142.43, 142.29, 141.71, 141.52, 140.78, 140.16, 139.78, 138.10, 138.04, 137.97, 137.93, 137.82, 137.74, 137.34, 137.27, 137.19, 137.06, 136.56, 136.11, 135.70, 135.43, 135.25, 135.14, 135.07, 134.07, 133.57, 132.87, 132.74, 132.30, 132.24, 131.01, 129.90, 129.66, 129.54, 129.43, 129.28, 125.91, 125.64, 124.90, 123.49, 123.39, 121.07, 121.01, 120.47, 120.44, 117.36, 117.34, 116.65, 116.61, 70.85 (J_{CP} = 120 Hz), 58.68, 55.10, 55.07, 37.73, 37.67, 37.60, 30.42, 30.11, 29.97 (The carbon signals of the empty and encapsulated ones were separately observed. The sum of carbon signal of each cage must be 81 in theory. Observed 110 (for two components, **4c** and H_2O@**4c**). One carbonyl, 48 sp^2, and 3 sp^3 carbon signals are overlapped.); ^{31}P (202 MHz, benzene-d_6) 13.00, 12.93 (The ^{31}P signal of the empty and encapsulated ones was separately observed.); HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{99}H_{42}N_2O_2PS_2$ (**4c**+H) 1386.2453; Found 1385.2362.

5c: ^{1}H NMR (500 MHz, benzene-d_6) δ 7.27 (d, 1H, J = 10.3 Hz), 7.184 (d, 1H, J = 8.0 Hz), 7.175 (d, 1H, J = 8.0 Hz), 7.14 (t, 1H, J = 8.0 Hz), 7.07 (t, 1H, J = 8.0 Hz), 6.81 (d, 1H, J = 8.0 Hz), 6.74 (d, 1H, J = 8.0 Hz), 6.79 (d, 1H, J = 10.3 Hz), 4.70 (d, 0.30H, J = 21.8 Hz), 4.68 (d, 0.70H, J = 21.8 Hz), 3.70 (d, 0.30H, J = 21.8 Hz), 3.68 (d, 0.70H, J = 21.8 Hz), 1.201 (s, 2.7H), 1.196 (s, 6.3H), 1.160 (s, 2.7H), 1.156 (s, 6.3H), –11.09 (s, 1.20H) (The proton signals of the empty and encapsulated ones were separately observed.); ^{13}C NMR (201 MHz, benzene-d_6) δ 197.38, 197.37, 196.66, 196.57, 168.43, 168.41, 168.39, 165.08, 164.92, 163.22, 163.09, 159.36, 155.12, 155.08, 154.43, 154.41, 153.09, 152.95, 151.06, 150.94, 150.89, 150.76, 150.68, 150.64, 150.16, 150.09, 149.86, 149.76, 149.67, 149.63, 149.47, 149.43, 149.35, 149.32, 149.26, 149.08, 149.05, 148.71,

148.69, 148.65, 148.64, 148.32, 148.17, 148.14, 146.88, 146.75, 146.02, 145.84, 145.51, 145.31, 145.18, 145.08, 144.94, 144.87, 144.80, 144.66, 144.59, 144.25, 144.02, 143.83, 143.53, 143.43, 143.40, 143.38, 143.33, 143.18, 143.07, 142.85, 142.16, 142.01, 141.14, 141.12, 141.05, 140.90, 139.68, 139.65, 139.21, 139.19, 139.04, 139.00, 138.64, 138.57, 138.46, 138.44, 137.86, 137.73, 137.64, 137.46, 137.19, 137.18, 137.16, 137.09, 137.07, 137.03, 136.93, 136.79, 136.64, 136.63, 136.50, 136.40, 136.23, 135.58, 135.49, 134.19, 134.17, 133.51, 132.97, 132.65, 132.60, 132.43, 131.79, 131.75, 131.63, 131.21, 131.18, 131.15, 130.65, 129.91, 129.10, 128.50, 128.44, 127.66, 126.93, 126.42, 125.47, 120.29, 120.25, 120.22, 120.20, 117.56, 117.52, 117.03, 116.99, 59.14, 59.12, 54.71, 54.69, 43.78, 43.71, 37.70, 29.99, 29.95 (The carbon signals of the empty and encapsulated ones were separately observed. The sum of carbon signal of each cage must be 77 in theory. Observed 142 (for two components, **5c** and H_2O@**5c**). The 12 sp^2 carbon signals are overlapped in the aromatic region.); HRMS (APCI) *m*/*z*: $[M]^{\bullet-}$ Calcd for $C_{81}H_{28}N_2O_2S_2$ (**5c**) 1124.1598; Found 1124.1559.

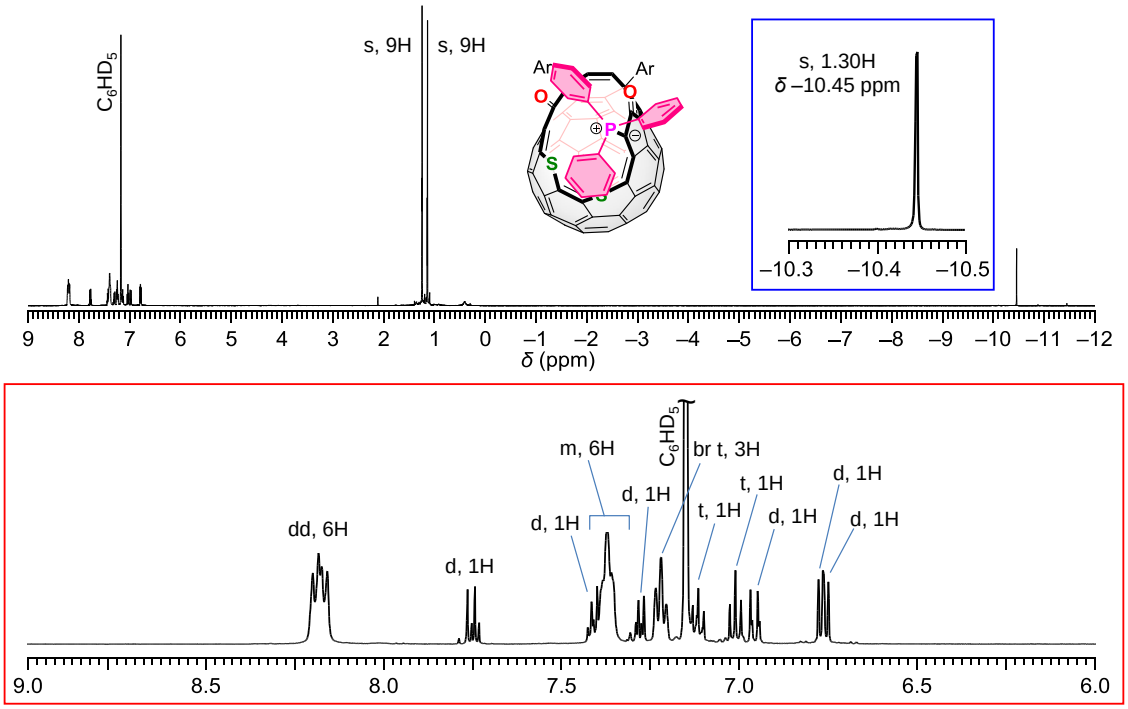


Figure S11. ^{1}H NMR spectra (500 MHz, benzene-d_6) of **4c**.

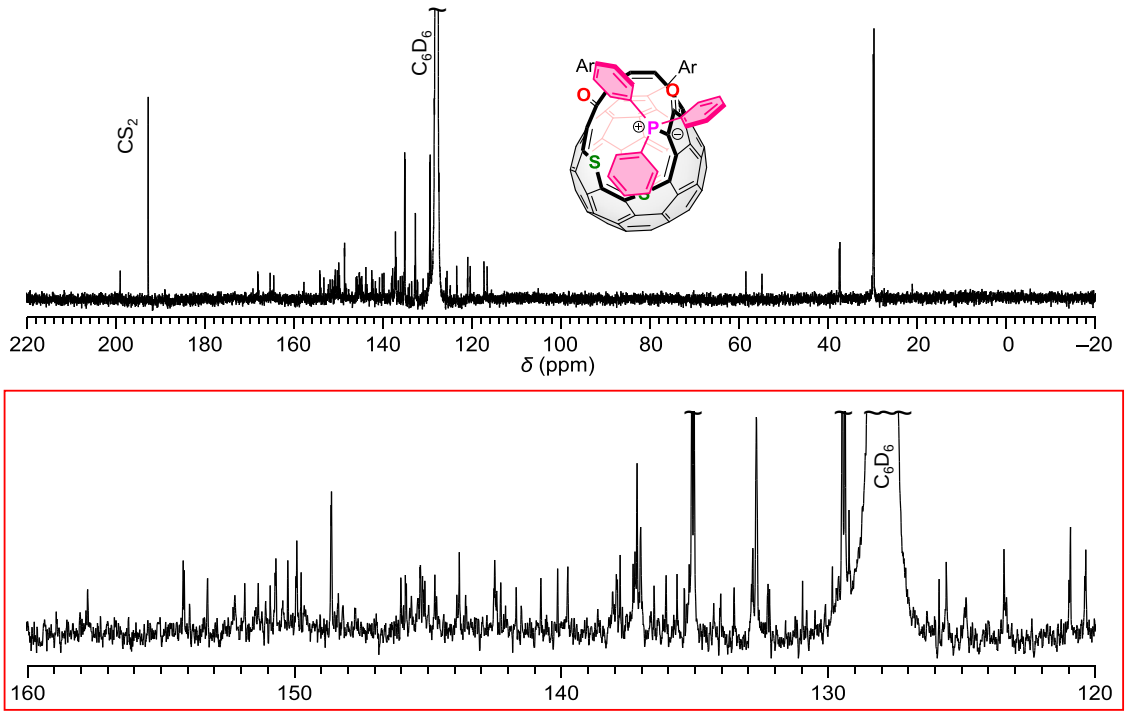


Figure S12. ^{13}C NMR spectra (126 MHz, benzene-d_6) of **4c**.

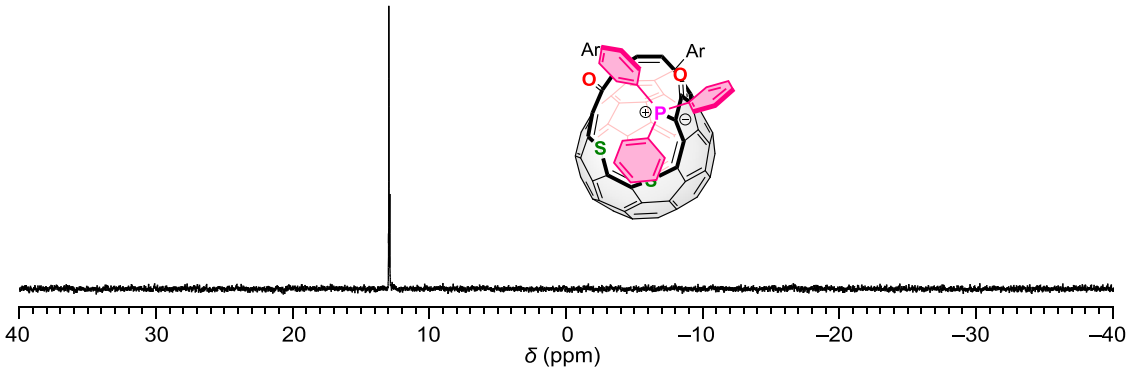


Figure S13. ^{31}P NMR spectrum (202 MHz, benzene-d_6) of **4c**.

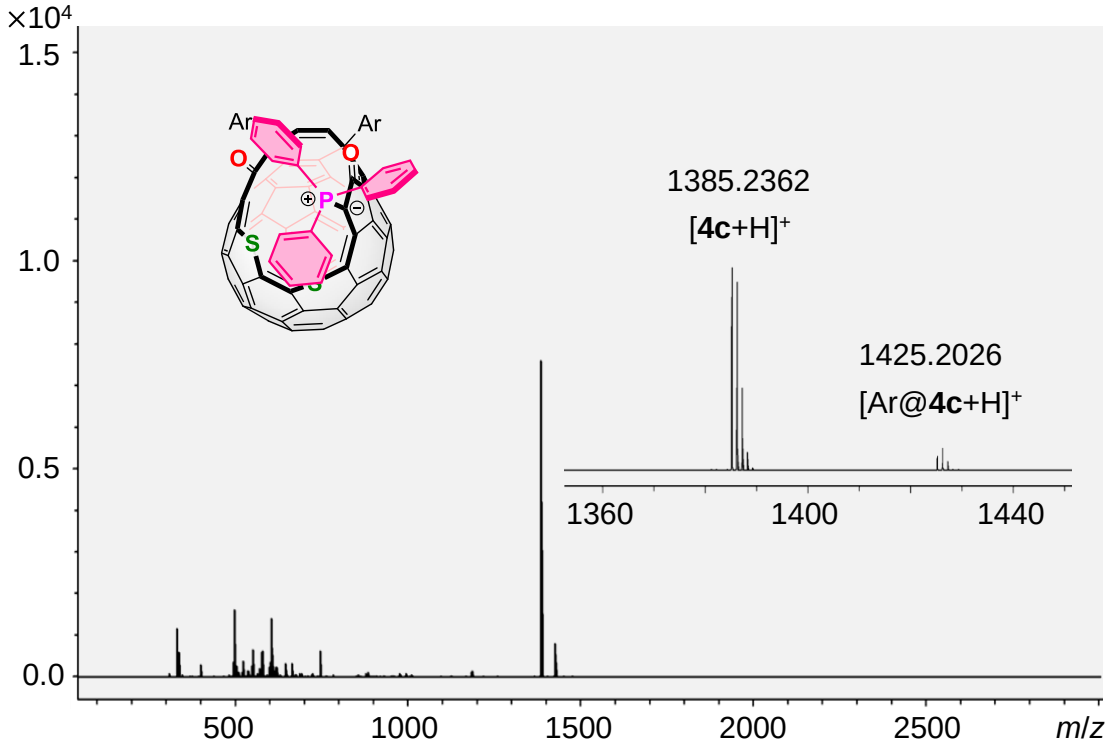


Figure S14. APCI mass spectra (positive ion mode) of **4c**.

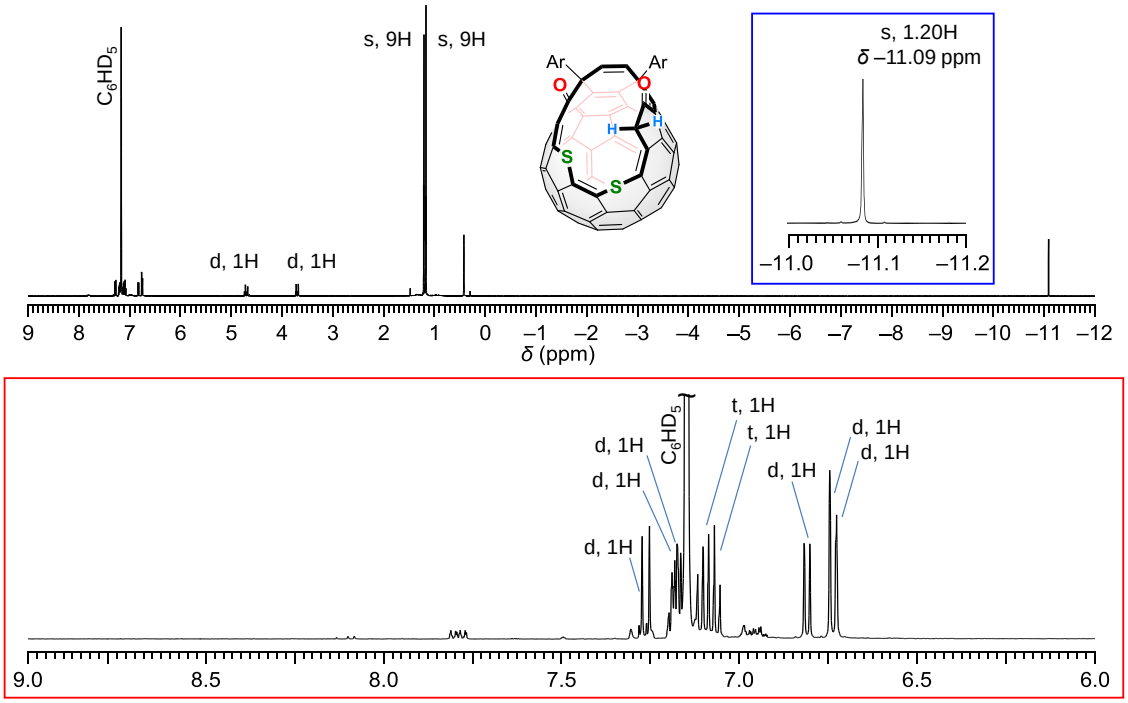


Figure S15. ^{1}H NMR spectra (500 MHz, benzene-d_6) of **5c**.

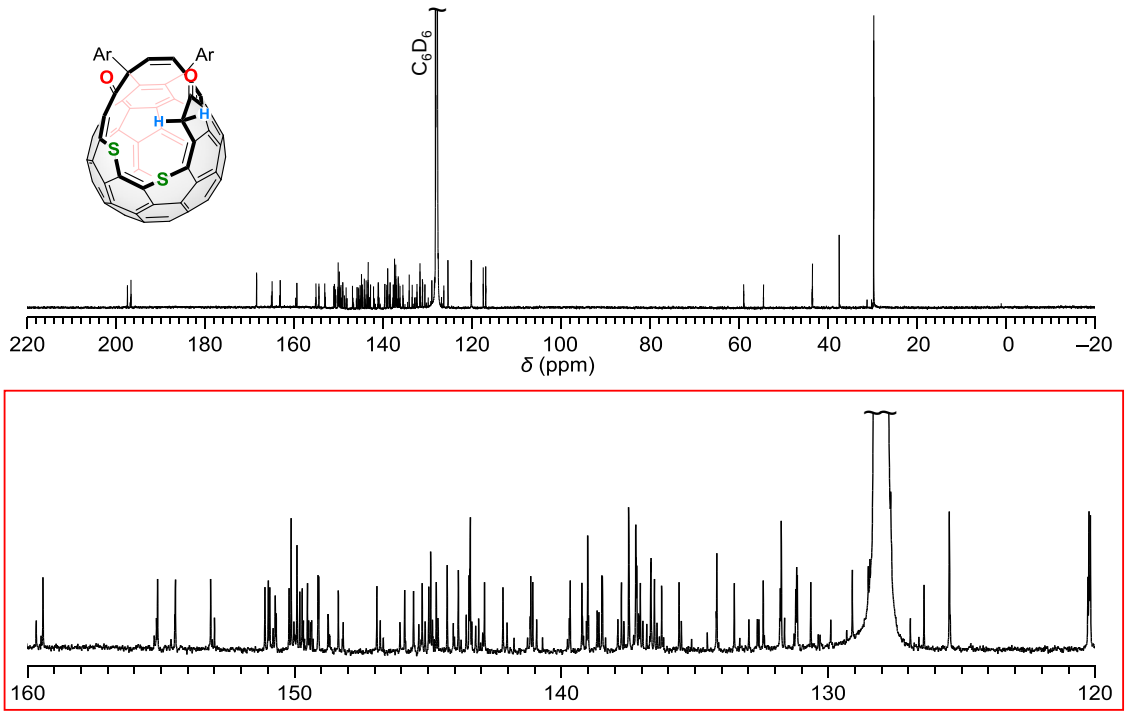


Figure S16. ^{13}C NMR spectra (201 MHz, benzene-d_6) of **5c**.

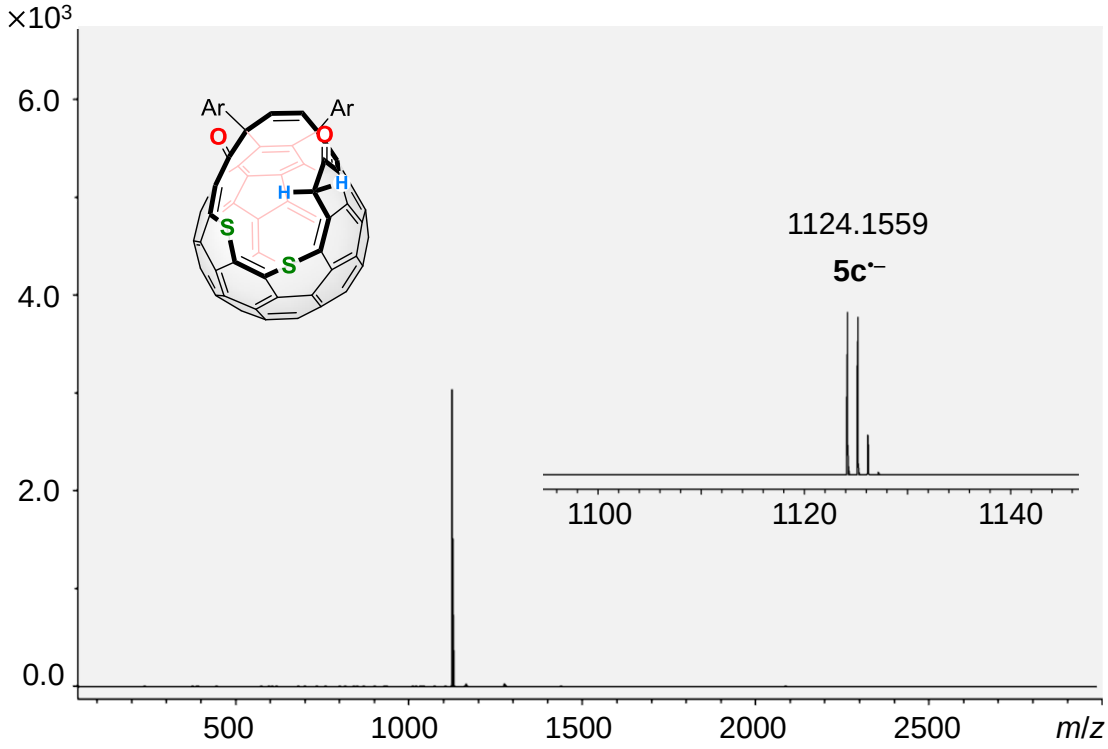


Figure S17. APCI mass spectra (negative ion mode) of **5c**.

4. H/D Exchange

Powdery **4a-Me** (5.00 mg, 4.18 μmol) was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (0.500 mL) and D_2O (7.57 μL, 4.18 μmol, 1.00 × 10^3 equiv) were added and the resulting solution was heated at 150 °C for 8 h (Aluminum block heater). After passing through a silica gel pad (CS_2/EtOAc (50:1)), the crude mixture was purified by HPLC equipped with the Buckyprep column (toluene, 7.5 mL/min, 50 °C) to give **5a**-d_2 (1.10 mg, 0.70 μmol, 23%) as a brown powder.

The reaction of **4a-Me** with water was conducted in a similar manner to obtain **5a**.[2]

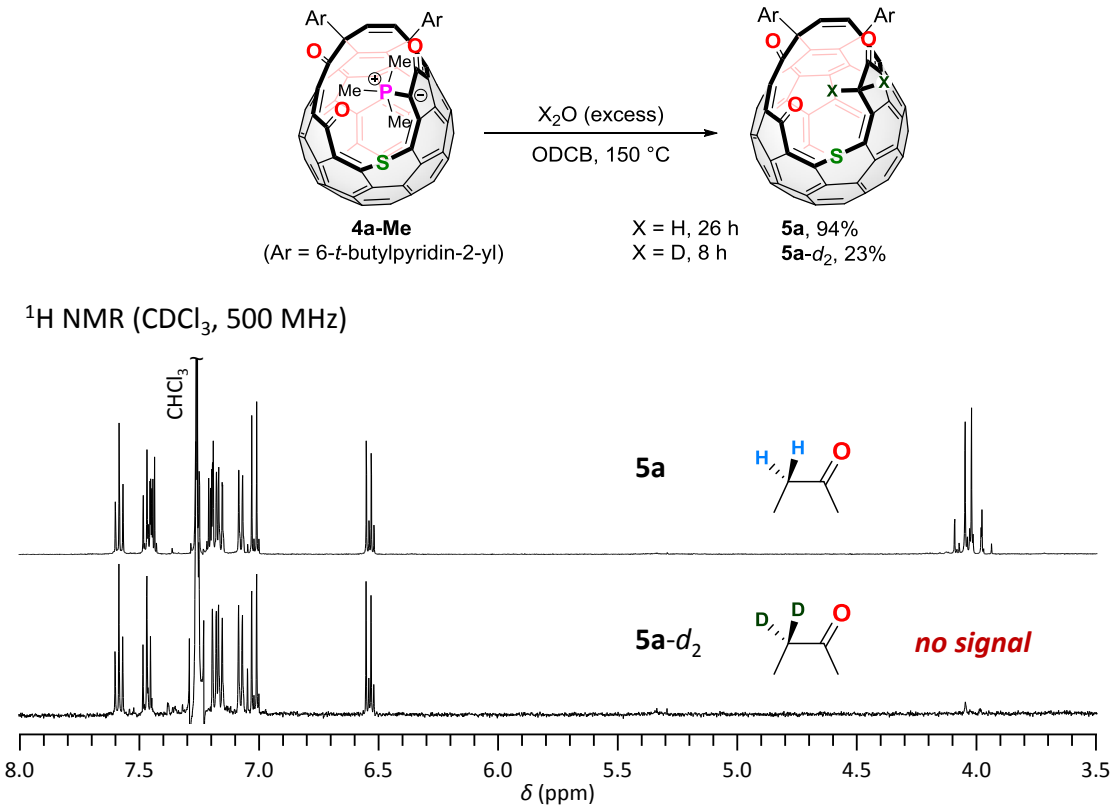


Figure S18. Hydrolysis of **4a-Me**.

To a solution of **5a** (5.03 mg, 4.47 μmol) in ODCB-d_4 (0.650 mL) which was placed into a shield NMR tube, three drops of D_2O were added and the resulting solution was heated at 150 °C for 37 h (oil bath). The quantitative conversion was confirmed by ^{1}H NMR as shown below. By passing through a silica gel pad, **6a**-*d* was converted into **5a**.

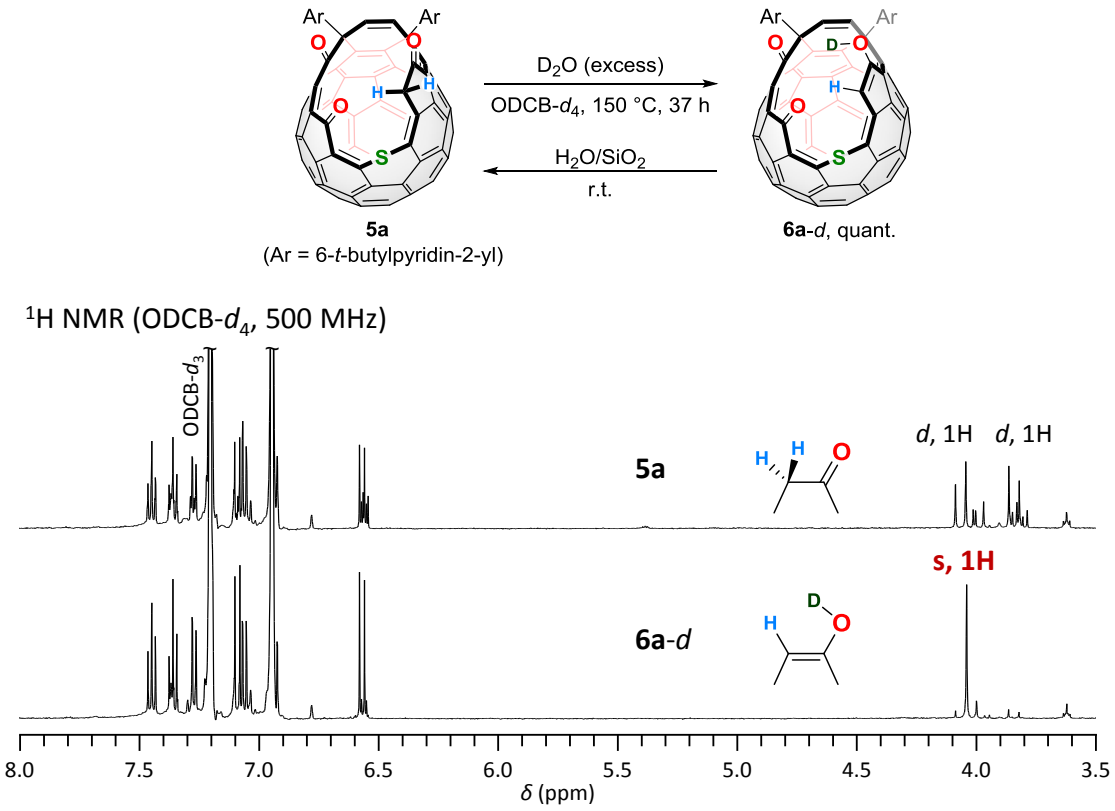


Figure S19. H/D exchange of **5a**.

5. DFT Calculations

5.1. Mulliken Charges

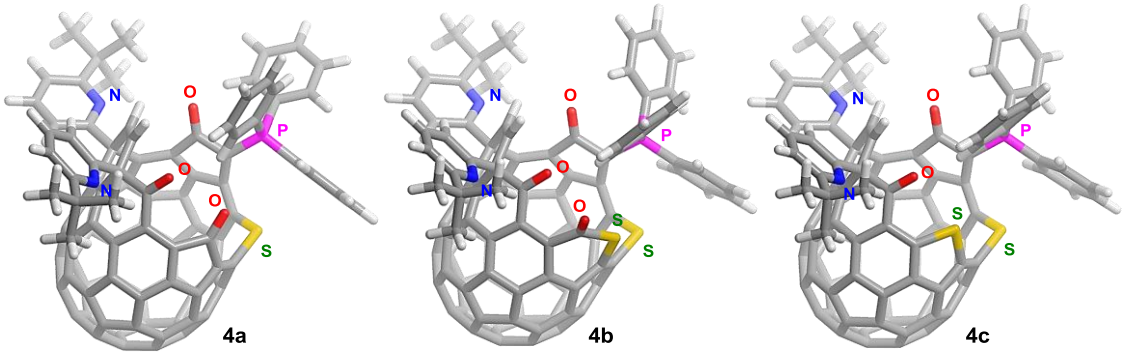
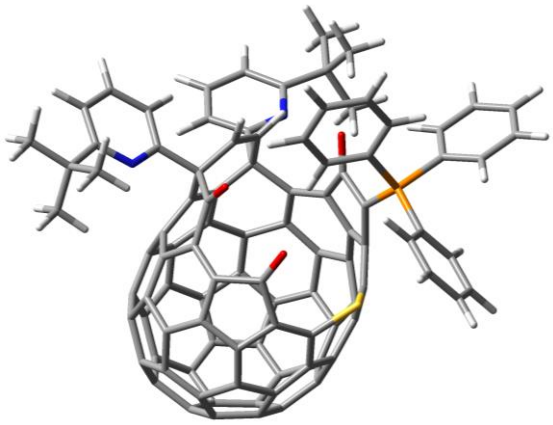


Figure S20. Optimized structures of **4a**–**c** (B3LYP/6-31G(d)) with Mulliken atomic charges (B3LYP/6-31G(d,p)).

Table S1. Optimized structure of **4a** (B3LYP/6-31G(d))



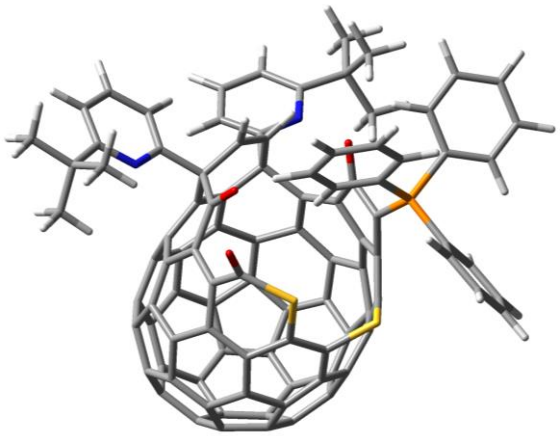
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.520897	3.068594	0.735046
2	6	0	0.935180	2.930852	-0.523420
3	6	0	0.120396	2.343320	-1.651925
4	6	0	0.689735	0.980735	-2.131787
5	6	0	1.785303	0.328488	-1.562593
6	6	0	2.858576	0.593456	-0.496753
7	6	0	3.158287	-0.697686	0.128662
8	6	0	2.390631	-1.734613	-0.560966
9	6	0	1.754167	-2.946151	-0.234487
10	6	0	0.814863	-3.602136	-1.143048
11	6	0	-0.338940	-4.407618	-0.686346
12	6	0	-0.764078	-4.343290	0.725774
13	6	0	0.010185	-3.572365	1.690990
14	6	0	-0.642462	-2.807652	2.656696
15	6	0	-0.249351	-1.413618	3.139722
16	6	0	-1.578674	-0.623351	3.058036
17	6	0	-1.817372	0.636651	2.496670
18	6	0	-0.759943	1.687455	2.395000
19	6	0	-0.862962	2.724368	1.220875
20	6	0	-1.733562	2.177080	0.106169
21	6	0	-1.316900	2.055799	-1.208594
22	6	0	-2.178842	1.420426	-2.182174
23	6	0	-1.593228	0.560530	-3.209214
24	6	0	-0.165327	0.244422	-3.071434
25	6	0	0.222595	-1.051325	-3.473412
26	6	0	1.186651	-1.753331	-2.691683
27	6	0	1.886270	-1.084795	-1.743417
28	6	0	0.742488	-3.097227	-2.463202
29	6	0	-0.367035	-3.305956	-3.338306
30	6	0	-0.688814	-2.037861	-3.978783
31	6	0	-2.000377	-1.696374	-4.222287
32	6	0	-2.453054	-0.368421	-3.852138
33	6	0	-3.848065	-0.507848	-3.484204
34	6	0	-4.383648	0.304598	-2.499519
35	6	0	-3.529486	1.263244	-1.845501
36	6	0	-3.942071	1.348325	-0.464870
37	6	0	-2.998988	1.618260	0.526010
38	6	0	-3.065370	0.866274	1.782202
39	6	0	-4.126121	-0.047589	1.942446
40	6	0	-3.899427	-1.309864	2.593357
41	6	0	-2.617103	-1.599159	3.035916
42	6	0	-2.054680	-2.908108	2.789131
43	6	0	-2.780833	-3.860483	2.103190
44	6	0	-2.118500	-4.587743	1.045992
45	6	0	-3.115699	-4.879911	0.052038
46	6	0	-2.732639	-4.949344	-1.272842
47	6	0	-1.344699	-4.744516	-1.641539
48	6	0	-1.373181	-4.174470	-2.974769
49	6	0	-2.744819	-3.875441	-3.341605
50	6	0	-3.057652	-2.655911	-3.958001
51	6	0	-4.221103	-1.915262	-3.530976
52	6	0	-5.086609	-2.446965	-2.568511
53	6	0	-5.659063	-1.583370	-1.549925
54	6	0	-5.316484	-0.229944	-1.527552
55	6	0	-5.036604	0.425393	-0.271146
56	6	0	-5.129434	-0.269593	0.924531
57	6	0	-5.485173	-1.678267	0.913675
58	6	0	-4.704324	-2.327816	1.942920
59	6	0	-4.147305	-3.588239	1.699731
60	6	0	-4.367136	-4.242421	0.431765
61	6	0	-5.164524	-3.641384	-0.545602
62	6	0	-4.769095	-3.717416	-1.941968
63	6	0	-3.598505	-4.393707	-2.300905
64	6	0	-5.729516	-2.326456	-0.303872
65	6	0	-1.539566	3.997788	1.796729
66	6	0	-1.413961	5.228333	1.141415
67	6	0	-2.055906	6.328471	1.697738
68	6	0	-2.788206	6.175645	2.875713
69	6	0	-2.866513	4.910904	3.469659
70	6	0	-3.636625	4.621798	4.766189
71	6	0	-4.258214	5.892074	5.373163
72	6	0	-2.660328	3.999694	5.790652
73	6	0	-4.763654	3.610624	4.452868
74	6	0	0.179709	3.369619	-2.809688
75	6	0	-0.805658	4.346985	-2.993612
76	6	0	-0.622236	5.274375	-4.014290
77	6	0	0.523745	5.209622	-4.806550
78	6	0	1.468083	4.207711	-4.550539
79	6	0	2.773020	4.035604	-5.342028
80	6	0	3.959027	4.141681	-4.355641
81	6	0	2.771163	2.630532	-5.986975
82	6	0	2.935910	5.095842	-6.444616
83	6	0	4.599590	0.485660	2.446658
84	6	0	3.380279	0.902831	2.995068
85	6	0	3.367186	1.840535	4.028094
86	6	0	4.566038	2.362721	4.515103
87	6	0	5.783791	1.948875	3.969111
88	6	0	5.804972	1.015057	2.934600
89	6	0	4.804141	-2.415296	1.898238
90	6	0	4.706400	-2.572038	3.286653
91	6	0	4.884467	-3.831506	3.860640
92	6	0	5.163179	-4.937257	3.056696
93	6	0	5.261695	-4.786108	1.671673
94	6	0	5.085022	-3.531190	1.091595
95	6	0	6.172275	-0.537375	0.183997
96	6	0	6.220193	0.332586	-0.918091
97	6	0	7.413845	0.510436	-1.617434
98	6	0	8.571299	-0.165369	-1.227830
99	6	0	8.534643	-1.022058	-0.127572

100	6	0	7.343227	-1.209270	0.574750
101	16	0	1.766414	-3.448994	1.483216
102	15	0	4.599562	-0.772529	1.127330
103	7	0	-2.248624	3.849665	2.916429
104	7	0	1.278142	3.313035	-3.565131
105	8	0	0.858229	-1.015542	3.413536
106	8	0	3.451542	1.656999	-0.282717
107	8	0	0.146967	1.763857	3.200921
108	1	0	1.199016	3.461594	1.486127
109	1	0	1.950297	3.201452	-0.783906
110	1	0	-0.823512	5.313044	0.235673
111	1	0	-1.983659	7.303459	1.222320
112	1	0	-3.284048	7.030740	3.319163
113	1	0	-4.990976	6.353732	4.700738
114	1	0	-3.497001	6.641745	5.619762
115	1	0	-4.781380	5.637923	6.301707
116	1	0	-3.198011	3.724297	6.705852
117	1	0	-1.870230	4.709967	6.062606
118	1	0	-2.184068	3.105585	5.380512
119	1	0	-5.486459	4.031999	3.743711
120	1	0	-5.303895	3.349147	5.370738
121	1	0	-4.355411	2.694614	4.017693
122	1	0	-1.687684	4.375383	-2.363065
123	1	0	-1.367958	6.044728	-4.194322
124	1	0	0.673052	5.927755	-5.603893
125	1	0	4.007721	5.139619	-3.903143
126	1	0	4.905327	3.962474	-4.880668
127	1	0	3.857971	3.408573	-3.550808
128	1	0	3.716229	2.454234	-6.514976
129	1	0	1.954623	2.530150	-6.712226
130	1	0	2.645815	1.857447	-5.224283
131	1	0	3.879845	4.932508	-6.976624
132	1	0	2.961410	6.112635	-6.034939
133	1	0	2.128974	5.043934	-7.185225
134	1	0	2.443986	0.501046	2.630055
135	1	0	2.410867	2.156518	4.431416
136	1	0	4.554087	3.096128	5.317335
137	1	0	6.718549	2.359677	4.341018
138	1	0	6.754109	0.713196	2.503666
139	1	0	4.478753	-1.718295	3.915650
140	1	0	4.803190	-3.945752	4.937816
141	1	0	5.301047	-5.916456	3.506915
142	1	0	5.474088	-5.644893	1.041363
143	1	0	5.169147	-3.421758	0.014330
144	1	0	5.337454	0.887258	-1.210270
145	1	0	7.436256	1.184663	-2.469066
146	1	0	9.497902	-0.023370	-1.777556
147	1	0	9.430755	-1.550870	0.185650
148	1	0	7.330344	-1.886257	1.422303

The total electronic energy was calculated to be –4909.8675845 Hartree.

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

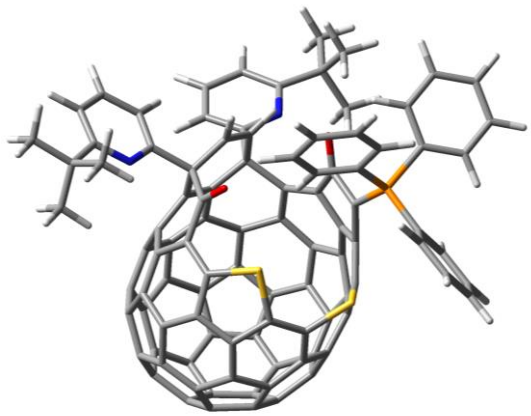


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.280572	3.269330	-0.509228
2	6	0	-0.706351	3.071307	0.737389
3	6	0	0.068901	2.365783	1.824796
4	6	0	-0.565008	1.008178	2.236283
5	6	0	-1.684880	0.416181	1.643349
6	6	0	-2.728171	0.743313	0.558381
7	6	0	-3.147421	-0.537337	-0.026358
8	6	0	-2.436712	-1.616045	0.651221
9	6	0	-1.935024	-2.890454	0.343784
10	6	0	-1.017248	-3.590160	1.242597
11	6	0	0.073064	-4.455538	0.758223
12	6	0	0.452656	-4.380824	-0.662583
13	6	0	-0.341200	-3.650900	-1.623947
14	6	0	0.260759	-2.919386	-2.644837
15	16	0	-0.706394	-1.928883	-3.759492
16	6	0	1.583605	-0.369650	-3.187100
17	6	0	1.897813	0.798067	-2.475726
18	6	0	0.856690	1.854304	-2.241836
19	6	0	1.066116	2.839482	-1.033152
20	6	0	1.902260	2.184868	0.049000
21	6	0	1.488427	2.028018	1.361056
22	6	0	2.321126	1.304210	2.297057
23	6	0	1.695811	0.445062	3.299844
24	6	0	0.252284	0.209994	3.161593
25	6	0	-0.204965	-1.066459	3.549479
26	6	0	-1.217356	-1.701315	2.772944
27	6	0	-1.864697	-0.989035	1.819098
28	6	0	-0.872712	-3.076985	2.550599
29	6	0	0.241785	-3.355160	3.398470
30	6	0	0.651190	-2.111566	4.036312
31	6	0	1.984610	-1.852423	4.261475
32	6	0	2.508246	-0.546881	3.909590
33	6	0	3.887351	-0.760848	3.516126
34	6	0	4.457879	0.044387	2.546179
35	6	0	3.657183	1.077213	1.938987
36	6	0	4.051723	1.180522	0.556053
37	6	0	3.116465	1.553807	-0.405279
38	6	0	3.100362	0.844720	-1.683060
39	6	0	4.055557	-0.167025	-1.883613
40	6	0	3.670701	-1.395732	-2.523638
41	6	0	2.361608	-1.568243	-2.997043
42	6	0	1.700085	-2.851204	-2.747349
43	6	0	2.415999	-3.835994	-2.060571
44	6	0	1.785534	-4.624134	-1.030961
45	6	0	2.798367	-4.998891	-0.079651
46	6	0	2.458298	-5.100191	1.255169
47	6	0	1.093147	-4.840453	1.675460
48	6	0	1.188841	-4.280798	3.008477
49	6	0	2.584810	-4.059868	3.339231
50	6	0	2.979365	-2.868188	3.962869
51	6	0	4.175312	-2.188714	3.525445

52	6	0	4.984874	-2.749094	2.530782	102	15	0	-4.605598	-0.538360	-1.000809
53	6	0	5.585598	-1.896066	1.518647	103	7	0	2.376934	3.928726	-2.796584
54	6	0	5.334162	-0.521839	1.539393	104	7	0	-1.020624	3.279149	3.808162
55	6	0	5.070826	0.186441	0.308058	105	8	0	-3.188555	1.848916	0.265540
56	6	0	5.073762	-0.483897	-0.905612	106	8	0	-0.174469	1.921834	-2.881350
57	6	0	5.321335	-1.910232	-0.934271	107	1	0	-0.930227	3.760599	-1.225871
58	6	0	4.435513	-2.466728	-1.932158	108	1	0	-1.698515	3.398195	1.020310
59	6	0	3.808125	-3.682429	-1.703816	109	1	0	1.428601	5.340124	0.113962
60	6	0	4.059214	-4.409158	-0.481112	110	1	0	2.681530	7.266338	-0.892285
61	6	0	4.930386	-3.892728	0.479391	111	1	0	3.698662	7.007482	-3.140789
62	6	0	4.576745	-3.985220	1.886518	112	1	0	5.145592	6.259719	-4.757089
63	6	0	3.381338	-4.605241	2.266199	113	1	0	3.596927	6.749838	-5.478697
64	6	0	5.568932	-2.607390	0.252978	114	1	0	4.686474	5.671415	-6.358098
65	6	0	1.822356	4.069723	-1.591940	115	1	0	2.873292	3.964003	-6.675209
66	6	0	1.903721	5.258408	-0.857803	116	1	0	1.729542	5.011402	-5.814411
67	6	0	2.593642	6.323110	-1.425605	117	1	0	1.966159	3.337936	-5.280261
68	6	0	3.167169	6.177818	-2.690293	118	1	0	5.502973	3.844215	-3.992377
69	6	0	3.039415	4.956362	-3.361188	119	1	0	5.062428	3.283117	-5.616900
70	6	0	3.620273	4.675971	-4.754097	120	1	0	4.210906	2.645508	-4.193674
71	6	0	4.298842	5.915469	-5.362840	121	1	0	1.979013	4.263279	2.623634
72	6	0	2.474389	4.216752	-5.685533	122	1	0	1.764033	5.840646	4.549361
73	6	0	4.662789	3.540815	-4.628857	123	1	0	-0.260162	5.738678	5.983828
74	6	0	0.069624	3.326059	3.040586	124	1	0	-3.656588	5.202165	4.303365
75	6	0	1.103837	4.243021	3.264064	125	1	0	-4.591392	4.019183	5.238318
76	6	0	0.979431	5.118421	4.337879	126	1	0	-3.601558	3.486026	3.858833
77	6	0	-0.157298	5.062086	5.143946	127	1	0	-3.442676	2.364096	6.757330
78	6	0	-1.152508	4.122603	4.847250	128	1	0	-1.675874	2.349062	6.920684
79	6	0	-2.449629	3.964920	5.654207	129	1	0	-2.426136	1.793303	5.412989
80	6	0	-3.648371	4.180284	4.701993	130	1	0	-3.483716	4.816548	7.358666
81	6	0	-2.500590	2.527007	6.219913	131	1	0	-2.528847	6.005793	6.465910
82	6	0	-2.542921	4.967232	6.817514	132	1	0	-1.726268	4.837244	7.537648
83	6	0	-4.445034	0.327982	-2.597038	133	1	0	-2.303277	0.524314	-2.452953
84	6	0	-3.182155	0.714944	-3.056575	134	1	0	-2.066422	1.658120	-4.625307
85	6	0	-3.053837	1.365357	-4.286141	135	1	0	-4.085933	2.130159	-6.014286
86	6	0	-4.186644	1.627257	-5.056129	136	1	0	-6.337537	1.470425	-5.190002
87	6	0	-5.453638	1.254834	-4.595812	137	1	0	-6.575672	0.344736	-3.004026
88	6	0	-5.587326	0.614028	-3.366274	138	1	0	-5.361714	-2.015979	-3.449759
89	6	0	-5.145167	-2.257238	-1.313637	139	1	0	-6.159048	-4.318179	-3.828288
90	6	0	-5.470048	-2.689182	-2.606893	140	1	0	-6.392290	-5.893161	-1.918423
91	6	0	-5.917269	-3.993669	-2.820198	141	1	0	-5.806482	-5.142611	0.379418
92	6	0	-6.046308	-4.877361	-1.748876	142	1	0	-5.003314	-2.846301	0.767068
93	6	0	-5.719835	-4.456662	-0.458294	143	1	0	-5.315864	2.281231	-0.638675
94	6	0	-5.269556	-3.155406	-0.238555	144	1	0	-7.195210	3.434784	0.467933
95	6	0	-6.034559	0.297131	-0.179199	145	1	0	-8.990783	2.121399	1.582139
96	6	0	-6.100406	1.701821	-0.170084	146	1	0	-8.894989	-0.365140	1.554453
97	6	0	-7.159902	2.348909	0.464106	147	1	0	-7.040435	-1.520615	0.435591
98	6	0	-8.166237	1.611956	1.090573	148	6	0	0.404408	-0.515457	-4.093240
99	6	0	-8.111600	0.218402	1.078580	149	8	0	0.165448	0.182275	-5.048356
100	6	0	-7.053627	-0.436993	0.447474	---					
101	16	0	-2.103101	-3.545613	-1.321204	The total electronic energy was calculated to be –5308.0840323 Hartree.					

Table S3. Optimized structure of **4c** (B3LYP/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.474272	3.219321	-0.445680
2	6	0	-0.882819	2.960923	0.795210
3	6	0	-0.070429	2.247700	1.849533
4	6	0	-0.641955	0.844517	2.193963
5	6	0	-1.737092	0.237849	1.571198
6	6	0	-2.801093	0.578649	0.511711
7	6	0	-3.134797	-0.678044	-0.170223
8	6	0	-2.359181	-1.755906	0.438477
9	6	0	-1.754873	-2.955113	0.030728
10	6	0	-0.808495	-3.677986	0.882436
11	6	0	0.329670	-4.464774	0.359742
12	6	0	0.731220	-4.310998	-1.056383
13	6	0	-0.065976	-3.494616	-1.950898
14	6	0	0.558379	-2.615379	-2.829903
15	16	0	-0.085694	-0.996303	-3.321272
16	6	0	1.549850	-0.296024	-3.070308
17	6	0	1.829960	0.919020	-2.432765
18	6	0	0.739711	1.883855	-2.186520
19	6	0	0.889906	2.875985	-0.986246
20	6	0	1.776641	2.241892	0.073350
21	6	0	1.365185	2.001389	1.373306
22	6	0	2.229203	1.278157	2.281080
23	6	0	1.643362	0.336088	3.232463
24	6	0	0.214169	0.034673	3.072077
25	6	0	-0.175077	-1.286358	3.376611
26	6	0	-1.145010	-1.923969	2.550422
27	6	0	-1.839066	-1.184117	1.653211
28	6	0	-0.714731	-3.254604	2.228725
29	6	0	0.399122	-3.530131	3.078246
30	6	0	0.732352	-2.312363	3.804942
31	6	0	2.046767	-1.995109	4.063981
32	6	0	2.502309	-0.644709	3.794215
33	6	0	3.894497	-0.760922	3.407716
34	6	0	4.428544	0.126061	2.488983
35	6	0	3.577332	1.141886	1.923833
36	6	0	3.981960	1.342817	0.552677
37	6	0	3.036781	1.714216	-0.402928
38	6	0	3.081631	1.065440	-1.717736
39	6	0	4.116015	0.140870	-1.959777
40	6	0	3.835426	-1.072374	-2.675893
41	6	0	2.540490	-1.323846	-3.125620
42	6	0	1.975809	-2.640078	-2.983672
43	6	0	2.717964	-3.650928	-2.382808
44	6	0	2.089096	-4.493770	-1.403186
45	6	0	3.101898	-4.853150	-0.443024
46	6	0	2.737904	-5.030218	0.875783
47	6	0	1.352291	-4.854109	1.275554
48	6	0	1.398502	-4.374151	2.643178
49	6	0	2.774834	-4.105968	3.017767
50	6	0	3.097847	-2.936098	3.720184
51	6	0	4.261742	-2.169355	3.344403
52	6	0	5.112289	-2.627236	2.332717
53	6	0	5.680407	-1.688194	1.379483
54	6	0	5.348323	-0.334187	1.467533
55	6	0	5.065234	0.426622	0.271946
56	6	0	5.128703	-0.174735	-0.975117
57	6	0	5.465087	-1.583796	-1.077860
58	6	0	4.646793	-2.142042	-2.131022
59	6	0	4.090363	-3.413676	-1.983502
60	6	0	4.342865	-4.178662	-0.785322
61	6	0	5.158395	-3.658801	0.221967
62	6	0	4.783226	-3.845067	1.613425
63	6	0	3.615392	-4.546232	1.932183
64	6	0	5.725870	-2.329476	0.077923
65	6	0	1.567741	4.164654	-1.514405
66	6	0	1.608058	5.317825	-0.720822
67	6	0	2.231844	6.443785	-1.243444
68	6	0	2.786044	6.391846	-2.524085
69	6	0	2.703102	5.201834	-3.254304
70	6	0	3.275320	5.022449	-4.667654
71	6	0	3.893679	6.319676	-5.218154
72	6	0	2.135530	4.567157	-5.607427
73	6	0	4.365728	3.927267	-4.617853
74	6	0	-0.116251	3.149016	3.108666
75	6	0	0.872039	4.103247	3.379672
76	6	0	0.703259	4.920212	4.492843
77	6	0	-0.431062	4.771522	5.290553
78	6	0	-1.378756	3.799949	4.945803
79	6	0	-2.667079	3.540509	5.740565
80	6	0	-3.874263	3.733454	4.794166
81	6	0	-2.642309	2.078710	6.243436
82	6	0	-2.814021	4.486093	6.945239
83	6	0	-4.517530	0.318401	-2.640706
84	6	0	-3.299374	0.878937	-3.036945
85	6	0	-3.238677	1.677235	-4.181100
86	6	0	-4.389935	1.912295	-4.931959
87	6	0	-5.612484	1.361350	-4.534408
88	6	0	-5.681731	0.574610	-3.386835
89	6	0	-4.971329	-2.438478	-1.629758
90	6	0	-5.229348	-2.772370	-2.966573
91	6	0	-5.554534	-4.084507	-3.312450
92	6	0	-5.627006	-5.073329	-2.331411
93	6	0	-5.366124	-4.750264	-0.998502
94	6	0	-5.037748	-3.441733	-0.646439
95	6	0	-6.096725	-0.105110	-0.256829
96	6	0	-6.253905	1.276890	-0.045698
97	6	0	-7.370452	1.757851	0.636376

98	6	0	-8.344909	0.877493	1.109749	124	1	0	-3.938494	4.771019	4.443970
99	6	0	-8.200184	-0.492958	0.895679	125	1	0	-4.807980	3.495174	5.317889
100	6	0	-7.084238	-0.983555	0.216198	126	1	0	-3.786981	3.083631	3.919403
101	16	0	-1.828867	-3.413363	-1.700983	127	1	0	-3.576428	1.840994	6.766697
102	15	0	-4.593243	-0.718147	-1.140891	128	1	0	-1.812044	1.915438	6.941228
103	7	0	2.099999	4.114088	-2.735716	129	1	0	-2.523752	1.386443	5.405757
104	7	0	-1.204315	3.013996	3.868894	130	1	0	-3.746608	4.264832	7.476431
105	8	0	-3.336810	1.671575	0.309436	131	1	0	-2.852791	5.537974	6.637818
106	8	0	-0.280357	1.868991	-2.860664	132	1	0	-1.992809	4.368213	7.662300
107	1	0	-1.149962	3.703332	-1.143571	133	1	0	-2.403254	0.711387	-2.452716
108	1	0	-1.888059	3.228858	1.093771	134	1	0	-2.285653	2.111181	-4.464323
109	1	0	1.153635	5.324469	0.264201	135	1	0	-4.341097	2.532677	-5.823084
110	1	0	2.285517	7.360996	-0.662374	136	1	0	-6.512935	1.553176	-5.111613
111	1	0	3.269836	7.267431	-2.939955	137	1	0	-6.638712	0.169764	-3.069067
112	1	0	4.734533	6.665815	-4.605505	138	1	0	-5.164815	-2.015219	-3.739915
113	1	0	3.157407	7.129761	-5.281163	139	1	0	-5.746115	-4.332033	-4.352686
114	1	0	4.276990	6.143974	-6.229450	140	1	0	-5.878196	-6.094504	-2.604190
115	1	0	2.530021	4.367901	-6.611005	141	1	0	-5.409324	-5.517308	-0.230712
116	1	0	1.363465	5.341317	-5.694471	142	1	0	-4.823129	-3.206042	0.390907
117	1	0	1.662718	3.657102	-5.229221	143	1	0	-5.493127	1.963816	-0.392743
118	1	0	5.200924	4.231542	-3.975476	144	1	0	-7.475800	2.827087	0.797966
119	1	0	4.762755	3.741523	-5.623140	145	1	0	-9.214176	1.258186	1.639368
120	1	0	3.959281	2.991099	-4.226070	146	1	0	-8.957569	-1.186366	1.251053
121	1	0	1.746868	4.195877	2.745196	147	1	0	-7.000277	-2.050765	0.047330
122	1	0	1.451731	5.668596	4.741207	----------					
123	1	0	-0.569320	5.401667	6.160917	The total electronic energy was calculated to be –5194.74652 Hartree.					

5.2. Keto-Enol Tautomerization

For the calculations to be simplified, 6-*t*-butylpyridin-2-yl groups were replaced with 2-pyridyl groups for the following calculations.

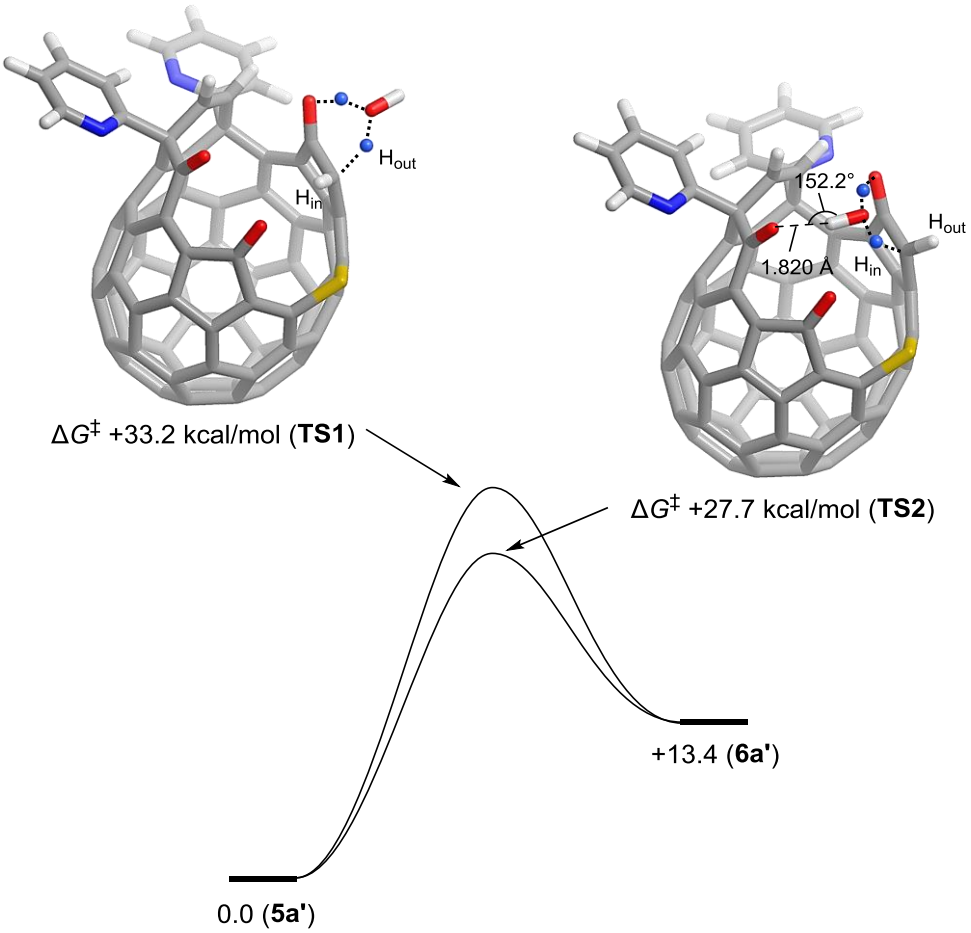


Figure S21. Two possible transition states, calculated at the M06-2X/6-31G(d,p) level of theory (298 K).

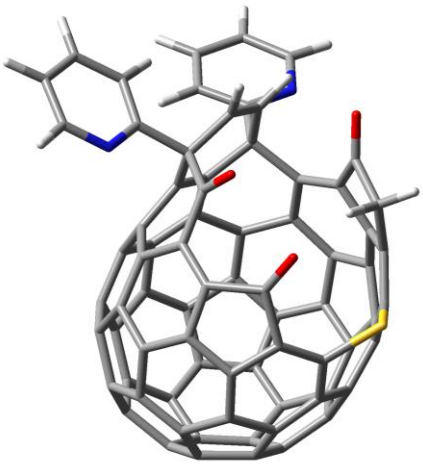
Table S4. Optimized structure of H_2O (M06-2X/6-31G(d,p))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.117808
2	1	0	0.000000	0.760256	-0.471232
3	1	0	0.000000	-0.760256	-0.471232

The total electronic energy was calculated to be –76.3839203 Hartree.

Table S5. Optimized structure of **5a'** (M06-2X/6-31G(d,p))



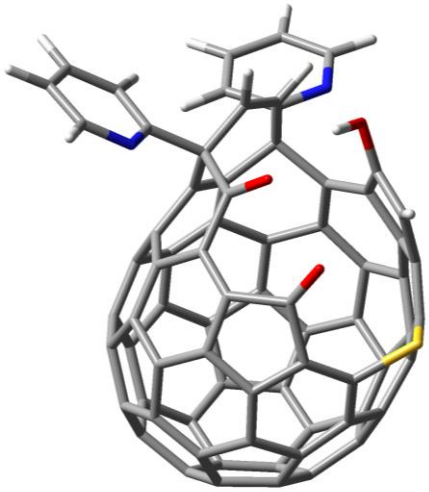
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.828553	0.615907	1.428005
2	6	0	3.845181	-0.700830	1.252686
3	6	0	3.030993	-1.437368	0.221722
4	6	0	1.859232	-2.208443	0.853598
5	6	0	1.490842	-2.123354	2.186944
6	6	0	1.987956	-1.413202	3.445583
7	6	0	-0.399847	-1.649563	3.542845
8	6	0	-1.738225	-1.337590	3.453049
9	6	0	-2.594180	-1.916798	2.428869
10	6	0	-3.694912	-1.160671	1.802940
11	6	0	-3.784703	0.295348	2.025290
12	6	0	-2.871058	0.949417	2.953211
13	6	0	-2.285867	2.153383	2.610380
14	6	0	-0.825875	2.548708	2.850502
15	6	0	-0.381805	3.102455	1.473903
16	6	0	0.775353	2.834836	0.752378
17	6	0	2.030048	2.356389	1.424709
18	6	0	3.060921	1.573196	0.560034
19	6	0	2.347883	0.876043	-0.572803
20	6	0	2.375031	-0.482943	-0.762372
21	6	0	1.551091	-1.089031	-1.782287
22	6	0	0.881942	-2.354582	-1.495773
23	6	0	0.937198	-2.824383	-0.102427
24	6	0	-0.203470	-3.478700	0.380509
25	6	0	-0.643738	-3.218090	1.714419
26	6	0	0.159734	-2.504674	2.550779
27	6	0	-2.059642	-2.998263	1.713961
28	6	0	-2.533298	-3.396330	0.422488
29	6	0	-1.383272	-3.697842	-0.408169
30	6	0	-1.388565	-3.360856	-1.738011
31	6	0	-0.227303	-2.693116	-2.293678
32	6	0	-0.726310	-1.812556	-3.330353
33	6	0	-0.097308	-0.609909	-3.568538
34	6	0	1.043644	-0.251391	-2.769936
35	6	0	0.995640	1.175854	-2.551394
36	6	0	1.472346	1.708360	-1.363224
37	6	0	0.706069	2.764911	-0.699128
38	6	0	-0.438360	3.237147	-1.353170
39	6	0	-1.611118	3.580894	-0.600360
40	6	0	-1.580232	3.419364	0.769290
41	6	0	-2.716354	2.832259	1.441082
42	6	0	-3.807328	2.403803	0.721813
43	6	0	-4.340741	1.097047	1.016991
44	6	0	-4.841173	0.560539	-0.220789
45	6	0	-4.786322	-0.797392	-0.425623
46	6	0	-4.231717	-1.661514	0.596970
47	6	0	-3.634679	-2.778626	-0.111465
48	6	0	-3.693594	-2.530829	-1.536874
49	6	0	-2.587864	-2.813485	-2.336457
50	6	0	-2.178709	-1.872077	-3.352103
51	6	0	-2.923586	-0.721695	-3.582522

52	6	0	-2.253617	0.538598	-3.849711
53	6	0	-0.867268	0.584507	-3.846422
54	6	0	-0.181558	1.684358	-3.211534
55	6	0	-0.890568	2.708955	-2.621708
56	6	0	-2.340358	2.675347	-2.627125
57	6	0	-2.788745	3.206189	-1.361293
58	6	0	-3.867253	2.619633	-0.709395
59	6	0	-4.534583	1.484702	-1.297993
60	6	0	-4.133701	0.997087	-2.535230
61	6	0	-4.082201	-0.436199	-2.758387
62	6	0	-4.434965	-1.311110	-1.738254
63	6	0	-3.007243	1.603375	-3.215801
64	6	0	4.025099	2.605114	-0.051973
65	6	0	5.259869	2.196198	-0.559499
66	6	0	6.083088	3.151506	-1.140451
67	6	0	5.648545	4.472668	-1.194467
68	6	0	4.400307	4.775898	-0.663220
69	6	0	3.980393	-2.414602	-0.485619
70	6	0	4.688437	-2.037661	-1.628508
71	6	0	5.591380	-2.940302	-2.176443
72	6	0	5.759966	-4.178021	-1.565134
73	6	0	5.014120	-4.452270	-0.423135
74	16	0	-2.316295	0.061375	4.381318
75	7	0	3.598822	3.866074	-0.104804
76	7	0	4.142792	-3.595142	0.111858
77	8	0	-0.173730	2.346090	3.835669
78	8	0	3.110684	-1.317333	3.865062
79	8	0	2.253622	2.572151	2.589347
80	6	0	0.740274	-0.948671	4.234175
81	1	0	4.395693	1.065147	2.237568
82	1	0	4.421179	-1.331690	1.920723
83	1	0	5.556101	1.154511	-0.487451
84	1	0	7.050861	2.869772	-1.543436
85	1	0	6.259870	5.251331	-1.636094
86	1	0	4.021536	5.794665	-0.683936
87	1	0	4.526140	-1.062190	-2.076113
88	1	0	6.153879	-2.681155	-3.067816
89	1	0	6.451739	-4.913757	-1.959087
90	1	0	5.118915	-5.406043	0.088572
91	1	0	0.661693	0.145096	4.187247
92	1	0	0.859698	-1.221819	5.286508

The total electronic energy was calculated to be –3559.2020868 Hartree.

Table S6. Optimized structure of **6a'** (M06-2X/6-31G(d,p))



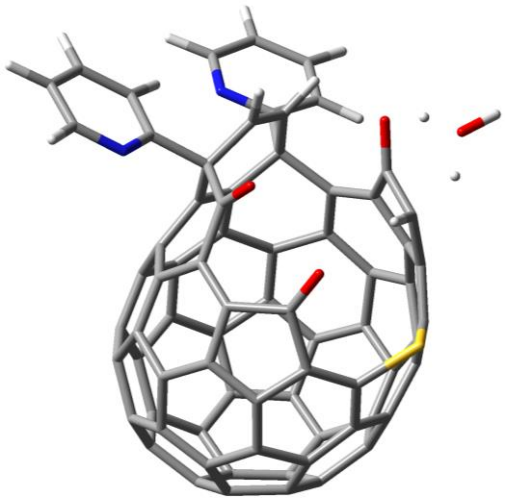
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.047690	0.697855	1.172456
2	6	0	3.977480	-0.627180	1.228581
3	6	0	3.049621	-1.468774	0.392627
4	6	0	1.836013	-2.048266	1.148892
5	6	0	1.445559	-1.731254	2.443534
6	6	0	1.789303	-0.680149	3.478934
7	6	0	-0.453350	-1.115537	3.690653
8	6	0	-1.804652	-0.857397	3.603046
9	6	0	-2.649136	-1.563080	2.653399
10	6	0	-3.732200	-0.880561	1.925400
11	6	0	-3.795904	0.594713	1.959786
12	6	0	-2.886568	1.345591	2.815839
13	6	0	-2.248769	2.467150	2.323701
14	6	0	-0.786406	2.859545	2.545031
15	6	0	-0.290835	3.169308	1.099224
16	6	0	0.865176	2.782344	0.426463
17	6	0	2.067835	2.247642	1.161937
18	6	0	3.160832	1.545880	0.306626
19	6	0	2.442075	0.718584	-0.726192
20	6	0	2.432844	-0.651816	-0.726945
21	6	0	1.579586	-1.363117	-1.645207
22	6	0	0.878394	-2.552932	-1.174962
23	6	0	0.916501	-2.808605	0.274818
24	6	0	-0.236850	-3.377812	0.824860
25	6	0	-0.682530	-2.928297	2.107084
26	6	0	0.110186	-2.101662	2.827065
27	6	0	-2.102700	-2.717995	2.073776
28	6	0	-2.570454	-3.273396	0.840577
29	6	0	-1.415108	-3.691540	0.064313
30	6	0	-1.410556	-3.538749	-1.297989
31	6	0	-0.238400	-2.971938	-1.927327
32	6	0	-0.718515	-2.227187	-3.077108
33	6	0	-0.065576	-1.081635	-3.475487
34	6	0	1.088144	-0.649960	-2.733757
35	6	0	1.068572	0.794955	-2.698509
36	6	0	1.560458	1.459518	-1.586839
37	6	0	0.807575	2.582903	-1.021981
38	6	0	-0.325377	2.998712	-1.733811
39	6	0	-1.491931	3.451354	-1.034267
40	6	0	-1.471064	3.451448	0.345055
41	6	0	-2.636354	2.996061	1.067736
42	6	0	-3.735120	2.513751	0.395511
43	6	0	-4.313046	1.272076	0.846845
44	6	0	-4.809327	0.594476	-0.321736
45	6	0	-4.779375	-0.779812	-0.353406
46	6	0	-4.254743	-1.518495	0.778542
47	6	0	-3.663903	-2.721482	0.223894
48	6	0	-3.705239	-2.654994	-1.226274
49	6	0	-2.601231	-3.053975	-1.973549
50	6	0	-2.172469	-2.260880	-3.098689
51	6	0	-2.896410	-1.135199	-3.480447
52	6	0	-2.198777	0.066508	-3.900929
53	6	0	-0.812165	0.083293	-3.902935
54	6	0	-0.102916	1.239234	-3.409272
55	6	0	-0.787312	2.339399	-2.939293
56	6	0	-2.237432	2.336864	-2.947275
57	6	0	-2.676690	3.025958	-1.756831

58	6	0	-3.774801	2.550981	-1.050565
59	6	0	-4.469944	1.370105	-1.501323
60	6	0	-4.073193	0.724298	-2.664474
61	6	0	-4.051527	-0.726803	-2.707698
62	6	0	-4.424817	-1.461217	-1.586606
63	6	0	-2.928936	1.217689	-3.406368
64	6	0	4.002181	2.625584	-0.381869
65	6	0	5.053450	2.247624	-1.220055
66	6	0	5.810516	3.243529	-1.818880
67	6	0	5.493145	4.575449	-1.560740
68	6	0	4.429688	4.846140	-0.708691
69	6	0	3.905649	-2.632018	-0.136507
70	6	0	4.535243	-2.583591	-1.380476
71	6	0	5.352108	-3.645711	-1.751510
72	6	0	5.516674	-4.708517	-0.870823
73	6	0	4.857058	-4.652754	0.353309
74	16	0	-2.398291	0.634281	4.360375
75	7	0	3.693488	3.895005	-0.125614
76	7	0	4.070737	-3.640896	0.719706
77	8	0	-0.181795	2.858785	3.577764
78	8	0	3.013389	-0.163961	3.696618
79	8	0	2.175272	2.307731	2.365308
80	6	0	0.671294	-0.315537	4.161863
81	1	0	4.738297	1.231656	1.819537
82	1	0	4.600816	-1.177701	1.926225
83	1	0	5.261012	1.193821	-1.380677
84	1	0	6.636746	2.988249	-2.474755
85	1	0	6.056825	5.386609	-2.007231
86	1	0	4.151541	5.871131	-0.477287
87	1	0	4.379166	-1.738014	-2.042137
88	1	0	5.851381	-3.642569	-2.715392
89	1	0	6.140634	-5.559063	-1.120354
90	1	0	4.964517	-5.457561	1.076608
91	1	0	0.624759	0.492160	4.879846
92	1	0	2.953024	0.803413	3.610782

The total electronic energy was calculated to be –3559.1797667 Hartree.

Table S7. Optimized structure of **TS1** (M06-2X/6-31G(d,p))



Standard orientation:

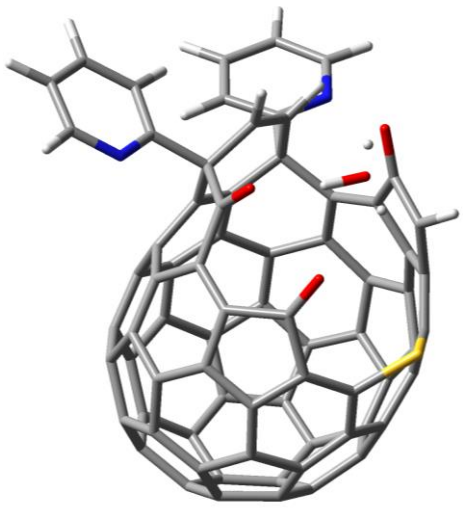
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.835663	-0.308191	1.259255
2	6	0	3.844649	-1.140880	0.225533
3	6	0	2.979407	-1.000527	-0.998330
4	6	0	1.842497	-2.037293	-1.035170
5	6	0	1.541465	-2.916257	-0.002190
6	6	0	2.035387	-3.185261	1.408410
7	6	0	-0.270542	-3.554768	1.376790
8	6	0	-1.620881	-3.338849	1.569818
9	6	0	-2.525512	-3.079860	0.459855
10	6	0	-3.654794	-2.138880	0.573223
11	6	0	-3.727385	-1.240706	1.742776
12	6	0	-2.766781	-1.375151	2.830604
13	6	0	-2.197337	-0.246801	3.390255
14	6	0	-0.727225	-0.072669	3.785567
15	6	0	-0.358729	1.299925	3.163534
16	6	0	0.760716	1.653133	2.418541
17	6	0	2.049147	0.889654	2.527212
18	6	0	3.018126	0.950189	1.315778
19	6	0	2.242784	1.189068	0.046754
20	6	0	2.267283	0.343195	-1.029932
21	6	0	1.398441	0.580973	-2.156669
22	6	0	0.745646	-0.554671	-2.799510
23	6	0	0.871175	-1.854627	-2.121120
24	6	0	-0.244572	-2.700342	-2.183874
25	6	0	-0.616662	-3.449556	-1.025463
26	6	0	0.224424	-3.483270	0.037410
27	6	0	-2.035180	-3.349737	-0.826855
28	6	0	-2.570900	-2.757279	-2.012653
29	6	0	-1.463525	-2.358630	-2.863491
30	6	0	-1.535177	-1.195851	-3.586245
31	6	0	-0.404299	-0.288916	-3.567872
32	6	0	-0.956958	1.044633	-3.690589
33	6	0	-0.341758	2.100213	-3.053551
34	6	0	0.838819	1.849436	-2.271240
35	6	0	0.802774	2.730311	-1.127572
36	6	0	1.337386	2.311549	0.080943
37	6	0	0.612487	2.597756	1.321036
38	6	0	-0.567249	3.346080	1.215500
39	6	0	-1.698100	3.029159	2.039716
40	6	0	-1.593477	1.967023	2.914523
41	6	0	-2.690105	1.034369	3.032998
42	6	0	-3.818691	1.181144	2.260981
43	6	0	-4.336509	0.014276	1.591586
44	6	0	-4.901518	0.463635	0.346463
45	6	0	-4.858636	-0.373331	-0.742696
46	6	0	-4.252441	-1.684359	-0.624170
47	6	0	-3.699166	-1.982196	-1.930902
48	6	0	-3.827066	-0.817124	-2.784516
49	6	0	-2.765934	-0.428928	-3.598716
50	6	0	-2.409426	0.965647	-3.694005
51	6	0	-3.166564	1.930187	-3.037862
52	6	0	-2.509895	3.047590	-2.383383
53	6	0	-1.125247	3.128877	-2.401826
54	6	0	-0.407379	3.511091	-1.209402
55	6	0	-1.084993	3.820453	-0.049275
56	6	0	-2.533109	3.745092	-0.022158
57	6	0	-2.913983	3.239301	1.275695
58	6	0	-3.954581	2.324063	1.380994
59	6	0	-4.653295	1.886484	0.197509
60	6	0	-4.318977	2.403556	-1.047469
61	6	0	-4.280002	1.525165	-2.202665
62	6	0	-4.578073	0.175009	-2.058294
63	6	0	-3.230456	3.352957	-1.162441

64	6	0	3.961821	2.149362	1.508937
65	6	0	4.995606	2.348739	0.589064
66	6	0	5.828023	3.443226	0.770614
67	6	0	5.599735	4.293094	1.851328
68	6	0	4.535354	4.010349	2.698020
69	6	0	3.908687	-1.121387	-2.215218
70	6	0	4.013919	-2.294007	-2.961352
71	6	0	4.928530	-2.338071	-4.008671
72	6	0	5.702825	-1.215860	-4.272609
73	6	0	5.530449	-0.096760	-3.461919
74	16	0	-2.151202	-2.985920	3.226263
75	7	0	3.723844	2.960592	2.535936
76	7	0	4.661918	-0.043337	-2.453624
77	8	0	-0.024244	-0.873727	4.333029
78	8	0	3.230346	-3.341927	1.769563
79	8	0	2.333386	0.249834	3.508354
80	6	0	0.896684	-3.495172	2.259314
81	1	0	4.446550	-0.514124	2.132450
82	1	0	4.469464	-2.026740	0.254900
83	1	0	5.115501	1.661652	-0.245611
84	1	0	6.642217	3.634658	0.078618
85	1	0	6.226923	5.158686	2.032768
86	1	0	4.316175	4.652497	3.547423
87	1	0	3.390777	-3.150127	-2.727956
88	1	0	5.029777	-3.236849	-4.608855
89	1	0	6.424218	-1.201436	-5.081639
90	1	0	6.120111	0.801372	-3.631312
91	1	0	3.136241	-4.183919	2.792254
92	1	0	0.837871	-2.982276	3.222290
93	8	0	2.625772	-4.935732	3.443138
94	1	0	1.626466	-4.617820	2.970322
95	1	0	2.873604	-5.828000	3.167282

The total electronic energy was calculated to be –3635.54621 Hartree.

The imaginary frequency was found at –1426.42 cm^{-1}.

Table S8. Optimized structure of **TS2** (M06-2X/6-31G(d,p))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.873425	-0.653049	1.059487
2	6	0	-3.812289	0.673539	1.093099
3	6	0	-2.922231	1.514491	0.218638
4	6	0	-1.762529	2.161502	1.002193
5	6	0	-1.465382	1.929395	2.339926
6	6	0	-1.992086	1.049643	3.499383
7	6	0	0.336749	1.258568	3.705163
8	6	0	1.672350	0.903813	3.620463
9	6	0	2.587544	1.557368	2.699839
10	6	0	3.677385	0.836968	2.018112
11	6	0	3.691195	-0.638708	2.046704
12	6	0	2.706007	-1.368570	2.837846
13	6	0	2.109325	-2.504342	2.314040
14	6	0	0.637478	-2.877221	2.422616
15	6	0	0.250341	-3.251467	0.970369
16	6	0	-0.863785	-2.867499	0.230396
17	6	0	-2.138444	-2.447196	0.885101
18	6	0	-3.092936	-1.510097	0.102041
19	6	0	-2.292072	-0.689223	-0.878326
20	6	0	-2.255014	0.681961	-0.865127
21	6	0	-1.369943	1.387167	-1.762010
22	6	0	-0.681967	2.581461	-1.281898
23	6	0	-0.788230	2.869542	0.156758
24	6	0	0.347188	3.431941	0.753503
25	6	0	0.721481	3.002623	2.061260
26	6	0	-0.137485	2.236720	2.774311
27	6	0	2.130662	2.741900	2.098615
28	6	0	2.669574	3.267735	0.883978
29	6	0	1.566562	3.708951	0.048065
30	6	0	1.622369	3.540612	-1.311049
31	6	0	0.469272	2.984179	-1.988678
32	6	0	0.989535	2.228203	-3.110812
33	6	0	0.337297	1.091808	-3.534455
34	6	0	-0.848304	0.672855	-2.836226
35	6	0	-0.857698	-0.771347	-2.817071
36	6	0	-1.414762	-1.442460	-1.740680
37	6	0	-0.717446	-2.608195	-1.193121
38	6	0	0.449850	-3.024903	-1.844930
39	6	0	1.572031	-3.496864	-1.084900
40	6	0	1.474690	-3.510908	0.292108
41	6	0	2.585122	-3.045917	1.090682
42	6	0	3.722695	-2.567520	0.487656
43	6	0	4.277347	-1.328443	0.974346
44	6	0	4.864174	-0.663000	-0.157823
45	6	0	4.864272	0.711110	-0.190458
46	6	0	4.292700	1.462439	0.908390
47	6	0	3.776885	2.684736	0.322932
48	6	0	3.888911	2.611043	-1.120287
49	6	0	2.832690	3.031543	-1.925317
50	6	0	2.443293	2.240131	-3.066336
51	6	0	3.165104	1.103007	-3.413358
52	6	0	2.469681	-0.086033	-3.870410
53	6	0	1.083688	-0.081734	-3.936332
54	6	0	0.335119	-1.230752	-3.487063
55	6	0	0.982968	-2.349521	-3.008298
56	6	0	2.431743	-2.364992	-2.938797
57	6	0	2.797400	-3.070012	-1.733063
58	6	0	3.851325	-2.605234	-0.954788
59	6	0	4.585820	-1.432180	-1.357892
60	6	0	4.266965	-0.777681	-2.540997
61	6	0	4.272244	0.673732	-2.582123
62	6	0	4.598903	1.399327	-1.441909
63	6	0	3.159162	-1.249851	-3.347493
64	6	0	-4.059433	-2.402998	-0.695058
65	6	0	-5.205773	-1.846482	-1.265374

66	6	0	-6.040962	-2.673362	-2.003407	83	1	0	-5.426223	-0.793939	-1.116996
67	6	0	-5.704633	-4.017009	-2.145508	84	1	0	-6.943095	-2.277153	-2.458682
68	6	0	-4.539654	-4.471568	-1.539385	85	1	0	-6.329569	-4.698411	-2.711304
69	6	0	-3.817313	2.608444	-0.385898	86	1	0	-4.240094	-5.513096	-1.623263
70	6	0	-4.434300	2.442341	-1.627718	87	1	0	-4.240109	1.555785	-2.222785
71	6	0	-5.285127	3.441392	-2.085284	88	1	0	-5.772727	3.346151	-3.050434
72	6	0	-5.495625	4.561678	-1.289605	89	1	0	-6.146705	5.368255	-1.606785
73	6	0	-4.844937	4.623689	-0.060980	90	1	0	-4.987090	5.478222	0.596503
74	16	0	2.118360	-0.657823	4.344466	91	1	0	-2.928041	-0.885966	4.209518
75	7	0	-3.726699	-3.685465	-0.827895	92	1	0	-1.351977	-0.903486	4.252975
76	7	0	-4.025369	3.673022	0.388620	93	8	0	-2.226058	-1.578398	4.414260
77	8	0	-0.071659	-2.778070	3.388616	94	1	0	-0.946180	0.455343	5.330601
78	8	0	-3.167040	0.710886	3.719511	95	1	0	-2.201445	-2.264342	3.713205
79	8	0	-2.441113	-2.823163	1.997976						
80	6	0	-0.844696	0.594380	4.255578						
81	1	0	-4.523623	-1.184634	1.748363						
82	1	0	-4.397109	1.225922	1.819536						

The total electronic energy was calculated to be –3635.5592081 Hartree.

The imaginary frequency was found at –769.78 cm^{-1}.

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