Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Hydrogenation of Cage-Opened C_{60} Derivatives Mediated by Frustrated Lewis Pairs

Yoshifumi Hashikawa and Yasujiro Murata*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
Fax: (+81)774-38-3178
E-mail: yasujiro@scl.kyoto-u.ac.jp

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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 and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.00 ppm in ^{13}C NMR) and CD_2Cl_2 (δ 5.32 ppm in ^{1}H NMR, δ 53.80 ppm in ^{13}C NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. 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. 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. Diethyl ether was purchased from Kanto Chemical Co., Inc. Carbon disulfide, trimethylamine, $NaBH_4$, $B(C_6F_5)_3$, and acetone were purchased from FUJIFILM Wako Pure Chemical Corporation. *o*-Dichlorobenzene (ODCB) was purchased from Sigma-Aldroch Co. LLC. Triphenylsilane, pinacol borane (HBpin), and *N*,*N*-dimethylaniline were purchased from Tokyo Chemical Industry Co. Ltd.

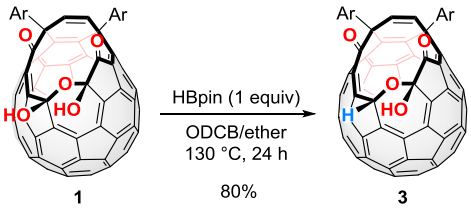
All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. Compounds **1**,[1] **4**,[2] and **6**[3] were synthesized according to literature procedures.

2. Computational Methods

All calculations were conducted using the Gaussian 09 program. All structures at the stationary states were optimized at the B3LYP-D3/6-31G(d) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory. Natural charges were obtained from the natural population analysis at the same level of theory.

3. Synthesis

3.1. Reduction of 1 by HBpin



(Ar = 6-*t*-butylpyridin-2-yl)

Powdery **1** (10.0 mg, 8.92 μmol) was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL), ether (0.10 mL), and HBpin (1.30 μL, ρ = 0.882 g/mL, 8.96 μmol, 1.00 equiv) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (40:1) to (20:1)) to give **3** (7.98 mg, 7.22 μmol, 80%) followed by unreacted **1** (1.17 mg, 1.04 μmol, 12%) as brown powders.

3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.61 (t, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 8.0 Hz), 7.40 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.20 (d, 1H, J = 8.0 Hz), 7.15 (d, 1H, J = 8.0 Hz), 7.02 (d, 1H, J = 10.0 Hz), 6.86 (d, 1H, J = 10.0 Hz), 5.90 (br s, 1H), 1.24 (s, 9H), 1.16 (s, 9H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{82}H_{28}N_2O_4$ (**3**) 1104.2055; Found 1104.2031. (These data were matched well with the reported one.[4])

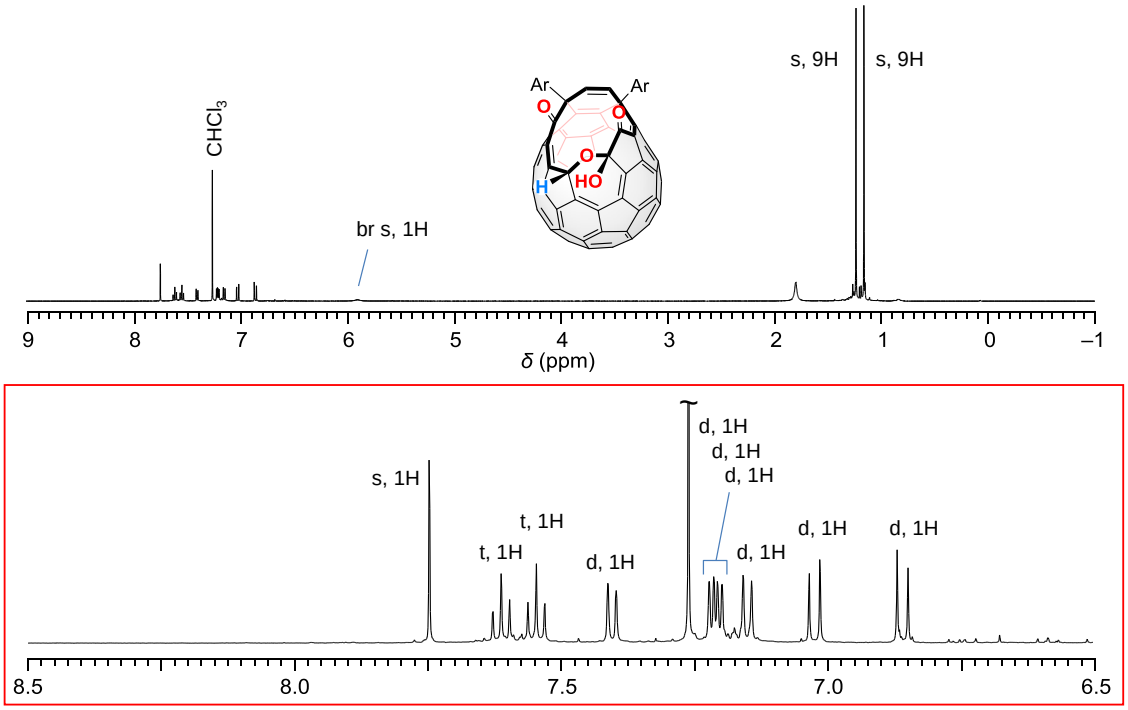


Figure S1. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **3**.

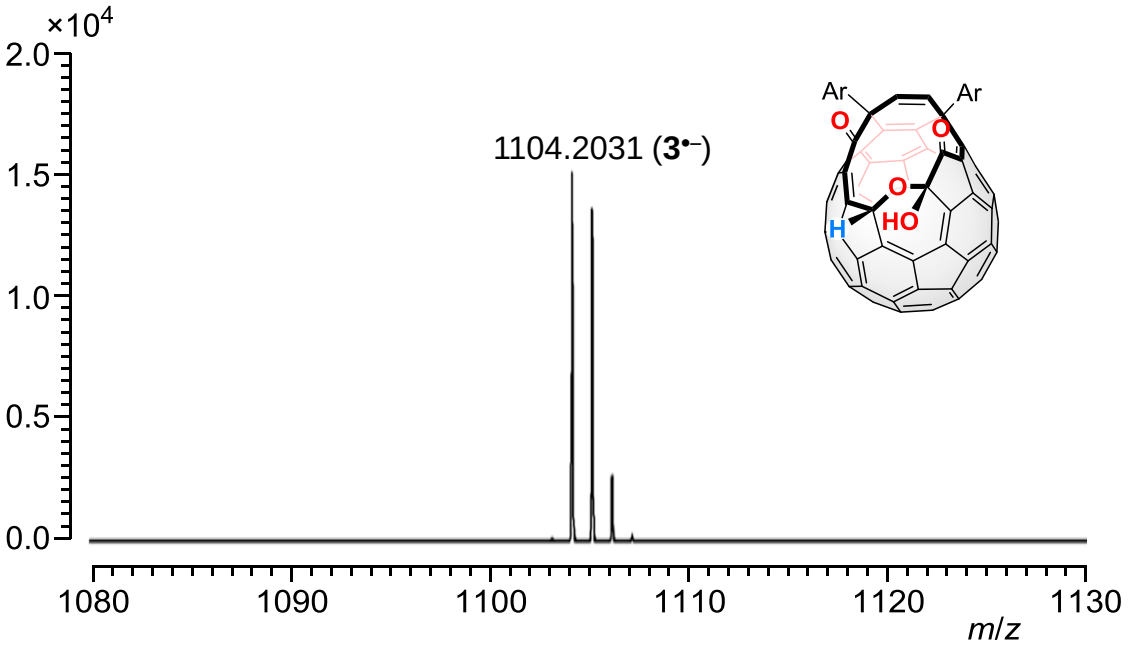
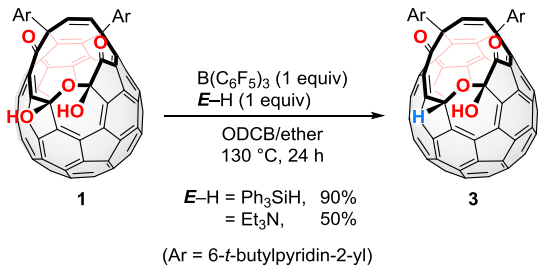


Figure 2. APCI mass spectrum (negative ion mode) of **3**.

3.2. Dehydroxyhydrogenation of 1



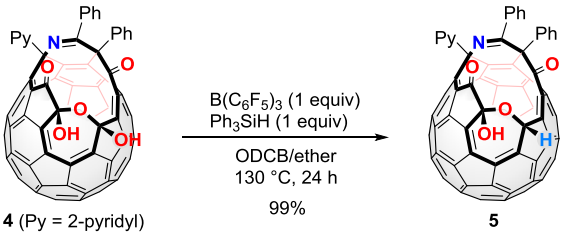
[The reaction using Ph_3SiH]

Powdery **1** (10.0 mg, 8.92 μmol) and $B(C_6F_5)_3$ (4.6 mg, 9.0 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL) and ether (0.10 mL) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (40:1) to (20:1)) to give **3** (4.91 mg, 4.44 μmol, 50%) followed by unreacted **1** (1.03 mg, 0.919 μmol, 10%) as brown powders. ***Note***: The use of crystalline $B(C_6F_5)_3$ is important.

[The reaction using Et_3N]

Powdery **1** (10.0 mg, 8.92 μmol) and $B(C_6F_5)_3$ (4.6 mg, 9.0 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL), ether (0.10 mL), and Et_3N (1.25 μL, ρ = 0.726 g/mL, 8.97 μmol, 1.01 equiv) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (40:1)) to give **3** (4.91 mg, 4.44 μmol, 50%) as a brown powder. In this reaction, **1** was completely consumed. ***Note***: The use of crystalline $B(C_6F_5)_3$ is important.

3.3. Dehydroxyhydrogenation of 4



4 (Py = 2-pyridyl) **5**

Powdery **4** (10.3 mg, 9.49 μmol) and $B(C_6F_5)_3$ (4.8 mg, 9.4 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL) and ether (0.10 mL) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (40:1)) to give **5** (10.0 mg, 9.36 μmol, 99%) as a brown powder. ***Note***: The use of crystalline $B(C_6F_5)_3$ is important.

5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, 1H, J = 5.2 Hz), 8.26 (d, 2H, J = 7.5 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.83–7.72 (m, 2H), 7.65 (s, 1H), 7.45–7.11 (m, 8H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{80}H_{16}N_2O_4$ (**5**) 1068.1116; Found 1068.1103. (These data were matched well with the reported one.[2c])

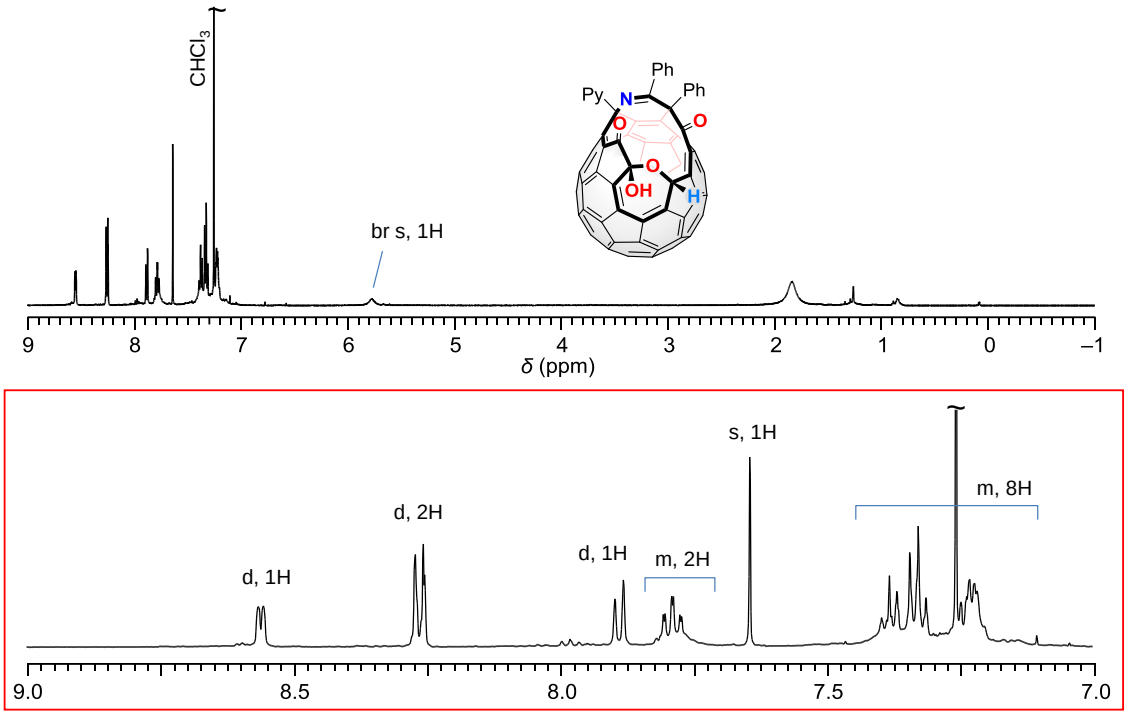


Figure S3. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **5**.

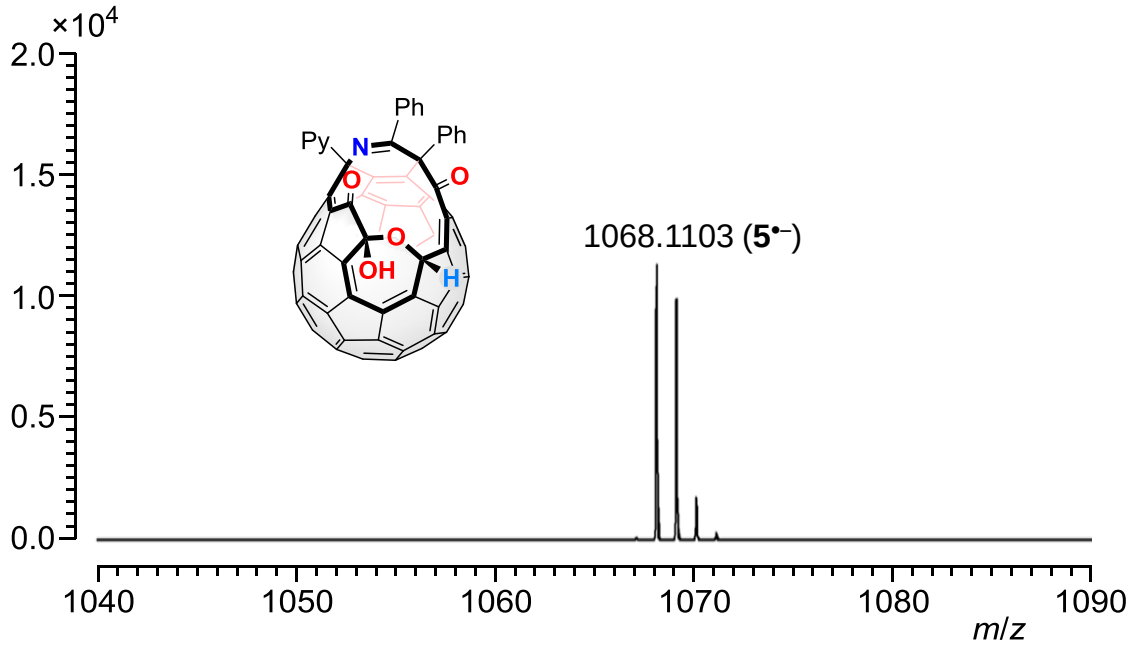
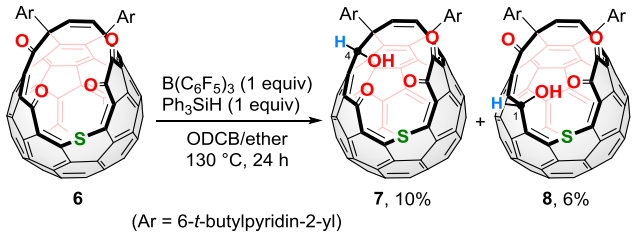


Figure 4. APCI mass spectrum (negative ion mode) of **5**.

3.4. Hydrogenation of 6



Powdery **6** (10.0 mg, 8.81 μmol), $B(C_6F_5)_3$ (4.6 mg, 8.9 μmol, 1.0 equiv), and Ph_3SiH (2.3 mg, 8.8 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL) and ether (0.10 mL) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1) to (40:1)) to give **7** (0.97 mg, 0.85 μmol, 10%) and **8** (0.62 mg, 0.55 μmol, 6%), followed by unreacted **6** (7.99 mg, 7.04 μmol, 80%) as reddish brown powders. ***Note***: The use of crystalline $B(C_6F_5)_3$ is important.

7: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (t, 1H, J = 8.0 Hz), 7.39 (t, 1H, J = 8.0 Hz), 7.29 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.03 (d, 1H, J = 8.0 Hz), 6.88 (d, 1H, J = 10.3 Hz), 6.84 (d, 1H, J = 8.0 Hz), 6.65 (d, 1H, J = 6.9 Hz), 6.05 (d, 1H, J = 10.3 Hz), 3.50 (d, 1H, J = 6.9 Hz), 1.22 (s, 9H), 1.17 (s, 9H), –10.70 (s, 1.70H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 193.55, 186.10, 184.09, 168.23, 167.81, 164.21, 161.20, 155.98, 152.57, 152.15, 152.01, 151.98, 151.01, 150.68, 150.61, 150.13, 149.77, 149.72, 149.62, 149.56, 149.44, 149.07, 147.96, 147.25, 147.04, 145.99, 145.60, 145.01, 144.06, 143.86, 143.78, 143.24, 143.20, 143.15, 143.11, 142.70, 142.30, 142.00, 141.74, 140.93, 140.20, 139.45, 139.27, 138.99, 138.02, 137.70, 137.57, 137.47, 137.44, 136.95, 136.92, 136.79, 136.60, 136.49, 136.46, 133.55, 132.28, 131.93, 131.06, 130.83, 128.74, 126.91, 125.15, 121.99, 120.91, 120.01, 119.82, 119.67, 117.48, 116.99, 116.82, 71.92, 62.19, 54.76, 37.58, 37.10, 29.90, 29.88 (The sum of carbon signals must be 78 in theory. Observed 78.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{82}H_{28}N_2O_4S$ (**7**) 1136.1775; Found 1136.1733.

8: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, 1H, J = 8.0 Hz), 7.50 (t, 1H, J = 8.0 Hz), 7.40 (d, 1H, J = 4.6 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.22 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 10.3 Hz), 7.20 (d, 1H, J = 8.0 Hz), 7.11 (d, 1H, J = 8.0 Hz), 6.65 (d, 1H, J = 10.3 Hz), 3.85 (d, 1H, J = 4.6 Hz), 1.20 (s, 9H), 1.10 (s, 9H), –11.06 (s, 1.70H); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{82}H_{28}N_2O_4S$ (**8**) 1136.1775; Found 1136.1777. (These data were matched well with the reported one.[5])

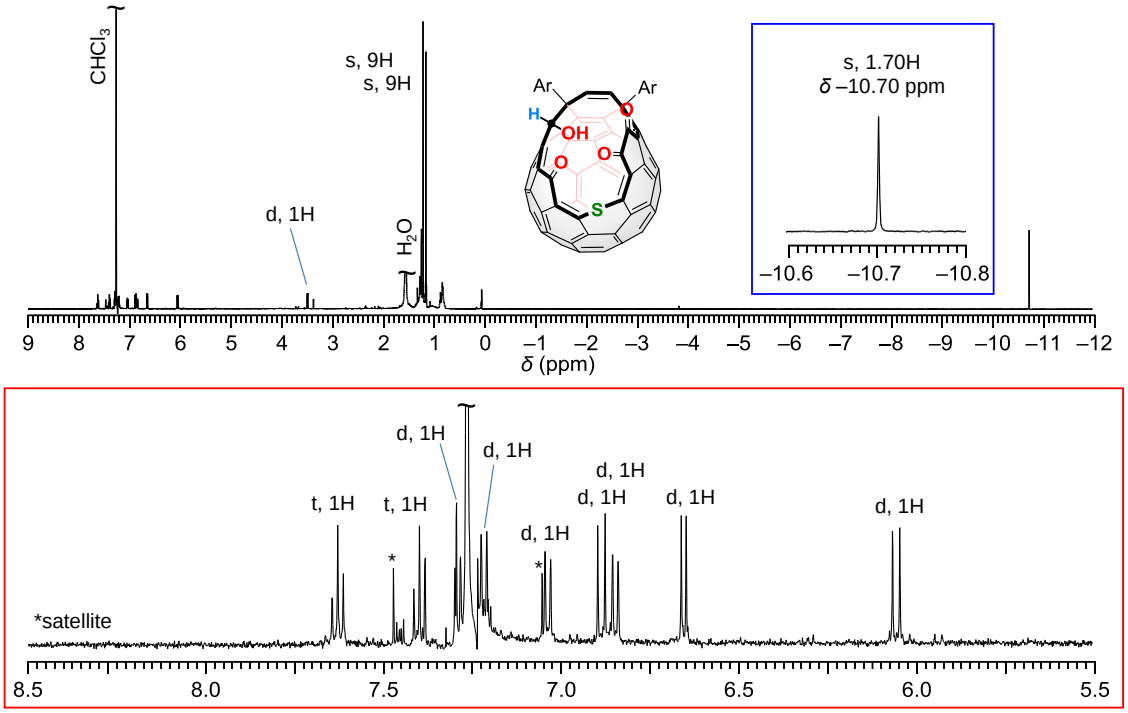


Figure S5. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **7**.

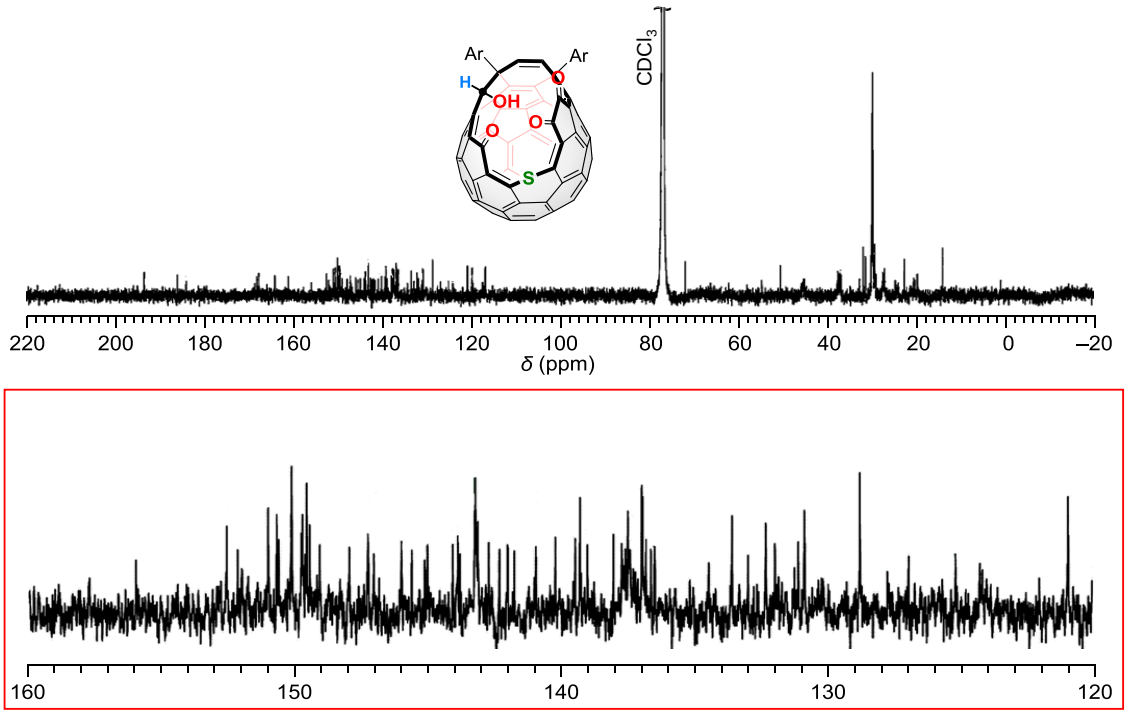


Figure S6. ^{13}C NMR spectra (201 MHz, $CDCl_3$) of **7**.

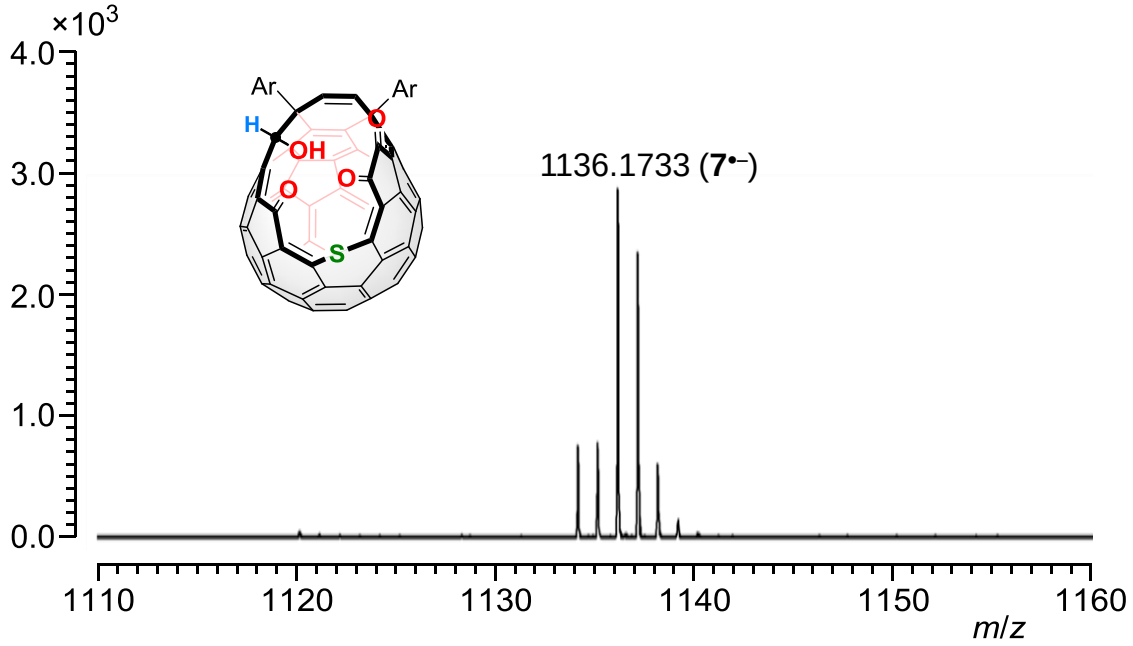


Figure 7. APCI mass spectrum (negative ion mode) of **7**.

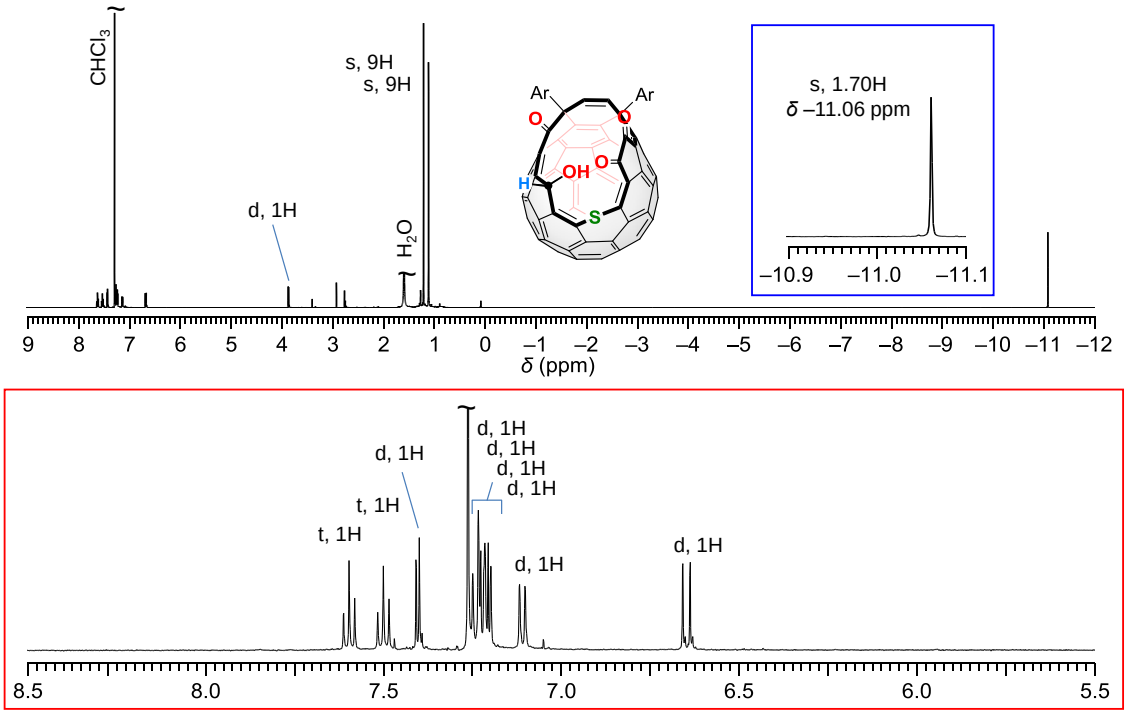


Figure S8. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of **8**.

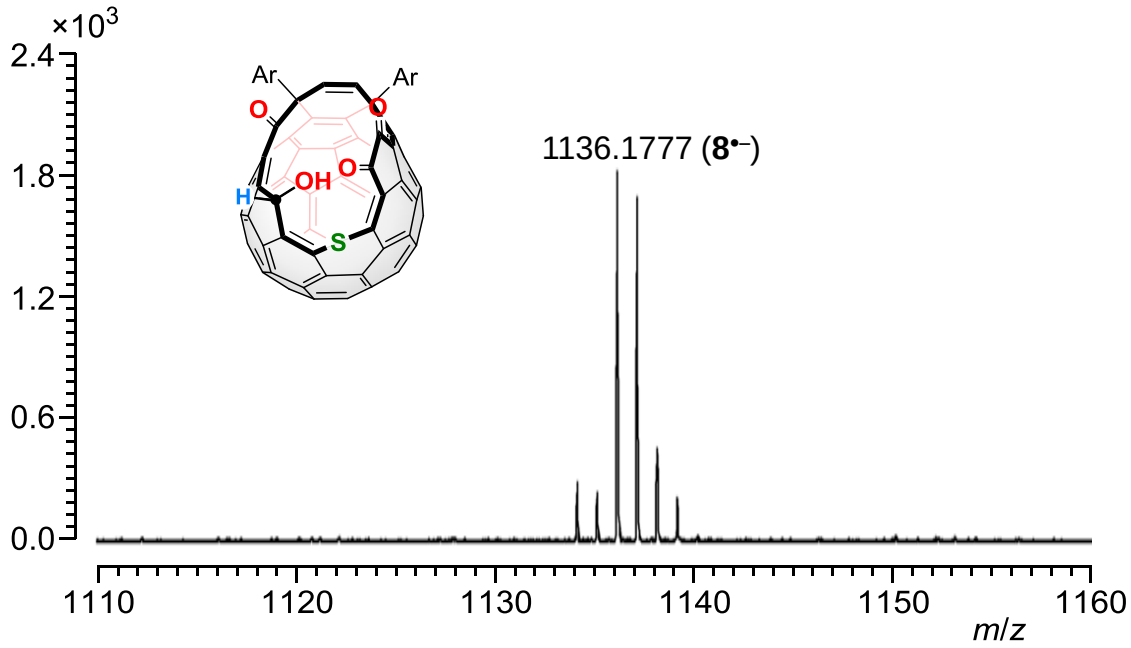
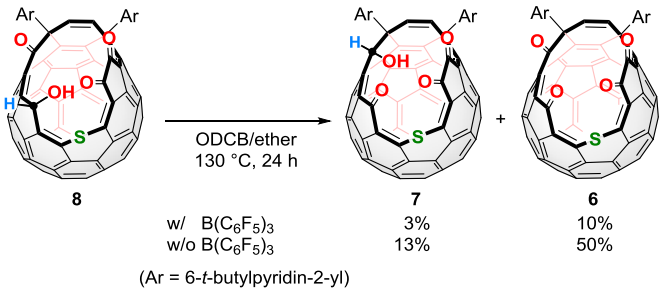


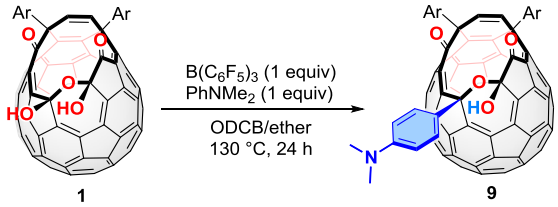
Figure 9. APCI mass spectrum (negative ion mode) of **8**.

3.5. Conversion of 8 into 7



Powdery **8** (8.0 mg, 7.0 μmol) and $B(C_6F_5)_3$ (3.7 mg, 7.2 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL) and ether (0.10 mL) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (200:1) to (100:1)) to give **7** (0.21 mg, 0.18 μmol, 3%), unreacted **8** (6.74 mg, 5.93 μmol, 84%), and **6** (0.80 mg, 0.70 μmol, 10%) as reddish brown powders.

3.6. Reductive Arylation of 1



w/ $B(C_6F_5)_3$ 42%
w/o $B(C_6F_5)_3$ Not formed

(Ar = 6-*t*-butylpyridin-2-yl)

Powdery **1** (10.0 mg, 8.92 μmol) and $B(C_6F_5)_3$ (4.6 mg, 9.0 μmol, 1.0 equiv) were placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.00 mL), ether (0.10 mL), and $PhNMe_2$ (1.14 μL, ρ = 0.956 g/mL, 8.99 μmol, 1.01 equiv) were added and the resulting solution was heated at 130 °C for 24 h (Aluminum block heater). The crude mixture was purified by column chromatography using silica gel (CS_2/acetone (40:1) to (20:1)) to give **9** (4.57 mg, 3.73 μmol, 42%) followed by unreacted **1** (5.89 mg, 5.25 μmol, 59%) as brown powders. ***Note***: The use of crystalline $B(C_6F_5)_3$ is important.

9: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.35 (d, 2H, J = 8.5 Hz), 7.68 (t, 1H, J = 8.0 Hz), 7.57 (t, 1H, J = 8.0 Hz), 7.49 (d, 1H, 8.0 Hz), 7.26 (d, 1H, 8.0 Hz), 7.22 (d, 1H, 8.0 Hz), 7.18 (d, 1H, 8.0 Hz), 7.05 (d, 1H, J = 10.3 Hz), 6.87 (d, 2H, 8.5 Hz), 6.86 (d, 1H, 10.3 Hz), 4.45 (s, 1H), 3.05 (s, 6H), 1.24 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (201 MHz, CD_2Cl_2) δ 197.47, 194.49, 169.36, 168.73, 164.68, 163.19, 154.64, 153.18, 151.29, 150.26, 150.11, 149.85, 149.68, 149.56, 149.50, 149.08, 148.83, 148.76, 148.39, 148.18, 147.97, 147.91, 147.73, 147.53, 147.27, 147.05, 146.59, 146.09, 146.01, 145.80, 145.63, 144.44, 144.41, 143.91, 143.84, 143.76, 143.15, 142.88, 141.83, 141.70, 141.66, 141.25, 141.12, 140.79, 139.98, 139.16, 138.53, 137.69, 137.59, 137.54, 137.27, 137.21, 137.15, 136.71, 136.31, 135.80, 135.34, 134.14, 133.98, 133.37, 132.82, 132.15, 132.13, 130.71, 130.48, 128.52, 128.45, 127.31, 127.25, 120.39, 119.94, 117.80, 117.22, 111.66, 98.73, 96.90, 60.09, 55.16, 40.53, 38.11, 37.84, 30.13, 29.94 (The sum of carbon signals must be 83 in theory. Observed 83.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{90}H_{37}N_3O_4$ (**9**) 1223.2790; Found 1223.2755.

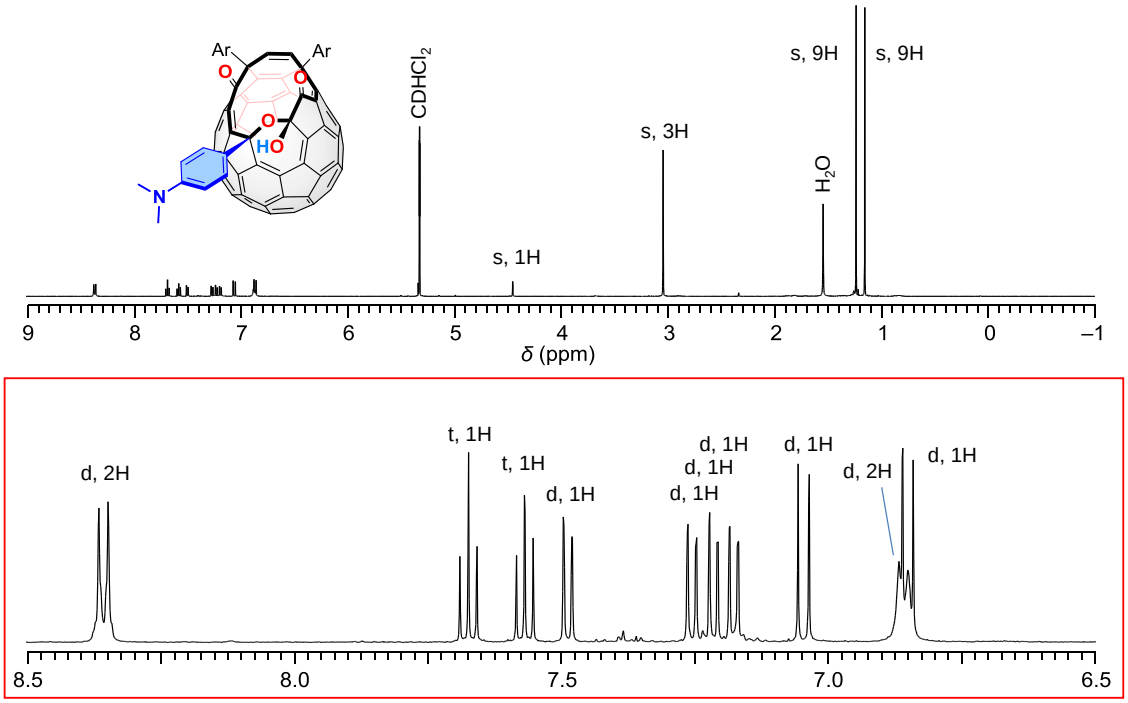


Figure S10. ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of **9**.

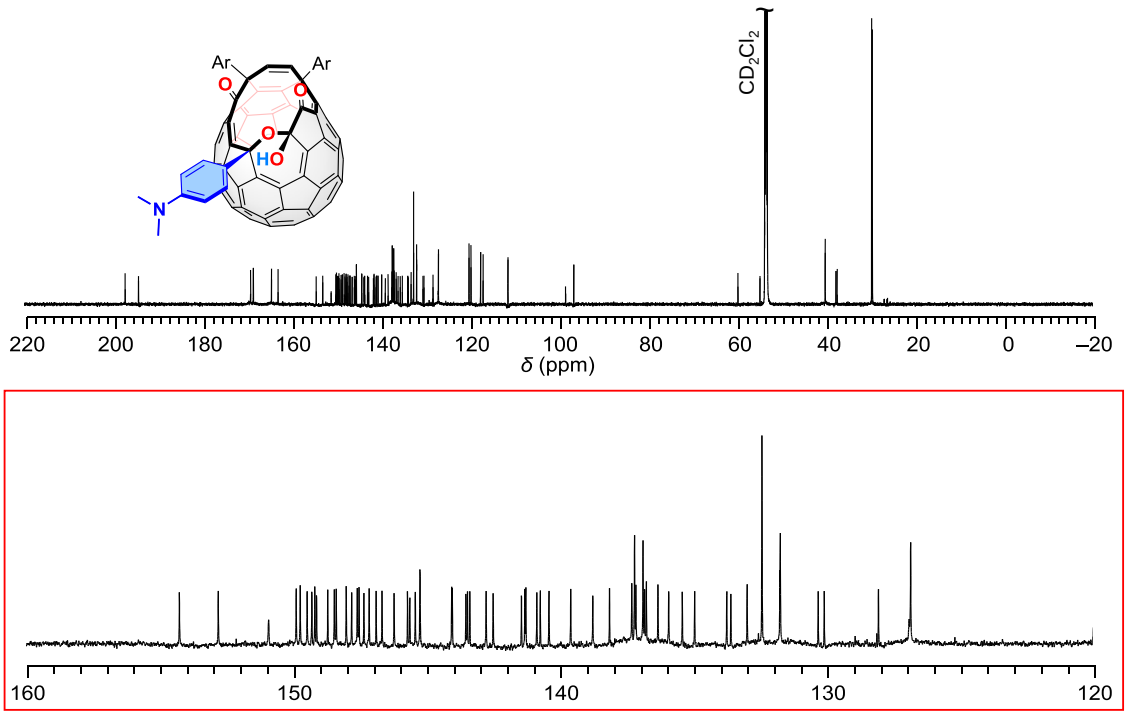


Figure S11. ^{13}C NMR spectra (201 MHz, CD_2Cl_2) of **9**.

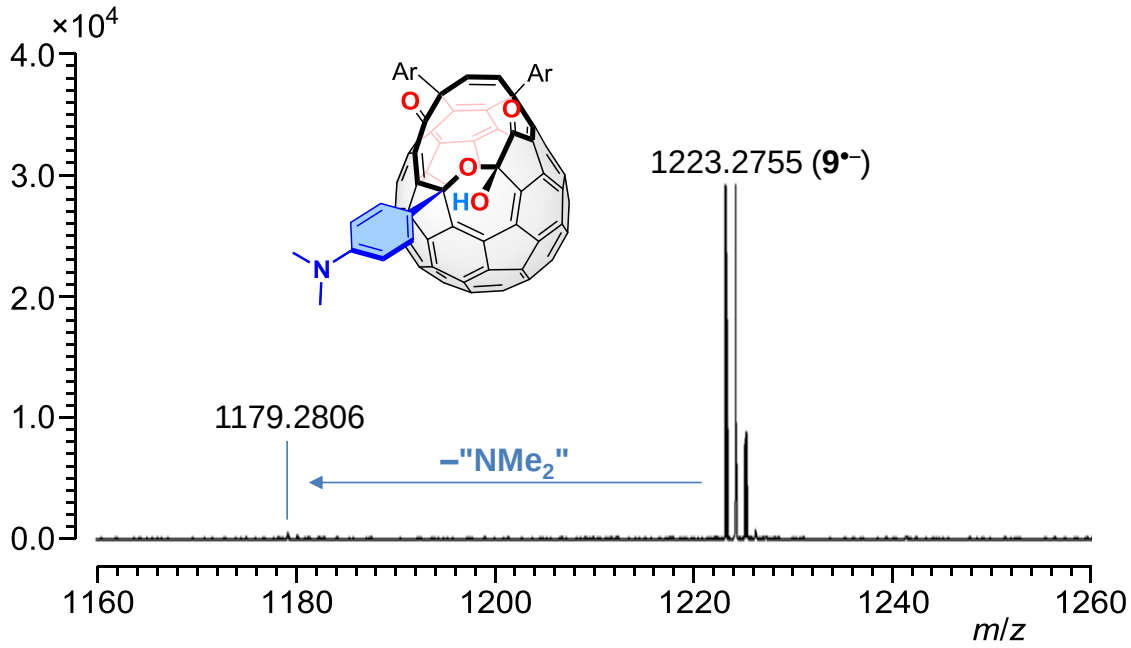


Figure 12. APCI mass spectrum (negative ion mode) of **9**.

4. Single Crystal X-Ray-Structures of (H_2O@**5**)•CS_2

Single crystals of H_2O@**5** were obtained from a CS_2 solution by slow evaporation. 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 monochromater. A total of 5401 reflections were measured at the maximum 2θ angle of 50.05°, of which 4814 were independent reflections (R_{int} = 0.0410). The structure was solved by direct methods (SHELXT-2014/5[6]) and refined by the full-matrix least-squares on F^2 (SHELXL-2018/3[6]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions except for the encapsulated H_2O molecule. A part of the fullerene skeleton was refined using SIMU and ISOR instructions. The crystal data are as follows: $C_{81}H_{18}N_2O_5S_2$; FW = 1163.09, crystal size 0.21 × 0.08 × 0.04 mm^3, monoclinic, *C*2/*c*, *a* = 30.736(8) Å, *b* = 9.788(2) Å, *c* = 32.682(8) Å, β = 107.241(3)°, *V* = 9391(4) Å^3, *Z* = 8, D_c = 1.645 g cm^{-3}. The refinement converged to R_1 = 0.1154, wR_2 = 0.2766 ($I > 2\sigma(I)$), GOF = 1.084. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2088803).

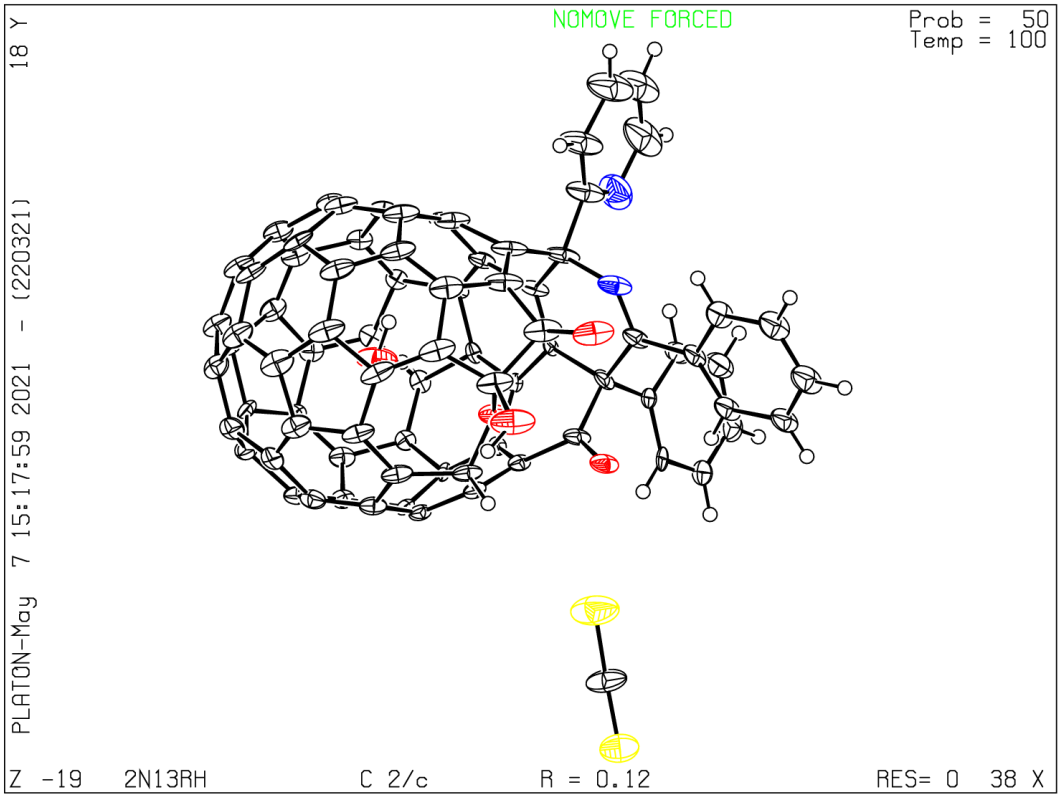
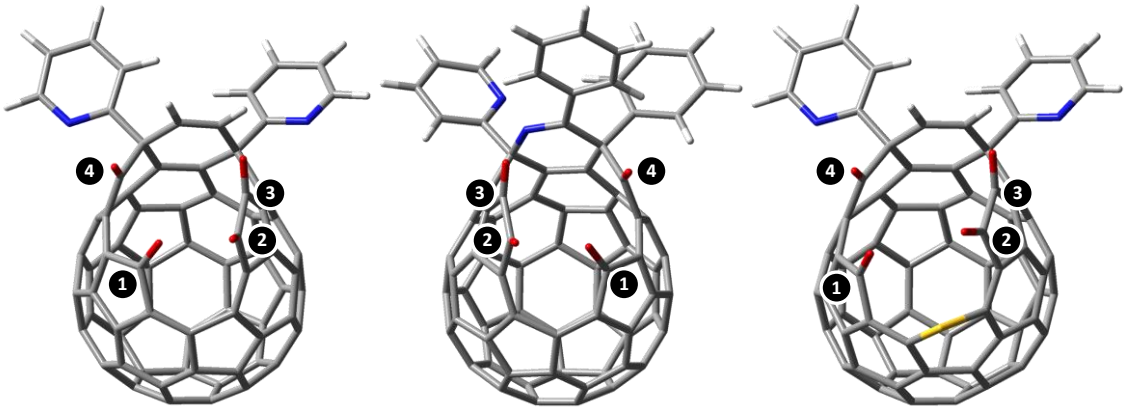


Figure S13. Single crystal X-ray structure of (H_2O@**5**)•CS_2. Thermal ellipsoids are shown at 50% probability.

5. Natural Charges

For the calculations to be simplified, 6-*t*-butylpyridin-2-yl groups were replaced with 2-pyridyl groups for **2'** and **6'**. The calculations were performed at the B3LYP-D3/6-31G(d) level of theory using Gaussian 09.[7]



2'

	q(O)	*q*(C)	Δ*q*
1	**–0.495**	+0.558	1.053
2	–0.466	+0.491	0.957
3	–0.478	+0.500	0.978
4	–0.482	+0.599	**1.081**

4-keto-form

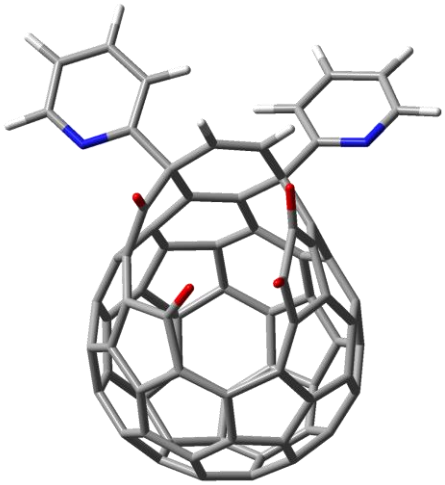
	q(O)	*q*(C)	Δ*q*
1	**–0.490**	+0.557	1.047
2	–0.464	+0.489	0.953
3	–0.457	+0.496	0.953
4	–0.476	+0.575	**1.051**

6'

	q(O)	*q*(C)	Δ*q*
1	–0.462	+0.555	1.017
2	–0.456	+0.488	0.944
3	–0.478	+0.497	0.975
4	**–0.485**	+0.597	**1.082**

Figure S14. Natural charges *q* of **2'**, **4-keto-form**, and **6'** (B3LYP-D3/6-31G(d)).

Table S1. Optimized structure of **2'** (B3LYP-D3/6-31G(d))

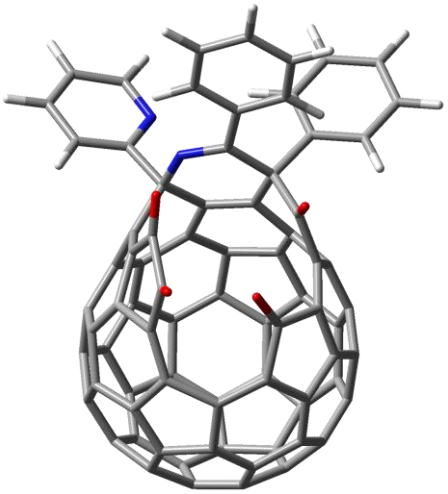


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.956568	-0.193956	1.295735
2	6	0	3.775285	1.089298	0.998279
3	6	0	2.824759	1.596474	-0.056318
4	6	0	1.587075	2.297062	0.547863
5	6	0	1.244510	2.286320	1.900151
6	6	0	1.826150	1.784429	3.203374
7	6	0	0.583615	1.443965	4.121891
8	6	0	-0.623065	1.694961	3.272939
9	6	0	-1.939418	1.242376	3.127234
10	6	0	-2.510279	-0.155252	3.083221
11	6	0	-1.836070	-1.381007	3.001700
12	6	0	-0.341857	-1.644147	3.110417
13	6	0	-0.031586	-2.666297	2.025856
14	6	0	1.077035	-2.619680	1.183732
15	6	0	2.403213	-2.107288	1.641709
16	6	0	3.265896	-1.329992	0.592214
17	7	0	3.954026	-3.607853	0.009941
18	8	0	2.963241	1.746009	3.605479
19	8	0	2.812979	-2.295509	2.765638
20	7	0	3.585168	3.865755	-0.563580
21	6	0	2.381414	-0.864709	-0.543369
22	6	0	1.286575	0.842208	-1.913793
23	8	0	0.644016	1.281474	5.313963
24	6	0	1.517821	-1.868315	-1.129425
25	6	0	0.592735	2.727724	-0.436682
26	8	0	0.453573	-1.030712	3.785307
27	6	0	-0.650722	2.226970	-2.531882
28	6	0	4.317492	4.741581	-1.263427
29	6	0	-1.828117	2.907291	-2.019512
30	6	0	3.623549	2.580777	-0.932395
31	6	0	0.520745	2.075419	-1.754809
32	6	0	0.792893	-0.169582	-2.747202
33	6	0	2.233453	0.460148	-0.891453
34	6	0	-1.790023	3.456062	-0.750474
35	6	0	-0.425478	-0.016546	-3.497562
36	6	0	-0.945376	3.263366	1.387211
37	6	0	-1.133932	1.169035	-3.400777
38	6	0	0.885583	-1.551513	-2.329101
39	6	0	0.873831	-2.833797	-0.235787
40	6	0	-0.567366	3.385868	0.010078
41	6	0	5.508531	-1.853558	-0.524039
42	6	0	4.301899	-2.315628	0.012184
43	6	0	-4.021241	2.537383	-0.248534
44	6	0	-0.319174	-3.443310	-0.666054
45	6	0	-0.307477	-2.230580	-2.785445
46	6	0	6.390334	-2.781510	-1.074487
47	6	0	-0.122515	2.591545	2.256055
48	6	0	-2.585942	1.133985	-3.342788
49	6	0	5.116191	4.384883	-2.349686
50	6	0	-4.585262	1.540182	0.648949
51	6	0	-3.259002	-0.091108	-3.332913
52	6	0	-2.358761	3.081941	1.478654
53	6	0	6.038889	-4.131507	-1.071802
54	6	0	4.404726	2.119346	-1.998896
55	6	0	-2.824655	2.051807	2.301967
56	6	0	4.809509	-4.490236	-0.518572
57	6	0	-1.119779	-1.291774	-3.525650
58	6	0	-5.060673	0.434046	-0.158287
59	6	0	-4.316726	-1.113097	1.609382
60	6	0	-2.913872	3.274307	0.157804
61	6	0	-1.409876	-3.649845	0.255355
62	6	0	-3.014347	2.209568	-2.474180
63	6	0	-4.357184	-0.302915	-2.405150
64	6	0	-3.963711	1.283978	1.874355
65	6	0	5.160005	3.040154	-2.720186
66	6	0	-1.277320	-3.148097	1.545567
67	6	0	-3.787394	-0.061190	2.362633
68	6	0	-4.757219	0.725158	-1.549502
69	6	0	-4.090050	2.015427	-1.597356
70	6	0	-2.374580	-2.438425	2.176938
71	6	0	-2.510276	-1.332307	-3.427665
72	6	0	-3.141415	-2.311309	-2.558949
73	6	0	-0.905458	-3.176052	-1.962148
74	6	0	-4.566861	-1.947393	-0.575089
75	6	0	-2.352171	-3.215624	-1.842058
76	6	0	-2.664033	-3.507882	-0.456918
77	6	0	-3.590405	-2.348557	1.516071
78	6	0	-4.948500	-0.867990	0.323877
79	6	0	-3.739713	-2.876012	0.166771
80	6	0	-4.274628	-1.669821	-1.915728
81	1	0	4.612844	-0.480571	2.110725
82	1	0	4.283469	1.857022	1.569404
83	1	0	4.258898	5.777894	-0.935688
84	1	0	5.743737	-0.794445	-0.501569
85	1	0	7.337064	-2.455230	-1.496479
86	1	0	5.686071	5.138088	-2.884943
87	1	0	6.697384	-4.888733	-1.485907
88	1	0	4.411113	1.064249	-2.254204
89	1	0	4.493212	-5.531314	-0.495828
90	1	0	5.770748	2.714230	-3.557818

The total electronic energy was calculated to be –3236.211551 Hartree.

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



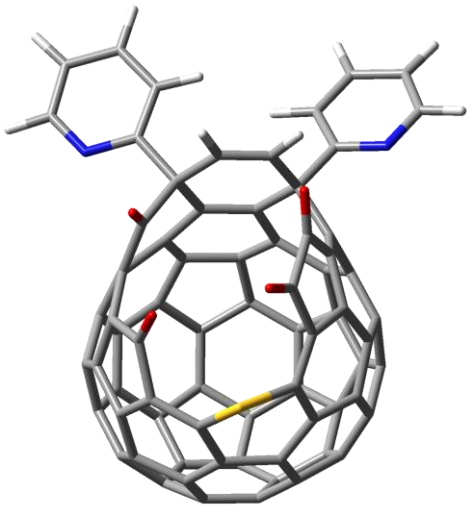
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.690557	1.119115	-2.925423
2	6	0	-2.276658	1.196985	-3.252778
3	6	0	-1.567681	0.032425	-3.499608
4	6	0	-2.221232	-1.261912	-3.415266
5	6	0	-3.567665	-1.343156	-3.061541
6	6	0	-4.317912	-0.124627	-2.810829
7	6	0	-1.668617	2.256938	-2.469247
8	6	0	-0.226945	-0.093333	-2.995553
9	6	0	-1.260387	-2.182883	-2.849669
10	6	0	-4.001972	-2.348565	-2.105820
11	6	0	-5.220038	-0.377233	-1.700207
12	6	0	-3.978619	2.172634	-1.975186
13	6	0	-3.069557	-3.235331	-1.559656
14	6	0	-1.671460	-3.154222	-1.945151
15	6	0	-3.113136	-3.548378	-0.145026
16	6	0	-0.850871	-3.411069	-0.781102
17	6	0	-0.370355	2.125812	-1.924856
18	6	0	-0.020099	-1.475552	-2.617934
19	6	0	-1.745502	-3.655231	0.322669
20	6	0	0.827507	-1.780655	-1.555895
21	6	0	0.382445	0.921931	-2.249928
22	6	0	-5.013365	-1.746099	-1.255351
23	6	0	-5.482238	0.629893	-0.769494
24	6	0	-0.072129	2.753653	-0.625260
25	6	0	-4.868743	1.939092	-0.918734
26	6	0	-2.746641	2.896762	-1.734509
27	6	0	-5.518513	0.316042	0.648526
28	6	0	-4.566234	2.448233	0.402473
29	6	0	-2.487702	3.430237	-0.484630
30	6	0	0.381083	-2.762117	-0.570492
31	6	0	-5.049009	-2.046357	0.111710
32	6	0	1.501739	0.553385	-1.421386
33	6	0	-4.932046	1.426534	1.372347
34	6	0	-3.420958	3.209440	0.611486
35	6	0	-1.144670	3.378030	0.038296
36	6	0	-1.260020	3.230794	1.459008
37	6	0	1.090208	2.327032	0.160067
38	6	0	1.748914	-0.755384	-1.115046
39	6	0	2.193259	-1.953169	1.015556
40	6	0	-2.628967	3.017746	1.805826
41	6	0	-2.913810	1.969361	2.686725
42	6	0	-1.874103	1.175940	3.326560
43	6	0	-4.093353	1.175880	2.461877
44	6	0	-4.074253	-2.957336	0.674463
45	6	0	1.833660	1.790425	2.716842
46	6	0	-5.287266	-0.987573	1.082038
47	6	0	-4.426495	-1.228230	2.227524
48	6	0	1.008250	2.301147	1.552133
49	6	0	0.830516	-2.531043	0.787604
50	6	0	-0.096866	-2.637902	1.823986
51	6	0	-0.275989	2.573773	2.156034
52	6	0	-0.563028	1.657905	3.236480
53	6	0	-3.797405	-0.169270	2.888888
54	6	0	-2.410765	-0.234912	3.367366
55	6	0	0.785346	1.425732	3.846297
56	6	0	-3.696179	-2.440848	1.982983
57	6	0	-1.392025	-3.162921	1.574429
58	6	0	-0.237407	-1.656550	2.981691
59	6	0	-2.378525	-2.501008	2.410020
60	6	0	-1.731795	-1.439408	3.144421
61	6	0	2.211860	1.658935	-0.660057
62	6	0	2.859015	-1.192438	-0.176347
63	6	0	3.668809	0.019516	0.358490
64	7	0	3.312337	1.233099	0.165895
65	6	0	3.753201	-2.123540	-1.028514
66	6	0	2.866323	2.651810	-1.647827
67	8	0	2.756401	-2.121638	2.076607
68	8	0	3.023175	1.767984	2.901224
69	6	0	3.011507	4.006437	-1.339309
70	6	0	3.682147	4.826002	-2.244381
71	6	0	4.185943	4.263858	-3.417564
72	6	0	4.000594	2.896976	-3.625224
73	7	0	3.357333	2.100782	-2.763115
74	6	0	3.828194	-3.504932	-0.826726
75	6	0	4.615098	-4.297279	-1.665135
76	6	0	5.329085	-3.717502	-2.713717
77	6	0	5.247341	-2.338833	-2.924183
78	6	0	4.460039	-1.545770	-2.091934
79	8	0	0.643631	-1.046288	3.542055
80	8	0	1.063621	1.266287	5.007259
81	6	0	6.726078	-1.508968	2.096537
82	6	0	5.509121	-1.418339	1.423016
83	6	0	4.947789	-0.169373	1.113278
84	6	0	5.648730	0.986365	1.510907
85	6	0	6.859497	0.894498	2.186562
86	6	0	7.408811	-0.356026	2.480777
87	1	0	2.612496	4.401557	-0.411286
88	1	0	3.810497	5.884628	-2.036088
89	1	0	4.713111	4.865064	-4.151897
90	1	0	4.384655	2.415192	-4.522465
91	1	0	3.293835	-3.971276	-0.004466
92	1	0	4.669389	-5.368724	-1.492657
93	1	0	5.942995	-4.334819	-3.363690
94	1	0	5.795763	-1.877795	-3.741152
95	1	0	4.376643	-0.476865	-2.274471

96	1	0	7.135685	-2.489481	2.323444	100	1	0	8.356706	-0.429767	3.007724
97	1	0	5.003732	-2.332078	1.154687						
98	1	0	5.213299	1.951922	1.291058						
99	1	0	7.374812	1.802475	2.488260						

The total electronic energy was calculated to be –3467.2768334 Hartree.

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



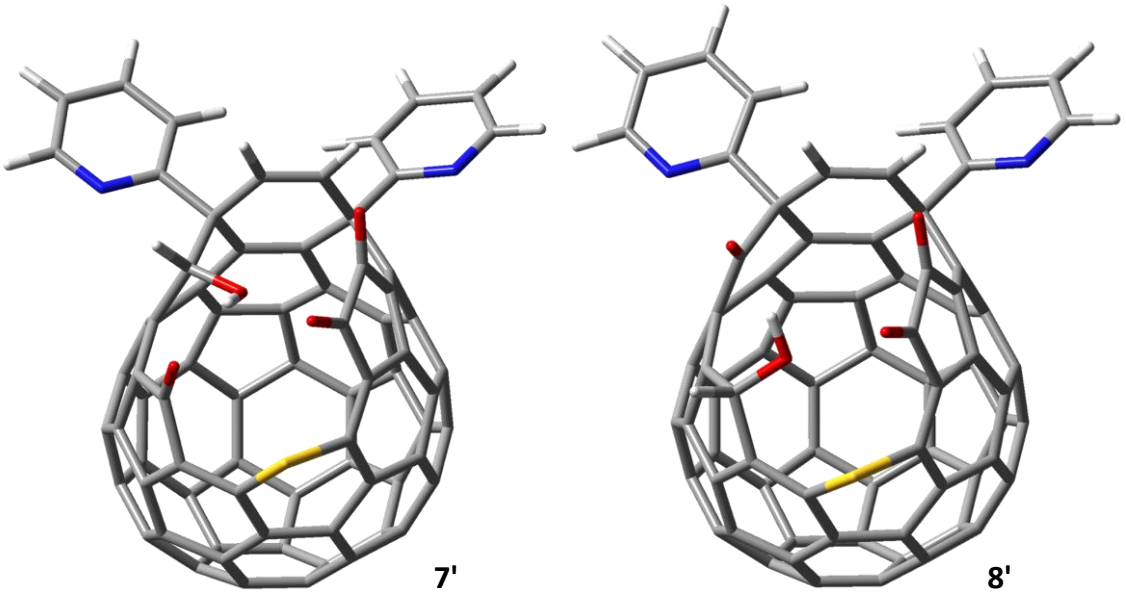
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.799468	0.317295	1.475004
2	6	0	3.808213	-0.936309	1.027266
3	6	0	3.002590	-1.439803	-0.145266
4	6	0	1.832075	-2.350711	0.295039
5	6	0	1.477941	-2.582589	1.623565
6	6	0	1.999513	-2.220246	2.996760
7	6	0	0.720943	-2.025103	3.911556
8	6	0	-0.432105	-2.446046	3.077558
9	6	0	-1.767712	-2.058500	3.061953
10	6	0	-2.864303	0.317652	3.058606
11	6	0	-2.262776	1.569781	2.975552
12	6	0	-0.787476	1.889869	3.267096
13	6	0	-0.370057	2.755722	2.053475
14	6	0	0.791312	2.660712	1.282036
15	6	0	2.073413	2.111168	1.826277
16	6	0	3.068102	1.449402	0.806778
17	16	0	-2.290848	-0.855025	4.267879
18	7	0	3.668871	3.807551	0.482432
19	8	0	3.120302	-2.177514	3.443653
20	8	0	2.364033	2.183083	2.999981
21	7	0	4.058551	-3.536182	-0.831256
22	6	0	2.326947	1.003745	-0.433312
23	6	0	1.509498	-0.662091	-2.028458
24	8	0	0.760313	-1.634993	5.053389
25	6	0	1.456040	1.989863	-1.028701
26	6	0	0.898538	-2.727830	-0.771661
27	8	0	-0.100117	1.436903	4.145976
28	6	0	-0.282009	-2.114786	-2.880520
29	6	0	4.938071	-4.238925	-1.556474
30	6	0	-1.444467	-2.885221	-2.478582
31	6	0	3.972409	-2.220130	-1.053546
32	6	0	0.835826	-1.957993	-2.023102
33	6	0	1.002893	0.373616	-2.821469
34	6	0	2.337311	-0.292584	-0.903820
35	6	0	-1.433916	-3.511448	-1.249462
36	6	0	-0.142617	0.200202	-3.677183
37	6	0	-0.678704	-3.518133	0.923526
38	6	0	-0.780894	-1.028342	-3.702314
39	6	0	0.967195	1.723933	-2.306609
40	6	0	0.701643	2.888799	-0.153441
41	6	0	-0.247547	-3.479346	-0.440720
42	6	0	5.326952	2.186532	-0.149832
43	6	0	4.078290	2.538562	0.375340
44	6	0	-3.682382	-2.654789	-0.743347
45	6	0	-0.451984	3.496485	-0.684604
46	6	0	-0.210364	2.370028	-2.838404
47	6	0	6.181000	3.202464	-0.572982
48	6	0	0.134093	-3.021525	1.900907
49	6	0	-2.235711	-1.074672	-3.728094
50	6	0	5.766347	-3.672598	-2.525026
51	6	0	-4.270933	-1.713532	0.195350
52	6	0	-2.979336	0.108186	-3.697090
53	6	0	-2.092566	-3.279255	0.980142
54	6	0	5.763117	4.528697	-0.458391
55	6	0	4.767609	-1.554944	-1.995012
56	6	0	-2.620422	-2.369591	1.925601
57	6	0	4.498734	4.775539	0.075810
58	6	0	-0.907798	1.432323	-3.688415
59	6	0	-4.827837	-0.645933	-0.611341
60	6	0	-4.354664	0.896152	1.207672
61	6	0	-2.579935	-3.388844	-0.362748
62	6	0	-1.618800	3.672075	0.137400
63	6	0	-2.644736	-2.214126	-2.936561
64	6	0	-4.134537	0.213612	-2.821160
65	6	0	-3.715021	-1.484815	1.482203
66	6	0	5.677052	-2.297172	-2.743821
67	6	0	-1.575333	3.210535	1.444452
68	6	0	-3.790363	-0.113200	2.017622
69	6	0	-4.488082	-0.866298	-2.008682
70	6	0	-3.752075	-2.106474	-2.083210
71	6	0	-2.705494	2.489029	1.986271
72	6	0	-2.302960	1.394782	-3.692015
73	6	0	-3.049025	2.301722	-2.837524
74	6	0	-0.915638	3.250817	-2.033447
75	6	0	-4.566019	1.779064	-0.967478
76	6	0	-2.368212	3.224254	-2.033241
77	6	0	-2.804880	3.473766	-0.676715
78	6	0	-3.813467	2.235102	1.199170
79	6	0	-4.869881	0.642173	-0.112569
80	6	0	-3.886120	2.758943	-0.151964
81	6	0	-4.176575	1.567101	-2.292465
82	1	0	4.358170	0.582921	2.366459
83	1	0	4.373158	-1.694505	1.555107
84	1	0	4.978083	-5.306720	-1.349107
85	1	0	5.614808	1.142581	-0.215933
86	1	0	7.157954	2.961965	-0.983596
87	1	0	6.459166	-4.291255	-3.086999
88	1	0	6.397752	5.351500	-0.772570
89	1	0	4.667486	-0.483181	-2.135216
90	1	0	4.130413	5.793789	0.184660
91	1	0	6.303942	-1.810890	-3.486363

The total electronic energy was calculated to be –3634.4345584 Hartree.

6. Differences in Energies between 7' and 8'

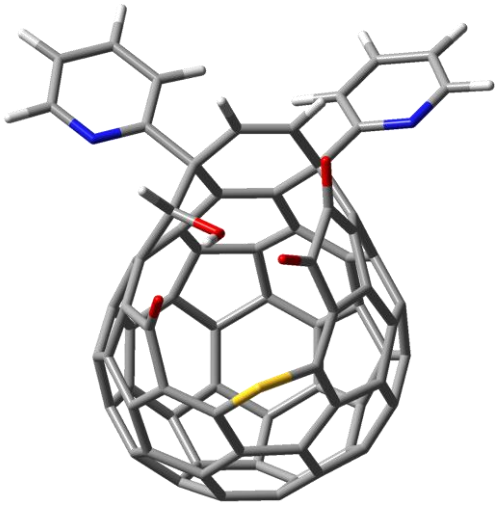
For the calculations to be simplified, 6-*t*-butylpyridin-2-yl groups were replaced with 2-pyridyl groups for **7'** and **8'**.



Δ*G*	0.00	+1.01
Δ*H*	0.00	+1.32
Δ*E*	0.00	+1.59

Figure S15. Difference in energies (units in kcal/mol) between two structural isomers, **7'** and **8'**, calculated at the B3LYP-D3/6-31G(d) level of theory (298 K).

Table S4. Optimized structure of **7'** (B3LYP-D3/6-31G(d))

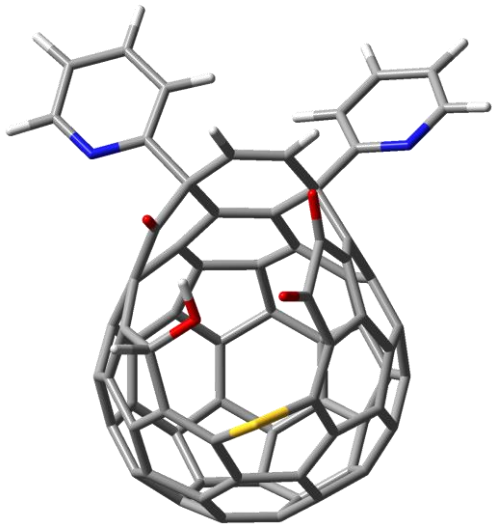


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.897887	0.898650	1.132940
2	6	0	3.986539	-0.428995	1.100326
3	6	0	3.140481	-1.322153	0.222361
4	6	0	2.014840	-2.067690	0.978134
5	6	0	1.682631	-1.841679	2.308539
6	6	0	2.207477	-0.986650	3.430792
7	6	0	0.929348	-0.493901	4.224312
8	6	0	-0.215254	-1.248766	3.659618
9	6	0	-1.570368	-0.943393	3.550031
10	6	0	-2.853312	1.239569	2.814301
11	6	0	-2.367488	2.449695	2.325995
12	6	0	-0.935120	2.948080	2.467950
13	6	0	-0.525631	3.271217	1.030800
14	6	0	0.634467	2.875766	0.367229
15	6	0	1.835786	2.343463	1.166954
16	6	0	2.961387	1.716154	0.277191
17	16	0	-2.150926	0.563864	4.303095
18	7	0	3.387398	4.083166	-0.283695
19	8	0	3.332306	-0.762177	3.807049
20	8	0	1.406701	1.327211	2.067939
21	7	0	4.304269	-3.466552	0.275301
22	6	0	2.291291	0.861959	-0.777451
23	6	0	1.576542	-1.259904	-1.756124
24	8	0	0.959811	0.355523	5.086442
25	6	0	1.356280	1.559234	-1.625236
26	6	0	1.080258	-2.812242	0.125639
27	8	0	-0.247606	2.975369	3.468739
28	6	0	-0.156624	-2.980227	-2.034841
29	6	0	5.182642	-4.354203	-0.207186
30	6	0	-1.279132	-3.613141	-1.367168
31	6	0	4.101679	-2.341339	-0.420002
32	6	0	0.966289	-2.509033	-1.308985
33	6	0	1.004871	-0.556540	-2.820667
34	6	0	2.395139	-0.510191	-0.833017
35	6	0	-1.226115	-3.785127	0.001271
36	6	0	-0.136022	-1.049443	-3.548266
37	6	0	-0.446110	-3.020591	2.026343
38	6	0	-0.713796	-2.245883	-3.156177
39	6	0	0.896038	0.883264	-2.755465
40	6	0	0.561298	2.657046	-1.068800
41	6	0	-0.032377	-3.440522	0.721259
42	6	0	4.884503	2.451155	-1.213081
43	6	0	3.776871	2.812926	-0.433339
44	6	0	-3.505952	-2.894844	0.244708
45	6	0	-0.605657	3.028744	-1.777319
46	6	0	-0.307012	1.269645	-3.450729
47	6	0	5.603048	3.448893	-1.862022
48	6	0	0.358090	-2.189806	2.751606
49	6	0	-2.165296	-2.357406	-3.129534
50	6	0	5.896638	-4.167450	-1.390478
51	6	0	-4.132354	-1.718764	0.824237
52	6	0	-2.964642	-1.264521	-3.477451
53	6	0	-1.867064	-2.823962	2.031707
54	6	0	5.197373	4.776894	-1.712161
55	6	0	4.777632	-2.055764	-1.612169
56	6	0	-2.424606	-1.664969	2.620784
57	6	0	4.087906	5.038172	-0.912019
58	6	0	-0.959311	0.077033	-3.943328
59	6	0	-4.755359	-1.017741	-0.280570
60	6	0	-4.370430	1.070418	0.902894
61	6	0	-2.365687	-3.408720	0.822230
62	6	0	-1.786656	3.445782	-1.072056
63	6	0	-2.513402	-3.182103	-1.993203
64	6	0	-4.119858	-0.922993	-2.664550
65	6	0	-3.575131	-1.038637	1.939939
66	6	0	5.687312	-2.987653	-2.104659
67	6	0	-1.740410	3.475363	0.309490
68	6	0	-3.739374	0.425464	1.990812
69	6	0	-4.415339	-1.682271	-1.529652
70	6	0	-3.616677	-2.838359	-1.199222
71	6	0	-2.847338	2.944698	1.079352
72	6	0	-2.350487	-0.020515	-3.911828
73	6	0	-3.137134	1.085846	-3.395455
74	6	0	-1.049415	2.336290	-2.970096
75	6	0	-4.630042	1.154225	-1.438797
76	6	0	-2.501053	2.253956	-2.954409
77	6	0	-2.958146	2.929126	-1.760604
78	6	0	-3.919060	2.361023	0.433651
79	6	0	-4.869571	0.358418	-0.244373
80	6	0	-4.010046	2.387809	-1.014950
81	6	0	-4.229051	0.526236	-2.620291
82	1	0	4.522034	1.458727	1.823937
83	1	0	4.666168	-0.944870	1.767308
84	1	0	5.167648	1.406621	-1.291164
85	1	0	6.465480	3.198060	-2.472566
86	1	0	6.593879	-4.922868	-1.737491
87	1	0	5.727107	5.588610	-2.199679
88	1	0	4.582918	-1.129235	-2.141636
89	1	0	6.222075	-2.797014	-3.030521
90	1	0	5.319258	-5.257719	0.383653
91	1	0	3.738918	6.058035	-0.764817
92	1	0	2.271951	3.185706	1.712456
93	1	0	1.184223	1.765700	2.904415

The total electronic energy was calculated to be – 3635.6737951 Hartree.

Table S5. Optimized structure of **8'** (B3LYP-D3/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.853846	0.184806	1.445100
2	6	0	3.821972	-1.038519	0.923010
3	6	0	2.985287	-1.448336	-0.263761
4	6	0	1.792230	-2.353994	0.126191
5	6	0	1.425298	-2.664652	1.436599
6	6	0	1.936403	-2.379345	2.829018
7	6	0	0.659203	-2.308456	3.765799
8	6	0	-0.489505	-2.658382	2.899801
9	6	0	-1.824119	-2.273347	2.912827
10	6	0	-2.853101	0.109778	3.063822
11	6	0	-2.186209	1.325638	3.043661
12	6	0	-0.713428	1.651574	3.423672
13	6	0	-0.313667	2.561543	2.218121
14	6	0	0.845897	2.532645	1.445943
15	6	0	2.099636	1.907035	1.940139
16	6	0	3.112284	1.367003	0.879263
17	16	0	-2.391301	-1.185665	4.204502
18	7	0	3.754107	3.736755	0.906591
19	8	0	3.055583	-2.299832	3.277699
20	8	0	2.350748	1.790004	3.130486
21	7	0	4.036732	-3.521743	-1.012691
22	6	0	2.365706	1.021912	-0.392181
23	6	0	1.509191	-0.517854	-2.088519
24	8	0	0.711468	-2.045849	4.944147
25	6	0	1.505150	2.058757	-0.911487
26	6	0	0.861971	-2.650770	-0.967428
27	8	0	0.033408	0.473583	3.516586
28	6	0	-0.304306	-1.882523	-3.032721
29	6	0	4.894096	-4.209958	-1.776689
30	6	0	-1.476625	-2.665004	-2.686673
31	6	0	3.927379	-2.204895	-1.221740
32	6	0	0.814216	-1.799611	-2.166638
33	6	0	1.017067	0.577383	-2.807442
34	6	0	2.348649	-0.239993	-0.946038
35	6	0	-1.475915	-3.377471	-1.505713
36	6	0	-0.133751	0.480126	-3.667549
37	6	0	-0.727671	-3.549126	0.663085
38	6	0	-0.788950	-0.734744	-3.776332
39	6	0	1.004053	1.890109	-2.201229
40	6	0	0.760703	2.889656	0.034522
41	6	0	-0.292464	-3.411416	-0.692615
42	6	0	5.306415	2.211488	-0.116787
43	6	0	4.111798	2.497423	0.554433
44	6	0	-3.717283	-2.539263	-0.943790
45	6	0	-0.384774	3.553460	-0.441764
46	6	0	-0.168276	2.587089	-2.677849
47	6	0	6.160562	3.264871	-0.430161
48	6	0	0.082167	-3.126645	1.677383
49	6	0	-2.244268	-0.761405	-3.805049
50	6	0	5.678039	-3.627752	-2.772368
51	6	0	-4.299713	-1.665152	0.062087
52	6	0	-2.971255	0.425883	-3.684925
53	6	0	-2.142441	-3.312097	0.732522
54	6	0	5.796485	4.561495	-0.063372
55	6	0	4.679104	-1.524977	-2.187546
56	6	0	-2.668369	-2.477633	1.744203
57	6	0	4.585513	4.741992	0.602711
58	6	0	-0.882137	1.720234	-3.587322
59	6	0	-4.838440	-0.531113	-0.663450
60	6	0	-4.342332	0.860008	1.268428
61	6	0	-2.624539	-3.313255	-0.616377
62	6	0	-1.547934	3.666674	0.396446
63	6	0	-2.668061	-1.948658	-3.096478
64	6	0	-4.125425	0.482309	-2.802915
65	6	0	-3.749228	-1.545499	1.366119
66	6	0	5.566463	-2.252350	-2.976430
67	6	0	-1.509410	3.095918	1.662765
68	6	0	-3.800888	-0.214694	2.001864
69	6	0	-4.494802	-0.649859	-2.072239
70	6	0	-3.775600	-1.890915	-2.238554
71	6	0	-2.635983	2.339410	2.148324
72	6	0	-2.277765	1.699924	-3.588260
73	6	0	-3.008254	2.549742	-2.665452
74	6	0	-0.859046	3.412185	-1.803374
75	6	0	-4.530329	1.908359	-0.834941
76	6	0	-2.312180	3.399786	-1.796814
77	6	0	-2.739488	3.546607	-0.422075
78	6	0	-3.762874	2.176782	1.358289
79	6	0	-4.857053	0.715869	-0.069363
80	6	0	-3.828111	2.807359	0.052838
81	6	0	-4.145538	1.792155	-2.173121
82	1	0	4.441082	0.381406	2.335073
83	1	0	4.382439	-1.839209	1.388195
84	1	0	5.550316	1.186644	-0.375392
85	1	0	7.095422	3.077786	-0.950254
86	1	0	6.353948	-4.234740	-3.365572
87	1	0	6.433189	5.411477	-0.285254
88	1	0	4.560757	-0.454644	-2.317957
89	1	0	6.158693	-1.754443	-3.738577
90	1	0	4.954058	-5.278547	-1.580461
91	1	0	4.263343	5.734958	0.908619
92	1	0	-0.671152	2.235641	4.356202
93	1	0	0.901523	0.704017	3.884005

The total electronic energy was calculated to be – 3635.6712615 Hartree.

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