Supporting Information

Synthesis and Structural Characterization of a Nonaromatic Dithia-di-2,6-naphthioctaphyrin(1.0.0.1.1.0.0.1)

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Contents

1. General Information

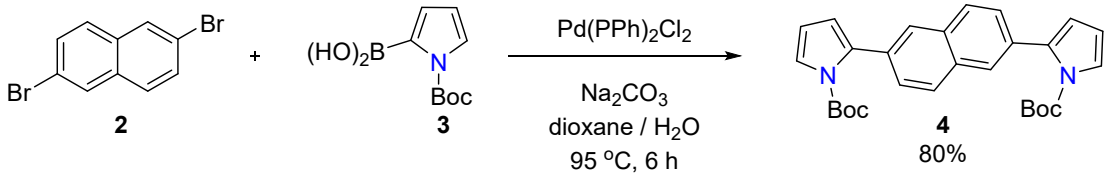
Materials: All reagents and solvents were purchased from Energy Chemical, Macklin, Adamas-beta®, TCI, Sigma-Aldrich and Innochem, and were used without further purification except where noted. Thin-layer chromatographic (TLC) analyses were carried out using pre-coated, glass-backed silica gel plates. Alumina column chromatography was performed on Merck deactivated Brockmann III neutral alumina oxide. Silica gel column chromatography was performed on Qingdao Haiyang silica gel of mesh size 200-300.

Instrumentation: All NMR spectra were acquired on either a Bruker 400 MHz instrument or a Bruker 500 MHz MHz NMR spectrometer. ^{1}H NMR Chemical shifts are reported in ppm relative to TMS (δ 0.00) or residual solvent signals as the internal reference standards ($CDCl_3$ δ = 7.26). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as *J* values in Hz. $^{13}C\{^{1}H\}$ NMR spectra were obtained at 100 MHz on the 400 MHz NMR instruments noted above. Chemical shifts were recorded relative to the solvent resonance ($CDCl_3$: δ 77.16). High-resolution mass spectrometrometric (HRMS) data were acquired on a Waters G2 XS mass spectrometer. UV−Vis−NIR spectra were recorded on a Varian Cary 5000 spectrophotometer.

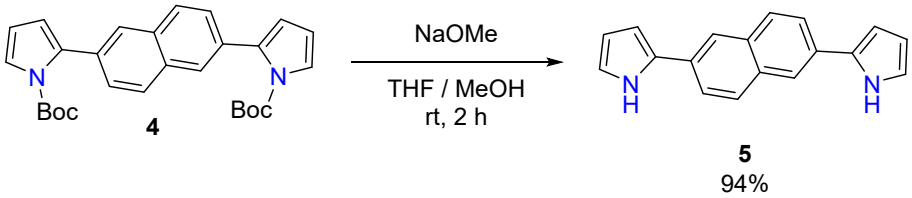
Computational Detail: All calculations were carried out using the Gaussian 16 program[1]. Initial geometrie of **1** was obtained from the X-ray diffraction coordinates. Geometry optimizations in the ground state (S_0) were performed by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals The time-dependent DFT (TD-DFT) method at the B3LYP/6-311G(d,p) level was employed to simulate the optical absorption properties of the macrocycle.

X-ray Crystal Structure Analysis: Single crystals of **1** were grown by slow diffusion of *n*-hexane into $CHCl_3$ solutions of the species in question at room temperature. The X-ray diffraction data for **1** was collected in Bruker D8 Venture diffractometer with a PHOTON III detector and a μ-focus Cu$K\alpha$ radiation source (λ = 1.5418 Å), or Ga$K\alpha$ radiation (λ = 1.34139 Å). The crystal was kept at 215.0 K during data collection. The crystal structure data have been deposited in the Cambridge Crystallographic Data Centre with reference no. CCDC 2521026 [**1**]

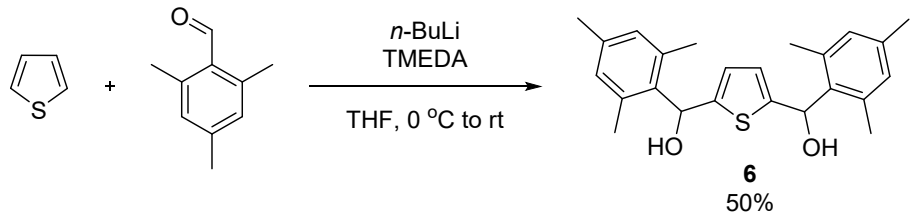
2. Synthetic Procedures and Compound Characterization Data



Compound 4. To a 250 mL round-bottom flask maintained under a nitrogen atmosphere was added a mixture of 2,6-dibromonaphthalene **2** (866.5 mg, 3.0 mmol), *N*-Boc-2-pyrroleboronic acid **3** (1.60 g, 7.6 mmol), bis(triphenylphosphine)palladium(II) chloride (210.6 mg, 0.30 mmol), and Na_2CO_3 (634.0 mg, 6.0 mmol) in 1,4-dioxane (50 mL) and water (3 mL). The reaction mixture was stirred at 95 °C in an oil bath for 6 h. After completion, the solvent was removed under reduced pressure, and the resulting dark residue was extracted with ethyl acetate and water (3×). The combined organic layers were concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography using dichloromethane as the eluent. The solvent was evaporated under reduced pressure, and the residue was washed with methanol to afford compound **4** as an off-white solid (1.10 g, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 4H), 7.46 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.41 (dd, *J* = 3.2, 1.9 Hz, 2H), 6.28 (dt, *J* = 6.5, 3.3 Hz, 4H), 1.32 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 149.58, 135.10, 132.13, 132.08, 128.27, 127.13, 126.87, 122.96, 115.06, 110.89, 83.87, 27.76.

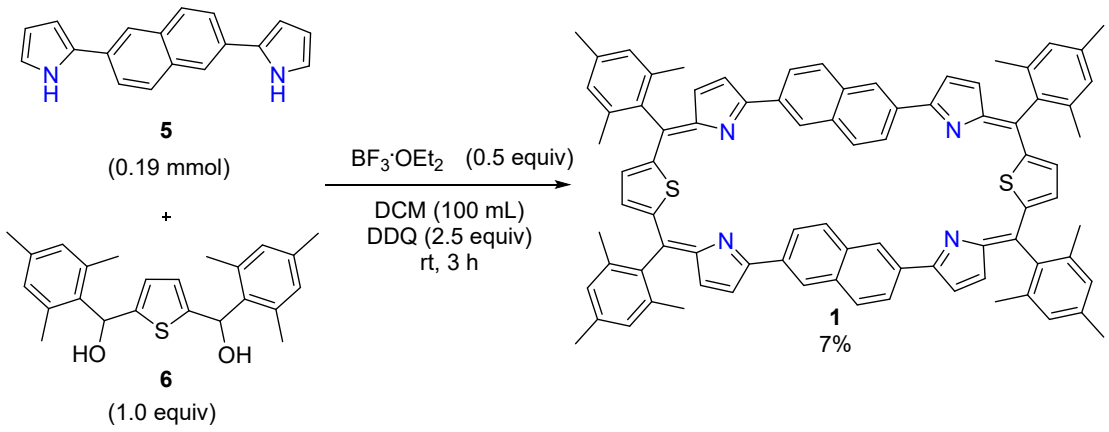


Compound 5. To a 100 mL round-bottom flask, a methanol–THF (1:10, v/v; 20 mL total volume) solution of compound **4** (1.00 g, 2.2 mmol) was treated with NaOMe (1.00 g, 18.5 mmol) at room temperature and stirred for 3 h. The progress of the reaction was monitored by TLC, which showed complete consumption of the starting material, indicating smooth deprotection. Upon completion, the reaction mixture was poured into water (200 mL). The resulting precipitate was collected by filtration and washed with methanol to afford compound **5** as a grayish-white solid (534.2 mg, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 2H), 8.03 (s, 2H), 7.79 (s, 4H), 7.00 – 6.82 (m, 2H), 6.64 (s, 2H), 6.26 – 6.09 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 131.78, 131.21, 129.72, 127.87, 123.60, 120.22, 119.75, 109.33, 106.22.



Compound 6. To a 100 mL round-bottomed flask equipped with a magnetic stir bar were added thiophene (562.8 μL, 7.13 mmol) and dry THF (25 mL). The reaction mixture was stirred under an inert atmosphere, after which *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 3.20 mL, 21.0 mmol) was added and the mixture was stirred at room temperature for 5 min. *n*-BuLi in hexane (1.6 M, 13.04 mL, 21.0 mmol) was then added dropwise via syringe. The reaction mixture was stirred at room temperature for 1 h and subsequently heated in an oil bath at 66 °C for an additional 1 h. The mixture was allowed to cool to room temperature and then to 0 °C. At this temperature, mesitaldehyde (2.51 mL, 17.0 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the product was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1, v/v) as the eluent, concentrated under reduced pressure, and washed with methanol to afford compound **6** as a white solid (1.36 g, 50%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.78 (s, 4H), 6.29 (s, 2H), 6.15 (d, J = 4.3 Hz, 2H), 5.88 (d, J = 4.3 Hz, 2H), 2.22 (s, 12H), 2.20 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 147.52, 137.32, 136.14, 135.93, 129.44, 121.91, 67.24, 20.49, 20.18.

Table S1. Synthetic optimization studies for macrocycle **1**.



entry	variation from the standard conditions	yield (%)[a]
1	none	7
2	1.3 equiv of compound **6** instead of 1.0 equiv	7
3	0.5 equiv of TFA instead of $BF_3 \cdot OEt_2$	5
4	0.5 equiv of MSA instead of $BF_3 \cdot OEt_2$	5
5	0.5 equiv of PTSA instead of $BF_3 \cdot OEt_2$	nd
6	1.0 equiv of $BF_3 \cdot OEt_2$ instead of 0.5 equiv	nd
7	1.5 equiv of DDQ instead of 2.5 equiv	7
8	2.5 equiv of TCQ instead of DDQ	nd
9	reaction time 12 h instead of 3 h	7
10	200 mL of DCM instead of 100 mL	7

[a]Isolated yield. [b]nd indicates not determined.

Compound 1. In a 250 mL round-bottomed flask, compound **5** (50.0 mg, 0.19 mmol) and compound **6** (72.3 mg, 0.19 mmol) were dissolved in dry CH_2Cl_2 (100 mL). $BF_3 \cdot OEt_2$ (12 μL, 0.10 mmol) was then added, and the reaction mixture was stirred at room temperature for 3 h. DDQ (108 mg, 0.475 mmol) was subsequently added, and the mixture was stirred for an additional 1 h under air. Triethylamine (0.50 mL, 3.60 mmol) was then added, and the resulting solution was passed through a short column of neutral alumina. All colored fractions were collected and concentrated under reduced pressure. The crude product was further purified by silica gel column chromatography using CH_2Cl_2 as the eluent to afford compound **1** as a green solid (8 mg, 7%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 4H), 7.70 (d, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 8.5 Hz, 4H), 7.12 (d, *J* = 4.6 Hz, 4H), 6.97 (s, 8H), 6.81 (d, *J* = 4.5 Hz, 4H), 6.70 (s, 4H), 2.37 (s, 12H), 2.19 (s, 24H). HRMS (ESI): *m/z* calculated for $C_{84}H_{69}N_4S_2$ $[M+H]^+$: 1197.4959; found: 1197.4971. The $^{13}C\{^1H\}$ NMR spectra could not be recorded because of the poor solubility of **1** in common organic solvents. This product was further characterized by single crystal X-ray diffraction analysis.

3. Mass and NMR spectra

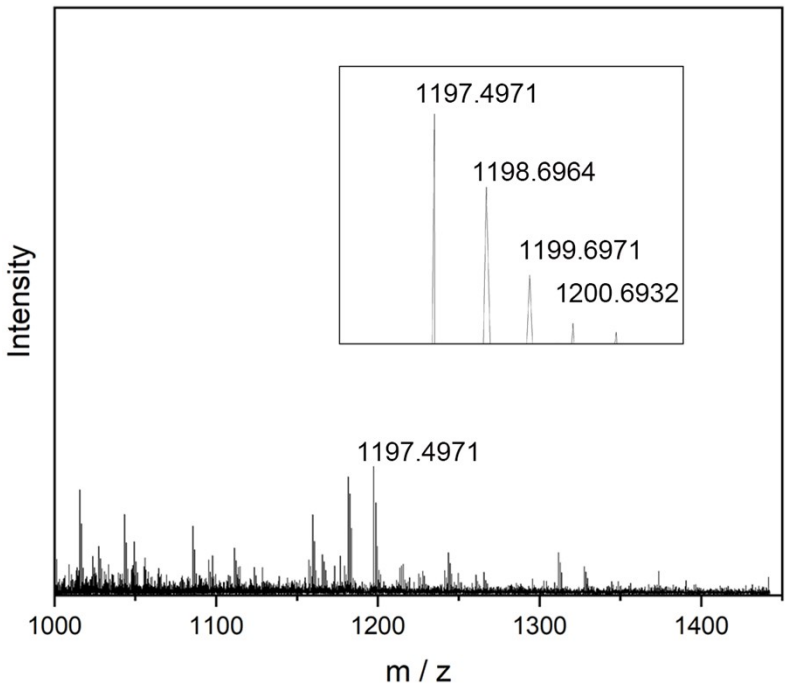


Figure S1. High-resolution mass spectrum of compound **1**.

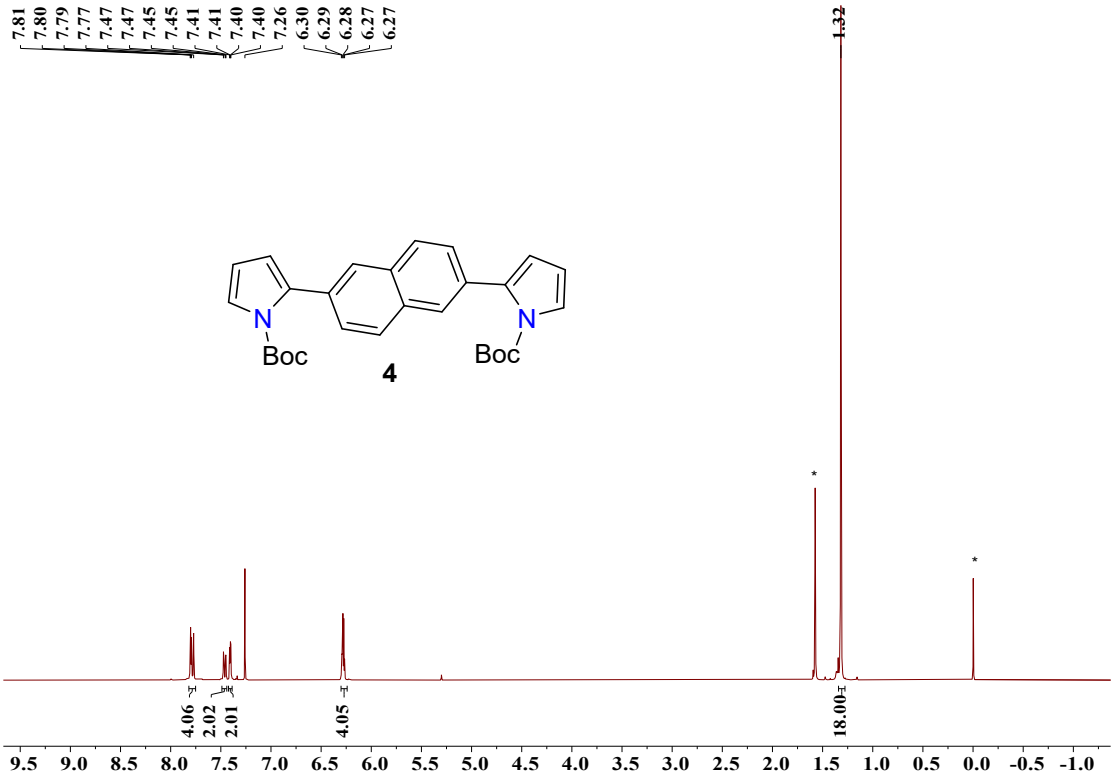


Figure S2. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

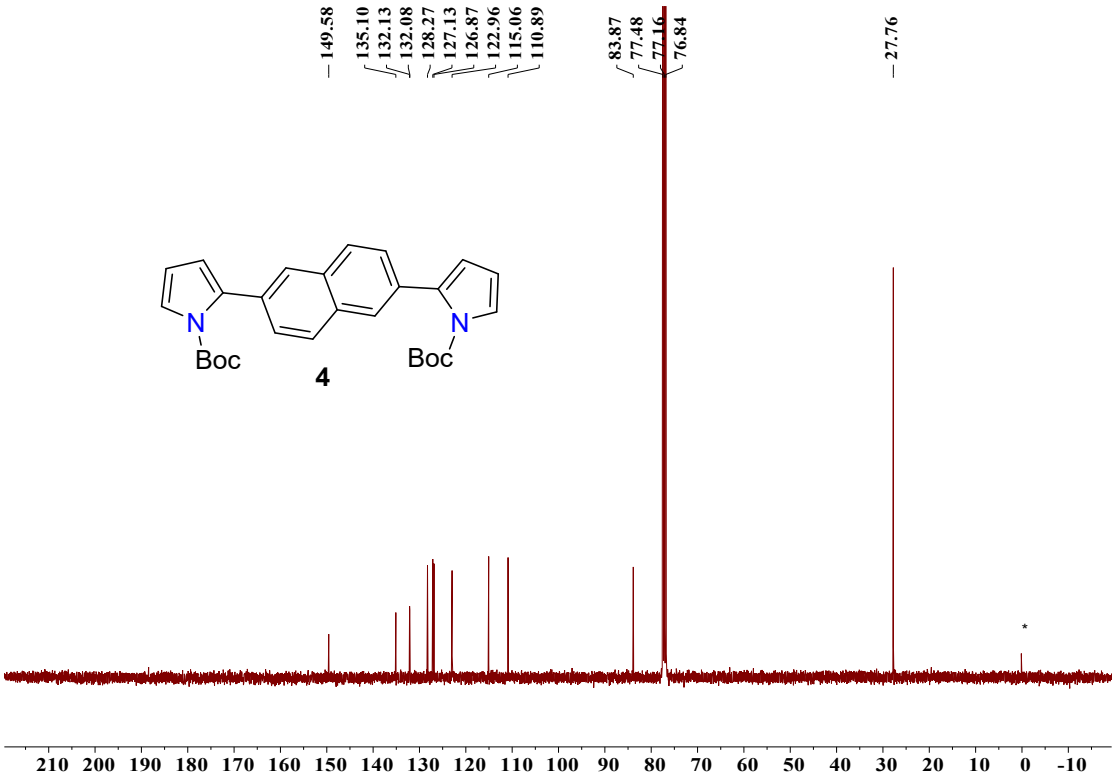


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **4** recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

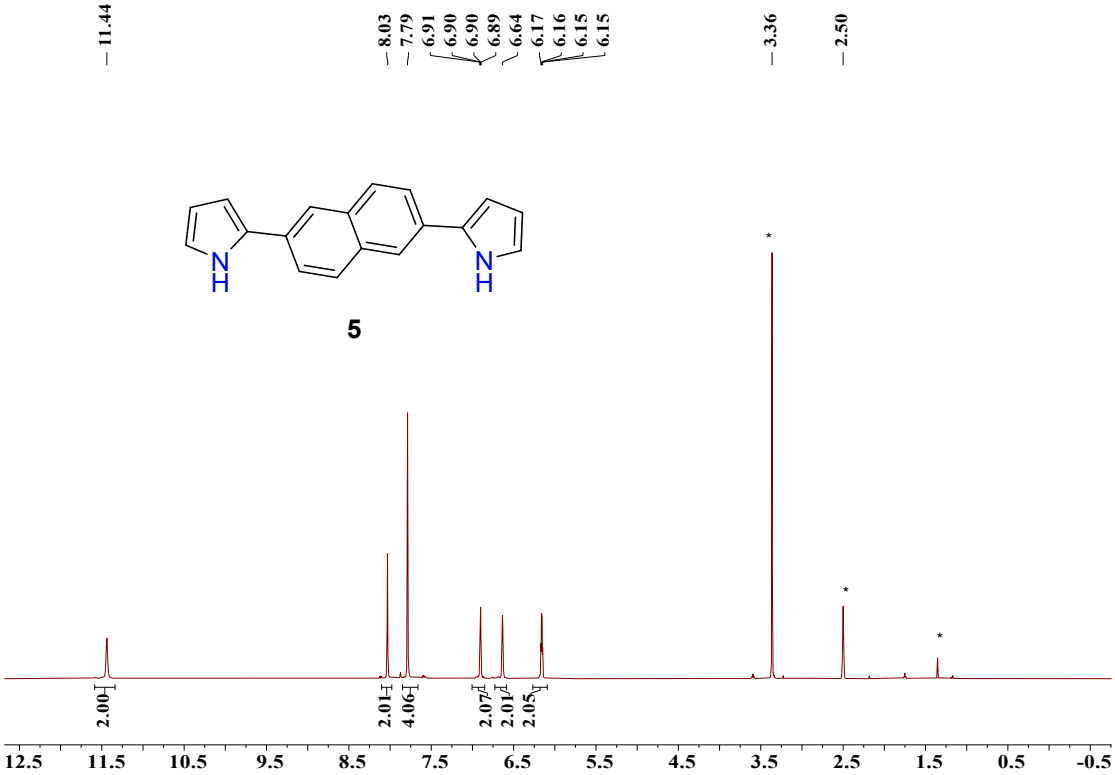


Figure S4. ^{1}H NMR spectrum of **5** recorded in DMSO-d_6 at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

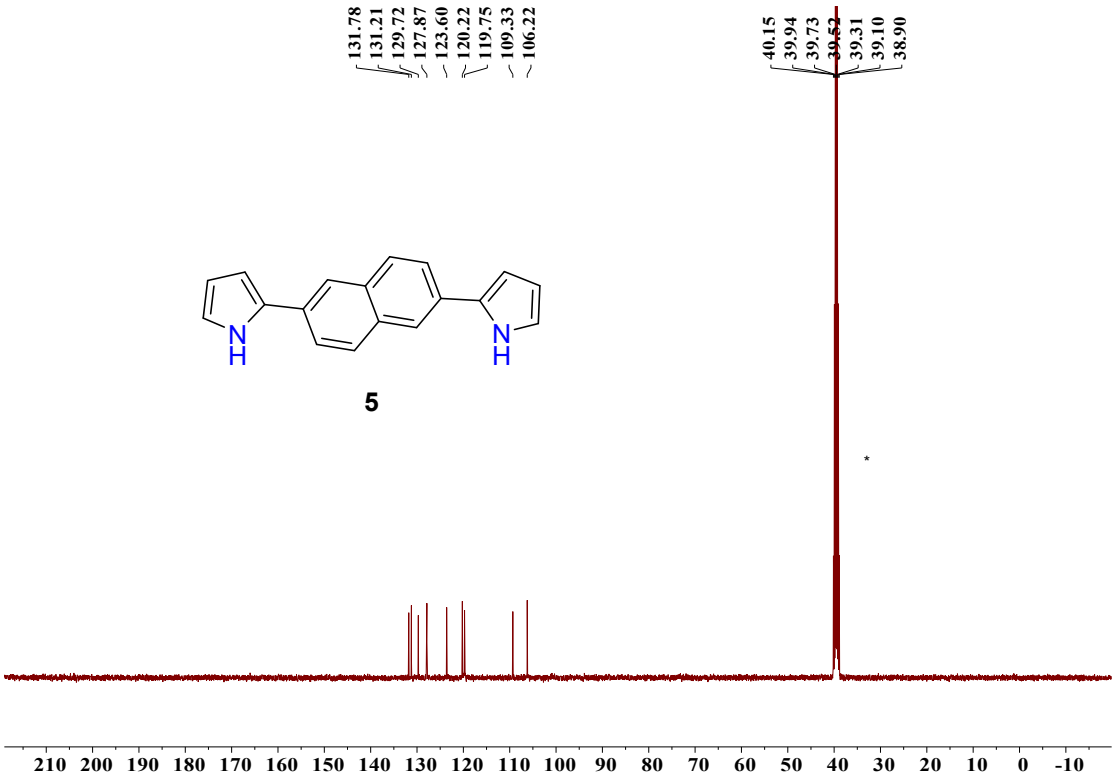


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **5** recorded in DMSO-d_6 at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

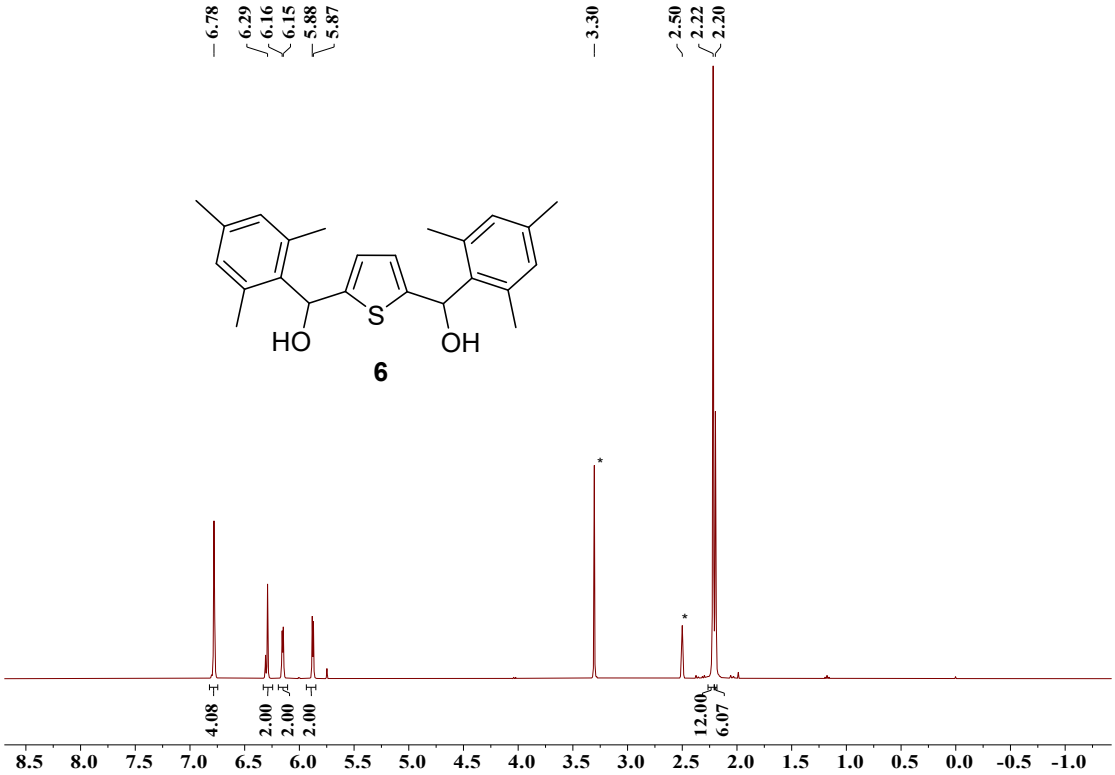


Figure S6. ^{1}H NMR spectrum of **6** recorded in DMSO-d_6 at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

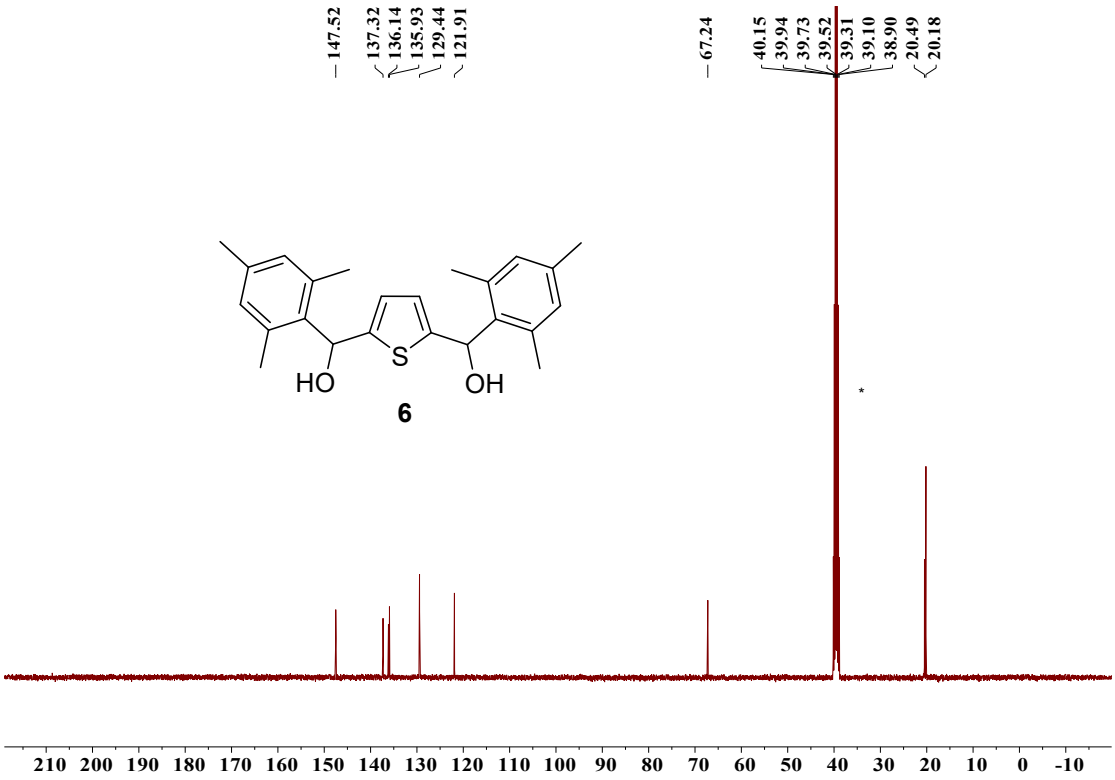


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **6** recorded in DMSO-d_6 at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

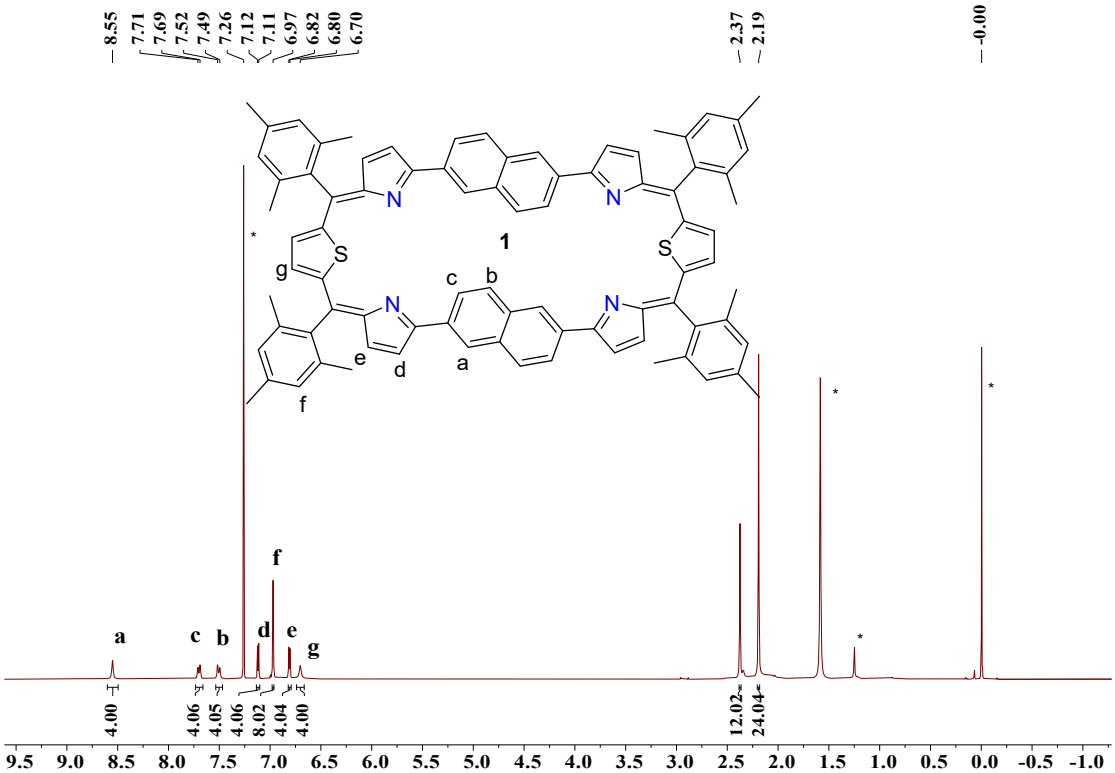


Figure S8. ^{1}H NMR spectrum of **1** recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

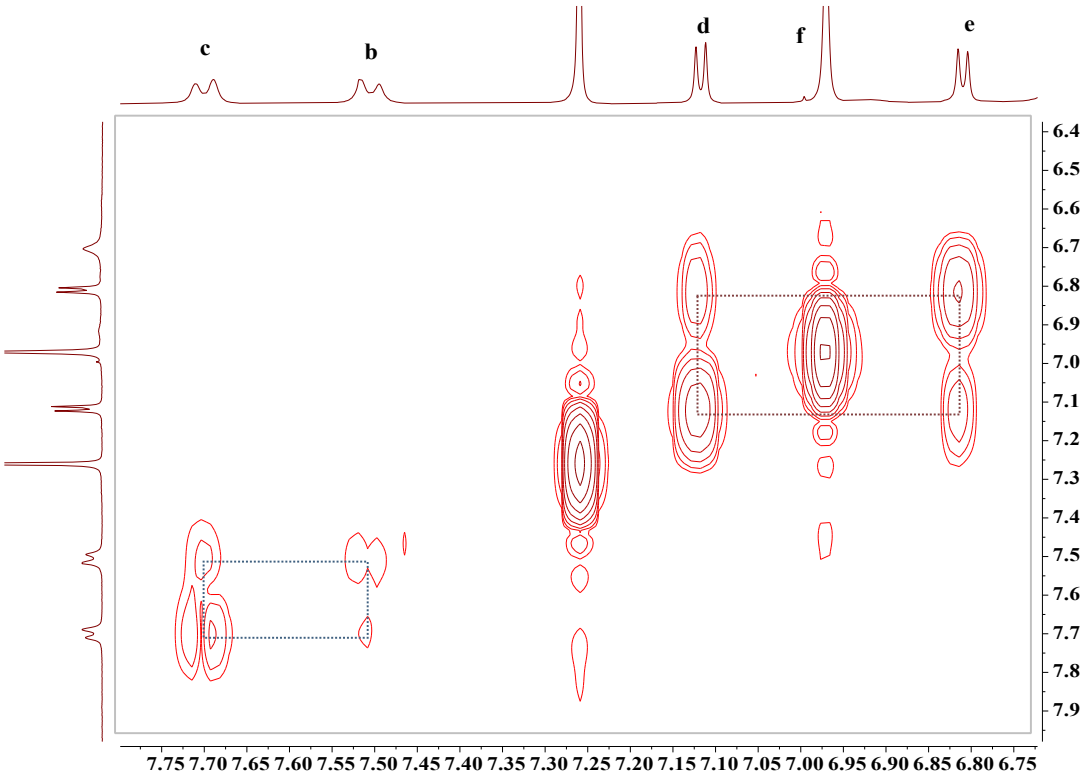


Figure S9. COSY spectrum of **1** recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

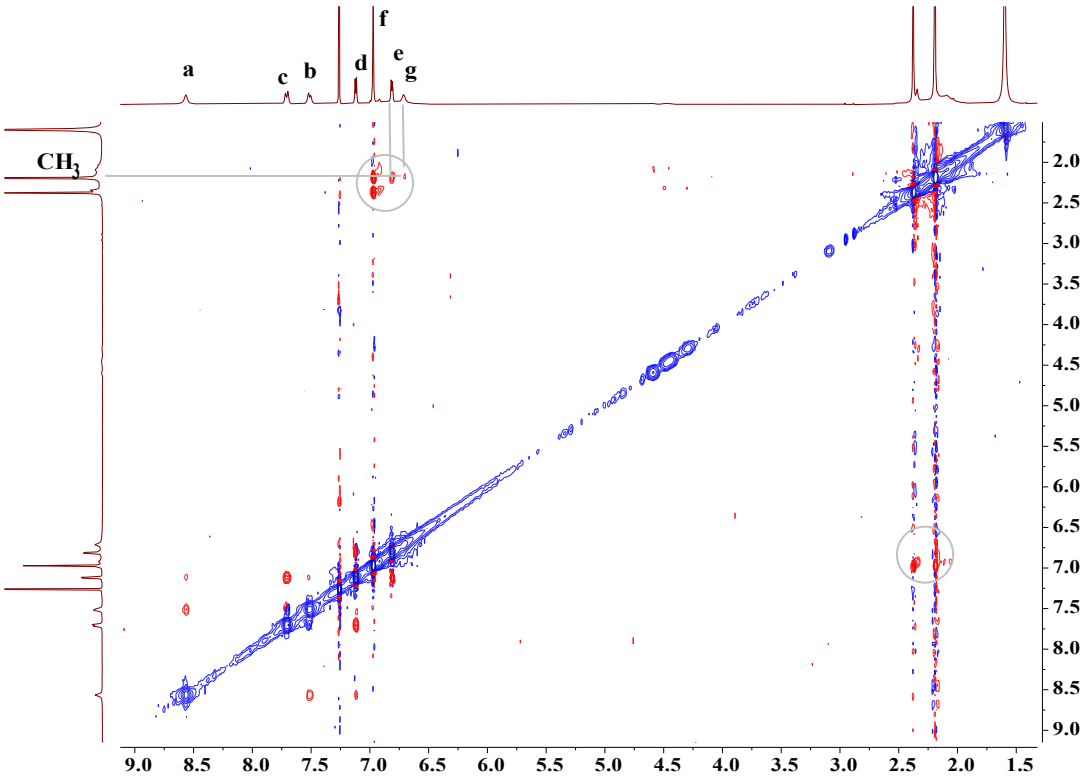


Figure S10. ROESY spectrum of **1** recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

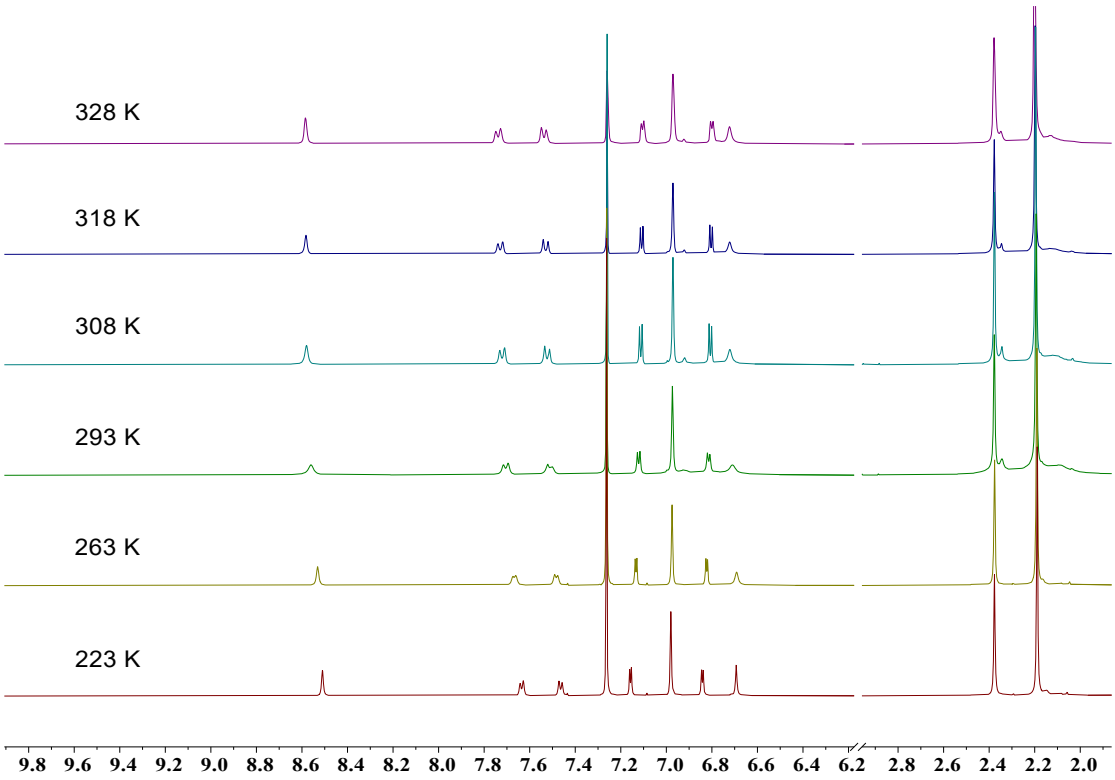


Figure S11. Variable-temperature ^{1}H NMR spectra of **1** recorded in $CDCl_3$ (400 MHz, 223–328 K).

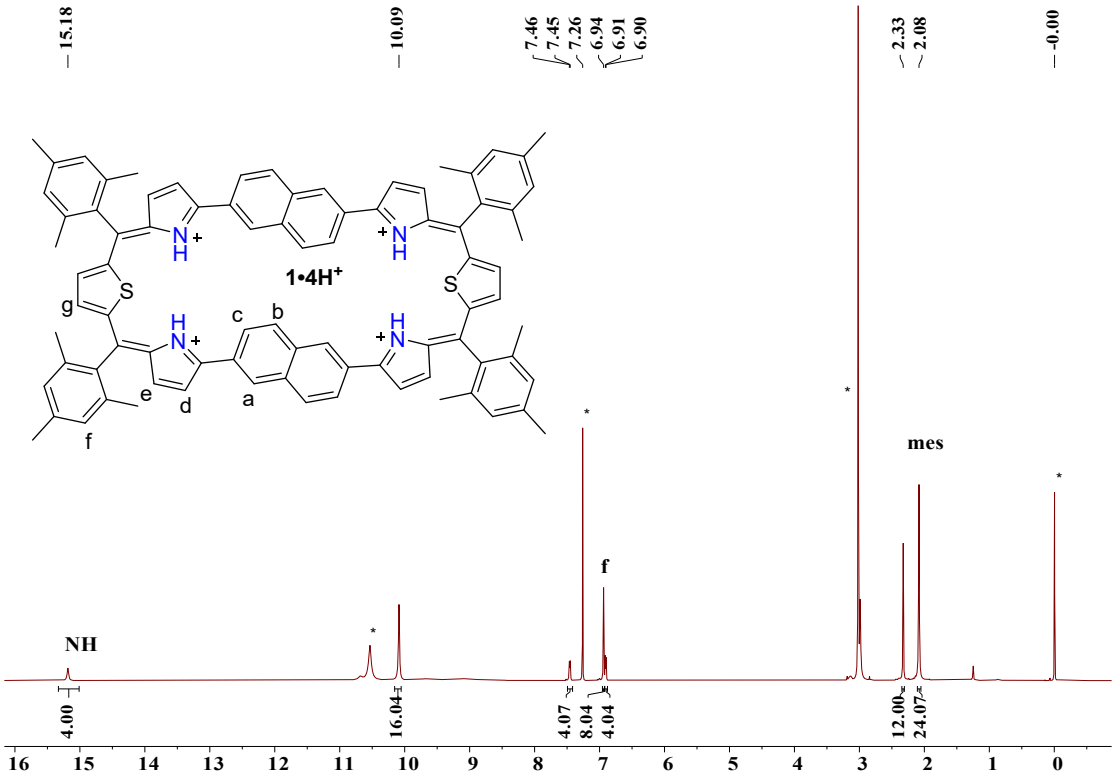


Figure S12. ^{1}H NMR spectrum of **1** after adding excess amount of MSA recorded in $CDCl_3$ at 25 °C (400 MHz). *Asterisk marks represent water and residual solvents in the sample.

4. Absorption and Emission Spectra

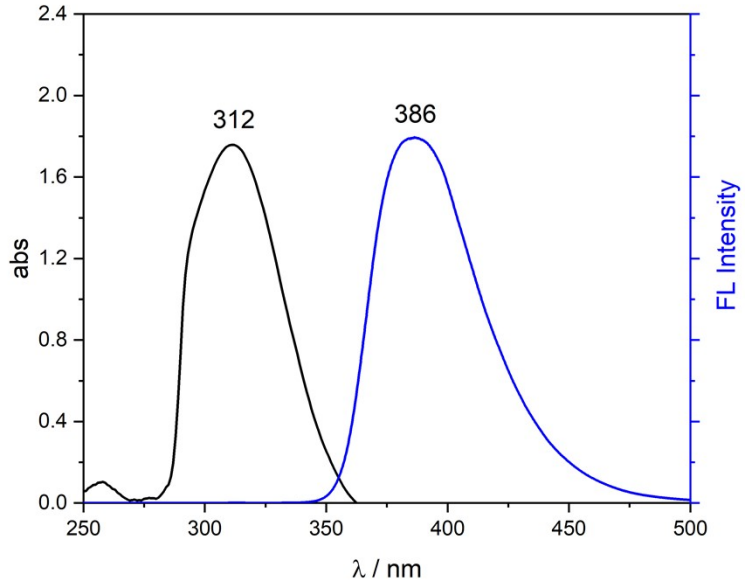


Figure S13. UV-Vis absorption and fluorescence spectra (λ_{ex} = 311) of **4** (8×10^{-5} M) recorded in THF at room temperature.

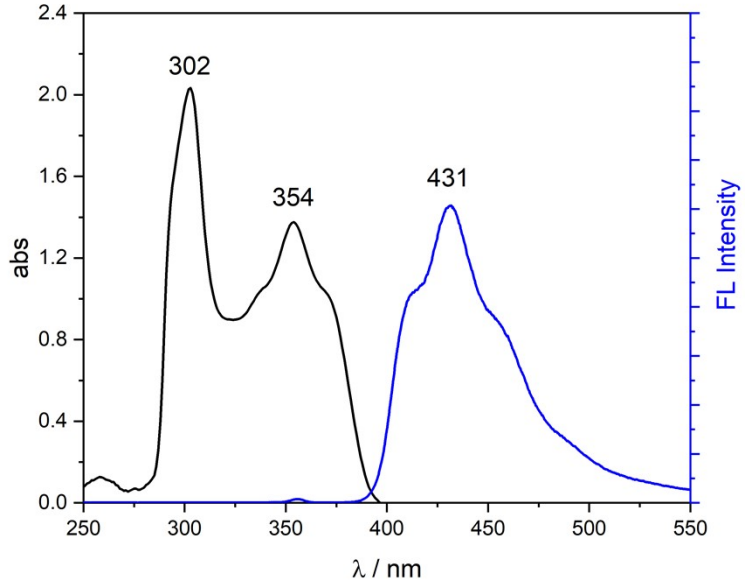


Figure S14. UV-Vis absorption and fluorescence spectra (λ_{ex} = 354) of **5** (8×10^{-5} M) recorded in THF at room temperature.

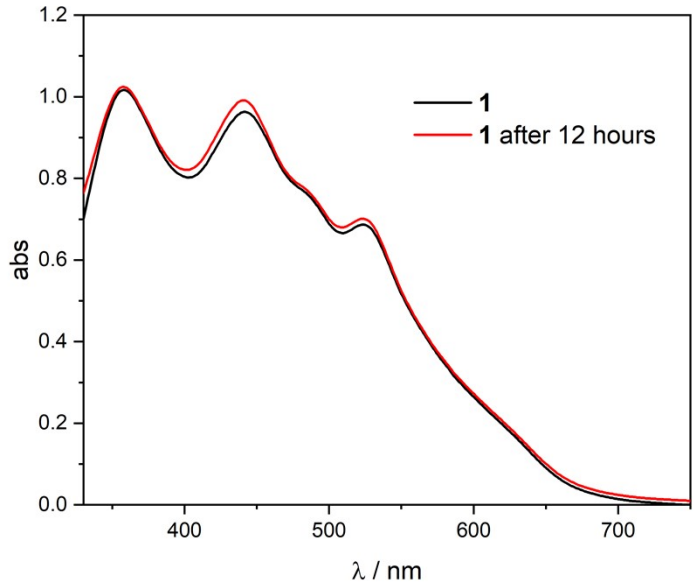


Figure S15. UV–Vis absorption spectra of **1** before (black) and after 12 h exposure to air (red) in THF at room temperature.

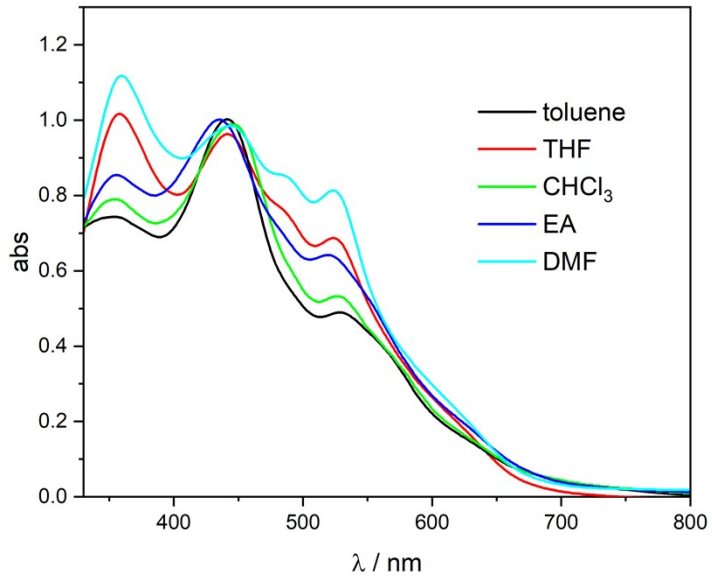


Figure S16. UV–Vis absorption spectra of compound **1** (1×10^{-5} M) recorded in various solvents at room temperature.

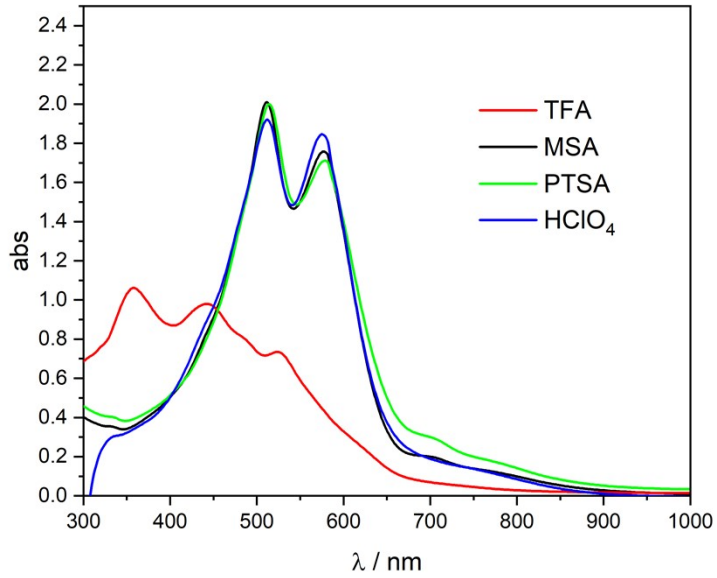


Figure S17. UV–Vis absorption spectra of compound **1** (1×10^{-5} M) after treatment with different acids (excess), recorded in THF at room temperature.

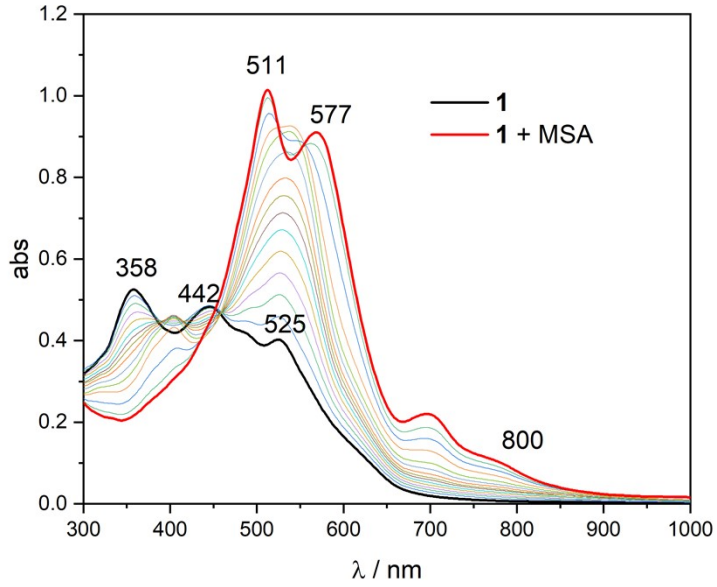


Figure S18. UV–Vis absorption spectra of **1** (5×10^{-6} M) before (black) and after addition of 3000 equiv. of MSA (red) in THF at room temperature.

5. Single Crystal X-ray Structure Analysis

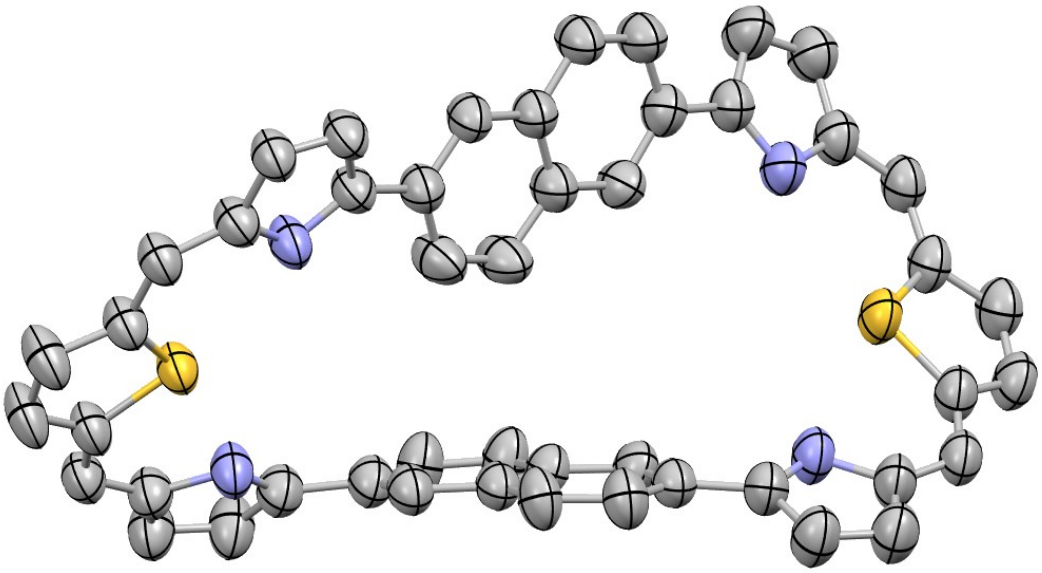


Figure S19. ORTEP drawings for **1**, thermal ellipsoids are set at 50% probability. Peripheral alkyl groups and hydrogen atoms have been omitted for clarity.

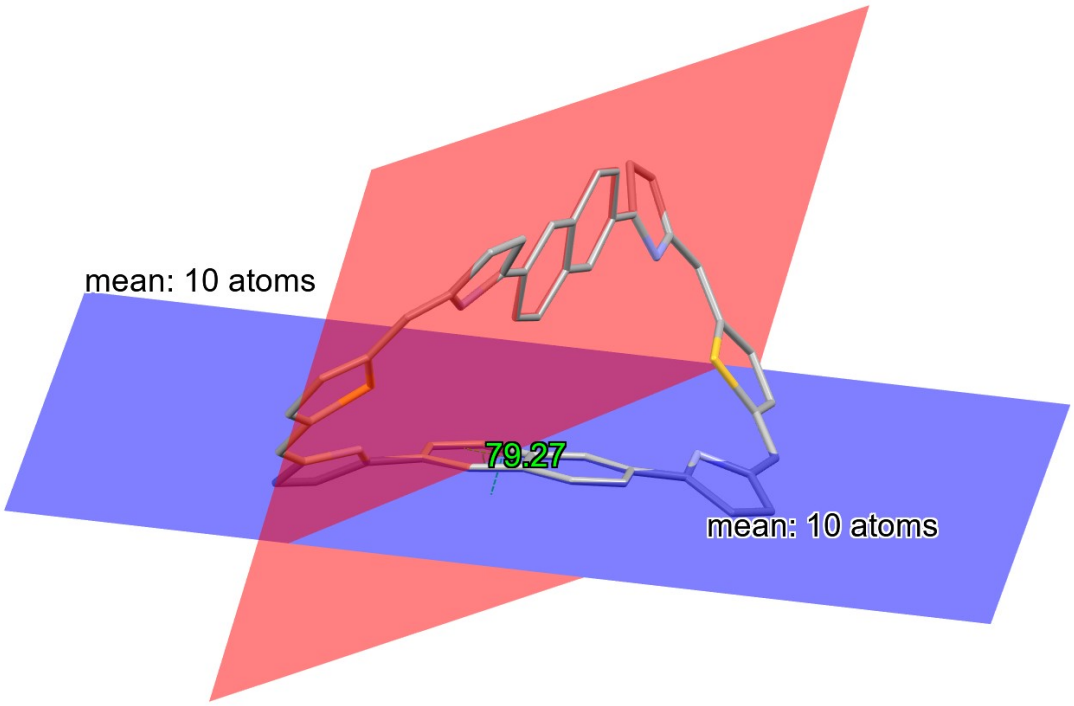


Figure S20. Selected dihedral angles (°) for **1** deduced from the corresponding single crystal X-ray diffraction structure. *Meso*-aryl groups and hydrogens have been omitted for clarity.

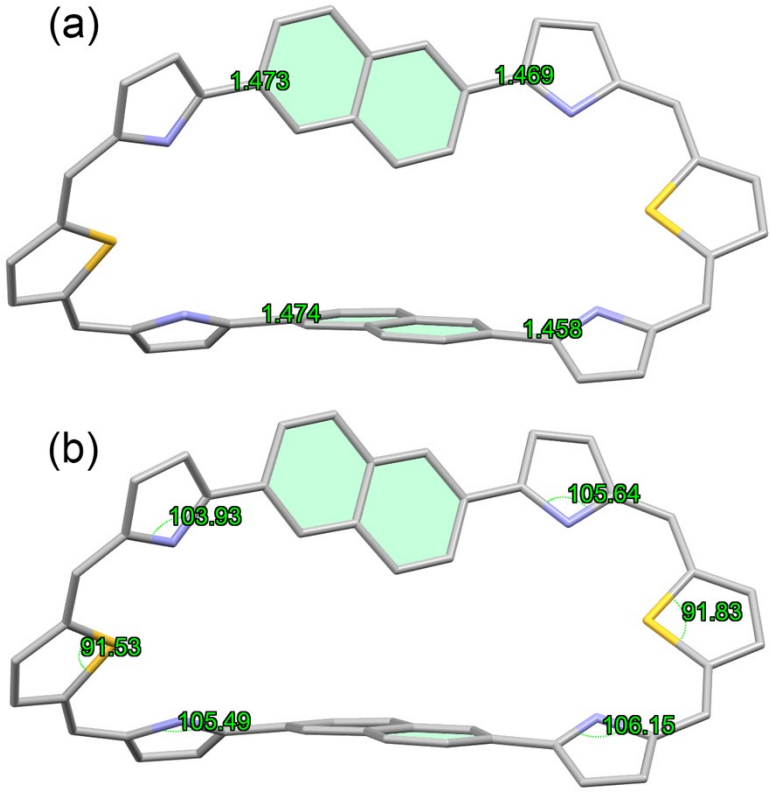


Figure S21. Selected bond lengths (a, Å) and bond angles (b, °) for **1** deduced from the corresponding single crystal X-ray diffraction structure. *Meso*-aryl groups and hydrogens have been omitted for clarity.

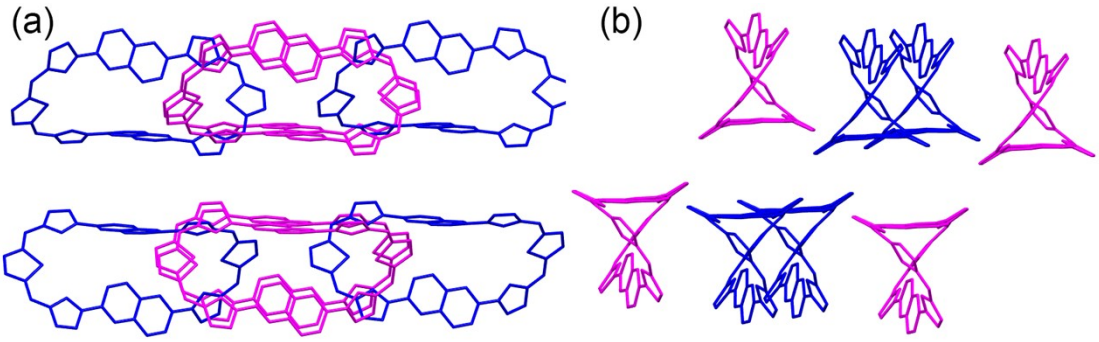


Figure S22. X-ray packing structures of **1**. Top view (a) and side view (b). *Meso*-aryl groups and hydrogens have been omitted for clarity.

Table S2. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{87}H_{71}Cl_9N_4S_2$
Formula weight	1555.64
Temperature/K	215
Crystal system,	triclinic
Space group	P -1
a/Å	13.5455(5)
b/Å	14.0485(5)
c/Å	22.4224(8)
α/°	95.993(2)
β/°	103.731(2)
γ/°	94.466(2)
Volume/Å^3	4098.9(3)
Z	2
ρ_{calc} g/cm^3	1.260
μ/mm^{-1}	3.643
F(000)	1612.0
Crystal size/mm^3	0.38 × 0.35 × 0.21
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	3.181 to 66.274
Limiting indices	-16≤h≤16, -16≤k≤16, -26≤l≤26
Reflections collected	14677
Independent reflections	14677
R(reflections)	0.0728
wR2(reflections)	0.2413

6. DFT Calculations

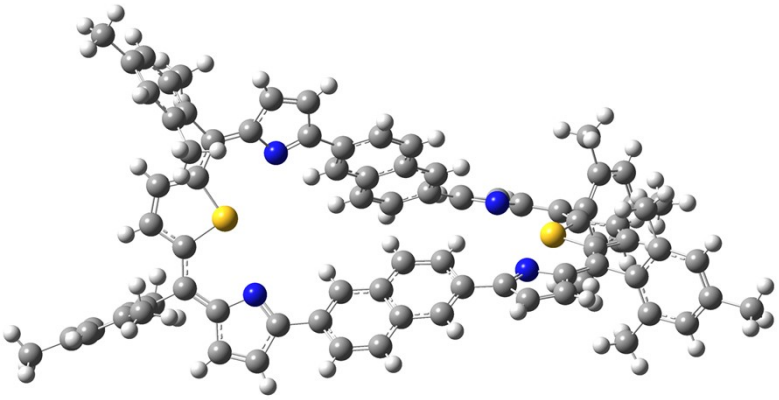


Figure S23. Optimized structures of **1**.

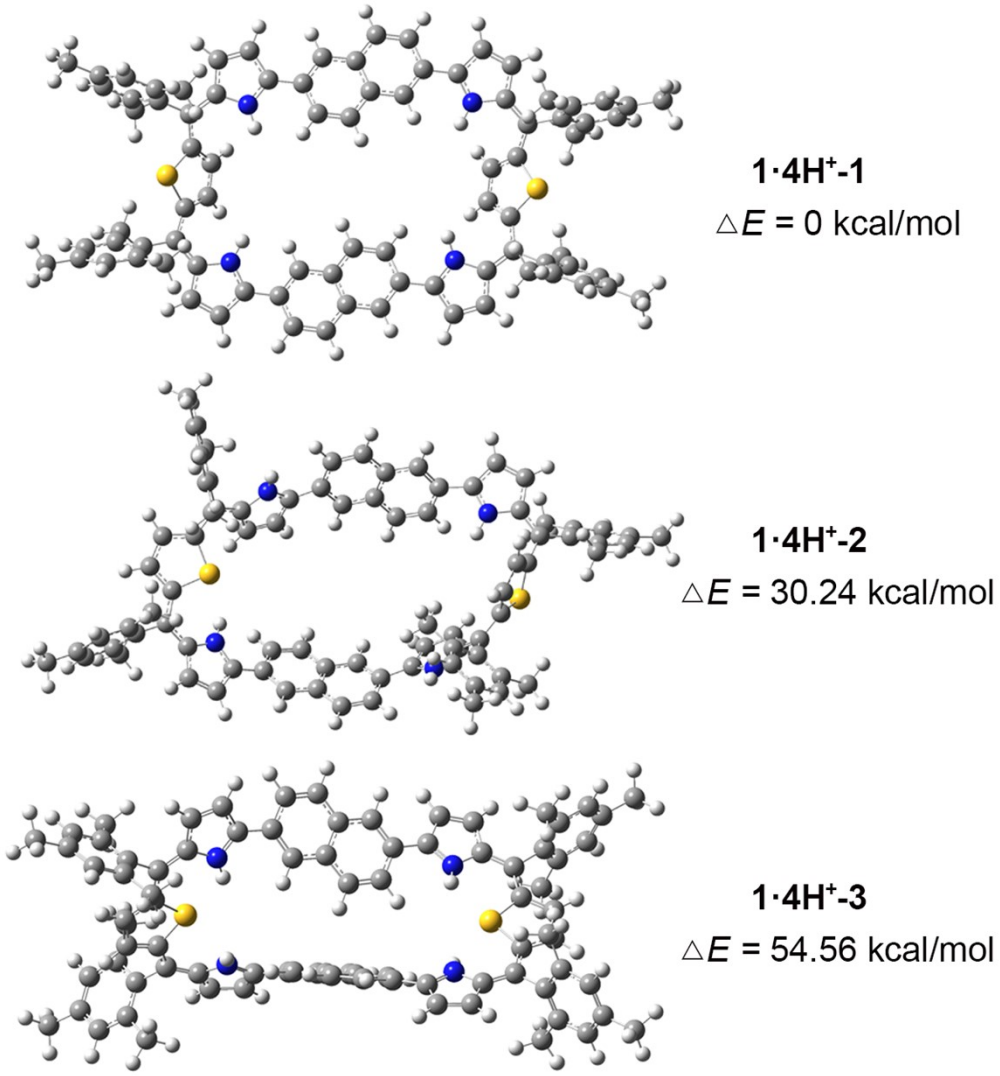


Figure S24. Geometries and calculated energies for selected conformers of **1·4H**$^+$. Note: The conformer of **1·4H**$^+$ with inversion of the thiophene rings(**1·4H**$^+$**-1**) is energetically more stable.

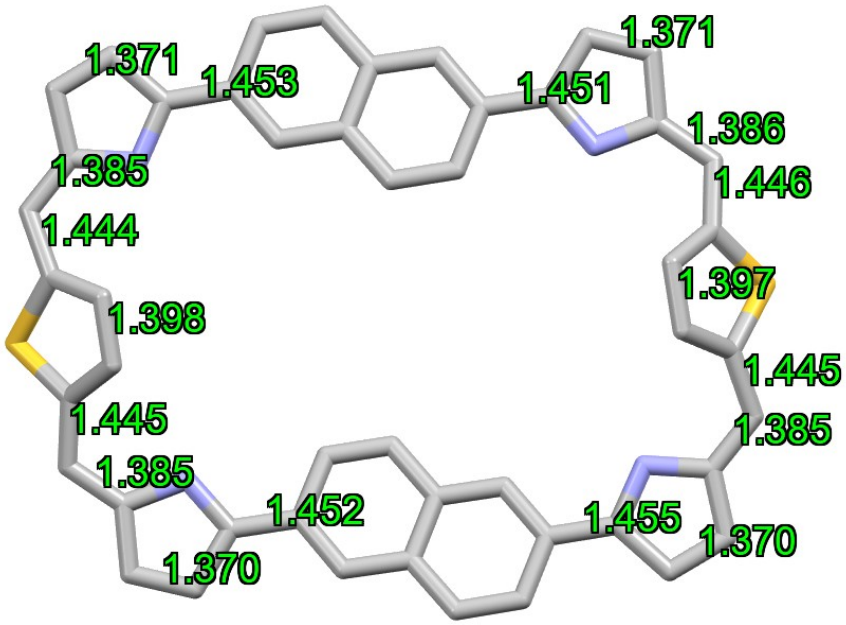


Figure S25. Selected bond lengths (a, Å) for **1**·4H$^+$(**1**·4H$^+$-**1**) obtained from the corresponding DFT-optimized structure. Meso-aryl groups and hydrogen atoms have been omitted for clarity.

7. Supporting References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

Appendix: Cartesian Coordinates of All Molecules for Theoretical Calculations

Table S3. Optimized coordinates of **1**.

* Sum of imaginary frequencies = 0

atom	X	Y	Z
S	-3.7928	6.8242	15.9585
S	5.3649	-0.7702	15.9946
N	-3.2355	5.1168	18.1603
N	-1.9456	6.8618	13.8911
N	5.3273	1.0488	18.1657
N	3.1196	-0.8923	14.1961
C	-1.2407	3.8637	18.8029
C	5.7287	-1.986	14.8244
C	-0.1643	2.9931	13.8277
C	-2.6228	4.3176	19.0096
C	-5.1893	6.9811	16.9655
C	-4.6447	4.6259	19.9499
H	-5.4026	4.6006	20.5052
C	-0.8812	1.7908	13.9416
H	-1.82	1.8177	13.9916
C	1.152	0.5131	13.9559
C	-4.3443	8.0767	14.9046
C	-3.4792	3.9813	20.1385
H	-3.2598	3.4213	20.8608
C	4.7165	-2.6845	14.0874
C	-3.5577	8.6545	13.8476
C	0.8588	3.0346	19.7109
C	-6.65	6.5729	18.9411
C	-2.383	8.1031	13.4278
C	-0.485	3.4571	19.868
H	-0.8668	3.4576	20.7268
C	1.2697	2.9234	13.8031
C	5.1055	-4.0218	13.5162
C	1.8503	-0.7843	13.9047
C	-0.0598	5.397	13.5279
C	7.0999	1.5792	19.5917
H	7.9684	1.6443	19.9444
C	3.5121	2.2036	19.3311
C	-5.3997	6.2416	18.17
C	7.4959	0.0944	17.6005
C	-4.4924	5.3676	18.7175
C	-4.0532	9.9332	13.2457
C	4.9143	1.779	19.1794

C	2.9641	2.3226	20.624
H	3.5021	2.1368	21.3725
C	-5.5881	8.5411	15.314
H	-6.0623	9.2135	14.8582
C	-4.3326	12.3022	13.3284
H	-4.1853	13.1258	13.7571
C	-0.7828	4.2429	13.7145
H	-1.7194	4.2943	13.7679
C	-3.8343	11.1381	13.9215
C	1.6617	2.7025	20.807
H	1.3048	2.7407	21.6756
C	6.698	0.882	18.4075
C	-1.3822	8.6585	12.5355
H	-1.4365	9.473	12.0702
C	-5.029	12.287	12.1445
C	-0.7652	6.6595	13.3375
C	-0.243	0.5841	13.9809
H	-0.7477	-0.2072	14.0255
C	1.3539	5.3237	13.4991
H	1.8592	6.1079	13.3826
C	1.8868	1.6705	13.8859
H	2.826	1.6197	13.8933
C	1.4049	2.9767	18.4012
C	-6.0654	7.9232	16.4552
H	-6.8974	8.1225	16.8442
C	2.7139	2.5055	18.2415
H	3.059	2.392	17.3745
C	9.8704	0.8557	17.3211
C	8.9651	-0.0292	17.8993
C	7.0852	-2.2603	14.7894
H	7.4766	-2.8733	14.194
C	-7.8482	5.9281	18.6283
C	-0.6656	3.8587	17.5279
H	-1.1645	4.1746	16.7968
C	-0.3585	7.7803	12.5031
H	0.452	7.8726	12.0349
C	-6.5816	7.5493	19.9255
C	0.6034	3.4059	17.3231
H	0.9488	3.3791	16.4496
C	7.0151	-0.6961	16.4993
C	5.4444	-4.1354	12.1704
C	-4.7577	9.8896	12.065
C	1.9877	4.1289	13.6417

H	2.928	4.1036	13.6298
C	3.4628	-2.2151	13.8891
C	5.9821	2.1216	20.0931
H	5.9074	2.6248	20.8834
C	-8.9633	7.2635	20.3416
C	1.2863	-2.0363	13.4213
H	0.3926	-2.198	13.1807
C	-5.2473	11.0951	11.5203
H	-5.7304	11.077	10.7142
C	5.1622	-5.1453	14.3612
C	-7.7602	7.8808	20.5965
H	-7.7306	8.5553	21.2504
C	7.8039	-1.5351	15.7223
H	8.7352	-1.6046	15.8234
C	2.3024	-2.9106	13.3911
H	2.266	-3.8042	13.0994
C	-9.0107	6.3058	19.365
H	-9.8308	5.8868	19.1755
C	-3.1186	11.1943	15.2449
H	-3.5797	10.6304	15.8857
H	-3.108	12.1089	15.5683
H	-2.2082	10.8799	15.1335
C	-5.3329	8.2868	20.2033
H	-4.6301	7.6577	20.4332
H	-5.4744	8.8977	20.942
H	-5.0708	8.7876	19.4142
C	9.4305	-1.0582	18.7169
C	5.823	-5.3853	11.6821
H	6.0516	-5.4665	10.775
C	11.228	0.681	17.5264
H	11.8301	1.2763	17.1189
C	-7.9162	4.9091	17.5502
H	-7.6121	5.301	16.7153
H	-8.832	4.6058	17.4487
H	-7.3492	4.1569	17.7788
C	5.8718	-6.4965	12.475
C	4.8099	-5.0501	15.8282
H	5.4424	-4.4658	16.2747
H	4.8483	-5.9334	16.2273
H	3.9145	-4.6907	15.9228
C	5.5362	-6.3696	13.8038
H	5.5607	-7.1316	14.3536
C	9.3775	1.9937	16.472

H	8.9356	1.6411	15.6831
H	10.1292	2.5446	16.2007
H	8.7507	2.5304	16.9808
C	-5.0237	8.5898	11.3429
H	-5.6964	8.7324	10.6589
H	-5.3433	7.9281	11.977
H	-4.2047	8.2749	10.9318
C	-5.5648	13.5703	11.5503
H	-6.4883	13.6916	11.8194
H	-5.513	13.5248	10.5825
H	-5.0347	14.3192	11.8668
C	11.7193	-0.3256	18.2999
C	8.4708	-2.0142	19.4018
H	8.2434	-2.7341	18.7929
H	7.665	-1.5368	19.6538
H	8.8916	-2.3807	20.1944
C	10.8049	-1.194	18.9027
H	11.125	-1.8893	19.4484
C	5.4398	-2.928	11.25
H	4.5321	-2.7447	10.9608
H	5.9948	-3.11	10.4748
H	5.7899	-2.1577	11.7239
C	-10.2408	7.6858	21.0697
H	-10.1884	7.4164	21.9993
H	-11.0069	7.2609	20.652
H	-10.3388	8.65	21.0171
C	6.3433	-7.8294	11.9241
H	5.5828	-8.3239	11.5794
H	6.7658	-8.3411	12.6326
H	6.981	-7.6772	11.2106
C	13.2166	-0.5381	18.5051
H	13.5318	-1.2273	17.8996
H	13.3807	-0.8134	19.4211
H	13.6886	0.2898	18.327

Table S4. Optimized coordinates of **1**·4H^+-**1**.

* Sum of imaginary frequencies = 0

atom	X	Y	Z
N	4.41794	-3.2182	-0.52649
C	5.78388	-3.56352	-0.20835
C	5.74762	-4.99041	0.1376
C	4.45476	-5.42899	0.04205
C	3.6245	-4.30743	-0.36905

C	1.60881	-3.50989	-1.62474
C	2.17358	-4.28396	-0.55901
C	1.35779	-4.99403	0.29894
C	-0.06367	-4.92112	0.16356
C	-0.62229	-4.11871	-0.86638
C	0.2496	-3.43354	-1.77231
C	-0.93683	-5.62835	1.05012
C	-2.29712	-5.50975	0.93272
C	-2.85973	-4.66569	-0.07867
C	-2.04201	-4.00006	-0.96938
C	-4.31703	-4.52007	-0.12045
C	-5.32082	-5.55546	0.06505
C	-6.55634	-4.96908	-0.0014
C	-6.37907	-3.52893	-0.22285
N	-4.94972	-3.33465	-0.30601
C	-6.08336	-0.63937	-1.47706
C	-5.96839	0.78089	-1.40641
C	-6.77679	1.34078	-0.43927
S	-7.72521	0.1206	0.33427
C	-6.97481	-1.15587	-0.56076
C	-7.32821	-2.53958	-0.29658
C	-6.90087	2.73671	-0.05738
N	-4.42046	3.09723	0.03585
C	-5.79585	3.53622	0.09861
C	-5.72718	4.97794	0.36302
C	-4.41064	5.34268	0.44921
C	-3.59719	4.15137	0.26118
C	-1.54319	2.92408	0.97802
C	-2.13789	4.04628	0.31281
C	-1.34728	5.02211	-0.25815
C	0.07799	4.90719	-0.21561
C	0.66484	3.78707	0.43063
C	-0.18116	2.80312	1.03704
C	0.92722	5.89302	-0.81111
C	2.29081	5.75685	-0.77331
C	2.88248	4.61797	-0.13843
C	2.08671	3.66032	0.45907
C	4.34066	4.48954	-0.14427
C	5.32886	5.55398	-0.05887
C	6.57387	4.98579	-0.08791
C	6.41902	3.53243	-0.21467
N	4.99273	3.30346	-0.24333
C	-8.75036	-2.83996	-0.09237

C	-8.25122	3.26829	0.16025
C	-9.23207	-3.27311	1.16796
C	-10.59283	-3.55241	1.32888
C	-11.48999	-3.41105	0.26014
C	-11.00971	-2.97984	-0.9873
C	-9.65638	-2.69148	-1.17503
C	-9.14715	3.38349	-0.93249
C	-10.42716	3.9067	-0.72552
C	-10.84202	4.31381	0.55098
C	-9.9552	4.1898	1.63282
C	-8.66943	3.67428	1.45395
C	-8.32462	-3.43173	2.33812
C	-9.19177	-2.24431	-2.51742
C	-12.93576	-3.70582	0.43657
C	-7.76994	3.55185	2.6347
C	-8.75473	2.96952	-2.30788
C	-12.20881	4.85592	0.76541
C	6.19067	0.70937	-1.60535
C	6.05478	-0.71131	-1.59218
C	6.76319	-1.31415	-0.57455
S	7.66129	-0.12984	0.31636
C	7.01738	1.18007	-0.60675
C	7.38071	2.55811	-0.31308
C	6.85781	-2.7096	-0.19449
C	8.80066	2.8728	-0.13306
C	8.17413	-3.18719	0.25797
C	9.29024	3.3325	1.11633
C	10.65002	3.62219	1.26104
C	11.53988	3.47024	0.18687
C	11.05202	3.0182	-1.04968
C	9.69888	2.71855	-1.22146
C	9.20925	-3.37708	-0.6948
C	10.45889	-3.83196	-0.27376
C	10.70833	-4.10235	1.08324
C	9.68347	-3.915	2.0199
C	8.41867	-3.46289	1.62281
C	8.39079	3.50949	2.28997
C	9.22125	2.26117	-2.55554
C	12.98542	3.76906	0.35702
C	7.37547	-3.26834	2.66733
C	8.9647	-3.113	-2.13942
C	12.05043	-4.57975	1.50756
H	4.11712	-2.27989	-0.79735

H	6.63304	-5.5547	0.41084
H	4.07286	-6.4257	0.22024
H	2.27219	-3.00116	-2.33008
H	1.77831	-5.60945	1.10345
H	-0.1919	-2.85262	-2.58759
H	-0.4975	-6.26577	1.82499
H	-2.96771	-6.04823	1.61034
H	-2.45696	-3.38231	-1.77278
H	-5.08556	-6.60109	0.2158
H	-7.52979	-5.44061	0.08149
H	-4.50872	-2.4277	-0.46957
H	-5.5297	-1.22708	-2.20812
H	-5.31827	1.34114	-2.07743
H	-4.14179	2.12625	-0.12972
H	-6.60724	5.60556	0.45341
H	-4.00129	6.32722	0.63282
H	-2.19179	2.18083	1.45063
H	-1.79131	5.89147	-0.7581
H	0.28452	1.95676	1.55062
H	0.4667	6.76024	-1.29694
H	2.94148	6.50919	-1.23123
H	2.5204	2.79557	0.9732
H	5.07786	6.60363	0.02249
H	7.53995	5.47742	-0.04906
H	4.57008	2.37303	-0.29397
H	-10.96224	-3.88443	2.30068
H	-11.70642	-2.86976	-1.82005
H	-11.1136	3.99942	-1.56883
H	-10.27877	4.49955	2.62811
H	-8.8482	-3.2805	3.29774
H	-7.47631	-2.73517	2.3486
H	-7.90614	-4.45214	2.38571
H	-8.14529	-2.49486	-2.73898
H	-9.78825	-2.68368	-3.33501
H	-9.29211	-1.15099	-2.62896
H	-13.18525	-4.11592	1.42669
H	-13.55296	-2.8001	0.30841
H	-13.30395	-4.43391	-0.30557
H	-7.15144	2.6439	2.63027
H	-7.08221	4.41125	2.70985
H	-8.32518	3.5309	3.58796
H	-7.67514	3.01261	-2.50517
H	-9.23024	3.59172	-3.08505

H	-9.07611	1.93397	-2.51594
H	-12.22637	5.70117	1.47197
H	-12.68951	5.21013	-0.15926
H	-12.88001	4.08843	1.18977
H	5.70235	1.33445	-2.35156
H	5.46301	-1.24055	-2.33685
H	11.02631	3.97174	2.22401
H	11.74151	2.90142	-1.88755
H	11.25586	-3.98205	-1.00403
H	9.87138	-4.12278	3.07454
H	7.56683	2.78534	2.33747
H	8.92805	3.41589	3.24921
H	7.9376	4.51585	2.29965
H	8.20867	2.6079	-2.80651
H	9.2107	1.1599	-2.62008
H	9.87213	2.60307	-3.37779
H	13.19126	4.47572	1.1757
H	13.5551	2.8519	0.59004
H	13.44546	4.19516	-0.54853
H	6.4294	-2.84367	2.31091
H	7.7306	-2.59507	3.46822
H	7.12528	-4.22088	3.16685
H	8.05364	-3.60626	-2.51161
H	8.85707	-2.03611	-2.34783
H	9.78628	-3.46463	-2.78507
H	12.8383	-3.84346	1.27495
H	12.12512	-4.78746	2.58547
H	12.33936	-5.50939	0.98875

Table S5. Optimized coordinates of **1**·**4H**$^{+}$**-2**.

* Sum of imaginary frequencies = 0

atom	X	Y	Z
N	5.5267	3.823	-1.9334
C	6.617	4.1917	-1.3095
C	6.1686	4.9113	-0.2629
C	4.8339	4.9946	-0.3261
C	4.425	4.2674	-1.3789
C	2.8931	3.1091	-2.7353
C	3.1516	3.9604	-1.7225
C	2.0735	4.4015	-1.0367
C	0.8261	3.9372	-1.2582
C	0.62	3.0171	-2.2145

C	1.6592	2.6443	-2.9789
C	-0.2386	4.315	-0.5269
C	-1.4443	3.7391	-0.6864
C	-1.6475	2.7462	-1.5752
C	-0.5917	2.4517	-2.3631
C	-2.7964	2.0308	-1.6285
C	-2.9649	0.9221	-2.3665
C	-4.1453	0.3899	-2.0483
C	-4.7323	1.1607	-1.1179
N	-3.9084	2.1741	-0.9439
C	-7.8744	-0.3115	0.1219
C	-8.3833	-1.5271	-0.1005
C	-7.6597	-2.2234	-0.9953
S	-6.4988	-1.3729	-1.31
C	-6.7437	-0.1277	-0.5776
C	-5.9264	0.956	-0.5017
C	-7.8128	-3.5588	-1.2509
N	-5.5224	-3.822	-1.9629
C	-6.6143	-4.1932	-1.3432
C	-6.1686	-4.917	-0.2984
C	-4.8337	-5	-0.3585
C	-4.4222	-4.2686	-1.4074
C	-2.8869	-3.1049	-2.7551
C	-3.1479	-3.9602	-1.7464
C	-2.0715	-4.4041	-1.0597
C	-0.8236	-3.9389	-1.2761
C	-0.6151	-3.015	-2.2282
C	-1.6523	-2.6392	-2.9937
C	0.2392	-4.3196	-0.5436
C	1.4453	-3.7432	-0.6976
C	1.6509	-2.7468	-1.582
C	0.597	-2.449	-2.3714
C	2.7998	-2.0311	-1.6295
C	2.9702	-0.9194	-2.3626
C	4.1498	-0.3885	-2.0392
C	4.7344	-1.1631	-1.1105
N	3.91	-2.1772	-0.9426
C	-6.3368	1.946	0.3211
C	-8.9945	-4.2123	-1.0356
C	-5.71	2.1569	1.5006
C	-6.1374	3.1537	2.296
C	-7.1646	3.9456	1.9526
C	-7.7738	3.7114	0.7804

C	-7.3824	2.7222	-0.0419
C	-10.1825	-3.5447	-1.1316
C	-11.3451	-4.0986	-0.7396
C	-11.4314	-5.3675	-0.3309
C	-10.321	-6.0912	-0.5036
C	-9.1462	-5.5627	-0.9021
C	-4.586	1.2768	2.0166
C	-8.1035	2.5692	-1.3683
C	-7.6413	5.0638	2.8488
C	-8.1246	-6.6476	-1.2233
C	-10.395	-2.1989	-1.8271
C	-12.7407	-5.9932	0.0856
C	7.8734	0.3041	0.1432
C	8.3828	1.5206	-0.073
C	7.6614	2.2206	-0.9668
S	6.5013	1.3713	-1.2879
C	6.7444	0.1232	-0.5599
C	5.9269	-0.9608	-0.4904
C	7.8152	3.557	-1.2166
C	6.3352	-1.9541	0.3294
C	8.9964	4.2096	-0.9958
C	5.7055	-2.1697	1.5065
C	6.1309	-3.1697	2.299
C	7.1588	-3.9602	1.9551
C	7.7711	-3.7214	0.7854
C	7.3817	-2.7289	-0.0339
C	10.1846	3.5423	-1.0914
C	11.3462	4.0946	-0.6943
C	11.4315	5.3618	-0.2803
C	10.3214	6.0863	-0.4527
C	9.1477	5.5594	-0.8564
C	4.5802	-1.2917	2.0232
C	8.1062	-2.5706	-1.3579
C	7.6334	-5.082	2.848
C	8.127	6.6456	-1.1758
C	10.3989	2.1994	-1.7918
C	12.7398	5.9857	0.1421
H	5.5632	3.3106	-2.8236
H	6.7494	5.267	0.5989
H	4.2194	5.4883	0.4366
H	3.6863	2.6927	-3.3749
H	2.2002	5.1122	-0.205
H	1.5294	1.8998	-3.7837

H	-0.122	5.0719	0.2684
H	-2.2422	4.0606	0.0026
H	-0.6644	1.6752	-3.139
H	-2.2811	0.4402	-3.0748
H	-4.4797	-0.5395	-2.5153
H	-4.0788	2.9546	-0.2984
H	-8.3224	0.3882	0.8419
H	-9.2478	-1.8894	0.4735
H	-5.5567	-3.3059	-2.851
H	-6.7517	-5.2761	0.5604
H	-4.2213	-5.4968	0.4038
H	-3.6783	-2.6859	-3.3951
H	-2.2004	-5.1182	-0.2312
H	-1.5206	-1.8914	-3.7952
H	0.1207	-5.0796	0.2484
H	2.2415	-4.0674	-0.0079
H	0.6717	-1.6694	-3.144
H	2.2883	-0.4347	-3.0707
H	4.4853	0.5428	-2.5016
H	4.0788	-2.9602	-0.2998
H	-5.6357	3.32	3.2632
H	-8.6177	4.3584	0.4891
H	-12.2781	-3.513	-0.7957
H	-10.4055	-7.1785	-0.3364
H	-4.5485	0.2775	1.5305
H	-3.601	1.7751	1.8706
H	-4.7058	1.0747	3.1051
H	-7.45	2.1609	-2.1706
H	-8.4679	3.5489	-1.7514
H	-8.9876	1.9018	-1.2569
H	-7.0596	5.1345	3.7948
H	-7.5492	6.0428	2.3255
H	-8.7095	4.91	3.1243
H	-7.3733	-6.3591	-1.9873
H	-7.6519	-7.083	-0.3155
H	-8.6214	-7.5066	-1.7306
H	-9.5493	-1.8607	-2.4623
H	-10.7292	-1.3864	-1.1445
H	-11.2147	-2.3054	-2.5753
H	-12.822	-7.0497	-0.2557
H	-12.8243	-5.9783	1.1961
H	-13.6171	-5.4503	-0.3343
H	8.3195	-0.3985	0.8616

H	9.2458	1.8806	0.5046
H	5.6267	-3.3399	3.2643
H	8.6156	-4.3672	0.4935
H	12.2795	3.5093	-0.7504
H	10.4056	7.1729	-0.281
H	4.5439	-0.2904	1.541
H	3.5955	-1.7893	1.8726
H	4.6972	-1.094	3.1128
H	7.4548	-2.1591	-2.1603
H	8.9901	-1.9036	-1.2416
H	8.4716	-3.5488	-1.744
H	7.0535	-5.1521	3.7952
H	8.7027	-4.9328	3.1216
H	7.5363	-6.0595	2.3228
H	7.3776	6.3601	-1.9428
H	7.6519	7.0773	-0.2674
H	8.625	7.5066	-1.6784
H	9.5548	1.8637	-2.4305
H	10.7312	1.3841	-1.1117
H	11.2204	2.3089	-2.5375
H	13.6171	5.4452	-0.279
H	12.8212	5.9649	1.2527
H	12.8215	7.0441	-0.1935

Table S6. Optimized coordinates of **1**·4H$^+$**-3**.

* Sum of imaginary frequencies = 0

atom	X	Y	Z
S	5.96026	-0.20564	-0.06692
S	-5.93453	0.02548	-0.07668
N	4.47733	1.95703	-1.16121
N	4.52912	-2.17087	1.26629
N	-4.70844	2.25801	1.16283
N	-4.31448	-1.89117	-1.48833
C	2.1529	2.65577	-0.89437
C	-7.01	-1.16866	-0.70699
C	0.68716	-2.28541	-0.5695
C	3.50952	2.80677	-1.43818
C	7.15144	0.73217	-0.89787
C	5.27746	3.65099	-2.54676
H	5.9711	4.19861	-3.16363
C	0.47287	-2.25406	-1.95714
H	1.32905	-2.28214	-2.62283

C	-1.90712	-2.18124	-1.64576
C	7.16709	-1.23945	0.61016
C	3.97221	3.87605	-2.31196
H	3.33933	4.65626	-2.70239
C	-6.68934	-1.98308	-1.84256
C	6.9135	-2.23162	1.62067
C	0.02302	3.64065	-0.25143
C	8.04706	2.61215	-2.26418
C	5.6507	-2.60975	1.97073
C	1.3293	3.74298	-0.79192
H	1.66928	4.72738	-1.09396
C	-0.46107	-2.23764	0.29137
C	-7.85195	-2.58267	-2.5874
C	-3.2737	-2.24425	-2.1953
C	2.13687	-2.48945	1.36344
C	-5.71019	3.79347	2.61051
H	-6.4596	4.21705	3.259
C	-2.5553	3.36925	0.82255
C	6.86087	1.8956	-1.675
C	-6.99568	1.77167	1.84489
C	5.61368	2.45677	-1.80319
C	8.10138	-2.81046	2.32548
C	-3.90778	3.27528	1.39827
C	-2.03647	4.6353	0.4849
H	-2.64424	5.51938	0.63616
C	8.42733	-0.87855	0.14988
H	9.32141	-1.40446	0.45208
C	9.83045	-2.65414	3.96345
H	10.3128	-2.10469	4.76696
C	1.95925	-2.38406	0.00445
H	2.79691	-2.46232	-0.68132
C	8.71345	-2.07966	3.34906
C	-0.78882	4.76405	-0.06359
H	-0.41811	5.74233	-0.34751
C	-5.8656	2.5647	1.89224
C	5.2207	-3.4272	3.09017
H	5.89464	-3.87781	3.80164
C	10.33713	-3.87255	3.5819
C	3.48266	-2.6692	1.89662
C	-0.78806	-2.22652	-2.48084
H	-0.9178	-2.22728	-3.55588
C	1.00189	-2.44706	2.20888
H	1.13402	-2.51349	3.28157

C	-1.73456	-2.16952	-0.28397
H	-2.5734	-2.1821	0.40372
C	-0.45561	2.36002	0.13302
C	8.41873	0.2123	-0.69978
H	9.30368	0.64693	-1.13976
C	-1.76627	2.25146	0.61408
H	-2.1264	1.26895	0.90456
C	-8.34106	1.6453	3.95909
C	-8.2001	2.142	2.66667
C	-8.22942	-1.14295	-0.05208
H	-9.036	-1.81657	-0.30056
C	8.55208	2.21334	-3.50321
C	1.6863	1.41326	-0.45295
H	2.32843	0.54003	-0.51607
C	3.87175	-3.43882	3.06885
H	3.17824	-3.91665	3.74146
C	8.63407	3.63452	-1.53121
C	0.41744	1.25829	0.01959
H	0.06739	0.28141	0.32708
C	-7.1486	0.61812	0.99951
C	-8.20732	-3.91223	-2.37543
C	8.59621	-4.02715	1.91674
C	-0.24636	-2.31622	1.68512
H	-1.10506	-2.28229	2.34787
C	-5.42826	-2.22896	-2.26758
C	-4.49558	4.25567	2.28469
H	-3.98984	5.1504	2.61096
C	10.29087	3.91467	-3.29298
C	-3.64716	-2.80283	-3.48673
H	-2.94565	-3.14595	-4.22954
C	9.73375	-4.55133	2.56549
H	10.12253	-5.50852	2.23508
C	-8.59913	-1.77837	-3.46735
C	9.76357	4.25493	-2.06837
H	10.23595	5.04268	-1.48796
C	-8.304	-0.14736	0.905
H	-9.17844	0.05166	1.50672
C	-4.98773	-2.8125	-3.51002
H	-5.6553	-3.14412	-4.28951
C	9.69977	2.90187	-3.99869
H	10.09781	2.59815	-4.96191
C	8.22039	-0.7195	3.76575
H	8.40996	0.03136	2.9924

H	8.72763	-0.389	4.67361
H	7.1448	-0.71827	3.96412
C	8.14882	4.0045	-0.1866
H	7.11543	4.36471	-0.19545
H	8.76241	4.79619	0.24674
H	8.18038	3.15453	0.50388
C	-9.20184	2.94383	2.12125
C	-9.30476	-4.42637	-3.06486
H	-9.5815	-5.46079	-2.88349
C	-9.49379	1.91459	4.67635
H	-9.58189	1.50363	5.67786
C	7.93602	1.09589	-4.26286
H	7.92901	0.16484	-3.68734
H	8.48132	0.90474	-5.1891
H	6.89668	1.31098	-4.53305
C	-10.03886	-3.67402	-3.93715
C	-8.24321	-0.32925	-3.70951
H	-8.30965	0.2634	-2.79232
H	-8.92179	0.11379	-4.43952
H	-7.2233	-0.22213	-4.09224
C	-9.67782	-2.36076	-4.13574
H	-10.24744	-1.74584	-4.82611
C	-7.24908	0.81466	4.57274
H	-6.97952	-0.0381	3.94123
H	-7.55835	0.42187	5.5428
H	-6.33767	1.40047	4.72988
C	7.95903	-4.81016	0.7931
H	8.54575	-5.70164	0.56656
H	7.8857	-4.21861	-0.12471
H	6.94694	-5.13594	1.05237
C	11.55909	-4.44563	4.2641
H	12.3896	-3.73367	4.24655
H	11.8888	-5.36666	3.78046
H	11.35204	-4.6709	5.31538
C	-10.50188	2.67461	4.16737
C	-9.06267	3.54151	0.73292
H	-8.92492	2.76848	-0.0288
H	-8.20216	4.21496	0.67504
H	-9.95351	4.11415	0.47129
C	-10.34297	3.19599	2.88031
H	-11.12477	3.81599	2.45275
C	-7.44788	-4.78592	-1.39315
H	-6.44535	-5.02499	-1.76077

H	-7.9756	-5.72757	-1.23497
H	-7.33263	-4.29614	-0.42226
C	11.55539	4.59028	-3.82685
H	11.53951	5.66605	-3.63514
H	11.66248	4.42972	-4.90089
H	12.44347	4.18165	-3.33387
C	-11.2618	-4.24888	-4.62735
H	-11.35618	-3.86989	-5.64776
H	-12.17246	-3.96633	-4.08823
H	-11.22246	-5.33938	-4.66343
C	-11.78622	2.94968	4.94452
H	-12.63989	2.46504	4.46071
H	-11.99731	4.02181	4.98248
H	-11.7163	2.57454	5.96715
H	-4.47453	1.49436	0.54902
H	-4.31667	-1.6863	-0.4988
H	4.49573	-1.88306	0.29787
H	4.42018	1.29976	-0.3984