Supporting Information

for

Dioxygen/Hydrogen Peroxide Interconversion Using Redox Couples of Saddle-Distorted Porphyrins and Isophlorins

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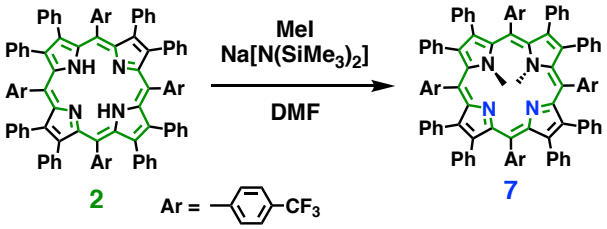
Experimental Section

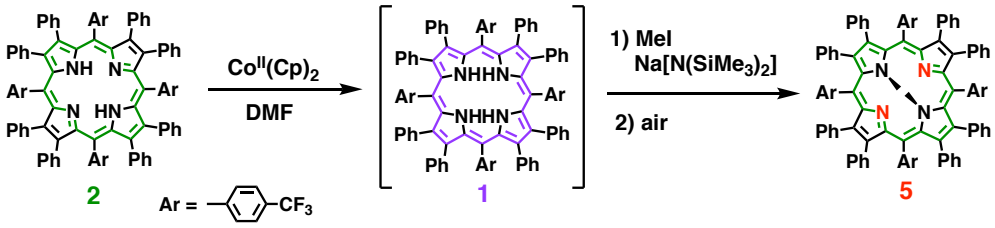
Materials.

General. *N*,*N*-Dimethylformamide (DMF) was used as a spectroscopic grade solvent. Sodium hydrosulfite ($Na_2S_2O_4$), cobaltocene ($Co^{II}(Cp)_2$), sodium bis(trimethylsilylamide) ($Na[N(SiMe_3)_2]$), iodomethane (MeI), hydrogen peroxide (H_2O_2, 50% aqueous solution) were purchased from commercial sources and used without further purification. **2** and **3** was synthesized based on the previous report.[1]

Synthesis.



***N*21,*N*22-Dimethyl-2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphyrin (7).** To a DMF solution (5 mL) of **2** (23.1 mg, 15.4 μmol), $Na[N(SiMe_3)_2]$ (25.0 mg, 136 μmol) was added under argon flow. After changing the color of solution from green to dark red, MeI (6.4 mg, 45 μmol) was added and the solution was stirred overnight at room temperature. Then, CH_2Cl_2 was added and washed with water for three times. The organic layer was dried over Na_2SO_4. The solution obtained was evaporated and dried under vacuum to obtain a green crude product containing a small amount of starting material (**2**) and trimethylated porphyrins. The crude product was purified by silica-gel column chromatography using CH_2Cl_2: THF = 20: 1 (v/v) as eluents. Pure **7** was obtained by recrystallization from acetone/hexane in 27% yield (6.3 mg, 4.1 μmol). ^{1}H NMR (acetone-d_6, 400 MHz): δ 7.98 (d, J = 8 Hz, 2H, *meso*-Ar), 7.96 (d, J = 8 Hz, 2H, *meso*-Ar), 7.87 (d, J = 8 Hz, 2H, *meso*-Ar), 7.82 (d, J = 8 Hz, 2H, *meso*-Ar), 7.21 (d, J = 8 Hz, 2H, *meso*-Ar), 7.17 (d, J = 8 Hz, 2H, *meso*-Ar), 7.13 (d, J = 8 Hz, 2H, *meso*-Ar), 7.09 (d, J = 8 Hz, 2H, *meso*-Ar), 6.71-6.84 (m, 40H, β-Ph) –2.68 (s, 6H, *N*-Me). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.85, 160.14, 159.98, 148.25, 147.30, 139.92, 138.57, 137.15, 136.51, 136.04, 135.92, 134.77, 134.77, 134.37, 134.05, 132.01, 131.73, 131.45, 131.38, 131.31, 130.55, 128.93, 126.95, 126.89, 126.48, 126.42, 126.36, 125.72, 125.65, 123.60, 123.34, 123.08, 122.63, 31.50. ^{19}F NMR (acetone-d_6, 376 MHz): δ –63.05, –63.19, –63.22. UV-Vis (DMF): λ_{max} (ε, cm^{-1} M^{-1}) = 511 (1.1×10^5), 702 (1.4×10^4), 777 (1.3×10^4). MS (MALDI-TOF, dithranol matrix): m/z = 1523.36 (Calcd. for $[M]^+$: 1523.29). Elemental analysis: Calcd for $C_{98}H_{62}F_{12}N_4 \bullet CH_2Cl_2$: C 73.92, H 4.01, N 3.48; Found: C 73.92, H 4.32, N 3.48.



***N*21,*N*23-*Di*methyl-2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphyrin (5). 2** (34.9 mg, 22.9 μmol) and $Co^{II}(Cp)_2$ (28.1 mg, 148 μmol) were mixed in DMF (5 mL) under Ar to form **1** *in situ* (color changed from green to reddish brown). After adding $Na[N(SiMe_3)_2]$ (42.6 mg, 232 μmol) to the mixture, MeI (2.8 μL, 46 μmol) was added. The mixture was stirred for 16 h at room temperature. After the reaction mixture was exposed to air, CH_2Cl_2 was added and the organic layer was washed with water for three times. The organic layer was dried over Na_2SO_4, evaporated to give crude red solid. The crude product was purified by silica-gel column chromatography using CH_2Cl_2: THF = 20: 1 (v/v) and THF as eluents. Pure **5** was obtained by recrystallization from acetone/hexane in 19% yield (6.6 mg, 4.3 μmol). ^{1}H NMR (acetone-d_6, 400 MHz): δ 8.34 (d, J = 8 Hz, 4H, *meso*-Ar), 7.93 (d, J = 8 Hz, 4H, *meso*-Ar), 7.48 (d, J = 8 Hz, 4H, *meso*-Ar), 7.19 (d, J = 8 Hz, 4H, *meso*-Ar), 7.16 (d, J = 7 Hz, 8H, β-Ph), 6.81-6.87 (m, 12 H, β-Ph), 6.64 (t, J = 7 Hz, 4H, β-Ph), 6.56 (t, J = 7 Hz, 8H, β-Ph), 6.37 (d, J = 7 Hz, 8H, β-Ph), –1.18 (s, 6H, *N*-Me). ^{13}C NMR (acetone-d_6, 100 MHz): δ 158.37, 154.45, 143.37, 142.60, 138.87, 137.29, 136.13, 134.90, 134.90, 132.66, 131.77, 127.11, 126.78, 126.60, 126.45, 123.91, 31.93. ^{19}F NMR (acetone-d_6, 376 MHz): δ –63.10. UV-Vis (DMF): λ_{max} (ε, cm^{-1} M^{-1}) = 509 (6.4×10^4), 708 (1.3×10^4). MS (MALDI-TOF, dithranol matrix): m/z = 1524.13 (Calcd. for $[M + H]^+$: 1524.29). Elemental analysis: Calcd for $C_{98}H_{62}F_{12}N_4 \cdot C_3H_6O \cdot 2H_2O$: C 74.99, H 4.49, N 3.46; Found: C 75.08, H 4.49, N 3.46.

Measurements.

X-ray Crystallography. Single crystals of **5** were grown by vapor diffusion of pentane into a dichloromethane solution of **5**. Single crystals of **7** were grown by vapor diffusion of hexane into a chloroform solution of **7**. The single crystals were mounted using a mounting loop. All measurements were performed at 120 K on a Bruker APEXII Ultra diffractometer. The structure was solved by a direct method (SIR-2014, SHELX-T) and expanded with differential Fourier techniques. All non-hydrogen atoms were refined anisotropically and the refinements were carried out with full matrix least squares on *F*. All calculations were performed using the Yadokari-XG crystallographic software package,[2,3] including SHELX-2014 and SHELX-2017.[4] In the structure refinements, contribution of the solvent molecules (3 molecules of dichloromethane in **5**, 2 molecules of chloroform in **7**) of crystallization were subtracted from the diffraction pattern by the "Squeeze" program.[5] In the crystallographic analysis of **7**, one of the two inner N-Me groups showed a crystallographic disorder and delocalized on two inner nitrogen atoms (N2 and N4) with different occupancies (0.81851 and 0.18149, respectively), and a co-crystallized chloroform molecule also existed showing the crystallographic disorder with the same occupancies with the Me groups to occupy the vacant space around one of the inner nitrogen atoms, formed when the Me groups localized on the other inner nitrogen. One of the disordered parts for the chloroform molecule, existing around N4, showed a further crystallographic disorder due to the rotation with the C-H bond as the axis. The latter disorder was very severe and difficult to treat with an appropriate disordered model, and thus, subtracted by the "Squeeze" program. As a result of this treatment, the molecular formula for the crystal structure of **7** is not integer value.

Supplementary crystallographic data of **5** and **7** are available from the Cambridge Crystallographic Data Centre as CCDC-1883310 and 1883312, respectively.

Spectroscopic Measurements. UV-Vis measurements were performed on a Shimadzu UV-3600 spectrophotometer, an Agilent 8453 spectrometer, and a UNISOKU USP-SFM-CRD10 double mixing stopped-flow spectrometer equipped with a multi-channel photodiode array at 298 K. The cell length (*l*) of a quartz cuvette was 10 mm. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on Bruker AVANCE400, and AVANCEHD400 spectrometers at 298 K. MALDI-TOF-MS spectra were measured on a Bruker UltrafleXtreme-TN and AB SCIEX TOF/TOF 5800 spectrometers using dithranol as a matrix.

Electrochemical Measurements. Cyclic voltammetric and differential pulse voltammetric measurements were carried out in DMF containing 0.1 M $TBAPF_6$ as an electrolyte at room temperature under Ar. All measurements were made using a BAS ALS-710D electrochemical analyzer with a glassy carbon as a working electrode, a platinum wire as a counter electrode, and $Ag/AgNO_3$ as a reference electrode. All redox potentials were calibrated relative to that of Fc/Fc^+ as 0 V. The number of electrons in the reduction of a diprotonated porphyrin was estimated by comparing the peak current value with that of ferrocene.

The reaction of isophlorin derivatives with dioxygen. Isophlorin derivatives (**1**, **6**, **8**) were generated in situ by the chemical reduction of the corresponding porphyrins (**2**, **5**, **7**) with 1 equivalent of aqueous $Na_2S_2O_4$ ($Na_2S_2O_4$aq) in DMF under Ar atmosphere. The concentration of water in the reaction mixture was within 1%. After the reduction, O_2 was bubbled into the solution of isophlorin derivatives to start the reaction. The concentration of dioxygen was controlled by changing the ratio of bubbled gas (O_2 only, air only, O_2/Ar = 1/1 mixed gas, air/O_2 = 1/1 mixed gas, and air/Ar = 1/1 mixed gas). In the reaction of Isophlorin **3** with O_2 in DMF, 10 equivalents of TFA were added as a proton source. Deuterated **6** was prepared by the reduction of **5** with $Na_2S_2O_4$ in D_2O. Quantification of hydrogen peroxide (H_2O_2) produced was conducted by adding excess amount of KI to the reaction mixture after the reaction and the amount of I_3^- formed (eqs S1 and S2) was determined from the absorption spectrum (λ_{max} = 365 nm, $\varepsilon = 2.8 \times 10^4$ M^{-1} cm^{-1}) in DMF.

$$2I^- + H_2O_2 + 2H^+ \rightleftharpoons I_2 + 2H_2O \qquad \text{(S1)}$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad \text{(S2)}$$

The reaction of porphyrin derivatives with hydrogen peroxide. In the reaction of porphyrin derivatives (**2**, **5**, **7**) with H_2O_2, 50% aqueous solution of H_2O_2 diluted by DMF was added to the deaerated DMF solution of porphyrin derivatives. The concentration of water in the reaction mixture was within 1%.

Interconversion between 5 and 6. To a DMF solution of **5** containing excess amounts of H_2O_2, O_2 or Ar was bubbled alternatively. When bubbling O_2 gas, **6** was converted to **5** in a few minutes. On the other hand, the conversion of **5** to **6** was much slower than that of **6** to **5**,

Ar bubbling was continued for 90 minutes. The amounts of O_2 were quantified by a fluorescence O_2 sensor (Ocean Photonics, Neo Fox with the FOXY Formulation).

Computational Methods. Geometry optimizations were performed using the hybrid (Hartree-Fock/DFT) B3LYP functional[6,7] combined with the 6-31G** or 6-31G basis set.[8] The B3LYP functional was used for the closed-shell molecules. The Gaussian 09 program[9] was used for all calculations.

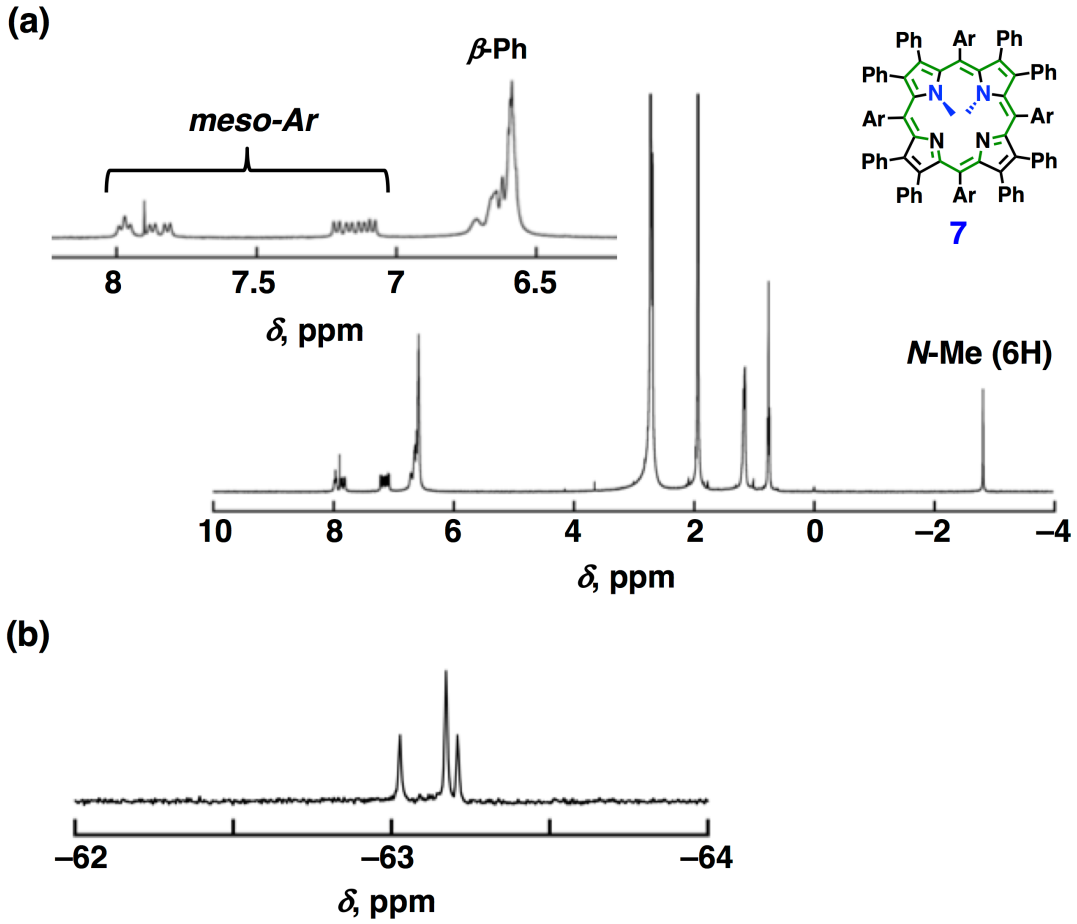


Figure S1. ^{1}H NMR spectrum (a) and ^{19}F NMR spectrum (b) of **7** in acetone-d_6.

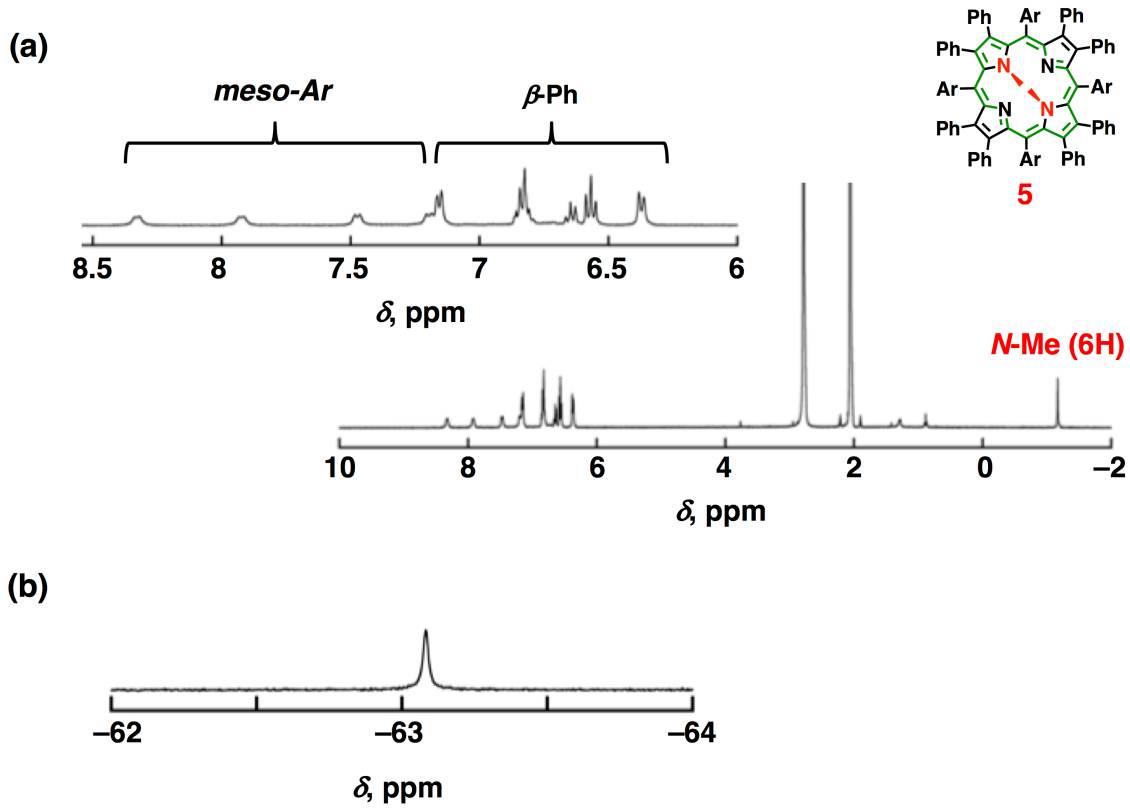


Figure S2. ^{1}H NMR spectrum (a) and ^{19}F NMR spectrum (b) of **5** in acetone-d_6.

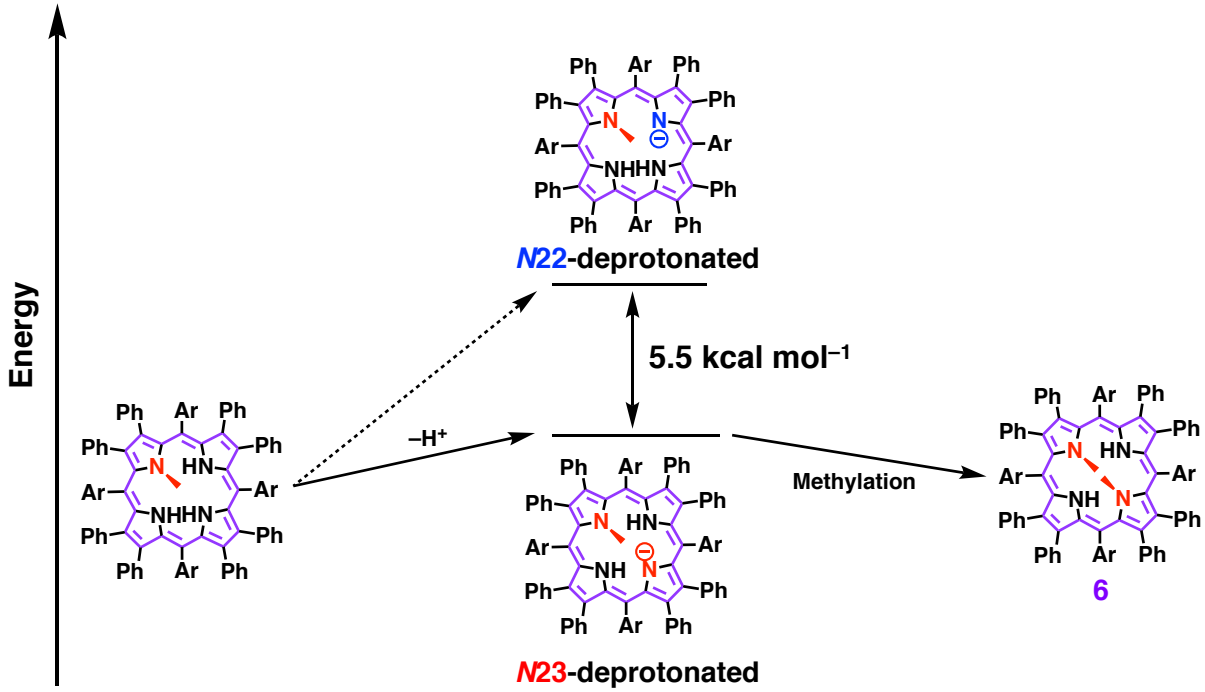


Figure S3. Comparison of thermodynamic stability of deprotonated monomethylated isophlorin derivatives in the course of methylation reaction of monomethylated isophlorin derivatives to afford **6**. The difference of energies was estimated by DFT calculations at the B3LYP/6-31G level of theory.

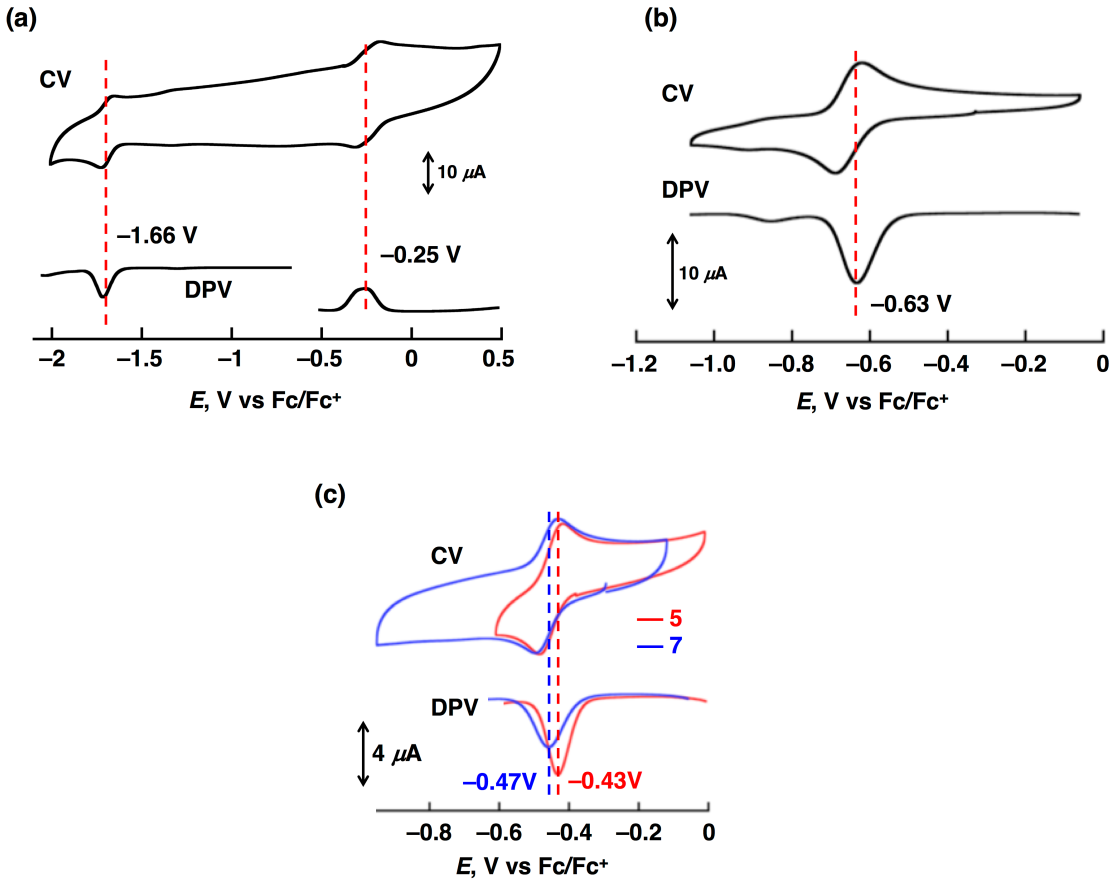


Figure S4. (a) Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of **3** (0.40 mM). (b) CV and DPV of **2** (0.40 mM). (c) CV and DPV of **5** (0.30 mM) and **7** (0.30 mM) in the presence of 2 equivalents of HCl. All measurements were conducted in deaerated DMF containing 0.1 M $TBAPF_6$ as an electrolyte at room temperature.

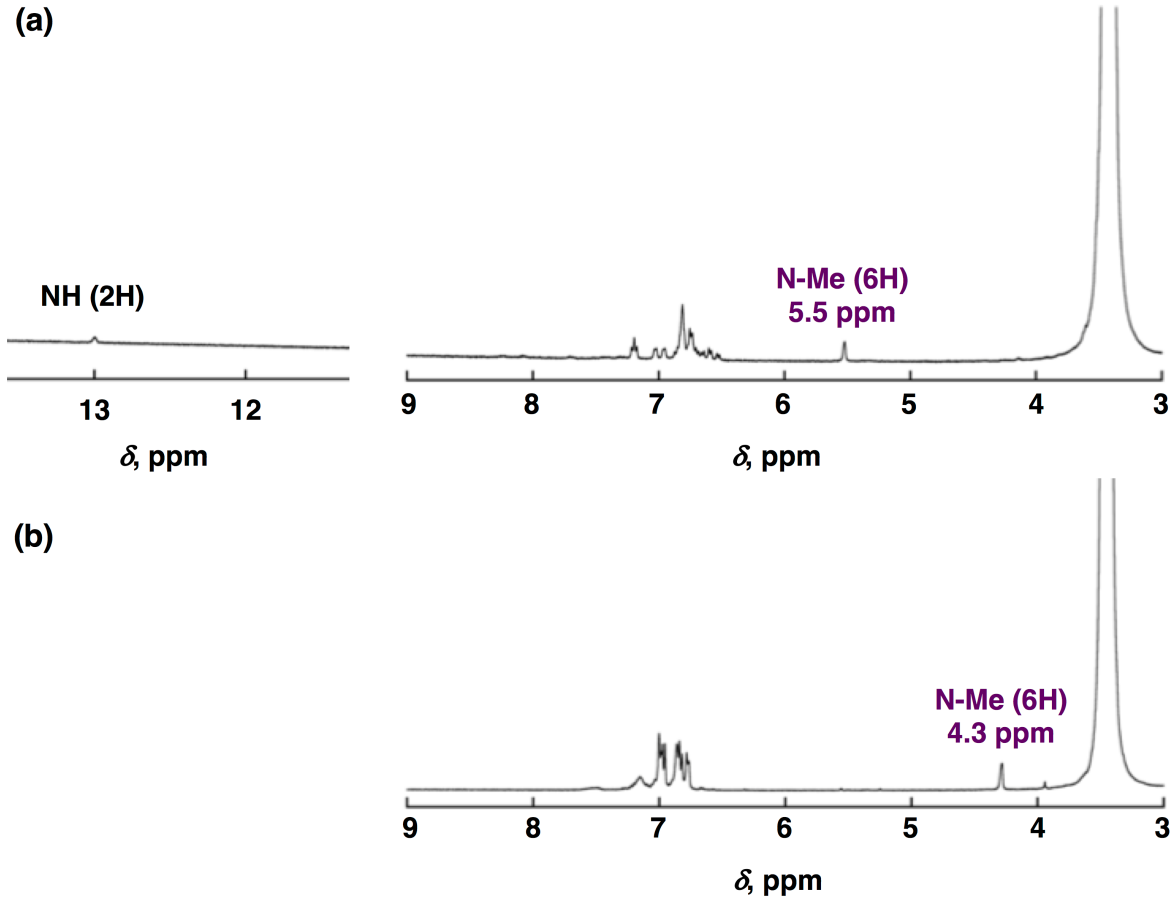


Figure S5. ^{1}H NMR spectra of **7** (a) and **5** (b) in DMSO-d_6 in the presence of 4 equivalent of $Na_2S_2O_4$aq as a reductant at 298 K.

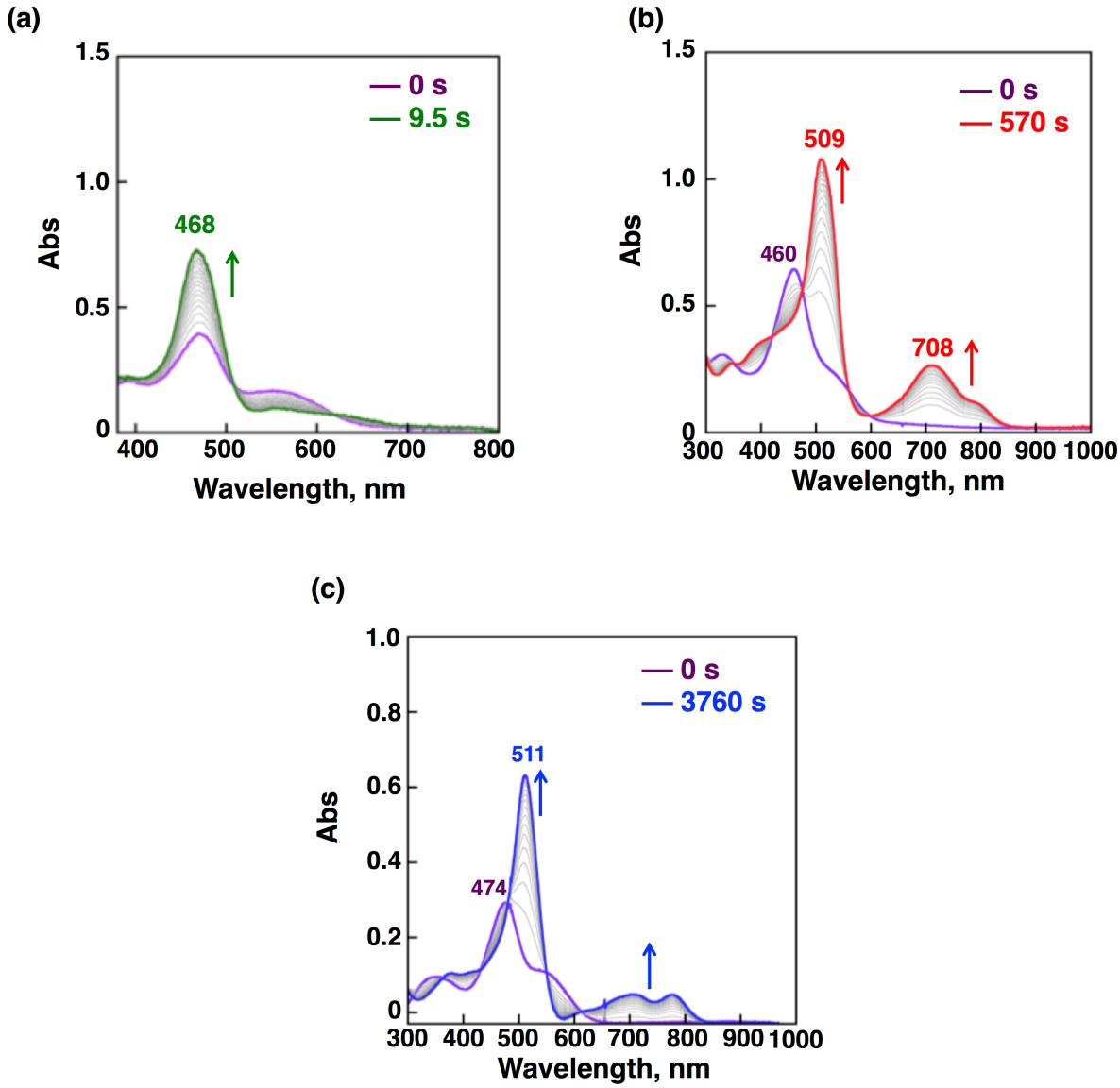


Figure S6. UV-Vis spectral changes of isophlorin derivatives (**1**, **6**, **8**) in the presence of O_2 in DMF. (a) The reaction of **1** (0.012 mM) with O_2 (0.31 mM) in DMF at 298 K monitored by stopped-flow measurement. (b) The reaction of **6** (0.017 mM) with O_2 (0.62 mM) in DMF at 298 K. (c) The reaction of **8** (0.0084 mM) with O_2 (0.62 mM) in DMF at 298 K. Isophlorin derivatives (**1**, **6**, **8**) were generated in situ through chemical reduction of the corresponding porphyrins (**2**, **5**, **7**) by 1 equivalent of $Na_2S_2O_4$aq.

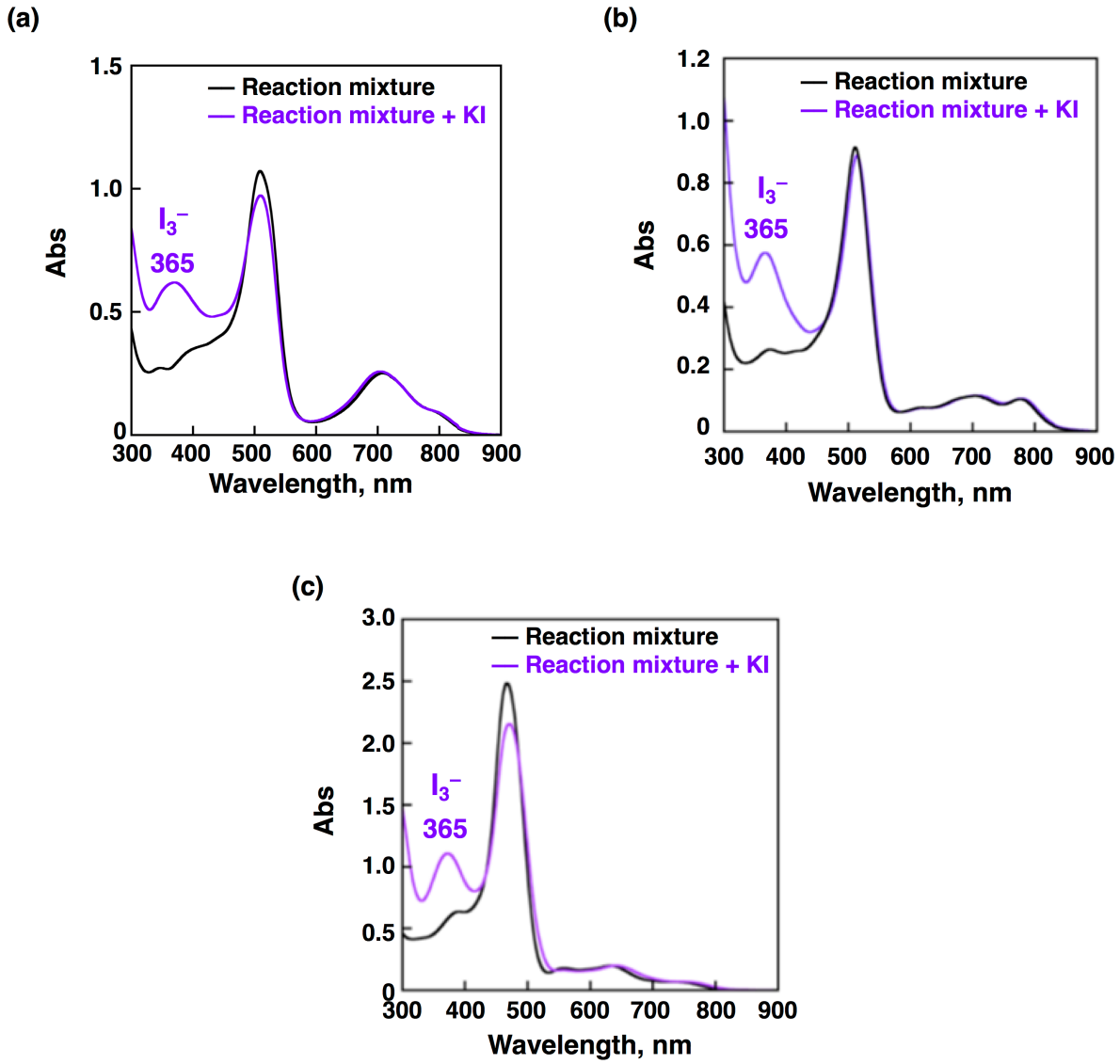


Figure S7. UV-Vis spectral changes after the reaction of (a) **6,**(b) **8**, and (c) **1** with O_2 in DMF at 298 K by adding KI for iodometric titration.

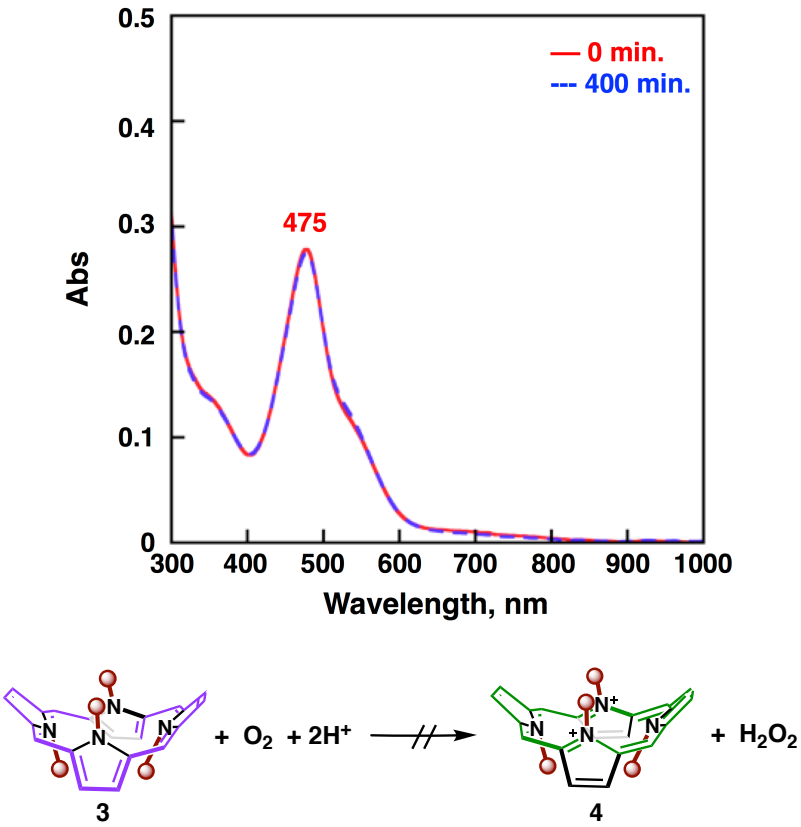


Figure S8. UV-Vis spectra of **3** in O_2-saturated DMF in the presence of 10 equivalents of trifluoroacetic acid (TFA) at 298 K after 0 min. (red solid line) and 400 min. (blue dotted line).

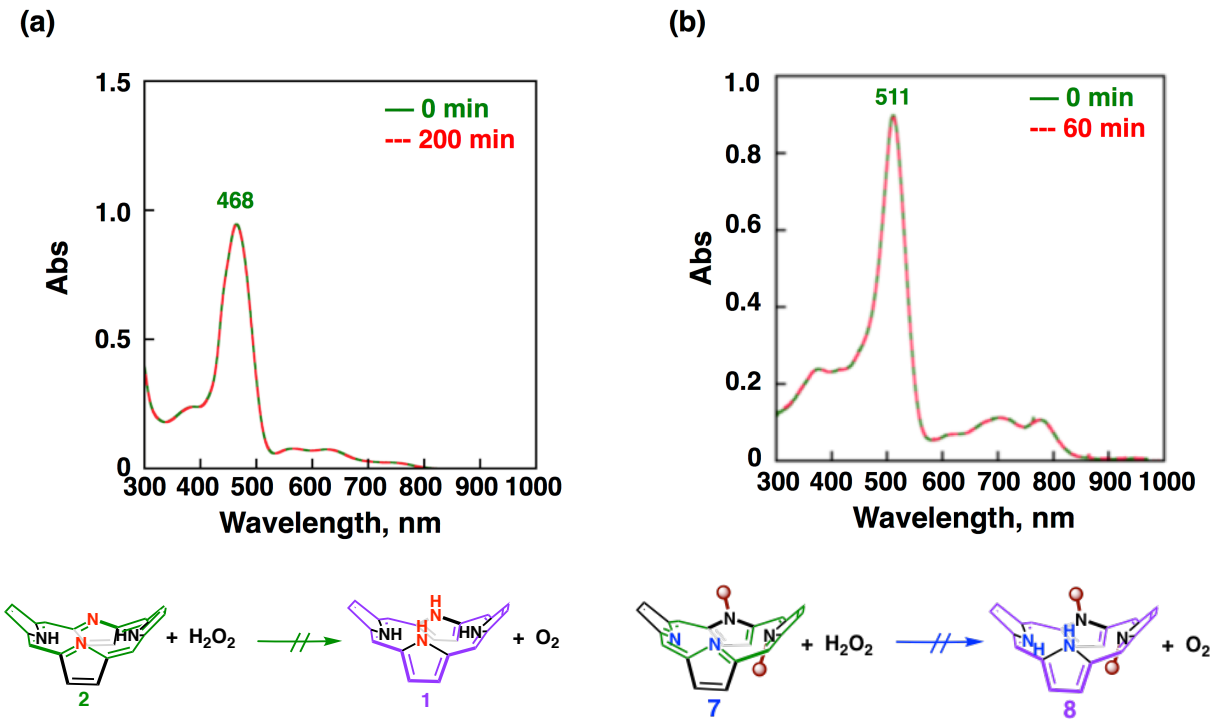


Figure S9. UV-Vis spectra of (a) **2** (0.010 mM) and (b) **7** (0.010 mM) in the presence of H_2O_2 (100 mM) in deaerated DMF at 298 K.

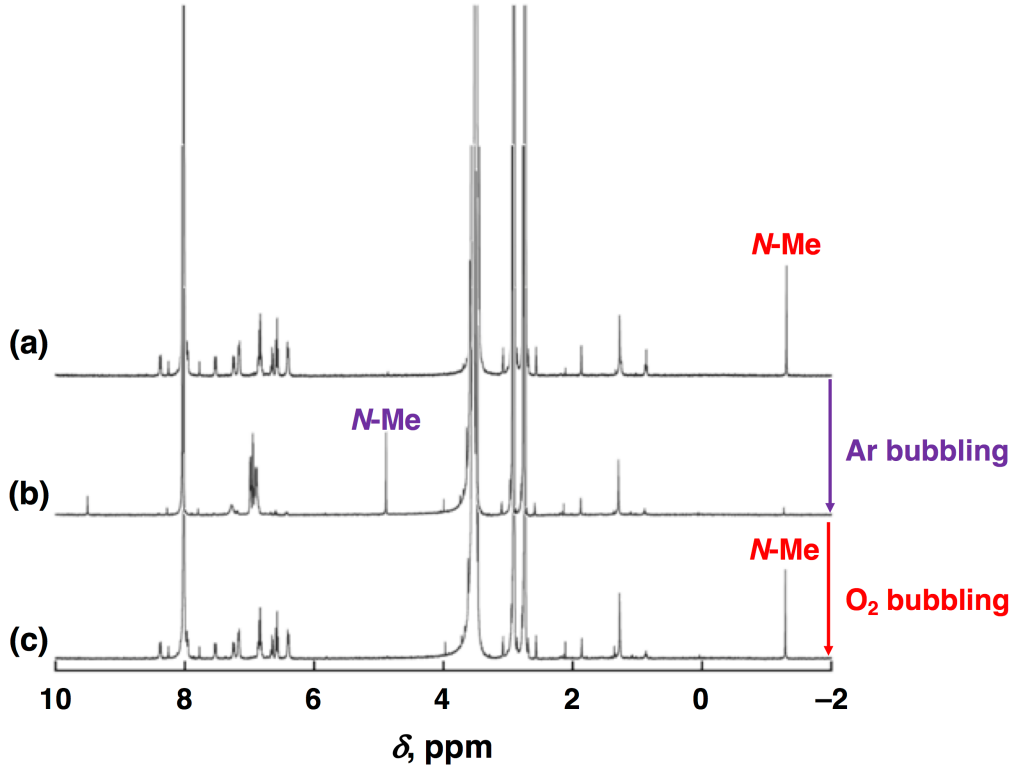


Figure S10. (a) ^{1}H NMR spectrum of **5** (0.32 mM) with H_2O_2 (70 mM) under O_2 in DMF-d_7. (b) ^{1}H NMR spectrum after Ar bubbling into the resultant DMF-d_7 solution affording the spectrum (a). (c) ^{1}H NMR spectrum after O_2 bubbling into the resultant DMF-d_7 solution showing the spectrum (b). "*N*-Me" in this Figure indicates the assignments of ^{1}H NMR signals derived from the inner *N*-Me groups of **5** or **6**.

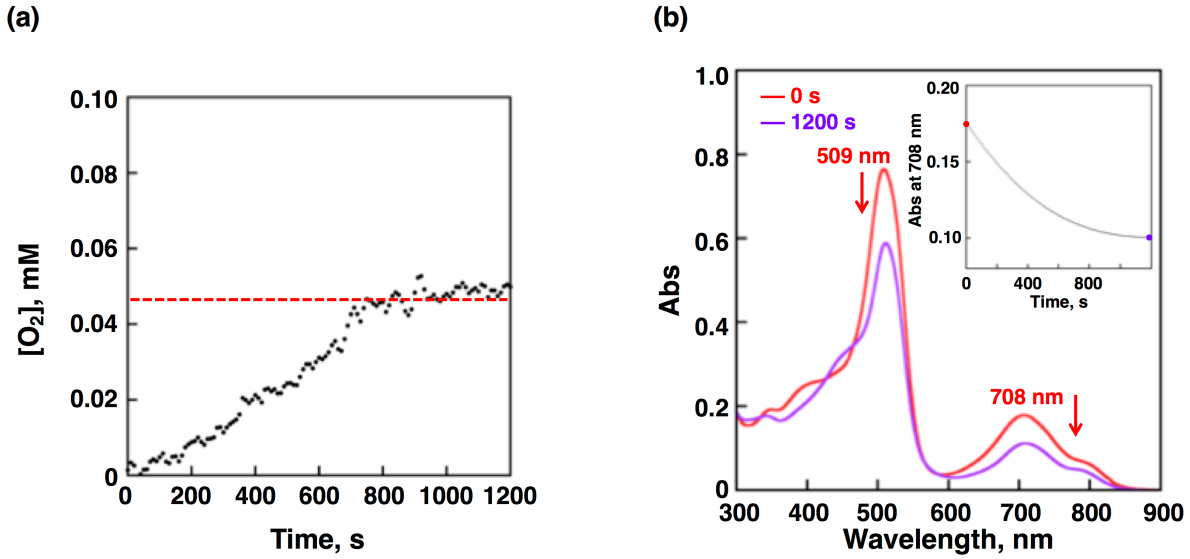


Figure S11. (a) Time-course of the concentration of O_2 in a DMF solution of the reaction mixture containing **5** (0.10 mM) and H_2O_2 (50 mM) monitored by a fluorescence O_2 sensor. (b) UV-Vis spectral change of **5** (0.10 mM) in the presence of H_2O_2 (50 mM) in DMF under Ar at 298 K (the optical cell length is 1 mm). Inset**:** Time-course of absorbance change at 708 nm.

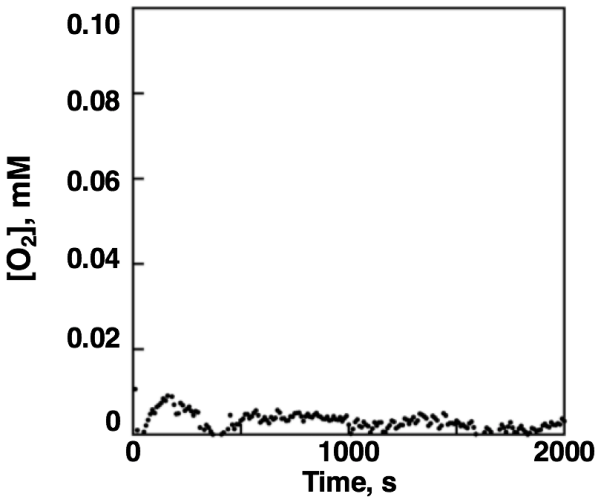


Figure S12. Time-course of the concentration of O_2 in a DMF solution of the reaction mixture H_2O_2 (50 mM) without **5** monitored by a fluorescence O_2 sensor.

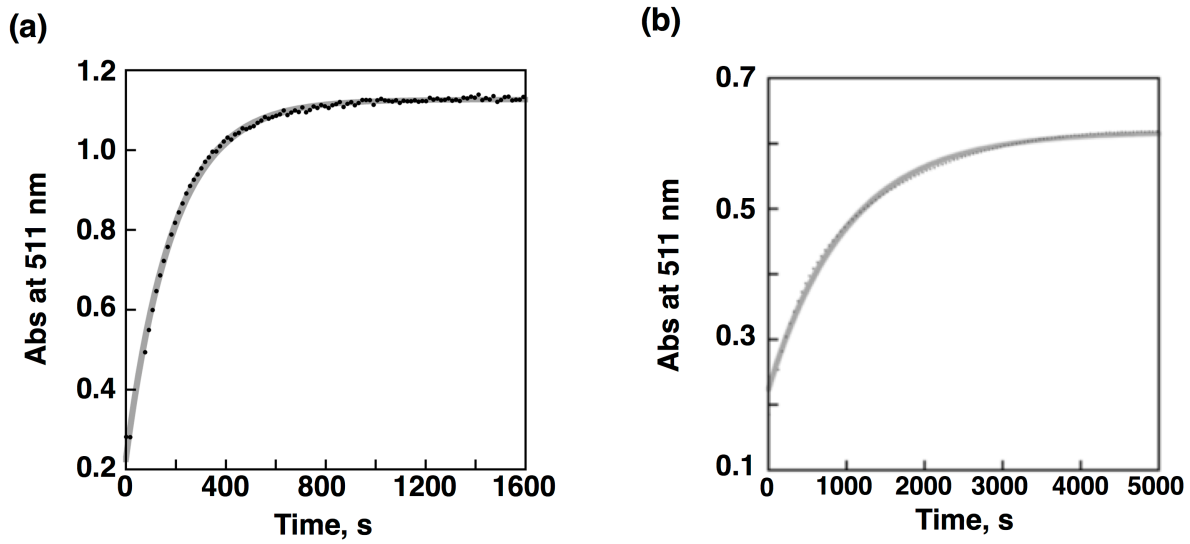


Figure S13. (a) Time-course of absorbance at 511 nm in the course of the reaction of **6** (17 μM) in air-saturated DMF at 298 K. Curve fitting was conducted to determine the pseudo first-order rate constants (k_{obs}). (b) Time-course of absorbance at 511 nm in the course of the reaction of **8** (8.4 μM) in air-saturated DMF at 298 K with curve fitting.

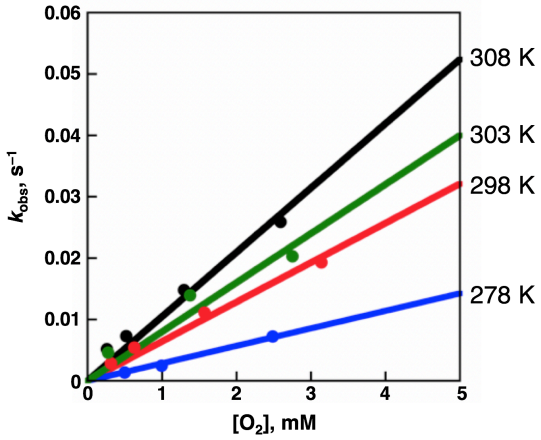


Figure S14. Plots of k_{obs} obtained in the reaction of **6** with O_2 relative to the concentration of O_2 at various temperature (278 K – 308 K).

Note: O_2 concentrations at various temperatures were calibrated by referring the temperature dependence of O_2 concentration in water.[10]

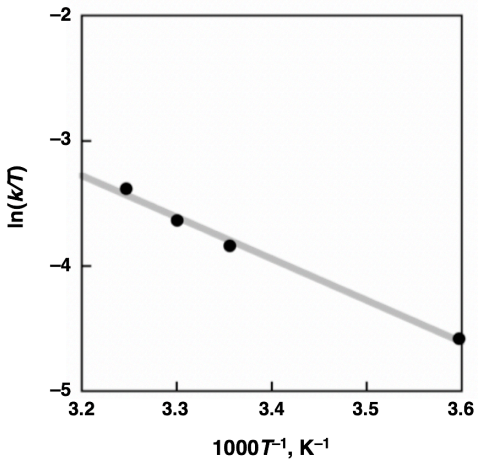


Figure S15. Temperature dependence of k in the reaction of **6** with O_2 (278 K – 308 K) to provide an Eyring plot.

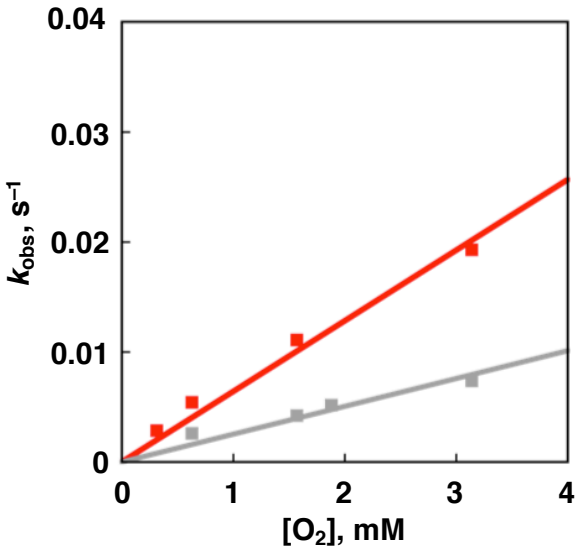


Figure S16. O_2 concentration dependence of the pseudo-first-order rate constant (k_{obs}) in the reaction of **6** (red) and deuterated **6** (gray) with O_2 in DMF containing 0.2% H_2O for **6** or D_2O for deuterated **6** at 298 K.

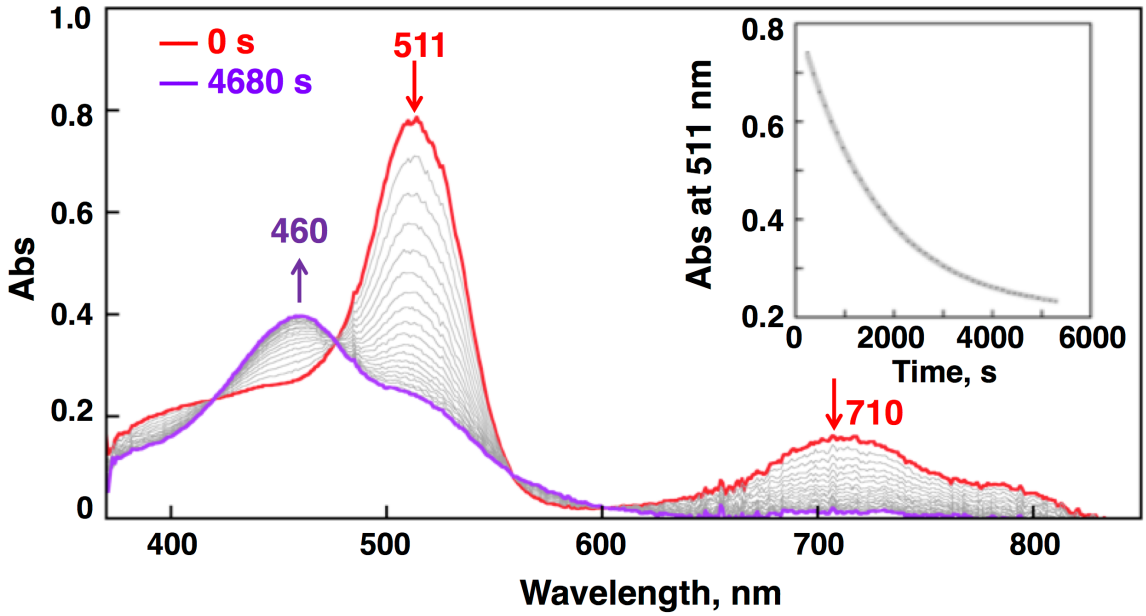


Figure S17. UV-Vis spectral change of **5** (0.010 mM) in the presence of H_2O_2 (40 mM) in DMF under Ar at 298 K. Inset: Time course of absorbance change at 511 nm with curve fitting.

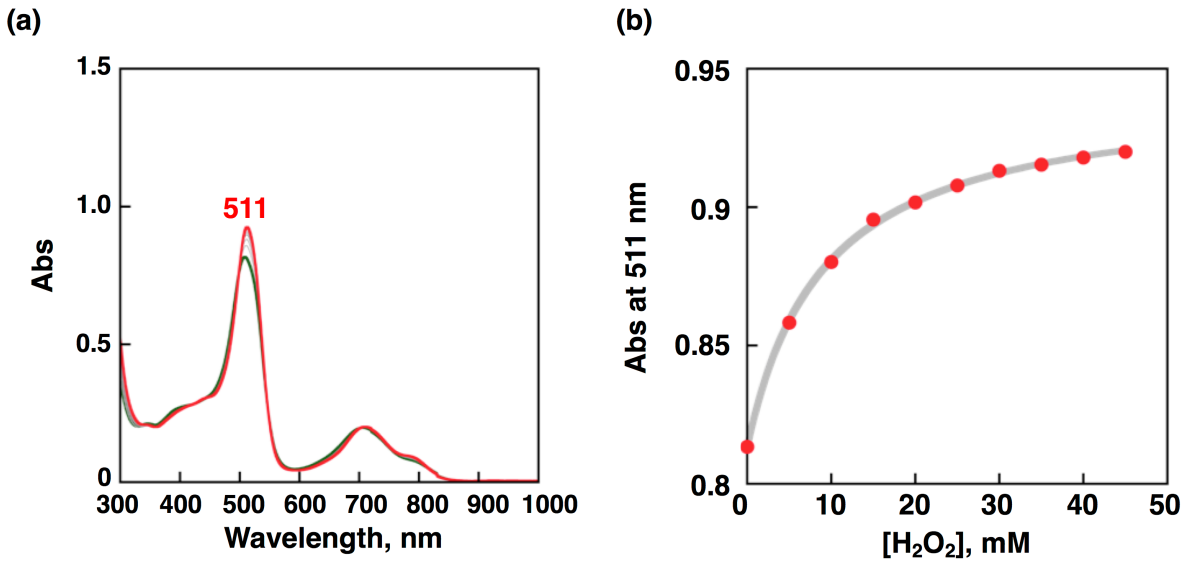


Figure S18. (a) UV-Vis titration of **5** (0.010 mM) with H_2O_2 in DMF under O_2 at 298 K. (b) Curve fitting of absorbance change at 511 nm against the concentration of H_2O_2.

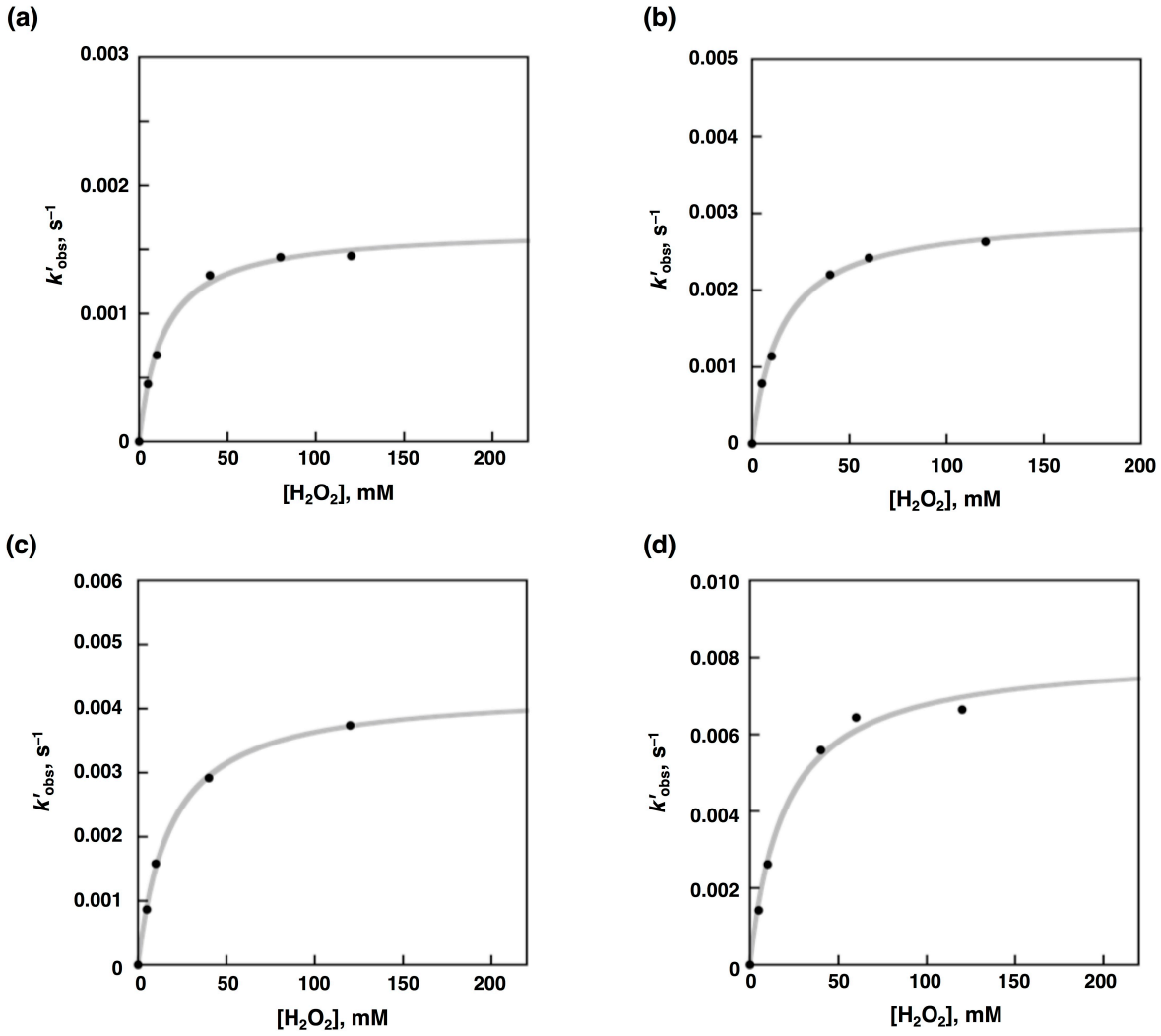


Figure S19. H_2O_2 concentration dependence of the pseudo-first-order rate constants (k'_{obs}) in the reaction of **5** (0.010 mM) with H_2O_2 in DMF at (a) 303 K, (b) 308 K, (c) 313 K, and (d) 318 K.

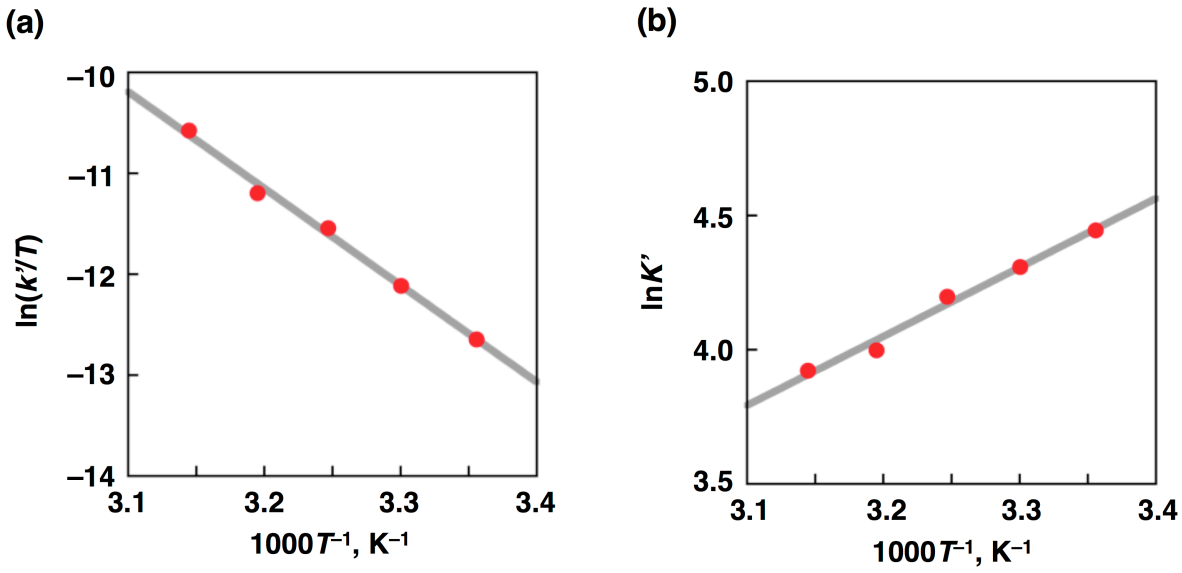


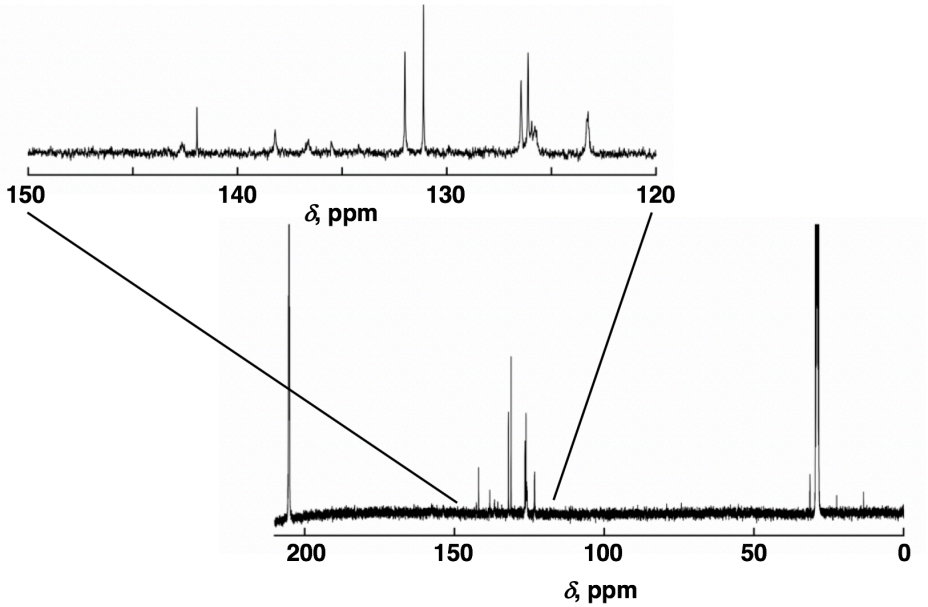
Figure S20. (a) Temperature dependence of *k*' (303 K -318 K) to provide an Eyring plot. (b) Temperature dependence of *K'* (303 K -318 K) to provide a van't Hoff plot for the equilibrium of adduct formation of **5** with H_2O_2.

Table S1. X-ray Crystallographic data for **5** and **7**.

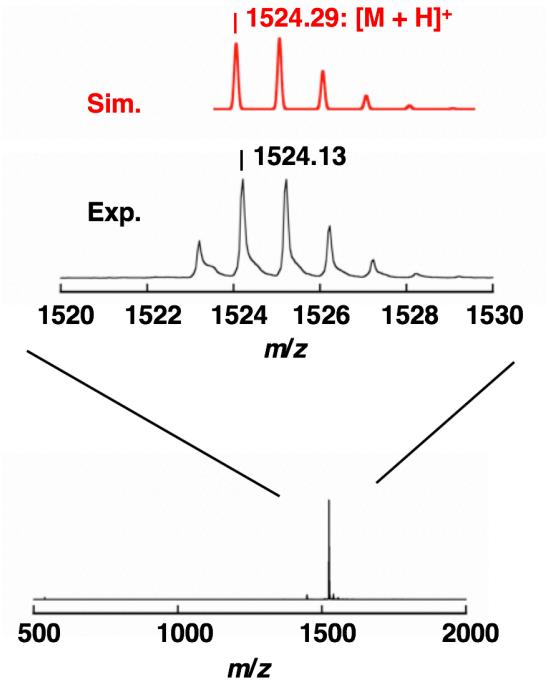
compound	**5**	**7**
crystal system	Triclinic	Triclinic
space group	$P\ \bar{1}$	$P\ \bar{1}$
T, K	120	120
formula	$C_{98}H_{64}F_{12}N_4O$	$C_{98}H_{62}F_{12}N_4$
FW	1541.60	1523.58
a, Å	15.1005(14)	16.181(2)
b, Å	16.7532(15)	16.229(2)
c, Å	18.7562(17)	18.735(3)
α, deg	90.1800(10)	64.770(2)
β, deg	109.1510(10)	76.472(2)
γ, deg	97.4620(10)	76.628(2)
V, Å^3	4439.1(7)	4278.3(11)
Z	2	2
λ, Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)
D_c, g cm^{-3}	1.153	1.292
reflns measured	25314	24424
reflns unique	13517	11103
R_1 (I > 2 (I))	0.0634	0.0897
wR_2 (all)	0.1878	0.2644
GOF	1.036	1.009

^{13}C NMR spectra and MALDI-TOF-MS of new compounds (5 and 7)

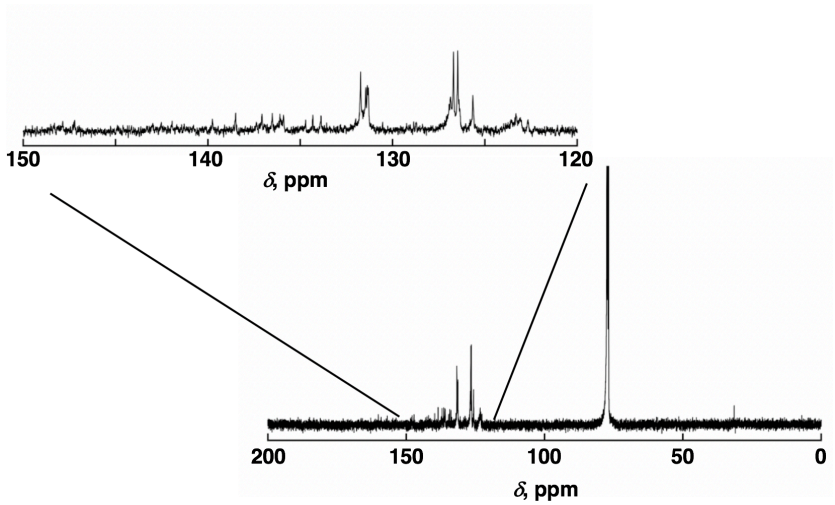
^{13}C NMR of **5** in acetone-d_6



MALDI-TOF-MS of **5** (dithranol matrix)



^{13}C NMR of **7** in $CDCl_3$



MALDI-TOF-MS of **7** (dithranol matrix)

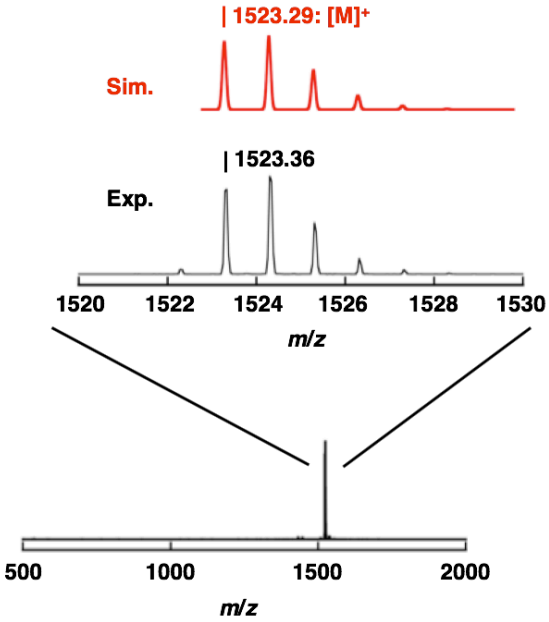


Table S2. Cartesian coordinates of *N*23-Deprotonated-*N*21-Monomethylated Isophlorin Derivative.

Atom	Coordinates (Å)		
	x	y	z
N	2.23994	-0.46661	-0.09055
N	0.48131	2.1178	-0.06443
H	0.30521	1.56598	0.76348
N	-2.19823	0.3716	-0.17807
C	2.45031	-1.6918	0.50648
C	3.16763	-1.45015	1.68476
C	3.39388	-0.03537	1.76973
C	2.82678	0.55522	0.63278
C	2.91105	1.92077	0.09194
C	1.77329	2.54982	-0.37853
C	1.59104	3.68458	-1.28625
C	0.24136	3.94764	-1.39456
C	-0.48833	2.99612	-0.54735
C	-1.83088	2.85855	-0.2528
C	-2.33594	1.63028	0.39593
C	-3.05744	1.47464	1.58448
C	-3.38513	0.08742	1.71815
C	-2.83679	-0.57874	0.61071
C	-2.89392	-1.99084	0.20073
C	-1.72908	-2.66952	-0.1479
C	-1.52239	-3.7309	-1.12986
C	-0.167	-3.93183	-1.27606
C	0.53944	-3.05249	-0.34049
C	1.89977	-2.92305	-0.09392
C	3.44737	-2.43114	2.7657
C	2.84285	-2.26154	4.02422
H	2.19017	-1.40921	4.18715

C	3.07871	-3.16185	5.06209
H	2.59932	-3.01032	6.02504
C	3.92939	-4.25087	4.86546
H	4.11531	-4.95292	5.6731
C	4.54443	-4.42643	3.62571
H	5.21533	-5.26523	3.46365
C	4.30784	-3.52537	2.58656
H	4.80084	-3.66689	1.63203
C	4.06816	0.68129	2.8717
C	5.27278	0.20364	3.41577
H	5.71649	-0.701	3.01361
C	5.90336	0.87933	4.45831
H	6.83567	0.4938	4.86082
C	5.34559	2.04748	4.9812
H	5.83816	2.57312	5.79391
C	4.14885	2.53295	4.45257
H	3.70196	3.43735	4.85578
C	3.51608	1.8553	3.41161
H	2.57684	2.23039	3.01646
C	4.24081	2.56911	0.1002
C	5.3989	1.83412	-0.21635
H	5.30532	0.78848	-0.49016
C	6.65623	2.42366	-0.18537
H	7.53738	1.84253	-0.43471
C	6.78954	3.76742	0.17736
C	5.65493	4.50918	0.51303
H	5.75957	5.54353	0.82174
C	4.39928	3.91355	0.48116
H	3.52749	4.48423	0.7816
C	2.65314	4.24816	-2.15861
C	3.2876	3.41452	-3.09321
H	3.01213	2.36542	-3.1421
C	4.25639	3.91893	-3.95833

H	4.7324	3.25865	-4.67731
C	4.61345	5.26708	-3.90183
H	5.37099	5.66045	-4.57287
C	3.99508	6.10432	-2.97353
H	4.27196	7.15285	-2.91618
C	3.02323	5.59914	-2.1105
H	2.56442	6.25303	-1.37704
C	-0.37861	4.85414	-2.39475
C	-0.22305	6.24607	-2.33459
H	0.31952	6.68674	-1.50523
C	-0.78386	7.07102	-3.30899
H	-0.65604	8.1473	-3.24081
C	-1.5105	6.51766	-4.36298
H	-1.94876	7.15958	-5.12118
C	-1.67375	5.13328	-4.43492
H	-2.23599	4.69278	-5.25307
C	-1.11408	4.31046	-3.45967
H	-1.23731	3.23375	-3.52724
C	-2.82412	3.92441	-0.51491
C	-2.58425	5.26513	-0.16771
H	-1.64535	5.52811	0.30629
C	-3.54351	6.24765	-0.38633
H	-3.34119	7.27675	-0.10975
C	-4.77518	5.91095	-0.95285
C	-5.03899	4.58098	-1.29676
H	-5.9917	4.31874	-1.74406
C	-4.07606	3.60373	-1.07497
H	-4.28984	2.57307	-1.34017
C	-3.27384	2.52583	2.61843
C	-2.49957	2.5077	3.78998
H	-1.75513	1.72732	3.91911
C	-2.67848	3.46849	4.78458
H	-2.06792	3.43469	5.6825

C	-3.64021	4.46782	4.62779
H	-3.78176	5.21679	5.40164
C	-4.42113	4.49527	3.47204
H	-5.1747	5.26646	3.34032
C	-4.2408	3.53264	2.47788
H	-4.85574	3.56081	1.58515
C	-4.14594	-0.52068	2.83297
C	-5.27375	0.13422	3.36149
H	-5.58366	1.08248	2.9382
C	-6.00212	-0.41824	4.41248
H	-6.87009	0.10965	4.79706
C	-5.62631	-1.6436	4.96472
H	-6.19446	-2.07461	5.78374
C	-4.51476	-2.31046	4.44992
H	-4.20964	-3.26537	4.86856
C	-3.7853	-1.7559	3.39959
H	-2.92639	-2.2946	3.01591
C	-4.22088	-2.63594	0.16916
C	-5.36715	-1.91328	-0.21607
H	-5.26307	-0.87635	-0.51731
C	-6.62428	-2.50315	-0.21482
H	-7.49509	-1.93111	-0.51604
C	-6.7724	-3.83504	0.18519
C	-5.65159	-4.56448	0.58836
H	-5.76862	-5.58845	0.92609
C	-4.39625	-3.96855	0.58706
H	-3.53672	-4.52728	0.94138
C	-2.5595	-4.28604	-2.0425
C	-3.0646	-3.50727	-3.0934
H	-2.70255	-2.49274	-3.22756
C	-4.00649	-4.02811	-3.97996
H	-4.38371	-3.40973	-4.78921
C	-4.45841	-5.33968	-3.83208

H	-5.19322	-5.74538	-4.52085
C	-3.96032	-6.1267	-2.79344
H	-4.30659	-7.14851	-2.66952
C	-3.01915	-5.60352	-1.90778
H	-2.64638	-6.21634	-1.09266
C	0.46205	-4.68804	-2.38737
C	0.23982	-6.06103	-2.56568
H	-0.36395	-6.60174	-1.84567
C	0.79941	-6.74062	-3.64691
H	0.61881	-7.80515	-3.76345
C	1.59033	-6.05961	-4.57221
H	2.02657	-6.58935	-5.41372
C	1.81914	-4.69245	-4.40717
H	2.43111	-4.15192	-5.12342
C	1.26144	-4.01481	-3.32538
H	1.44066	-2.95094	-3.20393
C	2.86694	-3.99141	-0.42201
C	2.59374	-5.34415	-0.14854
H	1.64869	-5.60915	0.3126
C	3.52438	-6.33775	-0.42974
H	3.29522	-7.37522	-0.21144
C	4.76178	-6.00286	-0.98552
C	5.05898	-4.66284	-1.25568
H	6.01541	-4.40127	-1.69543
C	4.12452	-3.67408	-0.97333
H	4.36288	-2.63684	-1.18616
C	5.79307	-7.06886	-1.22135
C	8.1406	4.4236	0.16117
C	-5.83671	6.9603	-1.11841
C	-8.1218	-4.49267	0.1373
F	8.22915	5.42202	1.06947
F	9.13438	3.54531	0.42567
F	8.41983	4.97313	-1.04681

F	-5.30837	8.1771	-1.38325
F	-6.69274	6.6624	-2.12223
F	-6.58578	7.09943	0.00359
F	-9.12507	-3.60784	0.33499
F	-8.35391	-5.08043	-1.06281
F	-8.24558	-5.46244	1.07235
F	6.55576	-7.28396	-0.12084
F	5.22909	-8.25653	-1.53882
F	6.64075	-6.74128	-2.22307
C	-1.68999	0.12824	-1.51941
H	-0.67259	-0.27145	-1.49464
H	-2.3352	-0.58763	-2.02987
H	-1.68871	1.06903	-2.06863
N	-0.44939	-2.29084	0.29963
H	-0.22219	-1.60697	0.99295

Table S3. Cartesian coordinates of *N*22-Deprotonated-*N*21-Monomethylated Isophlorin Derivative.

Atom	Coordinates (Å)		
	x	y	z
N	2.23994	-0.46661	-0.09055
H	1.84205	-0.35011	-1.00965
N	0.48131	2.1178	-0.06443
H	0.30521	1.56598	0.76348
N	-2.19823	0.3716	-0.17807
N	-0.44939	-2.29084	0.29963
C	2.45031	-1.6918	0.50648
C	3.16763	-1.45015	1.68476
C	3.39388	-0.03537	1.76973
C	2.82678	0.55522	0.63278
C	2.91105	1.92077	0.09194
C	1.77329	2.54982	-0.37853
C	1.59104	3.68458	-1.28625
C	0.24136	3.94764	-1.39456
C	-0.48833	2.99612	-0.54735
C	-1.83088	2.85855	-0.2528
C	-2.33594	1.63028	0.39593
C	-3.05744	1.47464	1.58448
C	-3.38513	0.08742	1.71815
C	-2.83679	-0.57874	0.61071
C	-2.89392	-1.99084	0.20073
C	-1.72908	-2.66952	-0.1479
C	-1.52239	-3.7309	-1.12986
C	-0.167	-3.93183	-1.27606
C	0.53944	-3.05249	-0.34049
C	1.89977	-2.92305	-0.09392
C	3.44737	-2.43114	2.7657
C	2.84285	-2.26154	4.02422
H	2.19017	-1.40921	4.18715

C	3.07871	-3.16185	5.06209
H	2.59932	-3.01032	6.02504
C	3.92939	-4.25087	4.86546
H	4.11531	-4.95292	5.6731
C	4.54443	-4.42643	3.62571
H	5.21533	-5.26523	3.46365
C	4.30784	-3.52537	2.58656
H	4.80084	-3.66689	1.63203
C	4.06816	0.68129	2.8717
C	5.27278	0.20364	3.41577
H	5.71649	-0.701	3.01361
C	5.90336	0.87933	4.45831
H	6.83567	0.4938	4.86082
C	5.34559	2.04748	4.9812
H	5.83816	2.57312	5.79391
C	4.14885	2.53295	4.45257
H	3.70196	3.43735	4.85578
C	3.51608	1.8553	3.41161
H	2.57684	2.23039	3.01646
C	4.24081	2.56911	0.1002
C	5.3989	1.83412	-0.21635
H	5.30532	0.78848	-0.49016
C	6.65623	2.42366	-0.18537
H	7.53738	1.84253	-0.43471
C	6.78954	3.76742	0.17736
C	5.65493	4.50918	0.51303
H	5.75957	5.54353	0.82174
C	4.39928	3.91355	0.48116
H	3.52749	4.48423	0.7816
C	2.65314	4.24816	-2.15861
C	3.2876	3.41452	-3.09321
H	3.01213	2.36542	-3.1421
C	4.25639	3.91893	-3.95833

H	4.7324	3.25865	-4.67731
C	4.61345	5.26708	-3.90183
H	5.37099	5.66045	-4.57287
C	3.99508	6.10432	-2.97353
H	4.27196	7.15285	-2.91618
C	3.02323	5.59914	-2.1105
H	2.56442	6.25303	-1.37704
C	-0.37861	4.85414	-2.39475
C	-0.22305	6.24607	-2.33459
H	0.31952	6.68674	-1.50523
C	-0.78386	7.07102	-3.30899
H	-0.65604	8.1473	-3.24081
C	-1.5105	6.51766	-4.36298
H	-1.94876	7.15958	-5.12118
C	-1.67375	5.13328	-4.43492
H	-2.23599	4.69278	-5.25307
C	-1.11408	4.31046	-3.45967
H	-1.23731	3.23375	-3.52724
C	-2.82412	3.92441	-0.51491
C	-2.58425	5.26513	-0.16771
H	-1.64535	5.52811	0.30629
C	-3.54351	6.24765	-0.38633
H	-3.34119	7.27675	-0.10975
C	-4.77518	5.91095	-0.95285
C	-5.03899	4.58098	-1.29676
H	-5.9917	4.31874	-1.74406
C	-4.07606	3.60373	-1.07497
H	-4.28984	2.57307	-1.34017
C	-3.27384	2.52583	2.61843
C	-2.49957	2.5077	3.78998
H	-1.75513	1.72732	3.91911
C	-2.67848	3.46849	4.78458
H	-2.06792	3.43469	5.6825

C	-3.64021	4.46782	4.62779
H	-3.78176	5.21679	5.40164
C	-4.42113	4.49527	3.47204
H	-5.1747	5.26646	3.34032
C	-4.2408	3.53264	2.47788
H	-4.85574	3.56081	1.58515
C	-4.14594	-0.52068	2.83297
C	-5.27375	0.13422	3.36149
H	-5.58366	1.08248	2.9382
C	-6.00212	-0.41824	4.41248
H	-6.87009	0.10965	4.79706
C	-5.62631	-1.6436	4.96472
H	-6.19446	-2.07461	5.78374
C	-4.51476	-2.31046	4.44992
H	-4.20964	-3.26537	4.86856
C	-3.7853	-1.7559	3.39959
H	-2.92639	-2.2946	3.01591
C	-4.22088	-2.63594	0.16916
C	-5.36715	-1.91328	-0.21607
H	-5.26307	-0.87635	-0.51731
C	-6.62428	-2.50315	-0.21482
H	-7.49509	-1.93111	-0.51604
C	-6.7724	-3.83504	0.18519
C	-5.65159	-4.56448	0.58836
H	-5.76862	-5.58845	0.92609
C	-4.39625	-3.96855	0.58706
H	-3.53672	-4.52728	0.94138
C	-2.5595	-4.28604	-2.0425
C	-3.0646	-3.50727	-3.0934
H	-2.70255	-2.49274	-3.22756
C	-4.00649	-4.02811	-3.97996
H	-4.38371	-3.40973	-4.78921
C	-4.45841	-5.33968	-3.83208

H	-5.19322	-5.74538	-4.52085
C	-3.96032	-6.1267	-2.79344
H	-4.30659	-7.14851	-2.66952
C	-3.01915	-5.60352	-1.90778
H	-2.64638	-6.21634	-1.09266
C	0.46205	-4.68804	-2.38737
C	0.23982	-6.06103	-2.56568
H	-0.36395	-6.60174	-1.84567
C	0.79941	-6.74062	-3.64691
H	0.61881	-7.80515	-3.76345
C	1.59033	-6.05961	-4.57221
H	2.02657	-6.58935	-5.41372
C	1.81914	-4.69245	-4.40717
H	2.43111	-4.15192	-5.12342
C	1.26144	-4.01481	-3.32538
H	1.44066	-2.95094	-3.20393
C	2.86694	-3.99141	-0.42201
C	2.59374	-5.34415	-0.14854
H	1.64869	-5.60915	0.3126
C	3.52438	-6.33775	-0.42974
H	3.29522	-7.37522	-0.21144
C	4.76178	-6.00286	-0.98552
C	5.05898	-4.66284	-1.25568
H	6.01541	-4.40127	-1.69543
C	4.12452	-3.67408	-0.97333
H	4.36288	-2.63684	-1.18616
C	5.79307	-7.06886	-1.22135
C	8.1406	4.4236	0.16117
C	-5.83671	6.9603	-1.11841
C	-8.1218	-4.49267	0.1373
F	8.22915	5.42202	1.06947
F	9.13438	3.54531	0.42567
F	8.41983	4.97313	-1.04681

F	-5.30837	8.1771	-1.38325
F	-6.69274	6.6624	-2.12223
F	-6.58578	7.09943	0.00359
F	-9.12507	-3.60784	0.33499
F	-8.35391	-5.08043	-1.06281
F	-8.24558	-5.46244	1.07235
F	6.55576	-7.28396	-0.12084
F	5.22909	-8.25653	-1.53882
F	6.64075	-6.74128	-2.22307
C	-1.68999	0.12824	-1.51941
H	-0.67259	-0.27145	-1.49464
H	-2.3352	-0.58763	-2.02987
H	-1.68871	1.06903	-2.06863

Table S4. Cartesian coordinates of **5-H_2O_2**

Atom	Coordinates (Å)		
	x	y	z
N	2.22999	0.00457	0.2772
H	1.41366	-0.00249	-0.57328
N	0.08588	2.27316	0.4634
N	-2.0664	0.00928	0.27686
H	-1.41766	-0.00435	-0.54741
N	0.07763	-2.27975	0.52071
C	2.8662	-1.11774	0.74423
C	3.90644	-0.69962	1.62395
C	3.90722	0.71265	1.6264
C	2.87179	1.13192	0.73484
C	2.5451	2.43157	0.20344
C	1.22801	2.74241	-0.19136
C	0.78602	3.49909	-1.33513
C	-0.6008	3.49874	-1.34027
C	-1.05127	2.74332	-0.19867
C	-2.37132	2.43799	0.19108
C	-2.70505	1.14149	0.72627
C	-3.74538	0.73133	1.6162
C	-3.75062	-0.68092	1.62144
C	-2.70887	-1.10835	0.74777
C	-2.37459	-2.42446	0.25484
C	-1.06411	-2.76538	-0.1116
C	-0.61905	-3.59056	-1.2158
C	0.76151	-3.59058	-1.22073
C	1.21489	-2.76679	-0.1185
C	2.52752	-2.43061	0.24398
C	4.66384	-1.59602	2.53979
C	4.0231	-2.12153	3.67283
H	2.98854	-1.85408	3.868
C	4.7014	-2.95816	4.55913

H	4.18697	-3.34904	5.43236
C	6.03705	-3.28721	4.32676
H	6.5673	-3.93984	5.01391
C	6.68733	-2.77328	3.20422
H	7.72474	-3.02963	3.01074
C	6.00705	-1.93487	2.32165
H	6.51504	-1.55728	1.44031
C	4.69407	1.5987	2.51188
C	6.08731	1.47232	2.63566
H	6.61	0.73119	2.04285
C	6.80845	2.29877	3.49571
H	7.88594	2.18475	3.5707
C	6.15388	3.27266	4.2505
H	6.71658	3.91677	4.91959
C	4.77012	3.41357	4.13664
H	4.24915	4.16629	4.72143
C	4.04978	2.58562	3.27834
H	2.97231	2.69444	3.20661
C	3.62151	3.41581	-0.0239
C	4.8903	3.02386	-0.49062
H	5.07379	1.97847	-0.7124
C	5.89939	3.95725	-0.69035
H	6.87035	3.64077	-1.05487
C	5.66667	5.30906	-0.42031
C	4.41494	5.71855	0.04597
H	4.23984	6.76469	0.27263
C	3.4076	4.78196	0.24135
H	2.44521	5.10067	0.62774
C	1.63989	3.88313	-2.48805
C	2.18753	2.87172	-3.29361
H	1.97257	1.832	-3.06114
C	2.9588	3.20461	-4.40682
H	3.37038	2.41497	-5.02898

C	3.1929	4.54253	-4.72917
H	3.79583	4.79833	-5.59563
C	2.64352	5.55128	-3.93708
H	2.81914	6.5945	-4.18284
C	1.86805	5.22332	-2.82534
H	1.44768	6.01051	-2.20706
C	-1.4461	3.88435	-2.49852
C	-1.6526	5.22494	-2.84818
H	-1.22166	6.01081	-2.23559
C	-2.41941	5.55509	-3.96522
H	-2.57716	6.59878	-4.22103
C	-2.98218	4.54806	-4.75012
H	-3.5781	4.8054	-5.62098
C	-2.76975	3.20953	-4.4154
H	-3.19139	2.42095	-5.03212
C	-2.0069	2.87455	-3.29708
H	-1.80768	1.83376	-3.05578
C	-3.44453	3.42376	-0.04425
C	-3.22699	4.79157	0.2083
H	-2.26235	5.11193	0.58769
C	-4.23079	5.72975	0.00143
H	-4.04734	6.77955	0.20289
C	-5.48247	5.3201	-0.4642
C	-5.71866	3.96639	-0.7229
H	-6.68464	3.65171	-1.10218
C	-4.71269	3.03207	-0.5138
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H	-2.79999	2.7029	3.20114
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C	-5.9821	3.3195	4.2213

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H	-7.72184	2.2519	3.52933
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C	-5.86615	-1.88516	2.3269
H	-6.37197	-1.50002	1.44755
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H	-2.8395	-1.85401	3.8591
C	-3.46453	-3.39687	0.0195
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C	-4.34469	-5.65849	0.21389
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C	-3.3266	-4.7357	0.42688
H	-2.41853	-5.04272	0.93526
C	-1.47061	-4.03005	-2.35087
C	-1.98316	-3.05902	-3.22643
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H	-3.1325	-2.68533	-5.00379
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H	-1.33098	-6.13882	-1.93452
C	1.60389	-4.03421	-2.36035
C	1.82671	-5.38991	-2.63181
H	1.4142	-6.14382	-1.96836
C	2.58386	-5.77498	-3.73814
H	2.75391	-6.82973	-3.93383
C	3.12021	-4.80875	-4.58985
H	3.70825	-5.10908	-5.45227
C	2.89154	-3.45567	-4.33257
H	3.29266	-2.69937	-5.00129
C	2.138	-3.06585	-3.22596
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C	5.67752	-5.25812	-0.46138
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H	0.96767	-2.2002	2.40484
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H	-0.81202	-2.18119	2.40353
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H	-0.79797	1.48	2.19688
H	0.96789	1.49621	2.20437
O	0.70613	-0.04479	-1.80373
O	-0.69385	-0.05205	-1.80293

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