Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Coerulein B: a water-soluble and water-compatible near-infrared photoredox catalyst

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1. Instrumentation and Materials

Instruments

^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). ^{1}H- and ^{13}C- spectra were referenced to $CHCl_3$ (δ: 7.26 and 77.16 ppm for ^{1}H- and ^{13}C-NMR, respectively), trifluoroacetic acid (δ: 11.50 and 164.20 ppm for ^{1}H- and ^{13}C-NMR, respectively) as an internal standard. The following abbreviations are used: s = singlet, d = doublet, m = multiplet. HRMS (ESI) spectra were recorded on Agilent 6230 Accurate-Mass TOF LC/MS system using electrospray ionization. UV/Vis spectra were recorded at room temperature on a HITACHI U-2900 spectrophotometer and fluorescence spectra on a HITACHI F-7100 spectrophotometer. Crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. These diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation).

Photoreactions

Photoreactions were performed in a Schlenck tube or two-neck round-bottom flask using a LED light (Techno Sigma PER-AMP series for 631 nm, ASAHI SPECTRA CL series for 730 nm, 830 nm).

Materials

Reagents were purchased from Wako Pure Chemical Industries, Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd. All solvents were used without further purification.

Computational Details

All calculations were carried out with the Gaussian 09[1] and Gaussian 16[2] program package. The molecular structures optimizations were conducted at the B3LYP level using 6-31+G(d,p) basis set for all the atoms. Excitation wavelengths and oscillator strengths were obtained at the density functional level using time-dependent perturbation theory (TDDFT) approach. Solvation was evaluated by the self-consistent reaction field (SCRF) method using the polarizable continuum model (PCM, solvent = DMSO).[3] The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point

vibrational energy and thermal corrections at 298 K. Intrinsic reaction coordinates (IRC) were calculated to confirm the connection between the transition states and the reactants/products. In this study, the Gibbs free energy was adopted as the basis for discussion.

Reference

[1]. Gaussian 09, Revision E. 01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.

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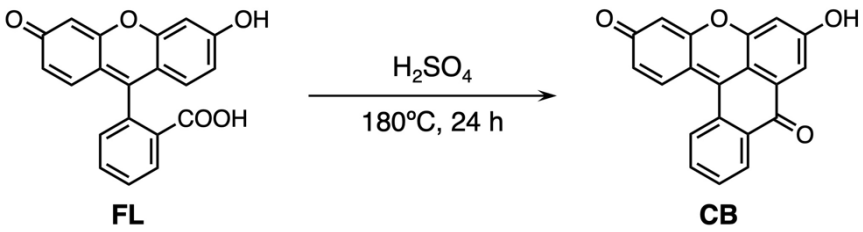
Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[3]. Miertuš, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* **1981**, *55*, 117-129.

2. Experimental Procedure



Synthesis of CB: **FL** (100 mg, 0.301 mmol) was dissolved in concentrated H_2SO_4 (5 ml). The resulting mixture was stirred for 24 h at 180°C. The reaction mixture was allowed to cool and slowly added to ice water. Then, methanol (100 ml) was added to the aqueous solution and stirred for 10 min. The water/methanol mixed solution was extracted 5 times with CH_2Cl_2 and concentrated in *vacuo*. After purification by column chromatography on silica gel using CH_2Cl_2/MeOH (15:1), **CB** was obtained as a black solid (27.1 mg, 29%). ^{1}H-NMR (500 MHz, trifluoroacetic acid-d): δ 8.79 (d, J = 9.0 Hz, 1H), 8.68-8.61 (m, 1H), 8.54-8.46 (m, 1H), 8.31 (d, J = 2.5 Hz, 1H), 8.12-8.04 (m, 2H), 7.69 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 7.60 (d, J = 2.5 Hz, 1H); **^{13}C NMR** (125 MHz, trifluoroacetic acid-d): δ ppm 185.7, 173.7, 170.0, 159.4, 156.8, 138.7, 137.5, 136.9, 135.7, 135.3, 133.6, 133.0, 124.0, 123.4, 116.1, 109.9, 105.8; HRMS (ESI, positive) *m*/*z* calcd. for $C_{20}H_{11}O_4$ ($M+H^+$): 315.0657, found: 315.0655.

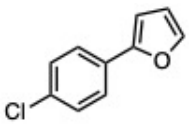
Table S1. Solubility of **CB** in various solvents.

Solvent	toluene	Et_2O	THF	AcOEt	CH_2Cl_2	DMF
Color [saturated solution]						
Solubility [mg/L]	< 1	< 1	200~500	10~20	< 1	> 1000
Solvent	DMSO	MeCN	MeOH	H_2O	H_2O (1M H_2SO_4 aq.)	H_2O (1M NaOH aq.)
Color [saturated solution]						
Solubility [mg/L]	> 1000	50~100	100~200	1~10	1~10	> 1000

Procedure for the reaction of aryl diazonium tetrafluoroborates with furan[1]

The photoreactions were performed with reference to the condition of ref [1]. In a 10 mL dried round bottom flask equipped with magnetic stirring bar, the **CB** (0.01 eq.), aryl diazonium tetrafluoroborate (1 eq.) and furan (10 eq.) were dissolved in dehydrated DMSO (0.23 mmol/mL). Then, LEDs was attached to the flask. After 0.5 h of irradiation the reaction mixture was transferred to separating funnel, diluted with diethyl ether and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate (100:0 to 10:1) as eluent.

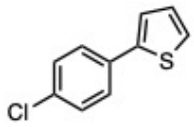
2-(4-Chloro-phenyl)-furan (2a)



2a was obtained as a colorless powder. ^{1}H and ^{13}C NMR of **2a** were in agreement with the literature[1].

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.60 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 1.5 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.48 (dd, *J* = 3.5 Hz, 1.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 153.1, 142.5, 133.2, 129.6, 129.1, 125.2, 120.0, 105.6.

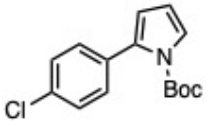
2-(4-Chloro-phenyl)-thiophene (2b)



2b was obtained as a colorless powder. ^{1}H and ^{13}C NMR of **2b** were in agreement with the literature[2].

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.54 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.30-7.29 (m, 2H), 7.09 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 143.0, 133.1, 132.8, 128.9, 128.1, 127.0, 125.1, 123.4.

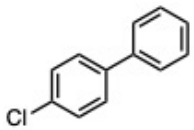
2-(4-Chlorophenyl)-*N*-Boc-pyrrole (2c)



2c was obtained as a colorless powder. ^{1}H and ^{13}C NMR of **2c** were in agreement with the literature[3].

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.45 (dd, *J* = 2.0, 3.0 Hz 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.31 (t, *J* = 2.0 Hz, 1H), 7.29 (t, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 1H), 6.22 (t, *J* = 3.0 Hz, 1H), 6.18 (dd, *J* = 2.0, 3.0 Hz, 1H), 1.39 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 149.3, 133.9, 133.3, 132.9, 130.6, 127.9, 123.0, 114.9, 110.8, 84.0, 27.8.

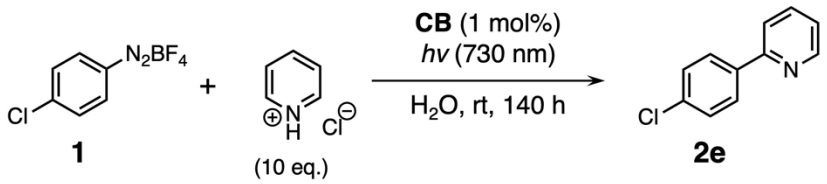
4-chloro-1,1'-biphenyl (2d)



2d was obtained as a colorless powder. ^{1}H and ^{13}C NMR of **2d** were in agreement with the literature[2].

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.59-7.53 (m, 4H), 7.48-7.42 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 140.1, 139.8, 133.5, 129.0, 129.0, 128.5, 127.7, 127.1.

Procedure for the reaction of aryl diazonium tetrafluoroborates with pyridine hydrochloride[4]

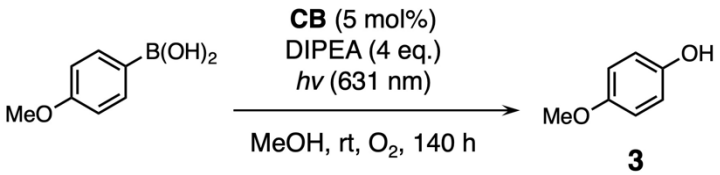


In a 10 mL dried round bottom flask equipped with magnetic stirring bar, the **CB** (0.01 mmol), aryl diazonium tetrafluoroborate (1 mmol) and pyridine hydrochloride (10 mmol) were dissolved in H_2O (4 mL). Then, 730 nm LED was attached to the flask. After 140 h of irradiation the reaction mixture was transferred to separating funnel, diluted with diethyl ether and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered and concentrated in *vacuo*. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate (100:0 to 10:1) as eluent. **2e** was obtained as a colorless powder.

^{1}H and ^{13}C NMR of **2e** were in agreement with the literature[4].

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.69 (dd, *J* = 4.3Hz, 1.5 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.74-7.73 (m, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.25-7.20 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 156.3, 149.9, 137.9, 137.1, 135.3, 129.1, 128.3, 122.6, 120.5.

Procedure for the oxidation of 4-methoxyphenylboronic acid[5]

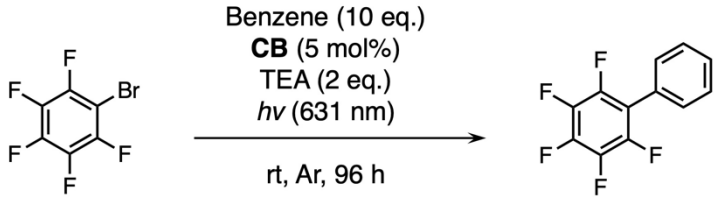


In a 100 mL dried round bottom flask equipped with magnetic stirring bar, the **CB** (0.01 mmol), 4-methoxyphenylboronic acid (0.2 mmol) and DIPEA (0.8 mmol) were dissolved in methanol (4 mL). Then, 631 nm LED was attached to the test tube. After 140 h of irradiation the reaction mixture was concentrated in *vacuo*. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate (3:1)

as eluent. **3** was obtained as a colorless powder.

^{1}H and ^{13}C NMR of **3** were in agreement with the literature[5]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 6.81-6.75 (m, 4H), 4.49 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ ppm 153.9, 149.5, 116.1, 114.9, 55.9.

Procedure for the reaction of bromopentafluorobenzene with benzene[6]



4

In a 5 mL dried screw cap test tube equipped with magnetic stirring bar, the **CB** (0.05 mmol), bromopentafluorobenzene (1 mmol) and triethylamine (2 mmol) were dissolved in benzene (20 eq.). Then, 631 nm LED was attached to the test tube. After 96 h of irradiation the reaction mixture was transferred to separating funnel, diluted with diethyl ether and washed twice with 100 mL of water. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using hexane as eluent. **4** was obtained as a colorless powder.

^{1}H and ^{13}C NMR of **4** were in agreement with the literature[6]. **^{1}H NMR** (500 MHz, $CDCl_3$): δ ppm 7.50-7.47 (m, 3H), 7.43-7.42 (m, 2H); **^{19}F NMR** (100 MHz, $CDCl_3$): δ ppm –162.1 (m, 2F), –155.5 (m, 1F), –143.1 (m, 2F).

Reference

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[4] Xue, D.; Jia, Z.-H.; Zhao, C.-J.; Zhang, Y.-Y.; Wang, C.; Xiao, J. *Chem.-Eur. J.* **2014**, *20*, 2960–2965.

[5] Meyer, A. U.; Slanina, T.; Yao, C.-J.; König, B. *ACS Catal*. **2016**, *6*, 369–375.

[6] Ravetz, B. D.; Tay, N. E. S.; Joe, C. L.; Sezen-Edmonds, M.; Schmidt, M. A.; Tan, Y.; Janey, J. M.; Eastgate, M. D.; Rovis, T. *ACS Cent. Sci.* **2020**, *6*, 2053– 2059.

3. Single X-ray Structure Analysis

Single crystals of **CB** and **CB-OTf** were obtained by slow diffusion of Et_2O into a $CHCl_3$ solution of **CB** at 10ºC. Single crystals of **CBH$^+$•HSO$_4^-$** was obtained by slow diffusion of H_2O into a H_2SO_4 solution of **CB** at 10ºC. These crystal structures were determined by the single-crystal X-ray diffraction method at T = 103 K. The diffraction data were collected using Rigaku XtaLAB Synergy-i diffractometer (Cu-Kα radiation). The structure was solved using the SHELXT[1] and refined with SHELXL-2018/3[2] via OLEX2[3]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were put on calculated geometrically, and were refined by applying riding models. Crystal data, structure refinement and included solvents are summarized in **Table S2-S4**. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 2272292 (**CB**), CCDC 2308442 (**CB-OTf**) and 2272293 (**CBH$^+$•HSO$_4^-$**).

Table S2. Crystal data and structure refinement for **CB**.

	CB
Chemical formula	$C_{20}H_{10}O_4$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	monoclinic
Space group [no.]	*C* 2/*c* [15]
Crystal color, habit	Metallic black, block
Crystal size, mm	0.19 × 0.11 × 0.07
a, Å	13.7163(5)
b, Å	11.3800(3)
c, Å	18.1174(5)
α, °	90
β, °	104.795(3)
γ, °	90
Volume, Å^3	2734.21(15)
Z	8
D_{calcd}, g/cm^3	1.527
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	0.884
$2\theta_{max}$ °	68.207
F(000)	1296
Reflns collected	2482
Unique reflns	2301
No. of parameters	218
R1 ($I > 2.00\sigma(i)$)	0.0495
R (all reflection)	0.0523
GOF	1.091

Table S3. Crystal data and structure refinement for **CB-OTf**.

	CB-OTf
Chemical formula	$C_{21}H_9F_3O_6S$
Recrystallization solvent	$CHCl_3$ / Et_2O
Included solvent	–
Crystal system	Triclinic
Space group [No.]	*P*-1 [2]
Crystal color, habit	Clear red, plate
Crystal size, mm	0.797 × 0.153 × 0.061
a, Å	5.78110(10)
b, Å	12.0613(4)
c, Å	12.5328(3)
α, °	100.454(2)
β, °	90.274(2)
γ, °	98.211(2)
Volume, Å^3	850.14(4)
Z	1
D_{calcd}, g/cm^3	1.744
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	2.395
$2\theta_{max}$ °	68.2320
F(000)	452
Reflns collected	3076
Unique reflns	2865
No. of parameters	281
R1 (*I* > 2.00σ(i))	0.0332
R (all reflection)	0.0349
GOF	1.046

Table S4. Crystal data and structure refinement for **$CBH^+ \bullet HSO_4^-$**

	$CBH^+ \cdot HSO_4^-$
Chemical formula	$C_{20}H_{12}O_8S$
Recrystallization solvent	H_2SO_4 / H_2O
Included solvent	–
Crystal system	triclinic
Space group [no.]	*P*-1
Crystal color, habit	Clear dark red, block
Crystal size, mm	0.20 × 0.11 × 0.08
a, Å	8.1750(5)
b, Å	8.5487(4)
c, Å	13.2740(6)
α, °	71.637(4)
β, °	81.162(4)
γ, °	68.995(5)
Volume, Å^3	821.05(8)
Z	2
D_{calcd}, g/cm^3	1.668
T, K	103.15
Radiation	Cu Kα
M, mm^{-1}	2.243
$2\theta_{max}$ °	67.5020
F(000)	424
Reflns collected	2607
Unique reflns	2968
No. of parameters	265
R1 (*I* > 2.00σ(i))	0.0599
R (all reflection)	0.0652
GOF	1.048

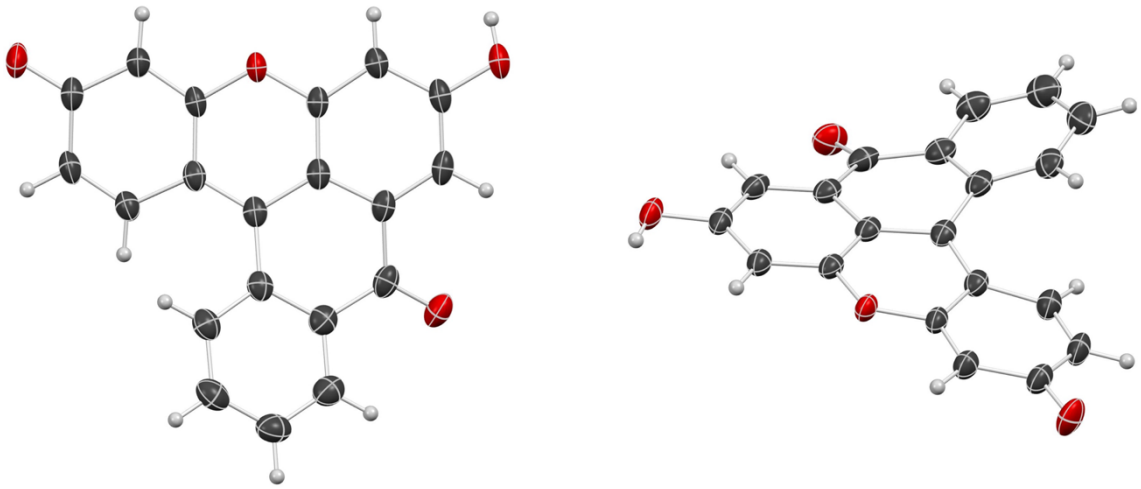

Figure S1. Top and side views of the X-ray crystal structure for **CB**. The thermal ellipsoids are scaled to the 50% probability level.

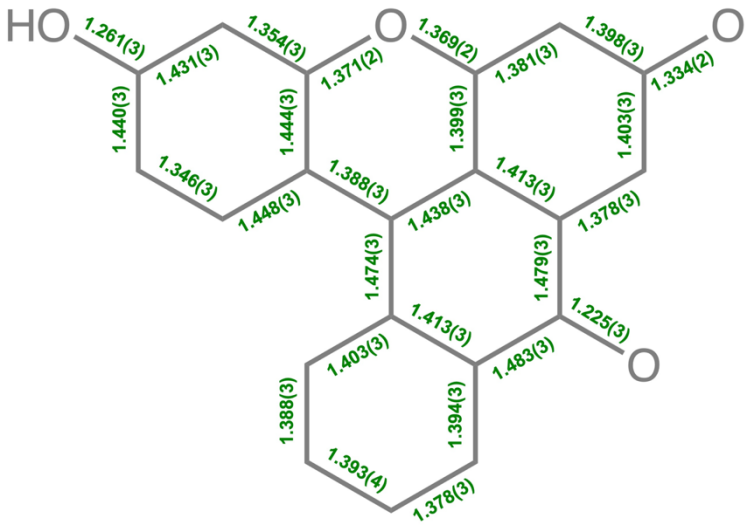

Figure S2. Bond distances (Å) obtained from X-ray crystallographic analysis of **CB**.

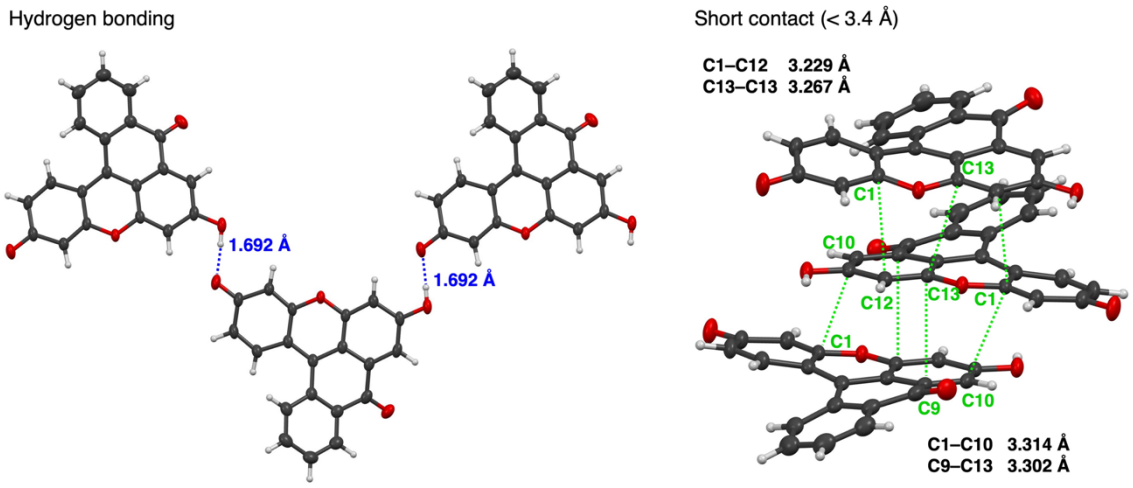

Figure S3. Hydrogen bonding and Short contact of **CB** in the X-ray structure. Intermolecular distances less than the van der Waals distance (3.4 Å) are shown in Å.

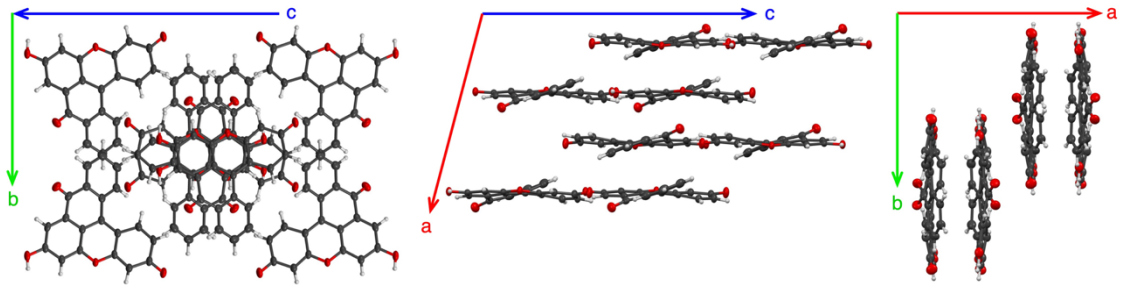

Figure S4. Crystal packing structure of **CB**.

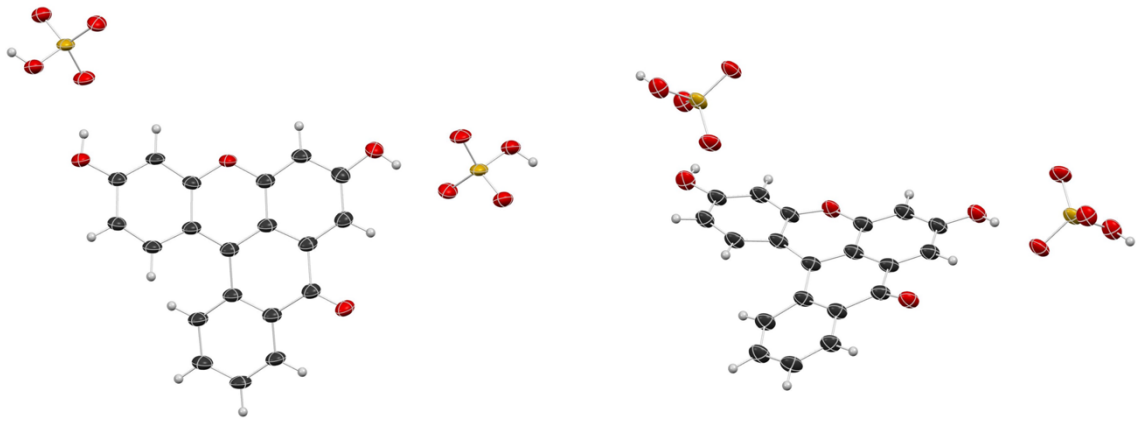

Figure S5. Top and side views of the X-ray crystal structure for **CBH$^+$•HSO$_4^-$**. The thermal ellipsoids are scaled to the 50% probability level.

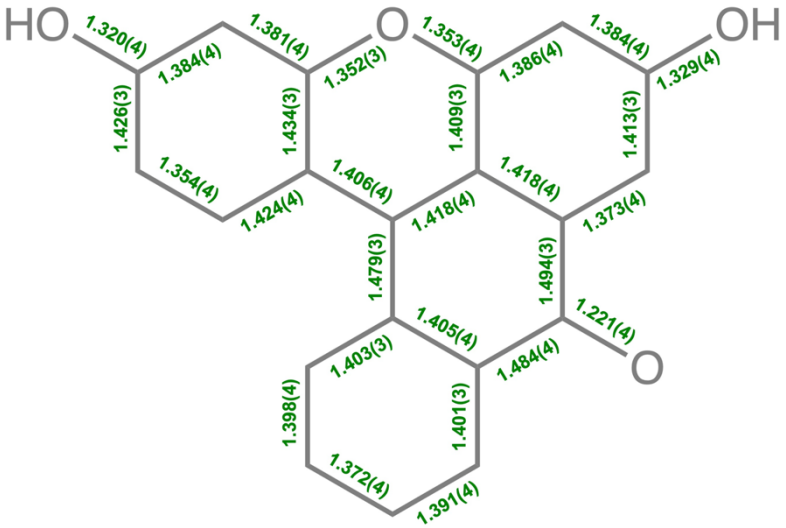

Figure S6. Bond distances (Å) obtained from X-ray crystallographic analysis of **CBH$^+$•HSO$_4^-$**.

Reference

[1] Sheldrick, G. M. *Acta Cryst*. **2015**, *A71*, 3–8.

[2] Sheldrick, G. M. *Acta Cryst*. **2015**, *C71*, 3–8.

[3] Dolomanov O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann. H. *J. Appl. Cryst.* **2009**, *42*, 339–341.

4. Optical properties of CB

Table S5. Optical properties of each molecular species of **CB** in DMSO

	λ_{abs} [nm]	ε	λ_{em} [nm]	Φ_{em} *1 [%]
CB	540	17700	–	–
CB⁻	716	27500	813	3
CBH⁺	533	26600	–	–

*1 The relative emission quantum yield Φ_{em} was measured by excitation at using reference material of Oxazine 170 (Φ_{em} = 58% in ethanol[1]).

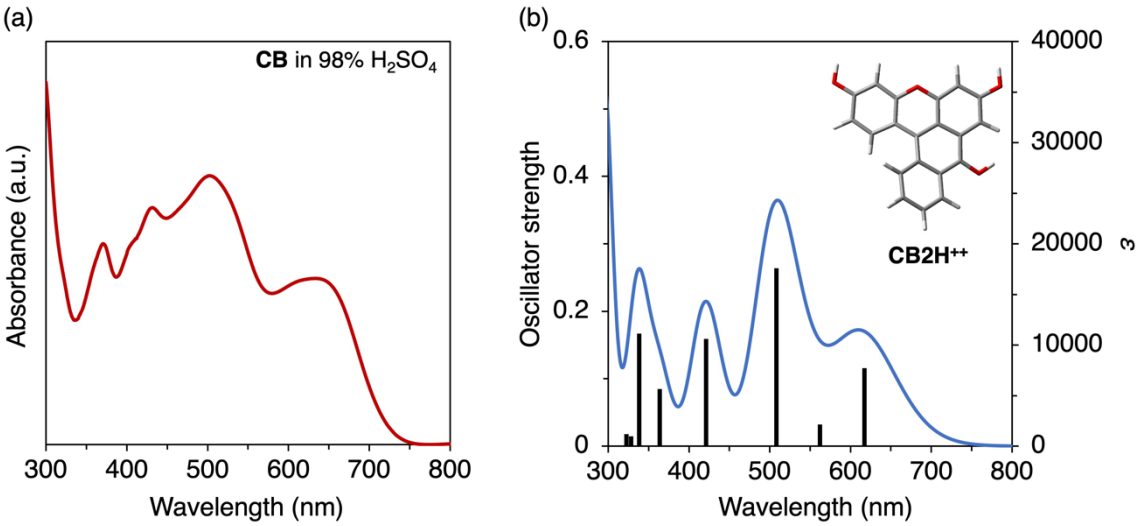

Figure S7. (a) Absorption spectrum of **CB** in concentrated sulfuric acid. (b) Calculated structure and absorption spectrum of **CB2H**$^{++}$. This calculation was performed at the B3LYP/6-31+G** level with PCM (water).

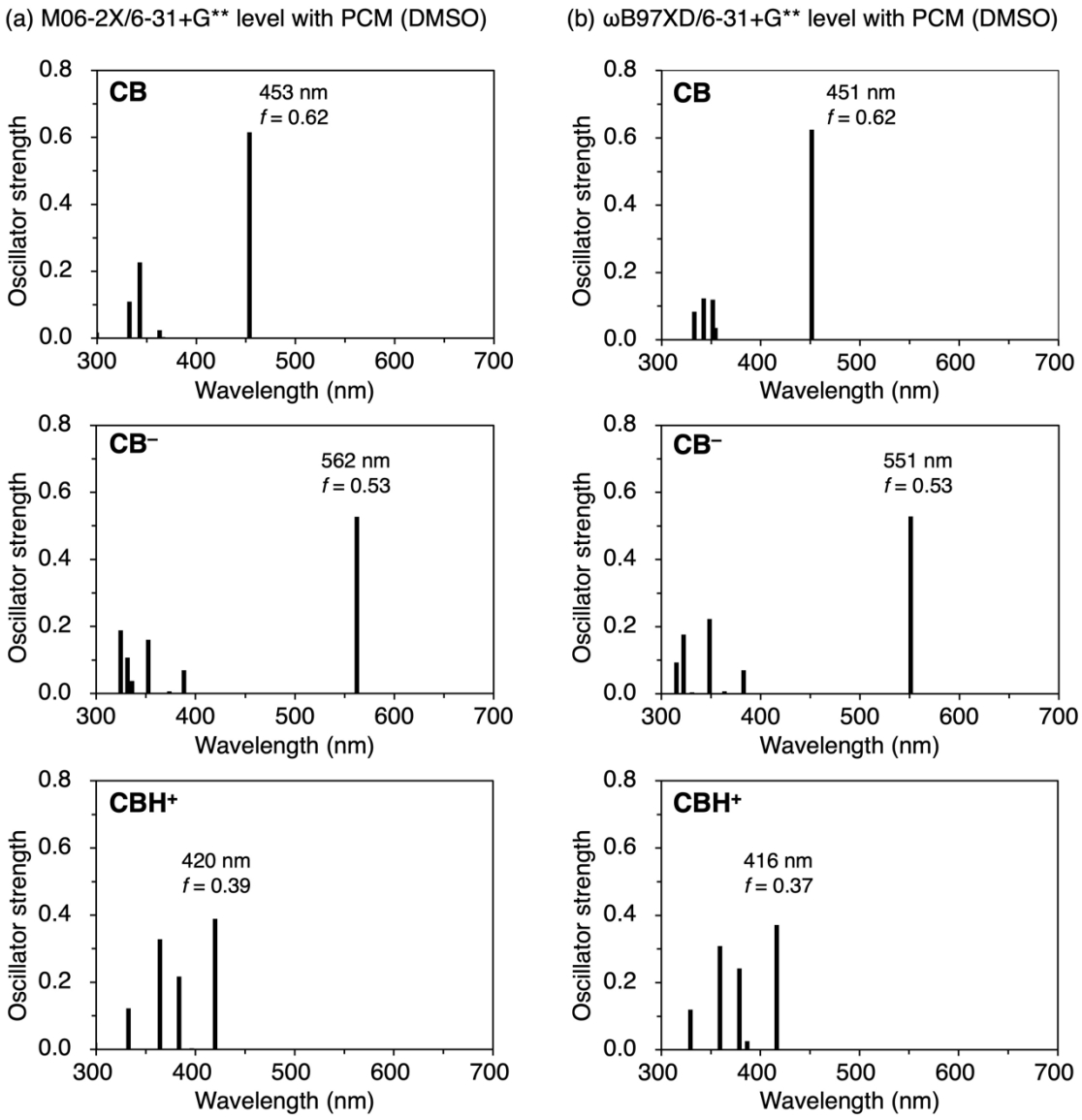

Figure S8. (a) Calculated absorption spectra of **CB**, **CB**$^{-}$, and **CBH**$^{+}$. These calculations were performed at the (a) M06-2X/6-31+G** level with PCM (DMSO) and (b) ωB97XD/6-31+G** level with PCM (DMSO).

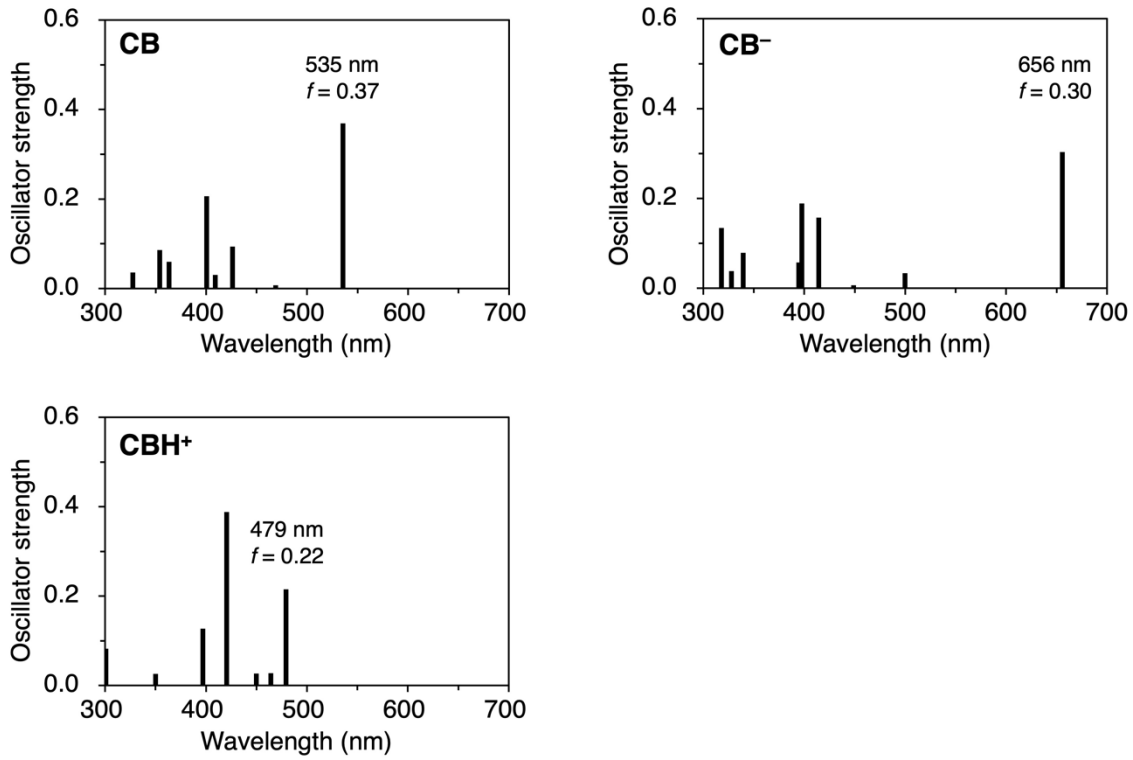

Figure S9. (a) Calculated absorption spectra of **CB**, **CB**$^{-}$, and **CBH**$^{+}$. These calculations were performed at the B3LYP/6-31+G** level with PCM (water).

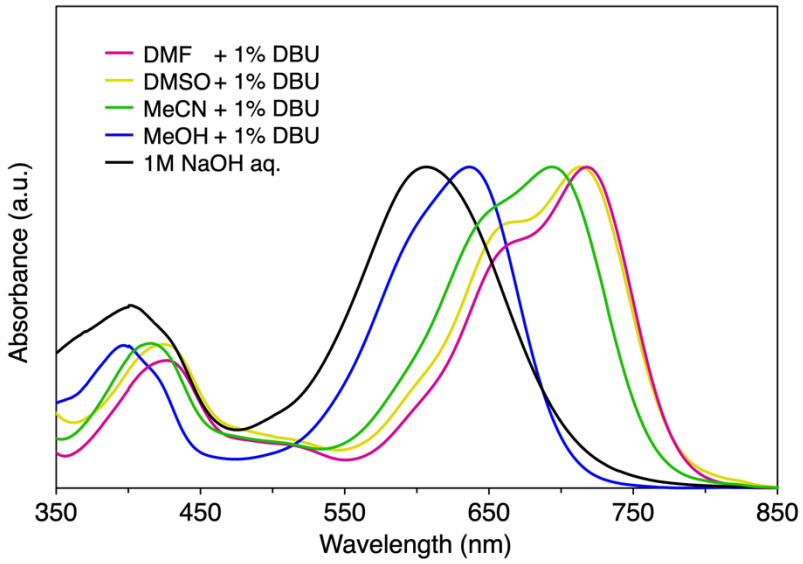

Figure S10. Absorption spectra of **CB** in various organic solvents containing bases.

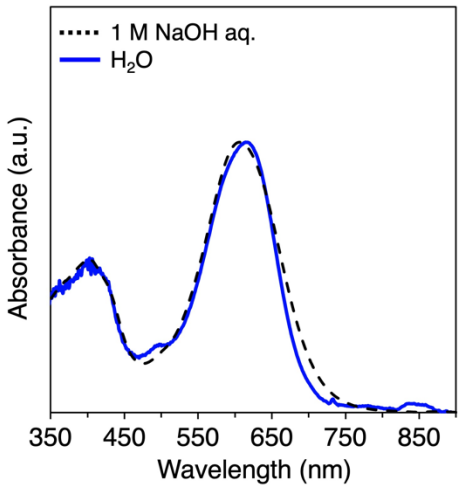

Figure S11. Absorption spectra of **CB** in water (blue solid line) and 1M NaOH aqueous solution (black dashed line).

Reference

[1] Rurack, K.; Spieles, M. *Anal. Chem.* **2011**, *83*, 1232–1242.

5. NMR Spectra of Compounds

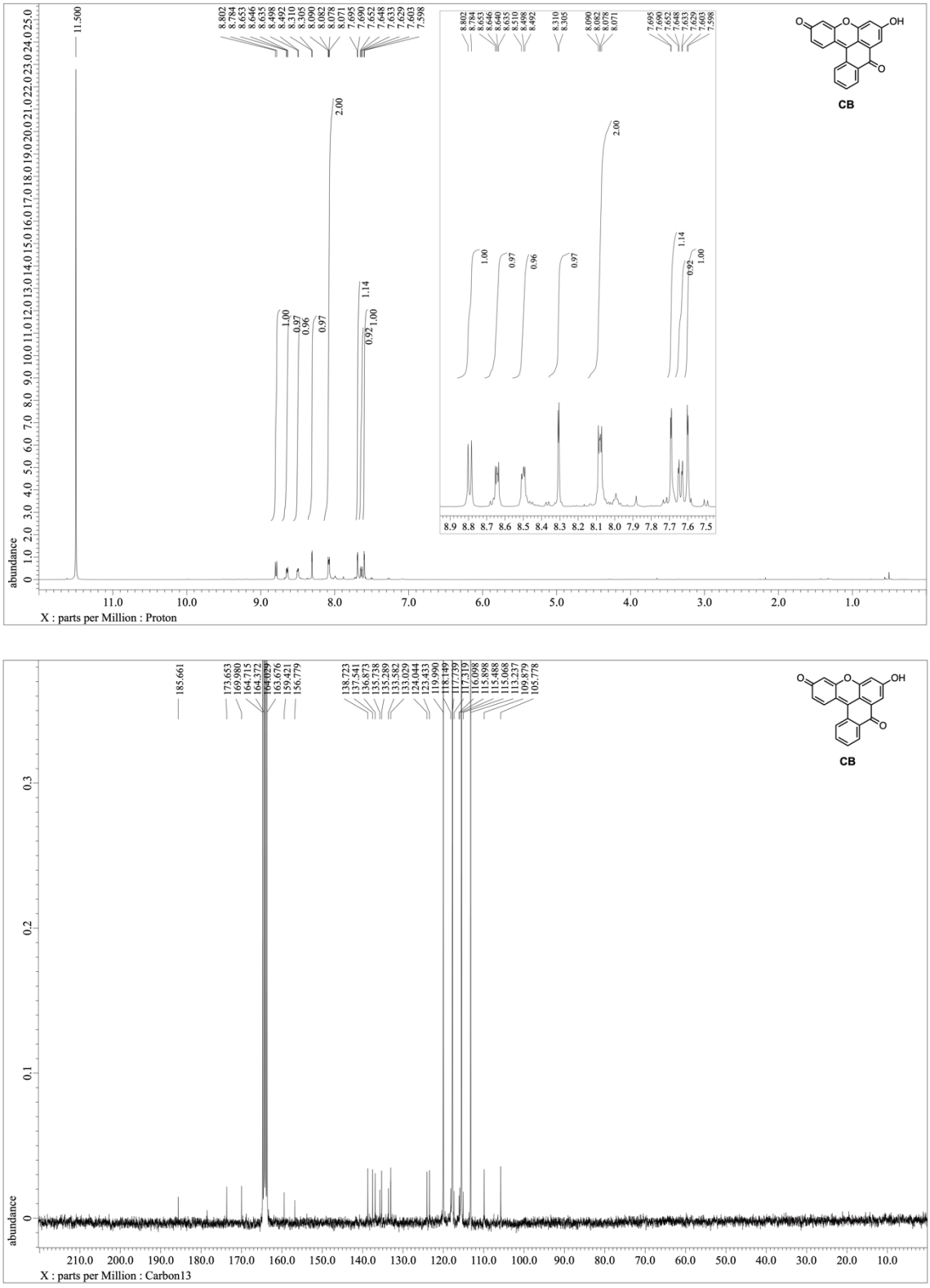

Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **CB** at 25°C in TFA-d.

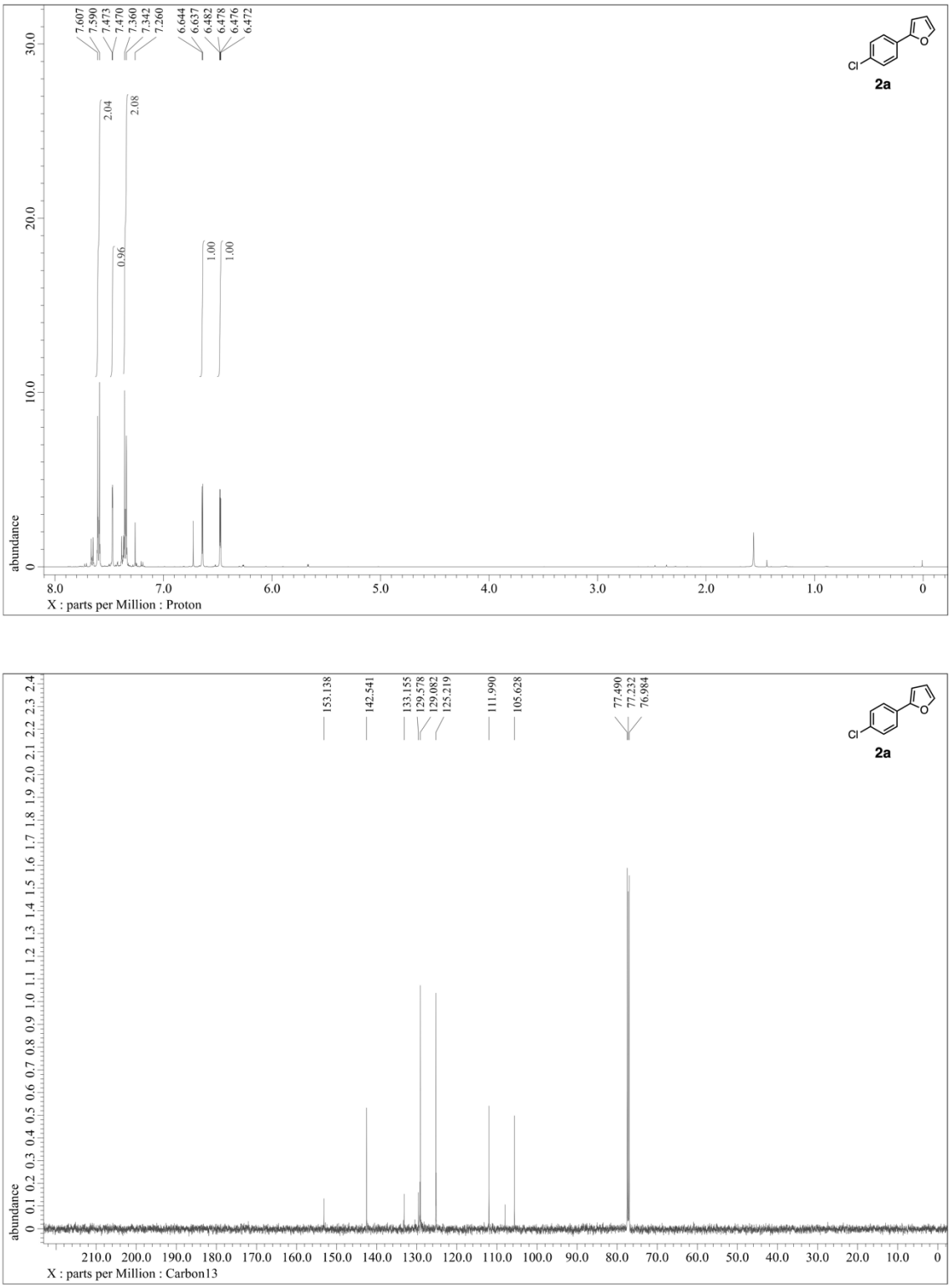

Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** at 25°C in $CDCl_3$.

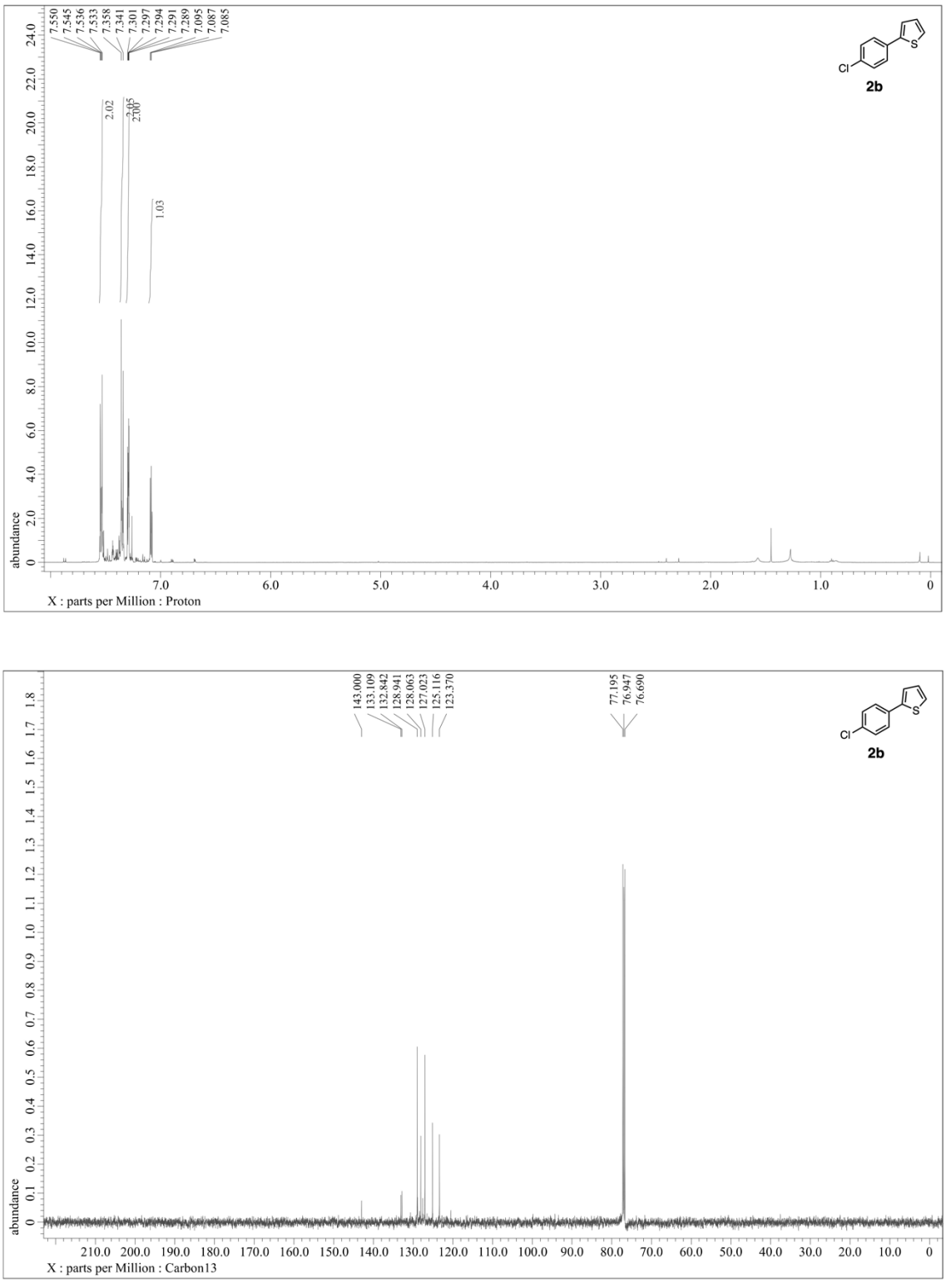

Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b** at 25°C in $CDCl_3$.

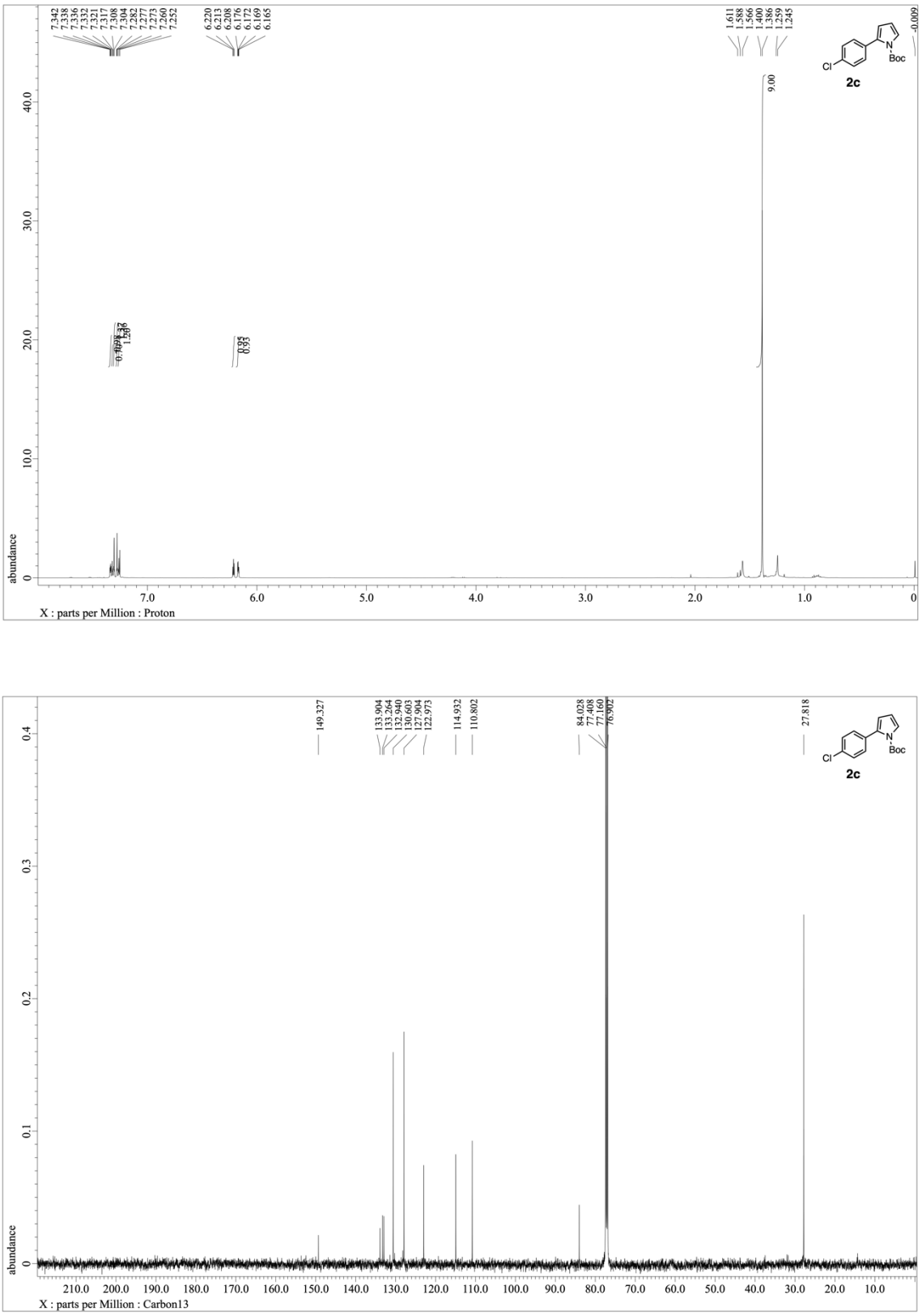

Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2c** at 25°C in $CDCl_3$.

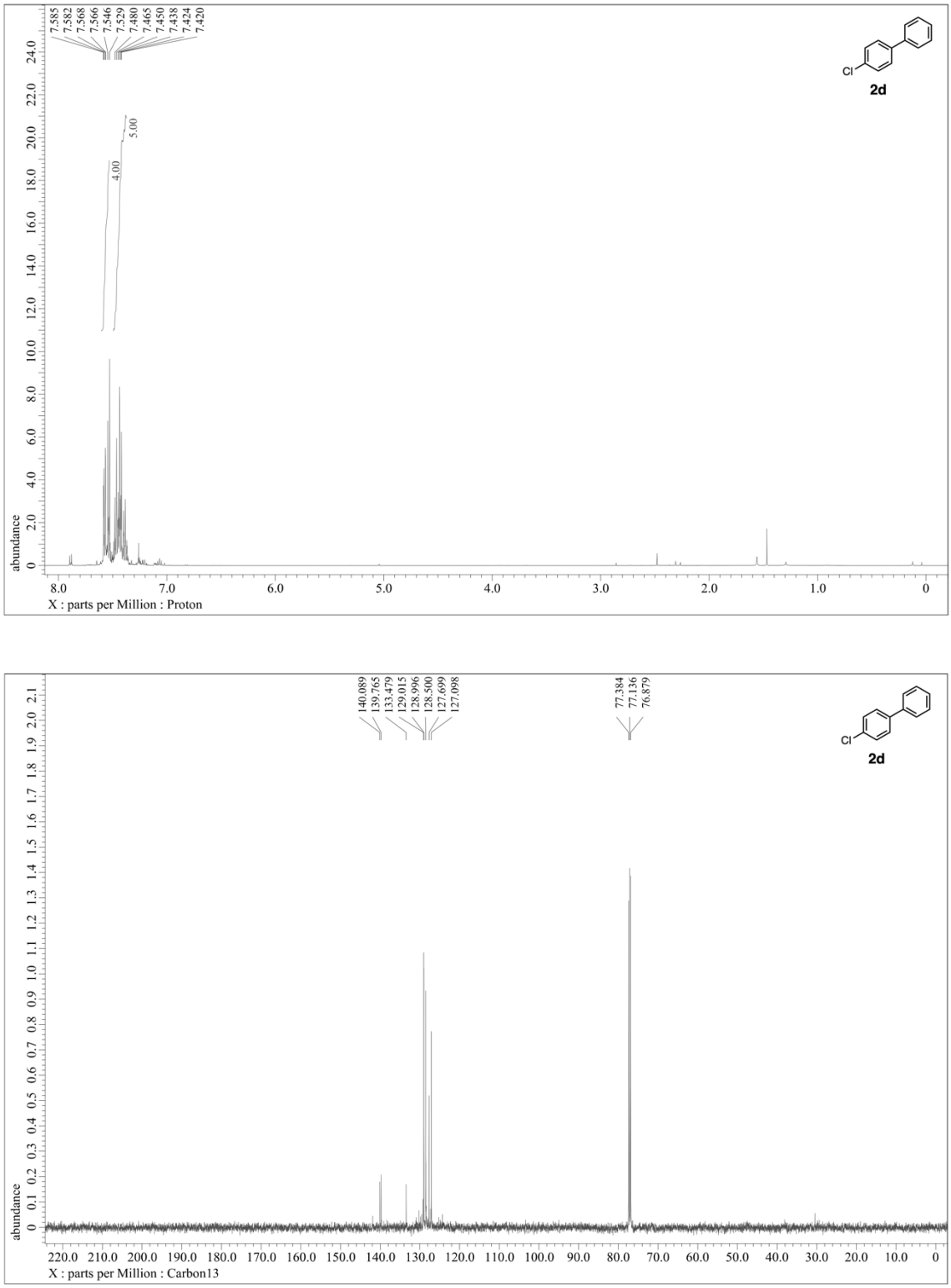

Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2d** at 25°C in $CDCl_3$.

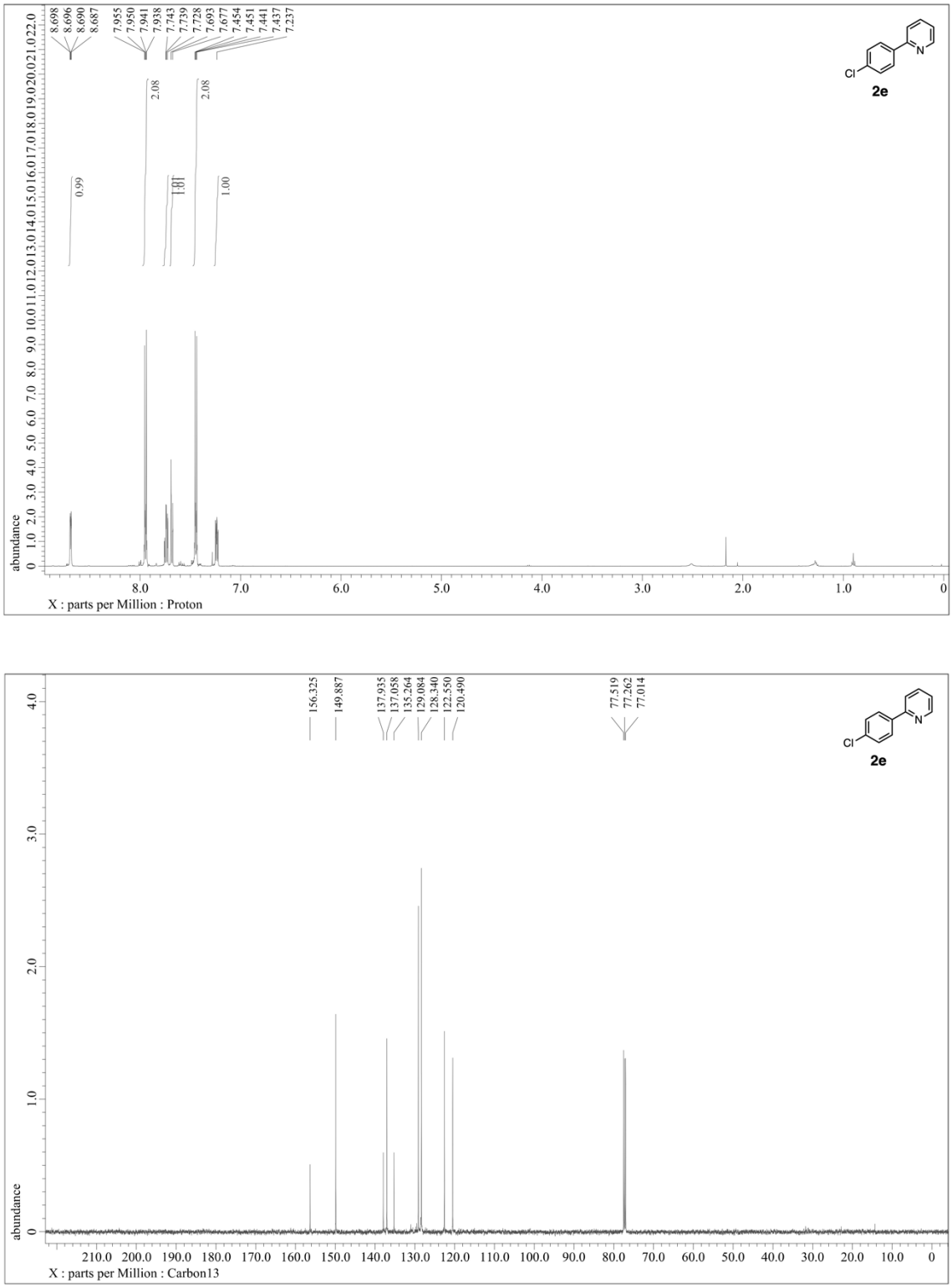

Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2e** at 25°C in $CDCl_3$.

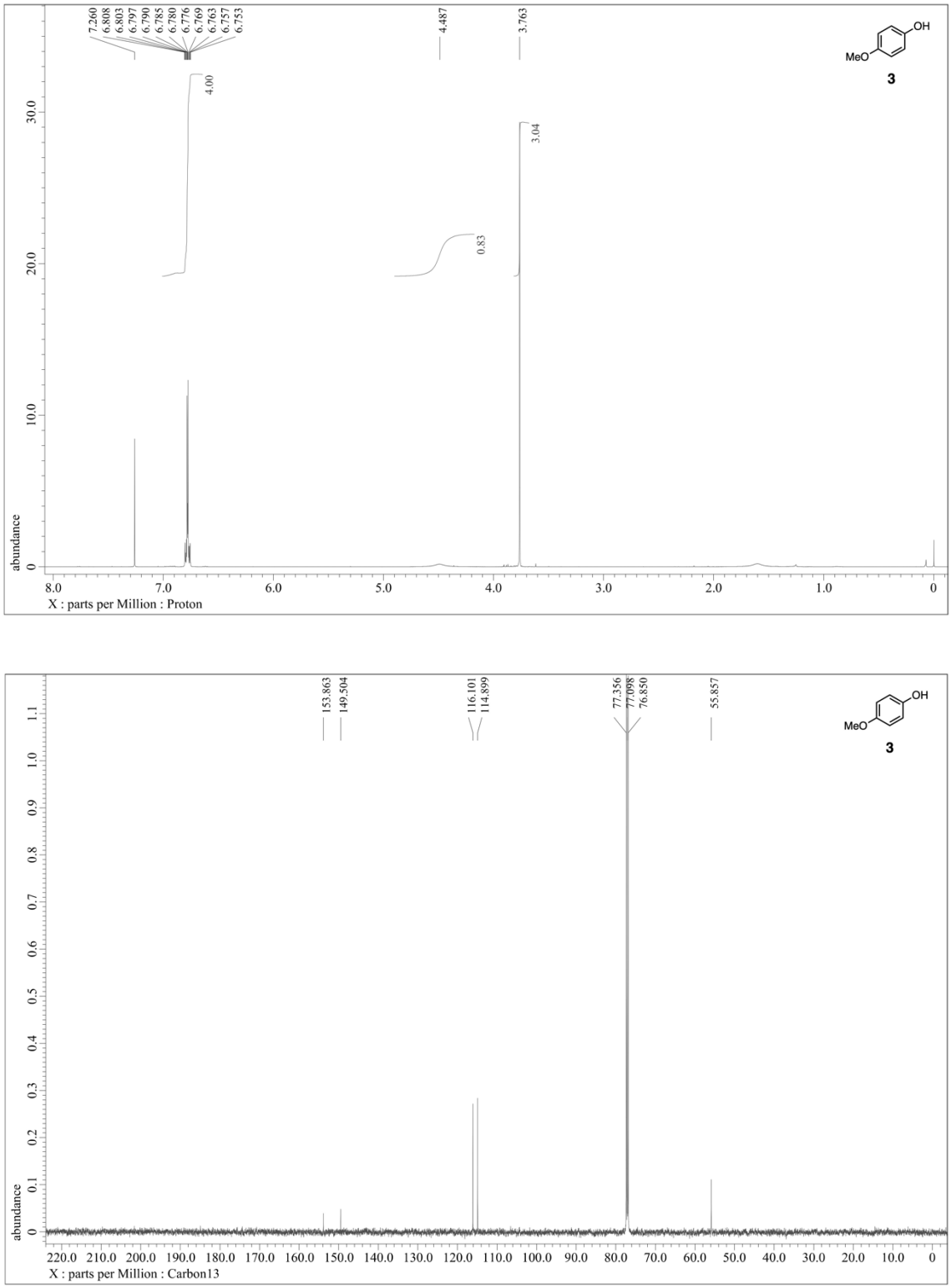

Figure S18. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3** at 25°C in $CDCl_3$.

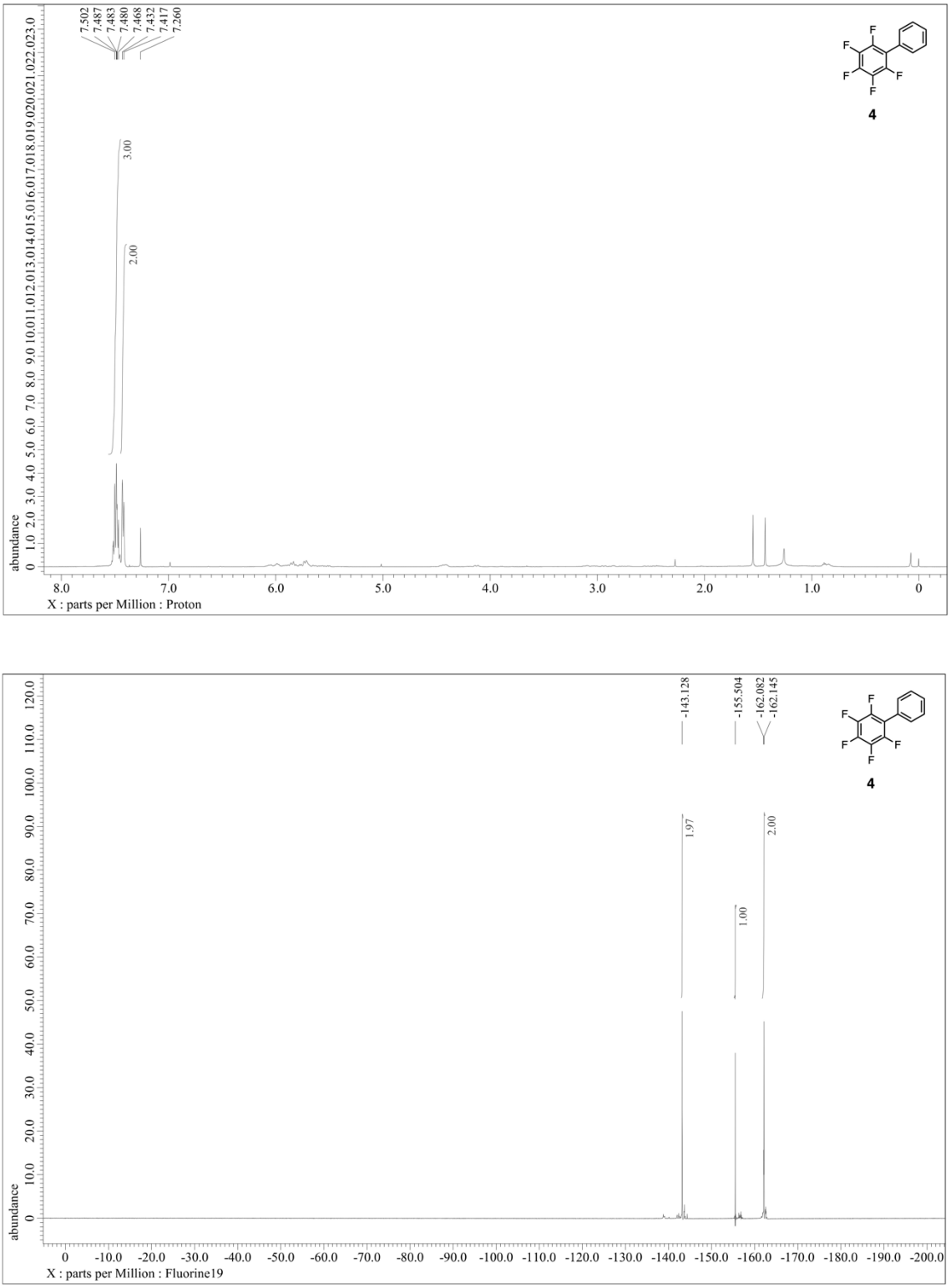

Figure S19. ^{1}H (top) and ^{19}F (bottom) NMR spectra of **4** at 25°C in $CDCl_3$.

6. Cartesian Coordinates (in Å) and Energies

CB (O3-H, Fig. 2b)

B3LYP/6-31+G(d,p)

G = –1068.897148 A. U.

C	-4.443547	-0.245337	0.168598
C	-3.486631	-1.306002	-0.112445
C	-2.148778	-1.061887	-0.113089
C	-1.574850	0.263592	0.085765
C	-2.524646	1.295519	0.455660
C	-3.859535	1.066325	0.504104
C	-0.198571	0.437042	-0.039409
C	0.623747	-0.756103	-0.064144
C	0.020589	-2.014798	-0.228922
C	0.762382	-3.193342	-0.270859
H	0.245887	-4.136435	-0.422401
C	2.147866	-3.128314	-0.096745
C	2.779380	-1.897271	0.125049
C	2.025522	-0.728516	0.133155
H	-3.864063	-2.302793	-0.310641
H	-2.139496	2.258204	0.766015
H	-4.553233	1.839200	0.820316
H	3.848584	-1.850638	0.295497
C	0.499653	1.731630	-0.132409
C	1.888592	1.798962	0.154506
C	-0.132576	2.910678	-0.579014
C	2.563104	3.026805	0.118581
C	0.553864	4.121348	-0.631734
H	-1.154889	2.875895	-0.931589
C	1.898809	4.191434	-0.252290
H	3.620472	3.031504	0.361203
H	0.039268	5.010119	-0.984606
H	2.429529	5.137939	-0.283746
C	2.698056	0.572064	0.393900
O	2.937727	-4.236439	-0.116888
H	2.408779	-5.031112	-0.269810
O	-5.669464	-0.428082	0.167562
O	-1.324897	-2.132100	-0.377233
O	3.877208	0.629765	0.732835

CB (O3-H, Fig. 2b)

CAM-B3LYP/6-31+G(d,p)

G = –1068.362951 A. U.

C	-4.421004	-0.259040	0.172213
C	-3.463170	-1.318393	-0.102879
C	-2.135182	-1.072737	-0.106481
C	-1.564016	0.256119	0.087753
C	-2.519251	1.287545	0.455008
C	-3.843210	1.055879	0.503756
C	-0.205504	0.432737	-0.041066
C	0.624503	-0.756491	-0.073009
C	0.030363	-2.008629	-0.235048
C	0.774904	-3.180325	-0.275374
H	0.262044	-4.124982	-0.424647
C	2.152462	-3.108904	-0.101032
C	2.775476	-1.879087	0.122842
C	2.016933	-0.722561	0.130241
H	-3.839861	-2.315013	-0.298631
H	-2.135878	2.250264	0.764841
H	-4.542275	1.823305	0.818535
H	3.843276	-1.827652	0.297575
C	0.489576	1.730735	-0.133571

C	1.867661	1.802872	0.156975
C	-0.143469	2.898153	-0.584422
C	2.538877	3.024456	0.118578
C	0.537338	4.106674	-0.638343
H	-1.164330	2.858277	-0.938809
C	1.874801	4.181801	-0.257201
H	3.594955	3.031122	0.364273
H	0.021454	4.992434	-0.994427
H	2.402658	5.128865	-0.291017
C	2.678441	0.580003	0.400764
O	2.944493	-4.208747	-0.120313
H	2.424336	-5.006892	-0.273581
O	-5.637404	-0.442115	0.168430
O	-1.310972	-2.130373	-0.376264
O	3.845688	0.641913	0.750354

CB (O3-H, Fig. 2b)

M06-2X/6-31+G(d,p)

G = –1068.467110 A. U.

C	-4.418619	-0.289087	0.167790
C	-3.453180	-1.347083	-0.112960
C	-2.124728	-1.094872	-0.107907
C	-1.564078	0.239554	0.094880
C	-2.521574	1.266010	0.477747
C	-3.846378	1.027962	0.521962
C	-0.206994	0.427070	-0.038407
C	0.634320	-0.754768	-0.074764
C	0.047349	-2.013452	-0.234987
C	0.804146	-3.179635	-0.273533
H	0.300298	-4.129820	-0.421918
C	2.183992	-3.094363	-0.098085
C	2.798784	-1.856939	0.123315
C	2.026671	-0.707308	0.127951
H	-3.825070	-2.344388	-0.317414
H	-2.135618	2.223620	0.805883
H	-4.550494	1.785656	0.851010
H	3.867096	-1.796441	0.298372
C	0.471436	1.733359	-0.131098
C	1.849606	1.822591	0.157250
C	-0.180207	2.890308	-0.587685
C	2.507871	3.052467	0.114625
C	0.486267	4.108826	-0.643813
H	-1.200758	2.830360	-0.945452
C	1.825455	4.201891	-0.262344
H	3.565549	3.072111	0.357323
H	-0.039958	4.987578	-1.003037
H	2.340477	5.156191	-0.299704
C	2.677210	0.605414	0.398708
O	2.984217	-4.185825	-0.115125
H	2.468132	-4.987340	-0.260346
O	-5.630665	-0.475694	0.154927
O	-1.292403	-2.145634	-0.379883
O	3.842130	0.679002	0.743008

CB (O3-H, Fig. 2b)

wB97XD/6-31+G(d,p)

G = –1068.527437A. U.

C	-4.417594	-0.275490	0.174040
C	-3.455588	-1.334243	-0.103094
C	-2.126453	-1.086522	-0.103687
C	-1.561345	0.245726	0.096388
C	-2.516998	1.274534	0.474076
C	-3.841505	1.040062	0.519610
C	-0.205551	0.428999	-0.040164

C	0.630248	-0.756091	-0.075333
C	0.039394	-2.010095	-0.239065
C	0.790837	-3.179498	-0.281845
H	0.283317	-4.126952	-0.433218
C	2.169724	-3.100880	-0.105880
C	2.786992	-1.866699	0.124138
C	2.022111	-0.713236	0.133142
H	-3.831325	-2.330451	-0.304271
H	-2.131558	2.234091	0.796186
H	-4.541069	1.803634	0.843210
H	3.854576	-1.810963	0.301916
C	0.480081	1.731382	-0.138207
C	1.856237	1.814628	0.160739
C	-0.162330	2.888352	-0.603740
C	2.517430	3.042639	0.119268
C	0.508438	4.104021	-0.658866
H	-1.179997	2.833554	-0.969285
C	1.843136	4.192782	-0.266911
H	3.572940	3.063051	0.369136
H	-0.011327	4.983403	-1.025105
H	2.362262	5.144681	-0.302240
C	2.674807	0.595252	0.412844
O	2.967505	-4.193527	-0.127899
H	2.450967	-4.989535	-0.285854
O	-5.632735	-0.460010	0.162866
O	-1.299839	-2.138129	-0.380276
O	3.837416	0.664382	0.773407

CB (O2-H, Fig. 2b)

B3LYP/6-31+G(d,p)

G = –1068.894040A. U.

C	-4.340202	0.056980	0.181076
C	-3.548491	-1.039500	-0.150294
C	-2.164898	-0.889714	-0.176498
C	-1.521634	0.352229	0.052735
C	-2.361618	1.418970	0.447148
C	-3.740154	1.285268	0.510995
C	-0.067230	0.397469	-0.035621
C	0.609924	-0.811961	-0.043294
C	-0.099876	-2.058302	-0.228380
C	0.515642	-3.271321	-0.281698
H	-0.054978	-4.175587	-0.459017
C	1.954629	-3.379076	-0.102615
C	2.674288	-2.112545	0.135608
C	2.043203	-0.905472	0.144051
H	-3.994334	-2.005745	-0.354086
H	-1.923105	2.359708	0.751366
H	-4.352331	2.124511	0.830460
H	3.743330	-2.169027	0.313949
C	0.715798	1.647506	-0.125321
C	2.105397	1.624554	0.160637
C	0.163885	2.863775	-0.573117
C	2.863685	2.799234	0.110838
C	0.935026	4.023736	-0.646058
H	-0.862647	2.901781	-0.912386
C	2.281879	4.004788	-0.274447
H	3.919109	2.732224	0.353285
H	0.480535	4.942868	-1.004022
H	2.877498	4.911306	-0.318365
C	2.817789	0.340180	0.414906
O	2.562617	-4.459429	-0.134315
O	-5.688136	-0.130316	0.201691
O	-1.455899	-2.022446	-0.435360
O	3.991814	0.313878	0.769289

H	-6.138497	0.683670	0.464482

CB (O2-H, Fig. 2b)

CAM-B3LYP/6-31+G(d,p)

G = –1068.360395 A. U.

C	4.322707	-0.069117	0.183334
C	3.539865	1.024303	-0.150706
C	2.160766	0.878241	-0.181607
C	1.518180	-0.352668	0.046275
C	2.346986	-1.417724	0.443243
C	3.720547	-1.290185	0.510907
C	0.062505	-0.389546	-0.038798
C	-0.602115	0.809241	-0.045868
C	0.111701	2.055060	-0.228697
C	-0.496970	3.261255	-0.278266
H	0.073180	4.164905	-0.454982
C	-1.934459	3.370955	-0.100372
C	-2.660803	2.106301	0.134890
C	-2.036112	0.909886	0.140547
H	3.988883	1.988529	-0.353727
H	1.903994	-2.356404	0.745197
H	4.328852	-2.130696	0.831595
H	-3.728748	2.167886	0.314769
C	-0.723107	-1.639645	-0.125030
C	-2.103116	-1.615140	0.162124
C	-0.175101	-2.848898	-0.572848
C	-2.863360	-2.780889	0.112661
C	-0.945821	-4.003027	-0.644622
H	0.850590	-2.888301	-0.912081
C	-2.286481	-3.982390	-0.272773
H	-3.917700	-2.709750	0.356091
H	-0.493946	-4.922337	-1.002951
H	-2.883210	-4.887157	-0.317098
C	-2.810414	-0.331432	0.414648
O	-2.535792	4.443725	-0.130447
O	5.666069	0.110771	0.209320
O	1.457464	2.009722	-0.440648
O	-3.976357	-0.300801	0.769954
H	6.114642	-0.701516	0.473511

CB (O2-H, Fig. 2b)

M06-2X/6-31+G(d,p)

G = –1068.464347 A. U.

C	-4.320950	0.058474	0.187070
C	-3.537441	-1.035766	-0.155142
C	-2.156729	-0.887863	-0.186595
C	-1.517524	0.346243	0.046607
C	-2.344187	1.409867	0.455168
C	-3.719495	1.280095	0.523704
C	-0.062101	0.386251	-0.038902
C	0.607317	-0.811248	-0.046648
C	-0.106176	-2.060053	-0.233164
C	0.507331	-3.265654	-0.283228
H	-0.058751	-4.171397	-0.465554
C	1.950170	-3.370293	-0.099995
C	2.674814	-2.099515	0.139877
C	2.042632	-0.905307	0.142335
H	-3.987708	-1.999671	-0.360225
H	-1.896546	2.345331	0.766392
H	-4.329718	2.116689	0.851723
H	3.743742	-2.157012	0.324074
C	0.714808	1.641846	-0.125434
C	2.094424	1.627397	0.166798
C	0.156754	2.844126	-0.585022

C	2.849561	2.797859	0.114427
C	0.921868	4.004686	-0.659066
H	-0.868583	2.869781	-0.932037
C	2.262896	3.995298	-0.278830
H	3.904696	2.734468	0.361286
H	0.466803	4.919295	-1.026118
H	2.852539	4.904933	-0.323980
C	2.811189	0.344269	0.422106
O	2.553112	-4.437859	-0.130084
O	-5.662276	-0.123238	0.213008
O	-1.451085	-2.015850	-0.451948
O	3.973510	0.320390	0.778736
H	-6.107528	0.685752	0.490346

CB (O2-H, Fig. 2b)

wB97XD/6-31+G(d,p)

G = –1068.525166 A. U.

C	4.320314	-0.072739	0.192686
C	3.539745	1.022425	-0.149461
C	2.159054	0.877359	-0.186972
C	1.516015	-0.353781	0.042143
C	2.339660	-1.419944	0.449028
C	3.714007	-1.293765	0.522366
C	0.060640	-0.389172	-0.044872
C	-0.602007	0.810147	-0.049981
C	0.116001	2.054801	-0.236610
C	-0.492379	3.262804	-0.288047
H	0.077683	4.166012	-0.468968
C	-1.931431	3.375035	-0.105906
C	-2.659516	2.109243	0.138590
C	-2.035994	0.910914	0.143435
H	3.991881	1.985717	-0.350717
H	1.891621	-2.356079	0.755863
H	4.318114	-2.134660	0.850788
H	-3.726638	2.174299	0.325469
C	-0.724622	-1.639222	-0.132555
C	-2.101721	-1.616760	0.170744
C	-0.177491	-2.842841	-0.599138
C	-2.861131	-2.784956	0.122383
C	-0.947447	-3.998982	-0.668279
H	0.844160	-2.875172	-0.955687
C	-2.284561	-3.983278	-0.277847
H	-3.914068	-2.719413	0.375373
H	-0.499474	-4.914374	-1.041478
H	-2.879189	-4.889666	-0.320772
C	-2.808233	-0.331315	0.431935
O	-2.531292	4.447348	-0.137723
O	5.661168	0.107173	0.225100
O	1.458935	2.007319	-0.452888
O	-3.968926	-0.300501	0.802177
H	6.103427	-0.703224	0.494953

CB^{-} (Fig. 4a, 4b)

B3LYP/6-31+G(d,p)

G = –1068.472792 A. U.

C	-4.441669	-0.024528	0.177055
C	-3.552933	-1.121121	-0.105330
C	-2.189855	-0.946482	-0.119709
C	-1.551815	0.330237	0.073082
C	-2.438312	1.403733	0.428673
C	-3.794280	1.244872	0.485042
C	-0.141271	0.406606	-0.027992
C	0.591568	-0.805730	-0.051346
C	-0.079999	-2.049237	-0.217007

C	0.574561	-3.260465	-0.279508
C	2.002423	-3.338219	-0.127476
C	2.679186	-2.073737	0.109732
C	2.009697	-0.870313	0.132383
H	-2.016063	2.357196	0.717948
H	-4.431805	2.071152	0.786430
H	3.750775	-2.092634	0.279896
C	0.629195	1.666259	-0.123144
C	2.019568	1.658622	0.166169
C	0.065603	2.873047	-0.580135
C	2.761936	2.846005	0.115879
C	0.820122	4.044544	-0.649032
H	-0.958600	2.898038	-0.925825
C	2.166093	4.043789	-0.271756
H	3.818649	2.802041	0.356187
H	0.353942	4.956594	-1.008833
H	2.750474	4.957375	-0.315177
C	2.749143	0.385851	0.416558
O	2.642229	-4.433629	-0.176822
O	-5.701363	-0.151071	0.194272
O	-1.439621	-2.066926	-0.366803
O	3.926435	0.382437	0.789262
H	-3.969172	-2.106588	-0.287700
H	0.006586	-4.172049	-0.435023
O	3.877208	0.629765	0.732835

CBH$^+$ (Fig. 4a)

B3LYP/6-31+G(d,p)

G = –1069.348026 A. U.

C	-4.337617	-0.105676	0.161549
C	-3.497394	-1.179591	-0.125362
C	-2.124305	-0.966272	-0.120462
C	-1.536278	0.321014	0.089440
C	-2.441857	1.368819	0.447119
C	-3.796828	1.167268	0.484872
C	-0.122944	0.445521	-0.020642
C	0.632854	-0.760865	-0.033455
C	-0.016949	-2.003485	-0.207554
C	0.672536	-3.212298	-0.278987
H	0.123331	-4.133325	-0.439463
C	2.056247	-3.194264	-0.117416
C	2.740290	-1.974682	0.117019
C	2.046463	-0.784861	0.143626
H	-3.883570	-2.173892	-0.321664
H	-2.051095	2.329788	0.749915
H	-4.472509	1.962191	0.778869
H	3.812377	-1.985325	0.276004
C	0.606384	1.714535	-0.126861
C	1.999627	1.743862	0.160071
C	0.000492	2.902089	-0.581342
C	2.703033	2.949863	0.112506
C	0.720963	4.094621	-0.650467
H	-1.022345	2.896110	-0.931863
C	2.065105	4.129862	-0.273538
H	3.760543	2.942557	0.351722
H	0.229600	4.992759	-1.009561
H	2.621914	5.060108	-0.315520
C	2.763689	0.493439	0.411246
O	2.817253	-4.303107	-0.156518
H	2.286148	-5.098234	-0.319880
O	-5.675745	-0.210250	0.191261
O	-1.360952	-2.062825	-0.343260
O	3.940157	0.503970	0.765987
H	-5.971169	-1.108452	-0.026487

FL^{-} (Fig. 4b)

B3LYP/6-31+G(d,p)

G = –1144.898260 A. U.

C	-3.544837	-2.390512	0.048117
C	-3.526968	-0.950620	0.087226
C	-2.347473	-0.253625	-0.038061
C	-1.077832	-0.892295	-0.216978
C	-1.091394	-2.324157	-0.250608
C	-2.250679	-3.039165	-0.127287
C	0.080176	-0.099833	-0.322372
C	-0.022781	1.303656	-0.281921
C	-1.311261	1.903966	-0.103924
C	-1.503297	3.265150	-0.048654
H	-2.503325	3.664916	0.086259
C	-0.394093	4.176151	-0.170211
C	0.915932	3.563579	-0.355564
H	-4.460710	-0.413244	0.219650
H	-0.147855	-2.845826	-0.377222
H	-2.236891	-4.125188	-0.155581
H	1.768536	4.229574	-0.454775
C	1.409950	-0.745005	-0.572698
C	2.384494	-1.011253	0.418246
C	1.707005	-1.069512	-1.905771
C	3.614544	-1.581543	0.044204
C	2.928030	-1.643041	-2.262501
H	0.966582	-0.860672	-2.671699
C	3.889106	-1.901027	-1.281841
H	4.347971	-1.773124	0.819198
H	3.125353	-1.883784	-3.302602
H	4.842442	-2.346371	-1.547409
O	-2.425392	1.114146	0.018179
C	2.224320	-0.730755	1.876498
C	1.081815	2.206955	-0.408195
H	2.074672	1.792362	-0.552666
O	3.150844	-0.743888	2.674264
O	-4.615662	-3.062438	0.159955
O	-0.538506	5.436225	-0.124153
O	0.961064	-0.476518	2.265215
H	0.975890	-0.301537	3.222939

CB (*P* helicity, Fig. 4c)

B3LYP/6-31+G(d,p)

G = –1068.472792 A. U.

C	4.441603	0.024541	-0.177263
C	3.552923	1.121088	0.105468
C	2.189841	0.946468	0.120004
C	1.551773	-0.330223	-0.072899
C	2.438205	-1.403666	-0.428831
C	3.794161	-1.244816	-0.485362
C	0.141260	-0.406605	0.028375
C	-0.591580	0.805736	0.051604
C	0.080001	2.049245	0.217235
C	-0.574543	3.260494	0.279507
C	-2.002378	3.338264	0.127227
C	-2.679145	2.073775	-0.109911
C	-2.009684	0.870326	-0.132337
H	2.015881	-2.357063	-0.718258
H	4.431650	-2.071063	-0.786920
H	-3.750716	2.092676	-0.280200
C	-0.629190	-1.666252	0.123347
C	-2.019543	-1.658624	-0.166087
C	-0.065572	-2.873088	0.580187
C	-2.761882	-2.846048	-0.115938
C	-0.820049	-4.044616	0.648898

H	0.958619	-2.898095	0.925925
C	-2.166022	-4.043861	0.271577
H	-3.818585	-2.802097	-0.356283
H	-0.353850	-4.956712	1.008559
H	-2.750367	-4.957478	0.314841
C	-2.749137	-0.385852	-0.416428
O	-2.642171	4.433708	0.176342
O	5.701309	0.151057	-0.194556
O	1.439602	2.066866	0.367268
O	-3.926432	-0.382444	-0.789161
H	3.969244	2.106503	0.287936
H	-0.006598	4.172100	0.435003
O	3.877208	0.629765	0.732835

CB (*P* helicity, Fig. 4c)

TD-B3LYP/6-31+G(d,p)

G = –1068.415288 A. U.

C	4.436639	-0.014062	-0.185673
C	3.564381	1.082479	0.159896
C	2.198966	0.920520	0.179063
C	1.551323	-0.333366	-0.069422
C	2.412817	-1.395282	-0.502139
C	3.773585	-1.257723	-0.558697
C	0.125376	-0.425771	0.061664
C	-0.586568	0.812920	0.048414
C	0.111638	2.043490	0.245435
C	-0.525659	3.258455	0.272320
C	-1.958076	3.344514	0.066158
C	-2.663228	2.097884	-0.156384
C	-2.014051	0.880765	-0.160508
H	1.966256	-2.324605	-0.832158
H	4.398028	-2.074991	-0.907428
H	-3.735775	2.132581	-0.313185
C	-0.643286	-1.647743	0.147155
C	-2.055324	-1.617488	-0.123123
C	-0.075838	-2.883737	0.555280
C	-2.788727	-2.827519	-0.098991
C	-0.825810	-4.047061	0.606112
H	0.955686	-2.916448	0.882496
C	-2.190860	-4.026877	0.243995
H	-3.847008	-2.780423	-0.332414
H	-0.363330	-4.970336	0.941302
H	-2.775010	-4.941948	0.269198
C	-2.769954	-0.372017	-0.370695
O	-2.554383	4.459589	0.079705
O	5.695866	0.102397	-0.206102
O	1.460083	2.039780	0.476224
O	-3.988597	-0.339248	-0.686848
H	3.996412	2.052637	0.382166
H	0.036929	4.169093	0.447022

CB (TS, Fig. 4c)

B3LYP/6-31+G(d,p)

G = –1068.465094 A. U.

C	-4.513291	-0.188457	0.000023
C	-3.635839	0.943360	0.000023
C	-2.267000	0.799075	0.000003
C	-1.564843	-0.467303	-0.000003
C	-2.471838	-1.589256	-0.000018
C	-3.833765	-1.472762	-0.000002
C	-0.130192	-0.466133	-0.000013
C	0.518917	0.806766	-0.000011
C	-0.230681	2.021592	-0.000016
C	0.321875	3.285526	-0.000018

C	1.740773	3.477091	-0.000014
C	2.516622	2.251954	0.000001
C	1.941940	1.000173	0.000004
H	-2.104732	-2.596523	-0.000042
H	-4.448768	-2.368435	-0.000013
H	3.598727	2.330674	0.000017
C	0.766552	-1.672556	-0.000016
C	2.184548	-1.506721	0.000010
C	0.323943	-3.013296	-0.000032
C	3.054008	-2.607262	0.000014
C	1.195171	-4.102263	-0.000028
H	-0.717122	-3.263205	-0.000047
C	2.575658	-3.910712	-0.000005
H	4.118785	-2.404434	0.000034
H	0.777358	-5.104204	-0.000042
H	3.258646	-4.754057	-0.000001
C	2.833206	-0.174065	0.000029
O	2.293853	4.619469	-0.000020
O	-5.776093	-0.092681	0.000039
O	-1.588040	1.981197	-0.000022
O	4.064509	-0.060605	0.000065
H	-4.054626	1.944517	0.000027
H	-0.336690	4.148103	-0.000022
O	3.877208	0.629765	0.732835

CB (TS, Fig. 4c)

TD-B3LYP/6-31+G(d,p)

G = –1068.406089 A. U.

C	4.528364	-0.206995	-0.000030
C	3.649586	0.932619	-0.000047
C	2.282634	0.796220	-0.000020
C	1.566554	-0.464656	0.000020
C	2.469195	-1.595044	0.000051
C	3.829083	-1.491223	0.000027
C	0.130988	-0.487658	0.000016
C	-0.516496	0.817446	0.000002
C	0.252401	2.013733	-0.000005
C	-0.300619	3.280495	0.000008
C	-1.734199	3.468559	0.000026
C	-2.528310	2.253013	0.000020
C	-1.956276	1.006986	0.000005
H	2.081358	-2.594747	0.000099
H	4.445110	-2.386384	0.000052
H	-3.609280	2.330200	0.000022
C	-0.764607	-1.662660	0.000022
C	-2.204228	-1.470124	-0.000009
C	-0.340739	-3.017335	0.000046
C	-3.075171	-2.593542	-0.000040
C	-1.208964	-4.098838	0.000018
H	0.700540	-3.274048	0.000087
C	-2.605363	-3.886198	-0.000030
H	-4.137471	-2.373549	-0.000071
H	-0.800445	-5.105420	0.000039
H	-3.294562	-4.726958	-0.000054
C	-2.846529	-0.177838	-0.000010
O	-2.238376	4.619516	0.000043
O	5.778547	-0.129534	-0.000056
O	1.607242	1.982942	-0.000025
O	-4.094141	-0.029215	-0.000026
H	4.078354	1.928904	-0.000079
H	0.346385	4.150569	0.000005

CB (*M* helicity, Fig. 4c)

B3LYP/6-31+G(d,p)

G = –1068.472791 A. U.

C	-4.441603	0.024541	-0.177263
C	-3.552923	1.121088	0.105468
C	-2.189841	0.946468	0.120004
C	-1.551773	-0.330223	-0.072899
C	-2.438205	-1.403666	-0.428831
C	-3.794161	-1.244816	-0.485362
C	-0.141260	-0.406605	0.028375
C	0.591580	0.805736	0.051604
C	-0.080001	2.049245	0.217235
C	0.574543	3.260494	0.279507
C	2.002378	3.338264	0.127227
C	2.679145	2.073775	-0.109911
C	2.009684	0.870326	-0.132337
H	-2.015881	-2.357063	-0.718258
H	-4.431649	-2.071063	-0.786921
H	3.750716	2.092676	-0.280200
C	0.629190	-1.666252	0.123347
C	2.019543	-1.658624	-0.166087
C	0.065572	-2.873088	0.580187
C	2.761882	-2.846048	-0.115938
C	0.820049	-4.044616	0.648898
H	-0.958619	-2.898096	0.925925
C	2.166022	-4.043861	0.271577
H	3.818585	-2.802097	-0.356283
H	0.353850	-4.956712	1.008559
H	2.750367	-4.957478	0.314841
C	2.749137	-0.385852	-0.416427
O	2.642170	4.433709	0.176342
O	-5.701309	0.151056	-0.194556
O	-1.439602	2.066866	0.367269
O	3.926432	-0.382444	-0.789161
H	-3.969244	2.106503	0.287936
H	0.006598	4.172100	0.435003
O	3.877208	0.629765	0.732835

CB (*M* helicity, Fig. 4c)

TD-B3LYP/6-31+G(d,p)

G = –1068.415299 A. U.

C	4.436639	-0.014062	0.185673
C	3.564381	1.082479	-0.159896
C	2.198966	0.920519	-0.179063
C	1.551323	-0.333366	0.069421
C	2.412817	-1.395282	0.502139
C	3.773585	-1.257723	0.558697
C	0.125376	-0.425771	-0.061663
C	-0.586568	0.812920	-0.048414
C	0.111638	2.043490	-0.245435
C	-0.525659	3.258455	-0.272321
C	-1.958076	3.344514	-0.066159
C	-2.663228	2.097885	0.156384
C	-2.014051	0.880765	0.160508
H	1.966256	-2.324605	0.832158
H	4.398028	-2.074991	0.907428
H	-3.735775	2.132581	0.313185
C	-0.643286	-1.647743	-0.147155
C	-2.055324	-1.617488	0.123123
C	-0.075838	-2.883737	-0.555280
C	-2.788727	-2.827519	0.098991
C	-0.825810	-4.047061	-0.606112
H	0.955686	-2.916449	-0.882496
C	-2.190861	-4.026877	-0.243996
H	-3.847009	-2.780422	0.332414
H	-0.363330	-4.970335	-0.941303

H	-2.775011	-4.941948	-0.269198
C	-2.769954	-0.372016	0.370696
O	-2.554383	4.459589	-0.079705
O	5.695866	0.102397	0.206103
O	1.460083	2.039780	-0.476224
O	-3.988597	-0.339247	0.686848
H	3.996412	2.052637	-0.382167
H	0.036929	4.169093	-0.447022