Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Strain-induced carbon-carbon bond cleavage of bowl-shaped sumanenone

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Instrumentations and Chemicals.

All manipulations of moisture or air-sensitive compounds were performed by standard Schlenk techniques in anhydrous solvents under nitrogen atmosphere using flame-dried glasswares. Reactions were conducted in an EYELA PPS-2511 personal organic synthesizer with an aluminum heat brock as heat source. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica-gel aluminum sheets (Merck silica gel 60 F254, Cat. No. 1.05554.0001). Column chromatography was conducted on a YAMAZEN automated flash chromatography system that consists of an AI-580S and a Parallel Frac FR-360 using silica-gel (Kanto Chemical Co., Inc. Silica Gel 60 N (spherical, neutral)). Preparative thin-layer chromatography (PTLC) was prepared using Wako Wakogel B-5F. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-ECZS400 spectrometer. Chloroform-d_1 ($CDCl_3$) and dimethylsulfoxide-d_6 (DMSO-d_6) were used as solvents for NMR measurements. Chemical shifts (δ) for ^{1}H NMR were given in parts per million (ppm) with coupling constants (*J*) in hertz (Hz) after correction by setting those of residual solvent to 7.26 ppm ($CHCl_3$) and 2.50 ppm (DMSO-d_6). Chemical shifts (δ) for ^{13}C{^{1}H} NMR were given in parts per million (ppm) with coupling constants (*J*) in hertz (Hz) after correction by setting those of solvent to 77.0 ppm ($CDCl_3$) and 39.5 ppm (DMSO-d_6). Melting points were determined on an Optimelt MPA100 automated melting point apparatus (Stanford Research Systems, Inc.), and expressed without correction. High resolution mass spectroscopy (HRMS) measurements were conducted on a JEOL JMS-700 double-focusing mass spectrometer using electron impact (EI) or fast atom bombardment (FAB) ionization mode. Infrared (IR) absorption spectroscopy measurements were performed on a JASCO FT/IR-4100 Fourier transform IR spectrometer by transmission method (KBr). The absorption bands were given in wavenumber (cm^{-1}).

Unless otherwise noted, all reagents purchased from commercial suppliers were used without further purification.

Acetic acid (AcOH), dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), methanol (MeOH), chloroform ($CHCl_3$), and *p*-bromophenol were purchased from FUJIFILM Wako Pure Chemical Corporation.

Fluorenone, trifluoromethanesulfonic acid (TfOH), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI·HCl), and 4-dimethylaminopyridine (DMAP) were purchased from Tokyo Chemical Industry Co., Ltd.

Deuterated chloroform ($CDCl_3$) was purchased from Kanto Chemical Co., Inc.

Anhydrous sodium sulfate (Na_2SO_4) was purchased from KISHIDA CHEMICAL Co., Ltd.

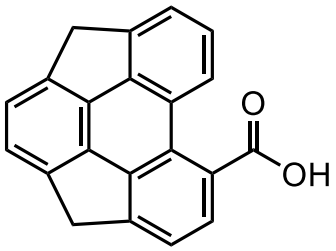
Dimethyl sulfoxide-d_6 (DMSO-d_6) was purchased from Nacalai Tesque, Inc.

Dichloromethane (CH_2Cl_2, dehydrated Super[2]) was purchased from Kanto Chemical Co., Inc., and purified by passing through a Glass Contour Ultimate Solvent System (Nikko Hansen & Co. Ltd.) under nitrogen atmosphere.

Sumanenone (**1**)[S1]and triphenylenone (**5**)[S2] were prepared according to the literatures.

Synthetic Procedure and Characterization Data.

1,8-dihydrodicyclopenta[def,jkl]triphenylene-4-carboxylic acid (2)



To a test tube equipped with a magnetic stir bar were added sumanenone (**1**) (10.0 mg, 36.0 μmol, 100 mol%) and AcOH (1.0 mL). To the mixture was added TfOH (14.0 μL, 110 μmol, 500 mol%) and the mixture was stirred for 6 h at 100 °C under air. After stirring for 6 h, the reaction mixture was cooled to room temperature. Then, the mixture was carefully poured into water (ca. 10 mL), and extracted with $CHCl_3$ (ca. 10 mL × 3). The combined organic extract was washed with brine (ca. 25 mL), dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. To this were added small amount of CH_2Cl_2 and *n*-hexane, then the precipitate formed was collected by filtration. This solid was washed by *n*-hexane to give **2** (9.7 mg, 33 μmol, 91%) as a white solid;

R_f = 0.11 (CH_2Cl_2: MeOH=9:1);

Melting point: 245 °C (dec.);

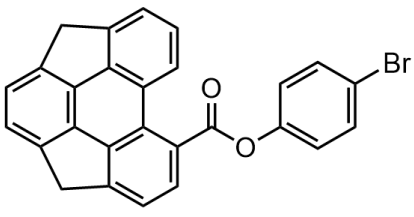
^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.4 (s, br, 1H), 8.58 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 6.9 Hz, 1H), 7.82 (d, J = 6.9 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.71 Hz (d, J = 7.6 Hz, 1H), 7.65 (dd, J = 8.4 Hz, J = 6.9 Hz, 1H), 4.50 (s, 2H), 4.47 (s, 2H);

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 171.0 (1C), 147.6 (1C), 144.6 (1C), 138.33 (1C), 138.29 (1C), 137.24 (1C), 137.17 (1C), 134.4 (1C), 133.6 (1C), 130.0 (1C), 129.1 (1C), 127.5 (1C), 126.2 (1C), 125.0 (1C), 123.98 (1C), 123.95 (1C), 123.6 (1C), 123.15 (1C), 123.10 (1C), two carbon signals are overlapped with the residual solvent signal;

IR (KBr, cm^{-1}) 2906, 1671, 1396, 1284, 1255, 765;

HRMS (EI$^+$) *m*/*z*: [M]$^+$ Calcd for $C_{21}H_{12}O_2$ 296.0837; Found 296.0841.

4-bromophenyl 1,8-dihydrodicyclopenta[def,jkl]triphenylene-4-carboxylate (3)



To a test tube equipped with a magnetic stir bar were added **2** (10.0 mg, 33.7 μmol, 100 mol%), EDCI·HCl (9.7 mg, 51 μmol, 150 mol%), and DMAP (1.2 mg, 10 μmol, 30 mol%). To this was added CH_2Cl_2 (2.0 mL) and the mixture was stirred for 1 min at 27 °C. To this was added *p*-bromophenol (11.7 mg, 67.5 μmol, 100 mol%) and the mixture was stirred at the same temperature. After stirring for 6 h, to the reaction mixture was added water (ca. 10 mL), and extracted with $CHCl_3$ (ca. 10 mL × 3). The combined organic extract was washed with water (ca. 15 mL) followed by brine (ca. 15 mL), and dried over Na_2SO_4. After

filtration, the filtrate was concentrated under reduced pressure. The residue was purified by PTLC (*n*-hexane/CH_2Cl_2 =1:1) to give **3** (12.7 mg, 28.1 μmol, 84%) as a pale yellow solid;

R_f = 0.40 (*n*-hexane/$CHCl_3$ =1:1);

Melting point: 213 °C (dec.);

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68 (d, *J* = 8.2 Hz, 1H), 8.32 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.71 Hz (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.62 (dd, *J* = 8.2 Hz, *J* = 7.3 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 4.51 (s, 2H), 4.46 (s, 2H);

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 167.5 (1C), 150.2 (1C), 149.9 (1C), 144.7 (1C), 139.8 (1C), 139.4 (1C), 137.6 (1C), 137.2 (1C), 135.5 (1C), 134.2 (1C), 132.7 (2C), 130.9 (1C), 127.5 (1C), 126.9 (1C), 126.8 (1C), 126.3 (1C), 125.9 (1C), 124.0 (1C), 123.6 (2C), 123.5 (1C), 122.8 (1C), 122.5 (1C), 119.1 (1C), 40.2 (1C), 40.1 (1C);

IR (KBr, cm^{-1}) 2961, 2923,1732, 1483, 1259, 1085, 1053, 797;

HRMS (FAB^+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{16}{}^{79}BrO_2$ 451.0334 Found 451.0338.

Preparation of single crystals. 3: Single crystals suitable for X-ray diffraction analysis were prepared by vapor diffusion method. In a small test tube, a solution of **3** in $CHCl_3$ (17 mM, 0.3 mL) was added. The test tube was put into the vial containing *n*-pentane, and this was stored at 20 °C. After 2 days, colorless plate-shaped crystals suitable for single crystal X-ray diffraction analysis were obtained.

Single Crystal X-ray Diffraction Analysis.

The diffraction data for **3** was recorded on a XtaLAB Synergy with a Cu-target (λ = 1.54184 Å) equipped with a Rigaku HyPix-6000HE as the detector at 123 K in house. The diffraction images were processed by using CrysAlisPro.[S3] All the structures were solved by dual-space algorithm using SHELXT program[S4]and refined by full-matrix least squares calculations on F^2 (SHELXL-2018/3)[S4] using the Olex2[S5] program package.

In order to obtain a high-quality data set, we tried the diffraction measurements several times. However, all the samples contained another domain, and therefore, we separately brought the data sets to the reduction process by using CrysAlisPro software to obtain both hkl4 and hkl5 style diffraction data. After the refinement process of the main component, the data was merged using HKLF5 and BASF commands.

Through the refinement process, we found two strong residual electron density peaks in all the sets. Even after several trials to assign the strongest residual density, no effective model with a better R factor was not constructed, and therefore, we concluded that the peak might be the crystallographic artifact. The second strongest peak could be 1/3 of oxygen, however we could not propose any possibility to generate a new C−O bond at the corresponding position in the present crystallization setting. After careful consideration above, we made the model without any atom assignment to the two residual peaks. Due to the remaining strong residual electron densities, the data quality is eventually low. Even with such a data quality, the flat structure is rigid in all the trials and could never collapse, no matter what atoms we assigned as the residual densities. The below ORTEP image was illustrated at 50% probability of the thermal ellipsoids.

CCDC 2323143 contains the supplementary crystallographic data. This data can be obtained free of charge via The Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/data_request/cif).

Formula	$C_{27}H_{15}BrO_2$
Crystal Size (mm^3)	0.27×0.10×0.03
Crystal System	Monoclinic
Space Group	$P2_1/c$ (No. 14)
***a* (Å)**	17.7637(6)
***b* (Å)**	15.5820(5)
***c* (Å)**	7.0233(3)
β (°)	95.518(3)
***V* (Å^3)**	1935.0(1)
Z	4
D_{calc} (g cm^{-3})	1.549
μ (mm^{-1})	3.069
Reflections collected/unique	4313/5418
R_1/wR_2 ($I > 2\sigma(I)$)	0.1178/0.3630
GOF on F^2	1.680

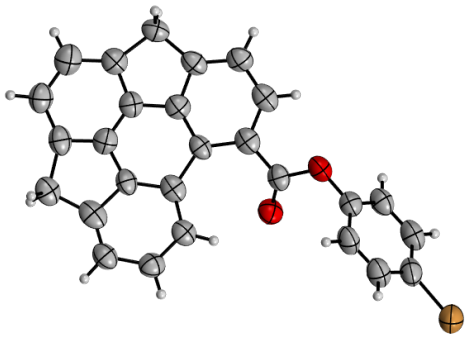
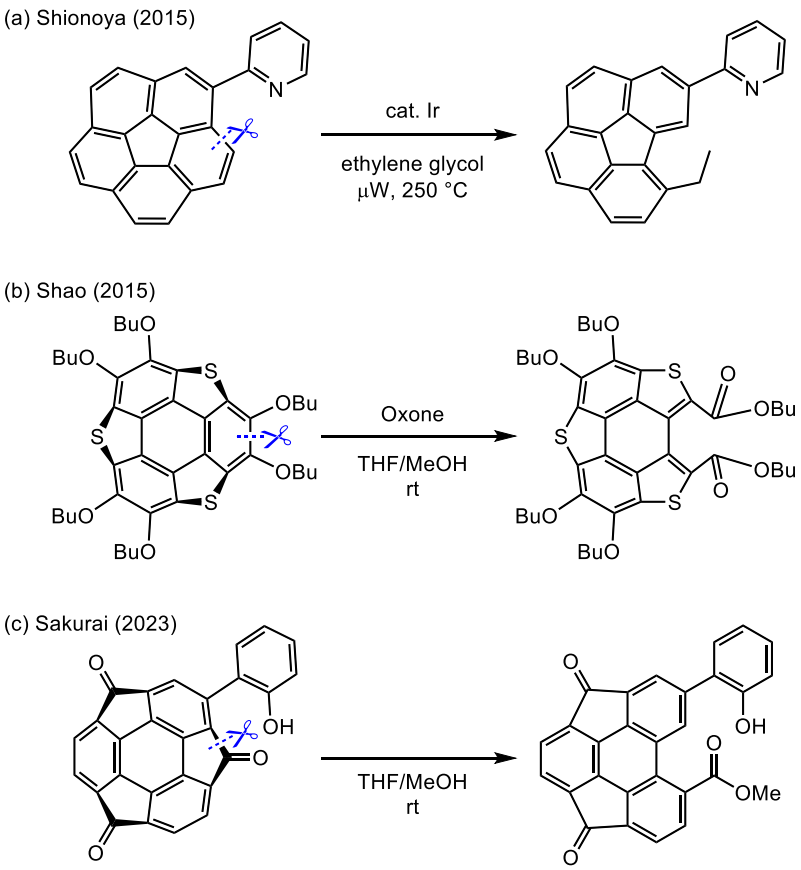


Figure S1. ORTEP image of **3**.



Scheme S1. Examples of reported C-C bond cleavage of buckybowls.

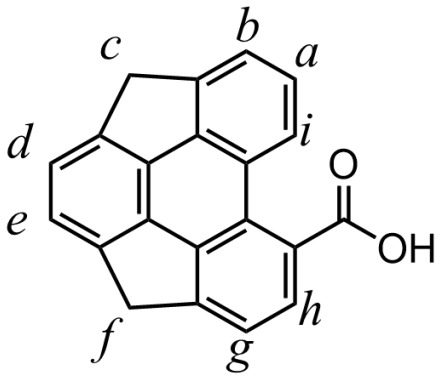
Computational study

Otherwise noted, all structure optimizations, self-consistent field (SCF) energies, and thermal energy correction calculations using density functional theory (DFT) were performed using Gaussian 16 (revision C.01)[S6] program package.

Geometry optimization and transition state (TS) calculations were performed by DFT method at the ωB97X-D level of theory with aug-cc-pVDZ[S7,S8] as a basis set for all atoms in AcOH using the Solvation Model Based on Density (SMD)[S9] solvation model. Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as either minima or first-order saddle points. Intrinsic reaction coordinate (IRC) calculations[S10] were carried out to confirm the transition states connecting the correct reactants and products on the potential energy surface. The zero-point energy (ZPE) and thermal energy corrections were calculated using vibrational frequencies. The self-consistent field energies (298.15 K, 1 atm) were corrected at the ωB97X-D level of theory in AcOH using SMD solvation model with aug-cc-pVTZ as a basis set for all atoms.

ωB97X-D/aug-cc-pVTZ/SMD(THF)//ωB97X-D/aug-cc-pVDZ/SMD(THF)

The simulation of NMR spectra was performed by the GIAO method using the optimized geometries at the B3LYP[S11] level of theory in the gas phase with 6-311+G(2d,p)[S12,S13] as a basis set.



Protons	Experimental (ppm)	Calculation (ppm)
a	7.65	7.93
b	7.82	8.03
c	4.50	4.89, 4.39
d	7.74	8.03
e	7.71	8.00
f	4.47	4.84, 4.44
g	7.85	8.00
h	7.98	8.58
i	8.58	9.09

Table S1. Experimental and calculated ^{1}H NMR chemical shifts of **2**. The chemical shifts were corrected using the value of tetramethylsilane (0 ppm) calculated at the B3LYP/6-311G+(2d,p) level of theory.

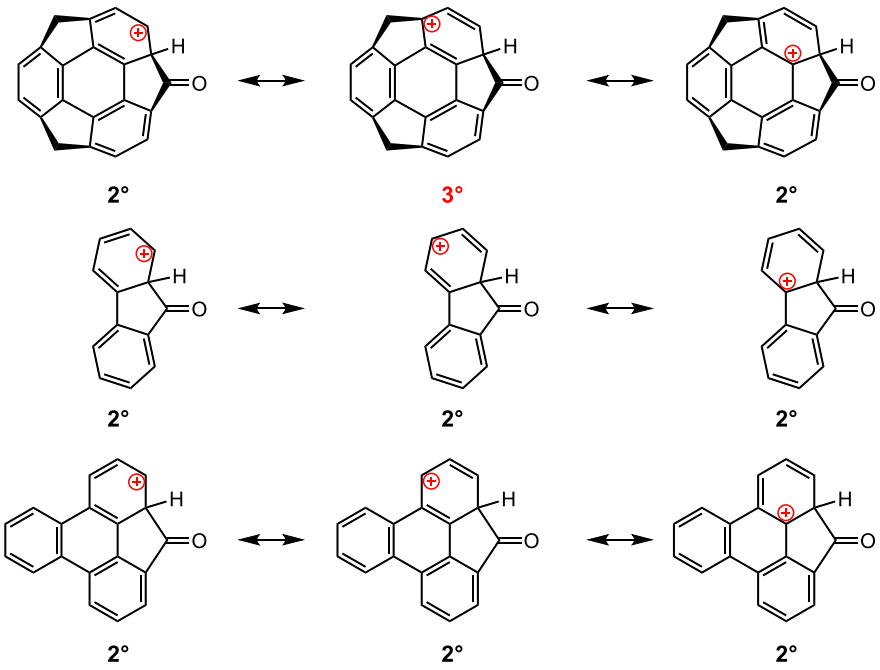


Figure S2. Resonance structures of carbocation intermediates **1**, **4**, and **5**.

Table S2. Calculated SCF energy (ωB97X-D/aug-cc-PVTZ/SMD(AcOH)), thermodynamic parameters (ωB97X-D/aug-cc-PVDZ/SMD(AcOH)), corrected enthalpy (*H*), and corrected Gibbs free energy (*G*) of TfOH and TfO^-.

	E (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs free energy (Hartree)	*H* (kcal mol^{-1})	*G* (kcal mol^{-1})
TfOH	-962.1283091	0.046911	0.003450	-603715.6981	-603742.9704
TfO^-	-961.7025263	0.034874	-0.005749	-603456.0685	-603481.5599

Table S3. Calculated SCF energy (ωB97X-D/aug-cc-PVTZ/SMD(AcOH)), thermodynamic parameters (ωB97X-D/aug-cc-PVDZ/SMD(AcOH)), corrected enthalpy (*H*), and corrected Gibbs free energy (*G*) of **1**.

	E (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs free energy (Hartree)	*H* (kcal mol^{-1})	*G* (kcal mol^{-1})
1-A	-1110.561078	0.32644	0.257474	-696683.3375	-696726.6143
1-B	-1110.552804	0.326803	0.262302	-696677.918	-696718.3931
1-C	-1110.955162	0.338898	0.274656	-696922.812	-696963.1245
1-D	-1111.007338	0.339411	0.272192	-696955.2311	-696997.4117
1-TS1	-1110.525807	0.321054	0.256716	-696664.5845	-696704.9572
1-TS2	-1110.937364	0.336629	0.272492	-696913.067	-696953.3136

Table S4. Calculated SCF energy (ωB97X-D/aug-cc-PVTZ/SMD(AcOH)), thermodynamic parameters (ωB97X-D/aug-cc-PVDZ/SMD(AcOH)), corrected enthalpy (*H*), and corrected Gibbs free energy (*G*) of **4**.

	E (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs free energy (Hartree)	*H* (kcal mol^{-1})	*G* (kcal mol^{-1})
4-A	-804.5560906	0.250515	0.187896	-504709.7917	-504749.0858
4-B	-804.5446718	0.250567	0.192735	-504702.5937	-504738.8839
4-C	-804.9260698	0.262382	0.204996	-504934.5107	-504970.5210
4-D	-804.9493244	0.262819	0.203704	-504948.8290	-504985.9242
4-TS1	-804.5192495	0.244823	0.186981	-504690.2454	-504726.5418
4-TS2	-804.9149926	0.260651	0.203509	-504928.6459	-504964.5031

Table S5. Calculated SCF energy (ωB97X-D/aug-cc-PVTZ/SMD(AcOH)), thermodynamic parameters (ωB97X-D/aug-cc-PVDZ/SMD(AcOH)), corrected enthalpy (*H*), and corrected Gibbs free energy (*G*) of **5**.

	E (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs free energy (Hartree)	*H* (kcal mol^{-1})	*G* (kcal mol^{-1})
5-A	-1034.415267	0.314386	0.245029	-648908.6438	-648952.166
5-B	-1034.405963	0.314552	0.249801	-648902.7014	-648943.3333
5-C	-1034.787928	0.325933	0.261105	-649135.2463	-649175.9266
5-D	-1034.808961	0.326250	0.260490	-649148.2458	-649189.5109
5-TS1	-1034.378831	0.308692	0.243605	-648889.3531	-648930.1958
5-TS2	-1034.772975	0.324515	0.260381	-649126.7530	-649166.9977

Optimized Cartesian coordinates of **2**.

C	-0.44126900	1.20933600	0.05448800
C	0.96176700	1.26587500	0.14570400
C	1.80230300	2.37457100	-0.03040600
C	3.27456700	1.89352500	-0.01205800
C	3.14389800	0.36218800	0.10671100
C	3.92869300	-0.79217600	-0.01116200
C	3.33935000	-2.09988500	-0.02422800
H	3.79727400	2.19114900	-0.93117100
H	3.82993600	2.32945800	0.83059200
H	5.01007600	-0.72935600	-0.13979200
H	4.00935700	-2.95035100	-0.15671800
C	-0.17246400	-1.24429900	0.12928600
C	-1.06492200	-0.15651400	0.09151300
C	-0.22790000	3.60722100	-0.33386400
C	1.18359100	3.59069200	-0.26375400
H	-0.72338500	4.55776600	-0.53389600
H	1.74268100	4.51324200	-0.42210500
C	1.78811200	0.12542400	0.24748200
C	1.23117300	-1.10624900	0.22334900
C	1.95322200	-2.27652200	0.07390000
C	0.89502400	-3.38868100	-0.05482700
C	-0.44167800	-2.61008800	-0.04143700
C	-1.76719300	-2.96410200	-0.22377300
C	-2.72546000	-1.93244600	-0.20334900
H	1.00511200	-3.95965600	-0.98689600
H	0.94420100	-4.11053500	0.77270000
H	-2.08773800	-3.99317400	-0.38439700
H	-3.77668600	-2.19062900	-0.32628600
C	-1.02611800	2.46967500	-0.19728000
H	-2.10055700	2.58057300	-0.30702500
C	-2.41827600	-0.57446300	-0.03289400
C	-3.61088800	0.31839600	0.05505900
O	-4.61102900	0.20991700	-0.61625900
O	-3.50717500	1.23983200	1.03629000
H	-4.33784800	1.73464500	1.03397900

Optimized Cartesian coordinates of **3**.

C	-6.38135500	0.15869400	-0.70253200
C	-2.81543200	-3.52390300	0.09297400
C	-6.11906100	1.56271300	-0.56905900
C	-4.82060700	2.04940800	-0.36783000
C	-3.83680200	1.07691700	-0.35415200
C	-3.64436900	-2.45917900	-0.21921200

C	-1.54468300	3.49099600	0.89703800
C	-1.46775700	-3.23955600	0.39539000
C	-0.93035000	-1.94626200	0.42437700
C	-5.34989000	-0.78666800	-0.62888300
C	-4.08689100	-0.24784800	-0.46467300
C	-2.65940900	2.88805800	0.33838500
C	-2.56521500	1.51342900	0.08021300
C	-3.06566500	-1.18302700	-0.18498000
C	-0.43131300	2.67221700	1.19547300
C	-1.75871200	-0.82095300	0.18161200
C	-0.39994300	1.29418700	0.97094600
C	-1.50294100	0.64177600	0.37944200
C	0.53716900	-1.85305900	0.67539700
O	1.11670200	-1.06115900	-0.26869800
O	1.13846600	-2.42593100	1.54692400
C	-4.09893400	3.35864200	0.01066400
C	-5.15172600	-2.31341900	-0.54131800
C	2.46327200	-0.73051700	-0.21271700
C	2.76478900	0.59123700	-0.52813800
C	4.09264700	1.00719700	-0.56752500
C	5.09959300	0.08651400	-0.29182200
C	4.79892400	-1.23801200	0.01262200
C	3.46991500	-1.65562800	0.05055400
Br	6.91621400	0.64578900	-0.33952600
H	-7.42175100	-0.14751500	-0.81845500
H	-3.16389500	-4.55618400	0.11554900
H	-6.97764900	2.23520800	-0.58544200
H	-1.51424100	4.55223200	1.14487800
H	-0.79580000	-4.06716000	0.62139000
H	0.43969100	3.13379700	1.66162100
H	0.47889900	0.74409100	1.29867900
H	-4.10674100	4.08958800	-0.81042900
H	-4.56056900	3.84562500	0.88019500
H	-5.41026400	-2.82220200	-1.48072200
H	-5.76584300	-2.76577400	0.24923300
H	1.95531500	1.28547800	-0.74826100
H	4.33789500	2.03825200	-0.81403700
H	5.59653500	-1.94879500	0.21954400
H	3.22805100	-2.68624400	0.29036100

Optimized Cartesian coordinates of **TfOH**.

S	-0.27122800	-0.82517100	0.00000000
O	0.07019000	-1.46631500	1.27142100
O	0.07019000	-1.46631500	-1.27142100

O	-1.79900500	-0.31783900	0.00000000
H	-2.42235200	-1.06705900	0.00000000
C	0.45912100	0.90314300	0.00000000
F	0.07019000	1.55312500	-1.08659200
F	0.07019000	1.55312500	1.08659200
F	1.77920400	0.76649200	0.00000000

Optimized Cartesian coordinates of **TfO$^-$**.

S	-0.40989700	-0.81321300	0.00000000
O	0.08621800	-1.44063800	1.25578900
O	0.08621800	-1.44063800	-1.25578900
O	-1.85678100	-0.46145000	0.00000000
C	0.43211100	0.85772200	0.00000000
F	0.08621800	1.56397100	-1.08575400
F	0.08621800	1.56397100	1.08575400
F	1.76539000	0.71726600	0.00000000

Optimized Cartesian coordinates of **1-A**.

C	-4.58540800	-0.85320700	0.45545400
C	-1.82341400	3.28928200	0.36696100
C	-3.95356800	-2.13168400	0.49423100
C	-2.67342500	-2.32161200	-0.03273700
C	-2.11538700	-1.23599100	-0.71083900
C	-1.53072300	-3.31465400	0.27158400
C	-2.60332900	2.25040300	-0.14579800
C	1.01376000	-2.45142200	0.54779800
C	-4.04689900	1.77624900	0.11554100
C	-0.40008500	3.19769200	0.37750800
C	0.24230300	2.07615400	-0.15013600
C	-3.94569800	0.25211700	-0.11172200
C	-2.72875900	0.00362200	-0.74956500
C	-0.27118700	-2.46798000	0.00129000
C	-0.68175200	-1.32265800	-0.69627500
C	-1.92704600	1.19482600	-0.77540800
C	1.80578500	-1.26594800	0.51883900
C	1.54465900	1.37635400	0.20966600
C	-0.55372000	1.11062400	-0.76851500
C	1.32111100	-0.10212900	-0.08147500
C	0.08639400	-0.18130400	-0.72782600
O	2.51553500	1.88621900	0.74662100
O	4.52664100	0.16057000	-1.25331100
O	4.78218100	0.41039000	0.95737200
C	5.13528900	-0.09166700	-0.22732900
C	6.32716900	-0.99335100	-0.14221900

H	-5.52062500	-0.73416100	1.00482400
H	-2.28418000	4.12066400	0.90145600
H	-4.44091600	-2.91941200	1.07096100
H	-1.56268500	-3.66607700	1.31000800
H	-1.56814500	-4.20297900	-0.37675900
H	1.38042700	-3.29396100	1.13501900
H	-4.76112800	2.25294000	-0.57248800
H	-4.36776800	2.01465200	1.13689000
H	0.16369900	3.95575900	0.92259800
H	2.73385600	-1.25402600	1.09082900
H	3.96868500	0.96519300	0.85624100
H	7.14784400	-0.48045100	0.37512600
H	6.06112500	-1.87950900	0.45067400
H	6.63853900	-1.29835800	-1.14500400

Optimized Cartesian coordinates of **1-B**.

C	-4.49332900	0.22446400	0.19246500
C	-0.58577300	3.29527500	0.53643100
C	-4.29189000	-1.18789200	0.20756800
C	-3.08909800	-1.75126400	-0.22750000
C	-2.16403400	-0.87359200	-0.79658000
C	-2.34049800	-3.06075900	0.10321300
C	-1.60343800	2.57438500	-0.09115300
C	0.31689900	-3.03950000	0.60213700
C	-3.14157100	2.56515200	0.04078900
C	0.73513200	2.76335700	0.64161400
C	1.03945900	1.51719400	0.10168900
C	-3.49481500	1.09190300	-0.25906400
C	-2.36042100	0.49507300	-0.81284500
C	-0.86077800	-2.64377800	-0.03357900
C	-0.83423400	-1.40616400	-0.68562300
C	-1.23292000	1.37962900	-0.71876400
C	1.43897600	-2.16113800	0.68744100
C	2.11885600	0.46274400	0.44512400
C	0.04445100	0.86749700	-0.62222400
C	1.39249900	-0.88701200	0.12484400
C	0.25136500	-0.55754300	-0.60518800
O	2.52730200	0.61649100	1.75970300
O	3.22690800	0.69277600	-0.47107100
O	4.38143200	-0.98933100	0.47059400
C	4.28679300	-0.12686600	-0.38363200
C	5.29786600	0.15294200	-1.44664500
H	-5.39308700	0.61224700	0.67305300
H	-0.80784800	4.21258300	1.08360700

H	-5.04916200	-1.80152700	0.69841700
H	-2.56620900	-3.40878000	1.11871100
H	-2.60285500	-3.87556000	-0.58810400
H	0.36095900	-3.97239100	1.16597000
H	-3.61798100	3.25894000	-0.66801100
H	-3.45885100	2.85897700	1.04890900
H	1.45563600	3.29375800	1.26469900
H	2.28136400	-2.46925700	1.30633700
H	3.13451100	-0.10781300	1.96896700
H	5.54083300	1.22266400	-1.45835500
H	6.19637900	-0.44381200	-1.26837600
H	4.86419400	-0.10416800	-2.42274500

Optimized Cartesian coordinates of **1-C**.

C	-4.31273200	1.09371400	0.37550000
C	0.29128000	3.05011700	0.47272300
C	-4.50019900	-0.31857300	0.34870700
C	-3.52313800	-1.16160100	-0.18064600
C	-2.44230700	-0.54014500	-0.81757700
C	-3.11600400	-2.61668000	0.11411500
C	-0.94106300	2.56875400	-0.08253000
C	-0.52718600	-3.23194300	0.53109600
C	-2.37926000	2.95138000	0.21739600
C	1.42576700	2.29126900	0.40244400
C	1.50098900	0.99079600	-0.34382100
C	-3.15469500	1.67622400	-0.14084800
C	-2.26990700	0.83276600	-0.81122600
C	-1.58944000	-2.56822000	-0.07829000
C	-1.28833000	-1.37499700	-0.74298700
C	-0.94158300	1.38715400	-0.82338000
C	0.77890100	-2.65379300	0.59142500
C	2.08383200	-0.35534700	0.31799300
C	0.17305900	0.56641100	-0.81762900
C	1.02221200	-1.42115800	0.00989200
C	-0.00857600	-0.82506100	-0.72662000
O	2.23336800	-0.27573700	1.69133300
O	3.30090100	-0.76881700	-0.32424800
O	4.33467300	1.07004800	0.43598700
C	4.38261900	0.02761800	-0.18807600
C	5.58235300	-0.53348600	-0.87098600
H	-5.02883500	1.69004200	0.94191400
H	0.30589400	3.98895700	1.02448800
H	-5.35229300	-0.72686600	0.89318700
H	-3.38489800	-2.91341100	1.13449900

H	-3.59150000	-3.33012100	-0.57473000
H	-0.70370600	-4.13838800	1.11141400
H	-2.66100800	3.82763200	-0.39043600
H	-2.50005400	3.24169800	1.26873600
H	1.52848500	-3.13394200	1.21932700
H	2.86048900	0.43396300	1.89400800
H	6.40424900	0.18529000	-0.82034200
H	5.86909800	-1.46757200	-0.36898800
H	5.34025300	-0.77376800	-1.91374400
H	2.13321000	1.23036100	-1.22159600
H	2.34952700	2.67097900	0.83762200

Optimized Cartesian coordinates of **1-D**.

C	-4.78989800	-0.61210700	-0.04838700
C	-1.84738400	3.60645300	-0.36941100
C	-4.26511600	-1.94737000	-0.04891200
C	-2.89401300	-2.19008800	0.09281400
C	-2.12115000	-1.05698700	0.28225900
C	-1.89318200	-3.34599000	-0.04904900
C	-2.52158500	2.43610300	-0.07439100
C	0.77140200	-3.07610200	-0.22700100
C	-4.01210000	2.03046700	-0.06183800
C	-0.43525000	3.55414000	-0.44282900
C	0.30919600	2.39121100	-0.25225900
C	-3.95589400	0.50262500	0.09908400
C	-2.61678400	0.20227800	0.29210300
C	-0.52894800	-2.63796300	-0.02059500
C	-0.72621500	-1.25998900	0.18728800
C	-1.73459900	1.29588600	0.16364600
C	1.78559400	-2.11558600	-0.18469100
C	2.73000000	0.05970600	0.23821000
C	-0.33317000	1.17050000	0.06848500
C	1.55497700	-0.73107700	0.01822800
C	0.21620200	-0.21896700	0.14132000
O	2.68527200	1.14635100	0.90516500
O	3.87440600	-0.41303700	-0.23280300
O	5.17907400	1.27599200	0.54682000
C	5.11453900	0.22312400	-0.03213800
C	6.20243200	-0.57686900	-0.62760700
H	-5.86024100	-0.49531200	-0.22424100
H	-2.36477800	4.54282000	-0.58011900
H	-4.96845300	-2.76371500	-0.21831600
H	-1.96870700	-4.08046200	0.76569300
H	-2.01705000	-3.89978600	-0.98966300

H	1.02059900	-4.12037000	-0.40833200
H	-4.50865100	2.32839500	-0.99485800
H	-4.55509500	2.51684700	0.76091700
H	2.81480500	-2.45407300	-0.28285100
H	3.59070500	1.55607200	0.96403700
H	7.15404300	-0.06313000	-0.47384200
H	6.21287900	-1.56944200	-0.15731400
H	5.99875100	-0.71381800	-1.69828700
H	1.38441100	2.45264700	-0.38587400
H	0.10243400	4.46850500	-0.69636900

Optimized Cartesian coordinates of **1-TS1**.

C	-4.52525800	0.25687100	0.13570700
C	-0.60553900	3.28966300	0.56865400
C	-4.33767500	-1.15710000	0.16262200
C	-3.13177500	-1.73359500	-0.24472500
C	-2.18692500	-0.86816600	-0.80062000
C	-2.40304900	-3.04732600	0.11215500
C	-1.61007800	2.57601100	-0.08721600
C	0.23494300	-3.04286500	0.68951900
C	-3.15005600	2.58251700	0.00472300
C	0.70643500	2.74565700	0.71074500
C	1.01647300	1.49991100	0.17262100
C	-3.50949800	1.11212400	-0.29926700
C	-2.36909900	0.50300200	-0.82747300
C	-0.91732500	-2.64326100	0.01170700
C	-0.86498500	-1.41124200	-0.65496300
C	-1.23518100	1.37733200	-0.70923000
C	1.35902600	-2.16895100	0.80507200
C	2.02533200	0.42512300	0.58391700
C	0.03424100	0.85622800	-0.58013600
C	1.33626500	-0.90789900	0.21775700
C	0.22459100	-0.57327700	-0.55458000
O	2.73075300	0.55412200	1.65530300
O	3.21683700	0.50036700	-0.76985200
O	4.59955100	-0.49713400	0.67142300
C	4.33562700	-0.03112900	-0.49077200
C	5.38446100	-0.10870400	-1.54593800
H	-5.43038000	0.65608700	0.59634600
H	-0.83747500	4.20649700	1.11214900
H	-5.11000000	-1.76083900	0.64203800
H	-2.65809500	-3.38918200	1.12270400
H	-2.65298000	-3.86297000	-0.58282100
H	0.24829700	-3.96666600	1.26942200

H	-3.59880700	3.27831100	-0.72006200
H	-3.49089100	2.88482700	1.00250800
H	1.41483700	3.26321400	1.35837000
H	2.17277600	-2.46006300	1.47026900
H	3.73319800	-0.10027200	1.35834600
H	6.22364200	0.53495700	-1.24979200
H	5.75485400	-1.14014600	-1.60295300
H	4.98819600	0.21187700	-2.51320500

Optimized Cartesian coordinates of 1-TS2.

C	-4.26026300	1.06372500	0.64814500
C	0.32236700	3.18930700	0.14647200
C	-4.43952100	-0.35078300	0.59172500
C	-3.50238000	-1.17780000	-0.03403700
C	-2.46560600	-0.53050400	-0.70659500
C	-3.08065200	-2.64815800	0.14075400
C	-0.94431400	2.63384000	-0.12998700
C	-0.48123700	-3.33628400	0.26798300
C	-2.36587000	2.97873600	0.32408800
C	1.47341300	2.48808800	-0.20865800
C	1.44415000	1.16269700	-0.76335600
C	-3.13809300	1.67007800	0.07726100
C	-2.29433900	0.83378300	-0.64831700
C	-1.57528400	-2.59778800	-0.18263600
C	-1.30690900	-1.36551800	-0.78489900
C	-0.98592400	1.39385200	-0.77311900
C	0.81614700	-2.76304500	0.27238100
C	2.08499200	-0.52393300	0.26929900
C	0.14048800	0.61266600	-0.97120200
C	1.01751300	-1.47092000	-0.21304300
C	-0.03245900	-0.80547200	-0.84360100
O	1.96039600	-0.21154900	1.54637300
O	3.33614000	-0.78173000	-0.21628500
O	4.27442600	0.90301500	0.95635800
C	4.41430300	-0.01026200	0.17861000
C	5.66187600	-0.45687300	-0.48582500
H	-4.95744200	1.63863300	1.25889300
H	0.41429700	4.15834400	0.63586800
H	-5.26013500	-0.77873100	1.16899200
H	-3.25653000	-3.00530600	1.16244400
H	-3.62121800	-3.32157100	-0.54062800
H	-0.61880000	-4.28989500	0.77821900
H	-2.76187700	3.82979600	-0.25090700
H	-2.37652900	3.27381200	1.38109100

H	1.61593600	-3.28427100	0.79755200
H	2.68144500	0.39978400	1.80050500
H	6.50017300	0.14698900	-0.13042700
H	5.82786900	-1.51960600	-0.26565000
H	5.54541300	-0.35409700	-1.57300100
H	2.24389300	0.92031700	-1.46705300
H	2.44143500	2.97132300	-0.07612100

Optimized Cartesian coordinates of **4-A**.

C	-0.17342500	3.44905300	0.02693900
C	1.03063100	2.87651700	-0.38633900
C	1.12137200	1.49787600	-0.60803400
C	-0.01511600	0.72993200	-0.40355500
C	-1.23114100	1.30452400	0.00706200
C	-1.32175100	2.66958100	0.22744100
H	-0.22245500	4.52526100	0.19598600
H	1.90552600	3.50862800	-0.53614800
H	2.05592500	1.04528200	-0.93644200
H	-2.25518900	3.13247200	0.54662800
C	-2.34606500	-2.18826700	-0.20942000
C	-3.69608000	-2.15050700	0.15820900
C	-4.30171800	-0.93961600	0.49947900
C	-3.58567600	0.26643000	0.48616600
C	-2.24929300	0.22793300	0.12104500
H	-1.85716900	-3.12531100	-0.47630100
H	-4.27965100	-3.07066000	0.17964200
H	-5.35444000	-0.93164200	0.78395700
H	-4.07460200	1.20185800	0.75728000
C	-1.64479900	-0.99269100	-0.22255400
C	-0.21771100	-0.73767100	-0.56011900
O	0.60708700	-1.57707600	-0.89587400
H	2.30373700	-1.35018800	-0.81387900
O	2.86459500	-0.70164900	1.34559100
C	3.66652200	-0.91639100	0.45193600
C	5.15162800	-0.78854600	0.58940100
H	5.51394600	-0.01853100	-0.10521100
H	5.41099400	-0.51855900	1.61664800
H	5.63039700	-1.73699800	0.31295300
O	3.29065800	-1.28509400	-0.77360000

Optimized Cartesian coordinates of **4-B**.

C	0.21431600	3.63822100	0.31949200
C	1.44868700	3.13518200	-0.09454300
C	1.60544200	1.77683100	-0.39406900

C	0.50611100	0.93864400	-0.26535500
C	-0.73902400	1.44702100	0.13739300
C	-0.89489800	2.79633100	0.43540700
H	0.11354800	4.69979300	0.54759200
H	2.30181100	3.80749100	-0.18862600
H	2.57072200	1.39589000	-0.72097000
H	-1.86148400	3.19255800	0.74692000
C	-1.77322100	-2.02505900	-0.37195000
C	-3.13758500	-2.03539700	-0.06260700
C	-3.78293200	-0.86421800	0.34402500
C	-3.08547400	0.34253100	0.44942800
C	-1.72874500	0.35075500	0.14044100
H	-1.26294600	-2.93466700	-0.68870900
H	-3.70319500	-2.96425800	-0.13900400
H	-4.84703700	-0.89301900	0.58078500
H	-3.59755200	1.25173000	0.76443700
C	-1.09088300	-0.82456800	-0.26499600
C	0.37784600	-0.56330200	-0.53591800
O	0.70620800	-0.97995700	-1.82074300
H	1.63394500	-0.75243600	-1.97934900
O	1.10052500	-1.34410000	0.46498700
C	2.43526800	-1.44142500	0.39059300
C	2.99288200	-2.24334900	1.52182500
H	4.07408800	-2.35059600	1.40012500
H	2.76740700	-1.73371000	2.46813200
H	2.51091300	-3.22886800	1.54811700
O	3.09489600	-0.93333000	-0.49854900

Optimized Cartesian coordinates of **4-C**.

C	3.87505700	-0.09744900	0.49095000
C	3.50551900	-1.39529500	0.10704200
C	2.20089900	-1.69610000	-0.29326500
C	1.28110900	-0.66236700	-0.29940000
C	1.64552800	0.64056800	0.06624700
C	2.94902000	0.93881400	0.47909900
H	4.90234700	0.09664100	0.79715800
H	4.25335700	-2.18811300	0.12905500
H	1.91769400	-2.70766600	-0.57963600
H	3.23307400	1.95133200	0.76259600
C	-1.91577400	1.32510800	-0.76926900
C	-2.12931800	2.53322600	-0.18140000
C	-1.04596900	3.24367900	0.41030400
C	0.25405700	2.75163800	0.46595800
C	0.49364800	1.49766600	-0.06936000

H	-2.71827800	0.79656100	-1.27919400
H	-3.12201900	2.97889800	-0.17149700
H	-1.25705700	4.21066000	0.86981400
H	1.03286700	3.29993100	0.99188800
C	-0.54960000	0.78035300	-0.83924000
H	-0.26712400	0.95828900	-1.90302300
C	-0.19325100	-0.74080400	-0.63131400
O	-0.41207200	-1.57140900	-1.70348800
H	-1.36958800	-1.65055800	-1.83953000
O	-0.82787100	-1.21428600	0.58098200
C	-2.12849200	-1.57159400	0.55111100
C	-2.60610100	-2.02353500	1.88870900
H	-2.02679500	-2.90295400	2.19924800
H	-2.43439100	-1.22976400	2.62695900
H	-3.66902300	-2.27204600	1.83333200
O	-2.79668900	-1.52488800	-0.46426900

Optimized Cartesian coordinates of **4-D**.

C	3.58121200	1.40579400	0.21933200
C	3.92311000	0.05923000	0.08179400
C	2.92041100	-0.88432100	-0.06187800
C	1.57031500	-0.48185200	-0.06162500
C	1.21425800	0.88745800	0.03535900
C	2.24747000	1.81105200	0.18865300
H	4.36492000	2.15411500	0.33789900
H	4.96647300	-0.25097900	0.09622300
H	3.16894300	-1.94140300	-0.13736100
H	2.00198300	2.87035700	0.25425400
C	-2.18785000	1.66194900	-1.42856300
C	-2.80377100	2.32533900	-0.36599300
C	-2.10566600	2.52501800	0.82450700
C	-0.79637100	2.06337200	0.95594700
C	-0.18281500	1.38396400	-0.09992900
H	-2.72331100	1.51614700	-2.36682700
H	-3.82502100	2.69250900	-0.46873500
H	-2.58049200	3.04634500	1.65590100
H	-0.25403700	2.21710500	1.88936900
C	-0.88396800	1.19021700	-1.29609700
H	-0.40172900	0.67576500	-2.12858000
C	0.58289200	-1.53449900	-0.09146400
O	0.88923300	-2.69026700	-0.53840300
H	0.11521600	-3.30894900	-0.45498300
O	-0.60701600	-1.27243000	0.39371100
C	-1.69481900	-2.17697000	0.33639600

C	-2.92465900	-1.50020300	0.78763900
H	-2.75586200	-1.07556200	1.78597200
H	-3.13025300	-0.66461000	0.10223200
H	-3.75179300	-2.21352500	0.79504800
O	-1.52640800	-3.30362800	-0.04341700

Optimized Cartesian coordinates of **4-TS1**.

C	0.26122000	3.61021200	0.33140400
C	1.43702300	3.12769700	-0.24743600
C	1.53769500	1.78977300	-0.64593500
C	0.44241300	0.96662100	-0.44102800
C	-0.74711300	1.44833700	0.12608900
C	-0.84725200	2.77618000	0.52018700
H	0.20308600	4.65635600	0.63348300
H	2.28198200	3.80075600	-0.39294600
H	2.45192300	1.40890900	-1.10068300
H	-1.76530500	3.16710100	0.95878300
C	-1.84571900	-1.98850500	-0.53702500
C	-3.17240900	-2.02571900	-0.09378200
C	-3.76368700	-0.89108500	0.46721100
C	-3.05492600	0.30961900	0.59742600
C	-1.73895200	0.34690500	0.15585600
H	-1.37000600	-2.86659000	-0.97349100
H	-3.74999100	-2.94549800	-0.18567900
H	-4.79851700	-0.94102600	0.80758700
H	-3.53196500	1.18850200	1.03077200
C	-1.15166200	-0.79835700	-0.40091800
C	0.26031500	-0.49033100	-0.77433200
O	0.86060900	-1.09162500	-1.74426900
H	1.98399500	-1.13333600	-1.38076800
O	1.13468100	-1.17078600	0.74137800
C	2.35689600	-1.44563000	0.54038500
C	3.17332900	-1.97334900	1.67365100
H	4.16194000	-1.49896600	1.66317500
H	2.66940400	-1.80342300	2.62957300
H	3.31305400	-3.05256300	1.51923700
O	2.91313100	-1.30689200	-0.60205400

Optimized Cartesian coordinates of **4-TS2**.

C	-3.90178800	-0.43762000	0.49936900
C	-3.75795000	0.93520600	0.25676300
C	-2.52341100	1.47550600	-0.09791000
C	-1.44537100	0.60194100	-0.19113100
C	-1.58872600	-0.77627100	0.00425300

C	-2.82121100	-1.30802900	0.38062500
H	-4.88038300	-0.83151200	0.77301500
H	-4.62132800	1.59182400	0.35964300
H	-2.40029000	2.54410100	-0.26698500
H	-2.94373800	-2.37907200	0.53599900
C	1.84056700	-1.01047300	-1.38927800
C	2.43851000	-1.91241100	-0.53712700
C	1.65469200	-2.62323400	0.39565300
C	0.28599500	-2.40551300	0.53083200
C	-0.31338100	-1.43652000	-0.26351300
H	2.41322800	-0.51812400	-2.17365500
H	3.50622200	-2.11513200	-0.60462000
H	2.14283200	-3.34232300	1.05416600
H	-0.28144600	-2.91486200	1.30799600
C	0.44944000	-0.73637700	-1.26029600
H	-0.07302900	-0.41407900	-2.16219500
C	-0.03604600	1.01008000	-0.45117900
O	0.15051700	1.97455400	-1.32277000
H	1.08803400	2.26490900	-1.28848500
O	0.72639100	1.01949400	0.69947600
C	2.04485900	1.40827000	0.66925900
C	2.69685600	1.18560900	1.98281000
H	2.13760100	1.72257700	2.76008700
H	2.66052900	0.11465500	2.22216800
H	3.73043300	1.53669200	1.94050100
O	2.54598100	1.87087200	-0.33075700

Optimized Cartesian coordinates of **5-A**.

C	5.29749000	-0.80815300	0.46820100
C	1.48599800	3.63220200	0.11680900
C	4.78945200	-2.10368400	0.31731800
C	3.43586900	-2.29299900	0.09100100
C	2.54561400	-1.20712900	0.00794400
C	2.48508600	2.66666500	0.22451100
C	-0.96923400	-2.63743600	-0.65717100
C	0.13045400	3.30868300	-0.12641500
C	-0.18421300	1.96997000	-0.25647800
C	4.44409100	0.28037000	0.39281900
C	3.06554800	0.11854200	0.16627800
C	0.40490000	-2.64356600	-0.42747200
C	1.10762100	-1.42791000	-0.23866600
C	2.17372300	1.29087000	0.09113400
C	-1.73274800	-1.44836900	-0.71294400
C	-1.45565000	1.20004000	-0.50572600

C	0.83975700	1.02505600	-0.14179100
C	-1.06001500	-0.25597200	-0.52609600
C	0.32036700	-0.29563000	-0.30091700
O	-2.57039000	1.67299100	-0.66025100
O	-4.15298700	-0.26741400	1.51207000
O	-4.84662200	0.20325800	-0.56381200
C	-4.98931100	-0.37341400	0.63057400
C	-6.25813900	-1.15887500	0.74714600
H	6.36198200	-0.65362200	0.64494100
H	1.76143100	4.68124100	0.22525100
H	5.45603200	-2.96416600	0.37684000
H	-1.47761900	-3.59089300	-0.79969700
H	-0.62290400	4.09213600	-0.20423800
H	-2.80426500	-1.49164900	-0.90145800
H	-3.99702700	0.70931000	-0.58964500
H	-6.35470000	-1.56759600	1.75663100
H	-7.11512800	-0.51426000	0.51287100
H	-6.24485700	-1.97468400	0.01140500
H	4.85327700	1.28324400	0.51066500
H	3.50635700	2.99592500	0.41458600
H	3.05742500	-3.30806900	-0.02388500
H	0.92003700	-3.60315300	-0.39867600

Optimized Cartesian coordinates of **5-B**.

C	5.09466600	0.26727800	0.47416100
C	0.26817900	3.51327600	-0.21356100
C	4.94292300	-1.12382600	0.42816300
C	3.68564100	-1.67440300	0.24246700
C	2.54265800	-0.86714300	0.09579400
C	1.48474500	2.85590300	-0.03851900
C	-0.45242000	-3.21972800	-0.38676600
C	-0.95737300	2.82773600	-0.38151700
C	-0.91689900	1.44931500	-0.36727000
C	3.98718100	1.08663000	0.33036700
C	2.69884600	0.55514500	0.13743000
C	0.87287400	-2.84559300	-0.18278700
C	1.21363100	-1.47771200	-0.09692600
C	1.53321100	1.44407400	-0.02138300
C	-1.50724400	-2.28550600	-0.51215300
C	-1.99831100	0.37556700	-0.52080700
C	0.30989500	0.81612800	-0.18732800
C	-1.19115600	-0.94287400	-0.41849800
C	0.14944000	-0.59912400	-0.21955700
O	-2.68533300	0.56612500	-1.71272500

O	-2.88089600	0.54294800	0.62411600
O	-4.30526300	-1.01829000	-0.15066300
C	-3.98275500	-0.21929400	0.70911200
C	-4.73925300	0.04292800	1.97045700
H	6.08122000	0.70683700	0.62221500
H	0.26158800	4.60360300	-0.22444900
H	5.81080400	-1.77422300	0.53855100
H	-0.69047900	-4.28157900	-0.45602100
H	-1.88564100	3.38142100	-0.51898700
H	-2.52387300	-2.63535800	-0.67791600
H	-3.29456300	-0.17719900	-1.82839800
H	-4.10811400	-0.22256000	2.82908200
H	-4.97353000	1.11252000	2.04429400
H	-5.65739300	-0.55045600	1.97999000
H	4.12013400	2.16729500	0.37006000
H	2.38822000	3.45360500	0.07904600
H	3.58260400	-2.75847000	0.20938500
H	1.63008700	-3.62434900	-0.09795200

Optimized Cartesian coordinates of **5-C**.

C	-4.84297600	-1.28905300	0.42349100
C	0.69656500	-3.10968800	-0.33867200
C	-5.05553900	0.09168100	0.51044000
C	-3.99453700	0.96751900	0.35227200
C	-2.69451400	0.49441000	0.10297100
C	-0.67149600	-2.75167200	-0.13905000
C	-0.34778000	3.52302400	0.00993000
C	1.64718100	-2.19688600	-0.69627600
C	1.24040200	-0.80202100	-0.96059900
C	-3.57114400	-1.78187700	0.18032400
C	-2.47945700	-0.91468000	0.01702900
C	-1.54734900	2.81967400	0.13165800
C	-1.56638300	1.42361100	-0.04028300
C	-1.13216200	-1.43878300	-0.26617300
C	0.89757000	2.90768600	-0.25615700
C	2.02512200	0.53483700	-0.59071700
C	-0.13884500	-0.50925800	-0.55085300
C	0.89143800	1.54278700	-0.42567500
C	-0.32718900	0.86014000	-0.35514500
O	2.93048200	0.97648500	-1.52736400
O	2.60551200	0.41118700	0.72538400
O	4.28582900	-0.85701400	-0.06649000
C	3.73591000	-0.31268900	0.87155700
C	4.19106800	-0.34387200	2.29056000

H	-5.67777600	-1.97960700	0.54039900
H	0.97429100	-4.15430300	-0.21044300
H	-6.05625800	0.47940800	0.69884300
H	-0.36738700	4.60258100	0.16028300
H	2.66764600	-2.50889600	-0.90775600
H	1.81168900	3.49754300	-0.29304600
H	3.65790300	0.33748000	-1.57936500
H	3.41095300	-0.80602700	2.90991300
H	5.12166000	-0.91209500	2.36516000
H	4.33938300	0.68281400	2.64887900
H	-3.42619200	-2.85815600	0.09965100
H	-1.35344400	-3.54553000	0.16951100
H	-4.17496600	2.03926300	0.42047400
H	-2.45315100	3.37129700	0.37694900
H	1.21574300	-0.78037400	-2.07547500

Optimized Cartesian coordinates of **5-D**.

C	-4.73077500	-0.84429200	0.93647700
C	-0.08307300	-3.42066700	-1.14922600
C	-4.81575600	0.55166300	0.86592900
C	-3.71860700	1.28783300	0.45861200
C	-2.50868000	0.65839500	0.10099400
C	-1.18505400	-2.81337000	-0.57605700
C	-0.18469300	3.60045700	-0.49137800
C	1.01324200	-2.64621500	-1.55267200
C	1.00707400	-1.28556900	-1.31853700
C	-3.55853900	-1.48183500	0.57469700
C	-2.43421100	-0.75254900	0.13735800
C	-1.33156500	2.84896700	-0.29551800
C	-1.30505500	1.44098500	-0.21270700
C	-1.21888100	-1.42366900	-0.34064300
C	1.05270100	2.96637100	-0.50299900
C	2.40868700	1.04109300	-0.08570200
C	-0.07285900	-0.66028100	-0.65679100
C	1.10846200	1.57145700	-0.40730000
C	-0.07772900	0.77642500	-0.39802300
O	3.46617100	1.60235700	-0.52724500
O	2.45746800	0.02859700	0.75641300
O	4.72061100	-0.16840300	0.76541100
C	3.66207200	-0.61101600	1.12516500
C	3.37080300	-1.79527800	1.95369400
H	-5.58575800	-1.42952100	1.27451600
H	-0.09072000	-4.49488800	-1.33221900
H	-5.73762000	1.06126800	1.14520600

H	-0.24438100	4.68432700	-0.56924700
H	1.85010400	-3.10747700	-2.07621500
H	1.97194300	3.54908900	-0.51373600
H	4.27298100	1.15772200	-0.14997800
H	2.72031500	-2.47322800	1.38333400
H	4.30683100	-2.28586900	2.22941000
H	2.81638200	-1.47519500	2.84646700
H	-3.51880500	-2.56696600	0.63870500
H	-2.04896300	-3.42920300	-0.33931800
H	-3.80538500	2.37188400	0.44191000
H	-2.27827600	3.37692200	-0.21298000
H	1.83197900	-0.69270900	-1.71472300

Optimized Cartesian coordinates of **5-TS1**.

C	5.05602900	0.23684500	0.62869100
C	0.29357500	3.52811000	-0.28926500
C	4.89955700	-1.15237800	0.55501900
C	3.65190700	-1.69275800	0.29011300
C	2.52406300	-0.87616500	0.08987700
C	1.49328500	2.85941000	-0.05083500
C	-0.45911600	-3.19413800	-0.63418600
C	-0.92648400	2.85397900	-0.53007600
C	-0.89708300	1.47524400	-0.51784800
C	3.96282200	1.06549100	0.43569400
C	2.68427800	0.54533800	0.16418400
C	0.85542500	-2.83566400	-0.34225500
C	1.20488400	-1.47369700	-0.19097300
C	1.53355900	1.44560800	-0.04141900
C	-1.49807900	-2.24636500	-0.79080900
C	-1.94307000	0.39941100	-0.73489300
C	0.31682400	0.83076000	-0.27487100
C	-1.16868800	-0.91601800	-0.63329000
C	0.15642500	-0.58494800	-0.34541200
O	-2.93810200	0.57081400	-1.53642200
O	-2.69322700	0.35483700	0.91955800
O	-4.44313200	-0.56368000	-0.11960900
C	-3.85219500	-0.16436900	0.94203000
C	-4.55917500	-0.28944100	2.24771200
H	6.03508900	0.66810500	0.83807600
H	0.29740000	4.61837200	-0.29493500
H	5.75597300	-1.80958100	0.70666200
H	-0.69653000	-4.25161000	-0.75322400
H	-1.84222700	3.41372400	-0.71799500
H	-2.51067000	-2.57304900	-1.02628200

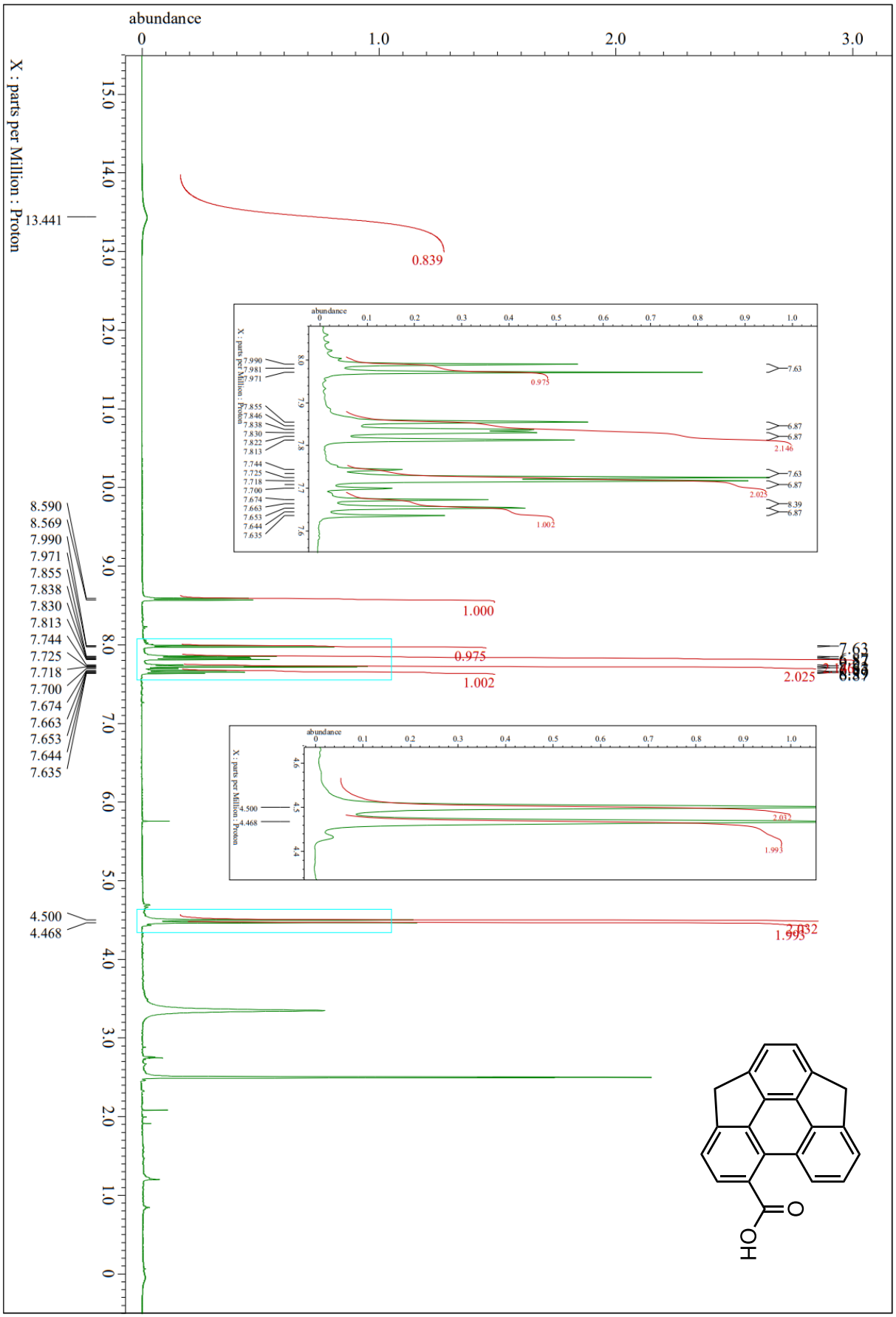
H	-3.80338700	-0.11615600	-1.00843100
H	-3.85524300	-0.20265500	3.08035500
H	-5.29978200	0.52059000	2.30942200
H	-5.09576300	-1.24463900	2.28307100
H	4.09940500	2.14460200	0.49832000
H	2.39292800	3.45024500	0.11951400
H	3.54442100	-2.77584400	0.23803600
H	1.60163200	-3.62340400	-0.24392200

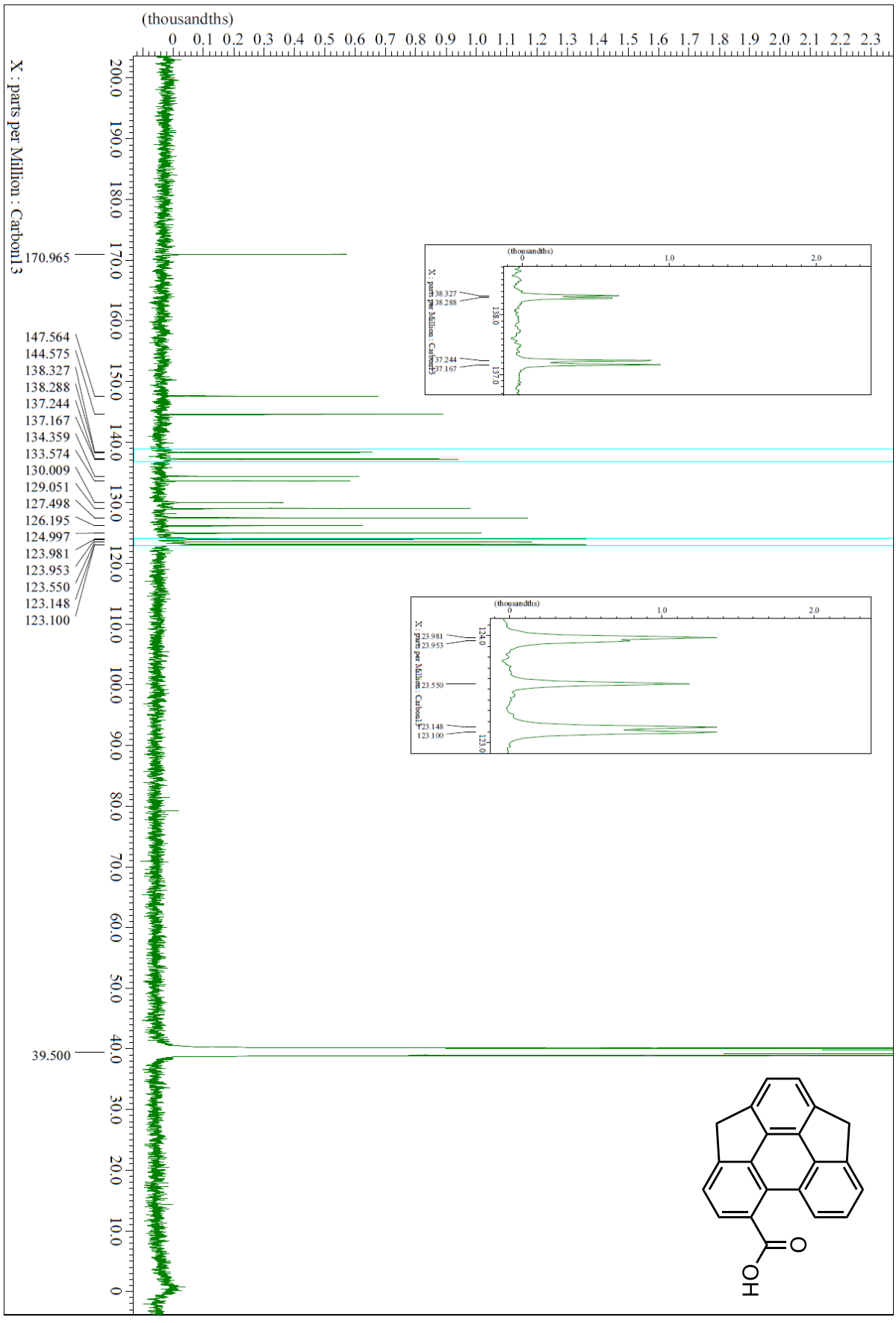
Optimized Cartesian coordinates of **5-TS2**.

C	4.61649600	1.49504500	0.50144400
C	-0.87465400	2.99895300	-0.76401700
C	4.92952900	0.13174000	0.54864100
C	3.94081400	-0.81322800	0.32921500
C	2.61872800	-0.42732600	0.04967900
C	0.44791000	2.70681400	-0.37993800
C	0.49468100	-3.61359000	0.06282100
C	-1.70991700	2.01968700	-1.27598000
C	-1.25867700	0.67369400	-1.31708500
C	3.32121100	1.89950000	0.22225800
C	2.30408700	0.96039100	-0.01845100
C	1.63524500	-2.81069100	0.12494100
C	1.55047200	-1.42648400	-0.09993600
C	0.94730700	1.39661300	-0.39547100
C	-0.78933800	-3.08522200	-0.15317600
C	-2.12068400	-0.89232300	-0.35509500
C	0.03529100	0.40787100	-0.76700700
C	-0.87971000	-1.71917300	-0.35720600
C	0.28199700	-0.94632500	-0.43090400
O	-3.14938800	-1.35315600	-1.02847300
O	-2.35046600	-0.33368000	0.88353700
O	-4.24278600	0.69541000	0.21151300
C	-3.42108200	0.51119000	1.07901000
C	-3.37806200	1.11818900	2.43120600
H	5.39201000	2.24075200	0.67449900
H	-1.21226700	4.03367500	-0.72923000
H	5.94976100	-0.18797300	0.75961100
H	0.59517200	-4.68171100	0.25383900
H	-2.67084400	2.28731500	-1.71242100
H	-1.67311800	-3.71841700	-0.09675300
H	-3.93760800	-0.80150400	-0.84773500
H	-2.50982100	1.79013500	2.48104800
H	-4.30041300	1.67536200	2.61159000
H	-3.23952500	0.33324000	3.18495800

H	3.10016000	2.96463100	0.17212300
H	1.07584100	3.53239000	-0.04620800
H	4.19663000	-1.87094600	0.37833700
H	2.58737100	-3.27745600	0.37066400
H	-1.56209900	0.09997000	-2.19661500

^{1}H NMR (400 MHz), ^{13}C{^{1}H}NMR (100 MHz), and ^{1}H-^{1}H COSY spectra (400 MHz) of **2** (DMSO-d_6, 25 °C).

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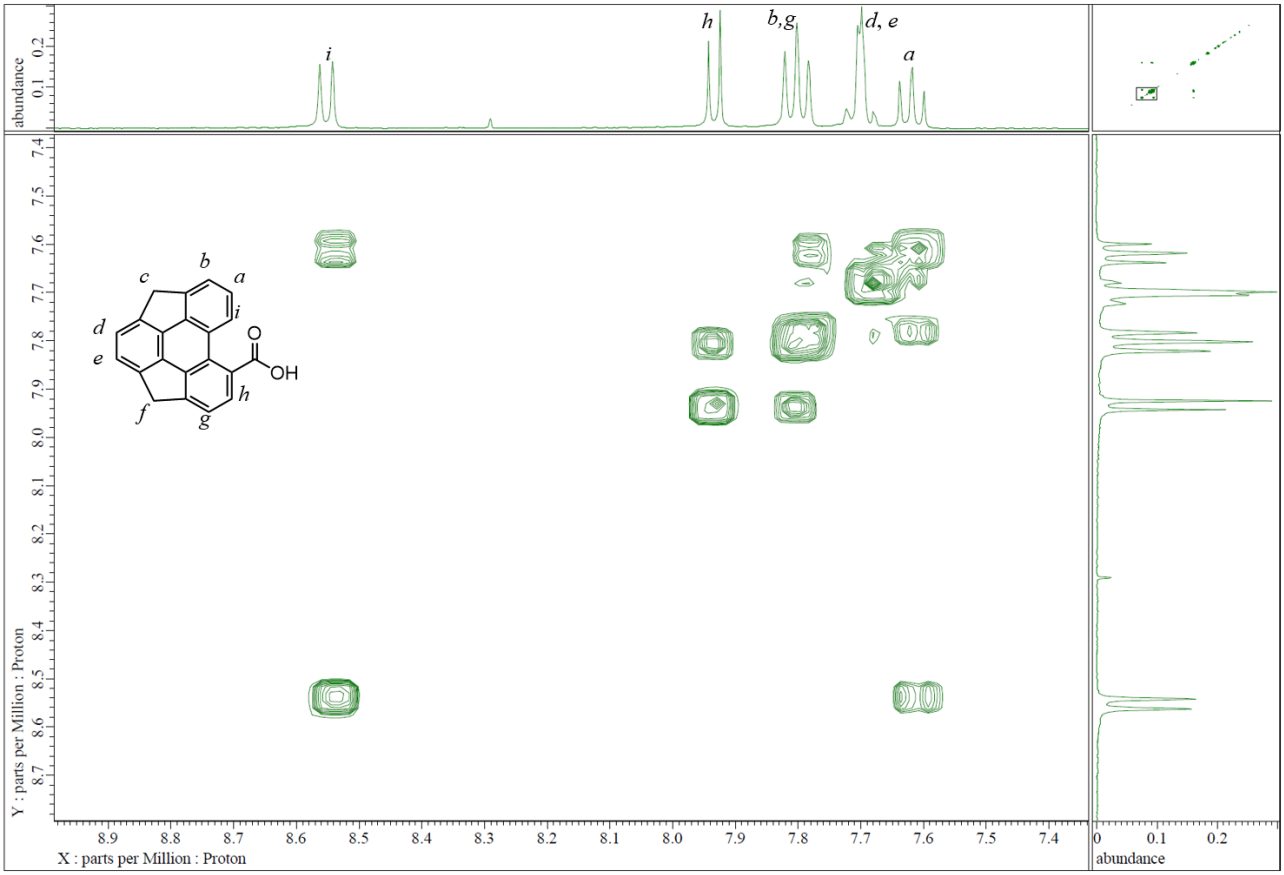
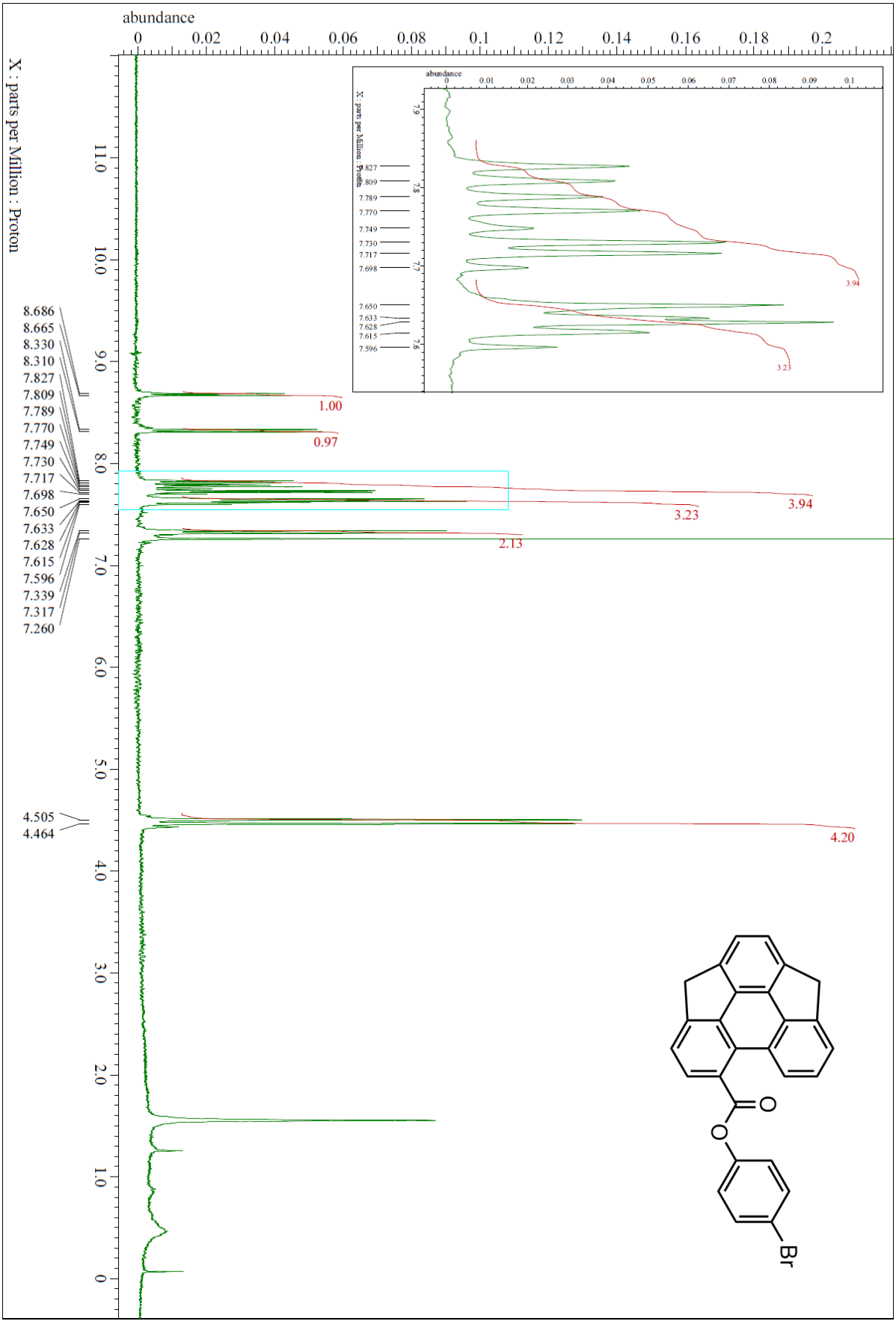
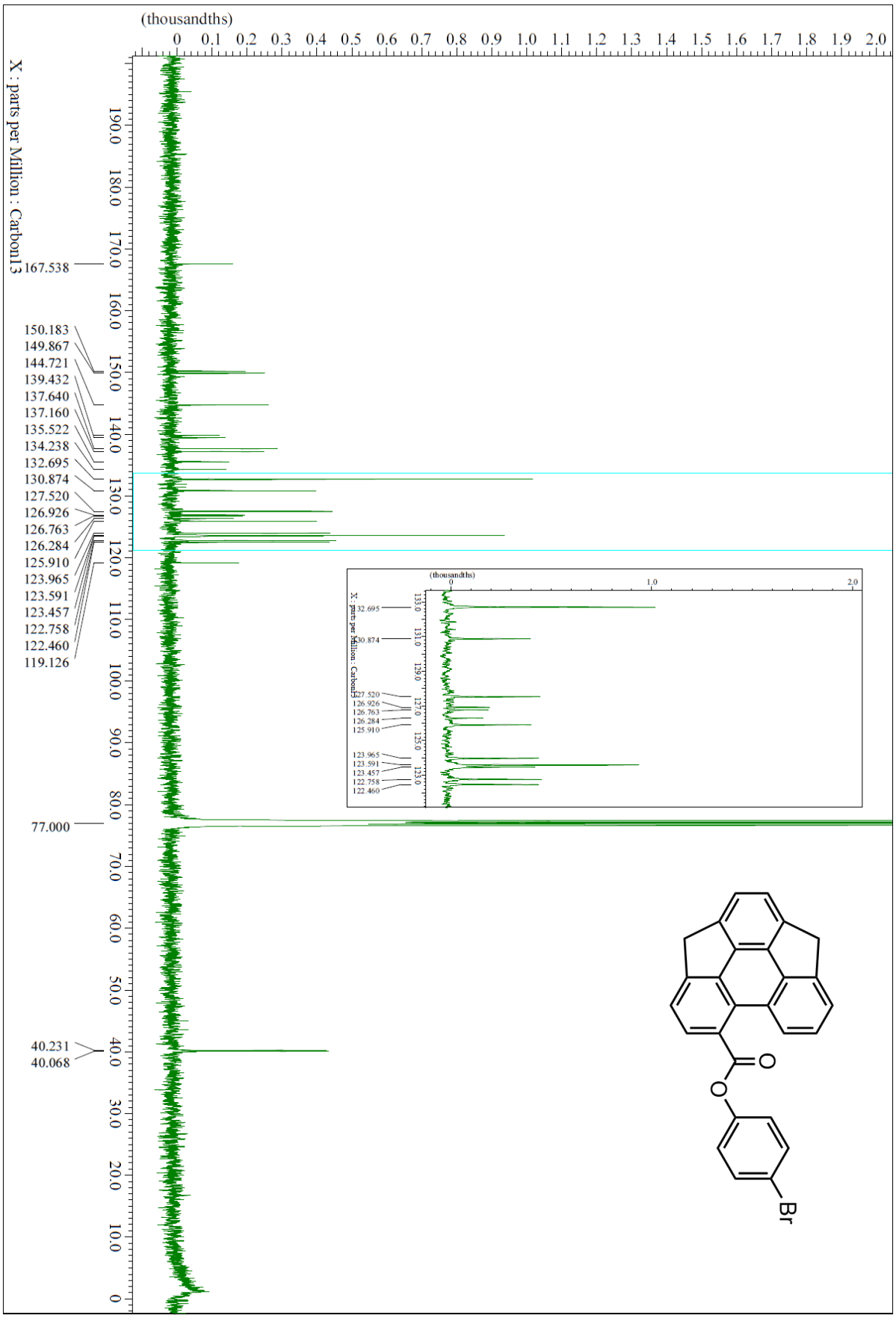
124.997
123.981
123.953
123.550
123.148
123.100
39.500
O
OH


abundance
i
h
b,g
d, e
a
c
b
a
i
d
e
OH
h
f
g
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

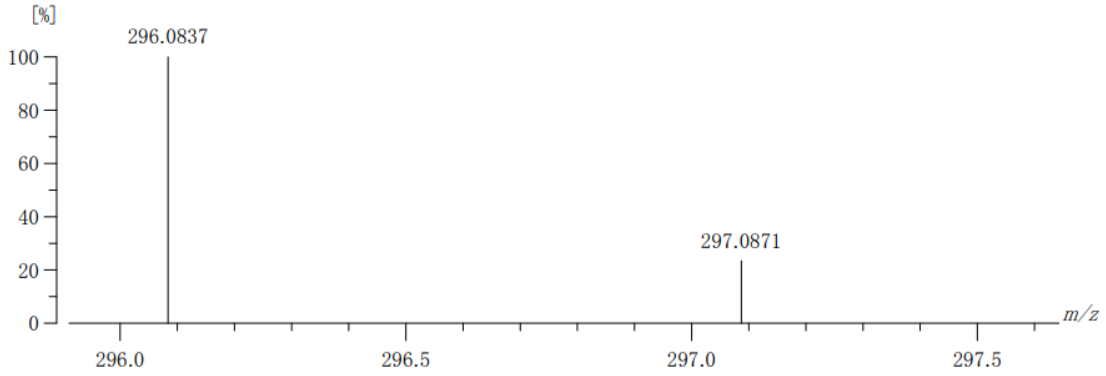
^{1}H NMR (400 MHz) and ^{13}C{^{1}H}NMR (100 MHz) of **3** ($CDCl_3$, 25 °C).



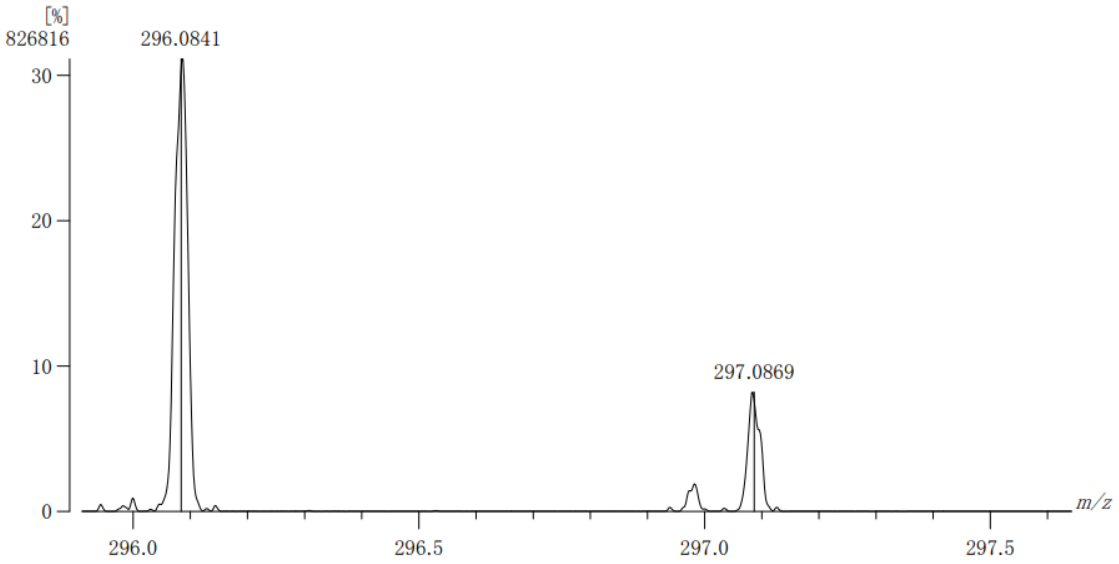

(thousandths)
X : parts per Million : Carbon13
167.538
150.183
149.867
144.721
139.432
137.640
137.160
135.522
134.238
132.695
130.874
127.520
126.926
126.763
126.284
125.910
123.965
123.591
123.457
122.758
122.460
119.126
77.000
40.231
40.068
O
O
Br

High-resolution mass spectrum of **2**.

[Molecular Formula]
Data : Sakurai_lab HR-007 Date : 02-Nov-2022 11:13
Instrument :
Sample : R-COOH
Inlet : Direct Ion Mode : -
RT : 0.29 min Molecular Formula : C21 H12 O2
Elements : 12C 80/0, 13C 1/0, H 100/0, O 2/2
Mass Tolerance : 3mmu
Unsaturation (U.S.) : -0.5 - 20.0

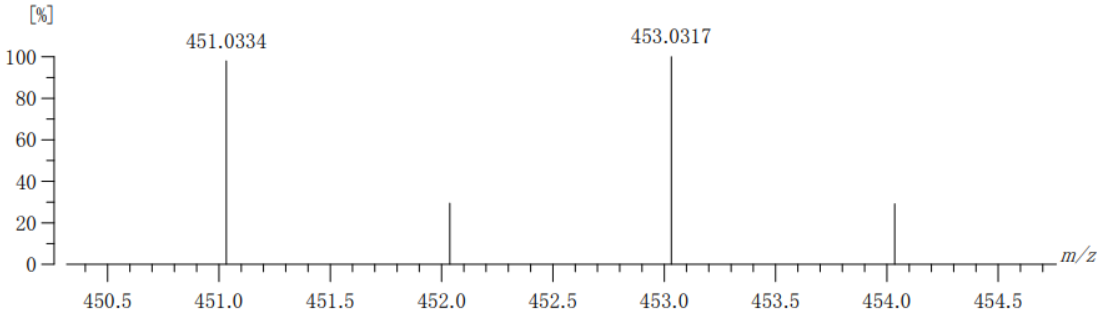


[Mass Spectrum]
Data : Sakurai_lab HR-007 Date : 02-Nov-2022 11:13
RT : 0.29 min Scan# : 6

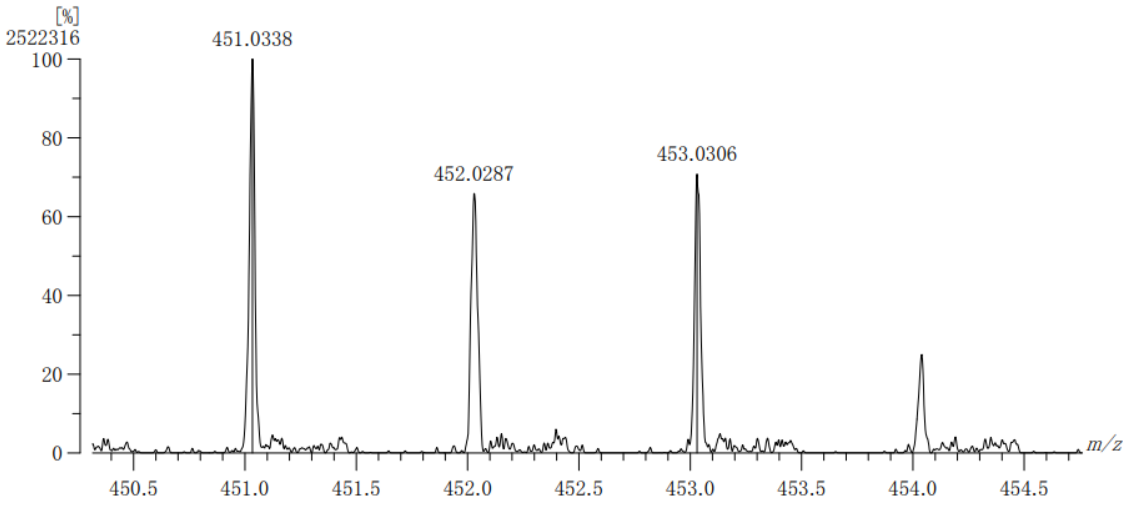


High-resolution mass spectrum of **3**.

[Molecular Formula]
Data : Sakurai_lab HR-23-003 Date : 04-Jan-2023 16:17
Instrument : JMS-700
Sample : Bromoester
Inlet : Direct Ion Mode : FAB+
RT : 2.66 min Molecular Formula : C27 H16 Br O2
Elements : C 80/0, H 100/0, 79Br 1/0, 81Br 1/0, O 2/2
Mass Tolerance : 10mmu
Unsaturation (U.S.) : -0.5 - 22.0



[Mass Spectrum]
Data : Sakurai_lab HR-23-003 Date : 04-Jan-2023 16:17
RT : 2.66 min Scan# : 30



References.

S1. M. Nishimoto, Y. Uetake, Y. Yakiyama, F. Ishiwari, A. Saeki, H. Sakurai, *J. Org. Chem.* 2022, **87**, 2508–2519.

S2. D.-C. Huang, C.-H, Kuo, M.-T. Ho, B.-C. Lin, W.-T. Peng, I. Chao, C.-P. Hsu, Y.-T. Tao, *J. Mater. Chem. C* 2017, **5**, 7935–7943.

S3. Rigaku Oxford Diffraction, Yarnton, England (**2015**).

S4. G. M. Sheldrick, *Acta Cryst. C* 2015, **71**, 3–8.

S5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339–341.

S6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S7. D. E. Woon, T. H. Dunning Jr., *J. Chem. Phys.* 1993, **98**, 1358–1371.

S8. R. A. Kendall, T. H. Dunning Jr., *J. Chem. Phys.* 1992, **96**, 6796–6806.

S9. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378–6396.

S10. K. Fukui, *Acc. Chem. Res.* 1981, **14**, 363–368.

S11. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623–11627.

S12. R. Krishnan, J. S. Binkley, R. Seeger, J. A. People, *J. Chem. Phys.* 1980, **72**, 650–654.

S13. T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comput. Chem.* 1983, **4**, 294–301.