Reactive Species Involved in the Regioselective Photooxidation of Heptamethine Cyanines

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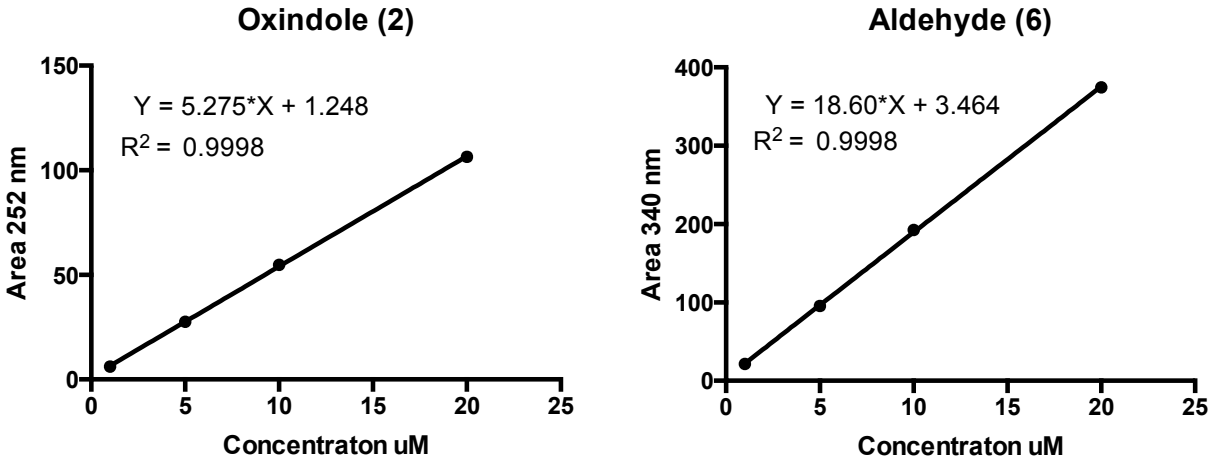
General Materials and Methods. All commercially obtained reagents were used as received. 1,1′,3,3,3′,3′-Hexamethylindotricarbocyanine iodide (HITC, **1**) of 97% purity, 2-(1,3,3-trimethylindolin-2-ylidene)acetaldehyde of 97% purity (aldehyde **6**), and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc were purchased from Sigma-Aldrich. Oxindole **2** was synthesized according to a known procedure.[1] 3-(4-Methylnaphthalen-1-yl)propanoic acid, the precursor to **12**, was purchased from OxChem (Irwindale, CA). LED light sources were obtained from Marubeni America Corporation (specification number L740-66-60 and L420-66-60). High-resolution LC/MS analyses were conducted on a Thermo-Fisher LTQ-Orbitrap-XL hybrid mass spectrometer system with an Ion MAX API electrospray ion source in positive ion mode. Analytical LC/MS was performed using a Shimadzu LCMS-2020 Single Quadrupole utilizing a Kinetex 2.6 μm C18 100 Å (2.1 x 50 mm) column obtained from Phenomenex Inc. Runs employed a gradient of 0→90% MeOH/0.1% aqueous formic acid over 4 1/2 minutes at a flow rate of 0.2 mL/min. Data analysis and curve fitting were performed using MS Excel 2011 and GraphPad Prism 6. See *JOC Standard Abbreviations and Acronyms* for abbreviations (available at http://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf).

[1] W. G. B. van Henegouwen, R. M. Fieseler, F. P. J. T. Rutjes and H. Hiemstra, *J. Org. Chem.*, 2000, **65**, 8317-8325.

Procedure for HPLC Calibration and Quantitative Analysis

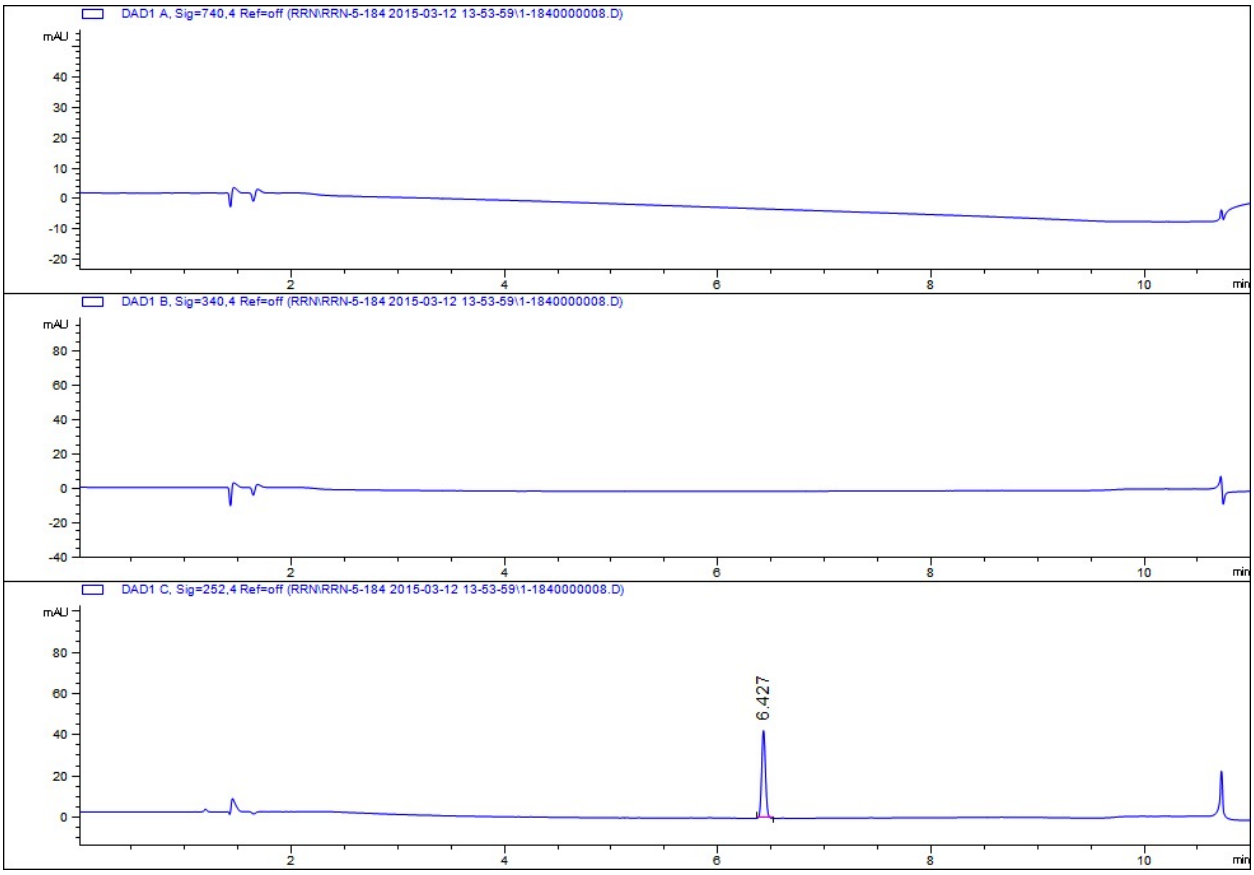
The HPLC yields of oxindole **2** and aldehyde **6** generated during photo- and chemical bleaching experiments were determined by an external calibration method.[2] A calibration curve was constructed with varying concentrations of **2** and **6** plotted against the integrated area of the peak (see below). The solutions for calibration were generated from a 1.00 mM DMSO stock solution of **2** or **6** diluted into 1:1 MeCN/H_2O to afford 1, 5, 10, and 20 μM solutions. The calibration samples were analyzed on an Agilent 1260 Infinity HPLC utilizing a Eclipse Plus C18 5 μm 110 Å (4.6 x 250 mm) column (Agilent Technologies) with a gradient of 5→95% (8 min), hold 95% (1 min), to 95→5% (0.5 min) MeCN/0.1% aqueous trifluoroacetic acid at a flow rate of 2.0 mL/min with a 20 μL injection volume. Samples of **1** were prepared from a 1.00 mM DMSO stock solution and diluted to 20 μM in the solvent mixture indicated in Tables 1 and 2.

HPLC Calibration Curves for 2 and 6



[2] D. Pigini, A. M. Cialdella, P. Faranda and G. Tranfo, *Rapid Commun. Mass Sp.*, 2006, **20**, 1013-1018.

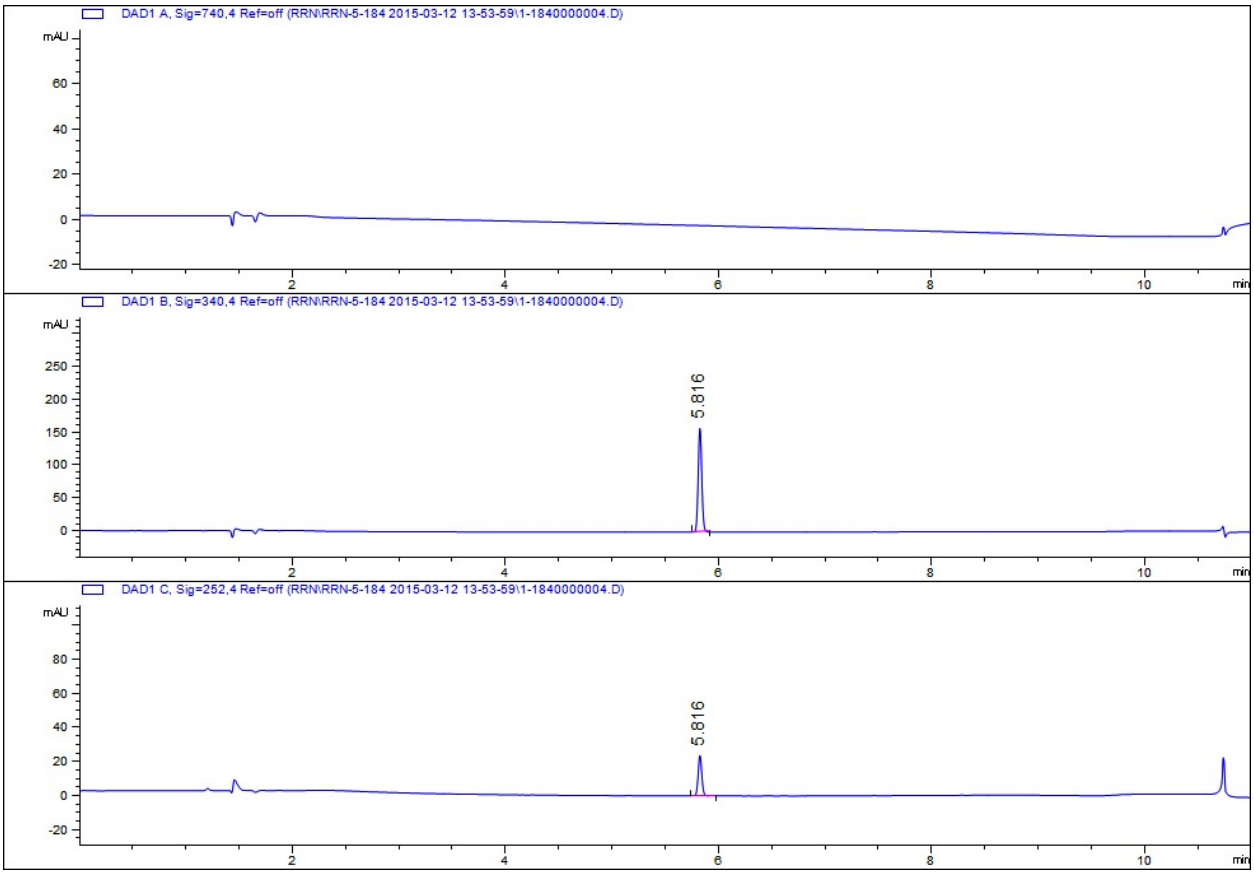
Chromatogram of 2 (MeCN:H_2O 1:1 20 μM)



Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.427	BB	0.0391	106.20425	42.61746	100.0000
Totals :				106.20425	42.61746	

Chromatogram of 6 (MeCN:H_2O 1:1 20 μM)



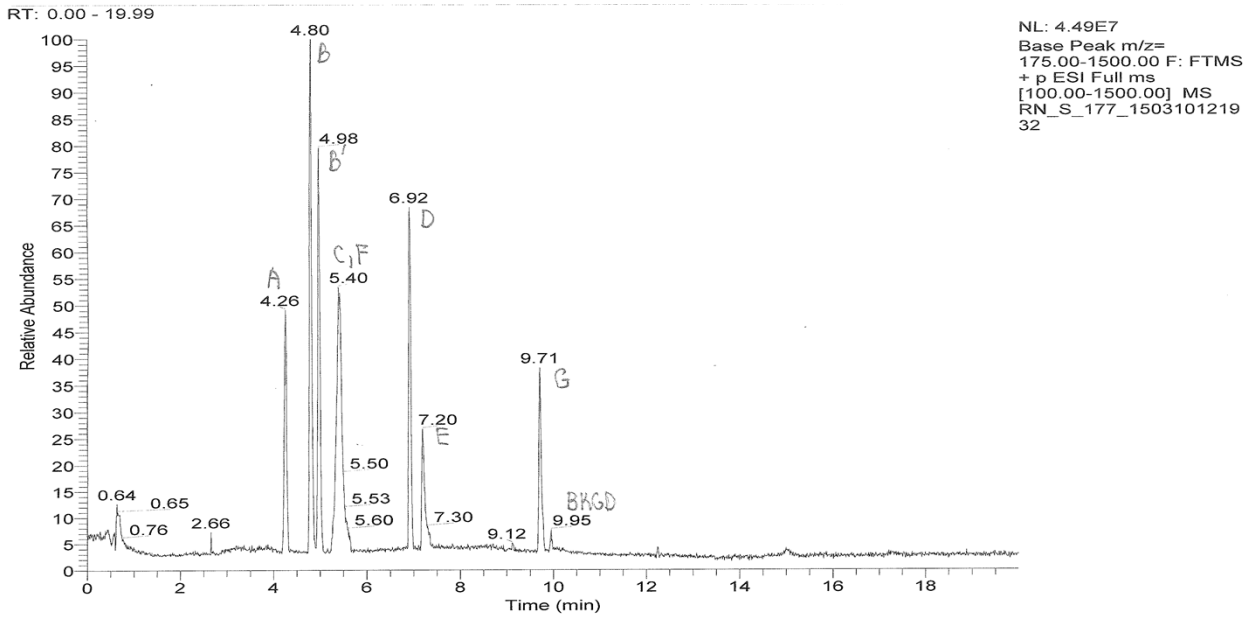
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.816	BB	0.0375	374.23874	159.04193	100.0000
Totals :				374.23874	159.04193	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.816	BV R	0.0381	56.62049	23.52851	100.0000
Totals :				56.62049	23.52851	

HRMS Chromatogram of Photolysis of 1 (1:1 MeCN:H_2O 740 nm hν)



Calculated and Observed HRMS Masses for Photolysis Products

Peak A (7): HRMS (ESI) calculated for $C_{16}H_{18}NO$ (M^+) 240.1383, observed 240.1385.

Peak B (3): HRMS (ESI) calculated for $C_{18}H_{20}NO$ (M^+) 266.1539, observed 266.1542.

Peak B′ (3): HRMS (ESI) calculated for $C_{18}H_{20}NO$ (M^+) 266.1539, observed 266.1543.

Peak C/F (10/12): HRMS (ESI) calculated for $C_{29}H_{33}N_2O_2$ (M^+) 441.2537, observed 441.2538.

Peak D (6): HRMS (ESI) calculated for $C_{13}H_{16}NO$ $(M+H)^+$ 202.1232, observed 202.1229.

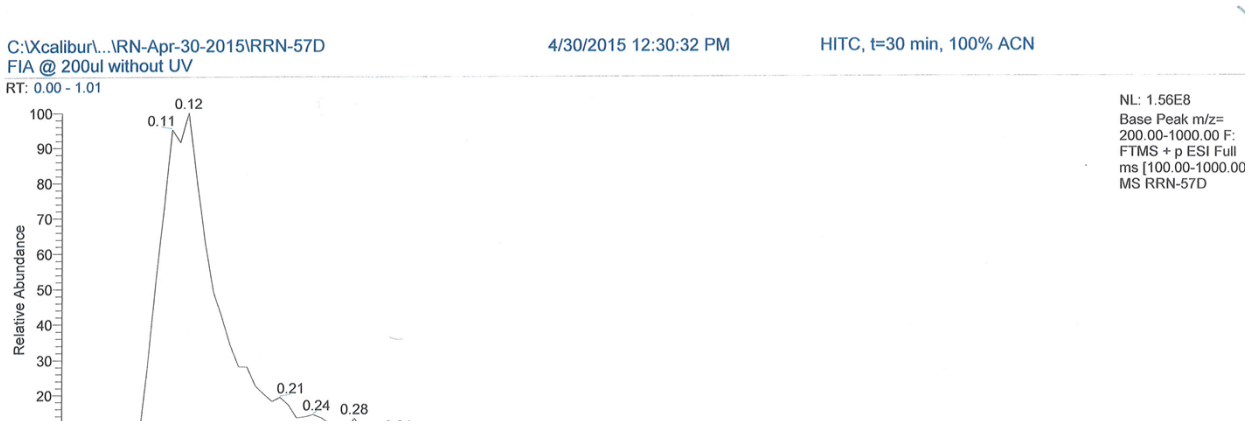
Peak E (2): HRMS (ESI) calculated for $C_{11}H_{14}NO$ $(M+H)^+$ 176.1075, observed 176.1075.

Peak G (1): HRMS (ESI) calculated for $C_{29}H_{33}N_2$ (M^+) 409.2638, observed 409.2639.

MS/MS Experiment of Photolysis of 1

A 20 μM solution of **1** in MeCN was generated from a 1 mM acetonitrile stock solution. The sample was irradiated with 20 mW/cm^2 740 nm (± 20 nm) light in a HPLC vial for 30 minutes at 22 °C, then immediately analyzed by direct inject HRMS. The m/*z* of 441.25 was analyzed by collision-induced dissociation MS/MS spectrometry.

HRMS Spectrum of Photolysis of 1



MS/MS Spectra of CID of 441.25 m/*z*

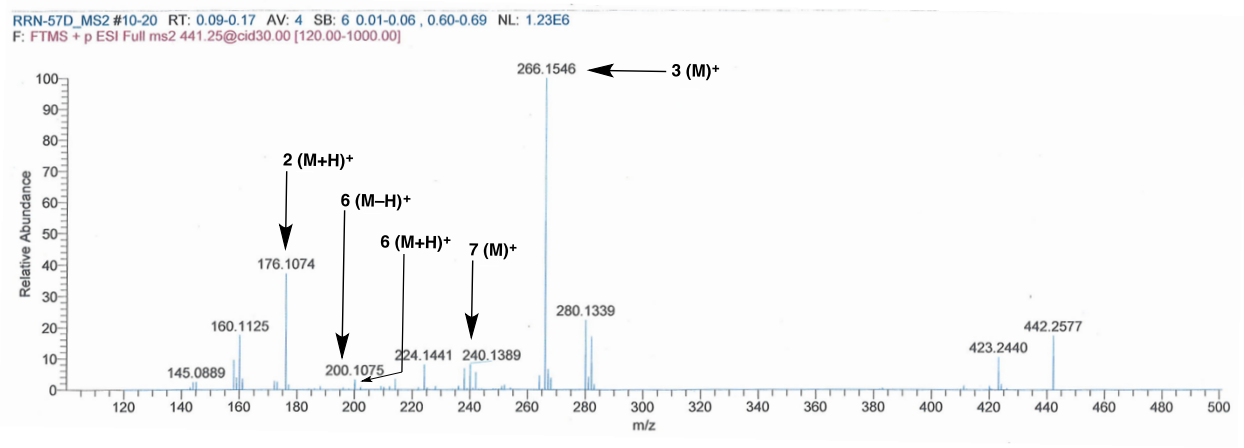


Figure S1: Time Course Yields of 740 nm and 420 nm Photobleaching of 1

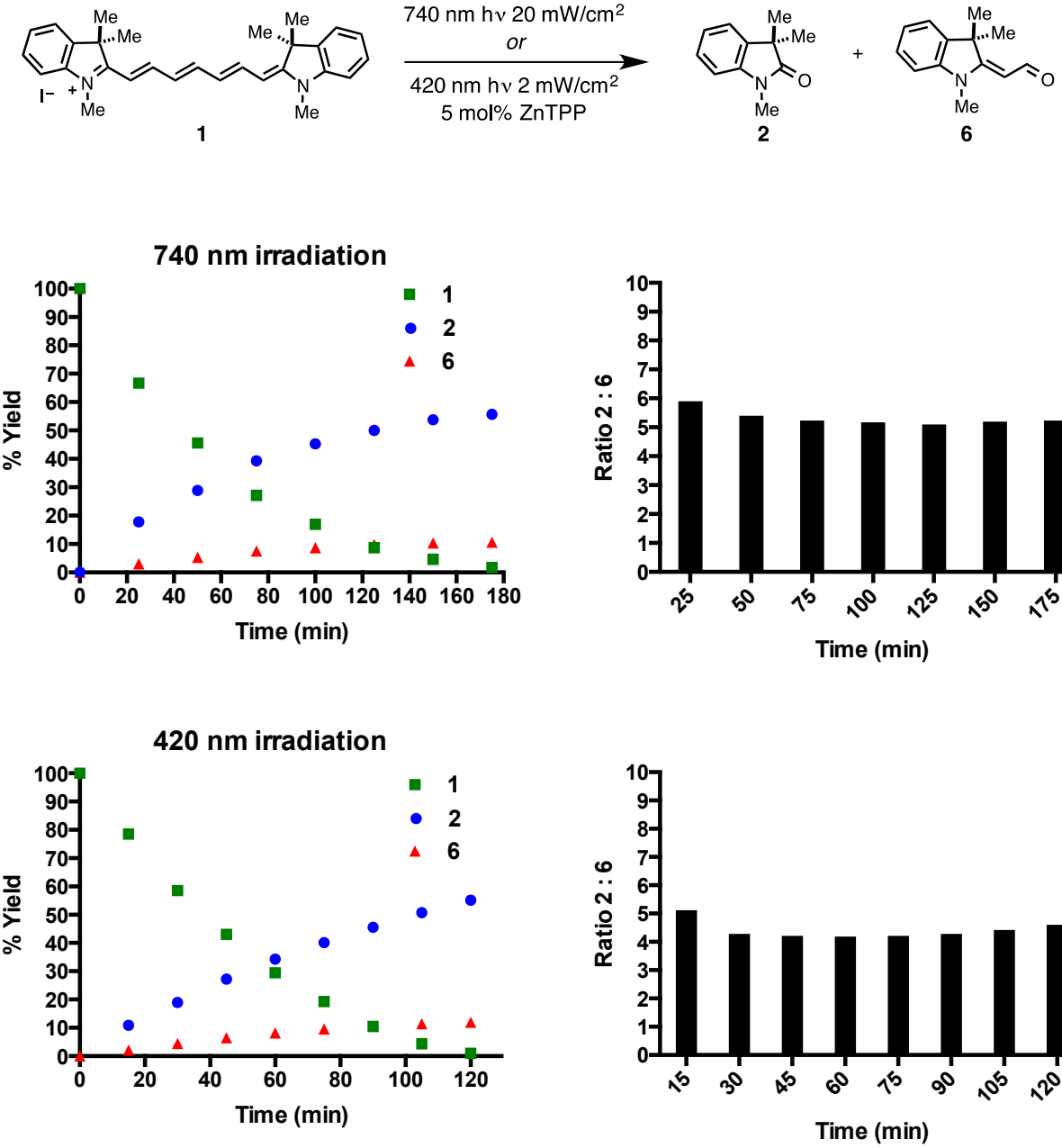
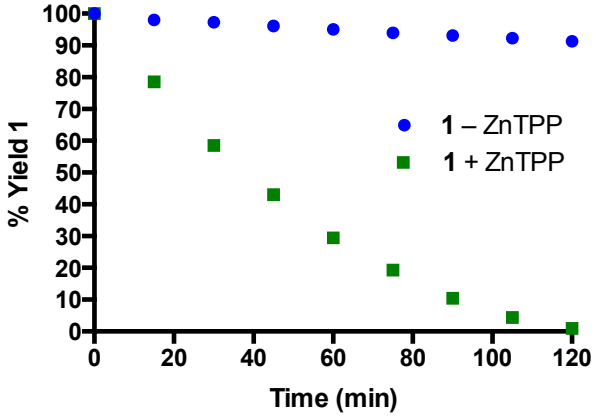


Figure S2: 420 nm hν (2 mW/cm^2) Photobleaching of 1 +/– ZnTPP



Procedures for Bleaching of 1 with Singlet Oxygen (Table 1)

740 nm irradiation: A 20 μM solution of **1** in 50 % MeCN/H_2O was generated from a 1 mM DMSO stock solution. The sample was irradiated at 22 °C with 20 mW/cm^2 740 nm (± 20 nm) light in a HPLC vial for 120 minutes. The sample was then analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

420 nm irradiation with ZnTPP: A 20 μM solution of **1** in 50 % MeCN/H_2O was generated from a 1 mM DMSO stock solution. A portion of a 1 mM THF stock solution of 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine zinc (ZnTPP) was added to achieve 5 mol % concentration of ZnTPP. The sample was irradiated at 22 °C with 2 mW/cm^2 420 nm light in a HPLC vial for 120 minutes. The sample was then analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

Thermal $^1O_2$ generation: Endoperoxide **12** was synthesized according to known procedures.[3] A 20 mM solution of **12** in H_2O was prepared. A solution of 20 μM **1** and 4 mM **12** in 50 % MeCN/H_2O was generated from their respective stock solutions. The sample was heated to 34 °C in a HPLC vial for 4 hours in the dark. The sample was then analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

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[3] J. M. Aubry, B. Cazin and F. Duprat, *J. Org. Chem.*, 1989, **54**, 726-728.

Procedures for Bleaching of 1 with ROS (Table 2)

Fenton conditions: A 20 μM solution of **1** in 50 mM $NaHPO_4$ (pH = 6) was generated from a 1 mM DMSO stock solution. Solutions of $FeCl_2$ tetrahydrate (50 mM H_2O stock) and hydrogen peroxide (100 mM H_2O stock) were added in succession such that the final concentration of each was 200 μ□□□□□□□□□□μ□□□□□□□□□□□□□□□□. After 5 minutes the sample was analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

Hydrogen peroxide: A 20 μM solution of **1** in 50 mM PBS (pH = 7.4) was generated from a 1 mM DMSO stock solution. A solution of hydrogen peroxide (100 mM H_2O stock) was added such that the final concentration of H_2O_2 was either 100 μ□ or 1 mM. After 120 minutes the sample was analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

Superoxide (100 μ□): A 20 μM solution of **1** in in 50 % MeCN/H_2O was generated from a 1 mM DMSO stock solution. A solution of potassium superoxide (3 mM DMSO stock) was added such that the final concentration of KO_2 was 100 μ□. After 120 minutes the sample was analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

Superoxide (1 mM): A 20 μM solution of **1** in in 50 % MeCN/H_2O was generated from a 1 mM DMSO stock solution. Solid potassium superoxide was added in one portion, and after 120 minutes the sample was analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

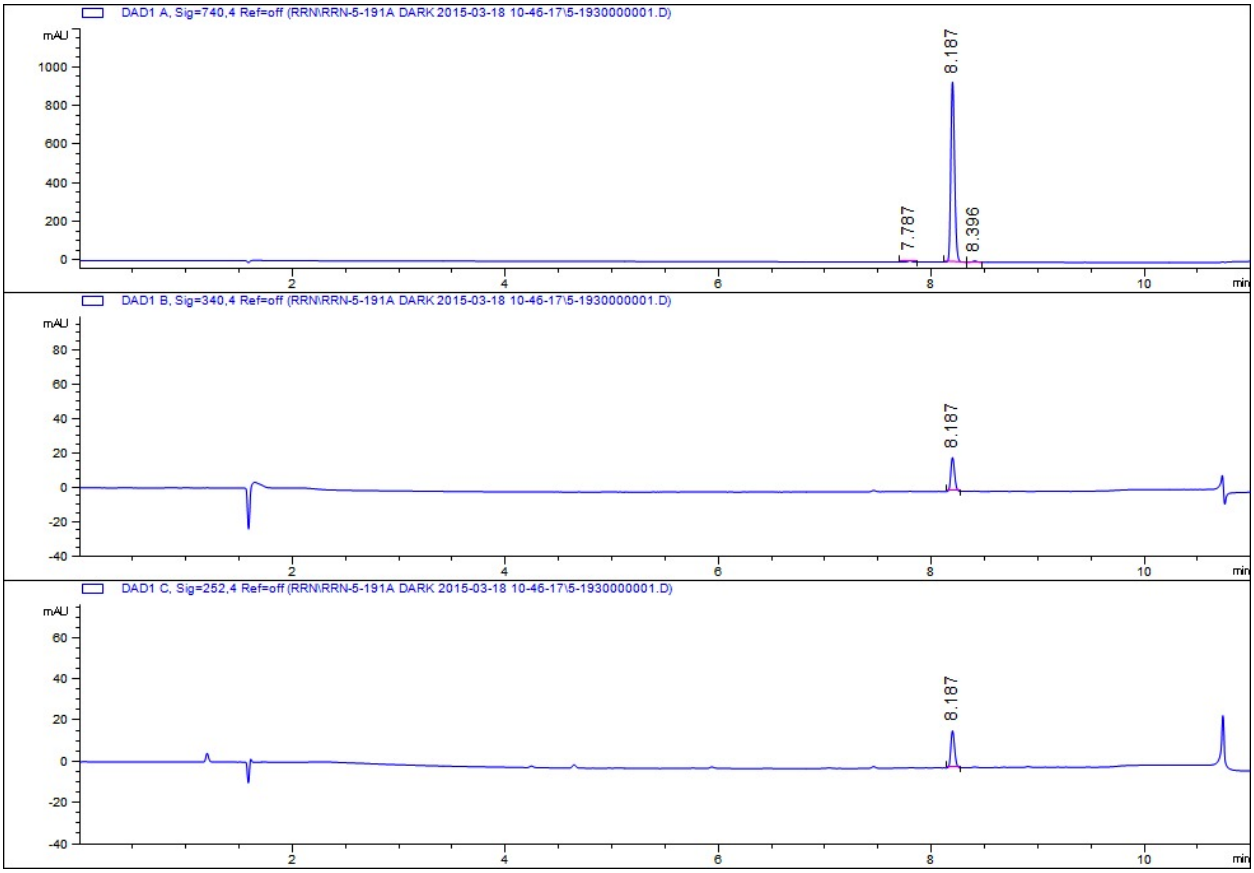
Hypochlorite: A 20 μM solution of **1** in 50 mM PBS (pH = 7.4) was generated from a 1 mM DMSO stock solution. A solution of sodium hypochlorite (100 mM H_2O stock) was added such that the final concentration of NaOCl was 100 μ□. After 20 minutes the sample was analyzed by HPLC according to

the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

Peroxynitrite: A 20 μM solution of **1** in 50 mM PBS (pH = 9) was generated from a 1 mM DMSO stock solution. A solution of sodium peroxynitrite (20 mM stock) was prepared with hydrogen peroxide and amyl nitrite and assayed according to Pryor et al.[4] A portion of this solution was added such that the final concentration of $NaONO_2$ was 150 μ□. After 5 minutes the sample was analyzed by HPLC according to the method outlined on page S4 and the yield determined by input of the peak area into the calibration equation. Reactions were run in experimental triplicate with the error expressed as the standard deviation of the mean.

[4] R. M. Uppu and W. A. Pryor, *Anal. Biochem.*, 1996, **236**, 242-249.

Chromatogram of 1 (MeCN:H_2O 1:1) t = 0 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.787	BB	0.0396	17.03045	6.48354	0.7334
2	8.187	BB	0.0387	2287.71387	929.53064	98.5214
3	8.396	VB	0.0425	17.30393	6.40259	0.7452
Totals :				2322.04824	942.41677	

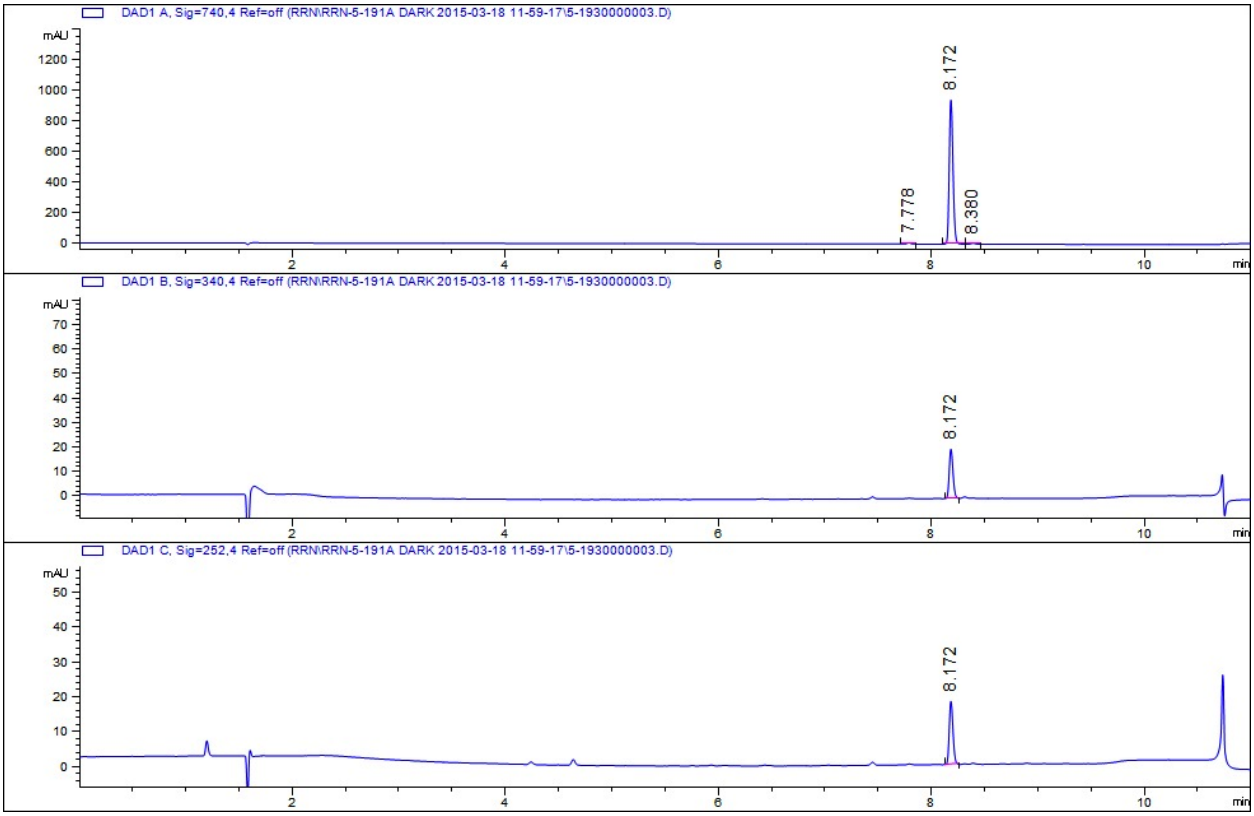
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.187	BB	0.0388	49.07401	19.86948	100.0000
Totals :				49.07401	19.86948	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.187	BB	0.0387	44.31171	17.98451	100.0000
Totals :				44.31171	17.98451	

Chromatogram of 1 (MeCN:H_2O 1:1) t = 120 min no irradiation



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.778	BB	0.0377	20.93714	8.49832	0.8937
2	8.172	BB	0.0375	2304.35303	942.23914	98.3654
3	8.380	VB	0.0424	17.35639	6.44228	0.7409
Totals :				2342.64655	957.17974	

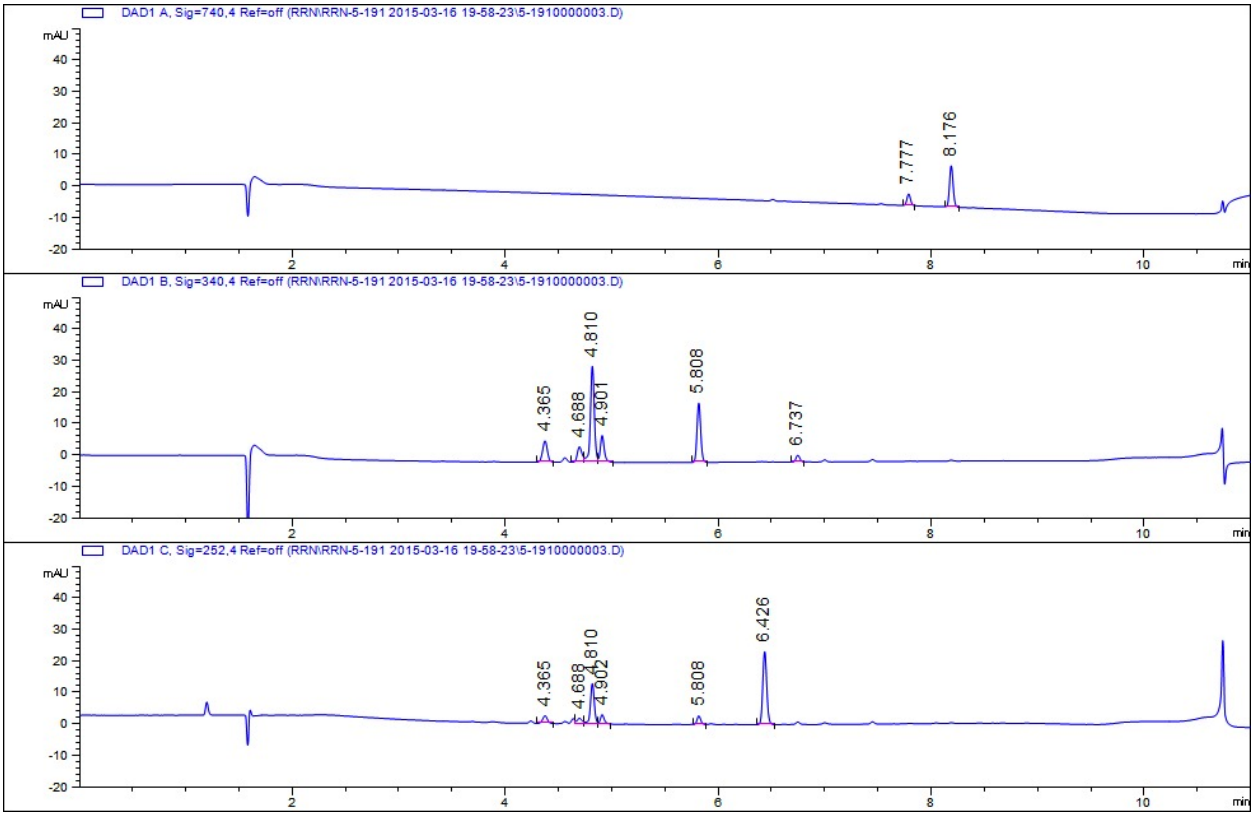
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.172	BB	0.0377	49.60467	20.18705	100.0000
Totals :				49.60467	20.18705	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.172	BB	0.0376	44.67307	18.22989	100.0000
Totals :				44.67307	18.22989	

Chromatogram of 740 nm irradiation of 1 at t = 120 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.777	BB	0.0373	8.98978	3.70399	22.3124
2	8.176	BB	0.0368	31.30081	13.15653	77.6876
Totals :				40.29060	16.86052	

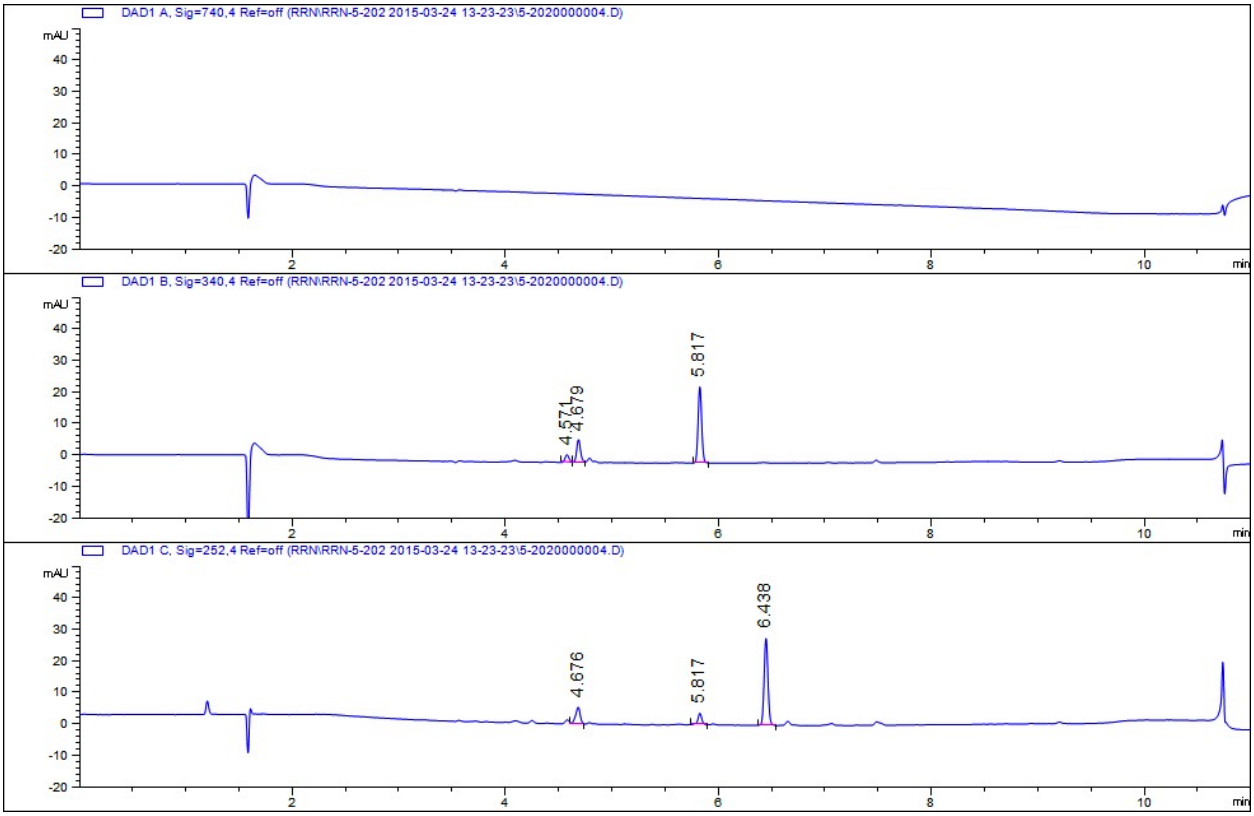
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.365	BB	0.0493	21.74986	6.80493	11.4397
2	4.688	VV	0.0489	16.01421	4.93590	8.4230
3	4.810	VV	0.0389	78.37814	30.61732	41.2244
4	4.901	VB	0.0395	22.40145	8.57631	11.7825
5	5.808	BB	0.0374	46.02819	18.87812	24.2094
6	6.737	BB	0.0389	5.55364	2.16650	2.9210
Totals :				190.12548	71.97907	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.365	BB	0.0487	7.71101	2.45066	6.3370
2	4.688	VV	0.0506	6.00769	1.76988	4.9372
3	4.810	VV	0.0385	32.61834	12.88191	26.8063
4	4.902	VB	0.0399	7.95900	3.00499	6.5408
5	5.808	BB	0.0387	6.82668	2.77771	5.6103
6	6.426	BB	0.0404	60.55895	23.25585	49.7683
Totals :				121.68167	46.14101	

Chromatogram of ZnTPP/420nm irradiation and 1 at t = 120 min



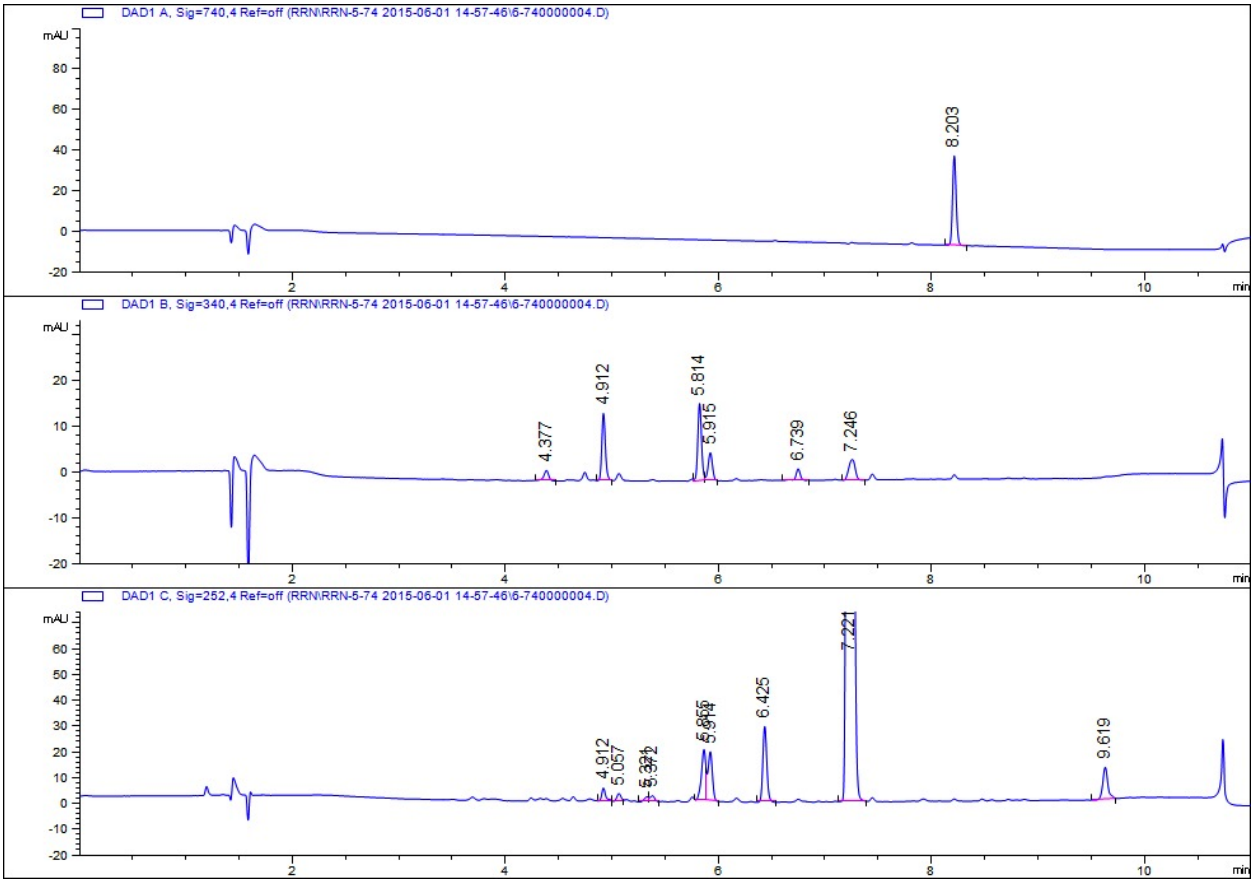
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.571	BV	0.0415	6.63607	2.46135	8.0326
2	4.679	VV	0.0390	18.74144	7.29395	22.6854
3	5.817	BB	0.0366	57.23690	24.22915	69.2820
Totals :				82.61441	33.98446	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.676	VV	0.0456	16.44247	5.38119	17.0759
2	5.817	BB	0.0401	9.82231	3.68486	10.2007
3	6.438	BB	0.0395	70.02566	27.70582	72.7234
Totals :				96.29044	36.77188	

Chromatogram of Endoperoxide 12 and 1 at t = 240 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.203	BB	0.0367	105.26933	44.37950	100.0000
Totals :				105.26933	44.37950	

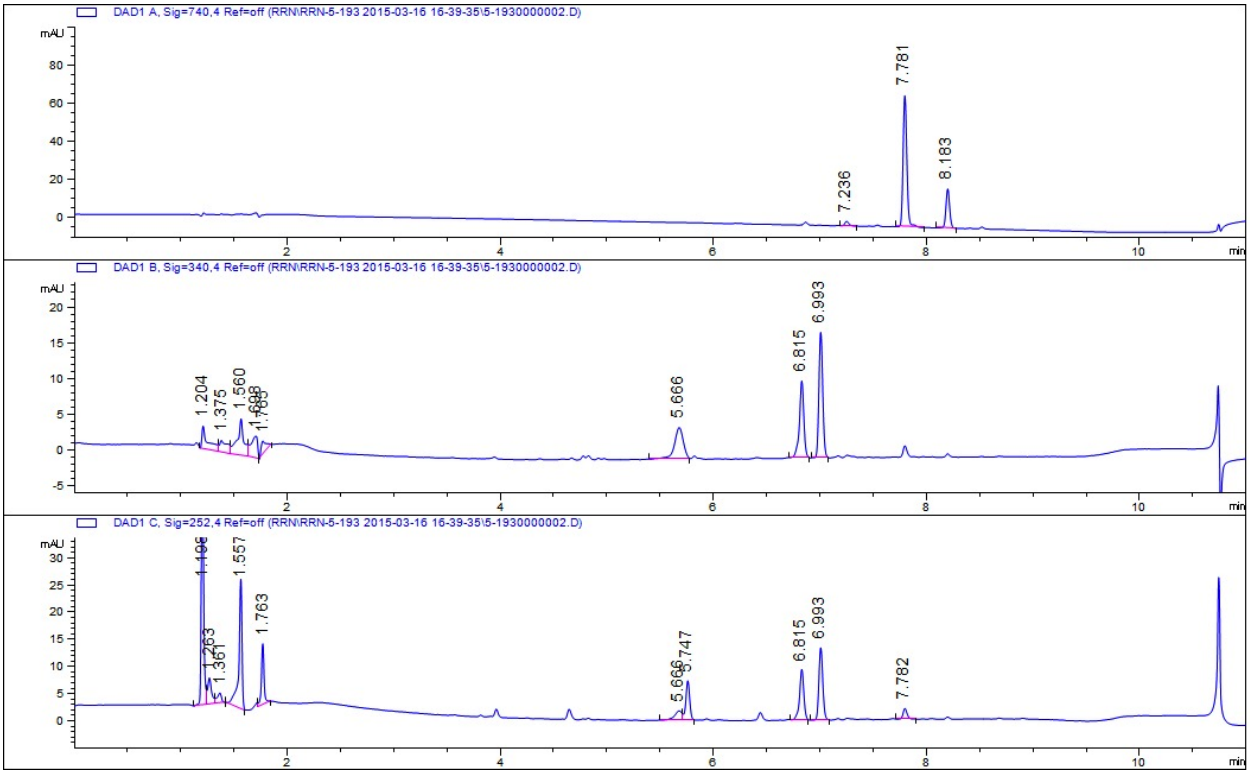
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.377	BB	0.0461	7.05976	2.28007	5.5265
2	4.912	BV	0.0366	34.97913	14.77940	27.3820
3	5.814	VV	0.0387	41.75775	16.99553	32.6884
4	5.915	VB	0.0445	17.76672	6.19384	13.9080
5	6.739	BB	0.0433	7.18031	2.51359	5.6208
6	7.246	BB	0.0680	19.00110	4.52105	14.8743
Totals :				127.74479	47.28346	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.912	VB	0.0398	13.51090	5.12290	0.2607
2	5.057	BV	0.0439	8.52217	3.02557	0.1644
3	5.321	BV	0.0447	5.99333	2.01362	0.1156
4	5.372	VV	0.0443	7.25110	2.39530	0.1399
5	5.855	BV	0.0452	60.10301	19.92372	1.1597
6	5.914	VB	0.0422	53.05488	19.22905	1.0237
7	6.425	BB	0.0404	76.84174	29.53230	1.4827
8	7.221	VV	0.0443	4915.65234	1724.34058	94.8517
9	9.619	BB	0.0497	41.53205	12.52099	0.8014
Totals :				5182.46153	1818.10403	

Chromatogram of $FeCl_2/H_2O_2$ and 1 at t = 5 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.236	BB	0.0415	6.38400	2.36486	2.8071
2	7.781	BV R	0.0390	171.61407	69.10564	75.4610
3	8.183	BB	0.0370	49.42271	20.56121	21.7318
Totals :				227.42078	92.03171	

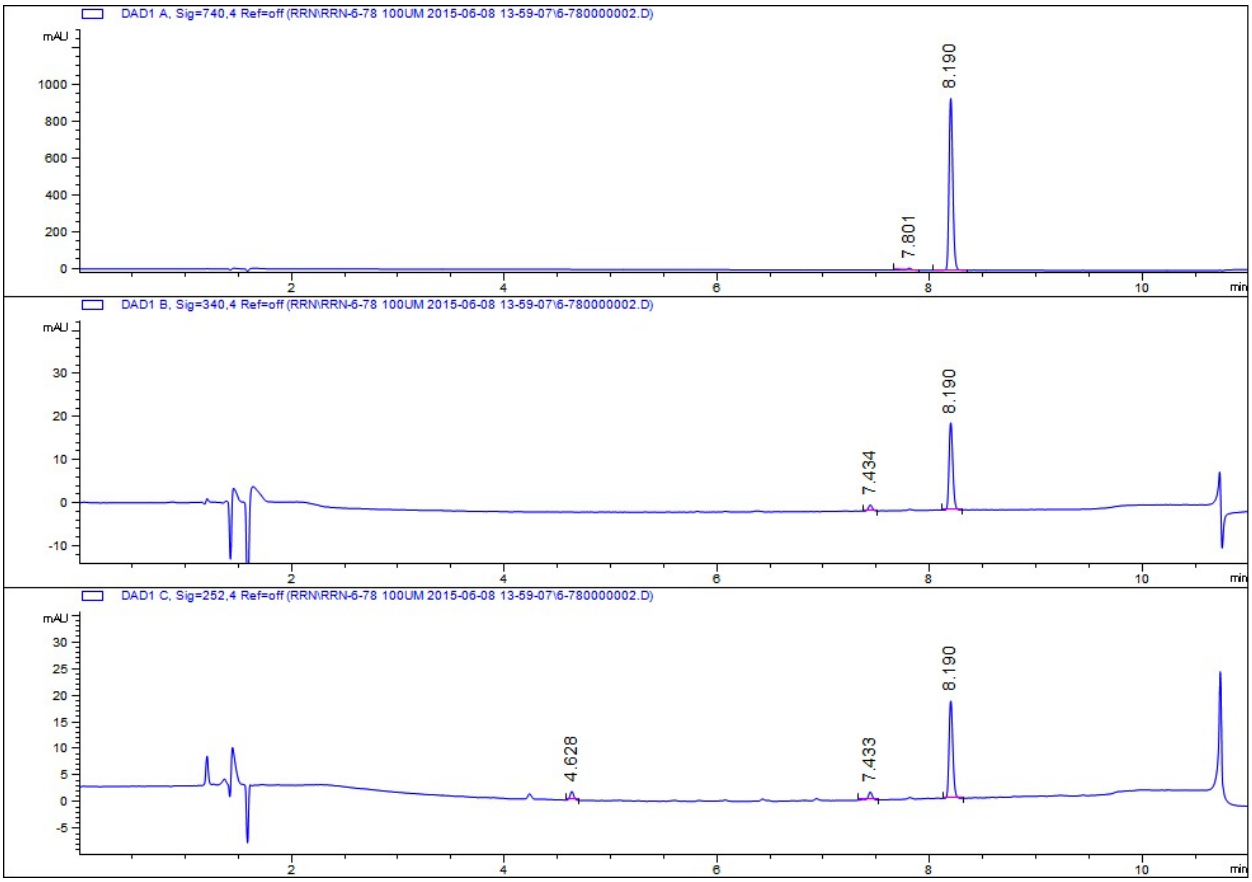
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.204	BB	0.0277	5.45006	2.93412	3.8201
2	1.560	BB	0.0519	18.88150	4.80026	13.2347
3	1.698	BV	0.0584	11.66782	3.06744	8.1784
4	1.765	BB	0.0526	7.52644	2.06332	5.2755
5	5.666	BV	0.0839	23.68478	4.32720	16.6015
6	6.815	BB	0.0430	31.32282	10.74834	21.9552
7	6.993	BB	0.0383	44.13330	17.59394	30.9345
Totals :				142.66671	45.53462	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.198	BV	0.0251	70.65514	43.23054	26.9743
2	1.263	VV	0.0413	15.25617	5.34695	5.8244
3	1.361	VV	0.0557	11.16594	2.72982	4.2629
4	1.557	VB	0.0327	54.48270	23.84456	20.8000
5	1.763	VB	0.0266	19.87379	11.26082	7.5873
6	5.666	BV	0.0725	8.16428	1.68548	3.1169
7	5.747	VB	0.0380	17.89293	7.19640	6.8310
8	6.815	BB	0.0417	25.78810	9.21399	9.8452
9	6.993	BB	0.0397	33.63025	13.21415	12.8391
10	7.782	BB	0.0394	5.02615	1.92629	1.9189
Totals :				261.93544	119.64900	

Chromatogram of 100 μ□ H_2O_2 and 1 at t = 120 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.801	BB	0.0381	26.36013	10.55824	1.1402
2	8.190	BB	0.0374	2285.58398	938.81262	98.8598
Totals :				2311.94411	949.37086	

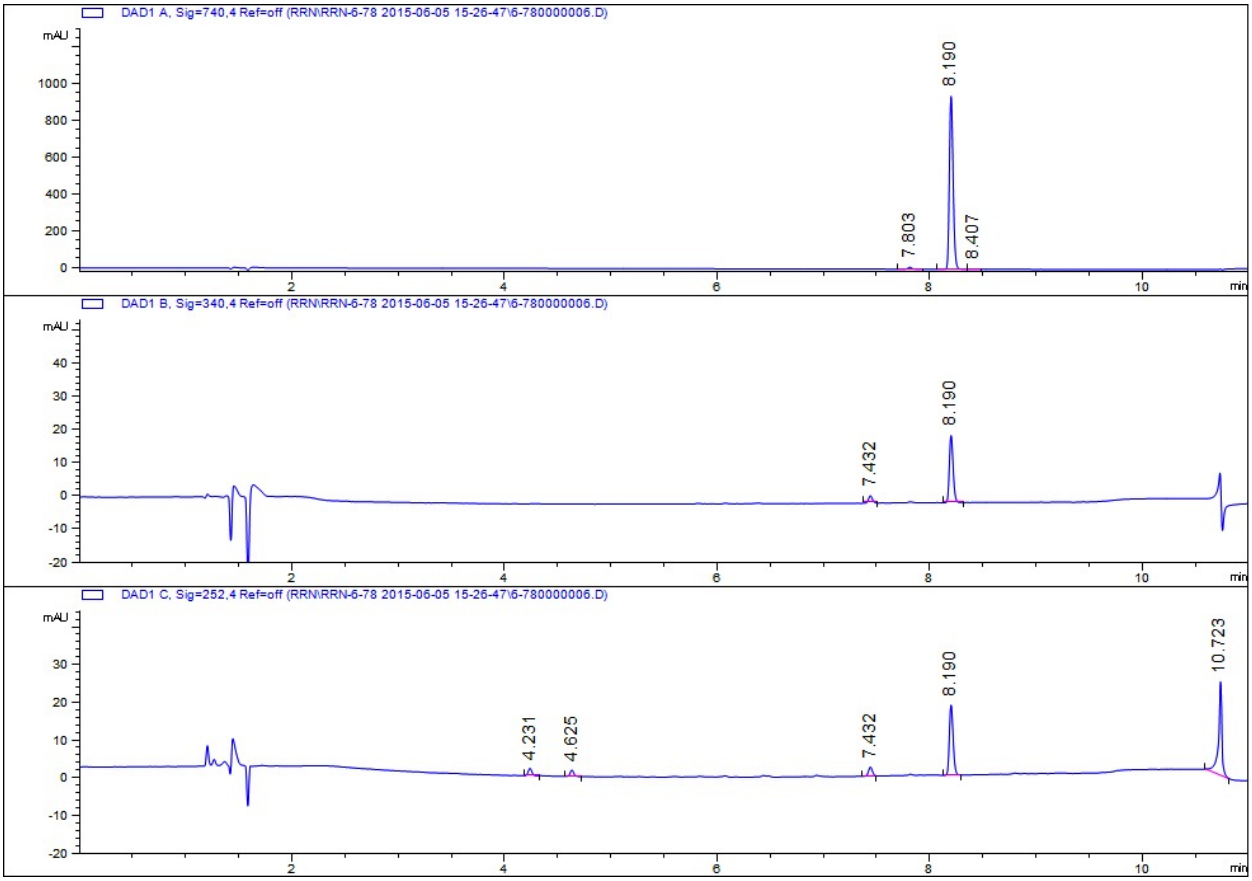
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.434	BB	0.0397	3.54736	1.39287	6.6929
2	8.190	BB	0.0375	49.45478	20.22903	93.3071
Totals :				53.00215	21.62190	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.628	BB	0.0372	4.02098	1.66182	7.5307
2	7.433	BB	0.0419	4.23775	1.50066	7.9366
3	8.190	BB	0.0377	45.13607	18.37856	84.5327
Totals :				53.39479	21.54104	

Chromatogram of 1 mM H_2O_2 and 1 at t = 120 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.803	BB	0.0375	25.70829	10.50994	1.0987
2	8.190	BB	0.0375	2311.75269	945.66095	98.7984
3	8.407	BB	0.0371	2.40874	1.00095	0.1029
Totals :				2339.86972	957.17184	

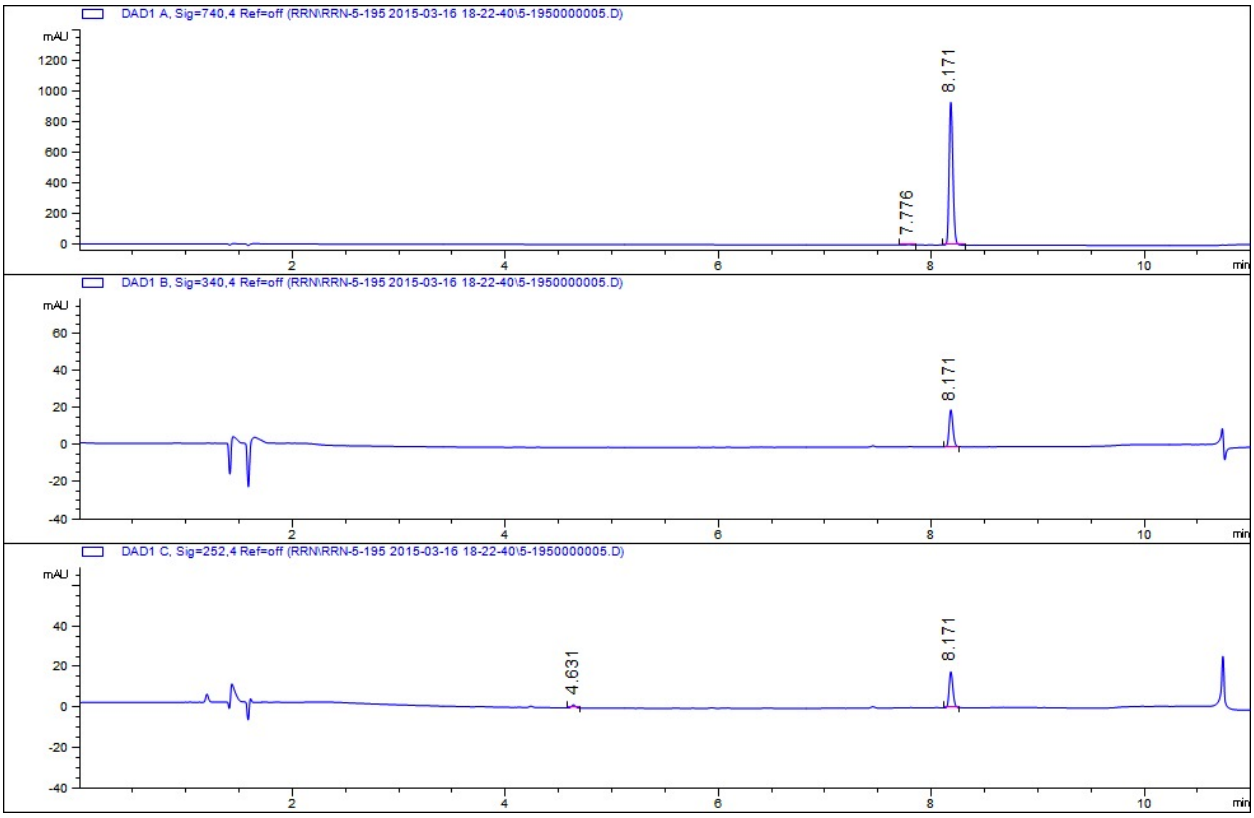
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.432	BB	0.0399	5.73573	2.23721	10.2519
2	8.190	BB	0.0377	50.21234	20.39607	89.7481
Totals :				55.94807	22.63327	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.231	BB	0.0373	4.76780	1.96385	4.1118
2	4.625	BB	0.0379	4.12173	1.66640	3.5546
3	7.432	BB	0.0401	6.20584	2.40600	5.3520
4	8.190	BB	0.0378	45.85848	18.55782	39.5488
5	10.723	BB	0.0320	55.00016	24.65057	47.4327
Totals :				115.95402	49.24464	

Chromatogram of 100 μ□ KO_2 and 1 at t = 120 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.776	BB	0.0407	10.86459	3.99486	0.4688
2	8.171	BB	0.0388	2306.44751	934.52399	99.5312
Totals :				2317.31210	938.51885	

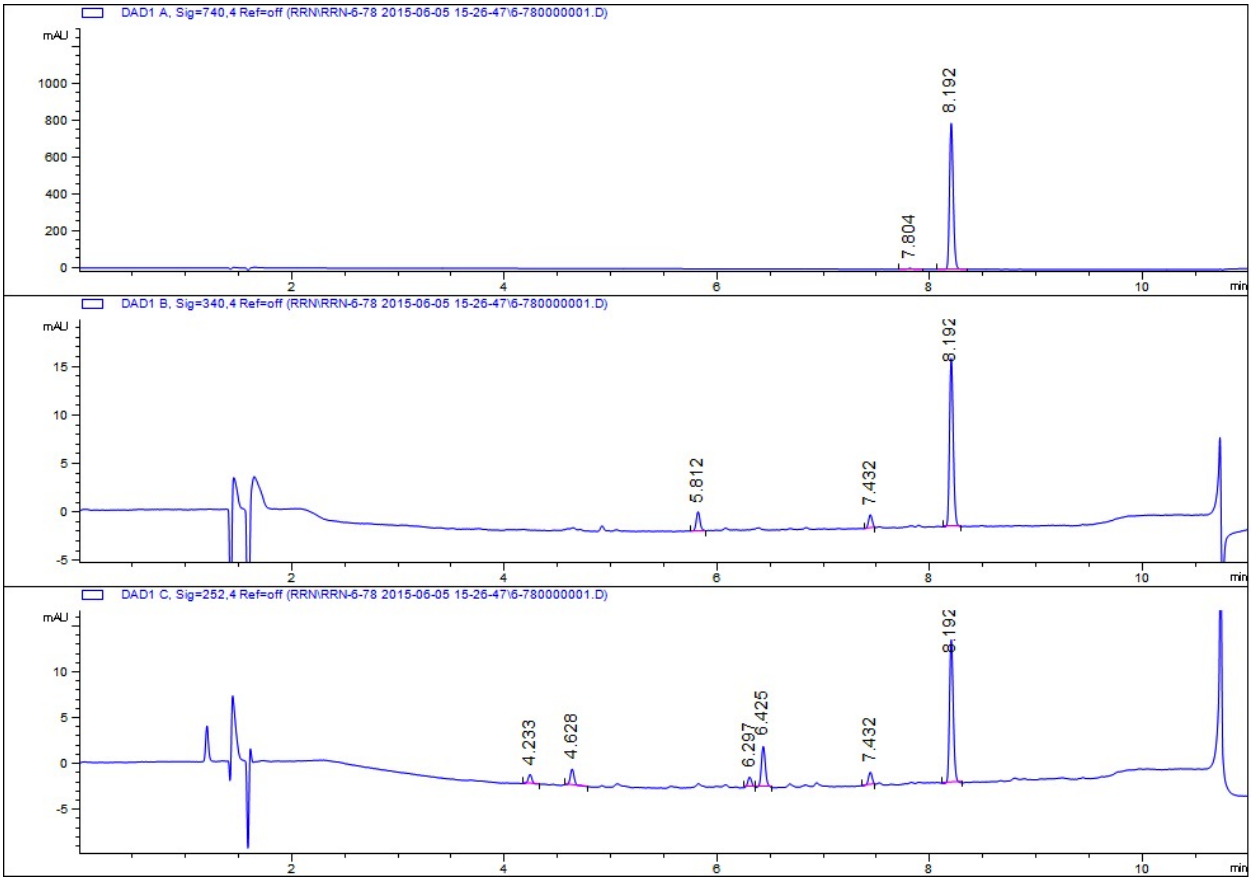
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.171	BB	0.0389	49.50911	19.95720	100.0000
Totals :				49.50911	19.95720	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.631	BB	0.0386	3.90878	1.59334	8.0426
2	8.171	BB	0.0389	44.69199	18.04410	91.9574
Totals :				48.60077	19.63743	

Chromatogram of 1 mM KO_2 and 1 at t = 120 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.804	BB	0.0384	12.50625	4.96880	0.6422
2	8.192	BB	0.0373	1935.01147	798.57294	99.3578
Totals :				1947.51772	803.54173	

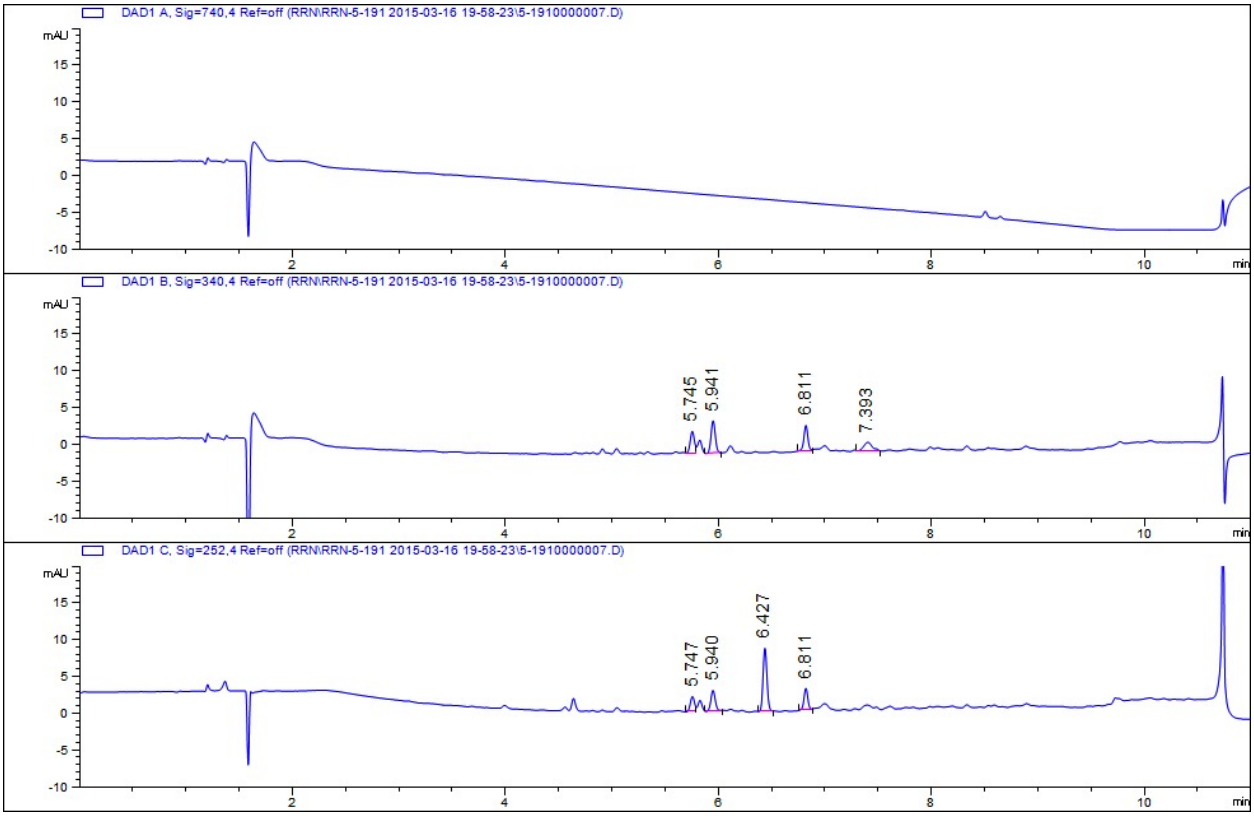
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.812	BB	0.0389	4.83695	1.95577	9.6064
2	7.432	BV	0.0392	3.49869	1.39877	6.9486
3	8.192	BB	0.0374	42.01563	17.25789	83.4450
Totals :				50.35127	20.61242	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.233	BB	0.0389	2.51560	1.01728	3.8682
2	4.628	BB	0.0405	4.64754	1.77530	7.1464
3	6.297	BV	0.0422	3.09358	1.15656	4.7569
4	6.425	VB	0.0415	12.28485	4.55358	18.8902
5	7.432	BV	0.0393	3.78139	1.45447	5.8146
6	8.192	BB	0.0377	38.71004	15.74824	59.5237
Totals :				65.03301	25.70544	

Chromatogram of NaOCl and 1 at t = 20 min



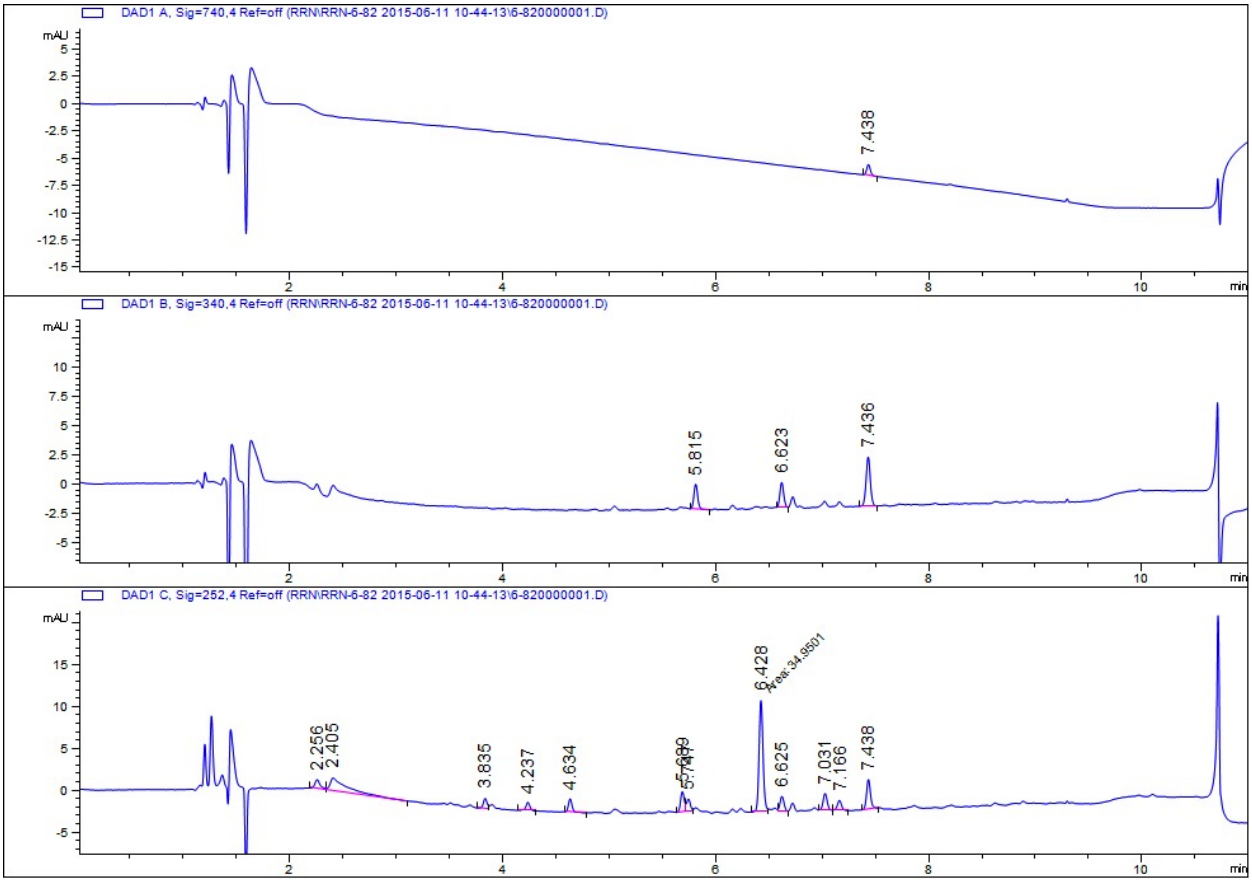
Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.745	BV	0.0433	8.64206	3.03190	22.4830
2	5.941	VB	0.0442	12.67113	4.44980	32.9650
3	6.811	BB	0.0415	9.93607	3.56841	25.8495
4	7.393	VB	0.0887	7.18890	1.22150	18.7025
Totals :				38.43816	12.27160	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.747	BV	0.0443	5.98218	2.09452	12.9818
2	5.940	VB	0.0481	9.30572	2.92626	20.1941
3	6.427	BB	0.0402	22.36613	8.63830	48.5363
4	6.811	BB	0.0411	8.42726	3.05847	18.2878
Totals :				46.08128	16.71756	

Chromatogram of $NaONO_2$ and 1 at t = 5 min



Signal 1: DAD1 A, Sig=740,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.438	BB	0.0382	2.41632	1.00037	100.0000
Totals :				2.41632	1.00037	

Signal 2: DAD1 B, Sig=340,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.815	BB	0.0394	5.37267	2.13081	23.8569
2	6.623	BV	0.0379	5.27317	2.12692	23.4151
3	7.436	BB	0.0429	11.87458	4.21037	52.7281
Totals :				22.52042	8.46811	

Signal 3: DAD1 C, Sig=252,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.256	BV	0.0549	4.13316	1.12474	4.0799
2	2.405	VB	0.1567	19.14813	1.56528	18.9012
3	3.835	BV	0.0374	3.03757	1.20696	2.9984
4	4.237	BB	0.0396	2.75049	1.01613	2.7150
5	4.634	BB	0.0371	3.83191	1.59029	3.7825
6	5.689	BV	0.0382	6.18078	2.46611	6.1011
7	5.747	VV	0.0387	3.96907	1.55797	3.9179
8	6.428	MF	0.0437	34.95007	13.32616	34.4993
9	6.625	VB	0.0424	4.82858	1.79561	4.7663
10	7.031	VV	0.0433	5.83467	2.04703	5.7594
11	7.166	VB	0.0433	3.50739	1.22974	3.4622
12	7.438	BB	0.0390	9.13475	3.55140	9.0169
Totals :				101.30657	32.47742	

Performance of MP2 and B3LYP vs. CCSD(T) and experiment for a model reaction

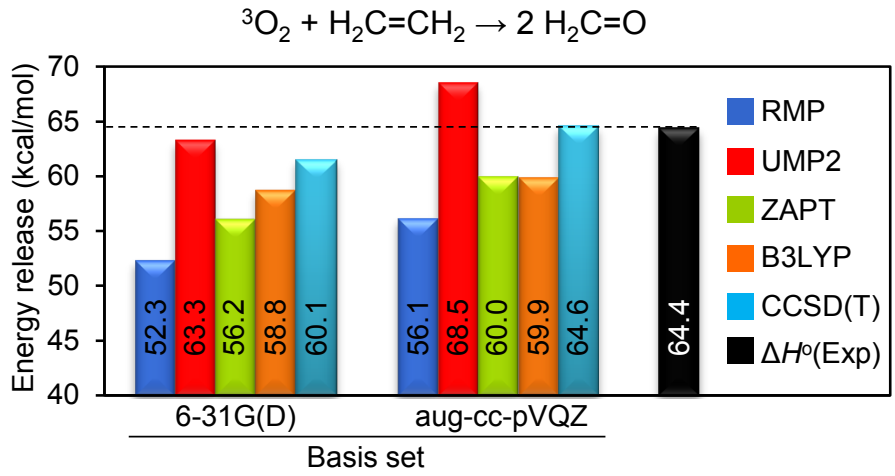


Figure S3. Computed exothermicities (electronic from optimized geometries) for the hypothetical reaction between triplet oxygen and ethylene to produce two equivalents of formaldehyde. All relevant energies were computed using GAMESS[1] except the following which were taken from the NIST Chemistry WebBook (webbook.nist.gov/chemistry): experimental standard enthalpy of reaction ($\Delta H°$), MP2/aug-cc-pVQZ energies for ethylene and formaldehyde, CCSD(T)/aug-cc-pVQZ energies for all species. Additionally, the UCCSD(T)/6-31G(d) computation for triplet oxygen was performed using Gaussian.[2] The 6-31G(d)[3] and aug-cc-pVQZ[4,5] basis sets used spherical functions. The three different open-shell second-order perturbation theory methods RMP, UMP2, and ZAPT are only relevant for the triplet oxygen, i.e., standard closed-shell MP2 energies were used for ethylene and formaldehyde. The methods used are:

- MP2: closed-shell second-order Møller-Plesset perturbation theory.[6]
- RMP: restricted open-shell second-order Møller-Plesset perturbation theory.[7,8]
- UMP2: unrestricted open-shell second-order Møller-Plesset perturbation theory.[6]
- ZAPT: Z-averaged restricted open-shell second-order Møller-Plesset perturbation theory.[9,10]
- B3LYP: density functional theory[11] using the B3LYP functional[12,13] as implemented in GAMESS.[1,14] A tight Lebedev grid was used: number of radial points in Euler-MacLaurin quadrature = 120, number of angular points in the Lebedev grid = 590.
- CCSD(T): coupled-cluster with singles and doubles and non-iterative triples.[15,16]

Computational References

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Geometrical conformations considered in minima searches for the O_2-Cy7 intermediates

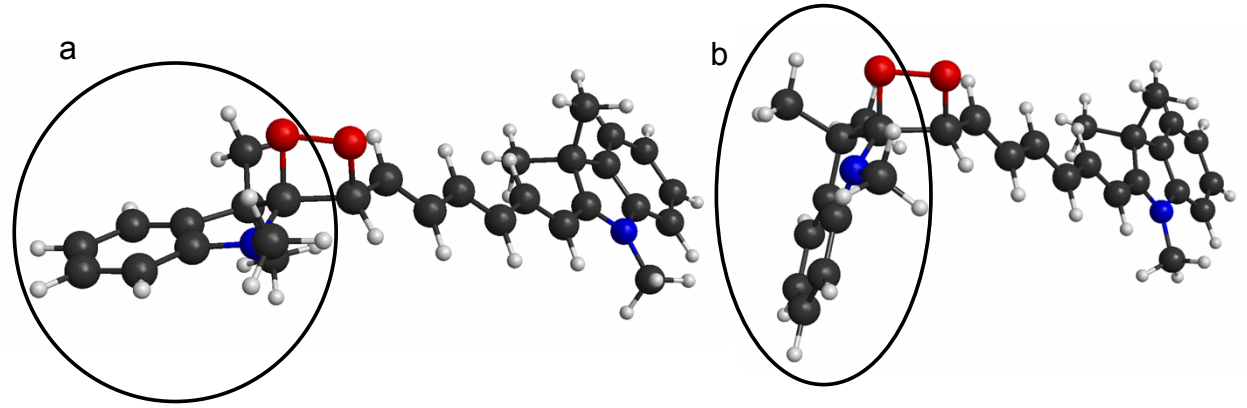

Figure S4. Illustrations of the possible "up" (a) and "down" (b) conformations of the affected terminal 1,3,3-trimethylindoline group for intermediate **10** (O_2 attached over C2/C1′).

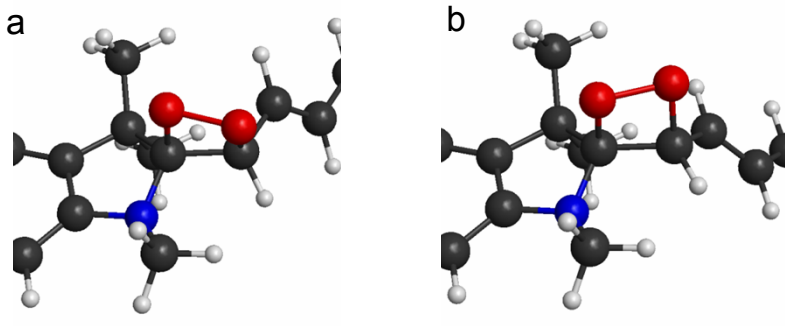

Figure S5. Illustrations of the possible "right" (a) and "left" (b) twist conformations of the dioxetane group using the model of intermediate **10** (O_2 attached over C2/C1′). Analogous dioxetane twist conformations were considered for the other three types of intermediate: intermediate **13** (O_2 attached over C1′/C2′), intermediate **11** (O_2 attached over C2′/C3′), and intermediate **14** (O_2 attached over C3′/C4′).

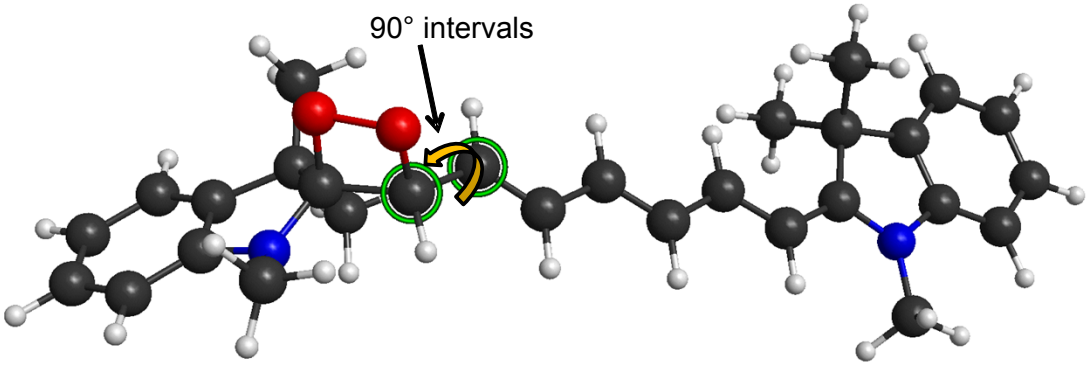

Figure S6. Illustration of the rotational degree of freedom about the C1′−C2′ bond for intermediate **10** (O_2 attached over C2/C1′). Starting structures for optimizations utilized 90° intervals for the H−C1′−C2′−H dihedral angle.

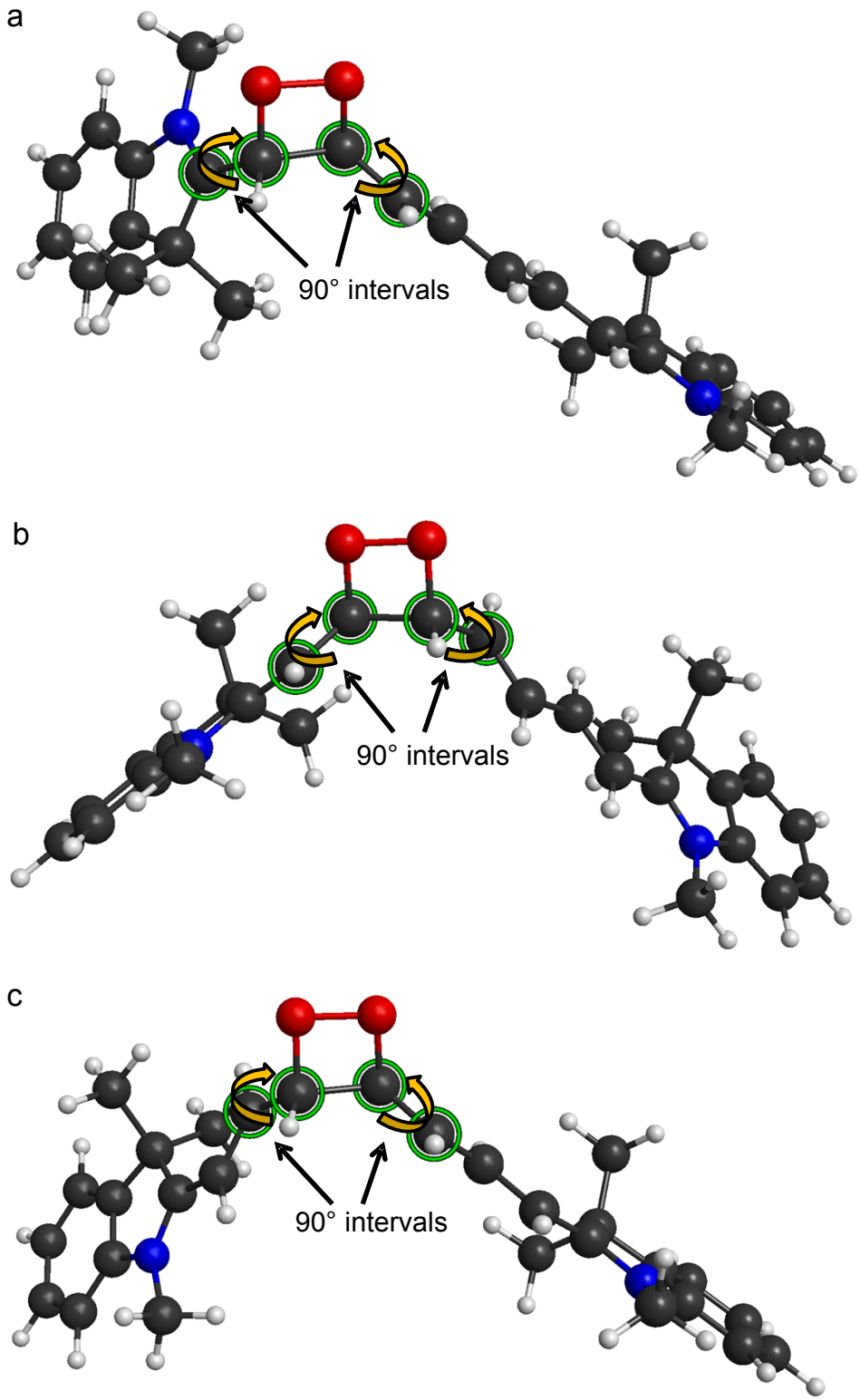

Figure S7. Illustration of the rotational degrees of freedom about the indicated C−C bonds for intermediates **13** (O_2 attached over C1′/C2′), **11** (O_2 attached over C2′/C3′), and **14** (O_2 attached over C3′/C4′). Starting structures for optimizations utilized 90° intervals for each of the H−C−C−H dihedral angles.

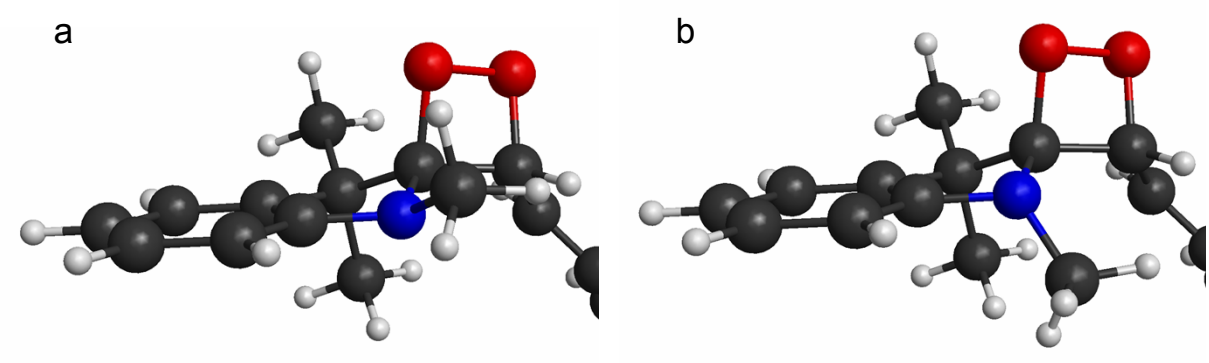

Figure S8. Illustrations of the considered "non-inverted" (a) and "inverted" (b) conformations of the affected N-Methyl group for the "up" conformation of intermediate **10** (O_2 attached over C2/C1′). Only the "non-inverted" exists, i.e., the "inverted" (b) structure optimizes to the "non-inverted" (a).

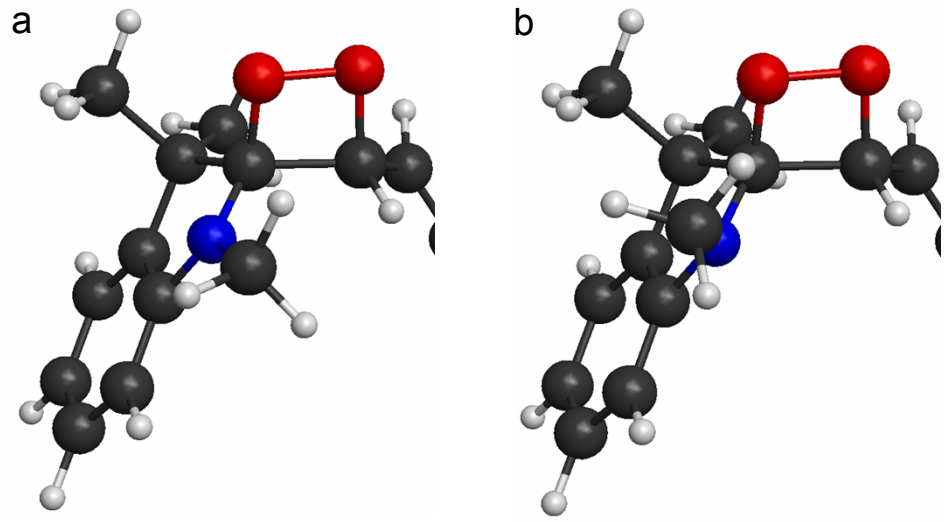

Figure S9. Illustrations of the considered "non-inverted" (a) and "inverted" (b) conformations of the affected N-Methyl group for the "down" conformation of intermediate **10** (O_2 attached over C2/C1′). Only the "non-inverted" exists, i.e., the "inverted" (b) structure optimizes to the "non-inverted" (a).

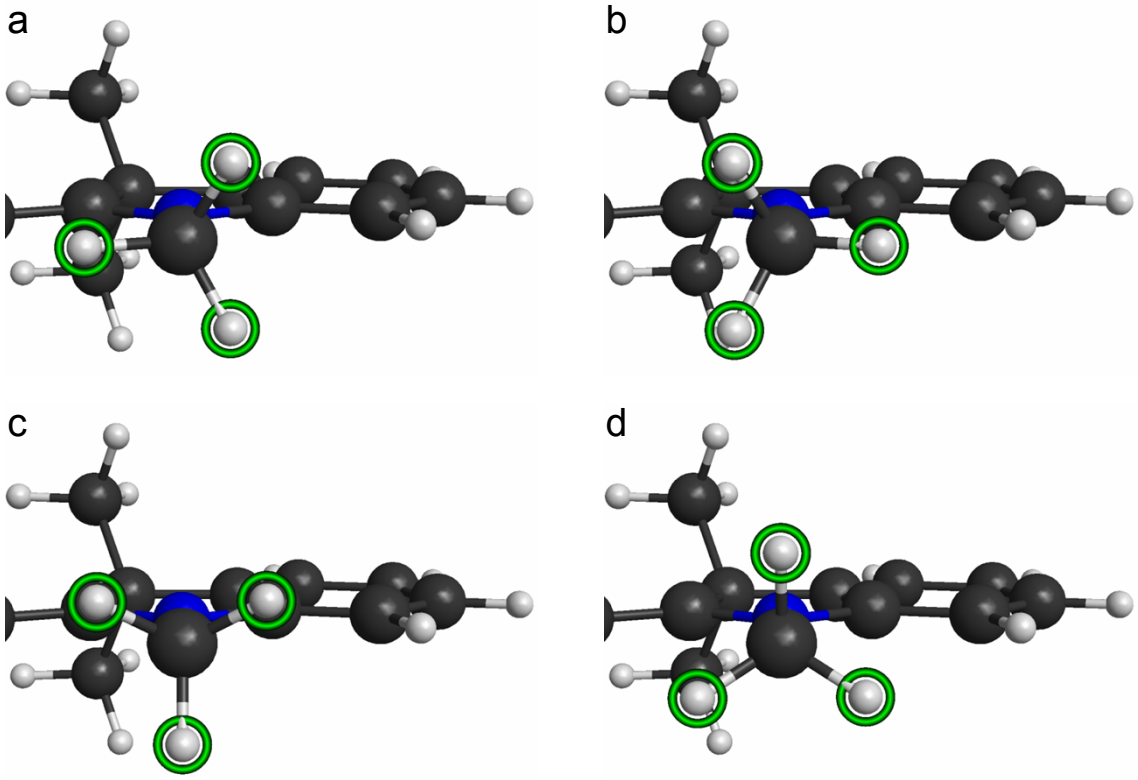

Figure S10. Illustrations of the considered N-methyl proton conformations of an indoline group, N-methyl proton orientations on both indole groups were probed. Typically, only one of the eclipsed conformations, (a) or (b), was a true minimum and if not then both staggered conformations (c) and (d) were true minima.

Lowest energy dioxetane intermediate structures

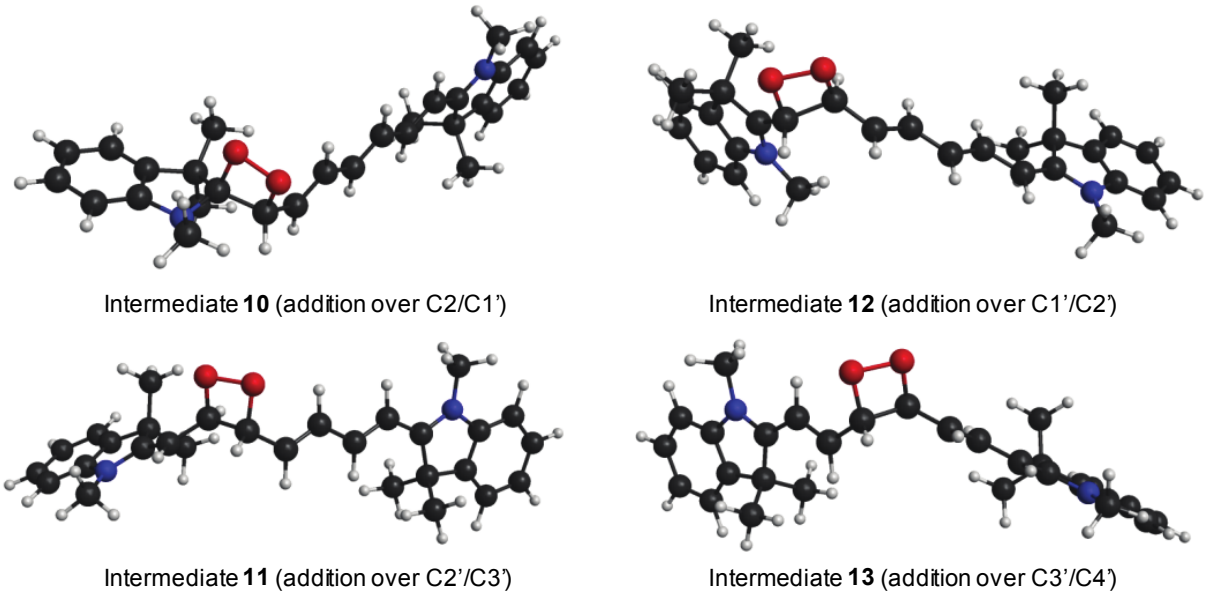

Figure S11. Lowest energy (electronic) MP2/6-31G(d) dioxetane intermediate minima.

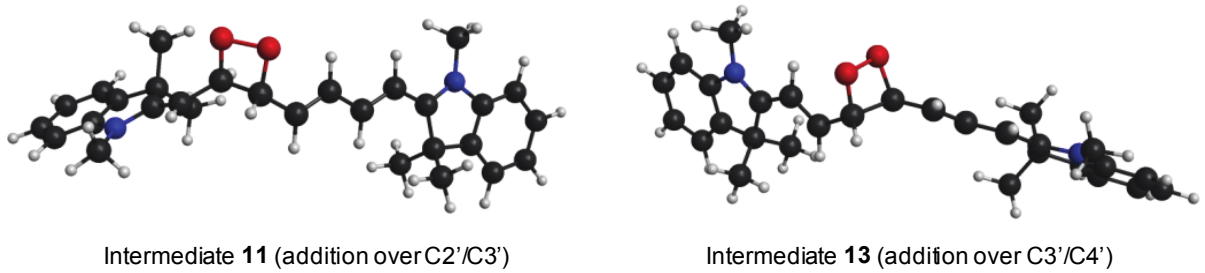

Figure S12. Lowest G_{298} energy MP2/6-31G(d) dioxetane intermediate structures where different from lowest electronic energy minima.

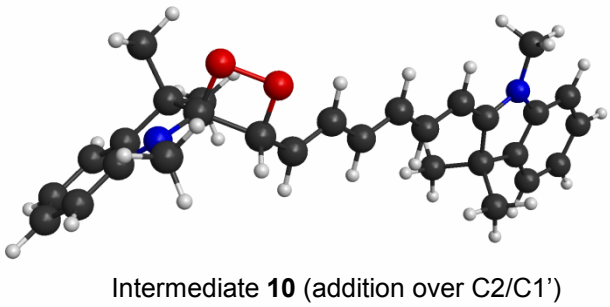

Figure S13. Lowest G_{298} energy B3LYP/cc-pVTZ dioxetane intermediate **10** structure which is the only difference from lowest electronic energy structures.

Optimized geometries (Cartesian coordinates (Å)) and energies

Electronic energies (E) given in hartree; Gibbs free energies (G_{298}), where given, are in kcal/mol and do not include electronic energies.

I. $^3\Sigma_g^-$ O_2

UB3LYP/6-31G(d)

E = –150.25665

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6072058350
O	8.0	0.0000000000	0.0000000000	0.6072058350

UB3LYP/cc-pVTZ

E = –150.32102

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6030514627
O	8.0	0.0000000000	0.0000000000	0.6030514627

UB3LYP/aug-cc-pVQZ

E = –150.33580

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6019322826
O	8.0	0.0000000000	0.0000000000	0.6019322826

ZAPT/6-31G(d)

E = –149.95546

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6286680957
O	8.0	0.0000000000	0.0000000000	0.6286680957

ZAPT/aug-cc-pVQZ

E = –150.17402

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6175091937
O	8.0	0.0000000000	0.0000000000	0.6175091937

UMP2/6-31G(d)

E = –149.94409

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6235011201
O	8.0	0.0000000000	0.0000000000	0.6235011201

UMP2/aug-cc-pVQZ

E = –150.16043

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6094391480
O	8.0	0.0000000000	0.0000000000	0.6094391480

ROMP2/6-31G(d)

E = –149.96155

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6353298799
O	8.0	0.0000000000	0.0000000000	0.6353298799

ROMP2/aug-cc-pVQZ

E = –150.18018

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6236252909
O	8.0	0.0000000000	0.0000000000	0.6236252909

UCCSD(T)(FULL)/6-31G(d)

E = –149.95876

ATOM	CHARGE	X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.6098500000
O	8.0	0.0000000000	0.0000000000	0.6098500000

II. Ethylene (C_2H_4)

B3LYP/6-31G(d)

E = –78.52760

ATOM	CHARGE	X	Y	Z
C	6.0	-0.6657957275	0.0000000000	0.0000000000
C	6.0	0.6657957275	0.0000000000	0.0000000000
H	1.0	1.2401530915	0.9238203865	0.0000000000
H	1.0	-1.2401530915	0.9238203865	0.0000000000
H	1.0	1.2401530915	-0.9238203865	0.0000000000
H	1.0	-1.2401530915	-0.9238203865	0.0000000000

B3LYP/aug-cc-pVQZ

E = –78.57145

ATOM	CHARGE	X	Y	Z
C	6.0	-0.6623283123	0.0000000000	0.0000000000
C	6.0	0.6623283123	0.0000000000	0.0000000000
H	1.0	1.2318298766	0.9203575123	0.0000000000
H	1.0	-1.2318298766	0.9203575123	0.0000000000
H	1.0	1.2318298766	-0.9203575123	0.0000000000
H	1.0	-1.2318298766	-0.9203575123	0.0000000000

MP2/6-31G(d)

E = –78.28225

ATOM	CHARGE	X	Y	Z
C	6.0	-0.6687768891	0.0000000000	0.0000000000
C	6.0	0.6687768891	0.0000000000	0.0000000000
H	1.0	1.2387800002	0.9235134650	0.0000000000
H	1.0	-1.2387800002	0.9235134650	0.0000000000
H	1.0	1.2387800002	-0.9235134650	0.0000000000
H	1.0	-1.2387800002	-0.9235134650	0.0000000000

CCSD(T)(FULL)/6-31G(d)

E = –78.32394

ATOM	CHARGE	X	Y	Z
C	6.0	-0.6714247134	0.0000000000	0.0000000000
C	6.0	0.6714247134	0.0000000000	0.0000000000
H	1.0	1.2453142772	0.9260327146	0.0000000000
H	1.0	-1.2453142772	0.9260327146	0.0000000000
H	1.0	1.2453142772	-0.9260327146	0.0000000000
H	1.0	-1.2453142772	-0.9260327146	0.0000000000

III. Formaldehyde (H_2CO)

B3LYP/6-31G(d)

E = –114.43894

ATOM	CHARGE	X	Y	Z
C	6.0	0.0000000000	0.0000000000	-0.6198942962
H	1.0	-0.9381982339	0.0000000000	-1.2148459777
H	1.0	0.9381982339	0.0000000000	-1.2148459777
O	8.0	-0.0000000000	0.0000000000	0.5867305615

B3LYP/aug-cc-pVQZ

E = –114.50135

ATOM	CHARGE	X	Y	Z
C	6.0	-0.0000000000	0.0000000000	-0.6225071759
H	1.0	-0.9381831164	0.0000000000	-1.2082675641
H	1.0	0.9381831164	0.0000000000	-1.2082675641
O	8.0	0.0000000000	0.0000000000	0.5761866141

MP2/6-31G(d)

E = –114.16360

ATOM	CHARGE	X	Y	Z
C	6.0	-0.0000000000	0.0000000000	-0.6275645188
H	1.0	-0.9350599657	0.0000000000	-1.2148135595
H	1.0	0.9350599657	0.0000000000	-1.2148135595
O	8.0	0.0000000000	0.0000000000	0.5943359477

CCSD(T)(FULL)/6-31G(d)

E = –114.19038

ATOM	CHARGE	X	Y	Z
C	6.0	0.0000000000	0.0000000000	-0.6265753261
H	1.0	-0.9389278820	0.0000000000	-1.2150505646
H	1.0	0.9389278820	0.0000000000	-1.2150505646
O	8.0	0.0000000000	0.0000000000	0.5938207653

IV. 1,1',3,3,3',3'-hexamethylindotricarbocyanine (Cy7)

B3LYP/6-31G(d): *Global minimum has C_{2v} point group.*

E = –1233.43446

ATOM	CHARGE	X	Y	Z
C	6.0	-0.0000000000	0.0000000000	-0.6338796796
H	1.0	-0.0000000000	0.0000000000	0.4578600423
C	6.0	-1.2405310955	0.0000000000	-1.2761718088
C	6.0	1.2405310955	0.0000000000	-1.2761718088
H	1.0	-1.2612806043	0.0000000000	-2.3656287964
H	1.0	1.2612806043	0.0000000000	-2.3656287964
C	6.0	-2.4513093031	0.0000000000	-0.5853083177
C	6.0	2.4513093031	0.0000000000	-0.5853083177
H	1.0	-2.3944883159	0.0000000000	0.5001120669
H	1.0	2.3944883159	0.0000000000	0.5001120669
C	6.0	-3.7088785319	0.0000000000	-1.2030706653
C	6.0	3.7088785319	0.0000000000	-1.2030706653
H	1.0	-3.7078369221	0.0000000000	-2.2900710756
H	1.0	3.7078369221	0.0000000000	-2.2900710756
C	6.0	-4.9490922856	0.0000000000	-0.5669938457
C	6.0	4.9490922856	0.0000000000	-0.5669938457
N	7.0	-6.1147769561	0.0000000000	-1.2670644969
N	7.0	6.1147769561	0.0000000000	-1.2670644969
C	6.0	-6.1963608777	0.0000000000	-2.7223297761
C	6.0	6.1963608777	0.0000000000	-2.7223297761
H	1.0	-7.2420628072	0.0000000000	-3.0252749598
H	1.0	7.2420628072	0.0000000000	-3.0252749598
H	1.0	-5.7126711874	-0.8926279882	-3.1331466213
H	1.0	5.7126711874	-0.8926279882	-3.1331466213
H	1.0	-5.7126711874	0.8926279882	-3.1331466213
H	1.0	5.7126711874	0.8926279882	-3.1331466213
C	6.0	-7.2410408394	0.0000000000	-0.4091338253
C	6.0	7.2410408394	0.0000000000	-0.4091338253
C	6.0	-8.5943883386	0.0000000000	-0.7371580117
C	6.0	8.5943883386	0.0000000000	-0.7371580117
H	1.0	-8.9460015281	0.0000000000	-1.7636572044
H	1.0	8.9460015281	0.0000000000	-1.7636572044
C	6.0	-9.5109526977	0.0000000000	0.3202570305
C	6.0	9.5109526977	0.0000000000	0.3202570305
H	1.0	-10.5738581157	0.0000000000	0.0974977336
H	1.0	10.5738581157	0.0000000000	0.0974977336
C	6.0	-9.0811080463	0.0000000000	1.6504390620
C	6.0	9.0811080463	0.0000000000	1.6504390620
H	1.0	-9.8121294341	0.0000000000	2.4532490771
H	1.0	9.8121294341	0.0000000000	2.4532490771
C	6.0	-7.7132186815	0.0000000000	1.9556645197
C	6.0	7.7132186815	0.0000000000	1.9556645197
H	1.0	-7.3851041270	0.0000000000	2.9919210028

H	1.0	7.3851041270	0.0000000000	2.9919210028
C	6.0	-6.7938535784	0.0000000000	0.9152270010
C	6.0	6.7938535784	0.0000000000	0.9152270010
C	6.0	-5.2731240012	0.0000000000	0.9372532356
C	6.0	5.2731240012	0.0000000000	0.9372532356
C	6.0	-4.7460608565	-1.2785086093	1.6355256251
C	6.0	4.7460608565	-1.2785086093	1.6355256251
C	6.0	-4.7460608565	1.2785086093	1.6355256251
C	6.0	4.7460608565	1.2785086093	1.6355256251
H	1.0	-5.1151801550	-2.1807549145	1.1378486299
H	1.0	5.1151801550	-2.1807549145	1.1378486299
H	1.0	-5.1151801550	2.1807549145	1.1378486299
H	1.0	5.1151801550	2.1807549145	1.1378486299
H	1.0	-5.0952211555	-1.2974512703	2.6732611716
H	1.0	5.0952211555	-1.2974512703	2.6732611716
H	1.0	-5.0952211555	1.2974512703	2.6732611716
H	1.0	5.0952211555	1.2974512703	2.6732611716
H	1.0	-3.6528889176	-1.3159073562	1.6462336315
H	1.0	3.6528889176	-1.3159073562	1.6462336315
H	1.0	-3.6528889176	1.3159073562	1.6462336315
H	1.0	3.6528889176	1.3159073562	1.6462336315

B3LYP/cc-pVTZ: C_{2v} *structure optimized from 6-31G(d) structure and Hessian.*

E = –1233.87514

ATOM	CHARGE	X	Y	Z
C	6.0	0.0000000000	0.0000000000	-0.6349886456
H	1.0	0.0000000000	0.0000000000	0.4523974481
C	6.0	-1.2355087797	0.0000000000	-1.2734741601
C	6.0	1.2355087797	0.0000000000	-1.2734741601
H	1.0	-1.2559585418	0.0000000000	-2.3586860294
H	1.0	1.2559585418	0.0000000000	-2.3586860294
C	6.0	-2.4413887731	0.0000000000	-0.5863520250
C	6.0	2.4413887731	0.0000000000	-0.5863520250
H	1.0	-2.3823926353	0.0000000000	0.4945275538
H	1.0	2.3823926353	0.0000000000	0.4945275538
C	6.0	-3.6943619882	0.0000000000	-1.1984046598
C	6.0	3.6943619882	0.0000000000	-1.1984046598
H	1.0	-3.6965850276	0.0000000000	-2.2809186825
H	1.0	3.6965850276	0.0000000000	-2.2809186825
C	6.0	-4.9299632882	0.0000000000	-0.5645142960
C	6.0	4.9299632882	0.0000000000	-0.5645142960
N	7.0	-6.0899456021	0.0000000000	-1.2610390449
N	7.0	6.0899456021	0.0000000000	-1.2610390449
C	6.0	-6.1760831720	0.0000000000	-2.7127118287
C	6.0	6.1760831720	0.0000000000	-2.7127118287
H	1.0	-7.2183037706	0.0000000000	-3.0102086631
H	1.0	7.2183037706	0.0000000000	-3.0102086631
H	1.0	-5.6966116953	-0.8883563528	-3.1250621405

H	1.0	5.6966116953	-0.8883563528	-3.1250621405
H	1.0	-5.6966116953	0.8883563528	-3.1250621405
H	1.0	5.6966116953	0.8883563528	-3.1250621405
C	6.0	-7.2131365716	0.0000000000	-0.4059574503
C	6.0	7.2131365716	0.0000000000	-0.4059574503
C	6.0	-8.5606171374	0.0000000000	-0.7338420272
C	6.0	8.5606171374	0.0000000000	-0.7338420272
H	1.0	-8.9091559063	0.0000000000	-1.7562785913
H	1.0	8.9091559063	0.0000000000	-1.7562785913
C	6.0	-9.4752378225	0.0000000000	0.3172717875
C	6.0	9.4752378225	0.0000000000	0.3172717875
H	1.0	-10.5334025316	0.0000000000	0.0950065851
H	1.0	10.5334025316	0.0000000000	0.0950065851
C	6.0	-9.0487408832	0.0000000000	1.6415275212
C	6.0	9.0487408832	0.0000000000	1.6415275212
H	1.0	-9.7779305772	0.0000000000	2.4395893639
H	1.0	9.7779305772	0.0000000000	2.4395893639
C	6.0	-7.6868711470	0.0000000000	1.9470858534
C	6.0	7.6868711470	0.0000000000	1.9470858534
H	1.0	-7.3641624625	0.0000000000	2.9801134413
H	1.0	7.3641624625	0.0000000000	2.9801134413
C	6.0	-6.7697655297	0.0000000000	0.9129879099
C	6.0	6.7697655297	0.0000000000	0.9129879099
C	6.0	-5.2528355460	0.0000000000	0.9365391658
C	6.0	5.2528355460	0.0000000000	0.9365391658
C	6.0	-4.7271357743	-1.2743103515	1.6330438509
C	6.0	4.7271357743	-1.2743103515	1.6330438509
C	6.0	-4.7271357743	1.2743103515	1.6330438509
C	6.0	4.7271357743	1.2743103515	1.6330438509
H	1.0	-5.0915777906	-2.1729033030	1.1362359822
H	1.0	5.0915777906	-2.1729033030	1.1362359822
H	1.0	-5.0915777906	2.1729033030	1.1362359822
H	1.0	5.0915777906	2.1729033030	1.1362359822
H	1.0	-5.0774954709	-1.2943156214	2.6648587195
H	1.0	5.0774954709	-1.2943156214	2.6648587195
H	1.0	-5.0774954709	1.2943156214	2.6648587195
H	1.0	5.0774954709	1.2943156214	2.6648587195
H	1.0	-3.6392548825	-1.3090365571	1.6460370258
H	1.0	3.6392548825	-1.3090365571	1.6460370258
H	1.0	-3.6392548825	1.3090365571	1.6460370258
H	1.0	3.6392548825	1.3090365571	1.6460370258

MP2/6-31G(d): *Global minimum has C_2 point group.*

E = –1230.08006

ATOM	CHARGE	X	Y	Z
C	6.0	-0.0000000000	-0.0000000000	0.7049591620
H	1.0	-0.0000000000	-0.0000000000	-0.3888910438
C	6.0	0.0054908422	-1.2370456759	1.3490731841
C	6.0	-0.0054908422	1.2370456759	1.3490731841
H	1.0	0.0056250227	-1.2629769001	2.4396667101
H	1.0	-0.0056250227	1.2629769001	2.4396667101
C	6.0	0.0108536181	-2.4408889191	0.6448954427
C	6.0	-0.0108536181	2.4408889191	0.6448954427
H	1.0	0.0114162055	-2.3699837310	-0.4410510640
H	1.0	-0.0114162055	2.3699837310	-0.4410510640
C	6.0	0.0173504021	-3.6976011767	1.2519031621
C	6.0	-0.0173504021	3.6976011767	1.2519031621
H	1.0	0.0164765019	-3.7130968545	2.3403523592
H	1.0	-0.0164765019	3.7130968545	2.3403523592
C	6.0	0.0178690335	-4.9242321097	0.5843148698
C	6.0	-0.0178690335	4.9242321097	0.5843148698
N	7.0	0.0417492286	-6.1031143973	1.2504969185
N	7.0	-0.0417492286	6.1031143973	1.2504969185
C	6.0	0.0828864944	-6.2208935901	2.7017679623
C	6.0	-0.0828864944	6.2208935901	2.7017679623
H	1.0	0.2039917629	-7.2689660367	2.9677896159
H	1.0	-0.2039917629	7.2689660367	2.9677896159
H	1.0	-0.8445156054	-5.8418750102	3.1411514271
H	1.0	0.8445156054	5.8418750102	3.1411514271
H	1.0	0.9327364858	-5.6567696677	3.0947207073
H	1.0	-0.9327364858	5.6567696677	3.0947207073
C	6.0	0.0101388034	-7.2060234890	0.3658038056
C	6.0	-0.0101388034	7.2060234890	0.3658038056
C	6.0	0.0068996457	-8.5694528660	0.6559500849
C	6.0	-0.0068996457	8.5694528660	0.6559500849
H	1.0	0.0192345489	-8.9581829183	1.6703115737
H	1.0	-0.0192345489	8.9581829183	1.6703115737
C	6.0	-0.0224215638	-9.4472499851	-0.4336010301
C	6.0	0.0224215638	9.4472499851	-0.4336010301
H	1.0	-0.0268606893	-10.5183850131	-0.2495309983
H	1.0	0.0268606893	10.5183850131	-0.2495309983
C	6.0	-0.0469685953	-8.9718404235	-1.7512603703
C	6.0	0.0469685953	8.9718404235	-1.7512603703
H	1.0	-0.0693386937	-9.6796759945	-2.5755595055
H	1.0	0.0693386937	9.6796759945	-2.5755595055
C	6.0	-0.0453669037	-7.5962659841	-2.0165429377
C	6.0	0.0453669037	7.5962659841	-2.0165429377
H	1.0	-0.0666617934	-7.2341524784	-3.0427094235
H	1.0	0.0666617934	7.2341524784	-3.0427094235
C	6.0	-0.0177994724	-6.7138468090	-0.9415857931

C	6.0	0.0177994724	6.7138468090	-0.9415857931
C	6.0	-0.0114827922	-5.2046198965	-0.9144057987
C	6.0	0.0114827922	5.2046198965	-0.9144057987
C	6.0	-1.2945529097	-4.6652724982	-1.5686986836
C	6.0	1.2945529097	4.6652724982	-1.5686986836
H	1.0	-2.1786773288	-5.0589622106	-1.0590799323
H	1.0	2.1786773288	5.0589622106	-1.0590799323
H	1.0	-1.3290170972	-4.9857414687	-2.6147815226
H	1.0	1.3290170972	4.9857414687	-2.6147815226
H	1.0	-1.3352511903	-3.5736439523	-1.5418260559
H	1.0	1.3352511903	3.5736439523	-1.5418260559
C	6.0	1.2512688808	-4.6752536507	-1.6157184572
C	6.0	-1.2512688808	4.6752536507	-1.6157184572
H	1.0	2.1503835826	-5.0752320516	-1.1382094789
H	1.0	-2.1503835826	5.0752320516	-1.1382094789
H	1.0	1.2449563856	-4.9970541694	-2.6619514169
H	1.0	-1.2449563856	4.9970541694	-2.6619514169
H	1.0	1.3010246507	-3.5838791056	-1.5919229136
H	1.0	-1.3010246507	3.5838791056	-1.5919229136

V. Intermediate 10 (O_2 attached over C2/C1')

B3LYP/6-31G(d): Global electronic and free energy minimum.

E = –1383.66732
G_{298} = 309.956

ATOM	CHARGE	X	Y	Z
C	6.0	0.6266109606	-0.0209720862	0.6984929785
H	1.0	1.4056952069	0.0543194567	-0.0616182128
C	6.0	0.3949387406	-1.3074677604	1.2788316039
C	6.0	-0.0652109778	1.1146551346	1.0411281679
H	1.0	-0.3689521619	-1.4031601228	2.0465979128
H	1.0	-0.8440806498	1.0505051994	1.7997544828
C	6.0	1.0993872209	-2.4114053306	0.9231353640
C	6.0	0.1930346924	2.3751075894	0.4480674031
H	1.0	1.8892827300	-2.3387583104	0.1771615551
H	1.0	0.9774876945	2.4074373367	-0.3027632719
C	6.0	0.9300416950	-3.7370210323	1.5796134041
C	6.0	-0.4914940085	3.5296169412	0.7765064275
H	1.0	1.9232118661	-4.1075846338	1.8714231003
H	1.0	-1.2664058870	3.4390478980	1.5328203512
C	6.0	0.0677738401	-4.9018709745	0.9655878876
C	6.0	-0.2790476290	4.8124135018	0.2252981396
N	7.0	0.6787382417	-6.1905687714	0.9931052274
N	7.0	-1.0072060158	5.8730993591	0.6148551054
C	6.0	1.2089337170	-6.7483106712	2.2328573254
C	6.0	-2.0724165901	5.8297269683	1.6186893541
H	1.0	0.4379173661	-7.2924558051	2.7935815899
H	1.0	-2.5015630409	6.8235117798	1.7281237450
H	1.0	1.5901456956	-5.9517650860	2.8743898030
H	1.0	-1.6694791031	5.5115232841	2.5846924379
H	1.0	2.0336515958	-7.4314740511	2.0063033377
H	1.0	-2.8602857158	5.1393548999	1.3038167340
C	6.0	0.0291414002	-7.0388839201	0.0727523937
C	6.0	-0.6187256422	7.0579831918	-0.0677383057
C	6.0	0.1362091775	-8.4227297505	-0.0468193567
C	6.0	-1.1277236151	8.3478918807	0.0576439925
H	1.0	0.7664409672	-9.0060001939	0.6170546425
H	1.0	-1.9324959801	8.5978108788	0.7407293292
C	6.0	-0.6091135356	-9.0492341867	-1.0547913880
C	6.0	-0.5532379941	9.3377971717	-0.7455630786
H	1.0	-0.5458778836	-10.1284216555	-1.1646803901
H	1.0	-0.9234316029	10.3559986643	-0.6758819541
C	6.0	-1.4329771790	-8.3139184106	-1.9093278704
C	6.0	0.4862313104	9.0365043345	-1.6327130095
H	1.0	-2.0069473839	-8.8211075765	-2.6791859710
H	1.0	0.9144296811	9.8243411246	-2.2447921136
C	6.0	-1.5261653740	-6.9207039517	-1.7722241041
C	6.0	0.9806233055	7.7302294372	-1.7398690687

H	1.0	-2.1716137516	-6.3494604774	-2.4354904101
H	1.0	1.7881296991	7.5062750288	-2.4315588969
C	6.0	-0.7966923015	-6.2918134826	-0.7734418191
C	6.0	0.4183606166	6.7378659494	-0.9471709251
C	6.0	-0.6568704158	-4.8153807413	-0.4274967282
C	6.0	0.7334482416	5.2558606042	-0.8396610434
C	6.0	-2.0005526496	-4.0746930600	-0.3421696117
C	6.0	2.1930604039	5.0469188601	-0.3594458619
H	1.0	-2.6771604587	-4.5492207918	0.3721165012
H	1.0	2.3689695750	5.5380523451	0.6026312049
H	1.0	-2.4813326932	-4.0756266888	-1.3269506031
H	1.0	2.8788822182	5.4831378376	-1.0924973937
H	1.0	-1.8606443621	-3.0315013559	-0.0379361156
H	1.0	2.4404556226	3.9868148443	-0.2555393557
C	6.0	0.2488824203	-4.1608393768	-1.4994645264
C	6.0	0.4787253809	4.5502754620	-2.1970481805
H	1.0	1.2566919530	-4.5915705474	-1.4938604721
H	1.0	-0.5537468455	4.6923335048	-2.5310643061
H	1.0	-0.1800279537	-4.3407362250	-2.4904995605
H	1.0	1.1416186264	4.9791704093	-2.9550972665
H	1.0	0.3205266691	-3.0763773895	-1.3649101684
H	1.0	0.6789447278	3.4765778154	-2.1430081055
O	8.0	0.0446630074	-3.6762014884	2.7092025502
O	8.0	-0.8492552876	-4.6969057731	2.1138690999

<u>B3LYP/cc-pVTZ:</u> Lowest electronic energy structure is analogous to that for 6-31G(d) above.

E = –1384.16462

ATOM	CHARGE	X	Y	Z
C	6.0	0.5830936898	-0.0094291838	0.7046556524
H	1.0	1.3595223981	0.0584148746	-0.0525812484
C	6.0	0.3436253006	-1.2888352160	1.2845940150
C	6.0	-0.0960973723	1.1265619285	1.0425102477
H	1.0	-0.4185121468	-1.3755970546	2.0493985365
H	1.0	-0.8721272751	1.0693979091	1.7985336998
C	6.0	1.0338892186	-2.3926653135	0.9296054602
C	6.0	0.1703336358	2.3797274834	0.4502389761
H	1.0	1.8167273452	-2.3235801398	0.1825403503
H	1.0	0.9529143579	2.4030403695	-0.2965497857
C	6.0	0.8698571354	-3.7129057563	1.5830903619
C	6.0	-0.5006356217	3.5348229377	0.7725315305
H	1.0	1.8624902881	-4.0630845186	1.8863345929
H	1.0	-1.2746476624	3.4541835740	1.5245032295
C	6.0	0.0461937852	-4.8986072738	0.9643447162
C	6.0	-0.2779006011	4.8115285419	0.2226431161
N	7.0	0.6893699520	-6.1666784634	0.9765102249
N	7.0	-0.9971312158	5.8713498546	0.6059847904
C	6.0	1.2865847726	-6.7108671162	2.1867926343
C	6.0	-2.0672861693	5.8399368675	1.6001160713

H	1.0	0.5526871494	-7.2446753490	2.7961857926
H	1.0	-2.4986716244	6.8295519293	1.6891890892
H	1.0	1.7083089251	-5.9144627349	2.7942937124
H	1.0	-1.6742247657	5.5399215872	2.5707384458
H	1.0	2.0916381071	-7.3951662034	1.9213670568
H	1.0	-2.8476392429	5.1454272883	1.2926490510
C	6.0	0.0510274190	-7.0256425878	0.0657719138
C	6.0	-0.5963392441	7.0510415021	-0.0710000831
C	6.0	0.1866087358	-8.4010947311	-0.0585941868
C	6.0	-1.0940763267	8.3390349427	0.0534064555
H	1.0	0.8324892213	-8.9706311637	0.5942805311
H	1.0	-1.8967293942	8.5919276253	0.7302998250
C	6.0	-0.5509444552	-9.0401435496	-1.0561936065
C	6.0	-0.5112307111	9.3225616841	-0.7409636668
H	1.0	-0.4649860561	-10.1125802599	-1.1693176110
H	1.0	-0.8721207512	10.3391756144	-0.6720635885
C	6.0	-1.3976097776	-8.3257217254	-1.8950095776
C	6.0	0.5257858105	9.0163591192	-1.6187744932
H	1.0	-1.9661479061	-8.8424939417	-2.6556494387
H	1.0	0.9609009217	9.7991277766	-2.2241946793
C	6.0	-1.5215064006	-6.9412068730	-1.7526579840
C	6.0	1.0091924974	7.7122680998	-1.7250834623
H	1.0	-2.1858710281	-6.3881519302	-2.4047410889
H	1.0	1.8155284841	7.4873133590	-2.4104996874
C	6.0	-0.7974034420	-6.2998946666	-0.7666961222
C	6.0	0.4384942887	6.7264972079	-0.9410861889
C	6.0	-0.6889252372	-4.8246106724	-0.4209310811
C	6.0	0.7414177791	5.2458065947	-0.8342812867
C	6.0	-2.0438813861	-4.1157748572	-0.3328234547
C	6.0	2.1922606115	5.0250229569	-0.3485076906
H	1.0	-2.7080529742	-4.6056671600	0.3750152083
H	1.0	2.3658869319	5.5080688185	0.6124824369
H	1.0	-2.5208075576	-4.1226810693	-1.3136414664
H	1.0	2.8818718345	5.4578572769	-1.0722370694
H	1.0	-1.9291056483	-3.0755482177	-0.0258601136
H	1.0	2.4297203801	3.9677255409	-0.2488386709
C	6.0	0.1952324088	-4.1516151390	-1.4935207098
C	6.0	0.4888946539	4.5450634840	-2.1891631088
H	1.0	1.2065916842	-4.5604438090	-1.4962894935
H	1.0	-0.5369028413	4.6917557508	-2.5255942342
H	1.0	-0.2354842103	-4.3363719173	-2.4771627793
H	1.0	1.1534989273	4.9695959245	-2.9406876978
H	1.0	0.2453855357	-3.0715944409	-1.3568822885
H	1.0	0.6826947095	3.4756258557	-2.1350875157
O	8.0	-0.0264037286	-3.6696999622	2.7008792369
O	8.0	-0.8707645448	-4.7295542684	2.1202319067

<u>B3LYP/cc-pVTZ:</u> Lowest free energy structure.

E = –1384.16425
G_{298} (B3LYP/6-31G(d) value) = 309.570

ATOM	CHARGE	X	Y	Z
C	6.0	-0.5515472952	-1.4028825558	1.6453091368
H	1.0	-0.2018720158	-0.3869482634	1.4821072811
C	6.0	-1.7798373703	-1.7746452069	1.0378097844
C	6.0	0.2173682950	-2.2381889066	2.4109100097
H	1.0	-2.1460858056	-2.7830525575	1.1890690982
H	1.0	-0.1208077420	-3.2556447434	2.5774513889
C	6.0	-2.5025480694	-0.9277951448	0.2684778988
C	6.0	1.4347580172	-1.8351912988	2.9919378992
H	1.0	-2.1396970176	0.0797431407	0.0894771788
H	1.0	1.7442470307	-0.8154184715	2.8046407907
C	6.0	-3.7226446891	-1.3008694149	-0.4567961221
C	6.0	2.2258260485	-2.6572916767	3.7634649615
H	1.0	-3.5731490933	-1.0570434324	-1.5157978692
H	1.0	1.8694972444	-3.6673555550	3.9183663164
C	6.0	-5.2345703068	-0.8839353721	-0.0858762779
C	6.0	3.4472276828	-2.3145795161	4.3665571179
N	7.0	-5.9471980741	-0.1898191454	-1.0972004120
N	7.0	4.1414907685	-3.1994136971	5.0943949036
C	6.0	-5.9460645852	-0.5946042507	-2.4857506272
C	6.0	3.7336026585	-4.5794516981	5.3399380359
H	1.0	-6.9063688839	-0.3498138182	-2.9388354662
H	1.0	4.4944845345	-5.0757336962	5.9301117307
H	1.0	-5.8146508842	-1.6722123303	-2.5434275660
H	1.0	2.7924647800	-4.6054862334	5.8882260024
H	1.0	-5.1589679528	-0.0988815643	-3.0668862356
H	1.0	3.6197255088	-5.1135548635	4.3975831532
C	6.0	-6.2623397732	1.1003031187	-0.6723298057
C	6.0	5.3352053621	-2.6349065287	5.6083021943
C	6.0	-6.7074488410	2.1767922927	-1.4271208625
C	6.0	6.3074920727	-3.2246198710	6.4015296292
H	1.0	-6.8541272118	2.1001514337	-2.4952645940
H	1.0	6.2465594109	-4.2507696471	6.7328592539
C	6.0	-6.9613373107	3.3759585492	-0.7590162570
C	6.0	7.3926975329	-2.4331960316	6.7684963941
H	1.0	-7.3083195305	4.2305550542	-1.3242974827
H	1.0	8.1708776886	-2.8584838943	7.3866893519
C	6.0	-6.7712338890	3.4904785822	0.6126511112
C	6.0	7.4889519875	-1.1077985265	6.3524841768
H	1.0	-6.9707021408	4.4307334063	1.1076787015
H	1.0	8.3420637618	-0.5150060300	6.6514857537
C	6.0	-6.3252190410	2.3926489058	1.3565585443
C	6.0	6.4967929508	-0.5371911083	5.5549733068
H	1.0	-6.1877740940	2.4854536029	2.4264660168
H	1.0	6.5826489696	0.4938529409	5.2383158509

C	6.0	-6.0694764258	1.2014015860	0.7086161120
C	6.0	5.4140175434	-1.3129965930	5.1840730692
C	6.0	-5.6586989694	-0.1583035043	1.2422740333
C	6.0	4.2002095430	-0.9808138486	4.3395465447
C	6.0	-6.9145722632	-0.8854886493	1.7864354131
C	6.0	3.3782521520	0.1500683516	4.9987396352
C	6.0	-4.6066534137	-0.0994026581	2.3465404350
C	6.0	4.6305952907	-0.5994775552	2.9046387109
H	1.0	-7.6909599340	-0.9670493953	1.0268450655
H	1.0	3.0650251341	-0.1240151726	6.0056070326
H	1.0	-3.7349841450	0.4862031101	2.0591159558
H	1.0	5.1980557989	-1.4024313550	2.4353670136
H	1.0	-7.3178667526	-0.3150331911	2.6224394647
H	1.0	3.9938174624	1.0461228028	5.0699966264
H	1.0	-5.0390401060	0.3735600857	3.2290995142
H	1.0	5.2670584732	0.2838319022	2.9442155854
H	1.0	-6.6657769077	-1.8877204587	2.1318470131
H	1.0	2.4910142937	0.3972408979	4.4190307076
H	1.0	-4.2818438681	-1.0979922328	2.6387500863
H	1.0	3.7753238131	-0.3692831583	2.2723250386
O	8.0	-4.0957115170	-2.6718223514	-0.3002693463
O	8.0	-5.5166823256	-2.3088748984	-0.1070679682

MP2/6-31G(d): *Global electronic and free energy minimum.*

E = –1380.01726
G_{298} = 314.348

ATOM	CHARGE	X	Y	Z
C	6.0	0.7924782882	-0.0552665465	0.7370399675
H	1.0	1.5844899410	0.0706155581	-0.0052530364
C	6.0	0.5984652349	-1.3629486414	1.2922972352
C	6.0	0.0406366407	1.0345017258	1.0869107583
H	1.0	-0.1784079153	-1.5109219917	2.0398556742
H	1.0	-0.7512704296	0.9205625096	1.8275472548
C	6.0	1.3492029130	-2.4295561316	0.9181509808
C	6.0	0.2599198207	2.3179109393	0.5127567197
H	1.0	2.1510815468	-2.3105272789	0.1892977085
H	1.0	1.0594452750	2.3927667410	-0.2204672127
C	6.0	1.1729042717	-3.7807930665	1.5206303323
C	6.0	-0.4772250742	3.4266316695	0.8494160161
H	1.0	2.1478765090	-4.2056928479	1.7942511952
H	1.0	-1.2671282469	3.2900103691	1.5845145240
C	6.0	0.2356319976	-4.8052843215	0.8517673636
C	6.0	-0.3056511930	4.7240206994	0.2951155093
N	7.0	0.6792465987	-6.1623843825	0.9802723990
N	7.0	-1.0204038235	5.7697590451	0.7169560383
C	6.0	0.9706306097	-6.6860024151	2.3130373064
C	6.0	-2.0124315353	5.7569430134	1.7954643796
H	1.0	0.0569233700	-6.8384604580	2.8988470023
H	1.0	-1.6809069070	5.0885243966	2.5889880171
H	1.0	1.6212921125	-5.9965886709	2.8518347364
H	1.0	-2.9836941987	5.4378705785	1.4091181988
H	1.0	1.4996517855	-7.6349676976	2.2044090170
H	1.0	-2.0877653972	6.7647841970	2.2001217117
C	6.0	-0.1505890024	-6.9430903439	0.1405654234
C	6.0	-0.7301191146	6.9437349914	-0.0299523454
C	6.0	-0.3576249139	-8.3211087087	0.1608947892
C	6.0	-1.2902014141	8.2145962985	0.0899729457
H	1.0	0.1108494273	-8.9645770562	0.9006735790
H	1.0	-2.0753492014	8.4541567686	0.8012598187
C	6.0	-1.2038278371	-8.8633826265	-0.8164724123
C	6.0	-0.8009039088	9.1908554192	-0.7828001266
H	1.0	-1.3882334848	-9.9350928811	-0.8205398934
H	1.0	-1.2061988330	10.1976637665	-0.7329153750
C	6.0	-1.8264873248	-8.0525162607	-1.7709479186
C	6.0	0.2002586954	8.8937120977	-1.7202951026
H	1.0	-2.4829674903	-8.4994495080	-2.5131087437
H	1.0	0.5579726292	9.6776532579	-2.3823886764
C	6.0	-1.6066735682	-6.6675943497	-1.7757086455
C	6.0	0.7413256298	7.6060992848	-1.8195476946
H	1.0	-2.0982377005	-6.0363815735	-2.5143139089
H	1.0	1.5138894976	7.3885830200	-2.5540204544

C	6.0	-0.7770097353	-6.1220352568	-0.8032081086
C	6.0	0.2588438604	6.6228489645	-0.9603211980
C	6.0	-0.3147295761	-4.6981712609	-0.5903727478
C	6.0	0.6251187096	5.1679367736	-0.8223134012
C	6.0	-1.4377023240	-3.6754811558	-0.7398176822
C	6.0	2.1044786138	5.0386798882	-0.4092529506
H	1.0	-2.2709549948	-3.9074574098	-0.0735933146
H	1.0	2.2927846495	5.5728038703	0.5264670833
H	1.0	-1.8010892795	-3.6901648654	-1.7729490066
H	1.0	2.7288822208	5.4825295117	-1.1902302198
H	1.0	-1.0835948345	-2.6648393932	-0.5180230820
H	1.0	2.4034810822	3.9957674816	-0.2838192744
C	6.0	0.8262973817	-4.4110715047	-1.5815529592
C	6.0	0.3289147492	4.4211886618	-2.1356253265
H	1.0	1.6736490777	-5.0802469027	-1.4029414842
H	1.0	-0.7233454938	4.5299155353	-2.4135649858
H	1.0	0.4631884812	-4.5843424900	-2.5993184299
H	1.0	0.9414956339	4.8502903054	-2.9339897448
H	1.0	1.1634356059	-3.3719541274	-1.5180830907
H	1.0	0.5618585638	3.3568983260	-2.0580877225
O	8.0	0.2893023241	-3.7370906832	2.6752510275
O	8.0	-0.7910094254	-4.4322710671	1.8640511326

VI. Intermediate 12 (O_2 attached over C1'/C2')

B3LYP/6-31G(d): *Global electronic and free energy minimum.*

E = –1383.65676
G_{298} = 309.289

ATOM	CHARGE	X	Y	Z
C	6.0	-0.3443939729	-0.4208213719	-0.9722239776
H	1.0	-0.6564768037	-0.9688938406	-0.0796380204
C	6.0	-1.2727000595	-0.2268832420	-1.9596469499
C	6.0	1.0092761318	0.0065559118	-1.0108294952
H	1.0	-0.9971002300	0.2873020188	-2.8790965072
H	1.0	1.3461311363	0.5538041411	-1.8909510959
C	6.0	-2.6390024985	-0.7157130439	-1.8692176554
C	6.0	1.9117428784	-0.2631371092	-0.0054647719
H	1.0	-2.8212604652	-1.2957005266	-0.9547478070
H	1.0	1.5412416113	-0.8178358245	0.8534769342
C	6.0	-3.9036248826	0.2316597312	-2.1936029551
C	6.0	3.2734910258	0.1256010082	-0.0271393368
H	1.0	-3.5784306412	1.1420588650	-2.7091250337
H	1.0	3.5930929298	0.6736609085	-0.9101174913
C	6.0	-4.8284831678	0.5770712072	-1.1002442843
C	6.0	4.2250098484	-0.1273234540	0.9425974572
N	7.0	-5.7367832398	-0.2080695282	-0.5459845201
N	7.0	5.5254111284	0.2870246185	0.8135122431
C	6.0	-6.1131411418	-1.5837706982	-0.9125044956
C	6.0	6.0325292805	1.0144558459	-0.3380616294
H	1.0	-5.9118152252	-2.2374138616	-0.0590751603
H	1.0	7.0971965971	1.2039991503	-0.2079749093
H	1.0	-5.5483674709	-1.8957875056	-1.7855756150
H	1.0	5.8918015240	0.4304413412	-1.2547851124
H	1.0	-7.1836886673	-1.6008367143	-1.1352750358
H	1.0	5.5167333805	1.9756677976	-0.4471119811
C	6.0	-6.3875796487	0.4530273067	0.5426238548
C	6.0	6.3039763755	-0.0834746540	1.9306648711
C	6.0	-7.3973709923	-0.0401557349	1.3618897389
C	6.0	7.6542508045	0.1522582710	2.1792147152
H	1.0	-7.8145334011	-1.0340479865	1.2395425457
H	1.0	8.2884984477	0.6880800980	1.4803945266
C	6.0	-7.8595492302	0.8146582568	2.3678419538
C	6.0	8.1840883758	-0.3306783524	3.3817031117
H	1.0	-8.6473865060	0.4745739204	3.0327625775
H	1.0	9.2344310880	-0.1611736607	3.6007474806
C	6.0	-7.3223714568	2.0977630161	2.5278619535
C	6.0	7.3879132400	-1.0226586312	4.2978551544
H	1.0	-7.7010394336	2.7401046786	3.3171274307
H	1.0	7.8216837418	-1.3880485315	5.2238103713
C	6.0	-6.3061685512	2.5674886210	1.6849028443
C	6.0	6.0308873580	-1.2480425609	4.0268422909

H	1.0	-5.9010540797	3.5665421329	1.8192711169
H	1.0	5.4141557906	-1.7874053956	4.7415954455
C	6.0	-5.8386557746	1.7286645191	0.6806944519
C	6.0	5.4936501484	-0.7741595863	2.8380932626
C	6.0	-4.7827401309	1.9240720675	-0.3887377969
C	6.0	4.0788278770	-0.8701250210	2.2849167361
C	6.0	-3.3742582631	2.1806211169	0.2076733819
C	6.0	3.6851401662	-2.3533078475	2.0780462637
C	6.0	-5.1732916307	3.0642529895	-1.3684508306
C	6.0	3.0839858552	-0.1546660109	3.2307801541
H	1.0	-3.0977633764	1.4060082594	0.9297886098
H	1.0	4.3883786221	-2.8563609492	1.4069613275
H	1.0	-6.1481356833	2.8825929532	-1.8314024861
H	1.0	3.3636708563	0.8938655752	3.3746001983
H	1.0	-3.3765700061	3.1441595707	0.7266963964
H	1.0	3.7027046217	-2.8764264405	3.0403784783
H	1.0	-5.2302560192	4.0056679251	-0.8130146660
H	1.0	3.0905492695	-0.6441308384	4.2108108317
H	1.0	-2.6071669533	2.2171819364	-0.5722520942
H	1.0	2.6804899544	-2.4536777609	1.6565215679
H	1.0	-4.4243504018	3.1832053530	-2.1578843080
H	1.0	2.0607964936	-0.1857404993	2.8441429972
O	8.0	-4.3685227744	-0.7467738783	-3.1228451181
O	8.0	-3.0498047689	-1.4713498222	-3.0511873547

<u>B3LYP/cc-pVTZ:</u> Lowest electronic and free energy structure is analogous to that for 6-31G(d) above.

E = –1384.15581

ATOM	CHARGE	X	Y	Z
C	6.0	-0.3223626978	-0.3917876326	-0.9326096572
H	1.0	-0.6271757595	-0.9501332907	-0.0492921580
C	6.0	-1.2552922872	-0.1807018741	-1.9014157762
C	6.0	1.0282955684	0.0298367033	-0.9748641762
H	1.0	-0.9866983806	0.3424619613	-2.8129131569
H	1.0	1.3588596744	0.5852510691	-1.8469716937
C	6.0	-2.6161138619	-0.6718284679	-1.8078513452
C	6.0	1.9330314044	-0.2543958612	0.0143223880
H	1.0	-2.7897776198	-1.2392841683	-0.8901180653
H	1.0	1.5657865050	-0.8167036595	0.8640641486
C	6.0	-3.8730426359	0.2605474089	-2.1517938289
C	6.0	3.2919735943	0.1256809677	-0.0092577715
H	1.0	-3.5529028913	1.1713365071	-2.6594884128
H	1.0	3.6095366466	0.6807275075	-0.8830660882
C	6.0	-4.8187309505	0.5953810835	-1.0751248657
C	6.0	4.2445004108	-0.1419196573	0.9467780769
N	7.0	-5.6946662719	-0.2085908779	-0.5161718151
N	7.0	5.5415084109	0.2633452759	0.8139784973
C	6.0	-5.9990934473	-1.6090875280	-0.8398355489

C	6.0	6.0487879229	0.9963641792	-0.3294312810
H	1.0	-5.8149079633	-2.2142272170	0.0466093622
H	1.0	7.1143952101	1.1585770727	-0.2107545751
H	1.0	-5.3894347130	-1.9402036197	-1.6685343292
H	1.0	5.8853023613	0.4337916874	-1.2500590487
H	1.0	-7.0519294914	-1.6810730766	-1.1088448838
H	1.0	5.5570557246	1.9670658122	-0.4182305812
C	6.0	-6.3897887742	0.4519848078	0.5422920437
C	6.0	6.3215845358	-0.1178418091	1.9205361589
C	6.0	-7.3851624779	-0.0585684705	1.3583052216
C	6.0	7.6687328507	0.1098343851	2.1625553440
H	1.0	-7.7575193608	-1.0676692498	1.2587772323
H	1.0	8.2976825004	0.6471393428	1.4675739482
C	6.0	-7.8957254575	0.7983145295	2.3299128999
C	6.0	8.2027408298	-0.3823563870	3.3526047481
H	1.0	-8.6746163877	0.4450063908	2.9908659867
H	1.0	9.2503203462	-0.2193775872	3.5664117379
C	6.0	-7.4177188450	2.1009195517	2.4607534900
C	6.0	7.4133096442	-1.0755350097	4.2634928643
H	1.0	-7.8325818432	2.7443712843	3.2241123204
H	1.0	7.8498981654	-1.4481218024	5.1796592104
C	6.0	-6.4155104855	2.5885957575	1.6215983887
C	6.0	6.0592570889	-1.2925339865	3.9998638613
H	1.0	-6.0581779371	3.6035063076	1.7342485107
H	1.0	5.4497705581	-1.8332171747	4.7127256360
C	6.0	-5.9010479452	1.7476017110	0.6510425306
C	6.0	5.5181617938	-0.8095487427	2.8238648700
C	6.0	-4.8461203892	1.9608865050	-0.4098481441
C	6.0	4.1028216944	-0.8951226805	2.2803784704
C	6.0	-3.4638633714	2.3133128325	0.1854176063
C	6.0	3.7027831888	-2.3702228660	2.0629613495
C	6.0	-5.2862369202	3.0393026172	-1.4315132648
C	6.0	3.1190934340	-0.1875510925	3.2360213369
H	1.0	-3.1435976839	1.5752027529	0.9200048838
H	1.0	4.3955291120	-2.8676710555	1.3848859371
H	1.0	-6.2414165726	2.7902576880	-1.8928631867
H	1.0	3.3998524016	0.8547579196	3.3850543102
H	1.0	-3.5286288559	3.2801850026	0.6829097977
H	1.0	3.7253883065	-2.8998757559	3.0157067675
H	1.0	-5.3984817637	3.9909092795	-0.9131299876
H	1.0	3.1324451708	-0.6822136422	4.2075868969
H	1.0	-2.7017385743	2.3844816890	-0.5896196947
H	1.0	2.6994712490	-2.4610427656	1.6498899290
H	1.0	-4.5405581278	3.1686462687	-2.2149759081
H	1.0	2.0983330840	-0.2144796314	2.8577628045
O	8.0	-4.3219877921	-0.7164428310	-3.0872051105
O	8.0	-3.0257018418	-1.4567541580	-2.9775704310

MP2/6-31G(d): *Global electronic and free energy minimum.*

E = –1380.00045
G_{298} = 312.918

ATOM	CHARGE	X	Y	Z
C	6.0	-0.3674601992	-0.0488499292	-0.8398418353
H	1.0	-0.7174200204	-0.7893420724	-0.1140262107
C	6.0	-1.2378001610	0.3477612196	-1.8153131223
C	6.0	0.9739494128	0.4074879511	-0.6854326220
H	1.0	-0.9237869552	1.0468813524	-2.5909118339
H	1.0	1.3575379699	1.1379023079	-1.3989910010
C	6.0	-2.5896922738	-0.2012727638	-1.9150194677
C	6.0	1.7968667289	-0.0627257292	0.3088634877
H	1.0	-2.8164580748	-0.9095905904	-1.1049719110
H	1.0	1.3737750687	-0.7988081467	0.9903301257
C	6.0	-3.7928718524	0.7311528986	-2.2033248908
C	6.0	3.1464406549	0.3399256434	0.4874762457
H	1.0	-3.4709921931	1.6817193890	-2.6551870040
H	1.0	3.5257582103	1.0712973234	-0.2243399895
C	6.0	-4.7948849386	0.9401010656	-1.1289141238
C	6.0	4.0063492789	-0.1171236512	1.4632907989
N	7.0	-4.5744728996	1.7382475708	-0.1084889806
N	7.0	5.3100313841	0.3050306907	1.5499907645
C	6.0	-3.3572217938	2.5233736013	0.1409618931
C	6.0	5.9103626296	1.2437515294	0.6231338436
H	1.0	-3.5701224587	3.5762742567	-0.0580306313
H	1.0	6.9708058219	1.3409491735	0.8505864968
H	1.0	-2.5479325595	2.1542131954	-0.4887082197
H	1.0	5.8036730335	0.8781041151	-0.4032244285
H	1.0	-3.0810928995	2.3900382462	1.1877913316
H	1.0	5.4359641175	2.2279680353	0.7041202032
C	6.0	-5.7037439718	1.7821943187	0.7658392314
C	6.0	5.9733474306	-0.2796867407	2.6436500605
C	6.0	-5.8576572621	2.5211686679	1.9356866755
C	6.0	7.2846955075	-0.1011124065	3.0828454186
H	1.0	-5.0901460207	3.1845250355	2.3249273550
H	1.0	7.9820323794	0.5701677671	2.5889916687
C	6.0	-7.0831095288	2.3711532872	2.5912068990
C	6.0	7.6873602305	-0.8257869970	4.2117891750
H	1.0	-7.2667315207	2.9243044800	3.5080155346
H	1.0	8.7039191341	-0.7084810519	4.5790813941
C	6.0	-8.0797093520	1.5201068824	2.0855344904
C	6.0	6.8095168016	-1.6925101890	4.8724928510
H	1.0	-9.0196602309	1.4287703434	2.6232983006
H	1.0	7.1508880405	-2.2421269135	5.7457398960
C	6.0	-7.8888793559	0.7896630438	0.9062179193
C	6.0	5.4945043199	-1.8551710180	4.4151040685
H	1.0	-8.6722748435	0.1363347944	0.5286546432
H	1.0	4.8133708617	-2.5299831325	4.9311600757

C	6.0	-6.6758870733	0.9317664299	0.2366040502
C	6.0	5.0836647229	-1.1398167070	3.2961666006
C	6.0	-6.1515839905	0.3025865502	-1.0262047571
C	6.0	3.7470241050	-1.1183372097	2.5899627307
C	6.0	-7.0123406397	0.6607272658	-2.2555423752
C	6.0	3.4266877474	-2.5183666841	2.0428222244
C	6.0	-6.0190947347	-1.2303176862	-0.8767661210
C	6.0	2.6578254567	-0.6251412713	3.5542703695
H	1.0	-7.1035339543	1.7447345026	-2.3705510250
H	1.0	4.2184796979	-2.8513057253	1.3657442371
H	1.0	-5.4057686132	-1.4877773981	-0.0078234208
H	1.0	2.9103407596	0.3684857300	3.9357430234
H	1.0	-8.0136718989	0.2453720311	-2.1090876493
H	1.0	3.3614113387	-3.2300743358	2.8725702203
H	1.0	-7.0192595398	-1.6464449028	-0.7242490582
H	1.0	2.5824969432	-1.3114807301	4.4042683586
H	1.0	-6.5845421013	0.2307216150	-3.1639934679
H	1.0	2.4781656691	-2.5344433911	1.4992906771
H	1.0	-5.5836396913	-1.6643771218	-1.7779821658
H	1.0	1.6801203946	-0.5719638817	3.0677491752
O	8.0	-4.2638888281	-0.1805640350	-3.2185728087
O	8.0	-2.8796798801	-0.8269493186	-3.2203550941

VII. Intermediate 11 (O_2 attached over C2'/C3')

B3LYP/6-31G(d): Global electronic and free energy minimum.

E = –1383.66163
G_{298} = 309.137

ATOM	CHARGE	X	Y	Z
C	6.0	0.0798308862	-2.1438905536	-1.3116662316
H	1.0	0.3176063090	-1.0884245563	-1.4487220704
C	6.0	-1.2039897241	-2.6023928863	-1.8730051303
C	6.0	0.9434436177	-2.9592906733	-0.6482269354
H	1.0	-1.3611289564	-2.2029630061	-2.8859971911
H	1.0	0.6803857233	-4.0084522697	-0.5337709662
C	6.0	-2.5223093374	-2.4509444674	-1.0116455872
C	6.0	2.1902532625	-2.5036411174	-0.1277496770
H	1.0	-2.2740600997	-2.3795581115	0.0491452103
H	1.0	2.4257253721	-1.4523777715	-0.2681244173
C	6.0	-3.5950723857	-1.5563148009	-1.4424350575
C	6.0	3.0825887551	-3.3315989610	0.5164442519
H	1.0	-3.8440731948	-1.6283978887	-2.4978167060
H	1.0	2.7910402740	-4.3729147108	0.6229260179
C	6.0	-4.3180840902	-0.7042614902	-0.6565841054
C	6.0	4.3430123359	-2.9601163047	1.0435640435
N	7.0	-5.3309823141	0.0834393823	-1.1640362414
N	7.0	5.1342969258	-3.8525802055	1.6594343473
C	6.0	-5.7347666671	0.0648111168	-2.5572879174
C	6.0	4.8025303209	-5.2655873764	1.8604984087
H	1.0	-6.5549533197	0.7657788805	-2.7090971231
H	1.0	5.5974414345	-5.7412918333	2.4310071420
H	1.0	-6.0722318559	-0.9367125954	-2.8504900401
H	1.0	3.8670338077	-5.3568298233	2.4191983100
H	1.0	-4.9011013966	0.3584681943	-3.2070055749
H	1.0	4.7062435188	-5.7730240655	0.8961096094
C	6.0	-5.9291812205	0.8709192990	-0.1622523187
C	6.0	6.3527107734	-3.2632031063	2.0960124829
C	6.0	-6.9737481594	1.7870129932	-0.2685419686
C	6.0	7.4225551651	-3.8553010927	2.7619590511
H	1.0	-7.4681739542	1.9939418559	-1.2122561544
H	1.0	7.4368179069	-4.9053380196	3.0337907445
C	6.0	-7.3797594847	2.4476003804	0.8975627283
C	6.0	8.5082037481	-3.0319626781	3.0755159387
H	1.0	-8.1926932800	3.1659834400	0.8399904147
H	1.0	9.3618223656	-3.4571270906	3.5943258435
C	6.0	-6.7613414677	2.1982205256	2.1247901978
C	6.0	8.5104488951	-1.6754553811	2.7312831855
H	1.0	-7.0943827141	2.7214439322	3.0160885400
H	1.0	9.3667473197	-1.0588180097	2.9866556813
C	6.0	-5.7123916852	1.2710666166	2.2095305232
C	6.0	7.4215542952	-1.1042625824	2.0603477352

H	1.0	-5.2343660404	1.0753307625	3.1665230970
H	1.0	7.4336672936	-0.0502611096	1.7966471252
C	6.0	-5.3008271795	0.6103632189	1.0610014016
C	6.0	6.3368895308	-1.9117943282	1.7427471211
C	6.0	-4.2113835195	-0.4356161437	0.8614367072
C	6.0	5.0348470021	-1.5910912146	1.0299362234
C	6.0	-4.5363098066	-1.7060079820	1.6842743486
C	6.0	4.2252769184	-0.5366956951	1.8289560958
C	6.0	-2.8341427454	0.1480386600	1.2539782280
C	6.0	5.3147769199	-1.1096907826	-0.4177001479
H	1.0	-5.5157346741	-2.1089600726	1.4088456398
H	1.0	4.0224621261	-0.8801780469	2.8481250525
H	1.0	-2.5995810128	1.0360839265	0.6577054323
H	1.0	5.8787468270	-1.8578513642	-0.9832763503
H	1.0	-4.5600718144	-1.4594884716	2.7516512119
H	1.0	4.8055829655	0.3891095930	1.8929032049
H	1.0	-2.8444260102	0.4437066089	2.3089439509
H	1.0	5.9104449087	-0.1921784578	-0.3822783535
H	1.0	-3.7917885861	-2.4943282873	1.5346626970
H	1.0	3.2717514926	-0.3045588338	1.3466543918
H	1.0	-2.0277016386	-0.5812202327	1.1206278177
H	1.0	4.3909291402	-0.8915143333	-0.9603943002
O	8.0	-2.7784236864	-3.8567060032	-1.3590367989
O	8.0	-1.3726704560	-4.0252141977	-1.8428004195

<u>B3LYP/cc-pVTZ:</u> Lowest electronic and free energy structure is analogous to that for 6-31G(d) above.

E = –1384.16117

ATOM	CHARGE	X	Y	Z
C	6.0	0.0777303505	-2.2060034343	-1.2214781190
H	1.0	0.3083172356	-1.1536741168	-1.3608278465
C	6.0	-1.2121826101	-2.6566148844	-1.7597997486
C	6.0	0.9586839608	-3.0132019803	-0.5878771138
H	1.0	-1.3499370601	-2.3024090008	-2.7883595981
H	1.0	0.7081620728	-4.0605426464	-0.4671744612
C	6.0	-2.5233918111	-2.4192828570	-0.9261427769
C	6.0	2.2080183372	-2.5492205968	-0.0930705624
H	1.0	-2.2890552665	-2.3219980316	0.1308448941
H	1.0	2.4270838787	-1.4991618320	-0.2348655580
C	6.0	-3.5500741540	-1.5003636619	-1.3986844352
C	6.0	3.1167969999	-3.3627020613	0.5282822356
H	1.0	-3.7525023408	-1.5548697436	-2.4604600614
H	1.0	2.8423752156	-4.4038708990	0.6360680839
C	6.0	-4.3039917051	-0.6600722919	-0.6390485281
C	6.0	4.3778360767	-2.9801100841	1.0354749653
N	7.0	-5.2788073254	0.1426711383	-1.1798915917
N	7.0	5.1835032821	-3.8614759051	1.6310343654
C	6.0	-5.6057946577	0.1644728805	-2.5893562504

C	6.0	4.8758200472	-5.2765544310	1.8331357266
H	1.0	-6.3912270479	0.8906256312	-2.7688517806
H	1.0	5.6692296799	-5.7324817513	2.4127287241
H	1.0	-5.9551245466	-0.8148164645	-2.9240851367
H	1.0	3.9402475510	-5.3837820471	2.3788315683
H	1.0	-4.7340489238	0.4451204903	-3.1843675842
H	1.0	4.8001723474	-5.7885309030	0.8746253048
C	6.0	-5.9300169986	0.9029271801	-0.1965033601
C	6.0	6.3999045287	-3.2626054111	2.0492874331
C	6.0	-6.9643216123	1.8174407782	-0.3375016878
C	6.0	7.4821471347	-3.8449644000	2.6907617643
H	1.0	-7.4044404763	2.0454538541	-1.2976122164
H	1.0	7.5112520261	-4.8920691002	2.9534627264
C	6.0	-7.4346585959	2.4469282588	0.8146155082
C	6.0	8.5598626439	-3.0165829389	2.9909072602
H	1.0	-8.2409323950	3.1629758053	0.7304317404
H	1.0	9.4229621766	-3.4334108758	3.4906089746
C	6.0	-6.8883281675	2.1685592186	2.0620925704
C	6.0	8.5418908847	-1.6644839465	2.6569179114
H	1.0	-7.2706102189	2.6672722984	2.9417816410
H	1.0	9.3922697233	-1.0434912289	2.9015475502
C	6.0	-5.8488647245	1.2432167634	2.1820510820
C	6.0	7.4411432996	-1.1030881911	2.0099867327
H	1.0	-5.4290291458	1.0263048717	3.1563110928
H	1.0	7.4405244430	-0.0517015123	1.7549460050
C	6.0	-5.3743929043	0.6132482655	1.0481072496
C	6.0	6.3644033293	-1.9158547965	1.7060009985
C	6.0	-4.2760004748	-0.4241200726	0.8848503478
C	6.0	5.0510323315	-1.6060263430	1.0179266328
C	6.0	-4.6340836154	-1.7074700772	1.6633175989
C	6.0	4.2440535310	-0.5694259402	1.8334998967
C	6.0	-2.9263285549	0.1542927197	1.3566786136
C	6.0	5.3002766196	-1.1143478814	-0.4266340229
H	1.0	-5.5913840531	-2.1086006605	1.3325197910
H	1.0	4.0574955262	-0.9215642884	2.8474852883
H	1.0	-2.6649695260	1.0480523449	0.7901569759
H	1.0	5.8579201538	-1.8501749857	-1.0049383580
H	1.0	-4.7131644548	-1.4823795262	2.7274677184
H	1.0	4.8140471955	0.3566040353	1.8982242709
H	1.0	-2.9923130080	0.4311116511	2.4093955058
H	1.0	5.8859445553	-0.1964158897	-0.3955321101
H	1.0	-3.8819703986	-2.4851058384	1.5368660654
H	1.0	3.2874554451	-0.3437156601	1.3666014224
H	1.0	-2.1173496741	-0.5686200710	1.2531088051
H	1.0	4.3693167265	-0.9018083435	-0.9482341049
O	8.0	-2.8259570568	-3.8339326017	-1.2181321680
O	8.0	-1.4268101453	-4.0686475799	-1.6699114906

MP2/6-31G(d): *Global electronic energy minimum.*

E = –1380.00566
G_{298} = 313.194

ATOM	CHARGE	X	Y	Z
C	6.0	0.0780270010	-2.3045114499	-1.3593683807
H	1.0	0.3767152775	-1.2991079620	-1.6626352291
C	6.0	-1.2587794966	-2.7665349691	-1.7934178069
C	6.0	0.9011999941	-3.0703848937	-0.5980841565
H	1.0	-1.4349217984	-2.5782208699	-2.8630283675
H	1.0	0.5715770506	-4.0677667193	-0.3126951024
C	6.0	-2.4798238188	-2.3725879701	-0.9459901390
C	6.0	2.1909182744	-2.6124410534	-0.1743003041
H	1.0	-2.1743506437	-2.2056229937	0.0896431017
H	1.0	2.4808836481	-1.6087903956	-0.4756293061
C	6.0	-3.4509938988	-1.4026803187	-1.4487839894
C	6.0	3.0399646161	-3.3903458096	0.5657745850
H	1.0	-3.6354220745	-1.4269980997	-2.5202123677
H	1.0	2.6876026551	-4.3827204929	0.8367137209
C	6.0	-4.2011935607	-0.5784858489	-0.6584433031
C	6.0	4.3295044033	-2.9926289366	1.0271295128
N	7.0	-5.1184552233	0.3156923680	-1.1696211922
N	7.0	5.1306299219	-3.8315220663	1.6825478081
C	6.0	-5.3913766830	0.4504446290	-2.5841323781
C	6.0	4.8596469620	-5.2418351035	1.9807776732
H	1.0	-6.0081409635	1.3341727936	-2.7458912754
H	1.0	5.8133893813	-5.7649413417	2.0312892872
H	1.0	-5.9117075223	-0.4305869080	-2.9783616233
H	1.0	4.3365468469	-5.3266295575	2.9363855771
H	1.0	-4.4507021868	0.5811067732	-3.1280145695
H	1.0	4.2654385598	-5.6795822339	1.1807590602
C	6.0	-5.8418277123	0.9526986194	-0.1482674787
C	6.0	6.3282496322	-3.1937441796	2.1089210136
C	6.0	-6.8857034504	1.8717650801	-0.2448108515
C	6.0	7.3855276978	-3.7293915137	2.8426978115
H	1.0	-7.2953438494	2.1913319173	-1.1992764302
H	1.0	7.3992687668	-4.7526647494	3.2067095249
C	6.0	-7.4169054251	2.3707642873	0.9519502826
C	6.0	8.4474618929	-2.8625939751	3.1157508772
H	1.0	-8.2348913214	3.0858133605	0.9082890040
H	1.0	9.2963423328	-3.2274223292	3.6872843264
C	6.0	-6.9207201947	1.9637257717	2.1948759446
C	6.0	8.4357702523	-1.5325369275	2.6669527393
H	1.0	-7.3545757445	2.3655511294	3.1067682842
H	1.0	9.2795216697	-0.8873296205	2.8965253503
C	6.0	-5.8721433568	1.0358593718	2.2693602090
C	6.0	7.3572084798	-1.0228380188	1.9340123906
H	1.0	-5.4926791581	0.7133902249	3.2378573242

H	1.0	7.3604374595	0.0113085558	1.5963235028
C	6.0	-5.3414123390	0.5307692404	1.0883417315
C	6.0	6.2895079441	-1.8734496097	1.6605038710
C	6.0	-4.2257974839	-0.4681901948	0.8708900678
C	6.0	5.0039359029	-1.6358319223	0.9126095469
C	6.0	-4.5880566670	-1.8094398245	1.5259092513
C	6.0	4.1806223339	-0.5351953049	1.6064780289
C	6.0	-2.9155764906	0.1076777999	1.4309623886
C	6.0	5.3123235105	-1.2827357197	-0.5563844084
H	1.0	-5.5470426503	-2.1678676308	1.1414559607
H	1.0	3.9776808191	-0.8014567675	2.6477577855
H	1.0	-2.6789630783	1.0562278426	0.9395089860
H	1.0	5.8922826693	-2.0785194789	-1.0324874333
H	1.0	-4.6801496242	-1.6768902380	2.6093081902
H	1.0	4.7540397560	0.3962917859	1.5952287792
H	1.0	-3.0287160581	0.2957855530	2.5038469991
H	1.0	5.9053364102	-0.3638212958	-0.5797892432
H	1.0	-3.8366518972	-2.5801684911	1.3325239540
H	1.0	3.2299544546	-0.3599492618	1.0981617824
H	1.0	-2.0731433768	-0.5772092990	1.2937024013
H	1.0	4.4018450133	-1.1171177838	-1.1360926997
O	8.0	-2.9217422268	-3.7824074091	-1.0795340858
O	8.0	-1.4956359546	-4.1617491641	-1.4776341433

<u>MP2/6-31G(d):</u> Global free energy minimum (differs from above minimum only in one methyl group's proton orientation).

E = –1380.00565
G_{298} = 313.170

ATOM	CHARGE	X	Y	Z
C	6.0	0.1109438789	-2.1816308739	-1.3377493032
H	1.0	0.4007193377	-1.1570704838	-1.5792923712
C	6.0	-1.2062121365	-2.6399869707	-1.8316337981
C	6.0	0.9261170414	-2.9741396732	-0.5953581475
H	1.0	-1.3561467552	-2.4002640332	-2.8949385290
H	1.0	0.6054226888	-3.9899901502	-0.3715884592
C	6.0	-2.4557079974	-2.3064350890	-0.9998858526
C	6.0	2.1966894655	-2.5201004080	-0.1135204756
H	1.0	-2.1810926423	-2.1872849853	0.0508869758
H	1.0	2.4765715269	-1.4966360286	-0.3509337193
C	6.0	-3.4278486608	-1.3264220060	-1.4806914574
C	6.0	3.0353672930	-3.3209698401	0.6137815310
H	1.0	-3.5825559396	-1.2994974662	-2.5567483361
H	1.0	2.6995224157	-4.3367649808	0.8080316766
C	6.0	-4.2123683578	-0.5539293955	-0.6716486667
C	6.0	4.3188232494	-2.9386847663	1.1042075218
N	7.0	-5.1292774873	0.3514894758	-1.1632490692
N	7.0	5.0524950979	-3.7531109768	1.8615728955
C	6.0	-5.3651668593	0.5535918456	-2.5763921347

C	6.0	4.6670482667	-5.0873791543	2.3332391137
H	1.0	-5.9908530848	1.4355686230	-2.7110802728
H	1.0	3.5927483420	-5.1209033613	2.5048544503
H	1.0	-5.8607095345	-0.3136423245	-3.0288151946
H	1.0	4.9606827124	-5.8411578409	1.5986494015
H	1.0	-4.4119939986	0.7248030431	-3.0861804555
H	1.0	5.1759115569	-5.2710476309	3.2782706612
C	6.0	-5.8903876150	0.9258411702	-0.1321975671
C	6.0	6.3222390937	-3.1897257686	2.1668780535
C	6.0	-6.9455797901	1.8334983989	-0.2121870738
C	6.0	7.3677863510	-3.7473020421	2.9011533923
H	1.0	-7.3338732205	2.1947254658	-1.1606974326
H	1.0	7.3284755814	-4.7444122990	3.3301119887
C	6.0	-7.5172177335	2.2640076862	0.9925148634
C	6.0	8.5094756280	-2.9543523075	3.0472829008
H	1.0	-8.3448511114	2.9685387297	0.9615316211
H	1.0	9.3559768300	-3.3415846390	3.6074896257
C	6.0	-7.0489371269	1.8021930227	2.2270879922
C	6.0	8.5819052765	-1.6709323868	2.4831942250
H	1.0	-7.5138869873	2.1514267730	3.1452927367
H	1.0	9.4850911639	-1.0819044475	2.6181291125
C	6.0	-5.9883133150	0.8869074219	2.2847430254
C	6.0	7.5154800359	-1.1396288414	1.7478588218
H	1.0	-5.6304628308	0.5217195618	3.2462716278
H	1.0	7.5879308724	-0.1452401950	1.3125985772
C	6.0	-5.4175020435	0.4494939832	1.0954413445
C	6.0	6.3743548305	-1.9212344183	1.5889506967
C	6.0	-4.2807066254	-0.5210970713	0.8599733957
C	6.0	5.0825335813	-1.6470699186	0.8646991608
C	6.0	-4.6396455442	-1.8987023827	1.4366727909
C	6.0	4.3676321416	-0.4419332252	1.5078921091
C	6.0	-2.9956326372	0.0445997315	1.4848945005
C	6.0	5.3526497231	-1.4208058462	-0.6343940331
H	1.0	-5.5819172182	-2.2510747633	1.0078508782
H	1.0	4.1812976547	-0.6239536120	2.5701965140
H	1.0	-2.7605346754	1.0199877988	1.0483371049
H	1.0	5.8638888382	-2.2837392824	-1.0706008909
H	1.0	-4.7635845504	-1.8222315439	2.5223052860
H	1.0	5.0113447198	0.4378870732	1.4174495191
H	1.0	-3.1411870595	0.1768135425	2.5621988198
H	1.0	5.9974656219	-0.5447226554	-0.7495849478
H	1.0	-3.8711259884	-2.6478084044	1.2263006582
H	1.0	3.4171138810	-0.2220841544	1.0172440313
H	1.0	-2.1390262084	-0.6203007438	1.3375002902
H	1.0	4.4292055113	-1.2436215820	-1.1899082346
O	8.0	-2.8718571193	-3.7139519042	-1.2156930647
O	8.0	-1.4299628847	-4.0525626025	-1.5930144240

VIII. Intermediate 13 (O_2 attached over C3'/C4')

B3LYP/6-31G(d): *Global electronic and free energy minimum.*

E = –1383.65813
G_{298} = 309.316

ATOM	CHARGE	X	Y	Z
C	6.0	-0.2021603173	-2.6362708834	-1.4680716314
H	1.0	-0.3096107837	-2.6130904268	-0.3760728997
C	6.0	-1.6012771080	-2.3623298370	-2.1788775654
C	6.0	1.0198817570	-1.9815029536	-1.9253711995
H	1.0	-1.4470174139	-1.8745951187	-3.1518328505
H	1.0	1.2094509799	-1.9917787515	-2.9979292826
C	6.0	-2.6709635755	-1.7027996361	-1.4118432081
C	6.0	1.9095927107	-1.3930958973	-1.0744924806
H	1.0	-2.6480007946	-0.6167727739	-1.4054556923
H	1.0	1.6794747123	-1.4309937399	-0.0118322465
C	6.0	-3.6196377700	-2.4101370403	-0.7360399366
C	6.0	3.1161816828	-0.7513814799	-1.4823625689
H	1.0	-3.5487824919	-3.4907251262	-0.8130580576
H	1.0	3.2991780689	-0.7354283729	-2.5538496260
C	6.0	-4.6961385770	-1.8716954151	0.0266986960
C	6.0	4.0650500004	-0.1786957385	-0.6661845524
N	7.0	-5.5719471820	-2.6726148572	0.6436883806
N	7.0	5.2064592896	0.4030629600	-1.1662418820
C	6.0	-5.5280011034	-4.1396008009	0.6198820901
C	6.0	5.5281286007	0.4601497240	-2.5812300549
H	1.0	-6.3426531140	-4.5296641322	1.2260841307
H	1.0	6.4924095884	0.9487642818	-2.7157753014
H	1.0	-4.5793357757	-4.4938147738	1.0313563446
H	1.0	5.5869019364	-0.5493641765	-3.0047257869
H	1.0	-5.6417702341	-4.5025418978	-0.4052422523
H	1.0	4.7683023445	1.0296264605	-3.1297951354
C	6.0	-6.5704608639	-1.9284279330	1.3328382466
C	6.0	6.0181313440	0.9241688507	-0.1388120833
C	6.0	-7.6469680288	-2.3931695559	2.0837451467
C	6.0	7.2405868645	1.5863121952	-0.2323403509
H	1.0	-7.8496532195	-3.4486593713	2.2301521420
H	1.0	7.7235943766	1.7803218978	-1.1846281372
C	6.0	-8.4816552398	-1.4291904818	2.6566868193
C	6.0	7.8439779451	2.0042194372	0.9599121377
H	1.0	-9.3323741578	-1.7511076549	3.2492552906
H	1.0	8.7978634888	2.5220233388	0.9144109157
C	6.0	-8.2378041159	-0.0624596840	2.4777126466
C	6.0	7.2428539612	1.7667591264	2.1984572195
H	1.0	-8.9026482828	0.6645467718	2.9339604510
H	1.0	7.7305322717	2.0996454792	3.1097474714
C	6.0	-7.1476989203	0.3788462318	1.7169651546
C	6.0	6.0118783005	1.0989713680	2.2692199872

H	1.0	-6.9683021085	1.4421064493	1.5835583998
H	1.0	5.5465647218	0.9141438797	3.2344700093
C	6.0	-6.3105341238	-0.5689801994	1.1420474250
C	6.0	5.4034810059	0.6800298899	1.0945109411
C	6.0	-5.0733813036	-0.4094067574	0.2767615323
C	6.0	4.0901462979	-0.0571775141	0.8711044805
C	6.0	-3.9573704687	0.3400563349	1.0510824450
C	6.0	4.1344344002	-1.4460843135	1.5535627385
C	6.0	-5.4253422989	0.3187109520	-1.0474008200
C	6.0	2.9067413865	0.7875316741	1.4010072099
H	1.0	-3.7026948594	-0.1769783698	1.9815092017
H	1.0	4.9701007012	-2.0425356612	1.1744501123
H	1.0	-6.2069990287	-0.2132604941	-1.5984413713
H	1.0	2.8745382661	1.7671959712	0.9134875715
H	1.0	-4.3103961289	1.3439194119	1.3069844957
H	1.0	4.2694814292	-1.3226804956	2.6337854667
H	1.0	-5.7959937244	1.3224885223	-0.8174595321
H	1.0	3.0218871179	0.9494312637	2.4784493580
H	1.0	-3.0484159543	0.4446445873	0.4522494163
H	1.0	3.2116822576	-2.0109115475	1.3897229765
H	1.0	-4.5525485857	0.4207698007	-1.6981291764
H	1.0	1.9456272273	0.2907140532	1.2354878319
O	8.0	-1.7812013968	-3.7747272315	-2.3221076611
O	8.0	-0.3483539338	-4.0091022088	-1.9609907899

<u>B3LYP/cc-pVTZ:</u> Lowest electronic and free energy structure is analogous to that for 6-31G(d) above.

E = –1384.15765

ATOM	CHARGE	X	Y	Z
C	6.0	-0.1807662058	-2.6380744792	-1.4108286789
H	1.0	-0.2689728851	-2.6148214125	-0.3219548142
C	6.0	-1.5878254607	-2.4143699898	-2.1015665168
C	6.0	1.0117358990	-1.9524119421	-1.8855792488
H	1.0	-1.4543246479	-1.9455227750	-3.0826967677
H	1.0	1.1730040668	-1.9372714415	-2.9584127152
C	6.0	-2.6579333718	-1.7548254266	-1.3468942710
C	6.0	1.9157181783	-1.3801414350	-1.0498996595
H	1.0	-2.6167806072	-0.6738278721	-1.3325996362
H	1.0	1.7134269072	-1.4489680485	0.0122692183
C	6.0	-3.6304375457	-2.4420640895	-0.7026130473
C	6.0	3.1019492302	-0.7185020641	-1.4676845400
H	1.0	-3.5836295310	-3.5195671613	-0.7800302072
H	1.0	3.2606777754	-0.6741959040	-2.5376683176
C	6.0	-4.7091818023	-1.8877346849	0.0395319242
C	6.0	4.0604274385	-0.1583946304	-0.6644987414
N	7.0	-5.6039690623	-2.6706102699	0.6339601437
N	7.0	5.1810804704	0.4416442344	-1.1742878602
C	6.0	-5.5866418350	-4.1352331651	0.6144340650

C	6.0	5.4726499336	0.5359536473	-2.5900300665
H	1.0	-6.3890453263	-4.5060362693	1.2404324520
H	1.0	6.4301756010	1.0253782190	-2.7305248349
H	1.0	-4.6392847890	-4.5042512396	1.0019257028
H	1.0	5.5226946575	-0.4569276166	-3.0407747588
H	1.0	-5.7313156179	-4.4995433939	-0.4015012991
H	1.0	4.7066831674	1.1172781620	-3.1074984177
C	6.0	-6.6046947823	-1.9132938148	1.2990828349
C	6.0	6.0075329394	0.9477802777	-0.1575866066
C	6.0	-7.7004587762	-2.3611090014	2.0205376257
C	6.0	7.2161280632	1.6215478371	-0.2641686970
H	1.0	-7.9214445041	-3.4092302456	2.1576331770
H	1.0	7.6727990712	1.8393947676	-1.2187488441
C	6.0	-8.5301924678	-1.3906792522	2.5745176591
C	6.0	7.8411890971	2.0193939325	0.9168771778
H	1.0	-9.3957577702	-1.6986253272	3.1439998101
H	1.0	8.7845426879	2.5454672642	0.8612531705
C	6.0	-8.2622450655	-0.0340594442	2.4051091771
C	6.0	7.2741573721	1.7512818788	2.1575939771
H	1.0	-8.9236365751	0.6985899809	2.8460535441
H	1.0	7.7778604632	2.0688448268	3.0598688884
C	6.0	-7.1534972104	0.3903732748	1.6733689179
C	6.0	6.0566110129	1.0723806771	2.2420325063
H	1.0	-6.9581334759	1.4470693440	1.5484982946
H	1.0	5.6199490417	0.8648686847	3.2107259904
C	6.0	-6.3213436290	-0.5642350914	1.1174648197
C	6.0	5.4272687706	0.6733144948	1.0789344199
C	6.0	-5.0656217545	-0.4229325165	0.2831470795
C	6.0	4.1193925366	-0.0706293770	0.8712339453
C	6.0	-3.9585446609	0.3036767514	1.0825586618
C	6.0	4.1924538112	-1.4688699637	1.5205814905
C	6.0	-5.3733843586	0.3117423020	-1.0427794917
C	6.0	2.9438068545	0.7471164030	1.4453241980
H	1.0	-3.7303510961	-0.2204001026	2.0100815991
H	1.0	5.0197360193	-2.0471051170	1.1105459566
H	1.0	-6.1431132175	-0.2061052508	-1.6139502177
H	1.0	2.8887627283	1.7312706439	0.9807166942
H	1.0	-4.3021912772	1.3054112831	1.3373561748
H	1.0	4.3524518738	-1.3670657186	2.5943463770
H	1.0	-5.7364813498	1.3140916995	-0.8194022869
H	1.0	3.0836766539	0.8881658967	2.5174768237
H	1.0	-3.0411558206	0.3998769501	0.5053717876
H	1.0	3.2751489029	-2.0353399450	1.3678538729
H	1.0	-4.4867627759	0.4053426377	-1.6665428938
H	1.0	1.9896517688	0.2442612754	1.2937038092
O	8.0	-1.7380029204	-3.8302363330	-2.2189550767
O	8.0	-0.2991987684	-4.0228979243	-1.8883147036

MP2/6-31G(d): *Global electronic energy minimum.*

E = –1380.00165
G_{298} = 312.579

ATOM	CHARGE	X	Y	Z
C	6.0	-0.2328165793	-2.8658084855	-1.4384408815
H	1.0	-0.3979917312	-2.7164077744	-0.3616067253
C	6.0	-1.5583885552	-2.7456642910	-2.2248896847
C	6.0	0.9842837527	-2.2070023337	-1.9139266959
H	1.0	-1.3833882945	-2.4522254970	-3.2698790047
H	1.0	1.2145762788	-2.2866158672	-2.9761751558
C	6.0	-2.6608186864	-1.9737780990	-1.6107482263
C	6.0	1.8209543513	-1.5443877149	-1.0668878867
H	1.0	-2.6301934945	-0.8963324042	-1.7499905247
H	1.0	1.5449563411	-1.5258290994	-0.0141255271
C	6.0	-3.6317027952	-2.5970703338	-0.8959475321
C	6.0	3.0275733364	-0.8907092404	-1.4674272050
H	1.0	-3.5428740044	-3.6766559633	-0.8195730905
H	1.0	3.2711309376	-0.9479148652	-2.5267417889
C	6.0	-4.7256960612	-1.9444274013	-0.2352424857
C	6.0	3.8948623682	-0.2217069939	-0.6390688066
N	7.0	-5.6863775483	-2.6317027754	0.3725942182
N	7.0	5.0610514310	0.3513211670	-1.0977391267
C	6.0	-5.8333765412	-4.0906983900	0.4473862814
C	6.0	5.4955488970	0.2790064442	-2.4770166161
H	1.0	-5.5050755114	-4.4351393668	1.4306268432
H	1.0	6.4984837559	0.6960758385	-2.5576893475
H	1.0	-5.2517171098	-4.5696318189	-0.3356915492
H	1.0	5.5238710017	-0.7649129981	-2.8059336159
H	1.0	-6.8876383317	-4.3266285652	0.3015890820
H	1.0	4.8206727143	0.8414184570	-3.1323906894
C	6.0	-6.6252989277	-1.7740754740	1.0110748796
C	6.0	5.7507175601	1.0149070676	-0.0703048992
C	6.0	-7.7461906737	-2.1258020426	1.7614214258
C	6.0	6.9440641507	1.7345324395	-0.1247709576
H	1.0	-8.0302284140	-3.1556011995	1.9584531466
H	1.0	7.4997421967	1.8762170674	-1.0478249890
C	6.0	-8.4973634139	-1.0647691052	2.2737717396
C	6.0	7.4154338117	2.2907938028	1.0714316580
H	1.0	-9.3808229910	-1.2782406282	2.8689219798
H	1.0	8.3434514522	2.8572857245	1.0598594094
C	6.0	-8.1306348439	0.2696665296	2.0340385780
C	6.0	6.7172391747	2.1329643971	2.2735026764
H	1.0	-8.7399303426	1.0689844374	2.4473686371
H	1.0	7.1079664415	2.5752243475	3.1861790881
C	6.0	-6.9974619712	0.5891426194	1.2764666857
C	6.0	5.5175440801	1.4082289448	2.3056609790
H	1.0	-6.7261744880	1.6280749348	1.1021307765

H	1.0	4.9751334651	1.2864419353	3.2420827876
C	6.0	-6.2354893791	-0.4580585789	0.7645934399
C	6.0	5.0396794705	0.8535875930	1.1241721757
C	6.0	-4.9855609179	-0.4583837441	-0.0740912534
C	6.0	3.7950541848	0.0334713946	0.8671080528
C	6.0	-3.8330750301	0.2339899521	0.6774586806
C	6.0	3.8618673538	-1.2749433213	1.6701121958
C	6.0	-5.2672439115	0.2126555925	-1.4342435073
C	6.0	2.5493219094	0.8553285379	1.2285217842
H	1.0	-3.6517706490	-0.2502475931	1.6413697097
H	1.0	4.7597189999	-1.8385113047	1.4011234827
H	1.0	-6.0807045536	-0.2974170627	-1.9580948465
H	1.0	2.5262240575	1.7828293139	0.6490057460
H	1.0	-4.1080539680	1.2764150618	0.8623180105
H	1.0	3.9060380074	-1.0475459283	2.7405664982
H	1.0	-5.5682828786	1.2492413255	-1.2574301580
H	1.0	2.5758836100	1.1143332904	2.2923407950
H	1.0	-2.9077697121	0.2197695877	0.0972367462
H	1.0	2.9898091720	-1.9090302787	1.4876471361
H	1.0	-4.3838594069	0.2172589403	-2.0758681943
H	1.0	1.6271700678	0.3008500979	1.0330751462
O	8.0	-1.7523721664	-4.1761269395	-2.1172929169
O	8.0	-0.2791321085	-4.3104582027	-1.7454477634

<u>MP2/6-31G(d):</u> Global free energy minimum (differs from above minimum in dioxetane "twist").

E = –1380.00142
G_{298} = 311.803

ATOM	CHARGE	X	Y	Z
C	6.0	0.3069469072	-2.9592828513	-0.4092494868
H	1.0	0.4202607079	-2.0471487051	0.1902934077
C	6.0	-1.0966738274	-3.1800322722	-1.0201425839
C	6.0	1.4634479091	-3.1993693645	-1.2793661141
H	1.0	-1.1408315867	-3.2275026146	-2.1145855491
H	1.0	1.4393237203	-4.0919327898	-1.9044976186
C	6.0	-2.1378047067	-2.2817670728	-0.4474882773
C	6.0	2.5330690065	-2.3585856226	-1.2986702521
H	1.0	-2.2278317605	-1.2970609814	-0.8990543944
H	1.0	2.4984388565	-1.4963271683	-0.6349539442
C	6.0	-2.8738291638	-2.6788542729	0.6195819237
C	6.0	3.6899080074	-2.5391906259	-2.1224611115
H	1.0	-2.6700384650	-3.6849795646	0.9724293653
H	1.0	3.6837354716	-3.4188617001	-2.7634357055
C	6.0	-3.8544080851	-1.8837955036	1.3002323698
C	6.0	4.7877503903	-1.7169797567	-2.1630424807
N	7.0	-4.5666849582	-2.3634734184	2.3142149419
N	7.0	5.8782973463	-1.9785446642	-2.9662284990
C	6.0	-4.5179660168	-3.7111518277	2.8940779367
C	6.0	5.9758299133	-3.1438430675	-3.8192223549

H	1.0	-4.0234199107	-3.6600184771	3.8665657072
H	1.0	6.9656497402	-3.1730417135	-4.2727725005
H	1.0	-3.9833730870	-4.3906280704	2.2366976722
H	1.0	5.8343985075	-4.0551885565	-3.2286567034
H	1.0	-5.5442587919	-4.0601016322	3.0143062901
H	1.0	5.2205296359	-3.1131375235	-4.6128906186
C	6.0	-5.4429513668	-1.3813944167	2.8544378384
C	6.0	6.8524374313	-0.9739062889	-2.8589571298
C	6.0	-6.3246245120	-1.5080128056	3.9266469320
C	6.0	8.0784906974	-0.8538512437	-3.5128890434
H	1.0	-6.4324652433	-2.4233640240	4.5016047572
H	1.0	8.4265258775	-1.5821072606	-4.2405219584
C	6.0	-7.0722241817	-0.3702732263	4.2416742202
C	6.0	8.8666561597	0.2625449052	-3.2045726353
H	1.0	-7.7748607840	-0.4087196052	5.0693915213
H	1.0	9.8274438524	0.3824895757	-3.6993777252
C	6.0	-6.9313689116	0.8194580175	3.5085686774
C	6.0	8.4421795696	1.2210714252	-2.2781782308
H	1.0	-7.5306433392	1.6839644497	3.7815123472
H	1.0	9.0752748302	2.0768278320	-2.0587722710
C	6.0	-6.0349474092	0.9137358732	2.4372773187
C	6.0	7.2047820204	1.0829519507	-1.6336603407
H	1.0	-5.9366999000	1.8435537399	1.8812525463
H	1.0	6.8749525878	1.8302701884	-0.9134352265
C	6.0	-5.2799948423	-0.2110392936	2.1144452915
C	6.0	6.4140640316	-0.0201682877	-1.9330864942
C	6.0	-4.2461517432	-0.4401896575	1.0449792707
C	6.0	5.0566367527	-0.4186448557	-1.3976195637
C	6.0	-3.0498339153	0.5090009972	1.2488973310
C	6.0	5.1475489265	-0.6600805606	0.1169430071
C	6.0	-4.8810683227	-0.2703299561	-0.3496913791
C	6.0	4.0269777329	0.6693941280	-1.7354507833
H	1.0	-2.6125956154	0.3748189789	2.2425135567
H	1.0	5.8911566146	-1.4324197610	0.3330933080
H	1.0	-5.7258720802	-0.9531832314	-0.4774839476
H	1.0	3.9838379718	0.8274383342	-2.8169192690
H	1.0	-3.4004434314	1.5415867299	1.1635155463
H	1.0	5.4543899289	0.2636538132	0.6191034969
H	1.0	-5.2497471278	0.7550480377	-0.4452432235
H	1.0	4.3189142674	1.6123304018	-1.2609231587
H	1.0	-2.2735667924	0.3460095667	0.4982237650
H	1.0	4.1887093492	-0.9782149247	0.5357627018
H	1.0	-4.1589760416	-0.4514076853	-1.1484796377
H	1.0	3.0259429063	0.4037685965	-1.3843491201
O	8.0	-1.1394606912	-4.5059351638	-0.4385927328
O	8.0	-0.0048970170	-4.1037687561	0.4923590074

IX. Products 2+3 (C2/C1' bond oxidized)

B3LYP/6-31G(d): *Lowest energy minimum of aldehyde fragment **2**.*

E = –556.65060

ATOM	CHARGE	X	Y	Z
C	6.0	-1.6180961546	-0.3460627348	0.0000000000
N	7.0	-0.6192002487	-1.3089388112	0.0000000000
C	6.0	-0.8871628358	-2.7316778649	0.0000000000
H	1.0	-0.4644284969	-3.2104124125	-0.8919467900
H	1.0	-0.4644284969	-3.2104124125	0.8919467900
H	1.0	-1.9717870613	-2.8565908201	0.0000000000
C	6.0	0.6545710707	-0.7190660194	0.0000000000
C	6.0	1.8955423763	-1.3485690820	0.0000000000
H	1.0	1.9830143214	-2.4310634754	0.0000000000
C	6.0	3.0378760958	-0.5351472363	0.0000000000
H	1.0	4.0196874856	-1.0016210024	0.0000000000
C	6.0	2.9325696939	0.8565611159	0.0000000000
H	1.0	3.8307139683	1.4679087204	0.0000000000
C	6.0	1.6697177611	1.4712674331	0.0000000000
H	1.0	1.5911118289	2.5561444319	0.0000000000
C	6.0	0.5296244998	0.6816155149	0.0000000000
C	6.0	-0.9425890901	1.0459680245	0.0000000000
C	6.0	-1.3769910606	1.8114303757	-1.2670723969
C	6.0	-1.3769910606	1.8114303757	1.2670723969
H	1.0	-1.0590303662	1.2901430366	-2.1765709609
H	1.0	-1.0590303662	1.2901430366	2.1765709609
H	1.0	-0.9355188328	2.8145893502	-1.2775321165
H	1.0	-0.9355188328	2.8145893502	1.2775321165
H	1.0	-2.4677952933	1.9066060015	-1.2867447223
H	1.0	-2.4677952933	1.9066060015	1.2867447223
O	8.0	-2.8161125915	-0.5736370071	0.0000000000

MP2/6-31G(d): *Lowest energy minimum of aldehyde fragment **2**.*

E = –555.19381

ATOM	CHARGE	X	Y	Z
C	6.0	-1.6167716001	-0.3386156246	0.0000000000
N	7.0	-0.6220329400	-1.3016334520	0.0000000000
C	6.0	-0.8918243066	-2.7227751574	0.0000000000
H	1.0	-0.4708589011	-3.1963302951	-0.8926399852
H	1.0	-0.4708589011	-3.1963302951	0.8926399852
H	1.0	-1.9767842052	-2.8382646198	0.0000000000
C	6.0	0.6513961410	-0.7156663081	0.0000000000
C	6.0	1.8923754130	-1.3473848969	0.0000000000
H	1.0	1.9842269664	-2.4308824788	0.0000000000
C	6.0	3.0304042352	-0.5286003833	0.0000000000

H	1.0	4.0155929141	-0.9894324572	0.0000000000
C	6.0	2.9200761130	0.8659468310	0.0000000000
H	1.0	3.8195582795	1.4766974582	0.0000000000
C	6.0	1.6590909743	1.4813562040	0.0000000000
H	1.0	1.5768618542	2.5672761598	0.0000000000
C	6.0	0.5217555137	0.6828379254	0.0000000000
C	6.0	-0.9404880555	1.0385077233	0.0000000000
C	6.0	-1.3662553165	1.7970131962	-1.2606294137
C	6.0	-1.3662553165	1.7970131962	1.2606294137
H	1.0	-1.0516794077	1.2620002244	-2.1618708927
H	1.0	-1.0516794077	1.2620002244	2.1618708927
H	1.0	-0.9129336009	2.7936454128	-1.2733946580
H	1.0	-0.9129336009	2.7936454128	1.2733946580
H	1.0	-2.4557474058	1.8992873296	-1.2753723135
H	1.0	-2.4557474058	1.8992873296	1.2753723135
O	8.0	-2.8265350131	-0.5587947692	0.0000000000

*B3LYP/6-31G(d): Lowest energy minimum of aldehyde fragment **3**.*

E = –827.14558

ATOM	CHARGE	X	Y	Z
C	6.0	3.7362725391	-0.1022610129	-0.0091230833
H	1.0	3.6189206074	-1.1848458039	0.0467806310
C	6.0	5.0726066521	0.4178792031	-0.0501664116
C	6.0	2.6177285273	0.6856448738	-0.0359487910
H	1.0	5.2103904929	1.4968322681	-0.1066675468
H	1.0	2.7321922283	1.7673178817	-0.0912040644
C	6.0	6.1834551748	-0.3580193265	-0.0222127131
C	6.0	1.2982041394	0.1513801542	0.0064009277
H	1.0	6.1165139695	-1.4434335933	0.0341621997
H	1.0	1.2129719912	-0.9298680107	0.0610010011
C	6.0	7.5378304097	0.2548784129	-0.0680118452
C	6.0	0.1671407169	0.9344261835	-0.0156514240
H	1.0	8.3892697141	-0.4522097618	-0.0402314385
H	1.0	0.3175179908	2.0086964493	-0.0735393467
C	6.0	-1.1739455884	0.4706572954	0.0162479635
N	7.0	-2.2120191955	1.3177031448	0.0308684316
C	6.0	-2.1256574162	2.7812097214	0.0520240603
H	1.0	-3.0621223484	3.1819276413	0.4382831023
H	1.0	-1.3194219077	3.0994132479	0.7144860253
H	1.0	-1.9541646469	3.1691858613	-0.9572765796
C	6.0	-3.4553382627	0.6278616874	0.0060968980
C	6.0	-4.7439931540	1.1553969268	-0.0173657785
H	1.0	-4.9415719612	2.2218598943	-0.0315429757
C	6.0	-5.7999826222	0.2398769504	-0.0340092713
H	1.0	-6.8205825784	0.6091390269	-0.0538541584
C	6.0	-5.5609980486	-1.1397657789	-0.0283337603
H	1.0	-6.4002914885	-1.8282764407	-0.0412456694
C	6.0	-4.2541125409	-1.6437098629	-0.0098907044

H	1.0	-4.0816446957	-2.7163577920	-0.0093060620
C	6.0	-3.1956371060	-0.7442177947	0.0042488351
C	6.0	-1.6949863414	-0.9726213457	0.0182923838
C	6.0	-1.2753949446	-1.7252866640	1.3093215144
C	6.0	-1.2528825064	-1.7410007751	-1.2544018395
H	1.0	-1.5775286697	-1.1762349650	2.2064834676
H	1.0	-1.5414009635	-1.2047037257	-2.1636695632
H	1.0	-1.7677112082	-2.7024494475	1.3287006555
H	1.0	-1.7417955371	-2.7199180515	-1.2694934086
H	1.0	-0.1956648956	-1.8918526042	1.3530982738
H	1.0	-0.1720380279	-1.9040858979	-1.2780264236
O	8.0	7.7157725017	1.4563743802	-0.1322621420

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **3**.*

E = –824.94314

ATOM	CHARGE	X	Y	Z
C	6.0	3.7194083823	-0.1113057596	0.0056792345
H	1.0	3.5848882438	-1.1913483970	0.0943620317
C	6.0	5.0614149913	0.3953903637	-0.0557522365
C	6.0	2.6133009457	0.6926526779	-0.0412874222
H	1.0	5.2162588516	1.4709644895	-0.1437795381
H	1.0	2.7422351931	1.7717829476	-0.1293989778
C	6.0	6.1631824149	-0.3969639970	-0.0100940292
C	6.0	1.2886118102	0.1661376108	0.0209628284
H	1.0	6.0813084687	-1.4797731534	0.0773676131
H	1.0	1.1960930742	-0.9133594827	0.1103553438
C	6.0	7.5164376064	0.2085408311	-0.0796559240
C	6.0	0.1699662984	0.9585141813	-0.0214788174
H	1.0	8.3725376477	-0.4874222562	-0.0383808059
H	1.0	0.3276307483	2.0302881818	-0.1174411831
C	6.0	-1.1733034611	0.4857906053	0.0204813755
N	7.0	-2.2130252857	1.3207081885	0.0414513627
C	6.0	-2.1540460785	2.7856493707	0.0726019989
H	1.0	-3.0433745820	3.1482656213	0.5855851847
H	1.0	-1.2766782330	3.1069553499	0.6308101781
H	1.0	-2.1249856926	3.1792462481	-0.9463049333
C	6.0	-3.4510247212	0.6235429694	0.0057984744
C	6.0	-4.7435906682	1.1459177080	-0.0176541456
H	1.0	-4.9549992890	2.2112176846	-0.0311322818
C	6.0	-5.7843707814	0.2137913959	-0.0453755300
H	1.0	-6.8117101351	0.5664093205	-0.0679231759
C	6.0	-5.5264085531	-1.1662699439	-0.0464034115
H	1.0	-6.3607316228	-1.8622178900	-0.0669103390
C	6.0	-4.2166042600	-1.6603645363	-0.0255274671
H	1.0	-4.0323772644	-2.7324949990	-0.0310275107
C	6.0	-3.1696813585	-0.7428830500	-0.0044004316
C	6.0	-1.6777018888	-0.9477793846	0.0173053338
C	6.0	-1.2715379709	-1.6914701537	1.3055787484

C	6.0	-1.2278794140	-1.7028039051	-1.2472144996
H	1.0	-1.5960288423	-1.1377710768	2.1912043809
H	1.0	-1.5299224207	-1.1627943113	-2.1491009783
H	1.0	-1.7588577217	-2.6707619300	1.3146525832
H	1.0	-1.7045796058	-2.6872284015	-1.2602208738
H	1.0	-0.1921880130	-1.8466199367	1.3646347826
H	1.0	-0.1453272572	-1.8452820463	-1.2706431355
O	8.0	7.6935614441	1.4216914150	-0.1786624370

X. Products 4+5 (C1'/C2' bond oxidized)

B3LYP/6-31G(d): *Lowest energy minimum of aldehyde fragment **4**.*

E = –595.05839

ATOM	CHARGE	X	Y	Z
C	6.0	-3.8442573705	0.1255813824	-2.1362896510
H	1.0	-3.1624782933	0.9252555769	-2.4720448233
C	6.0	-4.7574762765	0.5396964619	-1.0217871461
N	7.0	-5.6558466563	-0.2264826099	-0.4423320182
C	6.0	-5.9730489796	-1.6379145969	-0.7373008580
H	1.0	-5.8022065978	-2.2208125472	0.1715847783
H	1.0	-5.3401694317	-1.9895511270	-1.5457972547
H	1.0	-7.0283166445	-1.6968322134	-1.0162135885
C	6.0	-6.3496974335	0.4841710658	0.5762030592
C	6.0	-7.3668700837	0.0162429339	1.4076751326
H	1.0	-7.7476660821	-0.9979499574	1.3524312922
C	6.0	-7.8797272035	0.9291307763	2.3288156636
H	1.0	-8.6730474465	0.6188697290	3.0012920937
C	6.0	-7.3850870398	2.2419726710	2.3986410239
H	1.0	-7.8061842824	2.9282069458	3.1271389115
C	6.0	-6.3618778799	2.6848352234	1.5506073600
H	1.0	-5.9938368948	3.7041001320	1.6212912090
C	6.0	-5.8397606825	1.7877196583	0.6270498516
C	6.0	-4.7537301149	1.9267141506	-0.4167982691
C	6.0	-3.3668551701	2.2403215024	0.2188091877
C	6.0	-5.1079293418	2.9932295923	-1.4949594009
H	1.0	-3.0854226018	1.4924532327	0.9661453090
H	1.0	-6.0703243314	2.7836669095	-1.9712683452
H	1.0	-3.4210764360	3.2148300390	0.7133098282
H	1.0	-5.1714783689	3.9725278375	-1.0111452399
H	1.0	-2.5830522348	2.2948443397	-0.5428476556
H	1.0	-4.3340448926	3.0507766837	-2.2664265705
O	8.0	-3.8328328485	-0.9753002125	-2.6430169093

MP2/6-31G(d): *Lowest energy minimum of aldehyde fragment **4**.*

E = –593.50547

ATOM	CHARGE	X	Y	Z
C	6.0	-3.8371934208	0.1362937832	-2.1354496110
H	1.0	-3.1583561315	0.9305664658	-2.4823415405
C	6.0	-4.7499830612	0.5487745238	-1.0250939738
N	7.0	-5.6530982224	-0.2229015175	-0.4442083433
C	6.0	-5.9743070472	-1.6328110609	-0.7363198374
H	1.0	-5.8093291254	-2.2038731435	0.1790900851
H	1.0	-5.3364450199	-1.9877365366	-1.5385548557
H	1.0	-7.0268937586	-1.6777876493	-1.0216102151

C	6.0	-6.3459349537	0.4848567595	0.5717851763
C	6.0	-7.3649984067	0.0125615990	1.4019801384
H	1.0	-7.7515129270	-1.0013320985	1.3501270470
C	6.0	-7.8706381483	0.9322034123	2.3206150092
H	1.0	-8.6652173338	0.6278567548	2.9959687188
C	6.0	-7.3711073151	2.2465661949	2.3893122166
H	1.0	-7.7923361305	2.9326120159	3.1195061041
C	6.0	-6.3483662930	2.6893789476	1.5423993226
H	1.0	-5.9769622073	3.7092110214	1.6121465432
C	6.0	-5.8306271012	1.7854047407	0.6182016442
C	6.0	-4.7540486023	1.9206834570	-0.4187233579
C	6.0	-3.3819501676	2.2345248126	0.2198201294
C	6.0	-5.1157190614	2.9820151288	-1.4825170784
H	1.0	-3.1076328438	1.4788868521	0.9611373204
H	1.0	-6.0766736932	2.7589121060	-1.9543011083
H	1.0	-3.4461334768	3.2042110486	0.7213895483
H	1.0	-5.1896065568	3.9557490774	-0.9902101151
H	1.0	-2.5964827269	2.2977413183	-0.5385014339
H	1.0	-4.3428412064	3.0509003217	-2.2531736475
O	8.0	-3.8199066812	-0.9831647550	-2.6397069157

*<u>B3LYP/6-31G(d):</u> Lowest energy minimum of aldehyde fragment **5**.*

E = –788.67828

ATOM	CHARGE	X	Y	Z
C	6.0	-0.2548809013	-0.4409307544	-1.4072844661
H	1.0	-0.4319015757	-0.8693412337	-0.4172450281
C	6.0	-1.3272451733	-0.3014121699	-2.2327580133
C	6.0	1.0961406799	-0.0778074865	-1.7120357090
H	1.0	-1.2266507581	0.1171336460	-3.2324725795
H	1.0	1.2927566966	0.3511212765	-2.6949550808
C	6.0	-2.6615645394	-0.7069295188	-1.8146640066
C	6.0	2.1337012842	-0.2429796122	-0.8379885832
H	1.0	-2.7108621312	-1.1292717672	-0.7821025356
H	1.0	1.8992991846	-0.6738143523	0.1327964828
C	6.0	3.4912181446	0.1115209463	-1.1190188566
H	1.0	3.6641181987	0.5372629816	-2.1050680924
C	6.0	4.5736015442	-0.0271270087	-0.2914826938
N	7.0	5.8525664155	0.3525764751	-0.6720452230
C	6.0	6.1617721040	0.9257760149	-1.9654530874
H	1.0	7.2295355153	1.1364097485	-2.0265049036
H	1.0	5.8966123525	0.2316890185	-2.7730874011
H	1.0	5.6119293754	1.8631631172	-2.1184991773
C	6.0	6.7871854889	0.1125709872	0.3461928462
C	6.0	8.1609045379	0.3526204612	0.3597422037
H	1.0	8.6791669567	0.7852576518	-0.4904083382
C	6.0	8.8713194279	0.0160759772	1.5190458700
H	1.0	9.9428906767	0.1950841477	1.5502218161
C	6.0	8.2296674564	-0.5413215731	2.6266983341

H	1.0	8.8005335503	-0.7945339504	3.5153684894
C	6.0	6.8463851210	-0.7748070499	2.5928700897
H	1.0	6.3455958067	-1.2088307261	3.4553244370
C	6.0	6.1305869368	-0.4463722704	1.4512595581
C	6.0	4.6450252842	-0.5878627086	1.1434626077
C	6.0	4.2259622982	-2.0766640147	1.2001612274
C	6.0	3.8104776116	0.2599516267	2.1333391826
H	1.0	4.8182536436	-2.6763998114	0.5015848215
H	1.0	4.1094650183	1.3124069216	2.0951313247
H	1.0	4.3898279022	-2.4710468748	2.2096271980
H	1.0	3.9676814106	-0.1006133634	3.1564463879
H	1.0	3.1690190648	-2.2102182433	0.9515864025
H	1.0	2.7401519991	0.2024387505	1.9145068477
O	8.0	-3.6728824180	-0.6146929085	-2.4953673311

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **5**.*

E = –786.57483

ATOM	CHARGE	X	Y	Z
C	6.0	-0.2452719145	-0.4486512187	-1.3851686215
H	1.0	-0.4142895001	-0.8729617165	-0.3912042329
C	6.0	-1.3178299319	-0.3128393172	-2.2092533619
C	6.0	1.1037815123	-0.0803427235	-1.7080469185
H	1.0	-1.2232691888	0.1014419400	-3.2113577195
H	1.0	1.2934343992	0.3448059194	-2.6949157708
C	6.0	-2.6490881111	-0.7220411053	-1.7753036191
C	6.0	2.1435748180	-0.2410004618	-0.8359146695
H	1.0	-2.7001098283	-1.1395869089	-0.7454114999
H	1.0	1.9122380841	-0.6682246864	0.1379396720
C	6.0	3.4971874943	0.1181559198	-1.1328235873
H	1.0	3.6661397426	0.5414624151	-2.1221437416
C	6.0	4.5773475183	-0.0203118963	-0.3010416743
N	7.0	5.8580300133	0.3590780615	-0.6748549387
C	6.0	6.1668387309	0.9312143287	-1.9657984115
H	1.0	7.2322836948	1.1534758918	-2.0142079957
H	1.0	5.9144031046	0.2298794736	-2.7694613953
H	1.0	5.6048509252	1.8596006213	-2.1190215959
C	6.0	6.7846566021	0.1134077208	0.3436657309
C	6.0	8.1607826987	0.3458170463	0.3697275632
H	1.0	8.6948360198	0.7767941116	-0.4731196289
C	6.0	8.8539822844	0.0005062969	1.5372264090
H	1.0	9.9271756304	0.1714381188	1.5829975536
C	6.0	8.1955085114	-0.5567558077	2.6382498768
H	1.0	8.7589112205	-0.8150763962	3.5312962935
C	6.0	6.8121486165	-0.7830550551	2.5928398940
H	1.0	6.2983370568	-1.2171830479	3.4494037736
C	6.0	6.1137516090	-0.4448264368	1.4403116501
C	6.0	4.6406503257	-0.5778792975	1.1220522267
C	6.0	4.2280332158	-2.0565850612	1.1740781072

C	6.0	3.8170072750	0.2695936474	2.1034184922
H	1.0	4.8333324276	-2.6428891569	0.4766721727
H	1.0	4.1340617816	1.3155204005	2.0582587945
H	1.0	4.3871216175	-2.4493045606	2.1843419121
H	1.0	3.9707628159	-0.0943344067	3.1252260059
H	1.0	3.1748625011	-2.1907670887	0.9138758187
H	1.0	2.7484210227	0.2229454255	1.8778546874
O	8.0	-3.6672306052	-0.6304386391	-2.4634622315

XI. Products 6+7 (C2'/C3' bond oxidized)

*B3LYP/6-31G(d): Lowest energy minimum of aldehyde fragment **6**.*

E = –633.97583

ATOM	CHARGE	X	Y	Z
C	6.0	-2.6954453856	-2.4882375870	-0.4760361094
H	1.0	-2.2437033818	-3.1976688746	-1.2059667175
C	6.0	-3.7165099904	-1.6582089268	-1.0801560696
H	1.0	-3.8717358060	-1.8627495168	-2.1360667029
C	6.0	-4.4876516253	-0.6768177872	-0.5036123904
N	7.0	-5.4252604953	0.0254457322	-1.2295509044
C	6.0	-5.6828368822	-0.1990147315	-2.6386448307
H	1.0	-6.4698464356	0.4746006518	-2.9772557523
H	1.0	-6.0069832701	-1.2319927354	-2.8141968823
H	1.0	-4.7807738840	-0.0109466741	-3.2336203098
C	6.0	-6.0930372714	0.9799212754	-0.4354962630
C	6.0	-7.0949887177	1.8787982441	-0.7931908262
H	1.0	-7.4899508892	1.9340557436	-1.8029818781
C	6.0	-7.5915684568	2.7294641513	0.2037902608
H	1.0	-8.3737192824	3.4398887427	-0.0506323179
C	6.0	-7.0990705845	2.6772487149	1.5087708283
H	1.0	-7.4981415737	3.3458945346	2.2662631008
C	6.0	-6.0889430740	1.7629908384	1.8455156133
H	1.0	-5.7050623985	1.7225019123	2.8620645282
C	6.0	-5.5886618070	0.9155134764	0.8682179137
C	6.0	-4.5104824299	-0.1552320713	0.9457953904
C	6.0	-4.9119865480	-1.2727354543	1.9379684763
C	6.0	-3.1479000246	0.4616311265	1.3422495642
H	1.0	-5.8769998931	-1.7133801229	1.6645678025
H	1.0	-2.8566584457	1.2538723712	0.6438716173
H	1.0	-5.0066043682	-0.8491702847	2.9447375455
H	1.0	-3.2257155214	0.9042137059	2.3422514886
H	1.0	-4.1470936287	-2.0510347045	1.9534078649
H	1.0	-2.3777994376	-0.3115255386	1.3579549846
O	8.0	-2.2920664810	-2.4993603517	0.6862392853

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **6**.*

E = –632.30384

ATOM	CHARGE	X	Y	Z
C	6.0	-2.6980043692	-2.4821594321	-0.4667481821
H	1.0	-2.2337901218	-3.1955883430	-1.1795802091
C	6.0	-3.7166679367	-1.6568935208	-1.0816931013
H	1.0	-3.8678657082	-1.8629148252	-2.1380425589
C	6.0	-4.4863939496	-0.6772184001	-0.5024386397
N	7.0	-5.4235508754	0.0238390707	-1.2280574867

C	6.0	-5.6770074153	-0.2052306668	-2.6348905911
H	1.0	-6.4671484312	0.4655549081	-2.9693419093
H	1.0	-5.9952229967	-1.2397840921	-2.8021350544
H	1.0	-4.7738148850	-0.0125696705	-3.2238691899
C	6.0	-6.0895987582	0.9768917444	-0.4373938359
C	6.0	-7.0929479564	1.8777788531	-0.7915839356
H	1.0	-7.4945790483	1.9408624046	-1.7995343552
C	6.0	-7.5819586113	2.7230283761	0.2135723039
H	1.0	-8.3649030874	3.4369901288	-0.0314999884
C	6.0	-7.0828436996	2.6643856303	1.5189528790
H	1.0	-7.4808253652	3.3322736966	2.2788543548
C	6.0	-6.0730459159	1.7498804539	1.8514133031
H	1.0	-5.6842641744	1.7043207531	2.8673990944
C	6.0	-5.5799052840	0.9065226680	0.8632367593
C	6.0	-4.5106614330	-0.1582899636	0.9348591214
C	6.0	-4.9213400607	-1.2615555309	1.9214764003
C	6.0	-3.1629000910	0.4643228138	1.3285103152
H	1.0	-5.8869873575	-1.6891888606	1.6346435073
H	1.0	-2.8875233257	1.2543870456	0.6231226398
H	1.0	-5.0197164517	-0.8309460521	2.9238511206
H	1.0	-3.2481188256	0.9081668937	2.3263042593
H	1.0	-4.1624347630	-2.0445769757	1.9428457000
H	1.0	-2.3877861415	-0.3027617421	1.3447836033
O	8.0	-2.3053909506	-2.4815615054	0.7092419861

*B3LYP/6-31G(d): Lowest energy minimum of aldehyde fragment **7**.*

E = –749.78354

ATOM	CHARGE	X	Y	Z
C	6.0	-0.1809342935	-2.4214340738	-0.5240969931
H	1.0	-0.0572146242	-2.8282718368	0.4784679753
C	6.0	-1.4132403708	-2.7859830572	-1.2802115464
C	6.0	0.7489244094	-1.6079489907	-1.0792091679
H	1.0	-2.1239961015	-3.4534367635	-0.7576849876
H	1.0	0.5612816953	-1.2369441238	-2.0860124173
C	6.0	1.9583696999	-1.2150004205	-0.4123691943
H	1.0	2.1154912202	-1.6023080900	0.5895175097
C	6.0	2.8827512562	-0.3937484895	-0.9983320541
H	1.0	2.6556770632	-0.0414217510	-2.0000970547
C	6.0	4.1045296033	0.0543894292	-0.4106049816
N	7.0	4.9701730531	0.8223274026	-1.0768750226
C	6.0	4.8543235161	1.2881847939	-2.4640812860
H	1.0	5.8545616230	1.3350803993	-2.8965963472
H	1.0	4.2599365251	0.5914541265	-3.0525576871
H	1.0	4.3992447300	2.2833520795	-2.4892321821
C	6.0	6.0814090935	1.1881123299	-0.2674640396
C	6.0	7.1658633521	1.9970036906	-0.5991805886
H	1.0	7.2705127353	2.4680468941	-1.5706506138
C	6.0	8.1291318430	2.1917494495	0.3938954756

H	1.0	8.9912226184	2.8161128380	0.1813150552
C	6.0	7.9971346461	1.5968705484	1.6556177018
H	1.0	8.7618219763	1.7651102199	2.4077060125
C	6.0	6.8930466359	0.7914719621	1.9629807299
H	1.0	6.8025840125	0.3394855061	2.9466477964
C	6.0	5.9262201644	0.5922068452	0.9853763831
C	6.0	4.6352772145	-0.2041205604	1.0047435719
C	6.0	4.9338737393	-1.7116400107	1.2302068342
C	6.0	3.6714818381	0.3517095844	2.0864934032
H	1.0	5.6029328002	-2.1056958579	0.4590341972
H	1.0	3.4552915642	1.4117792570	1.9217930339
H	1.0	5.4255306037	-1.8345587299	2.2000032580
H	1.0	4.1432427513	0.2511798844	3.0686484040
H	1.0	4.0211819834	-2.3133224179	1.2376689222
H	1.0	2.7250168908	-0.1947721885	2.1101613099
O	8.0	-1.6322123079	-2.3788715485	-2.4040692901

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **7**.*

E = –747.79905

ATOM	CHARGE	X	Y	Z
C	6.0	-0.1608811507	-2.4354407688	-0.5042912494
H	1.0	-0.0068374972	-2.8662074297	0.4845822027
C	6.0	-1.4028846231	-2.7787656527	-1.2468774646
C	6.0	0.7507029540	-1.6002716259	-1.0655925856
H	1.0	-2.1100653171	-3.4607839490	-0.7452825126
H	1.0	0.5320073211	-1.2061431846	-2.0583321632
C	6.0	1.9729008281	-1.2214620261	-0.4130089242
H	1.0	2.1568184963	-1.6342987452	0.5751673692
C	6.0	2.8773288494	-0.3828559054	-1.0031178554
H	1.0	2.6234713620	-0.0031227274	-1.9898523912
C	6.0	4.1062234947	0.0539629597	-0.4138748068
N	7.0	4.9737631112	0.8139049185	-1.0785560618
C	6.0	4.8642776323	1.2749798202	-2.4680404160
H	1.0	5.8677598163	1.3006285599	-2.8914512997
H	1.0	4.2602806913	0.5791027497	-3.0456186816
H	1.0	4.4239491060	2.2746992464	-2.4885054715
C	6.0	6.0808095764	1.1839553811	-0.2675086328
C	6.0	7.1688280321	1.9905586909	-0.6003993014
H	1.0	7.2843189809	2.4640619077	-1.5711255649
C	6.0	8.1192322100	2.1832779307	0.4051643866
H	1.0	8.9865922102	2.8055985754	0.2035338983
C	6.0	7.9729424273	1.5892290018	1.6696766092
H	1.0	8.7335493234	1.7603909062	2.4267405179
C	6.0	6.8674998237	0.7857260934	1.9734703714
H	1.0	6.7675497027	0.3360931804	2.9589479717
C	6.0	5.9083109268	0.5902481777	0.9832130883
C	6.0	4.6273872014	-0.2004013363	0.9889397160
C	6.0	4.9373433814	-1.6952367955	1.2119799422

C	6.0	3.6648880372	0.3516726326	2.0576027163
H	1.0	5.6165881746	-2.0702381797	0.4411029268
H	1.0	3.4621327263	1.4128178938	1.8868968048
H	1.0	5.4240871042	-1.8100788758	2.1847342370
H	1.0	4.1311185479	0.2445731223	3.0412183323
H	1.0	4.0316061912	-2.3050560755	1.2095652244
H	1.0	2.7164071891	-0.1896132906	2.0664856313
O	8.0	-1.6395636814	-2.3293568502	-2.3666344436

XII. Products 8+9 (C3'/C4' bond oxidized)

*B3LYP/6-31G(d): Lowest energy minimum of aldehyde fragment **8**.*

E = –672.42097

ATOM	CHARGE	X	Y	Z
C	6.0	-1.2869613269	-2.6844073533	-1.3765913378
H	1.0	-0.9149507610	-3.6788187993	-1.0707720434
C	6.0	-2.4586031562	-2.1529542430	-0.6079284730
H	1.0	-2.8582748699	-2.7721765266	0.1877039172
C	6.0	-2.9568725440	-0.9395415395	-0.9389472596
H	1.0	-2.4428137273	-0.4471059330	-1.7601932327
C	6.0	-4.0683220412	-0.2646234448	-0.3231058509
N	7.0	-4.4802063060	0.9334083364	-0.7272380410
C	6.0	-3.9378956200	1.7695880721	-1.8074686413
H	1.0	-4.7253578799	1.9390682265	-2.5466583512
H	1.0	-3.0889180936	1.2914679240	-2.2870371816
H	1.0	-3.6234801575	2.7267648306	-1.3831998812
C	6.0	-5.5910895010	1.3909238829	0.0328816854
C	6.0	-6.2881141877	2.5904940532	-0.0991718622
H	1.0	-6.0323751025	3.3373580119	-0.8431618726
C	6.0	-7.3498504805	2.7926729714	0.7843620643
H	1.0	-7.9250415256	3.7110719767	0.7231111803
C	6.0	-7.6825185787	1.8282670423	1.7472559509
H	1.0	-8.5137169917	2.0139821159	2.4206211057
C	6.0	-6.9633774836	0.6313872107	1.8562525181
H	1.0	-7.2350223861	-0.1041485511	2.6078711159
C	6.0	-5.9038062859	0.4165789468	0.9830436513
C	6.0	-4.9429216899	-0.7457664342	0.8362875103
C	6.0	-5.7093133944	-2.0450558238	0.4633842275
C	6.0	-4.1085490430	-0.9334646880	2.1335785905
H	1.0	-6.2894075762	-1.9180991178	-0.4558193234
H	1.0	-3.5604711826	-0.0223878195	2.3925801125
H	1.0	-6.4043484016	-2.2893966766	1.2722130705
H	1.0	-4.7873028443	-1.1674113037	2.9591260547
H	1.0	-5.0317997050	-2.8925615451	0.3327466528
H	1.0	-3.3937876186	-1.7549222994	2.0409167109
O	8.0	-0.7747630274	-2.0604439227	-2.2828616171

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **8**.*

E = –670.65407

ATOM	CHARGE	X	Y	Z
C	6.0	-1.3012934006	-2.6888318248	-1.3586540681
H	1.0	-0.9187348017	-3.6798872974	-1.0661076471
C	6.0	-2.4703314777	-2.1615883449	-0.5912742376
H	1.0	-2.8782734489	-2.7737786437	0.2059845066

C	6.0	-2.9579631900	-0.9426881278	-0.9356966851
H	1.0	-2.4323223321	-0.4623730650	-1.7581961275
C	6.0	-4.0695104878	-0.2684157550	-0.3203589700
N	7.0	-4.4802226817	0.9294795814	-0.7256886241
C	6.0	-3.9372718263	1.7658619911	-1.8050840280
H	1.0	-4.7318228310	1.9355423355	-2.5340943371
H	1.0	-3.0938961471	1.2802253350	-2.2860591698
H	1.0	-3.6190114528	2.7151059895	-1.3701482722
C	6.0	-5.5896047640	1.3883725986	0.0321664552
C	6.0	-6.2858137483	2.5903243815	-0.1019076839
H	1.0	-6.0355001242	3.3427229025	-0.8444671924
C	6.0	-7.3452577897	2.7817378965	0.7867743503
H	1.0	-7.9259777862	3.6982392177	0.7323622967
C	6.0	-7.6736032957	1.8111133399	1.7497314419
H	1.0	-8.5053686936	1.9962707410	2.4242462222
C	6.0	-6.9544520029	0.6150959218	1.8577228765
H	1.0	-7.2235304711	-0.1238703705	2.6091388244
C	6.0	-5.8943026954	0.4087730710	0.9782966011
C	6.0	-4.9373953737	-0.7410813849	0.8271540585
C	6.0	-5.7040545284	-2.0273537941	0.4562197823
C	6.0	-4.1108140442	-0.9202943208	2.1172721123
H	1.0	-6.2848426534	-1.8848545274	-0.4595549837
H	1.0	-3.5734322961	-0.0010387720	2.3670282079
H	1.0	-6.3954048920	-2.2689616457	1.2684491111
H	1.0	-4.7924228588	-1.1550442156	2.9396498646
H	1.0	-5.0289461005	-2.8741603234	0.3172609231
H	1.0	-3.3905984283	-1.7357257007	2.0254588930
O	8.0	-0.7882568658	-2.0491696092	-2.2738433511

*<u>B3LYP/6-31G(d):</u> Lowest energy minimum of aldehyde fragment **9**.*

E = –711.32492

ATOM	CHARGE	X	Y	Z
C	6.0	0.0035623091	-2.8479663124	-0.7298516795
H	1.0	-0.0353108059	-2.6117143576	0.3616913408
C	6.0	1.1511007051	-2.2830810005	-1.4216689835
H	1.0	1.2365314429	-2.4837393219	-2.4881837944
C	6.0	2.0761135685	-1.5356888887	-0.7587487573
H	1.0	1.9090003095	-1.3872051332	0.3066980206
C	6.0	3.2342580949	-0.9409930439	-1.3547349010
H	1.0	3.3529989780	-1.1213854354	-2.4205238270
C	6.0	4.1875842158	-0.1828371089	-0.7290916482
N	7.0	5.2743916876	0.3472969386	-1.4061120206
C	6.0	5.5029846401	0.1516362828	-2.8231374210
H	1.0	6.4185475829	0.6632721731	-3.1197756834
H	1.0	5.6077452279	-0.9151749198	-3.0573943088
H	1.0	4.6703158957	0.5565966520	-3.4118811007
C	6.0	6.1077985882	1.0845489214	-0.5504558699
C	6.0	7.2882363871	1.7680380007	-0.8395590212

H	1.0	7.7085262280	1.7956661711	-1.8401112373
C	6.0	7.9325414446	2.4318827161	0.2122744232
H	1.0	8.8541613046	2.9707829885	0.0086414976
C	6.0	7.4134674213	2.4122453842	1.5082151384
H	1.0	7.9299686366	2.9340662014	2.3086486855
C	6.0	6.2239814232	1.7184744063	1.7779725647
H	1.0	5.8187847750	1.7027725392	2.7871990397
C	6.0	5.5757341283	1.0568772782	0.7456316094
C	6.0	4.2899886736	0.2393557696	0.7512520804
C	6.0	4.4371841486	-0.9831321176	1.6886338451
C	6.0	3.0951741528	1.1252349041	1.1786879733
H	1.0	5.2822584563	-1.6094007251	1.3850199379
H	1.0	2.9928541100	1.9901867003	0.5154394879
H	1.0	4.6175392311	-0.6442850320	2.7152837574
H	1.0	3.2533835219	1.4959563033	2.1979623726
H	1.0	3.5367071687	-1.6041213797	1.6903359175
H	1.0	2.1524367444	0.5706286550	1.1625356906
O	8.0	-0.8712834263	-3.5282821489	-1.2466166382

*MP2/6-31G(d): Lowest energy minimum of aldehyde fragment **9**.*

E = –709.43771

ATOM	CHARGE	X	Y	Z
C	6.0	0.0127807543	-2.8295968680	-0.6910962873
H	1.0	-0.0194529945	-2.5922244176	0.3962678202
C	6.0	1.1532455812	-2.2737362865	-1.4051167182
H	1.0	1.2275549426	-2.4793544599	-2.4715538038
C	6.0	2.0833626735	-1.5267130077	-0.7487911722
H	1.0	1.9253280661	-1.3745278354	0.3177779419
C	6.0	3.2361889166	-0.9399544807	-1.3640085998
H	1.0	3.3472082578	-1.1233965889	-2.4313197062
C	6.0	4.1904365166	-0.1832511117	-0.7363633336
N	7.0	5.2791060432	0.3455501412	-1.4095794059
C	6.0	5.5053907120	0.1474835505	-2.8240541893
H	1.0	6.4283406883	0.6488539912	-3.1130784153
H	1.0	5.5966698378	-0.9204339402	-3.0520317552
H	1.0	4.6774680520	0.5636883932	-3.4091712682
C	6.0	6.1059535634	1.0825787811	-0.5536016068
C	6.0	7.2875520907	1.7705098018	-0.8330881637
H	1.0	7.7191420876	1.8066059116	-1.8299271739
C	6.0	7.9185754281	2.4307092960	0.2293644095
H	1.0	8.8409861620	2.9745442145	0.0386774900
C	6.0	7.3871449916	2.4036535304	1.5229266121
H	1.0	7.8982848427	2.9251038821	2.3282159435
C	6.0	6.1982803174	1.7069722763	1.7835221863
H	1.0	5.7836071295	1.6856493478	2.7903313034
C	6.0	5.5633042771	1.0484608928	0.7376399744
C	6.0	4.2889122532	0.2332432453	0.7328536456
C	6.0	4.4449322314	-0.9811015307	1.6606798235

C	6.0	3.1053743745	1.1161993613	1.1562927201
H	1.0	5.2970310792	-1.5906805087	1.3462695002
H	1.0	3.0176319028	1.9776510220	0.4879336668
H	1.0	4.6234593780	-0.6406888976	2.6864439305
H	1.0	3.2663970280	1.4845390264	2.1752813727
H	1.0	3.5507850569	-1.6097826141	1.6573725390
H	1.0	2.1617276319	0.5650566759	1.1347202024
O	8.0	-0.8734429032	-3.5150987333	-1.2055129921