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

This copy of the ESI replaces the previous version published on 26.06.2023 to correct some errors in the calculations and the optimized geometries

ELECTRONIC SUPPLEMENTARY INFORMATION

Correction: The Reaction of Acetonitrile with Hydrogen Peroxide in Alkaline Medium: a DFT Mechanistic Study of Green Production of Amides.

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OPTIMIZED COORDINATES
M06L/6-311+G(d,p)

ACN
6

C	1.267096	0.457142	-0.007299
C	2.087703	-0.722182	0.017785
N	0.603688	1.410263	-0.027466
H	2.903178	-0.626188	-0.700625
H	2.509739	-0.863915	1.013787
H	1.491665	-1.598738	-0.240390

H_2O_2
4

O	-2.129018	0.348978	0.103132
O	-1.462253	-0.908325	-0.155535
H	-1.243196	-1.203756	0.741088
H	-1.415256	0.986221	-0.050700

HOO^-
3

O	-2.104031	0.376574	0.068278
O	-1.491880	-0.978838	-0.149258
H	-1.215917	-1.218808	0.742810

HO^-
2

O	0.000000	0.000000	-0.006607
H	0.000000	0.000000	0.953607

TS1
8

C	1.266687	-0.544687	-0.000043
C	0.100788	0.366041	-0.000019
N	-0.195913	1.531747	-0.000023
O	-1.198262	-0.875571	0.000060
H	1.260015	-1.194631	-0.877907
H	2.193670	0.031922	-0.000192
H	1.260186	-1.194434	0.877968
H	-1.961233	-0.288641	0.000187

TS2
8

C	-1.058617	-0.835045	-0.000044
C	-0.165577	0.350705	-0.000075
N	-0.214729	1.554927	0.000104
H	-0.886626	-1.461062	0.879440
H	-2.104493	-0.521203	-0.000599
H	-0.885847	-1.461889	-0.878821
O	1.427703	-0.397547	-0.000181
H	1.303615	-1.353916	0.001410
H	-1.844656	0.482998	-0.000839

INT1
8

C	0.979058	-1.042550	-0.000022
C	0.282276	0.293381	-0.000072
N	0.708797	1.460844	-0.000109
O	-1.166675	-0.048082	0.000263
H	0.706235	-1.639857	-0.876458
H	2.061100	-0.909831	-0.000155
H	0.706451	-1.639767	0.876544
H	-1.596069	0.817680	0.000247

INT2
8

C	1.059675	-1.023853	-0.000038
C	0.290891	0.273997	-0.000031
O	-1.173543	-0.079830	0.000092
N	0.650223	1.459296	-0.000068
H	0.818943	-1.634240	-0.877697
H	2.133740	-0.836841	-0.000131
H	0.819074	-1.634178	0.877699
H	-1.267324	-1.041185	0.000104

TS3
8

C	-1.424296	0.004343	0.000000
C	0.061923	0.131202	-0.000017
N	0.841269	1.140479	0.000008
O	0.773478	-1.066883	0.000001
H	-1.767731	-0.552527	0.877168
H	-1.908956	0.980586	-0.000662
H	-1.767695	-0.553668	-0.876455
H	1.541916	-0.135958	-0.000010

***cis*-EtIm$^-$**
8

C	-0.059741	0.137717	0.000052
C	1.437853	-0.070116	0.001136
N	1.864878	-1.314325	0.001997
O	2.159337	0.995253	0.000905
H	-0.618522	-0.799363	0.000161
H	-0.359066	0.721023	0.876013
H	-0.357969	0.720181	-0.876857
H	2.888279	-1.272003	0.002384

***trans-syn*-EtIm**
9

C	-0.079183	0.145054	0.000026
C	1.370010	-0.180977	0.000753
O	1.575333	-1.523968	0.001486
N	2.371966	0.611810	0.000387
H	-0.239081	1.221673	-0.000923
H	-0.563514	-0.288669	-0.878070
H	-0.564045	-0.287205	0.878551
H	2.029697	1.571238	-0.000423
H	2.531799	-1.677267	0.002040

***trans*-anti-EtIm**
9

C	-0.096293	0.158457	0.000035
C	1.349985	-0.190823	-0.000061
O	1.627053	-1.527142	0.000529
N	2.357597	0.593475	0.000352
H	-0.241698	1.237042	0.000024
H	-0.586940	-0.267577	-0.879320
H	-0.586887	-0.267534	0.879445
H	2.014866	1.552202	0.000570
H	0.801905	-2.028473	0.000658

OC1
12

C	-0.829727	2.689791	0.314677
C	-0.548098	1.428483	1.044880
O	-0.356918	1.647656	2.368380
N	-0.477899	0.236760	0.585589
O	-3.516053	0.265077	1.952429
O	-2.669669	-0.961894	2.112363
H	-0.650344	0.256409	-0.418006
H	-0.202269	0.791230	2.795417
H	-1.746951	3.142240	0.700072
H	-0.024912	3.410888	0.474590
H	-0.943186	2.507926	-0.752310
H	-1.866356	-0.709817	1.619234

TS4
12

C	-0.775660	1.213357	-0.817146
C	-0.205924	0.261216	0.183717
O	0.626763	-0.747102	-0.390719
O	2.034447	-0.232533	-0.311029
N	0.080529	0.533794	1.413717
O	-1.682061	-1.112652	-0.037649
H	-1.120387	0.705255	-1.716648
H	-1.605692	1.774220	-0.385096
H	0.000901	1.930310	-1.104761
H	-1.440874	-1.661197	0.715596
H	-0.399486	1.392572	1.677814
H	2.058149	0.013137	0.632821

OC2
12

C	-0.894297	2.656316	0.323108
C	-0.571944	1.417783	1.080247
O	-0.378193	1.574334	2.417188
N	-0.451911	0.225712	0.633870
O	-2.772080	-0.884098	2.061015
O	-2.916336	0.363728	2.877783
H	-0.623424	0.239394	-0.369503
H	-0.518120	2.497553	2.663671
H	-1.795097	3.120307	0.734457
H	-0.082848	3.382388	0.422795
H	-1.054229	2.441868	-0.732034
H	-1.927389	-0.664133	1.625404

TS5
12

C	-0.733007	1.070930	-0.975532
C	-0.201814	0.274422	0.174741
N	0.080024	0.740908	1.346570
O	0.621339	-0.825451	-0.221923
O	2.018447	-0.288632	-0.311132
O	-1.670187	-1.081530	0.259094
H	-1.067378	0.441783	-1.800305
H	-1.561983	1.704166	-0.655904
H	0.060323	1.726698	-1.351929
H	-1.855326	-1.298240	-0.661097
H	-0.383888	1.641168	1.456860
H	2.100222	0.090853	0.582813

***trans-syn*-PAIA**
10

C	-1.742018	-0.648180	-0.047003
C	-0.481149	0.098999	0.178947
N	-0.239049	1.348248	0.236205
O	0.558036	-0.772058	0.348122
O	1.802592	-0.074593	0.573280
H	-1.575520	-1.724648	-0.057310
H	-1.089199	1.887659	0.095940
H	1.491262	0.864884	0.531091
H	-2.179269	-0.346995	-1.000144
H	-2.455235	-0.408320	0.743279

OC3
10

C	0.863001	0.270552	-0.137925
C	1.795800	-0.695410	-0.643422
N	0.110148	1.054162	0.270402
O	-2.419548	-0.029665	1.051126
H	2.314312	-0.297154	-1.516551
H	2.530299	-0.943677	0.124114
H	1.264005	-1.604253	-0.931142
O	-2.036242	-1.296496	0.467479
H	-1.648383	-1.757757	1.226206
H	-1.639400	0.523012	0.835853

TS6
10

C	1.170479	0.239360	0.006923
C	1.883093	-0.989821	0.000000
N	0.878745	1.389279	0.016893
O	-1.086741	0.156746	-0.030745
H	1.632729	-1.560128	-0.896242
H	2.957164	-0.775990	0.005497
H	1.625934	-1.574692	0.884825
O	-2.397805	-0.444910	-0.093468
H	-2.627712	-0.560995	0.838827
H	-0.184395	1.554927	0.001008

OC4
9

C	-1.123235	0.618227	0.002644
C	-2.053717	-0.476083	-0.002354
N	-0.392467	1.522036	0.005945
O	1.394645	-1.339464	0.091898
H	-1.914363	-1.090790	0.888071
H	-3.075686	-0.092592	-0.013280
H	-1.897792	-1.096112	-0.886360
O	2.158390	-0.059934	-0.046830
H	1.445928	0.598091	-0.022858

TS7

9

C	-0.583832	0.362351	-0.000029
C	-1.796015	-0.473533	0.000024
N	-0.161888	1.490820	-0.000001
O	0.654691	-0.911890	-0.000044
H	-1.825954	-1.119785	0.880084
H	-2.688465	0.154188	0.000078
H	-1.826000	-1.119707	-0.880073
O	1.880125	-0.144869	0.000045
H	1.474185	0.770724	-0.000070

***cis*-PAIA$^-$**

9

C	2.421041	-0.337901	0.000061
C	1.007806	0.130510	0.000165
O	0.168315	-0.931271	0.000174
O	-1.239833	-0.553721	0.000243
N	0.657609	1.362314	0.000211
H	2.626491	-0.952506	-0.879564
H	3.099566	0.513410	0.000154
H	2.626554	-0.952757	0.879494
H	-0.368041	1.358540	0.000254

OC5

19

C	-1.983663	0.174435	-1.347742
C	-2.925992	-0.268325	-0.284123
O	-4.203977	-0.030342	-0.677158
O	-5.190586	-0.552570	0.256178
N	-2.565528	-0.820815	0.811372
O	-5.056099	-3.034414	-0.473605
O	-4.271551	-2.849232	-1.672573
C	-5.003357	-2.432501	-2.748532
C	-4.056389	-2.163133	-3.867439
N	-6.268751	-2.287976	-2.704419
H	-1.000279	0.372859	-0.923712
H	-1.878389	-0.615147	-2.097452
H	-2.344773	1.068548	-1.858205
H	-3.427173	-1.051110	1.316064
H	-5.150221	-2.060391	-0.145135
H	-4.547200	-2.335445	-4.824884
H	-3.742535	-1.116563	-3.824014
H	-3.161951	-2.783598	-3.801592
H	-6.572187	-1.973865	-3.625528

TS8

11

C	-2.202328	-0.751403	-0.355789
C	-1.105272	0.147659	0.119654
O	-1.129745	1.373877	-0.022101
N	-0.050024	-0.442523	0.768516
H	1.278953	0.387875	0.760878
H	0.061032	-1.425478	0.505491
H	-3.123578	-0.187342	-0.493516
H	-2.374943	-1.581675	0.331339
H	-1.900809	-1.183157	-1.315205
O	1.688880	0.353269	-0.197885
O	2.722754	-0.388408	-0.248987

AcAm + $^1O_2$

11

C	-2.038983	-0.373403	-0.444202
C	-0.594329	-0.371460	-0.065723
O	0.152244	0.540510	-0.487515
N	-0.146782	-1.350269	0.715939
O	2.241674	0.962419	1.477566
H	-0.765095	-2.075323	1.046393
H	-2.497315	0.557876	-0.107680
H	-2.577613	-1.217612	-0.015373
H	-2.123391	-0.405406	-1.531520
H	0.831806	-1.359674	0.973903
O	2.139882	0.315613	0.430570

OC6

19

C	1.773190	-1.564415	-1.352601
C	2.300512	-0.549046	-0.410240
O	3.012155	0.395639	-1.096974
O	3.541865	1.408037	-0.212779
N	2.216058	-0.442912	0.856212
O	-0.267049	1.493147	-0.991448
O	-1.017666	0.361951	-0.460689
C	-2.337265	0.621041	-0.322371
C	-3.038127	-0.568524	0.235195
N	-2.916224	1.724112	-0.619963
H	2.595909	-2.151821	-1.766580
H	1.090707	-2.232805	-0.830201
H	1.250163	-1.089094	-2.184115
H	1.655225	-1.197684	1.241605
H	3.205055	1.079850	0.658404
H	-4.109366	-0.381923	0.289516
H	-2.863980	-1.451710	-0.383749
H	-2.671151	-0.800074	1.238229
H	-2.171247	2.337527	-0.969347

TS9

19

C	1.320627	0.466367	0.163605
C	0.613394	1.197260	1.267941
N	2.219695	0.998537	-0.655889
O	1.709908	-0.784265	0.706673
H	1.325775	1.459987	2.053229
H	0.177715	2.115283	0.872027
H	-0.182356	0.595687	1.713652
H	2.038625	1.991809	-0.754381
O	-1.030239	-0.762513	-0.330572
C	-2.171517	-0.030646	-0.183693
C	-3.223399	-0.883746	0.433411
H	-4.162996	-0.337243	0.491240
H	-3.374755	-1.797413	-0.145006
H	-2.925139	-1.183644	1.441172
N	-2.340832	1.191884	-0.511318
H	-1.452070	1.530175	-0.890840
H	2.959398	-0.626338	-0.688323
O	0.086704	0.036243	-0.917258
O	2.634768	-1.436547	-0.210082

INT4 + *cis*-EtIm$^-$

19

C	0.981036	1.346441	1.376233
C	1.577609	0.668291	0.192225
O	0.970932	0.776099	-1.044139
O	-1.292572	-1.107776	0.087041
C	-2.298247	-0.308469	0.152530
N	-2.318917	0.968203	-0.165189
N	2.359113	1.331786	-0.794216
O	1.994329	-0.604933	0.603232
O	2.515003	-1.363458	-0.505962
C	-3.591944	-0.911922	0.650955
H	1.732332	1.482415	2.155251
H	0.601400	2.322695	1.074126
H	0.159415	0.751096	1.777430
H	2.186515	2.336459	-0.670276
H	-4.415032	-0.196052	0.676055
H	-3.882753	-1.755096	0.017258
H	-3.452181	-1.315593	1.658462
H	-1.370194	1.207617	-0.469950
H	3.458639	-1.137318	-0.479097

INT4
11

C	0.984207	1.346128	1.376308
C	1.573762	0.666157	0.191557
O	1.979728	-0.613063	0.594561
O	2.527688	-1.356324	-0.512767
O	0.959399	0.778400	-1.045270
N	2.350554	1.325306	-0.798541
H	1.735454	1.471743	2.156710
H	0.615169	2.327179	1.078335
H	0.155567	0.761228	1.776983
H	2.185042	2.331036	-0.672551
H	3.469753	-1.128216	-0.460518

TS10
11

C	1.537447	-0.964525	-0.006681
C	0.335075	-0.087220	0.049302
O	0.194157	0.807967	1.046811
N	0.428485	1.185231	-0.758588
O	-0.788406	-0.838049	-0.291370
O	-1.970264	-0.208860	0.053734
H	1.548977	-1.522735	-0.943101
H	1.499610	-1.666982	0.826362
H	1.237886	1.772186	-0.562064
H	-0.447130	1.706269	-0.812016
H	2.442230	-0.363343	0.071810

OPTIMIZED COORDINATES M06L/cc-PVTZ

ACN
6

C	1.267458	0.456370	-0.007295
C	2.087170	-0.721548	0.017640
N	0.606444	1.406412	-0.027284
H	2.900165	-0.626479	-0.697732
H	2.508113	-0.863045	1.009904
H	1.493719	-1.595328	-0.239441

H_2O_2
4

O	-2.132800	0.348983	0.097110
O	-1.468175	-0.911893	-0.157241
H	-1.238060	-1.190612	0.739366
H	-1.410688	0.976640	-0.041249

HOO^-
3

O	-2.104302	0.378242	0.071223
O	-1.489329	-0.984852	-0.151136
H	-1.218198	-1.214462	0.741742

HO^-
2

O	0.000000	0.000000	-0.005390
H	0.000000	0.000000	0.952390

TS1
8

C	-1.208803	-0.657049	0.000062
C	-0.156037	0.373661	0.000026
N	0.046750	1.549444	0.000042
O	1.292790	-0.782104	-0.000112
H	-1.124009	-1.299538	0.873961
H	-2.194335	-0.195745	0.000188
H	-1.124178	-1.299420	-0.873941
H	1.961995	-0.094246	-0.000135

TS2
8

C	0.750191	-1.111051	-0.000107
C	0.292524	0.293744	0.000009
N	0.687983	1.421375	0.000134
H	0.380720	-1.644705	-0.874269
H	1.838010	-1.156681	-0.002179
H	0.384280	-1.643523	0.876270
O	-1.504892	0.039026	-0.000327
H	-1.636042	-0.913086	0.002441

INT1
8

C	0.977548	-1.039712	-0.000051
C	0.287100	0.298465	-0.000054
N	0.706294	1.458096	-0.000026
O	-1.167186	-0.055779	0.000499
H	0.703435	-1.635236	-0.872664
H	2.056744	-0.912057	-0.000195
H	0.703652	-1.635113	0.872713
H	-1.586413	0.813154	0.000016

INT2
8

C	1.056245	-1.020758	-0.000018
C	0.298433	0.281519	0.000008
O	-1.176151	-0.087477	0.000239
N	0.652693	1.457374	-0.000093
H	0.813144	-1.628735	-0.874058
H	2.128484	-0.842202	-0.000184
H	0.813401	-1.628629	0.874170
H	-1.254570	-1.047926	-0.000132

TS3
8

C	-1.418850	0.006344	-0.000003
C	0.066441	0.131756	-0.000027
N	0.839335	1.142121	-0.000135
O	0.766730	-1.069436	0.000130
H	-1.762689	-0.549554	0.872971
H	-1.902459	0.978872	-0.000381
H	-1.762687	-0.550232	-0.872543
H	1.533101	-0.147046	0.000035

***cis*-EtIm$^-$**
8

C	-0.056908	0.136556	0.000072
C	1.440251	-0.069370	0.001143
N	1.860693	-1.312215	0.001837
O	2.155290	0.992618	0.001053
H	-0.614360	-0.797090	0.000269
H	-0.356236	0.718518	0.872240
H	-0.355130	0.717449	-0.873191
H	2.881448	-1.268098	0.002368

***trans-syn*-EtIm**
9

C	-0.077756	0.145042	-0.000027
C	1.368887	-0.181500	0.000458
O	1.573744	-1.521953	0.001619
N	2.369558	0.608947	0.000359
H	-0.237882	1.217697	-0.000918
H	-0.561582	-0.287386	-0.874176
H	-0.561866	-0.285955	0.874675
H	2.029990	1.565370	-0.000255
H	2.529890	-1.668573	0.002093

***trans-anti*-EtIm**

9

C	-0.093746	0.157763	0.000116
C	1.350000	-0.190372	0.000336
O	1.624408	-1.523878	0.000470
N	2.355465	0.593117	0.000411
H	-0.242229	1.232133	-0.000019
H	-0.583264	-0.267806	-0.875262
H	-0.583456	-0.267613	0.875484
H	2.013191	1.548006	0.000311
H	0.799217	-2.021723	0.000385

OC1

12

C	-0.941751	2.618729	0.369563
C	-0.527305	1.374829	1.060692
O	-0.351346	1.575398	2.386244
N	-0.319458	0.215542	0.567713
O	-3.425210	0.487459	1.685153
O	-2.673749	-0.736986	2.129760
H	-0.506305	0.242172	-0.429282
H	-0.103768	0.726447	2.779873
H	-1.821548	3.037837	0.853615
H	-0.152708	3.366653	0.437005
H	-1.162004	2.430325	-0.675571
H	-1.847229	-0.633657	1.632549

TS4

12

C	-0.849100	1.178139	-0.820789
C	-0.189531	0.281328	0.170273
O	0.616024	-0.726738	-0.418242
O	2.037745	-0.251067	-0.319093
N	0.152789	0.596506	1.370570
O	-1.682618	-1.145424	0.056326
H	-1.216798	0.629386	-1.681661
H	-1.676443	1.715491	-0.363728
H	-0.124152	1.915940	-1.171058
H	-1.287952	-1.705475	0.728156
H	-0.323571	1.452175	1.635626
H	2.021972	0.045967	0.609839

OC2

12

C	-0.977937	2.594984	0.362741
C	-0.543141	1.371864	1.083300
N	-0.319917	0.209619	0.604998
O	-0.336165	1.515497	2.416790
O	-2.765414	-0.698313	2.062540
H	-0.511352	0.232668	-0.390752
H	-0.569583	2.410263	2.688402
H	-1.840938	3.036925	0.858491
H	-0.181748	3.339267	0.376557
H	-1.234544	2.374476	-0.667867
H	-1.904744	-0.589552	1.628608
O	-3.473060	0.545694	1.599005

TS5

12

C	-0.741450	1.049351	-0.988550
C	-0.172326	0.298702	0.169474
N	0.128477	0.796505	1.316454
O	0.597697	-0.833048	-0.199815
O	2.016310	-0.335769	-0.322559
O	-1.698480	-1.082235	0.301384
H	-1.074580	0.389616	-1.784337
H	-1.576353	1.670215	-0.673523
H	0.025644	1.709880	-1.399565
H	-1.900365	-1.218518	-0.627113
H	-0.314262	1.706112	1.402466
H	2.099009	0.087251	0.549263

trans-syn-PAIA

10

C	-1.738783	-0.646238	-0.046128
C	-0.477475	0.096754	0.179578
N	-0.239757	1.344923	0.237189
O	0.557152	-0.771958	0.346181
O	1.799851	-0.071462	0.570332
H	-1.576353	-1.719511	-0.056466
H	-1.087153	1.881634	0.098763
H	1.478917	0.863265	0.528061
H	-2.175595	-0.346053	-0.995233
H	-2.450354	-0.406355	0.740128

OC3

10

C	0.855733	0.268130	-0.127943
C	1.782221	-0.698578	-0.639117
N	0.108931	1.050296	0.282977
O	-2.421669	-0.032503	1.035596
H	2.305392	-0.297506	-1.503242
H	2.509865	-0.960177	0.124886
H	1.246195	-1.596809	-0.937233
O	-2.022448	-1.302877	0.466691
H	-1.588257	-1.725126	1.220537
H	-1.641971	0.518466	0.822988

TS6

10

C	1.157453	0.241284	0.007009
C	1.865428	-0.989988	0.000044
N	0.872392	1.390425	0.016139
O	-1.069858	0.157925	-0.029423
H	1.611224	-1.559179	-0.890973
H	2.937120	-0.785514	0.003801
H	1.607075	-1.572379	0.881230
O	-2.379561	-0.444852	-0.094069
H	-2.604131	-0.556410	0.837885
H	-0.199962	1.528149	0.000699

OC4

9

C	-1.116481	0.658494	0.028760
C	-1.996782	-0.474571	-0.001171
N	-0.421216	1.585287	0.043610
O	1.259644	-1.346065	0.117524
H	-1.862958	-1.072837	0.896334
H	-3.031353	-0.143531	-0.057244
H	-1.772179	-1.091076	-0.867714
O	2.080148	-0.109438	-0.104651
H	1.402879	0.577117	-0.038573

TS7

9

C	-1.788019	-0.508213	0.000592
C	-0.629585	0.387106	-0.000726
N	-0.207302	1.502005	-0.000466
O	0.699300	-0.931563	-0.001443
O	1.896251	-0.109463	0.001200
H	-1.786021	-1.138331	0.887495
H	-2.712811	0.064546	-0.017748
H	-1.767531	-1.167313	-0.864684
H	1.458694	0.781914	0.000953

cis-PAIA$^-$

9

C	2.419430	-0.336092	0.000060
C	1.007464	0.131390	0.000159
O	0.170498	-0.924575	0.000158
O	-1.236735	-0.543898	0.000241
N	0.657647	1.361510	0.000221
H	2.624326	-0.950039	-0.875462
H	3.098475	0.509926	0.000142
H	2.624387	-0.950264	0.875409
H	-0.365983	1.338661	0.000264

OC5

19

C	-1.950003	0.193815	-1.288695
C	-2.938626	-0.247774	-0.270505
O	-4.192584	-0.051686	-0.740134
O	-5.216594	-0.563319	0.157659
N	-2.629423	-0.761181	0.856682
O	-4.939884	-3.041984	-0.476245
O	-4.210789	-2.863912	-1.711765
C	-4.990876	-2.446556	-2.745811
C	-4.105419	-2.197386	-3.915702
N	-6.248498	-2.286278	-2.637566
H	-0.986143	0.380313	-0.826339
H	-1.822023	-0.584968	-2.040600
H	-2.283179	1.092165	-1.803170
H	-3.515596	-0.991927	1.310502
H	-5.089145	-2.056447	-0.190756
H	-4.674867	-2.262015	-4.837592
H	-3.685340	-1.194816	-3.840502
H	-3.276695	-2.899964	-3.951764
H	-6.594918	-1.975664	-3.540197

TS8

11

C	-2.200336	-0.742561	-0.357263
C	-1.098461	0.147961	0.119760
O	-1.118681	1.371726	-0.016092
N	-0.050606	-0.452369	0.763703
H	1.274792	0.385072	0.758514
H	0.055850	-1.430578	0.498903
H	-3.104116	-0.168096	-0.532183
H	-2.404559	-1.545746	0.347118
H	-1.888106	-1.209291	-1.291804
O	1.680824	0.351837	-0.199073
O	2.714502	-0.385710	-0.247516

AcAm + $^1O_2$

11

C	-2.042574	-0.378449	-0.444381
C	-0.597738	-0.366026	-0.072621
O	0.142276	0.542715	-0.499459
N	-0.146322	-1.338864	0.710434
O	2.250933	0.943446	1.491927
H	-0.757670	-2.059783	1.048238
H	-2.504115	0.547153	-0.109288
H	-2.574245	-1.221356	-0.014409
H	-2.132164	-0.411455	-1.527273
H	0.828286	-1.339720	0.967171
O	2.155431	0.305610	0.442020

OC6

19

C	1.735183	-1.453668	-1.421030
C	2.271147	-0.525097	-0.399668
O	3.054344	0.416916	-0.995387
O	3.572052	1.357309	-0.028265
N	2.125954	-0.486129	0.863120
O	-0.227476	1.340107	-1.137983
O	-0.975059	0.299059	-0.441117
C	-2.291340	0.567788	-0.354833
C	-2.994243	-0.534898	0.353995
N	-2.871631	1.610765	-0.813513
H	2.546609	-1.990582	-1.908320
H	1.064094	-2.168304	-0.956516
H	1.195891	-0.899069	-2.185917
H	1.511406	-1.226957	1.176769
H	3.165997	0.994607	0.797117
H	-4.048195	-0.302263	0.463318
H	-2.898133	-1.471184	-0.193737
H	-2.566030	-0.697674	1.341667
H	-2.121806	2.160571	-1.241597

TS9

19

C	1.320084	0.462013	0.164346
C	0.614782	1.191877	1.266918
N	2.220848	0.992966	-0.647320
O	1.692148	-0.794014	0.697547
H	1.324616	1.455349	2.049165
H	0.175591	2.105108	0.874067
H	-0.175506	0.589552	1.712750
H	2.072184	1.990435	-0.712975
O	-1.025362	-0.754069	-0.329654
C	-2.165332	-0.029192	-0.182957
C	-3.212440	-0.885225	0.433262
H	-4.150403	-0.344502	0.497485
H	-3.362541	-1.793661	-0.146534
H	-2.911426	-1.190402	1.434369
N	-2.340886	1.190113	-0.511445
H	-1.454606	1.525777	-0.890619
H	2.948729	-0.606457	-0.675165
O	0.079686	0.047973	-0.918030
O	2.632412	-1.431089	-0.214939

INT4 +cis-EtIm$^-$

19

C	0.971601	1.341416	1.373240
C	1.564944	0.653706	0.195179
O	0.958378	0.759608	-1.038993
O	-1.268332	-1.075274	0.100066
C	-2.278173	-0.288564	0.156582
N	-2.319931	0.983801	-0.159247
N	2.346083	1.313260	-0.794953
O	1.977827	-0.613846	0.613858
O	2.498007	-1.376096	-0.493260
C	-3.566126	-0.910257	0.644861
H	1.719787	1.480466	2.149367
H	0.593047	2.312519	1.067083
H	0.153287	0.750460	1.778417
H	2.174333	2.314384	-0.674303
H	-4.397326	-0.209498	0.667779
H	-3.840088	-1.753194	0.009853
H	-3.427217	-1.314827	1.648009
H	-1.376228	1.235723	-0.459824
H	3.430609	-1.113302	-0.491746

INT4

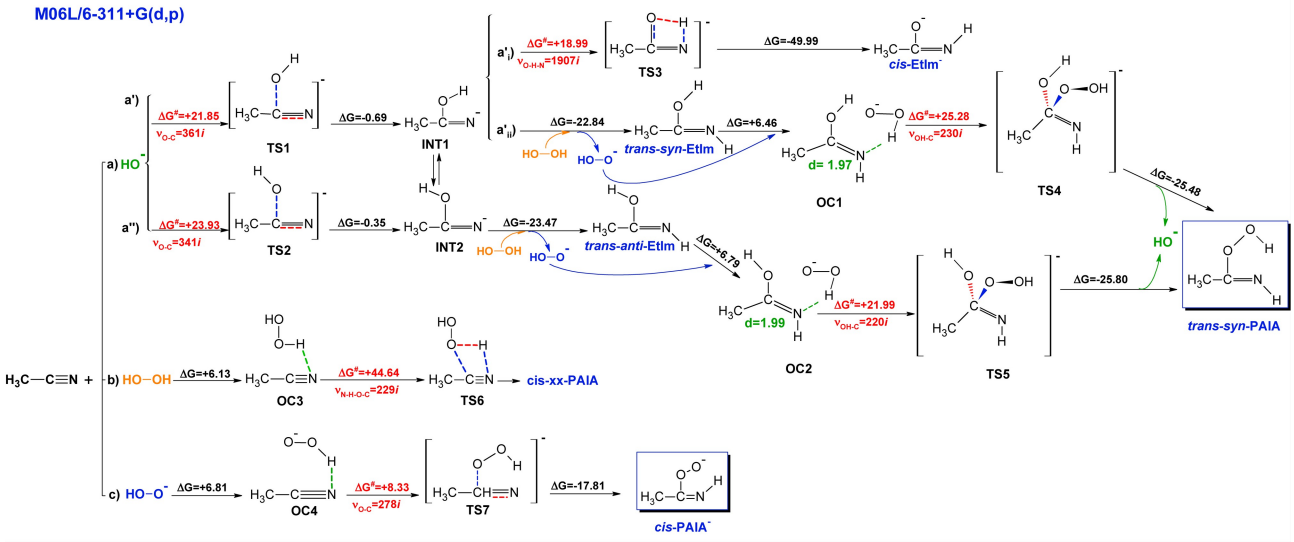
11

C	0.985113	1.345329	1.373615
C	1.575635	0.661040	0.193584
O	1.978517	-0.613608	0.601285
O	2.523932	-1.357557	-0.506292
O	0.964791	0.775721	-1.042621
N	2.354174	1.320517	-0.795483
H	1.731027	1.470620	2.153759
H	0.618864	2.322774	1.074850
H	0.158694	0.764130	1.773933
H	2.187956	2.322042	-0.669512
H	3.457619	-1.101434	-0.472312

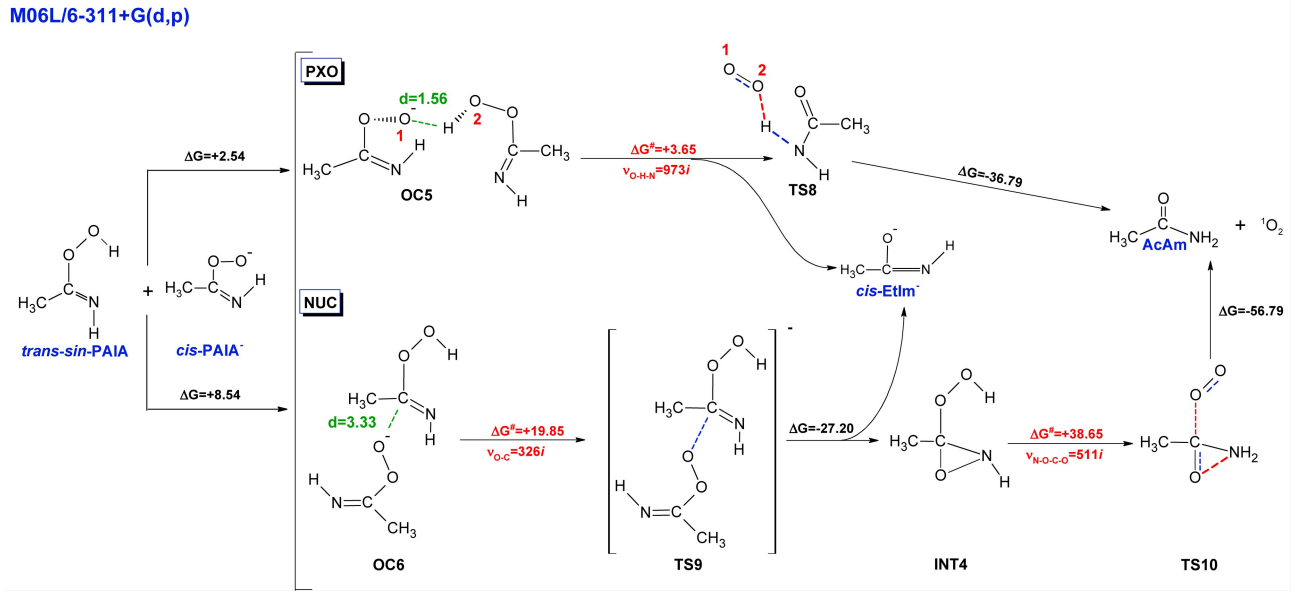
TS10

11

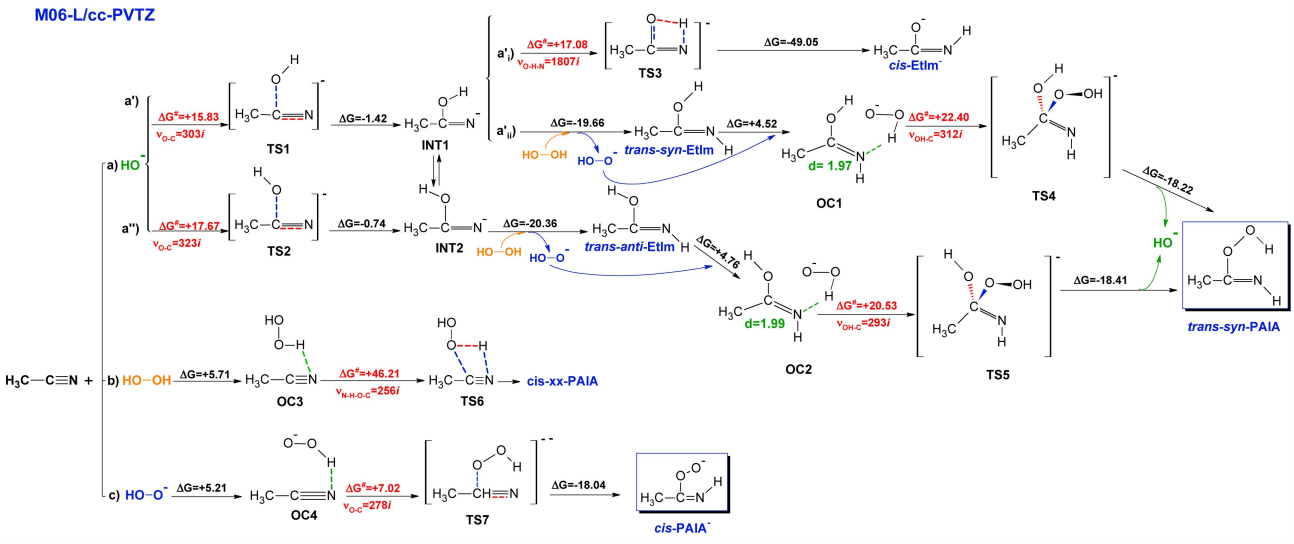
C	1.540863	-0.954881	-0.008654
C	0.333898	-0.086042	0.050009
O	0.192426	0.804387	1.047144
N	0.415922	1.186822	-0.762069
O	-0.782651	-0.841000	-0.291800
O	-1.961346	-0.215315	0.056003
H	1.551239	-1.518435	-0.937368
H	1.514300	-1.649989	0.825945
H	1.211936	1.780413	-0.556034
H	-0.464598	1.691729	-0.796573
H	2.439676	-0.350504	0.059608



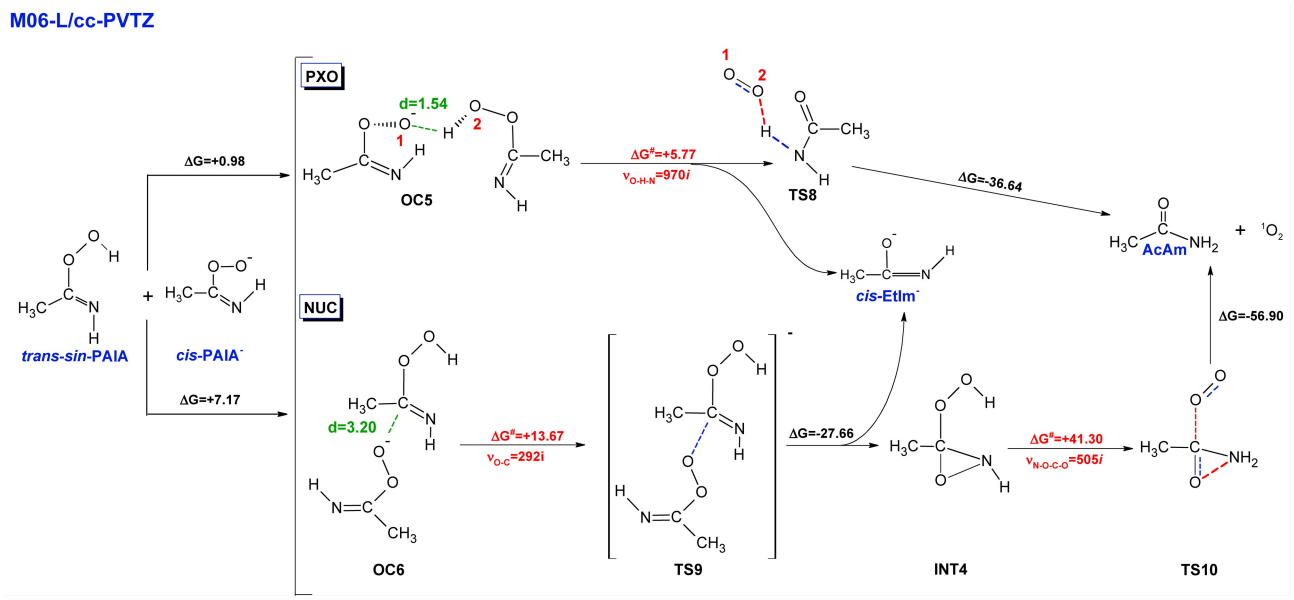
Scheme S1a revised formation mechanism of *trans-syn*-**PAIA** and cis-*PAIA*$^-$ at M06L/6-311G+(d,p) level of theory.



Scheme S1b revised formation mechanism of Acetamide (AcAm) at M06L/6-311G+(d,p) level of theory.



Scheme S2a revised formation mechanism of *trans-syn*-**PAIA** and cis-*PAIA*$^-$ at M06L/cc-PVTZ level of theory.



Scheme S2b revised formation mechanism of Acetamide (AcAm) at M06L/cc-PVTZ level of theory.