Supporting Information

Nature of Intermediates in Organo-SOMO Catalysis of α-Arylation of Aldehydes

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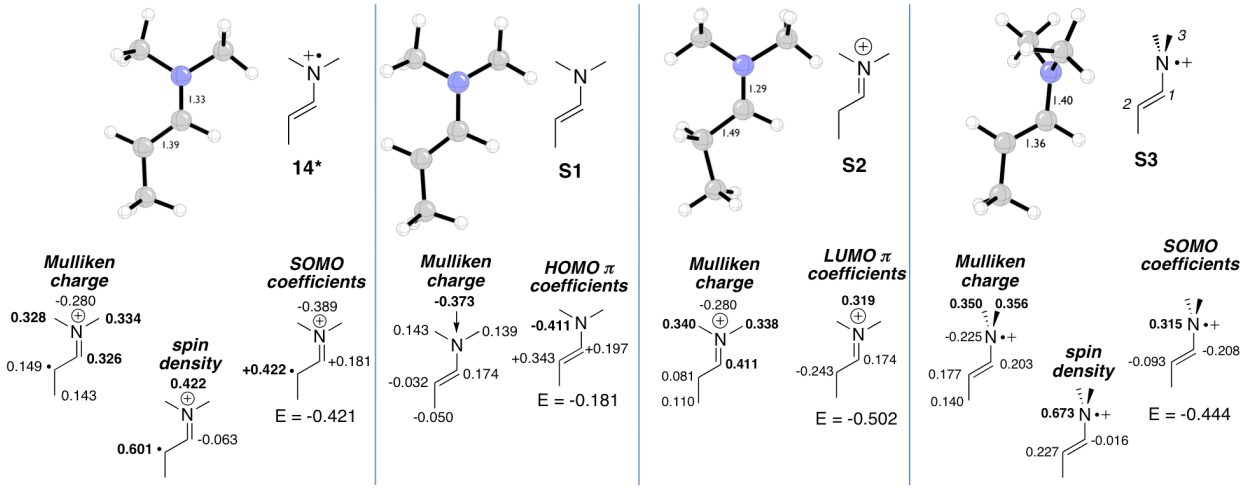
Contents

Comparison of 14* with enamine S1, iminium S2, and unconjugated radical cation S3



Oxidation of cyclized radical cations 17* and 18*

To understand the feasibility of oxidizing **17*** and **18*** to generate a dication, the oxidation and internal reorganization free energies were calculated. Single point energies (in water) were calculated on the gas-phase optimized geometries using CPCM B3LYP/6-31+G(d). The free energies of solvation from the single point energy calculations were used to obtain the energies used in the calculation of the internal reorganization energy (λ_i).

The Marcus equation allows the activation energy for the electron transfer to be calculated from the total reorganization energy (i.e., the total of the internal and solvent contributions) and the reaction free energy (ΔG_{rxn}). However, as a first approximation only the internal reorganization energies are used (eq. 1), as done elsewhere previously,[1] closely adopted to methodology successfully applied previously.[2-4]

$$\Delta G_{activation} = (\lambda_i/4)(1 + \Delta G_R/\lambda_i)^2 \qquad \text{(eq. 1)}$$

The following oxidations were calculated (see following page):

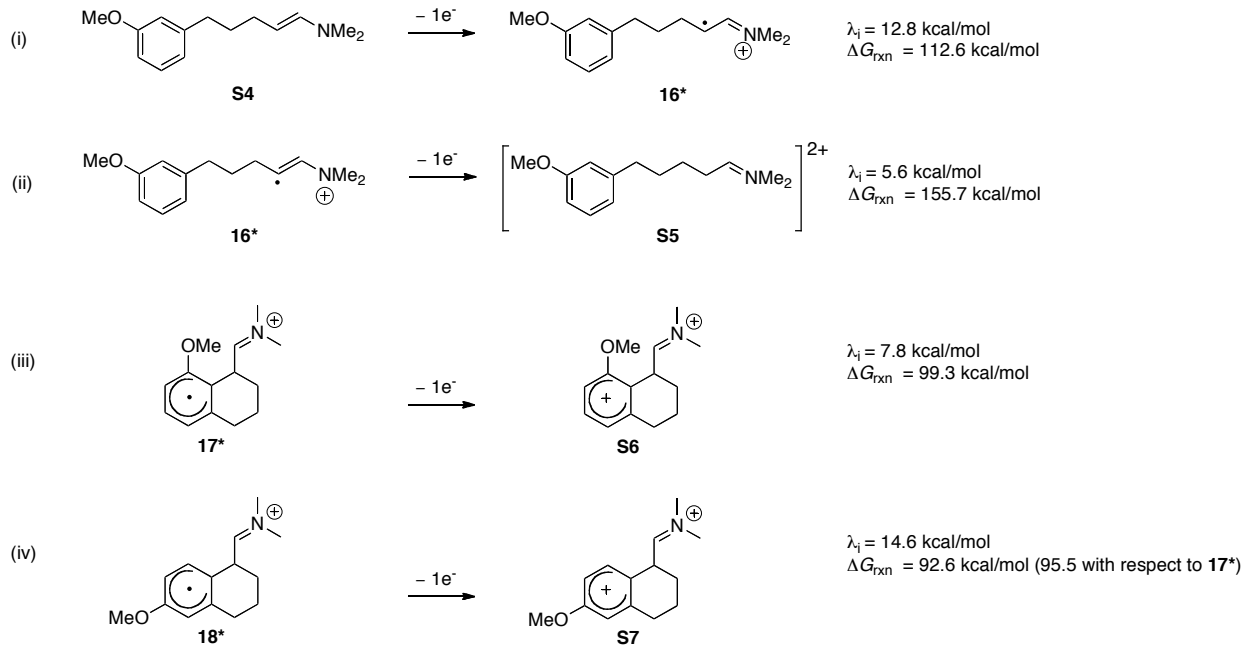
(i) Oxidation of the neutral enamine **S-4** to the radical cation **16***
(ii) Oxidation of the radical cation **16*** to the dication **S-5**
(iii) Oxidation of the ring-closed radical cation **17*** to the dication **S-6**
(iv) Oxidation of the ring-closed radical cation **18*** to the dication **S-7**

The four oxidations were considered in order to decide about their feasibility relative to each other. Since the oxidant is assumed to be identical in all three cases, it is neglected from this consideration. Only the half reactions for the oxidation of the organic compound are considered.

To calculate the internal reorganization energy (λ_i), the following approach was taken, as discussed for Reaction (i):[1]

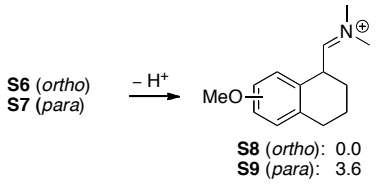
$$\lambda_i\,(1) = (E_N\,(R_c) - E_N(R_N)\,) + (E_C(R_N) - E_C(R_C))$$

$E_N(R_C)$: energy of the neutral species in the geometry of the radical cation;
$E_N(R_N)$: energy of the neutral species in its optimized geometry;
$E_C(R_N)$: energy of the cationic species in the geometry of the neutral compound
$E_C(R_C)$: energy of the cationic species in its optimized geometry.



The free energies and reorganization energies of the half reactions shown in above suggest that oxidation of the intermediate radical cation **17*** (and **18***) should be, at least as feasible as oxidation of the enamine **S4**. Furthermore, based on the greater endergonicity of the oxidation of radical cation **16***, it is reasonable to exclude dication **S5** as intermediate. Direct comparison of the SOMO-energies of species **16*** (E = -0.321 hartree) with **17*** (E = -0.278 hartree) and **18*** (E = -0.272 hartree) are in line with an easier oxidation of **17*** and **18***. The oxidation of **17*** and **18*** would be feasible with CAN (Ce^{4+} E° = +1.7 V). **S6** was calculated to be 3.8 kcal/mol destabilized with respect to **S7**.

Deprotonation of **S6**/**S7** would favor the more stable *ortho* iminium-aromatic product **S8**.



References

1. Murphy, J. A.; Zhou, S.-Z.; Thomson, D. W.; Schoenebeck, F.; Mohan, M.; Park, S. R.; Tuttle, T.; Berlouis, L. E. A. *Angew. Chem. Int. Ed.,* **2007**, *46*, 5178–5183.
2. Rosokha, S. V.; Dibrov, S. M.; Rosokha, T. Y.; Kochi, J. K. *Photochem. Photobiol. Sci.* **2006**, *5*, 914–924.
3. Rosokha, S. V.; Newton, M. D.; Head-Gordon, M. Kochi, J. K. *Chem. Phys.* **2006**, *324*, 117–128.
4. Rosokha, S. V.; Lu, J. M.; Newton, M. D.; Kochi, J. K. *J. Am. Chem. Soc.* **2005**, *127*, 7411–7420.

Molecular Geometries and Energies

Unless noted otherwise, all reported values are for the B3LYP/6-31G(d)-optimized geometries.

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of propanal, conjugated (14*)

Number of imaginary frequencies: 0
$\langle S^2 \rangle = 0.76$

C	-1.427923	0.325939	0.000023
H	-1.310964	1.406952	0.000096
C	-0.295676	-0.487528	-0.000027
H	-0.417686	-1.567154	-0.000054
N	0.966593	-0.053337	-0.000029
C	1.311509	1.378766	-0.000008
H	0.908033	1.860717	0.895108
H	2.396211	1.477061	-0.000542
H	0.907143	1.860971	-0.894578
C	2.086351	-1.002430	0.000023
H	1.712100	-2.026086	0.000108
H	2.699813	-0.832130	-0.890778
H	2.699831	-0.831993	0.890788
C	-2.807732	-0.213630	0.000000
H	-3.358708	0.161955	0.874986
H	-3.358720	0.162061	-0.874933
H	-2.842379	-1.305695	-0.000066

E (0 K) = -251.6339158
E +ZPE (0 K) = -251.479474
H (298 K) = -251.470374
G (298 K) = -251.512245

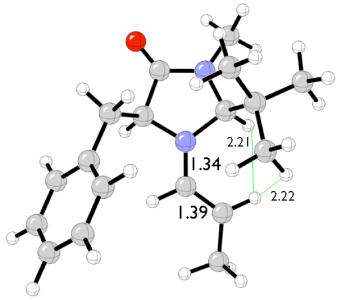
(*E*)-[(2*S*, 5*S*)-2-*tert*-butyl-5-benzyl-3-methyl-imidazolidin-4-one] enamine radical cation of propanal (15-*E)**

Number of imaginary frequencies: 0
$\langle S^2 \rangle = 0.76$

C	-2.063449	-0.355764	0.514050
C	-0.105008	1.135942	0.493320
H	-2.456344	-0.851930	1.412950
H	0.478463	1.452364	1.363318
C	0.734319	1.408513	-0.795280
H	0.749370	2.502627	-0.862200
N	-2.456861	1.046186	0.504273
C	-3.824271	1.524897	0.700193
H	-4.355501	0.864375	1.390701
H	-3.759068	2.527542	1.126666
H	-4.375960	1.585265	-0.241886
C	-1.414351	1.931130	0.474297
O	-1.479238	3.142179	0.450375
N	-0.580085	-0.232372	0.712167
C	2.136673	0.858325	-0.764480
C	2.450095	-0.366331	-1.380460
C	3.158122	1.561402	-0.102595
C	3.749694	-0.876131	-1.335390
H	1.678333	-0.908942	-1.921703
C	4.453742	1.050095	-0.051509
H	2.939787	2.523533	0.356103
C	4.751969	-0.172449	-0.666042
H	3.980215	-1.813617	-1.833119
H	5.236241	1.610719	0.451366
H	5.764938	-0.562660	-0.635516
H	0.183924	1.041772	-1.664511
C	0.122959	-1.207895	1.305747
H	-0.433154	-2.118414	1.503506
C	1.454398	-1.138142	1.687337
H	2.010271	-0.216070	1.552061
C	2.174405	-2.284650	2.296619
H	2.569628	-2.005365	3.283483
H	1.551602	-3.176746	2.403105
H	3.052912	-2.535029	1.684405
C	-2.518058	-1.214736	-0.728492
C	-4.046449	-1.427918	-0.616312
H	-4.614531	-0.510340	-0.780339
H	-4.363758	-2.144036	-1.380615
H	-4.331620	-1.842519	0.358117
C	-2.190327	-0.526488	-2.063089
H	-1.112895	-0.498990	-2.256369
H	-2.646459	-1.088110	-2.884559
H	-2.578862	0.495796	-2.107650
C	-1.854312	-2.606828	-0.690804
H	-0.769134	-2.562847	-0.830571
H	-2.071345	-3.146039	0.240379
H	-2.255456	-3.214311	-1.507862

E (0 K) = -886.059309
E +ZPE (0 K) = -885.647204
H (298 K) = -885.647204
G (298 K) = -885.69814

(*Z*)-[(2*S*, 5*S*)-2-*tert*-butyl-5-benzyl-3-methyl-imidazolidin-4-one] enamine radical cation of propanal (15-*Z)**



Number of imaginary frequencies: 0
$\langle S^2 \rangle$ = 0.76

C	-1.894608	0.333587	-0.382944
C	-0.012456	-1.225207	-0.648903
H	-2.299798	1.010003	-1.146395
H	0.528436	-1.419371	-1.580616
C	0.891507	-1.685919	0.528857
H	0.959139	-2.772437	0.396364
N	-2.352436	-1.027240	-0.633864
C	-3.745495	-1.402102	-0.857173
H	-4.243432	-0.641206	-1.465128
H	-3.741806	-2.353843	-1.391428
H	-4.293358	-1.534146	0.080532
C	-1.352386	-1.959503	-0.710436
O	-1.475111	-3.158735	-0.844041
N	-0.430737	0.185487	-0.655141
C	2.259173	-1.045090	0.525254
C	2.591902	-0.056682	1.463658
C	3.219753	-1.422112	-0.428471
C	3.854976	0.538769	1.454654
H	1.868141	0.228463	2.224315
C	4.479053	-0.824265	-0.442450
H	2.989022	-2.205307	-1.148271
C	4.798991	0.159189	0.499347
H	4.103417	1.289882	2.198827
H	5.216525	-1.135725	-1.176407
H	5.783729	0.617007	0.494017
H	0.379909	-1.512795	1.478267
C	0.388552	1.126583	-1.143404
H	1.411618	0.788293	-1.286669
C	0.054301	2.423997	-1.507590
H	-0.977407	2.755600	-1.443644
C	1.054589	3.394187	-2.018772
H	1.071296	4.290792	-1.381971
H	2.064012	2.977965	-2.064735
H	0.766310	3.746830	-3.019367
C	-2.278465	0.925177	1.039098
C	-3.758658	1.368977	0.962878
H	-4.446335	0.530286	0.835158
H	-4.032268	1.871469	1.895866
H	-3.929374	2.080719	0.146021
C	-2.112388	-0.118281	2.157998
H	-1.060926	-0.352111	2.351415
H	-2.523763	0.284594	3.088893
H	-2.639643	-1.051804	1.942486
C	-1.434201	2.167200	1.384633
H	-0.362808	1.950024	1.441044
H	-1.591634	2.991966	0.680747
H	-1.740750	2.535968	2.368646

E (0 K) = -886.054429
E +ZPE (0 K) = -885.642505
H (298 K) = -885.619678
G (298 K) = -885.694368

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of 5-(3-methoxyphenyl)-pentanal (16*)

Number of imaginary frequencies: 0
$\langle S^2 \rangle = 0.76$

C	-1.987802	-0.287804	1.342127
H	-1.825733	0.204243	2.314368
H	-2.241179	-1.336869	1.536111
C	-0.663460	-0.198769	0.535701
H	-0.429279	0.853567	0.330716
H	-0.796038	-0.693622	-0.434262
C	0.506251	-0.851863	1.299416
H	0.253197	-1.899134	1.510429
H	0.624147	-0.347963	2.267337
C	1.803414	-0.785994	0.521346
C	2.130237	-1.783313	-0.413767
C	2.678813	0.287162	0.698011
C	3.311662	-1.693021	-1.145870
H	1.459768	-2.629523	-0.559394
C	3.868605	0.376763	-0.040519
H	2.456022	1.073607	1.418201
C	4.191666	-0.618526	-0.970765
H	3.564747	-2.470333	-1.865784
H	5.107353	-0.575679	-1.552020
O	4.643480	1.472289	0.225410
C	5.867514	1.620407	-0.487980
H	5.694706	1.699496	-1.568760
H	6.315247	2.546975	-0.123726
H	6.550171	0.784057	-0.291593
C	-3.101083	0.406252	0.648415
H	-2.998655	1.480525	0.492230
C	-4.226309	-0.270701	0.181490
H	-4.304706	-1.348432	0.336382
N	-5.250196	0.297337	-0.455003
C	-5.302167	1.738421	-0.740023
H	-6.254285	1.965386	-1.219089
H	-5.219778	2.304918	0.192068
H	-4.482364	2.013349	-1.411223
C	-6.386599	-0.505393	-0.911754
H	-7.300397	-0.134420	-0.434742
H	-6.484735	-0.398639	-1.997642
H	-6.229128	-1.552897	-0.652843

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -675.917958
E +ZPE (0 K) = -675.2692624
H (268 K) = -675.577006
G (268 K) = -675.635609
H (298 K) = -675.573944
G (298 K) = -675.642365

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -675.603733
E +ZPE (0 K) = -675.278399
H (268 K) = -675.262781
G (268 K) = -675.321384

***ortho*-methoxy arylation (TS1)**

Number of imaginary frequencies: 1
$<S^2>$ = 0.77

C	-1.256948	-2.337092	-0.380536
C	-0.236171	-1.319998	0.135339
C	-0.822524	0.325347	-0.720845
C	-2.166430	0.448913	-0.180932
C	-3.151279	-0.614414	-0.575840
C	-2.705257	-1.984997	-0.017172
H	-0.381020	-1.064550	1.185500
H	-1.148771	-2.446295	-1.468898
H	-1.012571	-3.314820	0.056699
H	-4.152456	-0.369018	-0.204695
H	-3.210056	-0.678911	-1.671958
H	-2.811618	-1.977280	1.075978
H	-3.370913	-2.768425	-0.397936
H	-0.748012	-0.057236	-1.741806
C	1.115661	-1.530574	-0.274887
H	1.291134	-1.887227	-1.291669
C	2.207680	-0.848434	1.827396
H	2.244978	0.244397	1.893189
H	1.317289	-1.213085	2.340141
H	3.092443	-1.261101	2.318836
C	3.535127	-1.370270	-0.195197
H	4.027548	-0.392318	-0.153336
H	4.148429	-2.096304	0.348340
H	3.434556	-1.679541	-1.236476
N	2.211424	-1.281414	0.426883
C	0.110037	1.398753	-0.425395
C	-0.177608	2.351385	0.541140
H	0.536508	3.125455	0.806155
C	-1.443621	2.342936	1.149885
H	-1.671419	3.096149	1.902171
C	-2.429029	1.409574	0.778802
H	-3.416706	1.460211	1.235314
O	1.251543	1.328786	-1.148231
C	2.232413	2.359800	-0.983280
H	2.630593	2.368307	0.038087
H	3.029999	2.124544	-1.689070
H	1.805437	3.341073	-1.217766

UB3LYP/6-31G(d)
E (0 K) = -675.900021
E +ZPE (0 K) = -675.573395
H (268 K) = -675.559232
G (298 K) = -675.611328

M06-2X/6-31+G(d)
E (0 K) = -675.590768
E +ZPE (0 K) = -675.264141
H (268 K) = -675.249979
G (268 K) = -675.302075

***para*-methoxy arylation (TS2)**

Number of imaginary frequencies: 1
$<S^2>$ = 0.77

C	-1.327773	2.376985	0.443096
C	-1.289286	0.846780	0.349555
C	-0.068646	0.483767	-1.042957
C	1.138187	1.154437	-0.563561
C	1.070812	2.647196	-0.410464
C	0.046539	3.010706	0.688216
H	-0.778676	0.387689	1.197996
H	-1.773008	2.784518	-0.475696
H	-1.999022	2.655564	1.266543
H	2.054705	3.057168	-0.156677
H	0.753661	3.105082	-1.358521
H	0.433170	2.680311	1.661777
H	-0.063737	4.100262	0.740521
H	-0.605285	1.025789	-1.827559
C	-2.538038	0.248587	-0.020070
H	-3.188452	0.815537	-0.689565
C	-2.308913	-1.905514	1.177756
H	-1.329133	-1.539442	1.474472
H	-2.937329	-2.037918	2.066353
H	-2.192390	-2.873370	0.680944
C	-4.245675	-1.456328	-0.274350
H	-4.079008	-2.373795	-0.848682
H	-4.927079	-1.676779	0.554753
H	-4.689437	-0.697010	-0.919775
N	-2.967315	-0.973196	0.258458
C	0.041748	-0.953597	-1.259208
C	1.125333	-1.660727	-0.814510
C	2.218576	-0.988014	-0.205981
C	2.214986	0.418519	-0.102385
H	3.068182	0.945909	0.315765
H	-0.768025	-1.472587	-1.769230
O	3.224269	-1.786768	0.210543
C	4.382211	-1.196029	0.809756
H	4.893108	-0.530412	0.104945
H	4.115478	-0.641221	1.716353
H	5.036279	-2.029898	1.067568
H	1.192679	-2.739483	-0.945207

UB3LYP/6-31G(d)
E (0 K) = -675.899104
E +ZPE (0 K) = -675.572395
H (268 K) = -675.558274
G (268 K) = -675.610537

M06-2X/6-31+G(d)
E (0 K) = -675.588269
E +ZPE (0 K) = -675.261560
H (268 K) = -675.247439
G (268 K) = -675.299702

ortho-methoxy cyclized radical cation (17*)

Number of imaginary frequencies: 0
$<S^2> = 0.78$

C	-0.198483	-2.419210	-0.338456
C	0.185670	-0.961427	0.057111
C	-0.856482	0.055216	-0.595212
C	-2.252200	-0.340343	-0.179478
C	-2.646602	-1.751170	-0.512651
C	-1.635892	-2.753245	0.080881
H	0.113806	-0.856141	1.145289
H	-0.090121	-2.533797	-1.425988
H	0.504827	-3.117639	0.130594
H	-3.656327	-1.964370	-0.143880
H	-2.664688	-1.884435	-1.607022
H	-1.710213	-2.740355	1.176329
H	-1.874802	-3.771515	-0.248725
H	-0.740535	-0.086521	-1.688581
C	1.553281	-0.699456	-0.446623
H	1.661859	-0.596225	-1.529157
C	2.775951	-0.807179	1.689077
H	1.806637	-0.996890	2.143858
H	3.450383	-1.642717	1.898694
H	3.205415	0.110867	2.101730
C	3.949837	-0.426296	-0.446992
H	4.396251	0.492181	-0.053718
H	4.616610	-1.268215	-0.239131
H	3.790709	-0.333348	-1.521867
N	2.661301	-0.658912	0.229797
C	-0.520798	1.479748	-0.258480
C	-1.362858	2.307583	0.436773
H	-1.074412	3.327867	0.673347
C	-2.640749	1.841276	0.836794
H	-3.304763	2.506031	1.384008
C	-3.055108	0.527687	0.516473
H	-4.047989	0.196815	0.821943
O	0.718203	1.805151	-0.720971
C	1.227231	3.114875	-0.451747
H	1.296411	3.294440	0.627338
H	2.221219	3.149136	-0.900085
H	0.588193	3.877653	-0.910615

UB3LYP/6-31G(d)
E (0 K) = -675.906158
E +ZPE (0 K) = -675.578009
H (268 K) = -675.563841
G (268 K) = -675.616178
H (298 K) = -675.560897
G (298 K) = -675.622223

M06-2X/6-31+G(d)
E (0 K) = -675.601589
E +ZPE (0 K) = -675.273440
H (268 K) = -675.259272
G (268 K) = -675.311609

para-methoxy cyclized radical cation (18*)

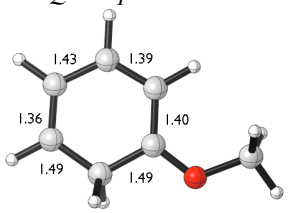
Number of imaginary frequencies: 0
$<S^2> = 0.78$

C	-1.397539	2.316823	0.332480
C	-1.255815	0.779096	0.226068
C	-0.102644	0.433137	-0.913017
C	1.144592	1.139479	-0.474164
C	1.038500	2.632140	-0.341143
C	-0.066215	2.996616	0.673562
H	-0.877325	0.375242	1.169959
H	-1.781835	2.704928	-0.621736
H	-2.144103	2.556512	1.099292
H	1.997257	3.064146	-0.032620
H	0.777853	3.073399	-1.316325
H	0.253699	2.693759	1.679679
H	-0.211292	4.083323	0.695575
H	-0.507303	0.904061	-1.824967
C	-2.529014	0.175228	-0.177924
H	-3.093445	0.687145	-0.962831
C	-2.489970	-1.814309	1.280028
H	-1.505035	-1.472271	1.586642
H	-3.171385	-1.813034	2.137329
H	-2.413928	-2.831477	0.885705
C	-4.329051	-1.432266	-0.318807
H	-4.172243	-2.412230	-0.779762
H	-5.051897	-1.530286	0.497018
H	-4.701709	-0.726674	-1.062203
N	-3.051196	-0.949238	0.231298
C	0.080220	-1.035279	-1.106881
C	1.217051	-1.683236	-0.727839
H	1.319458	-2.759752	-0.858522
C	2.320470	-0.968223	-0.181803
C	2.263473	0.440554	-0.080159
H	3.119032	1.000393	0.289761
H	-0.730494	-1.600112	-1.565267
O	3.384035	-1.731957	0.179488
C	4.544816	-1.089747	0.708462
H	5.250275	-1.891408	0.932565
H	4.987854	-0.405520	-0.024897
H	4.309406	-0.539901	1.627445

UB3LYP/6-31G(d)
E (0 K) = -675.900555
E +ZPE (0 K) = -675.573026
H (268 K) = -675.558713
G (268 K) = -675.611563
H (298 K) = -675.555741
G (298 K) = -675.617668

M06-2X/6-31+G(d)
E (0 K) = -675.593675
E +ZPE (0 K) = -675.266146
H (268 K) = -675.251833
G (268 K) = -675.304683

ortho-methoxy cyclohexadienyl cation (19*)
CBS-QB3-optimized



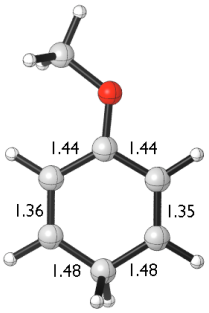
Number of imaginary frequencies: 0

C	-1.281884	1.391033	0.000003
C	-2.299331	0.386012	-0.000009
C	-1.939086	-0.921983	-0.000008
C	0.491502	-0.225765	0.000003
C	0.076572	1.114475	0.000009
H	-1.590228	2.433918	0.000004
H	-3.341554	0.685668	-0.000018
H	-2.682998	-1.713576	-0.000012
H	0.795211	1.924786	0.000015
C	-0.510892	-1.332861	0.000010
H	-0.310223	-1.989050	-0.864136
H	-0.310247	-1.989004	0.864198
O	1.726448	-0.637065	-0.000007
C	2.843210	0.297795	-0.000005
H	2.808966	0.911882	0.902670
H	3.730008	-0.332259	-0.000035
H	2.808935	0.911924	-0.902651

<u>B3LYP/6-31G(d)</u>
E (0 K) = -347.107802
E +ZPE (0 K) = -346.962825
H (298 K) = -346.954417
G (298 K) = -346.994486

<u>CBS-QB3</u>
E (0 K) = -346.457556
H (298 K) = -346.449043
G (298 K) = -346.489323

para-methoxy cyclohexadienyl cation (20*)
CBS-QB3-optimized



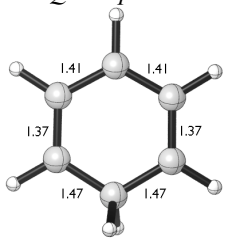
Number of imaginary frequencies: 0

C	0.500358	-0.269085	-0.000012
C	0.075430	1.102154	-0.000029
C	-1.253167	1.381191	-0.000026
C	-1.776138	-1.069666	-0.000010
C	-0.450401	-1.345314	-0.000018
H	0.808984	1.899334	-0.000059
H	-1.587762	2.415420	-0.000066
H	-0.063215	-2.358670	-0.000034
C	-2.289464	0.322078	0.000041
H	-2.966617	0.471099	-0.860998
H	-2.966396	0.471059	0.861268
H	-2.501748	-1.878506	-0.000016
O	1.746934	-0.641655	-0.000012
C	2.849643	0.308732	0.000034
H	2.809821	0.921661	0.903163
H	3.744082	-0.310457	-0.000004
H	2.809819	0.921761	-0.903028

<u>B3LYP/6-31G(d)</u>
E (0 K) = -347.110979
E +ZPE (0 K) = -346.965998
H (298 K) = -346.957671
G (298 K) = -346.997514

<u>CBS-QB3</u>
E (0 K) = -346.462400
H (298 K) = -346.453972
G (298 K) = -346.494006

cyclohexadienyl cation (21*)
CBS-QB3-optimized



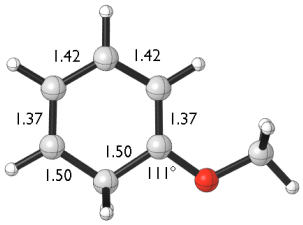
Number of imaginary frequencies: 0

C	1.412833	0.000327	0.000000
C	0.740274	-1.238833	0.000000
C	-0.627960	-1.253102	0.000000
C	-0.628542	1.252811	0.000000
C	0.739698	1.239176	0.000000
H	2.498638	0.000580	0.000000
H	1.309314	-2.159850	0.000000
H	-1.175992	-2.189286	-0.000001
H	-1.177008	2.188742	-0.000001
H	1.308313	2.160456	0.000000
C	-1.395131	-0.000324	0.000000
H	-2.105149	-0.000489	0.849933
H	-2.105153	-0.000489	-0.849930

B3LYP/6-31G(d)
E (0 K) = -232.556295
E +ZPE (0 K) = -232.445294
H (298 K) = -232.439350
G (298 K) = -232.473332

CBS-QB3
E (0 K) = -232.069295
H (298 K) = -232.063278
G (298 K) = -232.097379

***ortho*-methoxy cyclohexadienyl radical (22*)**
CBS-QB3-optimized



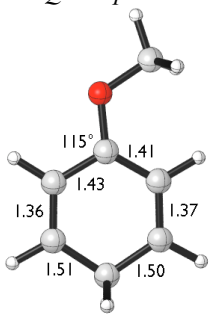
Number of imaginary frequencies: 0
$\langle S^2 \rangle = 0.78$

C	-1.317604	1.414558	0.000005
C	-2.287097	0.383438	-0.000010
C	-1.924231	-0.935474	-0.000012
C	0.477669	-0.212528	0.000005
C	0.068145	1.093783	-0.000016
H	-1.623755	2.455674	0.000022
H	-3.341698	0.649774	0.000002
H	-2.678469	-1.718003	0.000021
H	0.793837	1.900413	-0.000009
C	-0.484682	-1.368214	0.000045
H	-0.265819	-2.016164	-0.869454
H	-0.265850	-2.016091	0.869608
O	1.767832	-0.646458	-0.000108
C	2.800948	0.327625	0.000045
H	2.749921	0.962113	0.894425
H	3.740534	-0.227825	-0.000158
H	2.749749	0.962645	-0.893967

UB3LYP/6-31G(d)
E (0 K) = -347.321217
E +ZPE (0 K) = -347.178652
H (298 K) = -347.170249
G (298 K) = -347.210918

CBS-QB3
E (0 K) = -346.689579
H (298 K) = -346.681069
G (298 K) = -346.721933

para-methoxy cyclohexadienyl radical (23*)
CBS-QB3-optimized



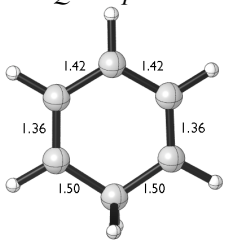
Number of imaginary frequencies: 0
$<S^2> = 0.79$

C	0.513012	-0.267212	-0.000074
C	0.069604	1.076149	-0.000161
C	-1.269078	1.376400	-0.000060
C	-1.778837	-1.076799	0.000056
C	-0.442833	1.326083	-0.000013
H	0.791166	1.887328	-0.000350
H	-1.584397	2.416632	-0.000215
H	-0.062284	-2.344200	-0.000053
C	-2.340320	0.320125	0.000145
H	-3.015058	0.458652	-0.867903
H	-3.014725	0.458657	0.868455
H	-2.483566	-1.904746	0.000101
O	1.821599	-0.664840	-0.000290
C	2.827970	0.332719	0.000276
H	2.769299	0.966876	0.895279
H	3.780682	-0.200553	-0.000266
H	2.768974	0.968279	-0.893739

UB3LYP/6-31G(d)
E (0 K) = -347.315831
E +ZPE (0 K) = -347.173727
H (298 K) = -347.165193
G (298 K) = -347.206275

CBS-QB3
E (0 K) = -346.684009
H (298 K) = -346.675351
G (298 K) = -346.716696

cyclohexadienyl radical (24*)
CBS-QB3-optimized



Number of imaginary frequencies: 0
$<S^2> = 1.17$

C	-1.452929	0.000081	0.000004
C	-0.739483	1.224541	-0.000002
C	0.622827	1.254818	-0.000004
C	0.622678	-1.254904	-0.000005
C	-0.739649	-1.224441	-0.000002
H	-2.535682	0.000156	0.000008
H	-1.293801	2.157721	-0.000006
H	1.149091	2.203547	-0.000012
H	1.148826	-2.203690	-0.000013
H	-1.294066	-2.157562	-0.000007
C	1.446294	-0.000077	0.000007
H	2.133585	-0.000141	0.865519
H	2.133617	-0.000141	-0.865478

UB3LYP/6-31G(d)
E (0 K) = -232.793385
E +ZPE (0 K) = -232.684325
H (298 K) = -232.678334
G (298 K) = -232.713076

CBS-QB3
E (0 K) = -232.324076
H (298 K) = -232.318016
G (298 K) = -232.352879

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of 5-(3,4-dimethoxyphenyl)-pentanal (25*)

Number of imaginary frequencies: 0
$<S^2> = 0.76$

C	-2.627212	0.294684	1.395673
H	-2.545393	1.170695	2.057938
H	-2.851940	-0.578808	2.019266
C	-1.257092	0.103358	0.686623
H	-1.048962	0.974401	0.052477
H	-1.308342	-0.770889	0.026330
C	-0.114812	-0.081976	1.707827
H	-0.339626	-0.950142	2.340186
H	-0.086687	0.796237	2.367091
C	1.226489	-0.273197	1.036029
C	1.747836	-1.546012	0.809857
C	1.960055	0.844070	0.590542
C	2.975504	-1.716516	0.155346
H	1.201266	-2.425569	1.147483
C	3.180450	0.691970	-0.061990
H	1.559213	1.837900	0.769178
C	3.699696	-0.610640	-0.285415
H	3.356642	-2.721104	0.000240
O	3.956888	1.718458	-0.520958
C	3.485597	3.048385	-0.324610
H	3.374019	3.280380	0.742120
H	4.244870	3.700126	-0.760943
H	2.526994	3.212785	-0.832838
C	-3.713899	0.541859	0.416545
H	-3.654493	1.456785	-0.173539
C	-4.757416	-0.358863	0.217531
H	-4.796220	-1.272404	0.813819
N	-5.749952	-0.199057	-0.658767
C	-5.845481	0.975546	-1.536487
H	-6.724066	0.866015	-2.171987
H	-5.944118	1.883726	-0.933706
H	-4.950925	1.046144	-2.162482
C	-6.810538	-1.201107	-0.780082
H	-7.775308	-0.729459	-0.563059
H	-6.825644	-1.583567	-1.806540
H	-6.630491	-2.018387	-0.080861
O	4.903365	-0.663180	-0.928777
C	5.467449	-1.947821	-1.176279
H	4.813691	-2.555947	-1.814217
H	6.411134	-1.763708	-1.693112
H	5.662273	-2.486480	-0.240263

UB3LYP/6-31G(d)
E (0 K) = -790.436961
E +ZPE (0 K) = -790.078535
H (268 K) = -790.060808
G (268 K) = -790.123717

M06-2X/6-31+G(d)
E (0 K) = -790.082538
E +ZPE (0 K) = -789.724112
H (268 K) = -789.706385
G (268 K) = -789.769294

TS3 (*ortho, meta* dimethoxy)

Number of imaginary frequencies: 1
$<S^2> = 0.78$

C	-3.060264	0.754356	-0.075946
C	-1.557291	0.833448	-0.357684
C	-0.803458	-0.465131	0.822121
C	-1.480560	-1.674497	0.361503
C	-2.969908	-1.731871	0.548509
C	-3.651987	-0.641766	-0.309386
H	-1.280567	0.409641	-1.323774
H	-3.254710	1.085349	0.954149
H	-3.571024	1.469738	-0.734887
H	-3.353872	-2.719575	0.269469
H	-3.223800	-1.564880	1.605292
H	-3.547842	-0.905853	-1.370376
H	-4.725804	-0.617761	-0.089168
H	-1.182493	-0.035810	1.753324
C	-0.942126	2.086521	-0.034638
H	-1.331756	2.636136	0.824706
C	0.808980	2.061985	-1.769196
H	1.652940	1.453368	-1.427113
H	0.132960	1.449303	-2.365411
H	1.185179	2.880642	-2.387999
C	0.751725	3.815244	-0.030571
H	1.753089	3.544185	0.322314
H	0.839787	4.598268	-0.789790
H	0.158829	4.180553	0.809081
N	0.109059	2.635507	-0.615693
C	0.642802	-0.430516	0.729774
C	1.320938	-1.340524	-0.093642
C	0.613488	-2.430850	-0.623563
H	1.122629	-3.166150	-1.238485
C	-0.766587	-2.595744	-0.370158
H	-1.268557	-3.475594	-0.770950
O	1.212979	0.620002	1.375187
C	2.502829	0.475792	2.002661
H	3.310976	0.550742	1.274361
H	2.561783	1.293775	2.723515
H	2.565508	-0.483759	2.525554
O	2.645707	-1.095877	-0.319899
C	3.414565	-2.089137	-0.998277
H	3.066624	-2.227114	-2.029030
H	4.438450	-1.712293	-1.008509
H	3.379905	-3.048319	-0.467773

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -790.413614
E +ZPE (0 K) = -790.054449
H (268 K) = -790.037966
G (268 K) = -790.095127

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -790.064330
E +ZPE (0 K) = -789.705165
H (268 K) = -789.688682
G (268 K) = -789.745843

TS4 (*para, meta* dimethoxy)

Number of imaginary frequencies: 1
$<S^2> = 0.77$

C	-1.887643	2.563777	0.095249
C	-1.582754	1.072360	0.274969
C	-0.252717	0.696046	-1.025765
C	0.791413	1.634350	-0.633866
C	0.475576	3.099961	-0.724542
C	-0.655464	3.459289	0.265179
H	-1.039855	0.862992	1.198036
H	-2.341042	2.725304	-0.893151
H	-2.643152	2.854869	0.837349
H	1.365838	3.701848	-0.510535
H	0.146428	3.346341	-1.744411
H	-0.276159	3.367174	1.291914
H	-0.947190	4.506699	0.124298
H	-0.839454	1.010315	-1.893815
C	-2.683526	0.203252	-0.007703
H	-3.377610	0.508050	-0.794045
C	-2.180699	-1.587687	1.619707
H	-1.231518	-1.081339	1.778054
H	-2.791795	-1.517931	2.527799
H	-1.990611	-2.643555	1.407243
C	-4.065744	-1.790755	0.044547
H	-3.724160	-2.766669	-0.316098
H	-4.752997	-1.945539	0.883831
H	-4.584027	-1.266014	-0.759294
N	-2.913817	-1.001316	0.493669
C	0.100328	-0.717863	-1.026986
C	1.269158	-1.160112	-0.462690
C	2.206517	-0.209107	0.079745
C	1.949709	1.165630	-0.034411
H	2.679433	1.885525	0.325679
H	-0.590999	-1.414646	-1.489215
O	3.306496	-0.746886	0.640826
C	4.303290	0.127631	1.181566
H	4.728177	0.768047	0.400594
H	3.887512	0.746601	1.984505
H	5.077735	-0.526925	1.583120
O	1.679943	-2.453279	-0.391426
C	0.847131	-3.449483	-0.980966
H	1.367322	-4.396976	-0.833047
H	-0.133346	-3.491110	-0.490430
H	0.709231	-3.266261	-2.053460

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -790.418207
E +ZPE (0 K) = -790.058528
H (268 K) = -790.042231
G (268 K) = -790.099037

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -790.068747
E +ZPE (0 K) = -789.709068
H (298 K) = -789.692771
G (298 K) = -789.749577

***Ortho*,*meta* dimethoxy cyclized radical cation (26*)**

Number of imaginary frequencies: 0
$<S^2> = 0.78$

C	-2.286158	1.906708	-0.138460
C	-1.378997	0.673100	0.142846
C	-0.002743	0.834136	-0.663917
C	0.621655	2.150630	-0.285428
C	-0.234908	3.366207	-0.501486
C	-1.581879	3.217514	0.234542
H	-1.130369	0.643464	1.208462
H	-2.555146	1.916391	-1.204018
H	-3.219417	1.804613	0.428242
H	0.287513	4.268236	-0.162986
H	-0.439492	3.493279	-1.577171
H	-1.409718	3.244630	1.318698
H	-2.241234	4.058944	-0.010108
H	-0.309147	0.862840	-1.728104
C	-2.095265	-0.541223	-0.306327
H	-2.301481	-0.615598	-1.377228
C	-2.404634	-1.627451	1.877968
H	-2.112738	-0.677964	2.321245
H	-3.358483	-1.948993	2.303476
H	-1.642936	-2.386037	2.085153
C	-3.246794	-2.655284	-0.202965
H	-2.673006	-3.562227	0.012169
H	-4.248789	-2.751305	0.224524
H	-3.313409	-2.504323	-1.280930
N	-2.567417	-1.506298	0.420342
C	0.894319	-0.348749	-0.465939
C	2.127812	-0.255562	0.163041
C	2.630546	1.013333	0.524538
H	3.599401	1.107790	1.002175
C	1.863096	2.184129	0.283472
H	2.291236	3.145566	0.568036
O	0.300438	-1.510144	-0.875053
C	1.062925	-2.499922	-1.588242
H	1.680370	-3.088256	-0.907967
H	0.326757	-3.138113	-2.082152
H	1.698824	-2.019969	-2.339785
O	2.794460	-1.430464	0.399142
C	4.157247	-1.363499	0.811595
H	4.254429	-0.920833	1.810655
H	4.507939	-2.396850	0.841387
H	4.764288	-0.790751	0.099686

UB3LYP/6-31G(d)
E (0 K) = -790.417453
E +ZPE (0 K) = -790.057381
H (268 K) = -790.040451
G (268 K) = -790.100331

M06-2X/6-31+G(d)
E (0 K) = -790.072030
E +ZPE (0 K) = -789.711958
H (268 K) = -789.695028
G (268 K) = -789.754908

***para* dimethoxy cyclized radical cation (27*)**

Number of imaginary frequencies: 0
$<S^2> = 0.77$

C	-1.897169	2.495906	0.028969
C	-1.513146	1.000061	0.156604
C	-0.281880	0.675486	-0.892381
C	0.821037	1.624858	-0.541109
C	0.489966	3.087731	-0.622510
C	-0.702871	3.417822	0.299623
H	-1.120780	0.803499	1.158680
H	-2.289061	2.677340	-0.982057
H	-2.708364	2.720351	0.732037
H	1.359749	3.697468	-0.352623
H	0.215156	3.349489	-1.656827
H	-0.389665	3.315280	1.347275
H	-1.011737	4.460146	0.155919
H	-0.709831	0.942756	-1.873815
C	-2.665641	0.155429	-0.174299
H	-3.237750	0.427787	-1.066470
C	-2.479182	-1.487755	1.654912
H	-1.545690	-0.990519	1.904739
H	-3.196658	-1.373107	2.474349
H	-2.293437	-2.553268	1.494070
C	-4.245743	-1.670095	-0.058393
H	-3.948089	-2.694693	-0.300927
H	-5.001629	-1.693661	0.732665
H	-4.650980	-1.180264	-0.944553
N	-3.070119	-0.927783	0.429274
C	0.122819	-0.762655	-0.877988
C	1.332935	-1.175041	-0.401852
C	2.301099	-0.211761	0.069797
C	2.016018	1.161943	-0.033531
H	2.762312	1.890341	0.273375
H	-0.580254	-1.481319	-1.286405
O	3.450159	-0.736317	0.560931
C	4.459350	0.158994	1.031765
H	4.823893	0.804420	0.223961
H	4.085576	0.777601	1.856239
H	5.272167	-0.475529	1.388282
O	1.765849	-2.465867	-0.346607
C	0.890577	-3.479583	-0.830911
H	1.427146	-4.421681	-0.706877
H	-0.041163	-3.511317	-0.251742
H	0.652847	-3.327206	-1.890980

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -790.420027
E +ZPE (0 K) = -790.059301
H (268 K) = -790.042855
G (268 K) = -790.100186

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -790.074894
E +ZPE (0 K) = -789.714168
H (268 K) = -789.697722
G (268 K) = -789.755053

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of 5-(3-methoxy-4-methyl-phenyl)-pentanal (28*)

Number of imaginary frequencies: 0
$<S^2> = 0.76$

C	-2.250935	0.206077	1.368028
H	-2.103862	1.028032	2.086441
H	-2.498600	-0.697098	1.938470
C	-0.917326	-0.000337	0.598287
H	-0.677659	0.907695	0.030594
H	-1.040333	-0.811818	-0.129421
C	0.241269	-0.335561	1.559921
H	-0.018761	-1.237543	2.128827
H	0.347540	0.481946	2.285403
C	1.548023	-0.552116	0.827680
C	1.923747	-1.823456	0.385934
C	2.389997	0.538143	0.550747
C	3.118960	-1.997839	-0.319431
H	1.286435	-2.681953	0.594684
C	3.583295	0.354155	-0.153448
H	2.099455	1.525149	0.899612
C	3.968613	-0.928354	-0.604076
H	3.402975	-2.995160	-0.655144
O	4.458240	1.362818	-0.454133
C	4.142104	2.683879	-0.029294
H	4.063236	2.746373	1.063551
H	4.967272	3.312523	-0.369609
H	3.205426	3.037376	-0.478885
C	-3.360229	0.574984	0.454207
H	-3.269582	1.517121	-0.087068
C	-4.467376	-0.248340	0.257689
H	-4.533389	-1.193219	0.800347
N	-5.488519	0.023150	-0.555123
C	-5.556131	1.254161	-1.355226
H	-6.496587	1.261307	-1.905836
H	-5.512986	2.127832	-0.698245
H	-4.720805	1.283994	-2.061817
C	-6.606580	-0.912642	-0.691238
H	-7.532855	-0.408739	-0.394117
H	-6.689836	-1.218670	-1.739856
H	-6.438159	-1.786024	-0.060397
C	5.260706	-1.112426	-1.359128
H	5.278390	-0.512343	-2.277377
H	6.123723	-0.791024	-0.762849
H	5.403852	-2.162328	-1.632307

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -715.235140
E +ZPE (0 K) = -714.881872
H (268 K) = -714.864816
G (268 K) = -714.926281

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -714.901664
E +ZPE (0 K) = -714.548396
H (268 K) = -714.531340
G (268 K) = -714.592805

TS5 (*ortho, meta* 3-methoxy-4-methyl)

Number of imaginary frequencies: 1
$\langle S^2 \rangle = 0.78$

C	1.270736	-2.492888	0.012509
C	0.271260	-1.382666	-0.342988
C	0.814579	0.068156	0.711486
C	2.180659	0.272915	0.220073
C	3.161913	-0.830059	0.493742
C	2.729564	-2.107937	-0.261617
H	0.433247	-0.983141	-1.345812
H	1.140583	-2.773534	1.067449
H	1.021358	-3.382733	-0.580673
H	4.170378	-0.535359	0.182992
H	3.195602	-1.046130	1.571440
H	2.864980	-1.947720	-1.339698
H	3.380850	-2.942805	0.022793
H	0.769087	-0.423115	1.686568
C	-1.09464	-1.705576	-0.033489
H	-1.277930	-2.332394	0.842621
C	-2.204430	-0.450548	-1.851893
H	-1.210107	-0.356210	-2.283453
H	-2.877544	-0.898918	-2.589229
H	-2.583494	0.540824	-1.582276
C	-3.514808	-1.605589	-0.120319
H	-4.006381	-0.675021	0.185639
H	-4.117700	-2.087553	-0.896263
H	-3.423506	-2.271817	0.738808
N	-2.185701	-1.297138	-0.657388
C	-0.109898	1.182590	0.532996
C	0.168227	2.237770	-0.332607
C	1.446717	2.287998	-0.915386
C	2.440962	1.331547	-0.621292
H	3.435288	1.447729	-1.051312
H	1.687395	3.118674	-1.577495
C	-0.852546	3.321653	-0.578514
H	-1.196038	3.764308	0.363047
H	-0.430693	4.115541	-1.201481
H	-1.744484	2.931628	-1.084740
O	-1.345863	1.158688	1.107673
C	-1.472547	0.679171	2.456103
H	-2.485909	0.940541	2.765553
H	-1.345687	-0.406381	2.522600
H	-0.746957	1.174812	3.110432

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -715.211548
E +ZPE (0 K) = -714.857072
H (268 K) = -714.841487
G (268 K) = -714.896396

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -714.884772
E +ZPE (0 K) = -714.530296
H (268 K) = -714.514711
G (268 K) = -714.569620

TS6 (*para, meta* 3-methoxy-4-methyl)

Number of imaginary frequencies:1
$<S^2> = 0.77$

C	-1.681398	2.458293	0.284014
C	-1.477234	0.938901	0.312039
C	-0.192264	0.608521	-1.028931
C	0.923006	1.434968	-0.579427
C	0.702115	2.919785	-0.530956
C	-0.389048	3.251815	0.511996
H	-0.940894	0.604927	1.201734
H	-2.136998	2.745050	-0.674424
H	-2.404124	2.725245	1.066658
H	1.631788	3.443049	-0.281065
H	0.373089	3.279338	-1.516738
H	-0.001447	3.036019	1.516809
H	-0.613971	4.324370	0.478879
H	-0.764890	1.033678	-1.858723
C	-2.643972	0.179607	-0.025902
H	-3.336971	0.613914	-0.749652
C	-2.208731	-1.826970	1.355964
H	-1.265060	-1.348836	1.606985
H	-2.825185	-1.920366	2.258045
H	-2.008598	-2.828076	0.962673
C	-4.150017	-1.719633	-0.154241
H	-3.875458	-2.661880	-0.640235
H	-4.823196	-1.936627	0.682654
H	-4.656935	-1.073037	-0.871940
N	-2.941865	-1.056836	0.347627
C	0.072361	-0.819121	-1.145128
C	1.208556	-1.406317	-0.649029
C	2.206136	-0.561251	-0.065003
C	2.055245	0.839554	-0.054828
H	2.842411	1.474070	0.343150
H	-0.674336	-1.442542	-1.635335
C	1.451386	-2.891723	-0.733935
H	2.373478	-3.113144	-1.283845
H	1.568593	-3.331325	0.263813
H	0.618465	-3.391289	-1.237003
O	3.283431	-1.209809	0.426437
C	4.350394	-0.456455	1.010034
H	3.996131	0.125308	1.868521
H	5.082357	-1.194092	1.341382
H	4.808142	0.212708	0.272770

UB3LYP/6-31G(d)
E (0 K) = -715.216837
E +ZPE (0 K) = -714.862251
H (268 K) = -714.846710
G (268 K) = -714.901820

M06-2X/6-31+G(d)
E (0 K) = -714.886653
E +ZPE (0 K) = -714.532067
H (268 K) = -714.516526
G (268 K) = -714.571636

***Ortho, meta* 3-methoxy-4-methyl cyclized radical cation (29*)**

Number of imaginary frequencies: 0
$<S^2> = 0.78$

C	-0.473814	2.609537	-0.300798
C	-0.511765	1.108140	0.113444
C	0.701453	0.337089	-0.579585
C	1.986762	1.033503	-0.217137
C	2.056396	2.492888	-0.565318
C	0.870375	3.254849	0.062227
H	-0.373858	1.032215	1.196888
H	-0.644784	2.685591	-1.383741
H	-1.295073	3.141814	0.193875
H	3.006711	2.924375	-0.230820
H	2.009884	2.617656	-1.659574
H	0.985167	3.272115	1.154088
H	0.868743	4.296930	-0.279302
H	0.518981	0.450972	-1.668158
C	-1.802630	0.537743	-0.335459
H	-1.958655	0.489615	-1.416622
C	-2.854873	0.165487	1.858329
H	-1.953802	0.605433	2.278511
H	-3.729222	0.735740	2.184619
H	-2.953486	-0.870251	2.198056
C	-4.044937	-0.341605	-0.241300
H	-4.188294	-1.382711	0.064421
H	-4.895845	0.255396	0.098797
H	-3.958437	-0.280014	-1.326697
N	-2.816612	0.174378	0.387951
C	0.684620	-1.119195	-0.221928
C	1.684604	-1.754596	0.469596
C	2.842930	-1.003026	0.817835
H	3.645983	-1.493637	1.364680
C	2.968858	0.360363	0.462709
H	3.879653	0.892604	0.738941
O	-0.490352	-1.766509	-0.566634
C	-0.466678	-2.437973	-1.838900
H	0.271300	-3.247507	-1.835151
H	-1.465661	-2.854291	-1.987003
H	-0.235272	-1.738410	-2.651412
C	1.589816	-3.215347	0.843090
H	2.138654	-3.846055	0.131353
H	2.028797	-3.388765	1.831648
H	0.550920	-3.554536	0.859180

UB3LYP/6-31G(d)
E (0 K) = -715.215896
E +ZPE (0 K) = -714.860638
H (268 K) = -714.844708
G (268 K) = -714.901176

M06-2X/6-31+G(d)
E (0 K) = -714.891781
E +ZPE (0 K) = -714.536523
H (268 K) = -714.520593
G (268 K) = -714.577061

***Para, meta* 3-methoxy-4-methyl cyclized radical cation (30*)**

Number of imaginary frequencies: 0
$<S^2>$ = 0.78

C -1.720949 2.398844 0.201609
C -1.431999 0.878352 0.202546
C -0.230188 0.570982 -0.905401
C 0.930851 1.421086 -0.500596
C 0.685998 2.902552 -0.462619
C -0.466917 3.224623 0.512154
H -1.026313 0.576857 1.172839
H -2.122862 2.683709 -0.781299
H -2.500956 2.616464 0.941271
H 1.594943 3.439073 -0.167561
H 0.405898 3.258892 -1.466678
H -0.138525 3.019696 1.539986
H -0.715068 4.291492 0.460072
H -0.667585 0.941154 -1.847858
C -2.632514 0.125956 -0.167329
H -3.234622 0.524175 -0.989065
C -2.417399 -1.746014 1.426259
H -1.491948 -1.268172 1.736810
H -3.120911 -1.778752 2.264895
H -2.207172 -2.768109 1.098624
C -4.257527 -1.664705 -0.212704
H -3.997113 -2.657056 -0.593453
H -4.985142 -1.770714 0.597987
H -4.681062 -1.058501 -1.014293
N -3.044903 -1.017153 0.314231
C 0.094549 -0.879865 -1.003312
C 1.272934 -1.421856 -0.575192
C 2.286753 -0.549374 -0.054436
C 2.098036 0.849650 -0.047134
H 2.893041 1.505414 0.298860
C 1.548922 -2.902523 -0.659880
H 2.445532 -3.106667 -1.256667
H 1.731352 -3.327826 0.334208
H 0.703251 -3.429157 -1.111575
H -0.656381 -1.536380 -1.442145
O 3.412150 -1.171707 0.380964
C 4.485896 -0.383921 0.894553
H 4.167216 0.200058 1.766160
H 5.257750 -1.095184 1.192751
H 4.885121 0.290538 0.127700

UB3LYP/6-31G(d)
E (0 K) = -715.218154
E +ZPE (0 K) = -714.862598
H (268 K) = -714.846868
G (268 K) = -714.902601

M06-2X/6-31+G(d)
E (0 K) = -714.892151
E +ZPE (0 K) = -714.536595
H (268 K) = -714.520865
G (268 K) = -714.576598

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of 5-(3,4-methylenedioxyphenyl)-pentanal (31*)

Number of imaginary frequencies: 0
$<S^2> = 0.76$

C	-2.292761	-0.599300	1.283621
H	-2.187914	-0.362565	2.354108
H	-2.524943	-1.667478	1.197236
C	-0.935268	-0.292847	0.592033
H	-0.712918	0.778081	0.680984
H	-1.013479	-0.517885	-0.478594
C	0.210827	-1.117591	1.214282
H	-0.028578	-2.184671	1.123705
H	0.266373	-0.891625	2.287545
C	1.544094	-0.834427	0.556781
C	1.993189	-1.622381	-0.510944
C	2.325461	0.258260	0.999955
C	3.210591	-1.368559	-1.170429
H	1.383970	-2.461846	-0.843088
C	3.514522	0.499337	0.342770
H	2.005968	0.881824	1.833098
C	3.949847	-0.293178	-0.717925
H	3.556255	-1.991684	-1.992194
O	4.454419	1.468793	0.611003
C	5.416162	1.380681	-0.452576
H	5.279193	2.226193	-1.140604
H	6.425019	1.369706	-0.031125
C	-3.389766	0.227612	0.723183
H	-3.319847	1.307439	0.857291
C	-4.458977	-0.330027	0.025538
H	-4.505920	-1.413083	-0.102578
N	-5.467507	0.357926	-0.510522
C	-5.558274	1.822047	-0.425407
H	-6.437316	2.150150	-0.979854
H	-5.653427	2.128013	0.621308
H	-4.663591	2.276697	-0.860666
C	-6.556798	-0.330361	-1.205949
H	-7.502691	-0.104282	-0.701371
H	-6.609218	0.034485	-2.237544
H	-6.379737	-1.406365	-1.199591
O	5.177863	0.149685	-1.154005

UB3LYP/6-31G(d)
E (0 K) = -749.924281
E +ZPE (0 K) = -749.616170
H (268 K) = -749.600802
G (268 K) = -749.659210

M06-2X/6-31+G(d)
E (0 K) = -749.596801
E +ZPE (0 K) = -749.288690
H (268 K) = -749.273322
G (268 K) = -749.331730

TS7 (*ortho, meta* methylenedioxy)

Number of imaginary frequencies: 1
$<S^2> = 0.77$

C	-1.692399	-2.345206	-0.120075
C	-0.484490	-1.467865	0.217023
C	-0.810443	0.139358	-0.793338
C	-2.107219	0.569988	-0.248218
C	-3.266336	-0.355122	-0.494055
C	-3.039164	-1.699782	0.231400
H	-0.507712	-1.077276	1.235261
H	-1.662602	-2.612359	-1.185916
H	-1.592779	-3.285091	0.440072
H	-4.199748	0.101152	-0.146444
H	-3.373262	-0.544873	-1.571970
H	-3.090126	-1.534224	1.315986
H	-3.845873	-2.396577	-0.025009
H	-0.834827	-0.339879	-1.775937
C	0.778713	-1.965237	-0.238394
H	0.797732	-2.493846	-1.194346
C	2.167700	-1.127389	1.614799
H	1.274899	-1.196006	2.236105
H	2.998663	-1.615208	2.130495
H	2.421860	-0.074620	1.450627
C	3.188004	-2.193511	-0.368075
H	3.786827	-1.300583	-0.579603
H	3.766900	-2.869981	0.268047
H	2.937477	-2.692013	-1.305528
N	1.959829	-1.798208	0.328724
C	0.238710	1.090485	-0.580268
C	0.117293	2.181313	0.259868
C	-1.082479	2.509031	0.868334
H	-1.175902	3.375123	1.519044
C	-2.193217	1.669915	0.581513
H	-3.157744	1.925069	1.018459
O	1.515349	1.002400	-1.059154
C	2.131068	2.261225	-0.693545
H	3.143956	2.077323	-0.330835
H	2.122121	2.920851	-1.571558
O	1.334262	2.824755	0.352924

UB3LYP/6-31G(d)
E (0 K) = -749.9022692
E +ZPE (0 K) = -749.592920
H (268 K) = -749.579131
G (268 K) = -749.630784

M06-2X/6-31+G(d)
E (0 K) = -749.579771
E +ZPE (0 K) = -749.270422
H (268 K) = -749.256633
G (268 K) = -749.308286

TS8 (*para, meta* methylenedioxy)

Number of imaginary frequencies: 1
$<S^2>$ = 0.77

C	-2.190650	2.050886	0.309708
C	-1.594421	0.640990	0.319760
C	-0.173963	0.698098	-0.965531
C	0.646020	1.780664	-0.414281
C	0.021880	3.146392	-0.365948
C	-1.167557	3.149025	0.621092
H	-1.027143	0.422054	1.225843
H	-2.662303	2.237897	-0.665621
H	-2.993999	2.092701	1.057844
H	0.760092	3.896870	-0.062466
H	-0.343735	3.425062	-1.364564
H	-0.785843	3.014515	1.642149
H	-1.665193	4.125460	0.590947
H	-0.794462	1.001844	-1.812899
C	-2.481245	-0.387260	-0.128990
H	-3.211169	-0.120621	-0.896674
C	-1.622476	-2.270750	1.229265
H	-1.050671	-1.510460	1.756952
H	-2.269510	-2.795527	1.940653
H	-0.935332	-2.993071	0.777541
C	-3.370276	-2.619442	-0.469477
H	-2.787822	-3.423983	-0.930908
H	-4.045111	-3.054092	0.275958
H	-3.951859	-2.105180	-1.235876
N	-2.460564	-1.672871	0.185639
C	0.433239	-0.624196	-1.106928
C	1.632992	-0.830051	-0.500866
C	2.338033	0.205892	0.153058
C	1.867721	1.513112	0.196879
H	2.452646	2.302290	0.666150
H	-0.069491	-1.412219	-1.661046
O	3.504298	-0.274511	0.650901
C	3.577482	-1.664033	0.271944
H	3.646442	-2.277735	1.175680
H	4.442331	-1.810044	-0.383736
O	2.372627	-1.980693	-0.437591

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -749.906067
E +ZPE (0 K) = -749.596707
H (268 K) = -749.582723
G (268 K) = -749.635659

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -749.582349
E +ZPE (0 K) = -749.272989
H (268 K) = -749.259005
G (268 K) = -749.311941

***Ortho, meta* methylenedioxy cyclized radical cation (32*)**

Number of imaginary frequencies: 0
$<S^2>$ = 0.78

C	-0.059595	-2.759619	-0.141815
C	0.335104	-1.278353	0.111449
C	-0.705767	-0.319967	-0.655911
C	-2.114384	-0.663915	-0.199929
C	-2.504914	-2.102895	-0.396388
C	-1.500565	-3.042962	0.301044
H	0.253602	-1.056349	1.180204
H	0.053247	-2.981125	-1.212467
H	0.637466	-3.411719	0.397678
H	-3.517290	-2.278521	-0.015582
H	-2.516504	-2.343051	-1.472062
H	-1.581389	-2.919781	1.389196
H	-1.743621	-4.088091	0.074898
H	-0.588198	-0.574506	-1.727475
C	1.693028	-1.045917	-0.423089
H	1.837234	-1.261504	-1.486898
C	2.785947	-0.228713	1.620679
H	1.908807	-0.589536	2.153052
H	3.687484	-0.653871	2.068810
H	2.834600	0.863460	1.677748
C	4.014813	-0.403804	-0.514412
H	4.288107	0.652771	-0.433514
H	4.792503	-1.016140	-0.049351
H	3.897213	-0.679053	-1.562966
N	2.745296	-0.619098	0.202872
C	-0.441265	1.114634	-0.425061
C	-1.295588	1.989678	0.192004
C	-2.562579	1.620017	0.633650
H	-3.233577	2.321585	1.120497
C	-2.927557	0.255877	0.408145
H	-3.918275	-0.064629	0.730218
O	0.752915	1.729186	-0.718541
O	-0.682493	3.224746	0.315883
C	0.515367	3.131356	-0.461778
H	1.356304	3.543981	0.100675
H	0.379560	3.645814	-1.423039

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -749.907386
E +ZPE (0 K) = -749.596830
H (268 K) = -749.582804
G (268 K) = -749.635601

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -749.588893
E +ZPE (0 K) = -749.275377
H (268 K) = -749.264311
G (268 K) = - -749.317108

***Para, meta* methylenedioxy cyclized radical cation (33*)**

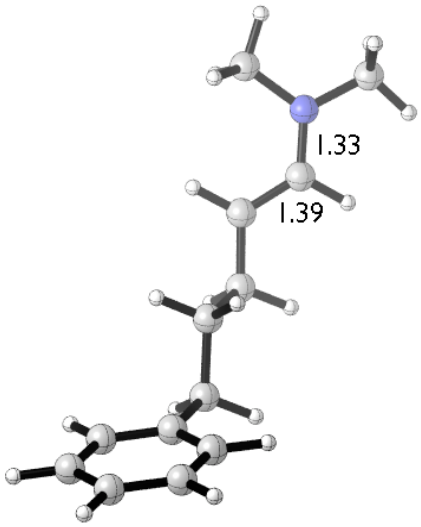
Number of imaginary frequencies: 0
$<S^2> = 0.78$

C	-2.096675	2.087876	0.182199
C	-1.475704	0.668753	0.177873
C	-0.175973	0.646594	-0.821807
C	0.756084	1.727551	-0.320348
C	0.181518	3.115460	-0.286011
C	-1.079309	3.154173	0.602910
H	-1.099969	0.428888	1.177322
H	-2.478452	2.312137	-0.824177
H	-2.957157	2.102837	0.862115
H	0.926510	3.831333	0.079271
H	-0.099381	3.426791	-1.304855
H	-0.789261	2.993484	1.649916
H	-1.548416	4.143756	0.546196
H	-0.593364	0.954629	-1.795907
C	-2.468762	-0.307734	-0.295857
H	-3.069928	-0.019998	-1.164202
C	-2.012948	-2.124064	1.306519
H	-1.219988	-1.484053	1.683678
H	-2.754446	-2.307207	2.090819
H	-1.588654	-3.079028	0.984259
C	-3.718296	-2.369416	-0.459233
H	-3.242181	-3.284785	-0.823147
H	-4.462359	-2.627316	0.300381
H	-4.196775	-1.842692	-1.285707
N	-2.692233	-1.507636	0.155500
C	0.433672	-0.724459	-0.932665
C	1.670297	-0.922724	-0.422598
C	2.448303	0.113596	0.151663
C	2.006058	1.435540	0.193300
H	2.642407	2.221330	0.598157
H	-0.113701	-1.527772	-1.420566
O	3.643746	-0.386753	0.579950
C	3.676723	-1.765772	0.172289
H	3.870229	-2.394513	1.046744
H	4.450218	-1.895494	-0.593955
O	2.393800	-2.089637	-0.377980

<u>UB3LYP/6-31G(d)</u>
E (0 K) = -749.908830
E + ZPE (0 K) = -749.598398
H (268 K) = -749.584251
G (268 K) = -749.637589

<u>M06-2X/6-31+G(d)</u>
E (0 K) = -749.589886
E +ZPE (0 K) = -749.279454
H (268 K) = -749.265307
G (268 K) = -749.318645

(*E*)-[*N*,*N*-dimethylamine] enamine radical cation of 5-phenylpentanal (34*)



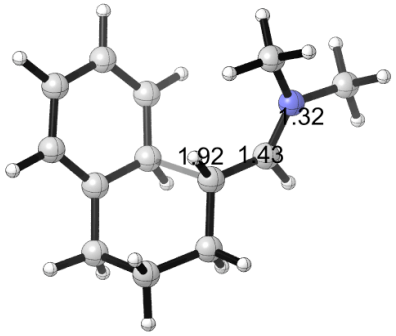
Number of imaginary frequencies: 0
$<S^2> = 0.76$

C	-1.122938	-0.655261	-1.173408
H	-1.007338	-1.643938	-1.645602
H	-1.245578	0.084974	-1.973048
C	0.169015	-0.358547	-0.364170
H	0.279297	-1.102738	0.434837
H	0.076934	0.621555	0.119834
C	1.418506	-0.377361	-1.268094
H	1.290152	0.363185	-2.068248
H	1.492555	-1.361235	-1.749882
C	2.686272	-0.085438	-0.494068
C	3.146190	1.230847	-0.338629
C	3.409718	-1.122821	0.113538
C	4.297403	1.504762	0.403703
H	2.598687	2.048206	-0.808753
C	4.561460	-0.853563	0.856481
H	3.069300	-2.152194	-0.002032
C	5.008796	0.462446	1.004709
H	4.641201	2.533007	0.509134
H	5.908198	0.673842	1.581334
C	-2.320813	-0.692911	-0.298212
H	-2.347696	-1.458976	0.477405
C	-3.366634	0.219516	-0.426451
H	-3.318289	0.981742	-1.206481
N	-4.458279	0.243900	0.338073
C	-4.679033	-0.712843	1.431702
H	-5.616048	-0.463910	1.929435
H	-4.739767	-1.728793	1.029138
H	-3.857452	-0.651142	2.151355
C	-5.509124	1.238221	0.111283
H	-6.449959	0.720347	-0.105211
H	-5.634931	1.837888	1.019385
H	-5.236616	1.881592	-0.725958
H	5.112393	-1.672992	1.316547

UB3LYP/6-31G(d)
E (0 K) = -561.394091
E +ZPE (0 K) = -561.101444
H (268 K) = -561.088003
G (268 K) = -561.141329

M06-2X/6-31+G(d)
E (0 K) = --561.120899
E +ZPE (0 K) = -560.828252
H (268 K) = -560.814811
G (268 K) = -560.868137

Arylation TS, unsubstituted benzene (TS9*)



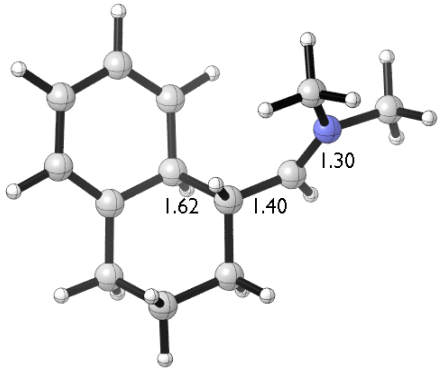
Number of imaginary frequencies: 1
$<S^2> = 0.78$

C	-0.384751	-2.297442	0.178146
C	0.321476	-0.943239	0.274177
C	-0.675748	0.206086	-0.903730
C	-2.008897	0.091769	-0.318630
C	-2.662334	-1.259456	-0.353820
C	-1.873195	-2.243122	0.540227
H	0.161716	-0.442014	1.229363
H	-0.255878	-2.702623	-0.835431
H	0.120966	-2.994853	0.860471
H	-3.701116	-1.195461	-0.011093
H	-2.674243	-1.645025	-1.383443
H	-1.984162	-1.940838	1.590354
H	-2.301901	-3.248042	0.449120
H	-0.512249	-0.395139	-1.803167
C	1.666318	-0.938619	-0.221183
H	1.898767	-1.618403	-1.044566
C	2.615049	0.820787	1.235158
H	1.624265	0.866513	1.680307
H	3.346315	0.521354	1.994225
H	2.884650	1.810585	0.854806
C	3.959551	-0.224901	-0.545095
H	4.203276	0.749167	-0.981798
H	4.730901	-0.489906	0.185715
H	3.922473	-0.980691	-1.330736
N	2.658302	-0.143316	0.130618
C	-0.074269	1.528462	-0.922883
H	0.842103	1.680499	-1.490489
C	-0.638754	2.572334	-0.223609
H	-0.157243	3.549180	-0.217864
C	-1.863954	2.393113	0.453662
H	-2.305600	3.221288	1.005204
C	-2.538003	1.161821	0.384499
H	-3.506084	1.052062	0.873179

UB3LYP/6-31G(d)
E (0 K) = -561.370614
E +ZPE (0 K) = -561.077051
H (268 K) = -561.065144
G (268 K) = -561.112157

M06-2X/6-31+G(d)
E (0 K) = -561.101091
E +ZPE (0 K) = -560.807527
H (268 K) = -560.795621
G (268 K) = -560.842634

Cyclized radical cation, unsubstituted benzene (35*)



Number of imaginary frequencies: 0
$<S^2>$ = 0.79

C	-0.088554	-2.244549	0.062580
C	0.356141	-0.760006	0.136733
C	-0.648606	0.154649	-0.746009
C	-2.042790	-0.095952	-0.228011
C	-2.505896	-1.525197	-0.255097
C	-1.534524	-2.423227	0.539013
H	0.276872	-0.409553	1.170447
H	0.009511	-2.594774	-0.974744
H	0.587167	-2.855000	0.673911
H	-3.520847	-1.608609	0.149895
H	-2.539323	-1.884732	-1.296352
H	-1.602324	-2.176887	1.607127
H	-1.821795	-3.476055	0.432109
H	-0.557572	-0.257328	-1.769137
C	1.725548	-0.634230	-0.398138
H	1.924639	-1.130841	-1.353518
C	2.707150	0.780810	1.362548
H	1.738021	0.710380	1.849380
H	3.485300	0.380716	2.019122
H	2.931525	1.827134	1.135805
C	4.033938	0.048450	-0.584982
H	4.294886	1.087956	-0.803845
H	4.788774	-0.382388	0.079219
H	3.977310	-0.526167	-1.510102
N	2.728139	0.019896	0.101826
C	-0.251603	1.600799	-0.738988
H	0.700394	1.870694	-1.195745
C	-1.046496	2.572617	-0.195706
H	-0.709564	3.608867	-0.202692
C	-2.313392	2.258299	0.357770
H	-2.930743	3.040492	0.793662
C	-2.783540	0.923881	0.316249
H	-3.773462	0.698762	0.714897

UB3LYP/6-31G(d)
E (0 K) = -561.3749443
E +ZPE (0 K) = -561.080285
H (268 K) = -561.068256
G (268 K) = -561.115842

M06-2X/6-31+G(d)
E (0 K) = -561.1101459
E +ZPE (0 K) = -560.815487
H (268 K) = -560.803458
G (268 K) = -560.851044

(*E*)-[*N,N*-dimethylamine] enamine of propanal (S1)

Number of imaginary frequencies: 0

C	-1.389578	0.329902	0.078438
H	-1.266368	1.388497	0.296285
C	-0.316598	-0.439351	-0.174321
H	-0.458323	-1.503121	-0.366597
N	1.018070	-0.047312	-0.282386
C	1.335594	1.336043	0.010917
H	1.164511	1.604158	1.069202
H	2.387316	1.523131	0.227068
H	0.719951	1.994944	-0.610011
C	2.009746	-1.011726	0.168444
H	1.740591	-2.009516	-0.193103
H	2.990665	-0.753174	-0.245509
H	2.102192	-1.060912	1.268047
C	-2.799458	-0.191862	0.055631
H	-3.314947	-0.013653	1.010031
H	-3.406700	0.293711	-0.722192
H	-2.823618	-1.270926	-0.137034

E (0 K) = -251.879305
E +ZPE (0 K) = -251.724756
H (298 K) = -251.716021
G (298 K) = -251.755953

***N,N*-dimethyliminium of propanal (S2)**

Number of imaginary frequencies: 0

C	-0.260342	-0.431482	-0.004375
H	-0.428018	-1.508258	-0.007252
N	0.979049	-0.067820	-0.000455
C	1.420157	1.340969	0.002764
H	2.022668	1.513849	0.898652
H	2.038320	1.512550	-0.882589
H	0.567148	2.015048	-0.005579
C	2.077854	-1.058177	0.001086
H	1.668142	-2.068213	0.000574
H	2.691966	-0.903753	-0.889795
H	2.689291	-0.903702	0.893800
C	-1.453980	0.468282	-0.005892
H	-1.392448	1.137116	0.864930
H	-1.399047	1.121721	-0.889101
C	-2.776729	-0.310694	0.005512
H	-2.865709	-0.934527	0.900392
H	-3.615404	0.389346	0.002451
H	-2.872011	-0.949831	-0.877871

E (0 K) = -252.2703126
E + ZPE (0 K) = -252.102482
H (298 K) = -252.093187
G (298 K) = -252.136415

(*E*)-[*N,N*-dimethylamine] enamine radical cation of propanal, unconjugated (S3)

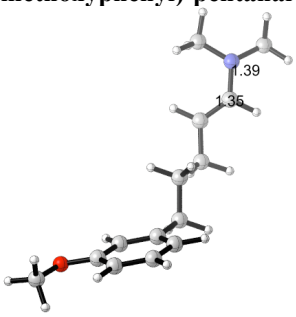
The C2-C2-N-C3 dihedral was constrained at 90°

Number of imaginary frequencies: 1
$\langle S^2 \rangle = 0.76$

C	-1.326480	0.232380	0.291237
H	-1.052937	0.735656	1.219254
C	-0.351791	-0.082657	-0.599404
H	-0.580690	-0.758451	-1.424689
N	1.012759	-0.035181	-0.282988
C	1.635409	1.245056	0.046336
H	0.927886	2.057932	-0.115113
H	2.008178	1.238836	1.077231
H	2.496882	1.383016	-0.622193
C	1.662649	-1.230536	0.259471
H	1.254448	-2.128419	-0.209348
H	2.742458	-1.175469	0.103017
H	1.447608	-1.258152	1.336462
C	-2.766899	-0.070934	0.080309
H	-3.139186	-0.714677	0.888137
H	-3.349213	0.859244	0.140754
H	-2.962078	-0.553105	-0.880287

E (0 K) = -251.5986156
E + ZPE (0 K) = -251.445898
H (298 K) = -251.437342
G (298 K) = -251.478105

(*E*)-[*N*,*N*-dimethylamine] enamine of 5-(3-methoxyphenyl)-pentanal (S4)

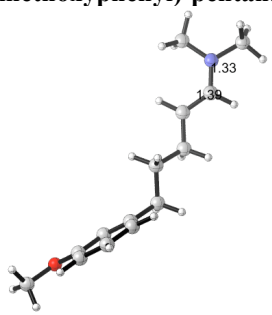


Number of imaginary frequencies: 0

C	-1.990011	-0.423034	1.238260
H	-1.842002	-0.068549	2.271142
H	-2.247064	-1.489139	1.315976
C	-0.654663	-0.278820	0.482328
H	-0.404589	0.786032	0.378459
H	-0.771592	-0.665504	-0.538347
C	0.513823	-1.004329	1.179745
H	0.265906	-2.070027	1.276476
H	0.616523	-0.614233	2.201197
C	1.827847	-0.855139	0.442780
C	2.200939	-1.769693	-0.556266
C	2.674238	0.219025	0.717125
C	3.392325	-1.597710	-1.254001
H	1.555766	-2.616066	-0.779163
C	3.874173	0.393555	0.013720
H	2.422417	0.944086	1.486609
C	4.240439	-0.519711	-0.980776
H	3.677037	-2.311719	-2.022865
H	5.165339	-0.407710	-1.534854
O	4.615307	1.484271	0.377870
C	5.838831	1.717417	-0.298011
H	5.684384	1.873275	-1.374313
H	6.255807	2.626254	0.140433
H	6.546247	0.889456	-0.154314
C	-3.125760	0.327936	0.596265
H	-3.027332	1.411135	0.557232
C	-4.197983	-0.277578	0.055218
H	-4.287757	-1.361868	0.125475
N	-5.244523	0.302750	-0.659361
C	-5.262982	1.748059	-0.767946
H	-6.065071	2.048602	-1.449093
H	-5.421831	2.251836	0.202365
H	-4.311432	2.098436	-1.180719
C	-6.551398	-0.319556	-0.513624
H	-7.055667	-0.058146	0.433629
H	-7.200515	-0.013600	-1.341545
H	-6.444283	-1.408511	-0.550107

E (0 K) = -676.079697
E +ZPE (0 K) = -675.753426
H (298 K) = -675.735069
G (298 K) = -675.801623

(*E*)-[*N*,*N*-dimethylamine] enamine of 5-(3-methoxyphenyl)-pentanal, dication (S5)

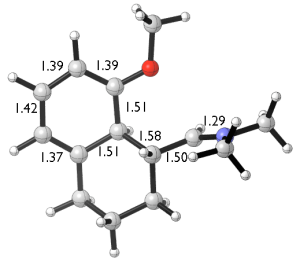


Number of imaginary frequencies: 0

C	2.003137	0.016077	1.071081
H	1.878050	-0.717129	1.887105
H	2.213242	0.978227	1.553051
C	0.673233	0.081681	0.278762
H	0.475367	-0.888793	-0.192962
H	0.764907	0.816337	-0.530656
C	-0.503898	0.455281	1.210013
H	-0.296045	1.422773	1.685086
H	-0.574416	-0.280538	2.018721
C	-1.840733	0.539773	0.503256
C	-2.165146	1.671720	-0.301575
C	-2.793723	-0.446943	0.629555
C	-3.414521	1.798012	-0.960725
H	-1.440645	2.475408	-0.404338
C	-4.066453	-0.324843	-0.029212
H	-2.634941	-1.332124	1.237811
C	-4.371639	0.819310	-0.837800
H	-3.613615	2.681420	-1.558904
H	-5.331828	0.910072	-1.331849
O	-4.885277	-1.320573	0.182205
C	-6.233276	-1.378570	-0.375962
H	-6.175041	-1.384200	-1.466746
H	-6.641309	-2.316561	-0.006341
H	-6.814919	-0.530844	-0.007005
C	3.171665	-0.431413	0.259035
H	3.045408	-1.317089	-0.359770
C	4.412277	0.204007	0.310255
H	4.530643	1.088108	0.931001
N	5.511960	-0.185600	-0.338101
C	5.544900	-1.369859	-1.214821
H	6.510274	-1.405360	-1.718088
H	5.418946	-2.277560	-0.616093
H	4.752643	-1.304629	-1.964594
C	6.775870	0.546965	-0.177276
H	7.535983	-0.138380	0.212694
H	7.101399	0.914615	-1.156065
H	6.644247	1.382838	0.509495

E (0 K) = -675.488273
E +ZPE (0 K) = -675.162586
H (298 K) = -675.143572
G (298 K) = -675.211228

Dication of 17* (S6)

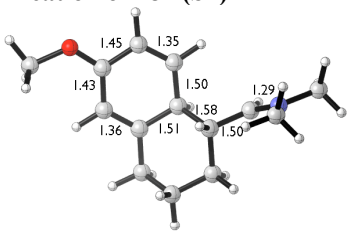


Number of imaginary frequencies: 0

C	0.343313	-2.332292	-0.258153
C	0.401357	-0.809903	0.100174
C	-0.850314	-0.041877	-0.477013
C	-2.140848	-0.775416	-0.180827
C	-2.177291	-2.243657	-0.470259
C	-0.979816	-2.968709	0.175746
H	0.379799	-0.706737	1.188751
H	0.482007	-2.459141	-1.339971
H	1.183027	-2.835317	0.233015
H	-3.125127	-2.669827	-0.130981
H	-2.136997	-2.390799	-1.560956
H	-1.072635	-2.947038	1.268088
H	-0.987979	-4.020925	-0.123614
H	-0.765250	-0.064841	-1.580514
C	1.688448	-0.294572	-0.471590
H	1.688728	-0.024058	-1.525681
C	3.110891	-0.605494	1.517174
H	2.194919	-0.844844	2.051247
H	3.784140	-1.467086	1.535471
H	3.608611	0.242447	1.994286
C	4.058185	0.141157	-0.651759
H	4.512568	1.004371	-0.159092
H	4.763984	-0.693537	-0.638612
H	3.795524	0.389530	-1.680001
N	2.843113	-0.254123	0.104960
C	-0.855960	1.429360	-0.129197
C	-1.999484	2.064128	0.338212
H	-2.010248	3.125910	0.551953
C	-3.149126	1.303259	0.545742
C	-3.221643	-0.091717	0.300720
H	-4.155110	-0.611090	0.493000
H	-4.037289	1.808189	0.919057
O	0.298642	2.016952	-0.348282
C	0.452786	3.463152	-0.174832
H	0.281684	3.727586	0.870805
H	1.481501	3.671742	-0.460679
H	-0.239773	3.984195	-0.838867

E (0 K) = -675.510304
E +ZPE (0 K) = -675.179126
H (298 K) = -675.161953
G (298 K) = -675.223103

Dication of 18* (S7)

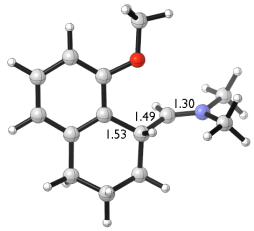


Number of imaginary frequencies: 0

C	-1.552769	1.961149	-0.024983
C	-1.234444	0.432971	0.068449
C	0.076355	0.078614	-0.740222
C	1.204081	1.010496	-0.367015
C	0.907323	2.479526	-0.395688
C	-0.357145	2.805224	0.428163
H	-1.062158	0.172105	1.116294
H	-1.823726	2.216537	-1.057820
H	-2.425679	2.179473	0.599407
H	1.765590	3.052499	-0.034443
H	0.739892	2.782041	-1.440689
H	-0.160622	2.640180	1.494256
H	-0.599704	3.865518	0.310496
H	-0.147592	0.296470	-1.802148
C	-2.415666	-0.301121	-0.488721
H	-2.484824	-0.368490	-1.574883
C	-3.581329	-0.804532	1.623016
H	-2.725020	-0.356441	2.120067
H	-4.486905	-0.243478	1.869738
H	-3.705585	-1.840108	1.950250
C	-4.563829	-1.407474	-0.576094
H	-4.677876	-2.441510	-0.241063
H	-5.469956	-0.846498	-0.332931
H	-4.383408	-1.377796	-1.650550
N	-3.420827	-0.797716	0.151725
C	0.419670	-1.377265	-0.664317
C	1.644762	-1.826321	-0.330490
H	1.895126	-2.881784	-0.298081
C	2.690543	-0.879484	-0.016574
C	2.435342	0.527713	-0.031085
H	3.233995	1.217840	0.217617
H	-0.355556	-2.096204	-0.921517
O	3.833171	-1.414674	0.266015
C	5.029583	-0.637093	0.594359
H	5.802398	-1.385928	0.752355
H	5.284717	0.009318	-0.247694
H	4.852458	-0.066760	1.508364

E (0 K) = -675.516269
E +ZPE (0 K) = -675.185246
H (298 K) = -675.168021
G (298 K) = -675.229474

_N,N_-dimethyl iminium of 6-methoxy-1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (S8, _ortho_)

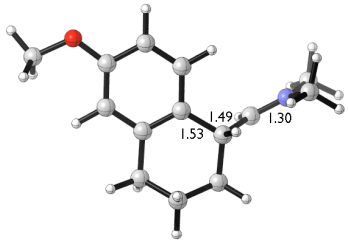


Number of imaginary frequencies: 0

C	-0.273267	-2.361436	0.094510
C	-0.408999	-0.859267	-0.306047
C	0.879039	-0.073254	-0.070971
C	2.116018	-0.701645	0.130243
C	2.234295	-2.212419	0.191581
C	1.042330	-2.928966	-0.446784
H	-0.664562	-0.809261	-1.371199
H	-0.288093	-2.460076	1.188455
H	-1.136410	-2.915603	-0.290858
H	3.166207	-2.523960	-0.292957
H	2.323734	-2.523607	1.242861
H	1.070275	-2.814326	-1.538167
H	1.087878	-4.002612	-0.236396
C	-1.520079	-0.290929	0.509734
H	-1.260128	0.049138	1.509992
C	0.815210	1.334023	-0.131834
C	1.956672	2.115727	0.023852
H	1.909634	3.197102	-0.020410
C	3.182488	1.477316	0.233972
H	4.079516	2.077630	0.352468
C	3.262964	0.091372	0.283371
H	4.223918	-0.391232	0.437395
O	-0.447209	1.838194	-0.348687
C	-0.613292	3.256586	-0.418808
H	-0.033840	3.675805	-1.248207
H	-1.675962	3.426761	-0.598347
H	-0.316442	3.737041	0.520322
N	-2.784338	-0.260839	0.227264
C	-3.369197	-0.679828	-1.058883
H	-4.131793	-1.438495	-0.864502
H	-3.839605	0.187891	-1.529715
H	-2.609604	-1.087805	-1.720060
C	-3.768990	0.261071	1.195199
H	-3.264559	0.564134	2.112692
H	-4.280949	1.120707	0.754180
H	-4.502337	-0.519024	1.416283

E (0 K) = -675.284430
E +ZPE (0 K) = -674.964710
H (298 K) = -674.947896
G (298 K) = -675.007954

_N,N_-dimethyl iminium of 6-methoxy-1,2,3,4-tetrahydronaphthalene-1-carbaldehyde (S9, _para_)



Number of imaginary frequencies: 0

C	1.561449	2.179438	0.128493
C	1.413033	0.709971	-0.369948
C	-0.017453	0.167368	-0.251608
C	-1.102583	0.996503	0.079659
C	-0.919879	2.482692	0.323132
C	0.362522	3.020428	-0.316511
H	1.739876	0.666317	-1.413760
H	1.619354	2.200882	1.225587
H	2.504921	2.587555	-0.248806
H	-1.791642	3.024145	-0.060390
H	-0.894629	2.678834	1.405399
H	0.277433	3.002775	-1.410565
H	0.524653	4.063225	-0.024517
C	2.247235	-0.152905	0.506128
H	1.960293	-0.167700	1.555996
C	-0.253391	-1.197144	-0.513029
C	-1.521175	-1.742644	-0.431873
H	-1.705002	-2.791539	-0.638201
C	-2.607708	-0.918272	-0.086802
C	-2.387480	0.444140	0.153036
H	-3.218339	1.099449	0.390753
N	3.260360	-0.906714	0.202705
C	3.836983	-1.050522	-1.146963
H	3.853375	-2.112117	-1.407548
H	3.254318	-0.502349	-1.882398
H	4.862528	-0.671144	-1.131873
C	3.946139	-1.710462	1.235781
H	3.483886	-1.540204	2.208048
H	3.872219	-2.768752	0.971237
H	4.999817	-1.421040	1.270696
H	0.572155	-1.844225	-0.804601
O	-3.809140	-1.528602	-0.028242
C	-4.965910	-0.758705	0.300108
H	-5.798629	-1.461981	0.288878
H	-4.875250	-0.313955	1.298164
H	-5.141431	0.028314	-0.442715

E (0 K) = -675.279684
E +ZPE (0 K) = -674.960237
H (298 K) = -674.943370
G (298 K) = -675.004258

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Gaussian 09, revision A.1

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