Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Ab initio insight into ultrafast nonadiabatic decay of hypoxanthine: keto-N7H and keto-N9H tautomers

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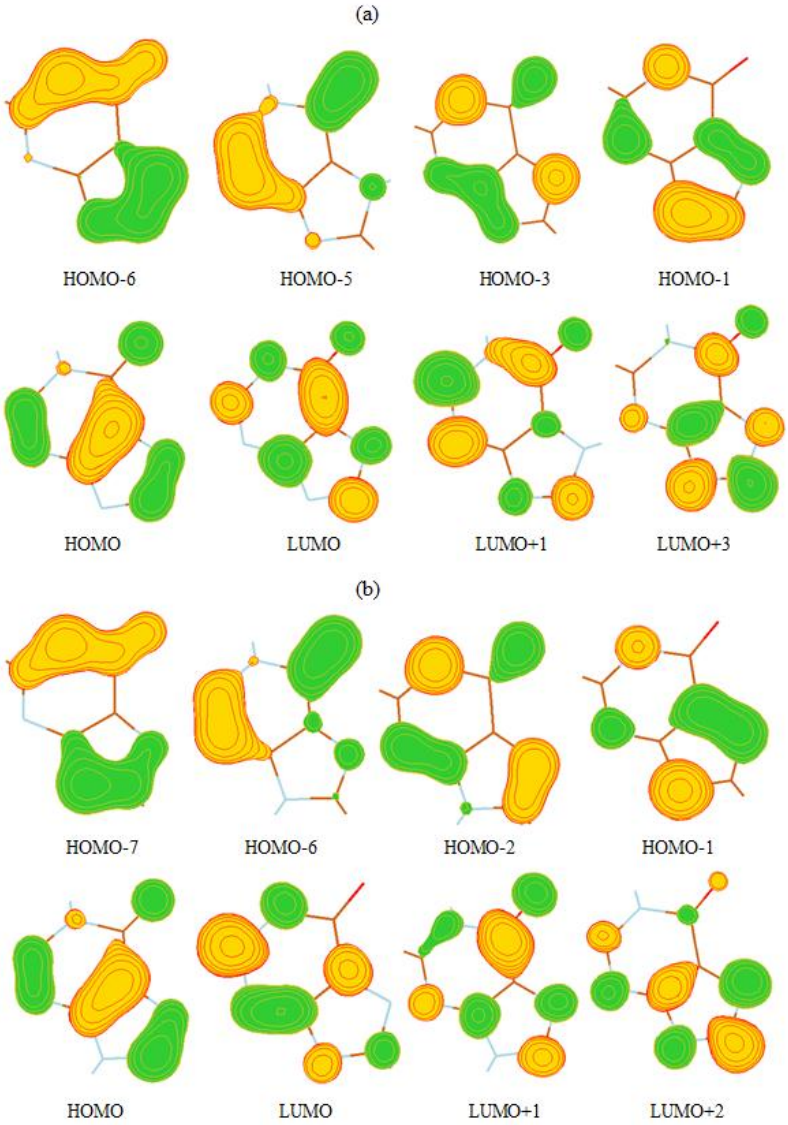

Fig. S1. Schematic plots of HOMO and LUMO molecular orbitals for keto-N7H (a) and keto-N9H (b) with an isosurface value of 0.05.

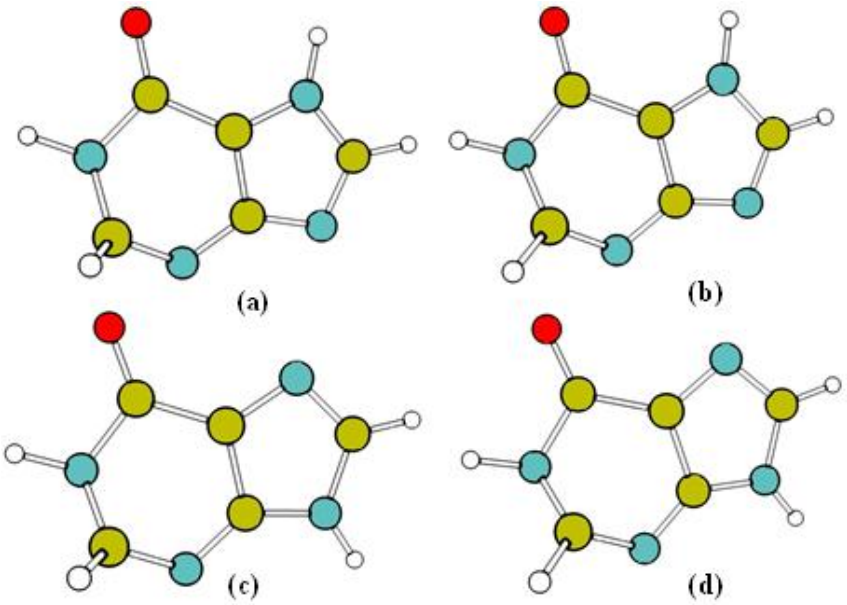

Fig. S2. Minima on the crossing seams (MXSs) between the S_1 and S_0 states of keto-N7H and keto-N9H (^{2}E conformation). (a) (c): *Ethylenic I*; (b) (d): *Ethylenic II*.

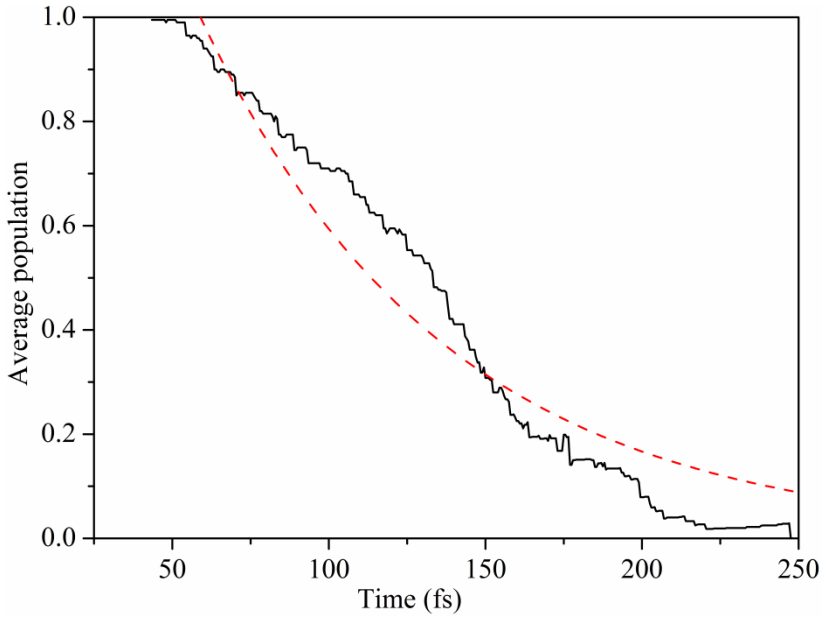

Fig. S3. Time evolution of the S_1 excited state population of keto-N7H averaged over all trajectories along with the fitting parameters.

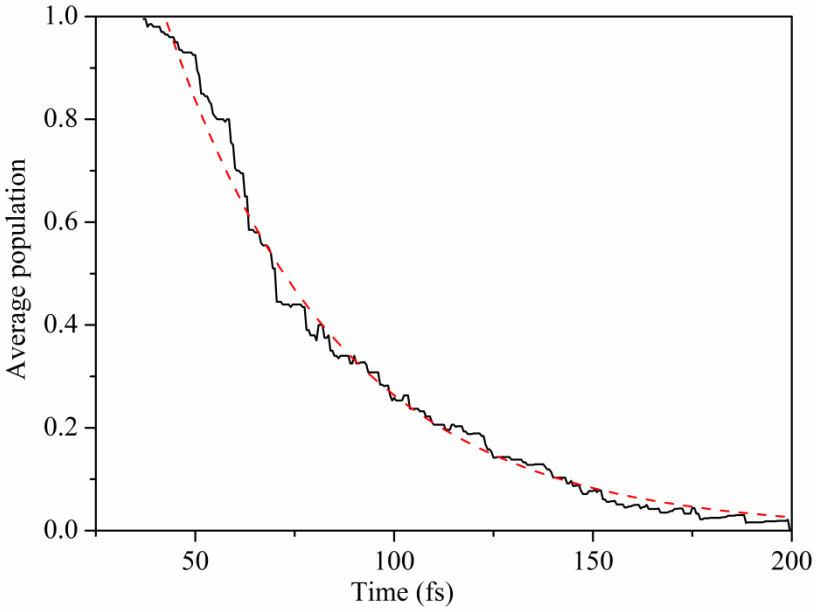

Fig. S4. Time evolution of the S_1 excited state population of keto-N9H averaged over all trajectories along with the fitting parameters.

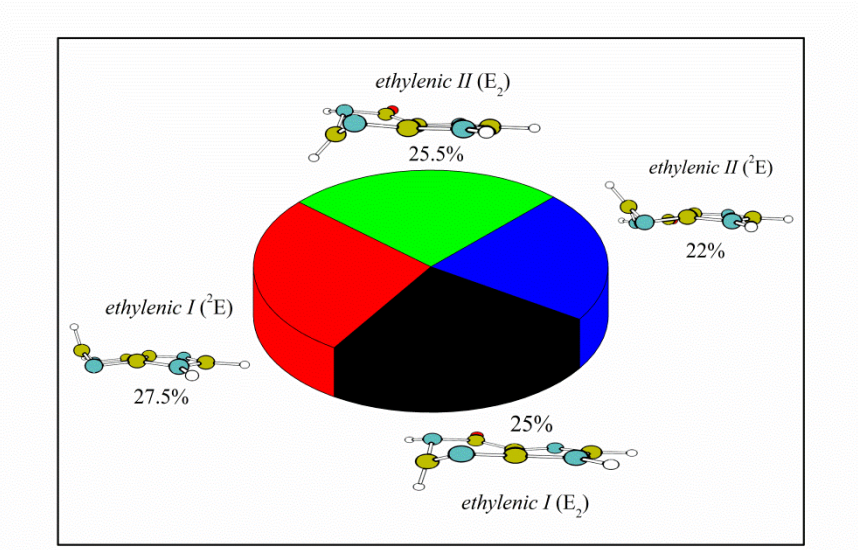

Fig. S5. Four of the main S_1/S_0 conical intersections of keto-N9H. The percentages show how often each type of structure is accessed for decay in the current dynamics simulations.

Table S1. Cartesian coordinates (Å) of the CCSD optimized ground-state geometry of keto-N7H.

Atom	X	Y	Z
C	−0.004666	0.549382	0.000000
C	−0.947387	−0.466811	0.000000
C	0.645807	−2.038175	0.000000
C	1.415917	0.317474	0.000000
C	−2.038982	1.358718	0.000000
N	−0.630054	−1.814154	0.000000
N	1.634645	−1.069538	0.000000
N	−0.721882	1.722166	0.000000
N	−2.222460	0.051135	0.000000
O	2.328069	1.137030	0.000000
H	1.010549	−3.063972	0.000000
H	2.609729	−1.353884	0.000000
H	−2.834953	2.094398	0.000000
H	−0.333125	2.656644	0.000000

Table S2. Cartesian coordinates (Å) of the CCSD optimized ground-state geometry of keto-N9H.

Atom	X	Y	Z
C	−0.002247	0.617965	0.000000
C	−0.882882	−0.452179	0.000000
C	0.676229	−2.019481	0.000000
C	1.425199	0.362252	0.000000
C	−1.948463	1.475076	0.000000
N	−0.606011	−1.798988	0.000000
N	1.640893	−1.045957	0.000000
N	−0.683279	1.823327	0.000000
N	−2.132325	0.108658	0.000000
O	2.369982	1.132836	0.000000
H	1.040253	−3.045433	0.000000
H	2.619874	−1.317299	0.000000
H	−2.785622	2.163295	0.000000
H	−3.006895	−0.400345	0.000000

Table S3. Cartesian coordinates (Å) of the MR-CIS optimized ground-state geometry of keto-N7H.

Atom	X	Y	Z
C	−0.003447	0.545246	−0.000000
C	−0.952488	−0.473986	−0.000000
C	0.647476	−2.024060	0.000000
C	1.403831	0.314582	−0.000000
C	−2.024603	1.355357	0.000000
N	−0.628087	−1.801586	−0.000000
N	1.621784	−1.060359	−0.000000
N	−0.716319	1.710233	0.000000
N	−2.207655	0.048450	−0.000000
O	2.304093	1.109149	−0.000000
H	1.013938	−3.034923	−0.000000
H	2.580724	−1.343265	0.000000
H	−2.806784	2.087637	0.000000
H	−0.336352	2.633283	0.000000

Table S4. Cartesian coordinates (Å) of the MR-CIS optimized ground-state geometry of keto-N9H.

Atom	X	Y	Z
C	0.000815	0.617994	−0.000000
C	−0.885057	−0.456299	−0.000000
C	0.675876	−2.006162	0.000000
C	1.415800	0.358949	0.000000
C	−1.940262	1.464488	−0.000000
N	−0.605684	−1.784661	−0.000000
N	1.628420	−1.039012	0.000000
N	−0.674420	1.806844	−0.000000
N	−2.120607	0.108265	0.000000
O	2.348878	1.102246	0.000000
H	1.039813	−3.017725	0.000000
H	2.590442	−1.311948	−0.000000
H	−2.769742	2.142442	−0.000000
H	−2.986707	−0.387927	0.000000

Table S5. Cartesian coordinates (Å) of the CASSCF optimized ground-state geometry of keto-N7H.

Atom	X	Y	Z
C	−0.009743	0.548567	0.000000
C	−0.942236	−0.460104	0.000000
C	0.641310	−2.028437	−0.000000
C	1.409843	0.303328	0.000000
C	−2.027419	1.351557	−0.000000
N	−0.617660	−1.799191	0.000000
N	1.628433	−1.059620	−0.000000
N	−0.718998	1.712831	−0.000000
N	−2.203888	0.057623	0.000000
O	2.296428	1.111436	0.000000
H	1.002837	−3.038678	−0.000000
H	2.584582	−1.343387	−0.000000
H	−2.813926	2.076299	−0.000000
H	−0.342298	2.633068	−0.000000

Table S6. Cartesian coordinates (Å) of the CASSCF optimized ground-state geometry of keto-N9H.

Atom	X	Y	Z
C	−0.006316	0.609614	0.000000
C	−0.883649	−0.445312	−0.000000
C	0.671663	−2.006976	0.000000
C	1.420178	0.346406	−0.000000
C	−1.939070	1.464574	0.000000
N	−0.592442	−1.782931	−0.000000
N	1.636795	−1.035248	0.000000
N	−0.686058	1.804015	0.000000
N	−2.123732	0.108011	−0.000000
O	2.335382	1.111864	−0.000000
H	1.032520	−3.017464	0.000000
H	2.596064	−1.308530	0.000000
H	−2.763528	2.145733	0.000000
H	−2.986692	−0.385617	−0.000000

Table S7. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic I* (^{2}E) for keto-N7H.

Atom	X	Y	Z
C	−0.200769	0.442144	−0.234843
C	−0.689973	−0.867299	−0.024357
C	1.412880	−1.449997	−0.320903
C	1.184871	0.827786	0.050052
C	−2.380205	0.402714	−0.039315
N	0.225165	−1.814395	0.241992
N	1.982428	−0.305160	0.267812
N	−1.319138	1.233063	−0.197954
N	−2.048346	−0.867802	0.088550
O	1.598288	1.946883	0.103792
H	1.587814	−1.647675	−1.370462
H	2.962459	−0.132560	0.183892
H	−3.385211	0.775032	−0.025886
H	−1.337738	2.228677	−0.268772

Table S8. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic I* (^{2}E) for keto-N9H.

Atom	X	Y	Z
C	0.224537	−0.508369	−0.144790
C	0.660451	0.833502	−0.018843
C	−1.372554	1.420419	−0.408245
C	−1.197426	−0.828941	0.084368
C	2.340122	−0.575807	0.022236
N	−0.206139	1.827245	0.168794
N	−1.986672	0.353697	0.244207
N	1.292417	−1.357153	−0.094979
N	2.015054	0.758775	0.094393
O	−1.692085	−1.906497	0.138295
H	−1.541061	1.587885	−1.464294
H	−2.955422	0.175942	0.073653
H	3.359161	−0.904260	0.062822
H	2.644996	1.524567	0.202113

Table S9. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic I* (^{2}E) for keto-N7H.

Atom	X	Y	Z
C	−0.209858	0.442656	−0.211682
C	−0.697814	−0.844564	−0.023890
C	1.419116	−1.462853	−0.317339
C	1.185447	0.814956	0.065251
C	−2.386315	0.403372	−0.051876
N	0.260106	−1.767336	0.268531
N	2.005441	−0.316288	0.238604
N	−1.330032	1.235418	−0.196875
N	−2.050022	−0.858344	0.074467
O	1.601316	1.931359	0.135410
H	1.575686	−1.667370	−1.369890
H	2.978649	−0.129806	0.116306
H	−3.394305	0.760887	−0.065334
H	−1.352658	2.225108	−0.290479

Table S10. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic I* (^{2}E) for keto-N9H.

Atom	X	Y	Z
C	−0.080532	−0.035438	−0.059300
C	0.000764	0.212259	2.088892
C	1.383088	0.299314	1.954163
C	2.047361	−0.301163	0.778753
C	0.949063	0.724676	3.988011
O	3.213346	−0.430516	0.602944
N	1.107494	−0.733890	−0.216468
N	−0.713091	−0.316867	1.082171
N	1.948877	0.609403	3.173317
N	−0.272603	0.476187	3.389954
H	1.528117	−0.793329	−1.121015
H	−1.166235	0.486855	3.824222
H	1.017942	0.996233	5.020080
H	−0.218375	0.918064	−0.552869

Table S11. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic I* (E_2) for keto-N7H.

Atom	X	Y	Z
C	−0.234070	0.422072	0.220979
C	−0.688217	−0.906422	0.056240
C	1.411266	−1.427992	0.468689
C	1.154576	0.823147	−0.026195
C	−2.402144	0.326081	−0.063290
N	0.255949	−1.845360	−0.124199
N	1.982798	−0.301461	−0.152371
N	−1.365140	1.185833	0.097631
N	−2.040303	−0.941732	−0.113080
O	1.547548	1.946941	−0.120229
H	1.545442	−1.570124	1.533119
H	2.954964	−0.103734	−0.038130
H	−3.412760	0.675537	−0.137083
H	−1.406073	2.183112	0.116537

Table S12. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic I* (E_2) for keto-N9H.

Atom	X	Y	Z
C	0.244971	−0.511619	0.116976
C	0.691706	0.829884	0.031592
C	−1.351432	1.420810	0.356525
C	−1.169084	−0.820225	−0.170207
C	2.364920	−0.587664	0.026966
N	−0.162585	1.831577	−0.169708
N	−1.946191	0.369407	−0.337406
N	1.309847	−1.365231	0.091218
N	2.049181	0.749756	−0.033150
O	−1.666583	−1.893912	−0.261933
H	−1.557996	1.570165	1.408523
H	−2.921421	0.193924	−0.205900
H	3.383167	−0.920922	0.018025
H	2.686401	1.513923	−0.102921

Table S13. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic I* (E_2) for keto-N7H.

Atom	X	Y	Z
C	−0.242120	0.421298	0.199409
C	−0.696459	−0.883847	0.055792
C	1.418021	−1.440800	0.465422
C	1.155737	0.809395	−0.040571
C	−2.408382	0.327263	−0.051857
N	0.290309	−1.799255	−0.150175
N	2.004324	−0.311278	−0.124481
N	−1.375812	1.188088	0.096462
N	−2.042700	−0.931554	−0.099754
O	1.552303	1.929597	−0.149971
H	1.535406	−1.589246	1.532352
H	2.967247	−0.097459	0.030485
H	−3.422769	0.663151	−0.099570
H	−1.421468	2.180568	0.136941

Table S14. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic I* (E_2) for keto-N9H.

Atom	X	Y	Z
C	0.248887	−0.496361	0.117563
C	0.700764	0.817513	0.039947
C	−1.353886	1.424141	0.348401
C	−1.163701	−0.807985	−0.182985
C	2.367313	−0.593365	0.025190
N	−0.191593	1.793043	−0.194465
N	−1.965278	0.375120	−0.322386
N	1.325193	−1.358824	0.091211
N	2.052773	0.752102	−0.029024
O	−1.651951	−1.883112	−0.296760
H	−1.554452	1.585680	1.399858
H	−2.933280	0.185824	−0.161675
H	3.383270	−0.927239	0.023400
H	2.686984	1.514137	−0.094996

Table S15. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic II* (^{2}E) for keto-N7H.

Atom	X	Y	Z
C	−0.186986	0.409316	−0.274589
C	−0.691929	−0.905243	−0.014904
C	1.377387	−1.386591	−0.374287
C	1.195510	0.817917	0.067865
C	−2.366180	0.393455	−0.025283
N	0.208279	−1.839847	0.275019
N	1.978683	−0.317021	0.313109
N	−1.295725	1.210846	−0.234642
N	−2.056342	−0.871187	0.137382
O	1.579621	1.944190	0.131002
H	1.804101	−1.887453	−1.218747
H	2.964379	−0.162422	0.276346
H	−3.364535	0.784374	−0.001743
H	−1.304859	2.206361	−0.308638

Table S16. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic II* (^{2}E) for keto-N9H.

Atom	X	Y	Z
C	0.208953	−0.480513	−0.183867
C	0.661112	0.872936	−0.017029
C	−1.347724	1.361762	−0.456201
C	−1.213532	−0.813767	0.101287
C	2.319339	−0.569083	0.017936
N	−0.191922	1.856453	0.179703
N	−1.985270	0.369829	0.286949
N	1.266248	−1.338591	−0.142772
N	2.016037	0.765005	0.132517
O	−1.683696	−1.900333	0.165516
H	−1.745830	1.813464	−1.343073
H	−2.964160	0.209344	0.165062
H	3.332802	−0.915098	0.064100
H	2.659589	1.514025	0.272114

Table S17. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic II* (^{2}E) for keto-N7H.

Atom	X	Y	Z
C	−0.186986	0.409059	−0.288777
C	−0.687634	−0.887333	−0.021753
C	1.372377	−1.379207	−0.368766
C	1.186008	0.803636	0.094891
C	−2.363018	0.391996	−0.017703
N	0.234443	−1.804511	0.283126
N	1.998915	−0.340846	0.311890
N	−1.304441	1.212970	−0.246400
N	−2.048787	−0.861393	0.145567
O	1.587374	1.920200	0.185271
H	1.778963	−1.874916	−1.226063
H	2.976395	−0.163988	0.207602
H	−3.365193	0.767704	0.003767
H	−1.326330	2.200340	−0.356932

Table S18. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic II* (^{2}E) for keto-N9H.

Atom	X	Y	Z
C	0.205658	−0.464364	−0.207950
C	0.663740	0.870795	−0.024921
C	−1.344009	1.352594	−0.446624
C	−1.198049	−0.803790	0.122652
C	2.314227	−0.577517	0.025361
N	−0.207323	1.835675	0.176956
N	−1.996321	0.383169	0.290054
N	1.279180	−1.331472	−0.158658
N	2.011564	0.769497	0.139689
O	−1.671022	−1.886121	0.212030
H	−1.736031	1.795432	−1.340174
H	−2.964989	0.202282	0.122531
H	3.324921	−0.923928	0.081155
H	2.650617	1.512935	0.300031

Table S19. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic II* (E_2) for keto-N7H.

Atom	X	Y	Z
C	−0.221054	0.391149	0.261857
C	−0.688514	−0.945388	0.048211
C	1.372561	−1.363074	0.517658
C	1.166513	0.812176	−0.043072
C	−2.386838	0.315478	−0.077247
N	0.241483	−1.873427	−0.156155
N	1.981617	−0.316227	−0.197289
N	−1.342595	1.165376	0.135011
N	−2.045552	−0.948655	−0.162523
O	1.530696	1.941997	−0.147471
H	1.772522	−1.811932	1.403444
H	2.961653	−0.138660	−0.127756
H	−3.390751	0.682920	−0.162284
H	−1.374421	2.162908	0.157928

Table S20. Cartesian coordinates (Å) of the MR-CIS optimized structure of *ethylenic II* (E_2) for keto-N9H.

Atom	X	Y	Z
C	0.228012	−0.484282	0.155963
C	0.692835	0.869331	0.030384
C	−1.328414	1.361656	0.403741
C	−1.184581	−0.804312	−0.187544
C	2.343956	−0.581238	0.030808
N	−0.147378	1.861030	−0.179994
N	−1.942958	0.386772	−0.380224
N	1.281779	−1.347489	0.138559
N	2.051812	0.756380	−0.070898
O	−1.657486	−1.886871	−0.288698
H	−1.756851	1.799748	1.283276
H	−2.926489	0.229713	−0.297548
H	3.356684	−0.932130	0.015942
H	2.703858	1.504107	−0.172965

Table S21. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic II* (E_2) for keto-N7H.

Atom	X	Y	Z
C	−0.221598	0.391669	0.275579
C	−0.684978	−0.926931	0.054350
C	1.367634	−1.356221	0.511240
C	1.158625	0.796284	−0.069995
C	−2.383357	0.313944	−0.084236
N	0.267155	−1.837928	−0.165231
N	2.002254	−0.339642	−0.194388
N	−1.351717	1.168060	0.146121
N	−2.037995	−0.938950	−0.170371
O	1.541474	1.915413	−0.200252
H	1.746908	−1.799802	1.408669
H	2.970811	−0.136744	−0.058949
H	−3.390872	0.666285	−0.166311
H	−1.397535	2.159027	0.205154

Table S22. Cartesian coordinates (Å) of the CASSCF optimized structure of *ethylenic II* (E_2) for keto-N9H.

Atom	X	Y	Z
C	0.223762	−0.468682	0.179772
C	0.695038	0.866897	0.038362
C	−1.324413	1.352585	0.394190
C	−1.168532	−0.794027	−0.208341
C	2.338929	−0.589598	0.023119
N	−0.163051	1.840247	−0.178174
N	−1.953985	0.400297	−0.383498
N	1.293952	−1.340860	0.154756
N	2.047534	0.760938	−0.077904
O	−1.643352	−1.871863	−0.334725
H	−1.746976	1.781555	1.280562
H	−2.929138	0.222098	−0.255358
H	3.349241	−0.940709	−0.001305
H	2.695885	1.503512	−0.200503