Supplementary Material

Internal Proton Transfer in the External Pyridoxal-5´-Phosphate Schiff Base in Dopa Decarboxylase

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Fully optimized structures and atomic geometries of oxoenamino and hydroxyimino tautomers in reactions **a**–**d** (Scheme 2) are shown in Figure S1 and Table S1. Energies and free energies in the gas phase, solvation free energies and solution free energies in aqueous solution for the tautomerization reactions of **a**–**d** (Scheme 2) are listed in Table S2.

Figure S1. Gas-phase structures of oxoenamino and hydroxyimino Schiff bases fully optimized at B3LYP/6-311+G(d,p) for reactions **a1**, **a2**, **b1**, and **c1**; HF/6-311+G(d,p) for reactions **b2**, **c2**, and **d2**; HF/6-31+G(d) for reaction **d1**

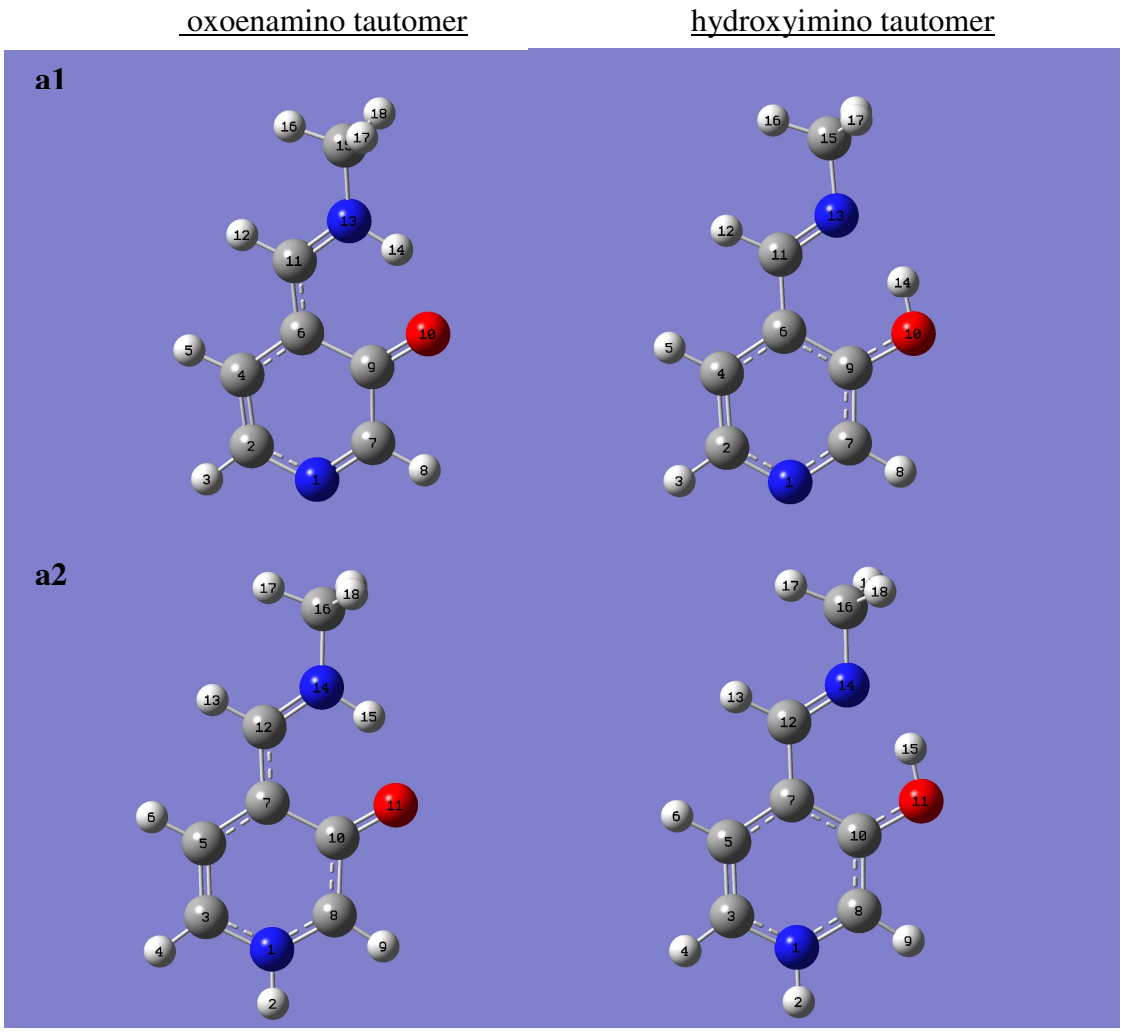

Figure S1 (continued)

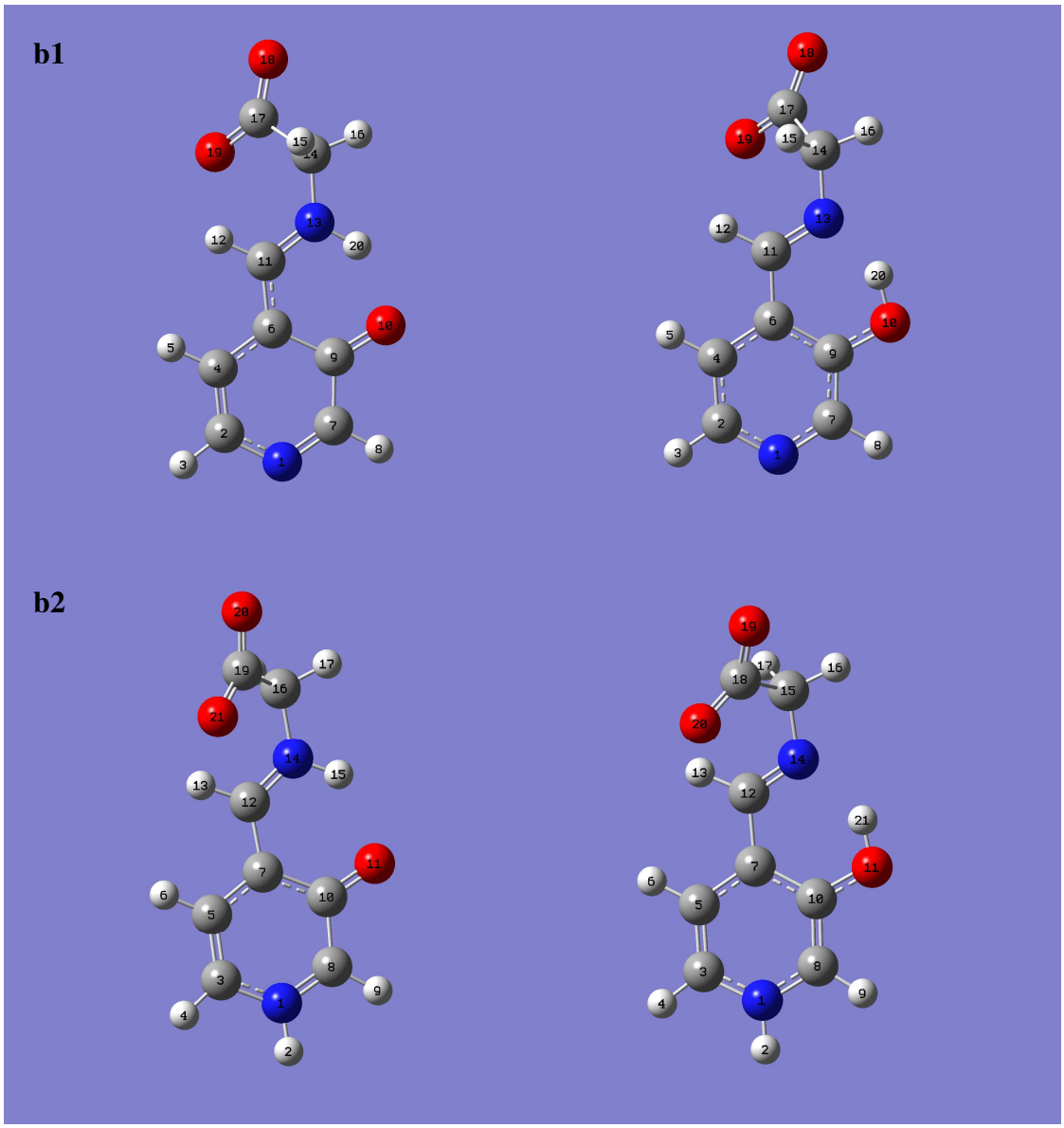

Figure S1 (continued)

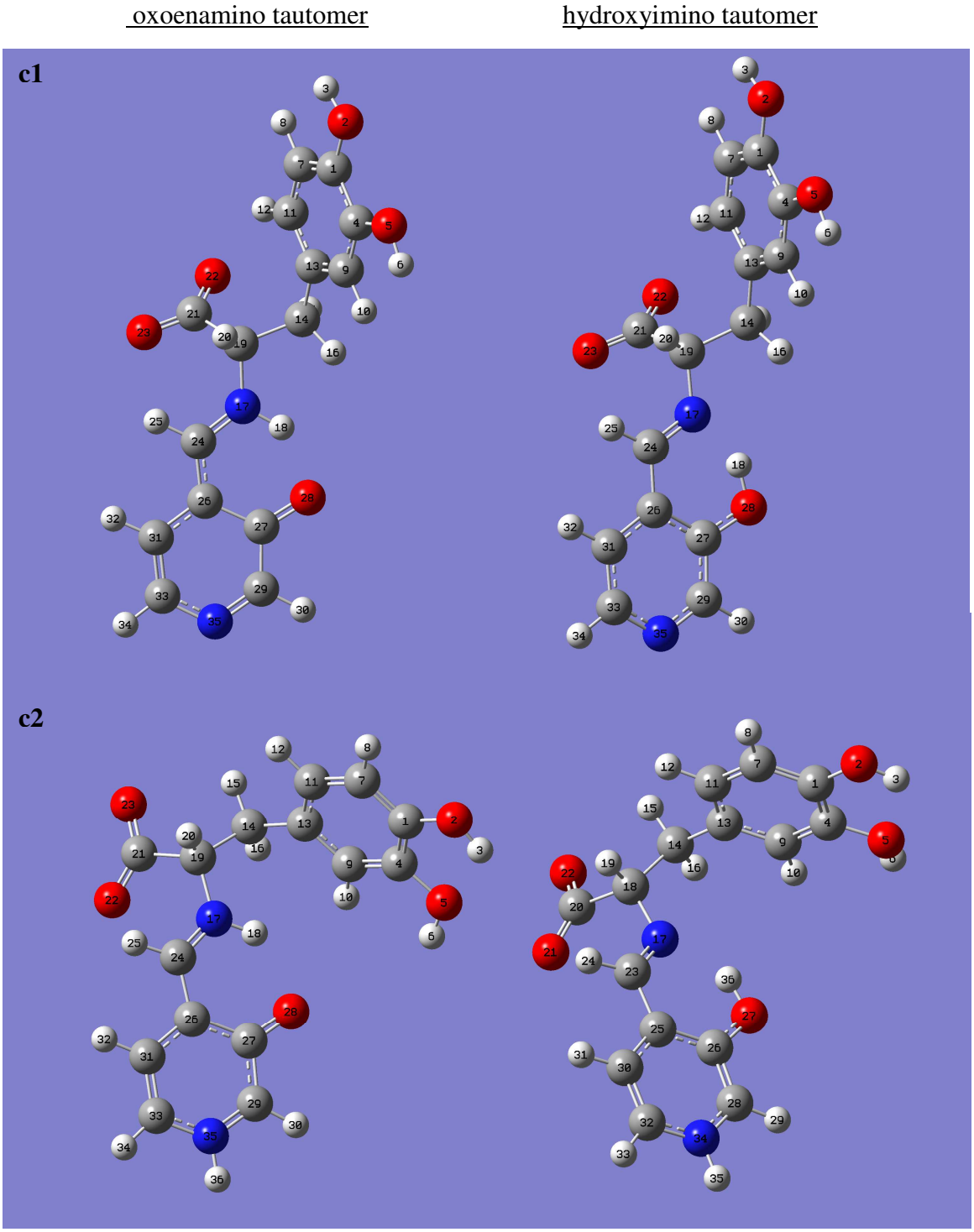

Figure S1 (continued)

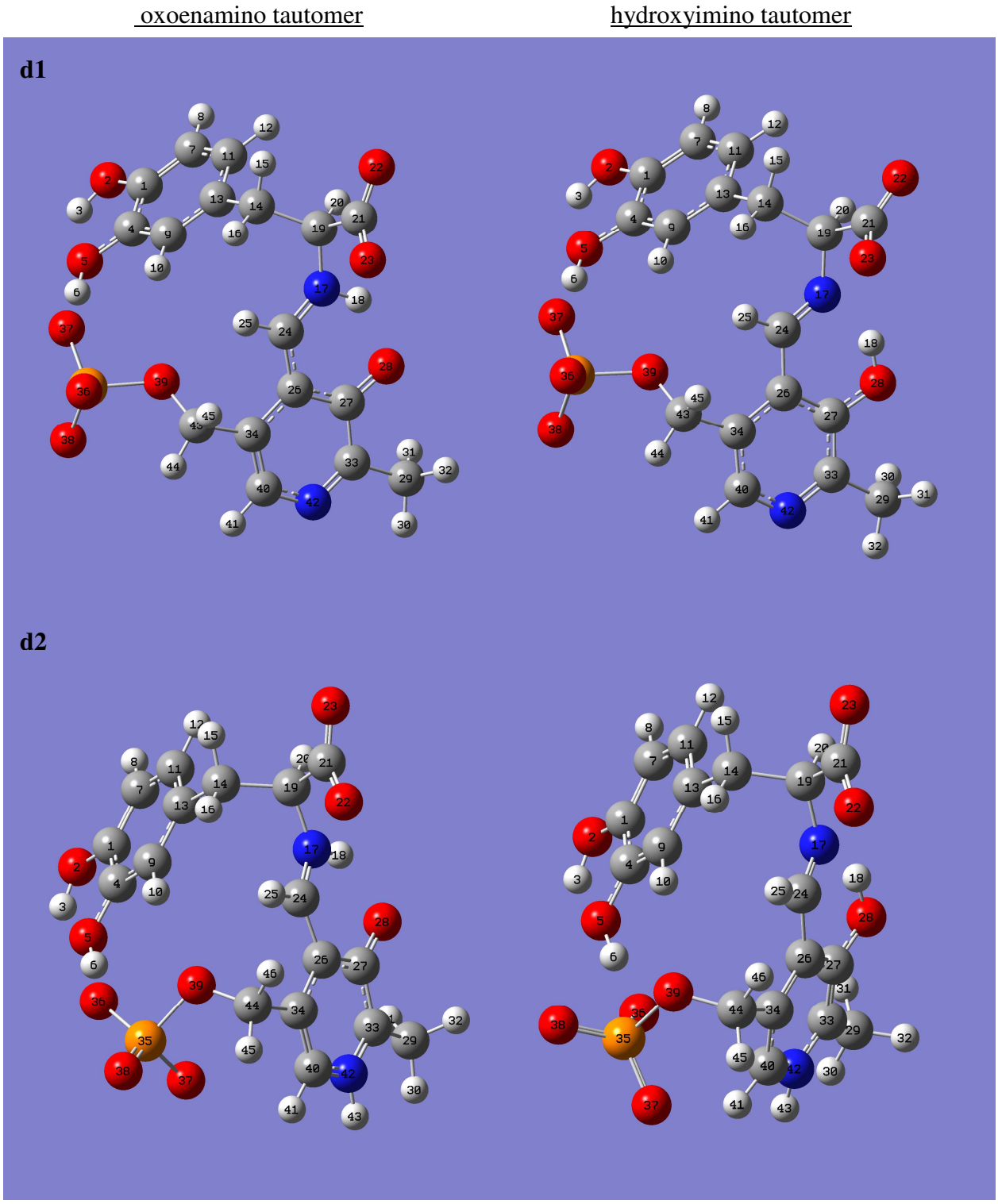

Table S1. Atomic Coordinates of the Fully Optimized Oxoenamino/Hydroxyimino Tautomers in Reactions **a–d** in the Gas Phase

reaction	tautomeric state	
a1 [a]	oxoenamino	N,0,2.83444974,0.1944606003,0.000078857 C,0,2.4381635778,-1.1178602128,-0.0004995841 H,0,3.2360934076,-1.8511212499,-0.0008998659 C,0,1.1246099014,-1.4920277806,-0.0006082279 H,0,0.8529799133,-2.5438524461,-0.0011071375 C,0,0.1063067337,-0.4971155533,-0.0000726827 C,0,1.9301355379,1.134302632,0.0005748102 H,0,2.2615339149,2.170467091,0.001006973 C,0,0.4936175178,0.9029291695,0.0006519341 O,0,-0.3382357345,1.8500034752,0.0010189154 C,0,-1.2547169008,-0.8390424614,-0.0001977601 H,0,-1.5538620442,-1.886166933,-0.0007118454 N,0,-2.2160217261,0.0626528305,0.0002981078 H,0,-1.8457015376,1.0369386114,0.000740986 C,0,-3.6372746593,-0.2300666349,0.0001138512 H,0,-3.7947361008,-1.3098942168,0.0001070357 H,0,-4.1127558516,0.1961805299,0.8870679486 H,0,-4.1125701339,0.1961715044,-0.8869514282
a1 [a]	hydroxyimino	N,0,-2.838330711,0.1306793385,-0.0001167351 C,0,-2.413249445,-1.1430761336,0.0000610482 H,0,-3.1820500412,-1.9085129412,0.0001026225 C,0,-1.0701783808,-1.4831166806,0.000170936 H,0,-0.7684016109,-2.5255867581,0.0002839756 C,0,-0.0970058563,-0.4729702485,0.0001006054 C,0,-1.9311636937,1.09896027,-0.0001726359 H,0,-2.2859176981,2.1254647514,-0.0002821559 C,0,-0.5451084822,0.86539563,-0.0000443195 O,0,0.2908999999,1.9132190841,-0.000002479 C,0,1.3257212135,-0.7982469432,0.0001319946 H,0,1.5874102731,-1.8655256504,0.0002236818 N,0,2.2284386279,0.1065729486,-0.0000920551 H,0,1.2151308252,1.5529750669,0.0002927613 C,0,3.6263833128,-0.2799023437,-0.0001376851 H,0,3.7681624118,-1.3686931814,0.0000928359 H,0,4.1183694612,0.1438599556,-0.8802077007 H,0,4.1185386024,0.1442558475,0.8796473459

[a] Calculated using the B3LYP/6-311+G(d,p) method

Table S1 (continued)

reaction	tautomeric state	
a2 [a]	oxoenamino	N,0,3.9397036378,2.0000379275,-0.0956814617 H,0,3.4120517699,2.0661401404,0.7709895908 C,0,5.3034072026,1.9924500897,-0.0024674223 H,0,5.7272262822,2.0573224608,0.9873468227 C,0,6.0298463798,1.9035410088,-1.1641864407 H,0,7.1117299259,1.8966826757,-1.1007508302 C,0,5.3880382921,1.8228390683,-2.4119090175 C,0,3.2526016278,1.927909521,-1.2284428792 H,0,2.1719201155,1.9424686924,-1.1802865126 C,0,3.9338999617,1.8320747009,-2.4995152709 O,0,3.2976521325,1.7635036045,-3.5694487928 C,0,6.1559225578,1.7303739071,-3.6162485541 H,0,7.2424195534,1.7227045458,-3.5651032957 N,0,5.6019619977,1.6537941252,-4.7885964066 H,0,4.5611134699,1.6663775089,-4.7602901134 C,0,6.3119556079,1.5571683338,-6.0609317685 H,0,7.3877737604,1.5580685485,-5.8899315468 H,0,6.0192536505,0.6350424797,-6.5661358534 H,0,6.0375220744,2.405500661,-6.6904102471
a2 [a]	hydroxyimino	N,0,3.6997322949,1.6709321232,-0.2926507177 H,0,3.0902371452,1.7000570576,0.5192900415 C,0,5.0354646069,1.6655530762,-0.0913148064 H,0,5.3814038531,1.6927959252,0.9315637232 C,0,5.8665002679,1.6260179194,-1.1923547969 H,0,6.9387251343,1.6214039738,-1.0398831541 C,0,5.3382160771,1.5923048751,-2.4865082454 C,0,3.1229213739,1.6400112259,-1.5066086747 H,0,2.0432142074,1.647540378,-1.5624901537 C,0,3.9233989791,1.5994380415,-2.6522809222 O,0,3.3313725912,1.5699106792,-3.8267263798 C,0,6.2181011746,1.5500867337,-3.6616073244 H,0,7.2990930994,1.5461758041,-3.4860555906 N,0,5.7111096618,1.519588293,-4.8312251501 H,0,4.057598618,1.5432687137,-4.5267952523 C,0,6.5643412539,1.4775883633,-6.0043549185 H,0,7.6302476256,1.476082143,-5.7560967175 H,0,6.3173369727,0.5832774386,-6.5823307873 H,0,6.331985063,2.3399672354,-6.6345701732

Table S1 (continued)

reaction	tautomeric state	
b1 [a]	oxoenamino	N,0,3.4290763435,0.6098044989,2.639438662 C,0,2.892984463,1.8248487743,2.9418745763 H,0,3.2074569621,2.2668117472,3.8816194518 C,0,2.0015086838,2.4636743234,2.1128249916 H,0,1.5909957187,3.4306390862,2.3908554083 C,0,1.6040333638,1.8656519493,0.8952816311 C,0,3.0770555268,0.0281005125,1.5161632119 H,0,3.5115078986,-0.9437719112,1.2877836741 C,0,2.1473734736,0.570049615,0.5441916111 O,0,1.8519086084,-0.0505216877,-0.5200228917 C,0,0.6948104371,2.5352482863,0.028089262 H,0,0.2827445957,3.5019494784,0.2948208347 N,0,0.3082821753,2.0192201214,-1.1092939638 C,0,-0.637467147,2.6360479511,-2.0298997835 H,0,-0.1631532365,3.4867038721,-2.5300443875 H,0,-0.8885737647,1.9010277692,-2.7925261415 C,0,-1.9836885204,3.2048525698,-1.3922635408 O,0,-2.8443965998,3.4345112178,-2.259454265 O,0,-1.9785775296,3.3861805751,-0.1594818234 H,0,0.6997476187,1.0772789534,-1.2792452288
b1	hydroxyimino	N,0,3.3696641582,0.5759102043,2.6675834708 C,0,2.9238266864,1.8151749956,2.9232030083 H,0,3.2644161951,2.2687692978,3.8497047196 C,0,2.0712230202,2.5026724885,2.0695190396 H,0,1.7307378564,3.5020938347,2.3214591829 C,0,1.6370488126,1.9055154622,0.8799289439 C,0,2.9622327017,-0.0082973844,1.541018776 H,0,3.322147388,-1.0134408233,1.3374216352 C,0,2.101360445,0.5955484514,0.6120376313 O,0,1.745610508,-0.0687696253,-0.4959888734 C,0,0.750149759,2.5984979406,-0.0527058745 H,0,0.4193379091,3.6045858594,0.2121661325 N,0,0.3760698834,2.0247492652,-1.1392735015 C,0,-0.5553996393,2.6939100358,-2.0078229972 H,0,-0.1868954359,3.6895778243,-2.2890394294 H,0,-0.6951353607,2.1103005797,-2.9158823166 C,0,-2.0069855295,2.9913382396,-1.3637316429 O,0,-2.9031723289,3.0555149782,-2.2237214938 O,0,-2.0209793006,3.1745330358,-0.1338156739 H,0,1.1246723912,0.5555085741,-1.000893591

Table S1 (continued)

reaction	tautomeric state	
b2 [b]	oxoenamino	N,0,3.3664942173,0.6217487109,2.5427039893 H,0,3.9948860463,0.1402719424,3.1534581224 C,0,3.475224152,1.9699902987,2.4706313785 H,0,4.2297505945,2.4334994774,3.0692410034 C,0,2.6197982085,2.6215651447,1.6308640373 H,0,2.6940018701,3.6898114833,1.5431322212 C,0,1.6719208467,1.9294583469,0.8785807416 C,0,2.5094724976,-0.0993743127,1.8728501096 H,0,2.5221174369,-1.1632975463,2.009441439 C,0,1.5654296756,0.5033919323,0.9549014059 O,0,0.7761105682,-0.1886362767,0.3302485644 C,0,0.8221582604,2.6900327411,-0.0190700702 H,0,0.9215273699,3.7569385978,-0.0394283394 N,0,-0.0257414139,2.1660562827,-0.8077663674 H,0,-0.087820826,1.163511001,-0.7975749523 C,0,-0.764216148,2.9350572141,-1.8176124208 H,0,-1.2297449091,2.2276527744,-2.4858777499 H,0,-1.5437272125,3.5079925561,-1.32999853 C,0,0.1397735923,3.9333898237,-2.6369508591 O,0,-0.446775038,4.3927846892,-3.5918028854 O,0,1.2645387812,4.124421879,-2.1823175983
b2	hydroxyimino	N,0,3.3784924295,0.6105182438,2.4817657698 H,0,4.0221067071,0.0991158757,3.0472529678 C,0,3.4281854457,1.9407387348,2.4956604381 H,0,4.1674565897,2.3971597226,3.1230259326 C,0,2.5522142321,2.6452632441,1.71560515 H,0,2.5955731883,3.717308513,1.7078783278 C,0,1.6228145538,1.9836489244,0.9184084693 C,0,2.5114445685,-0.0820350741,1.7322206241 H,0,2.5535431263,-1.1518634237,1.7791958406 C,0,1.6094679997,0.5707676328,0.9276500944 O,0,0.7840724078,-0.1538974674,0.2083966562 C,0,0.719149358,2.7606906381,0.0533077006 H,0,0.8084937247,3.8338789132,0.0964099002 N,0,-0.0430464878,2.1580114598,-0.7365081467 C,0,-0.7606460445,2.9371127245,-1.7170401844 H,0,-1.4191010513,2.2931915749,-2.2772911805 H,0,-1.3541772051,3.7079697091,-1.2307546569 C,0,0.2135854706,3.7083843982,-2.713150228 O,0,-0.3188420796,3.9697751256,-3.7716039731 O,0,1.3235478542,3.9677516932,-2.2610457903 H,0,0.2676925814,0.4373704765,-0.3576620761

[b] Calculated using the HF/6-311+G(d,p) method

Table S1 (continued)

reaction	tautomeric state	
c1 [a]	oxoenamino	C,0,-5.0656338407,-0.321110353,-0.2811825559 O,0,-6.3668893501,-0.4833563427,-0.7001549312 H,0,-6.808559806,0.369812227,-0.6449371768 C,0,-4.2198284075,-1.4343916286,-0.3134096772 O,0,-4.7404344363,-2.6267414299,-0.7605336611 H,0,-4.0404736797,-3.2871649247,-0.7446183372 C,0,-4.559916999,0.8947644823,0.1716804971 H,0,-5.2175439446,1.7609526744,0.1940463785 C,0,-2.897960133,-1.3012952907,0.1057027835 H,0,-2.2542680653,-2.1784081632,0.0777200061 C,0,-3.2367131217,1.0226184568,0.5900768854 H,0,-2.8445797475,1.9761747626,0.9237129154 C,0,-2.3813121842,-0.0827148884,0.5617970058 C,0,-0.9348819836,0.0179406289,0.999167902 H,0,-0.871613114,0.5656389651,1.9425178654 H,0,-0.5557677148,-0.9962591527,1.1676719616 N,0,1.3375628072,0.202333521,0.1141371585 H,0,1.5424425059,-0.5836798277,0.7580389739 C,0,-0.0285472661,0.7384399778,-0.0154682377 H,0,-0.3689309106,0.5259789164,-1.0340598052 C,0,-0.0214113787,2.3362910662,0.1117060102 O,0,-0.7035815073,2.8135948362,1.0353329504 O,0,0.6734004835,2.8962417448,-0.7630435036 C,0,2.3937201078,0.6116210315,-0.5408558065 H,0,2.2439067571,1.4539594264,-1.2114907114 C,0,3.6683434127,0.0037737227,-0.3712631548 C,0,3.8412377727,-1.1226671102,0.5224846877 O,0,2.9023543619,-1.6195159191,1.2127482642 C,0,5.1901436064,-1.6531388352,0.5652553069 H,0,5.3609120646,-2.5038926426,1.2227861154 C,0,4.7889390744,0.4799334017,-1.0915671562 H,0,4.6718894227,1.3289104468,-1.7593874727 C,0,6.0149541534,-0.1225436757,-0.9429826582 H,0,6.8870919642,0.2299122847,-1.483567888 N,0,6.2107116278,-1.1881475859,-0.1163405505

Table S1 (continued)

reaction	tautomeric state	
c1 [a]	hydroxyimino	C,0,-5.0796772793,-0.3001180738,-0.2804106651 O,0,-6.3801910776,-0.4589935886,-0.7082786485 H,0,-6.7939552437,0.4094013599,-0.7322475481 C,0,-4.2675083493,-1.4346644773,-0.2002673684 O,0,-4.8147479189,-2.6486163265,-0.5530178776 H,0,-4.1294647276,-3.3197226863,-0.4746409898 C,0,-4.5437676054,0.9356212378,0.0742926213 H,0,-5.1751863923,1.8192001782,0.0080836075 C,0,-2.9491296572,-1.3031910555,0.2313648392 H,0,-2.3316749024,-2.1977770585,0.2910433751 C,0,-3.2243425972,1.0614176834,0.5044298488 H,0,-2.8075018406,2.0285896008,0.7598749753 C,0,-2.4007517347,-0.0660662339,0.5907026692 C,0,-0.959105487,0.0306651088,1.0425527781 H,0,-0.8929288639,0.657341867,1.9354434818 H,0,-0.6057169576,-0.9723472961,1.3033565907 N,0,1.3367236047,0.1425966048,0.2093712872 H,0,2.2884998997,-0.4590802559,1.4678479349 C,0,-0.005690265,0.6257772424,-0.0117093652 H,0,-0.3422138846,0.3542616723,-1.0205467922 C,0,0.0227531026,2.2564054917,-0.0306531681 O,0,-0.662509727,2.8139554572,0.845402125 O,0,0.7226664097,2.7167491241,-0.9482116911 C,0,2.2023098181,0.2145916805,-0.736415358 H,0,1.9388963799,0.6016132763,-1.7232270127 C,0,3.5850986341,-0.2016572274,-0.5140934837 C,0,4.0126780213,-0.6991119136,0.7393478107 O,0,3.1796124139,-0.807123858,1.7846715098 C,0,5.3518591806,-1.0933517102,0.8779455223 H,0,5.6827240878,-1.4765109612,1.8396201862 C,0,4.5450501009,-0.1345685477,-1.5318973337 H,0,4.2644650043,0.2498193173,-2.5073991607 C,0,5.8474200117,-0.5492266869,-1.2888611569 H,0,6.5999751466,-0.4986859293,-2.0705041895 N,0,6.2522218504,-1.0258558858,-0.101882293

Table S1 (continued)

reaction	tautomeric state	
c2 [b]	oxoenamino	C,0,-2.6956818756,-4.1950866282,-4.546769881 O,0,-3.8912924709,-3.6180174031,-4.3038801269 H,0,-3.8818906144,-2.7264168657,-4.6100718435 C,0,-1.6719324614,-3.4929782644,-5.1614046849 O,0,-1.9440107969,-2.2040714061,-5.5053888967 H,0,-1.1510043777,-1.7199627623,-5.6559908132 C,0,-2.4797784332,-5.509171926,-4.1797007841 H,0,-3.2812778339,-6.0500712379,-3.7104076719 C,0,-0.4573221501,-4.101315133,-5.4102858062 H,0,0.3105065836,-3.5338559231,-5.9103565055 C,0,-1.254223671,-6.1105509658,-4.411672777 H,0,-1.1079498902,-7.1351390666,-4.1173762871 C,0,-0.2202632822,-5.4150059815,-5.024939104 C,0,1.1358542491,-6.0549455917,-5.240782069 H,0,1.0315868791,-7.0918192211,-5.5236895063 H,0,1.6556250593,-5.5614945139,-6.057939485 N,0,2.3007206142,-4.6524873589,-3.5961977964 H,0,1.8712301556,-3.8976336405,-4.1005309705 C,0,2.0379387303,-6.0464911775,-4.0028665032 H,0,1.5257295897,-6.5322945403,-3.1797630256 C,0,3.3848359333,-6.8482835464,-4.2343953072 O,0,4.4129513942,-6.2782767367,-3.8795515194 O,0,3.1897135141,-7.9487574584,-4.7054982193 C,0,3.1549723742,-4.3260132473,-2.7166315144 H,0,3.6290859592,-5.1121571924,-2.1645901999 C,0,3.5368099122,-2.9530464206,-2.4271571546 C,0,2.9428892507,-1.8565345856,-3.1318473629 O,0,2.0744998389,-1.94236725,-3.9900828126 C,0,3.4668717894,-0.5671438479,-2.7408943145 H,0,3.0962045959,0.3271453787,-3.2027790895 C,0,4.530824348,-2.7408163335,-1.4744953588 H,0,4.976666505,-3.5797124986,-0.9728515627 C,0,4.9690868469,-1.484230024,-1.1698374337 H,0,5.7302108344,-1.249610524,-0.4568762889 N,0,4.3998188091,-0.4526803752,-1.8332282752 H,0,4.7199940912,0.4692942694,-1.6162690487

Table S1 (continued)

reaction	tautomeric state	
c2 [b]	hydroxyimino	C,0,-2.6716649163,-4.1426987323,-4.3560398265 O,0,-3.8599055837,-3.5779071707,-4.0429666875 H,0,-3.9938257867,-2.8091000911,-4.5714551961 C,0,-1.8120140611,-3.5509084518,-5.2646996448 O,0,-2.2334030608,-2.3754955625,-5.8139946955 H,0,-1.7203232538,-2.150091803,-6.5691101647 C,0,-2.3006501567,-5.3361623731,-3.7680350463 H,0,-2.9786920691,-5.7994598179,-3.0742519522 C,0,-0.5988952657,-4.1395293632,-5.5708108352 H,0,0.0487018279,-3.6572666992,-6.2853724894 C,0,-1.0874881515,-5.9257833372,-4.0800512809 H,0,-0.8288599749,-6.8626863997,-3.6184402187 C,0,-0.2110108554,-5.3374647379,-4.9845137948 C,0,1.1250014457,-5.9714982227,-5.3167521887 H,0,0.9930252857,-7.0081249006,-5.5939571029 H,0,1.5612519282,-5.4820082227,-6.1812532893 N,0,2.408347991,-4.5737604493,-3.7703800152 C,0,2.1325839609,-5.9341254013,-4.1703683742 H,0,1.740011597,-6.4831248085,-3.3159125836 C,0,3.5145139513,-6.6768263279,-4.5109087047 O,0,4.4498124134,-6.3465751138,-3.7913652522 O,0,3.4241242973,-7.4990919616,-5.3988895228 C,0,2.99817249,-4.3772518915,-2.6850615654 H,0,3.2433164666,-5.161896398,-1.9875890334 C,0,3.4648075247,-3.0213055674,-2.3503650637 C,0,3.1961866793,-1.9150063734,-3.1871959444 O,0,2.4995893737,-1.9942604341,-4.2974221279 C,0,3.6916107974,-0.6875852491,-2.8202089859 H,0,3.5232503604,0.188676031,-3.4137366194 C,0,4.223800208,-2.8173746974,-1.2017929764 H,0,4.4568339797,-3.6459444031,-0.5612212771 C,0,4.6938591119,-1.5710162293,-0.8891423139 H,0,5.28667971,-1.3578951422,-0.0222104123 N,0,4.4128763215,-0.5534229754,-1.6999568305 H,0,4.7596384926,0.3538237587,-1.4714621567 H,0,2.2667412724,-2.9204858293,-4.4494674575

Table S1 (continued)

reaction	tautomeric state	
d1 [c]	oxoenamino	C,0,3.6469094129,1.0276854343,1.9170703877 O,0,4.4673830565,0.5522287872,2.9036811723 H,0,4.5080127981,-0.3902802458,2.7676201237 C,0,3.1331366634,0.1189055978,0.9875785488 O,0,3.4857945678,-1.1502789157,1.1446528635 H,0,3.0830830263,-1.7729801784,0.4141103129 C,0,3.3328206602,2.3666630067,1.8383565503 H,0,3.7432268237,3.0451349401,2.5686777457 C,0,2.3010357495,0.591776522,-0.0220612188 H,0,1.9223385064,-0.12854312,-0.7222183127 C,0,2.4924117706,2.8270365891,0.8266669872 H,0,2.2517116395,3.8762781383,0.7728842596 C,0,1.9650148824,1.9404303865,-0.1072382042 C,0,1.0549392602,2.4365937125,-1.2197206145 H,0,1.5211977532,3.279658223,-1.7164374715 H,0,0.9402842735,1.6654204316,-1.9735824097 N,0,-1.205165994,1.9195033707,-0.2161648337 H,0,-1.9518877298,2.2434152953,0.3758800123 C,0,-0.3235488473,2.9501560745,-0.7721309386 H,0,-0.171190649,3.650131767,0.0383820587 C,0,-0.9961510646,3.7567368369,-1.9332511489 O,0,-0.5569096382,4.9118006949,-2.0393699037 O,0,-1.8392460453,3.1761840848,-2.6118930988 C,0,-1.2283960005,0.6493154292,-0.4291564427 H,0,-0.4762128155,0.225834008,-1.0637903209 C,0,-2.1882126462,-0.2404880299,0.15699243 C,0,-3.1885251262,0.2667779087,1.0382937554 O,0,-3.3122877009,1.4667015368,1.3733019624 C,0,-5.2087195067,-0.236072128,2.4883033353 H,0,-5.8244671049,-1.0757012568,2.7942530527 H,0,-4.7867438575,0.2423963034,3.3686642826 H,0,-5.8303210587,0.5112897494,2.001203198 C,0,-4.1227243432,-0.7245280072,1.5650278896 C,0,-2.1381741007,-1.6407989774,-0.1266087781 P,0,1.3324252482,-3.2123328553,-1.178767107 O,0,1.179420491,-3.2874460606,-2.6718666056 O,0,2.6164061511,-2.51913389,-0.7188379667 O,0,0.9710528159,-4.4509921204,-0.410086526 O,0,0.1746404622,-2.0419387643,-0.695207009 C,0,-3.0783737468,-2.4404197866,0.454153261 H,0,-3.0723549511,-3.5018243185,0.2908641764 N,0,-4.0548100054,-1.9785687663,1.2810624281 C,0,-1.1344299628,-2.275024438,-1.0816110696 H,0,-1.3419863799,-3.3375908889,-1.1164160586 H,0,-1.3067453351,-1.884583729,-2.0855504136

[c] Calculated using the HF/6-31+G(d) method

Table S1 (continued)

reaction	tautomeric state	
d1 [c]	hydroxyimino	C,0,3.9079854051,0.6662247725,1.717853096 O,0,4.747819366,0.0958549779,2.6368964037 H,0,4.6572828473,-0.8447285646,2.5121868637 C,0,3.1921493998,-0.1760590922,0.8616543099 O,0,3.3937297938,-1.479221137,1.0282331032 H,0,2.8923994805,-2.0762275236,0.353547807 C,0,3.769589185,2.033369308,1.634234056 H,0,4.3340356737,2.6602923107,2.3057336305 C,0,2.3380335732,0.3892130567,-0.0790752757 H,0,1.7953410484,-0.2811950239,-0.7189629204 C,0,2.9072060217,2.588199615,0.6903463472 H,0,2.8019130852,3.6593004144,0.6323531537 C,0,2.1795924095,1.7725177864,-0.1707503126 C,0,1.2437309895,2.3918202476,-1.1985996971 H,0,1.7616414804,3.2105621104,-1.6896877532 H,0,1.01415045,1.6724452676,-1.9755188701 N,0,-1.0381980871,2.0770813105,-0.0827157825 H,0,-2.4313520277,2.23062781,1.0117549907 C,0,-0.0544306897,3.0039243338,-0.6249792322 H,0,0.2240524437,3.6411576629,0.2033933321 C,0,-0.6934142854,3.9487601833,-1.6991747048 O,0,-0.3310356338,5.1338752538,-1.6157400875 O,0,-1.4394268911,3.4293704276,-2.5299164446 C,0,-1.1437456715,0.8765720536,-0.4375421381 H,0,-0.49496432,0.4116780845,-1.157883128 C,0,-2.1928871473,-0.0079330544,0.1435301112 C,0,-3.1374108622,0.4896896687,1.0449648656 O,0,-3.1648754553,1.7707558187,1.4490374772 C,0,-5.1430691729,0.181611189,2.5300071056 H,0,-4.6717458696,0.5858233219,3.4223171399 H,0,-5.7183051739,0.990471786,2.086344686 H,0,-5.8159342277,-0.6191143735,2.8160865858 C,0,-4.1176683718,-0.3581686746,1.5648837615 C,0,-2.2667349759,-1.3683405042,-0.1949351342 P,0,0.938277887,-3.4076791609,-1.1527651775 O,0,0.7855370038,-3.519324645,-2.6446807229 O,0,2.3070113872,-2.911775391,-0.6930299295 O,0,0.3657049909,-4.5411906508,-0.3475777962 O,0,-0.0251591935,-2.0505659048,-0.7333594159 C,0,-3.2734668337,-2.1171696932,0.3951553585 H,0,-3.3436780829,-3.1681051457,0.1794833965 N,0,-4.1743867767,-1.6333002515,1.2404823739 C,0,-1.330664113,-2.0547498938,-1.1830026456 H,0,-1.6914350245,-3.0665481245,-1.3266350675 H,0,-1.4028174523,-1.5563633262,-2.1499361134

Table S1 (continued)

reaction	tautomeric state	
d2 [b]	oxoenamino	C,0,-2.8883351436,2.4338486827,1.5896969964 O,0,-2.8912064442,3.4851698843,2.4531120135 H,0,-2.1306333847,4.0052282359,2.2371953844 C,0,-1.8691117165,2.3602335741,0.632338793 O,0,-0.9799133998,3.33806169,0.6563869668 H,0,-0.224555997,3.2510205723,-0.0325695829 C,0,-3.86283556,1.4676167046,1.6519859437 H,0,-4.6364421685,1.5538095167,2.3961601217 C,0,-1.8628199977,1.2917521787,-0.2540042973 H,0,-1.0756154352,1.2568392422,-0.9857907704 C,0,-3.8423879063,0.3967106587,0.7616139671 H,0,-4.6126026137,-0.3546775065,0.8177303895 C,0,-2.8417561652,0.2997425619,-0.1925957586 C,0,-2.7983681099,-0.8750665741,-1.1525288629 H,0,-3.787993392,-1.0814252664,-1.543406961 H,0,-2.1770626437,-0.6252331784,-2.0059001731 N,0,-0.9912954961,-2.0773236896,0.0883456041 H,0,-0.8535710154,-2.4202519558,1.0245228583 C,0,-2.3145746074,-2.2028218882,-0.5365982405 H,0,-2.9819602207,-2.4828554804,0.2651184283 C,0,-2.3364410086,-3.3384388659,-1.61771435 O,0,-1.2720793838,-3.5571911555,-2.1852494667 O,0,-3.4455804822,-3.8366347913,-1.7749983372 C,0,0.049027601,-1.6288026488,-0.4833375209 H,0,-0.0463411929,-1.268933061,-1.4856256648 C,0,1.3457018732,-1.524405161,0.1775102986 C,0,1.4935647447,-2.0139000058,1.5134607446 O,0,0.6204599054,-2.6308789717,2.1525580399 C,0,3.0112125362,-2.1169835945,3.5445961093 H,0,4.0014307696,-1.8063622305,3.8682937936 H,0,2.269288604,-1.6691753558,4.1969272369 H,0,2.922368086,-3.1928093018,3.6544541514 C,0,2.7480985895,-1.7189104455,2.1277188045 C,0,2.3688460778,-0.8362945864,-0.4813223351 P,0,2.0280752061,2.3974901974,-1.3939486853 O,0,0.7773622676,3.177245098,-1.0601795805 O,0,2.9103423958,2.0596622461,-0.2220335218 O,0,2.7384864996,2.7953798611,-2.6395077629 O,0,1.3268484836,0.8611386661,-1.7742372238 C,0,3.5414520576,-0.6065347366,0.1929243779 H,0,4.3080493438,0.036691079,-0.1786812718 N,0,3.6612133431,-1.047276124,1.4481554111 H,0,4.4944859861,-0.7897543362,1.9319183843 C,0,2.1943867434,-0.1988809044,-1.8560502398 H,0,3.1704571058,0.1015805587,-2.2252671848 H,0,1.8052039981,-0.9396035034,-2.5522590278

Table S1 (continued)

reaction	tautomeric state	
d2 [b]	hydroxyimino	C,0,-1.1898532853,3.5709495045,0.8049016684 O,0,-0.6141733317,4.6047772779,1.4783178482 H,0,0.3163232661,4.5346513497,1.3225205451 C,0,-0.3646806677,2.7002154261,0.0839267883 O,0,0.936093876,2.9682519904,0.1302549807 H,0,1.5472789373,2.2171026023,-0.1587029864 C,0,-2.5498475974,3.3817237157,0.8313742647 H,0,-3.1618307982,4.0685741056,1.3913408517 C,0,-0.9467909541,1.6545832011,-0.6146063638 H,0,-0.2993495074,1.0140126762,-1.1859363111 C,0,-3.1190538788,2.3088980132,0.148128142 H,0,-4.1854391869,2.161447892,0.1876861907 C,0,-2.3260548567,1.4315036992,-0.572875267 C,0,-2.9376581258,0.2275646449,-1.2706300807 H,0,-3.8929439375,0.493225681,-1.7086776104 H,0,-2.2932788064,-0.0834291089,-2.0862431198 N,0,-2.0134903847,-1.3278814791,0.4256939262 H,0,-1.5681016253,-1.4332078845,2.0993870186 C,0,-3.2058453548,-0.982636864,-0.3386317956 H,0,-3.9514503925,-0.6852552686,0.3859735904 C,0,-3.8200389043,-2.1660130712,-1.1651869723 O,0,-3.0448497341,-3.0380118404,-1.5464778462 O,0,-5.0289400985,-2.048902967,-1.3549732052 C,0,-0.9521886005,-1.6351580369,-0.159344444 H,0,-0.880333105,-1.7353237823,-1.2255403382 C,0,0.3141328646,-1.7344557394,0.6153921767 C,0,0.288564107,-1.5930517776,2.0318153821 O,0,-0.8453420833,-1.5657392188,2.7309246011 C,0,1.5137311632,-1.2243207816,4.2025816556 H,0,2.482801512,-0.8329254068,4.4976088862 H,0,0.7496679821,-0.5174234073,4.4978320299 H,0,1.3355537528,-2.1500835993,4.743207535 C,0,1.4555498065,-1.4445717711,2.7206643662 C,0,1.530765699,-1.7972819477,-0.0391098389 P,0,3.0560928195,0.4558962155,-1.6809383546 O,0,2.4881205195,1.0675924997,-0.3978635795 O,0,4.1872812228,-0.4945142539,-1.365747008 O,0,3.193196568,1.3710219882,-2.8312158946 O,0,1.7902911858,-0.6091666931,-2.1269546379 C,0,2.6864649558,-1.6300375516,0.7144804658 H,0,3.6410358533,-1.5123230968,0.2244111493 N,0,2.6109687919,-1.4724140439,2.0196401398 H,0,3.4565172255,-1.2578007962,2.5000779798 C,0,1.7282767191,-1.8585002931,-1.5569591405 H,0,2.6450139067,-2.4128397437,-1.7364380492 H,0,0.9144400997,-2.4098208204,-2.0127589508

Table S2. Calculated Energies for Intramolecular Proton Transfer Reaction in Reactions **a**–**d** in the Gas Phase at 298.15 K [a,b]

Oxoenamino (keto) → hydroxyimino (enol)							
	ΔE_{elec} [b]	ΔE_T	$T\Delta S$	ΔG_{gas} [h]	ΔG_s (keto) [h]	ΔG_s (enol) [h]	ΔG_{PCM} [i]
a1 [c]	–4.9	0.1 [f]	–0.4	–4.4	–13.2	–8.1	0.7
a2 [c]	–0.6	0.7 [f]	–0.3	0.4	–59.1	–57.6	1.9
b1 [c]	2.7	–0.6 [f]	–0.2	2.3	–59.7	–59.7	2.3
b2 [d]	7.7	–0.5 [g]	–0.2	7.4	–42.6	–46.4	3.6
c1 [c]	0.9	–0.4 [f]	–0.4	0.9	–69.3	–69.5	0.7
c2 [d]	7.9	–0.7 [g]	0.2	7.0	–49.7	–55.3	1.4
d1 [e]	5.4	–0.1 [g]	0.3	5.0	–310.2	–311.9	3.4
d2 [d]	7.0	0.1 [g]	0.0	7.1	–179.0	–176.7	9.4

[a] All energies are reported to 1 decimal place in kcal/mol. [b] Single-point B3LYP/6-311+G(d,p) energy. [c] Geometries optimized at the B3LYP/6-311+G(d,p) level. [d] Geometries optimized at the HF/6-311+G(d,p) level. [e] Geometries optimized at the HF/6-31+G(d) level. [f] The frequencies were scaled by an empirical factor of 0.9613 (*1*). [g] The frequencies were scaled by an empirical factor of 0.8929 (*1*). [h] Gas-phase free energy of tautomerization reaction, ΔG_{gas}, was computed according to $\Delta G_{gas} = \Delta E_{elec} + \Delta E_T - T\Delta S$, where ΔE_{elec}, ΔE_T, and ΔS are the differences in the electronic energy, thermal energy, and entropy between the hydroxyimino conformation and oxoenamino isomer, respectively. Note that the thermal energy includes the zero-point energy (*2*). [h] Solvation free energies in aqueous solution were calculated at the B3LYP/6-311+G(d,p) level. [i] Solution free energies were computed according to $\Delta G_{PCM} = \Delta G_{gas} + \Delta G_s(\text{enol}) - \Delta G_s(\text{keto})$.

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