Supporting Information

Ultrafast Excited-State Dynamics of Hydrogen-Bonded Cytosine Microsolvated Clusters with Protic and Aprotic Polar Solvents

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S1. Chemical structures and relative energies of low-energy Cy microhydrates.

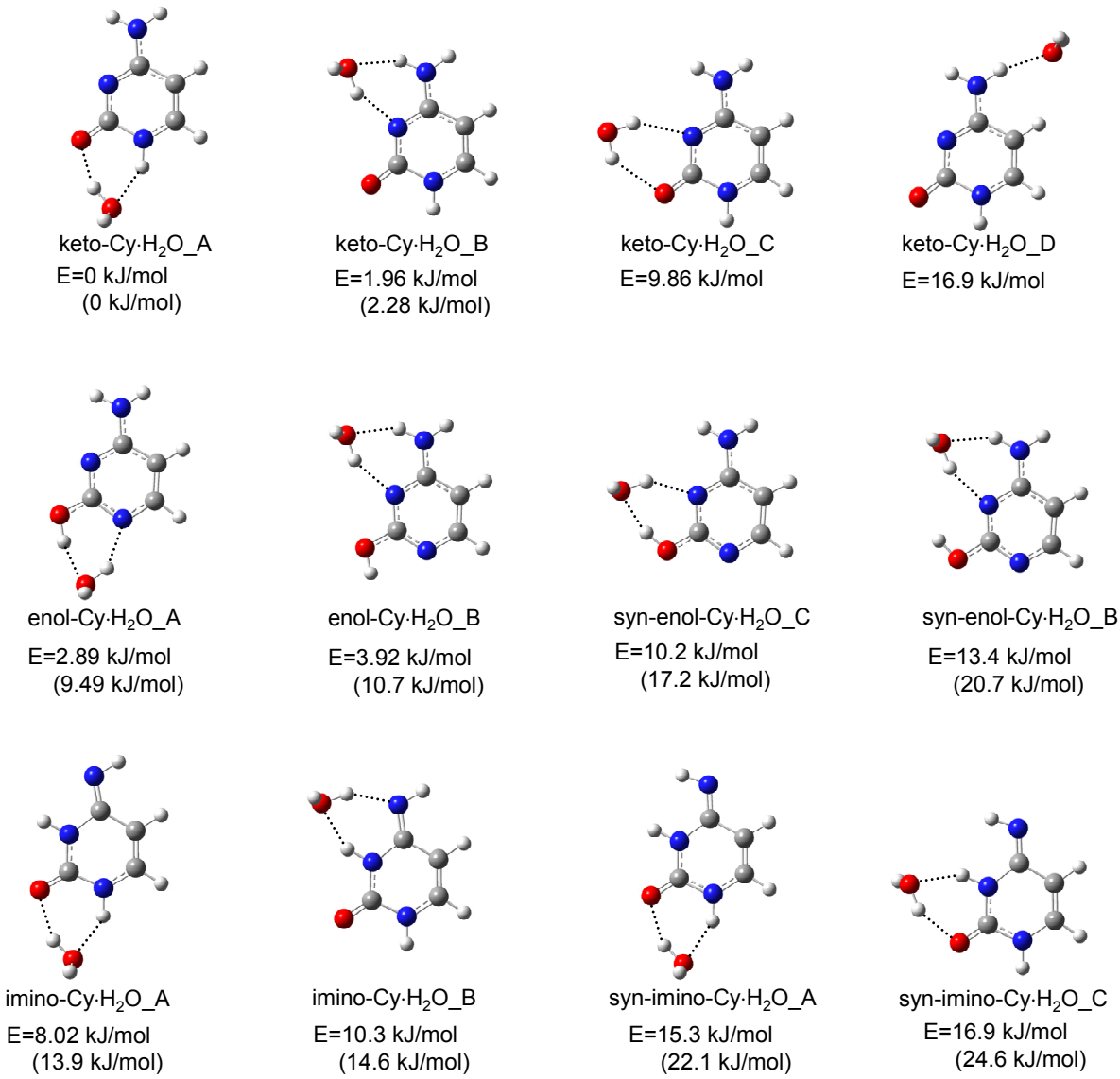


Figure S1. Chemical structures of low-energy Cy monohydrates, Cy·H_2O, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Structures optimized at the wB97XD/aug-cc-pVTZ level of theory are very similar. Zero-point-energy corrected relative energies (E) calculated at G4MP2 and ωB97XD/aug-cc-pVTZ (in parentheses) are also given for each structure.

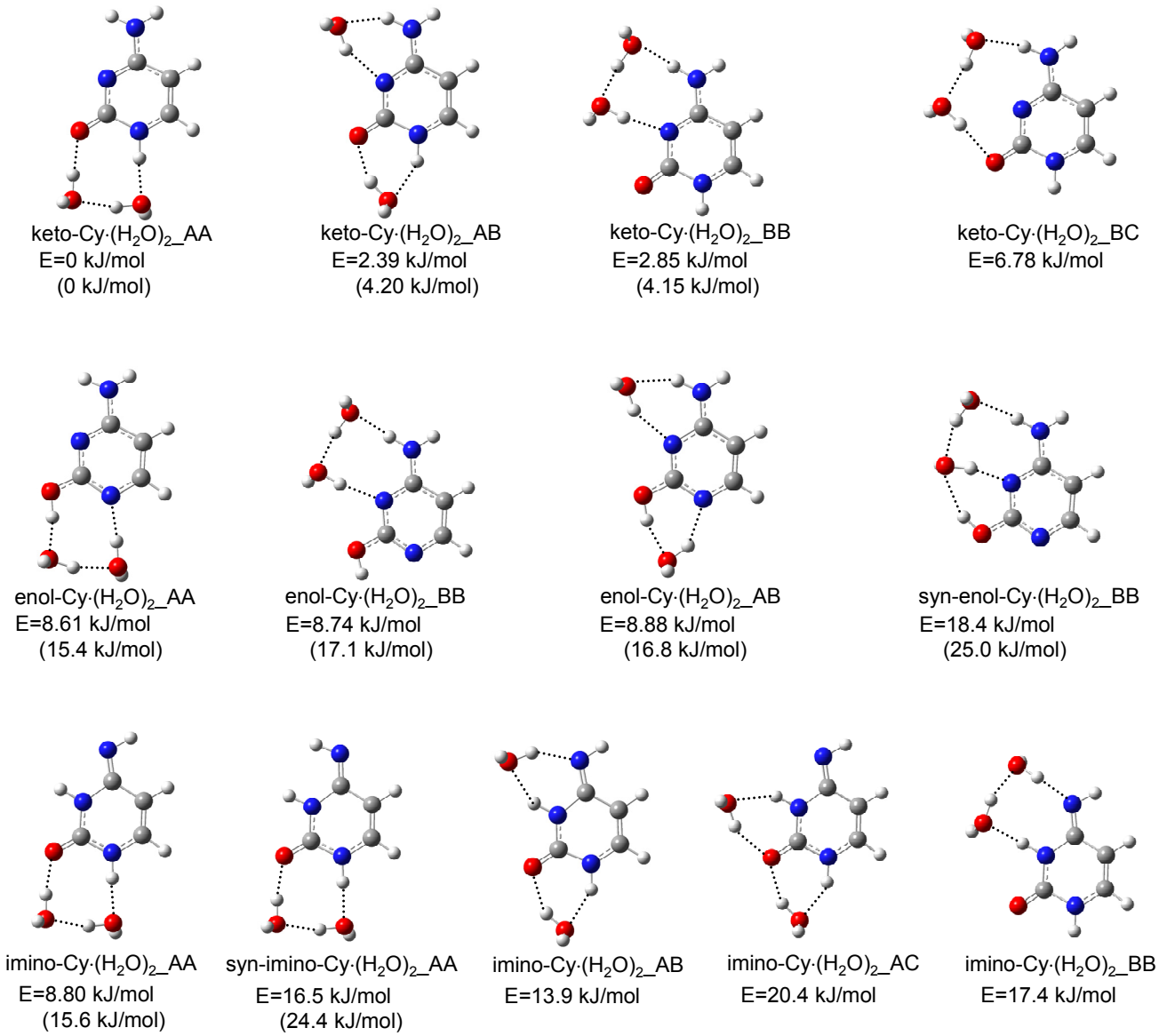


Figure S2. Chemical structures of low-energy isomeric Cy dihydrates, $Cy{\cdot}(H_2O)_2$, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Structures optimized at the ωB97XD/aug-cc-pVTZ level of theory are very similar. Zero-point-energy corrected relative energies (E) calculated at G4MP2 and ωB97XD/aug-cc-pVTZ (in parentheses) are also given for each structure.

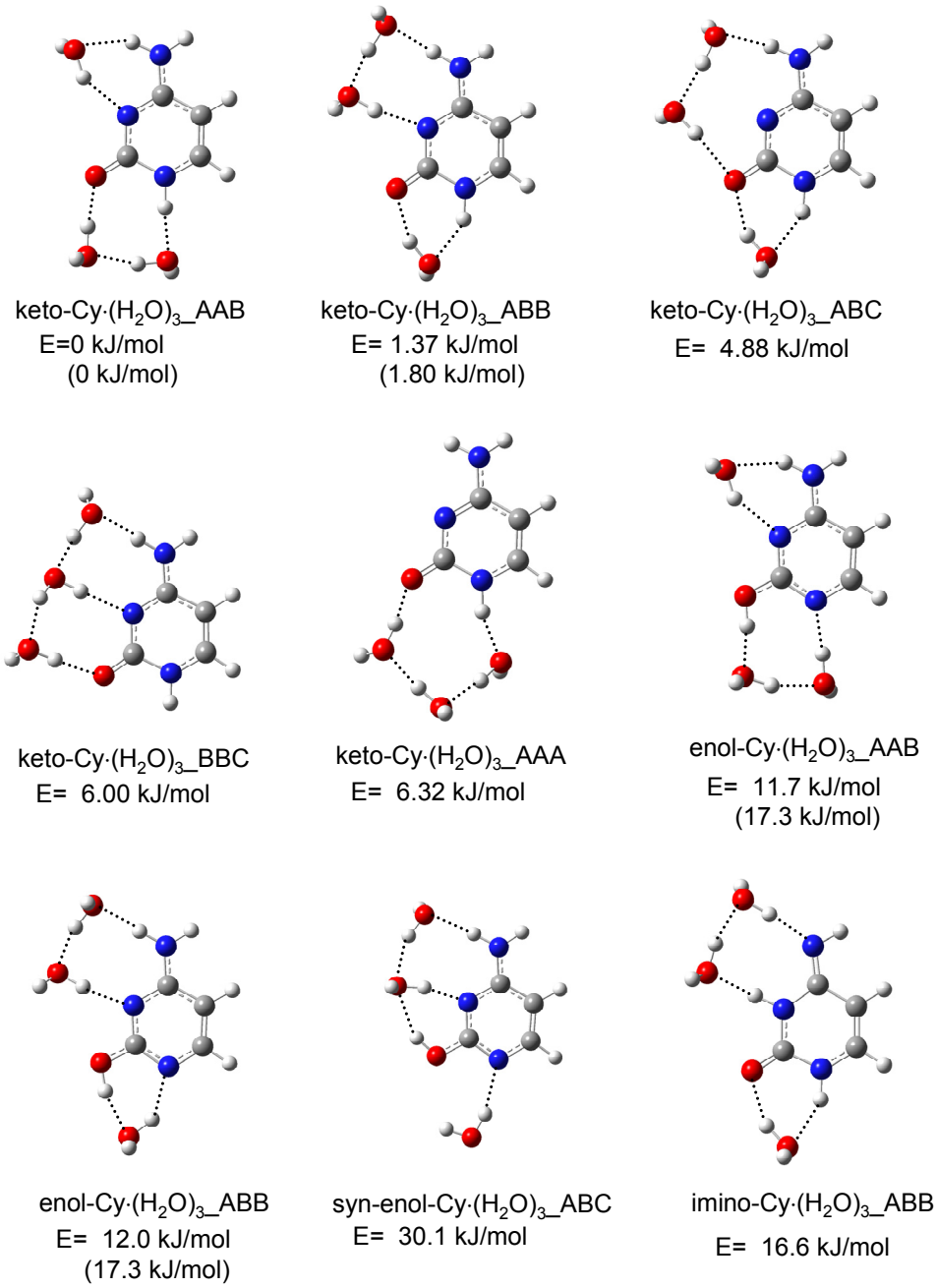
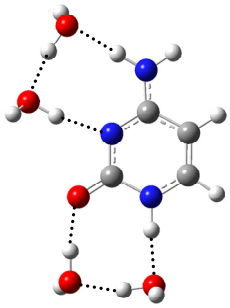
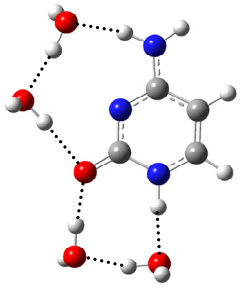


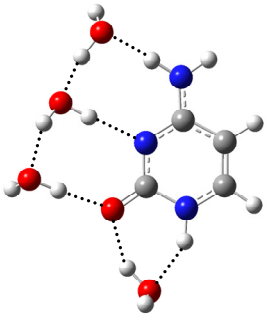
Figure S3. Chemical structures of low-energy isomeric Cy trihydrates, $Cy{\cdot}(H_2O)_3$, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Structures optimized at the wB97XD/aug-cc-pVTZ level of theory are very similar. Zero-point-energy corrected relative energies (E) calculated at G4MP2 and ωB97XD/aug-cc-pVTZ (in parentheses) are also given for each structure.



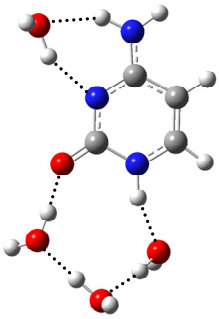
keto-Cy·$(H_2O)_4$_AABB
E=0 kJ/mol



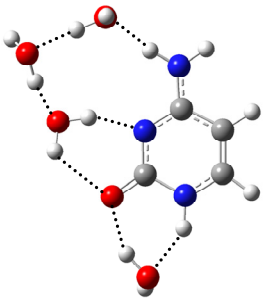
keto-Cy·$(H_2O)_4$_AABC
E=1.39 kJ/mol



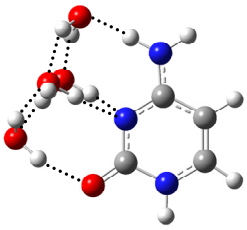
keto-Cy·$(H_2O)_4$_ABBC
E=6.97 kJ/mol



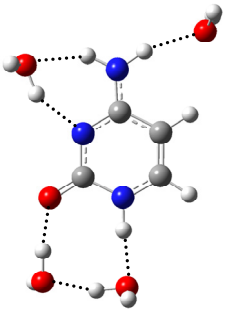
keto-Cy·$(H_2O)_4$_AAAB
E=7.38 kJ/mol



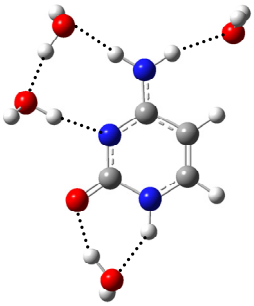
keto-Cy·$(H_2O)_4$_ABBB
E=9.64 kJ/mol



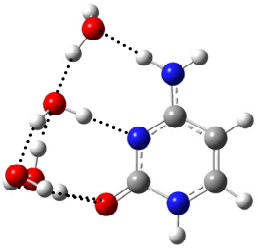
keto-Cy·$(H_2O)_4$_BBCC_cage
E=13.5 kJ/mol



keto-Cy·$(H_2O)_4$_AABD
E=16.6 kJ/mol

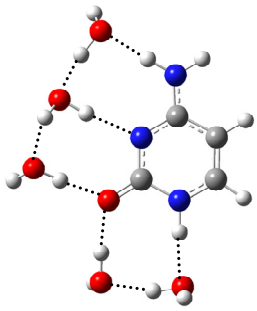


keto-Cy·$(H_2O)_4$_ABBD
E=17.7 kJ/mol

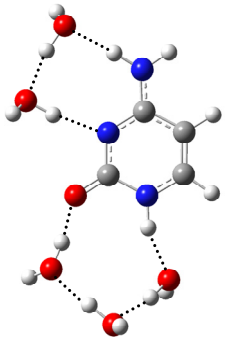


keto-Cy·$(H_2O)_4$_BBCC
E=21.9 kJ/mol

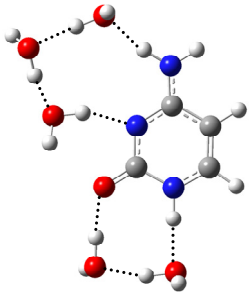
Figure S4. Chemical structures of low-energy isomeric keto-Cy tetrahydrates, keto-Cy·$(H_2O)_4$, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.



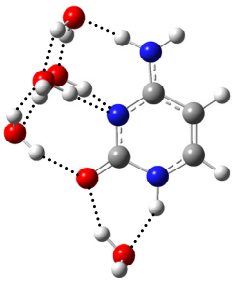
keto-Cy·$(H_2O)_5$_AABBC
E=0 kJ/mol



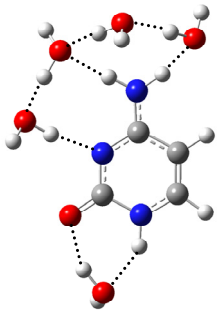
keto-Cy·$(H_2O)_5$_AAABB
E=0.87 kJ/mol



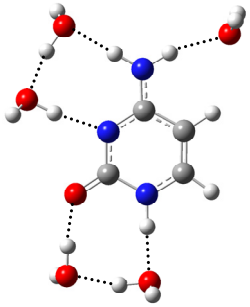
keto-Cy·$(H_2O)_5$_AABBB
E=1.83 kJ/mol



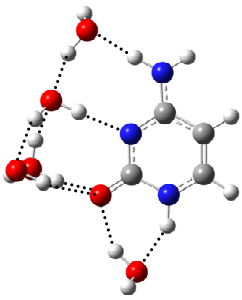
keto-Cy·$(H_2O)_5$_ABBCC_cage
E=5.69 kJ/mol



keto-Cy·$(H_2O)_5$_ABBDD
E=6.71 kJ/mol



keto-Cy·$(H_2O)_5$_AABBD
E=9.79 kJ/mol



keto-Cy·$(H_2O)_5$_ABBCC
E=15.9 kJ/mol

Figure S5. Chemical structures of low-energy isomeric keto-Cy pentahydrates, keto-Cy·$(H_2O)_5$, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.

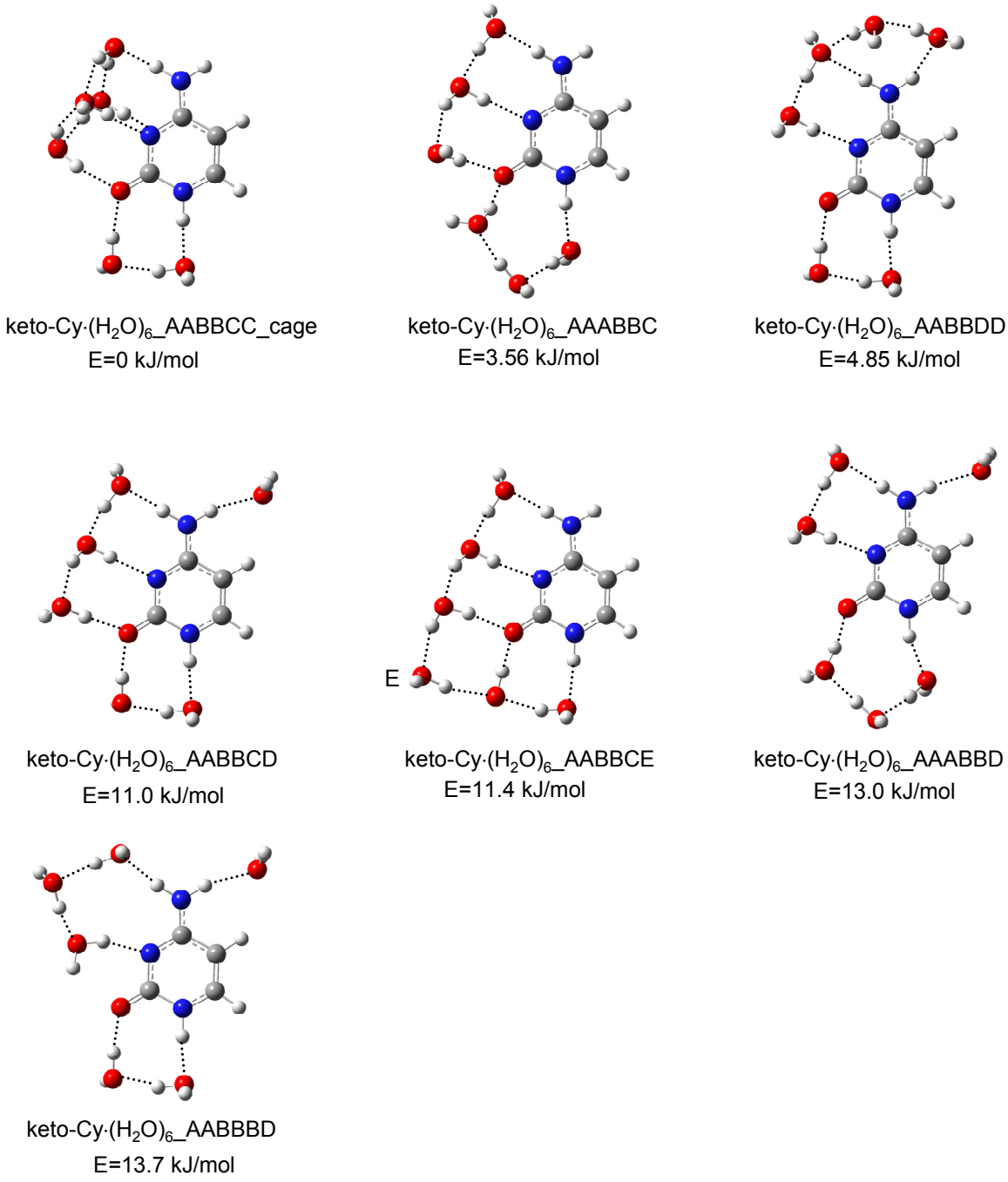


Figure S6. Chemical structures of low-energy isomeric keto-Cy hexahydrates, keto-Cy·$(H_2O)_6$, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.

S2. Chemical structures and relative energies of low-energy 1mCy monohydrates.

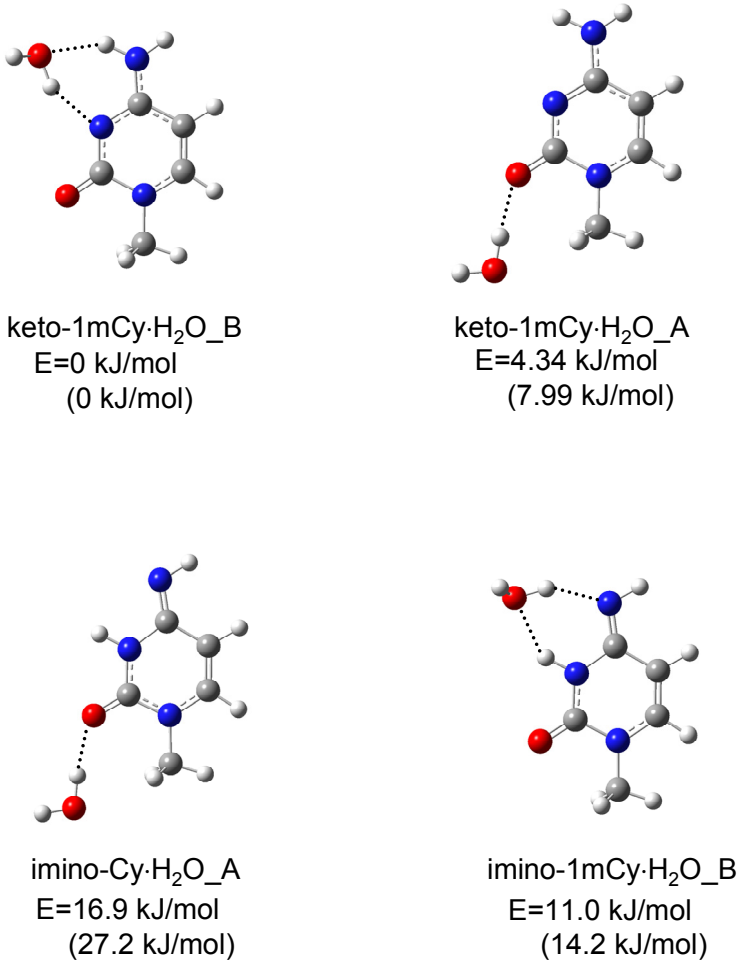


Figure S7. Chemical structures of low-energy isomeric 1mCy monhydrates, 1mCy·H_2O, calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 and ωB97XD/aug-cc-pVTZ (in parentheses) are also given

S3. Chemical structures and relative energies of low-energy Cy microsolvated clusters listed in Table 3.

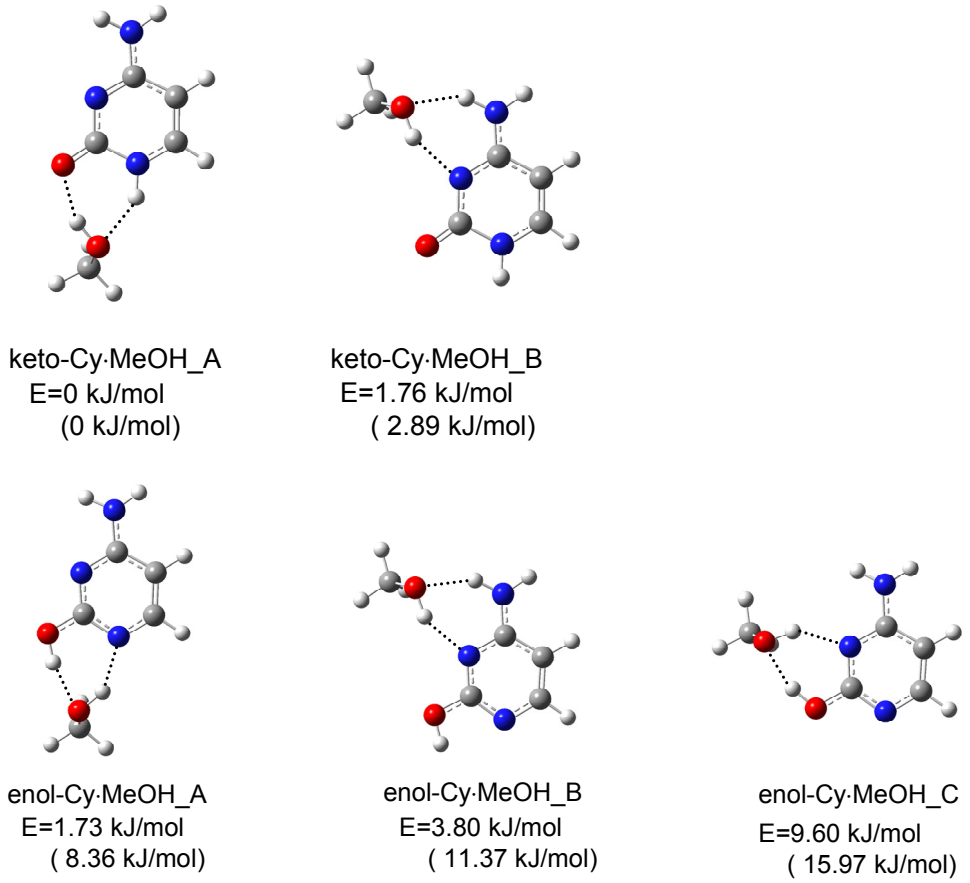


Figure S8. Chemical structures of low-energy isomeric Cy·MeOH microsolvated clusters calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.

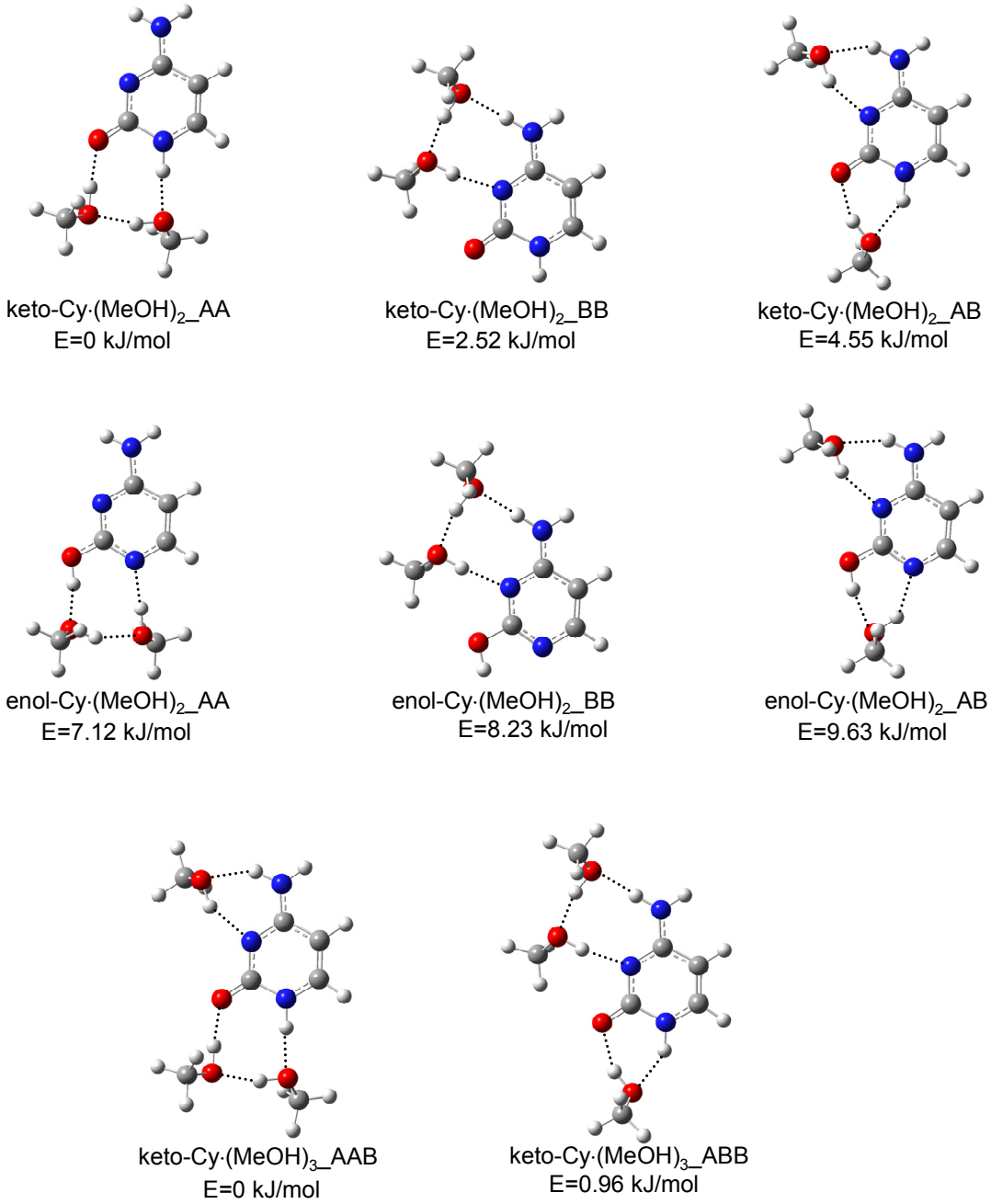


Figure S9. Chemical structures of low-energy isomeric Cy·(MeOH)$_{2,3}$ microsolvated clusters calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.

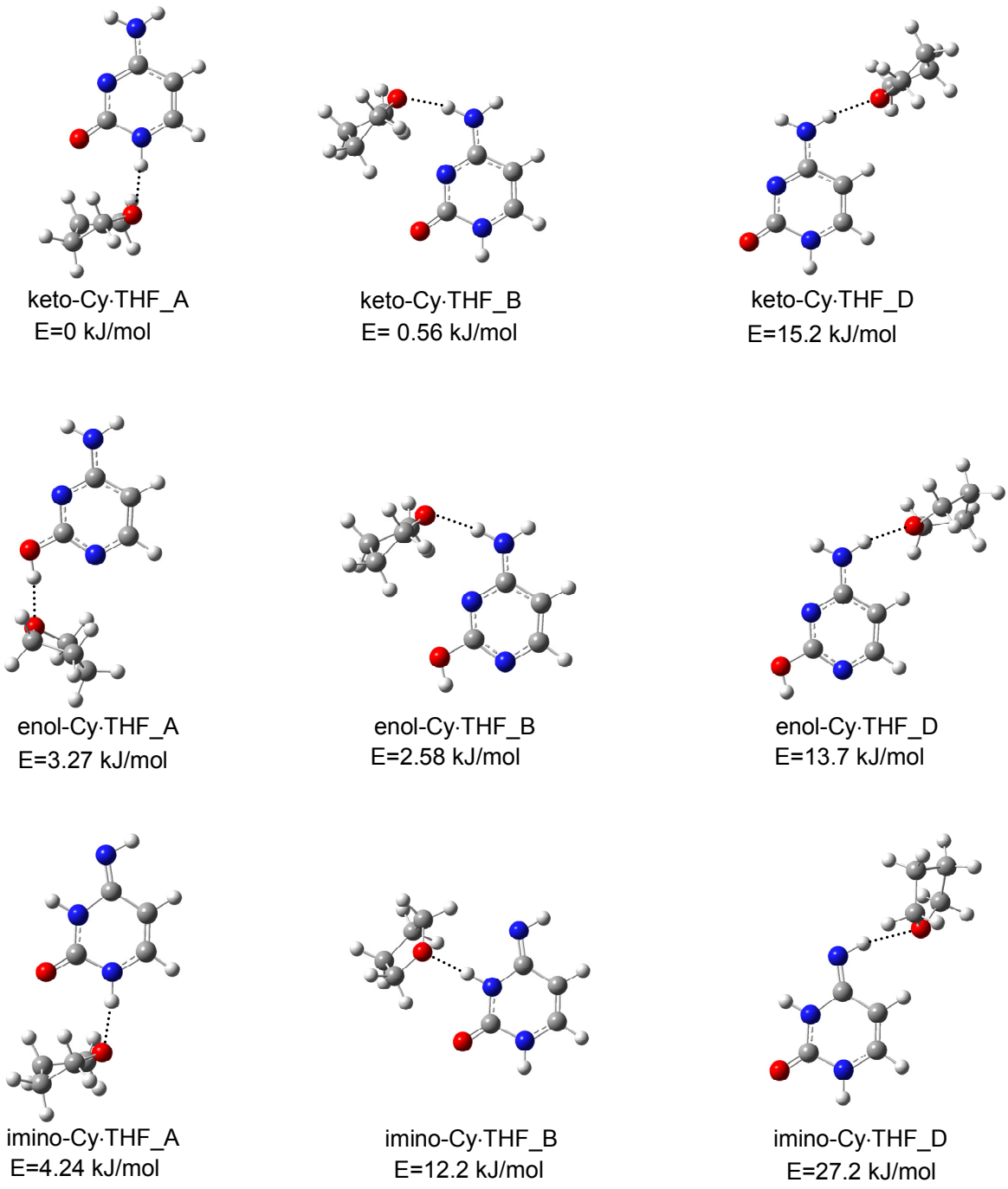


Figure S10. Chemical structures of low-energy isomeric Cy·THF microsolvated clusters calculated at the G4MP2 level of theory. H-bonds are represented as dotted lines. Zero-point-energy corrected relative energies (E) calculated at G4MP2 are also given for each structure.

S4. Cartesian coordinates of the most stable isomers of Cy microhydrates displayed in Figure 4

(1) keto-Cy· H_2O_A

Cartesian coordinates (G4MP2)

	X	Y	Z
N	0.7749200	0.7005870	-0.0132990
C	-0.1946410	1.6366730	-0.0137140
H	0.1318870	2.6707300	-0.0237140
C	-1.5031820	1.2735060	-0.0014210
H	-2.2968930	2.0072940	0.0056670
C	-1.7616310	-0.1363800	0.0109020
N	-3.0457430	-0.5787740	0.0605840
H	-3.1895880	-1.5671630	-0.0694290
H	-3.8081530	0.0427460	-0.1431370
N	-0.8155190	-1.0569090	0.0024430
C	0.4939730	-0.6845380	-0.0109230
O	1.4350120	-1.4756370	-0.0248720
H	1.7731200	0.9341910	-0.0207080
O	3.5444420	0.2580780	-0.0636380
H	3.9459980	0.2266580	0.8104810
H	3.0052750	-0.5638760	-0.1082390

(2) keto-Cy·$(H_2O)_2$_AA

Cartesian coordinates (G4MP2)

	X	Y	Z
N	0.2907624	0.6619871	-0.0242107
C	-0.6658060	1.6058599	0.0907414
H	-0.3162369	2.6309788	0.1455271
C	-1.9799565	1.2656095	0.1351155
H	-2.7584875	2.0088380	0.2353779
C	-2.2617667	-0.1352074	0.0491666
N	-3.5502794	-0.5653878	0.1121599
H	-3.7120802	-1.5388030	-0.0897003
H	-4.3092679	0.0788545	-0.0220471
N	-1.3296735	-1.0631994	-0.0628084
C	-0.0149964	-0.7092108	-0.0926520
O	0.8977755	-1.5308671	-0.1819487
H	1.2831813	0.9484125	-0.0597364

O	3.5361091	-1.1084950	0.1205458
H	3.7098603	-1.4374015	1.0077422
H	2.5878434	-1.3354140	-0.0437096
O	2.9798520	1.5043735	-0.0406394
H	3.3417314	0.5911247	0.0884924
H	3.2689103	1.7447685	-0.9267195

(3) keto-Cy·$(H_2O)_3$_AAB

Cartesian coordinates (G4MP2)

	X	Y	Z
N	0.8637190	-0.8462610	0.0428460
C	0.1825550	-2.0088300	-0.0440460
H	0.7867010	-2.9086800	-0.0788830
C	-1.1737990	-2.0267110	-0.0842460
H	-1.7290980	-2.9517090	-0.1514550
C	-1.8254190	-0.7518700	-0.0320320
N	-3.1688940	-0.6688990	-0.0491580
H	-3.5900580	0.2610080	-0.0587310
H	-3.7304000	-1.4906630	-0.1781140
N	-1.1472990	0.3917450	0.0425780
C	0.2127580	0.3960090	0.0808560
O	0.8722310	1.4340580	0.1474020
H	1.8971240	-0.8629740	0.0754120
O	3.5357110	1.7164170	-0.1504270
H	3.6213990	2.0668610	-1.0422810
H	2.5615240	1.6914780	0.0112280
O	3.6743540	-0.9488110	0.0565030
H	3.7885310	0.0241450	-0.0903900
H	4.0207540	-1.0920870	0.9430580
O	-3.3310000	2.1797050	-0.0509830
H	-2.3998660	1.8686920	-0.0545870
H	-3.4462410	2.5552950	0.8277290

(4) keto-Cy·$(H_2O)_4$_AABB

Cartesian coordinates (G4MP2)

	X	Y	Z
N	1.3714680	-0.9095030	-0.0449980
C	0.8820830	-2.1675120	0.0292770

H	1.6203560	-2.9615410	0.0373470
C	-0.4524530	-2.3981480	0.0865730
H	-0.8527870	-3.4008070	0.1424260
C	-1.3066050	-1.2443430	0.0675390
N	-2.6381600	-1.3944630	0.1127660
H	-3.2759830	-0.5915660	0.0208730
H	-3.0268420	-2.3209030	0.0963000
N	-0.8117650	-0.0077480	0.0126700
C	0.5301730	0.2075540	-0.0518300
O	1.0077200	1.3436320	-0.1195850
H	2.3934440	-0.7608730	-0.0974970
O	3.5967510	2.0472370	0.1614270
H	3.6415220	2.3870970	1.0603450
H	2.6368960	1.8693320	0.0124960
O	4.1594290	-0.5573430	-0.1116620
H	4.1191320	0.4178380	0.0559350
H	4.5061210	-0.6255590	-1.0070250
O	-4.3950510	0.8301200	-0.1990150
H	-3.6961450	1.5286970	-0.2086120
H	-4.8712950	0.9966640	0.6205430
O	-2.2456460	2.4237640	0.0755710
H	-1.6582950	1.6327990	0.1252170
H	-1.8917230	2.9262290	-0.6646620

(5) keto-Cy·$(H_2O)_5$_AABBC

Cartesian coordinates (G4MP2)

	X	Y	Z
N	1.4628480	1.1525630	0.0879820
C	1.0337600	2.4359620	0.1075610
H	1.8087250	3.1910700	0.1720740
C	-0.2876770	2.7298230	0.0549640
H	-0.6423100	3.7509490	0.0777160
C	-1.1931080	1.6186540	-0.0276470
N	-2.5135770	1.8286240	-0.0676210
H	-3.1934030	1.0511480	-0.0231580
H	-2.8589320	2.7683440	0.0233750
N	-0.7518680	0.3573720	-0.0769740
C	0.5700460	0.0885390	-0.0026780

O	1.0189300	-1.0746780	-0.0100710
H	2.4760990	0.9536640	0.1554110
O	3.5879400	-1.7975430	-0.5422120
H	3.5911900	-1.9478870	-1.4925870
H	2.6451740	-1.6173820	-0.3215410
O	4.2279860	0.7093570	0.1799240
H	4.1762260	-0.2234370	-0.1437980
H	4.5569010	0.6287200	1.0810380
O	-4.3852750	-0.2737880	0.1352200
H	-3.7566730	-1.0285450	-0.0109360
H	-4.9619770	-0.3089960	-0.6343980
O	-2.4550040	-1.9555740	-0.5851100
H	-1.8416270	-1.1956130	-0.5913180
H	-2.0007040	-2.5643040	0.0291020
O	-0.4901130	-3.3036020	0.8722330
H	0.0583110	-2.5271240	0.6447580
H	-0.2126510	-3.9717670	0.2374730

(6) keto-Cy·$(H_2O)_6$_AABBCC_cage

Cartesian coordinates (G4MP2)

	X	Y	Z
N	1.7909920	1.0707800	0.0103890
C	1.4887760	2.3804650	-0.1488220
H	2.3341010	3.0440540	-0.2908390
C	0.2036390	2.8104670	-0.1375910
H	-0.0459550	3.8531300	-0.2757990
C	-0.8100520	1.8129310	0.0508770
N	-2.1035600	2.1430190	0.0550200
H	-2.8441200	1.4091690	0.0509410
H	-2.3635610	3.0982390	-0.1223610
N	-0.4941160	0.5204680	0.2304350
C	0.7992030	0.1110150	0.1920400
O	1.1199810	-1.0826140	0.3155710
H	2.7822730	0.7689850	-0.0150460
O	4.4760980	0.3254850	-0.1566620
H	4.3151870	-0.6500880	-0.1963760
H	4.9575220	0.4512690	0.6673300
O	-3.9763530	0.1063420	-0.0623190

H	-3.7264700	-0.4008980	0.7268300
H	-3.5707770	-0.4228100	-0.7866610
O	-2.2196430	-1.2007930	1.7104440
H	-1.6040490	-0.5963030	1.2320430
H	-1.9826960	-1.1415030	2.6406310
O	-2.3782920	-1.2451530	-1.8806130
H	-1.9558910	-1.9629750	-1.3537000
H	-1.7040280	-0.5576400	-1.8636940
O	-1.0494120	-2.9569650	-0.1618690
H	-1.5595630	-2.6737870	0.6150740
H	-0.2266870	-2.4491110	-0.0517500
O	3.5956630	-2.2000630	-0.0259040
H	3.5236170	-2.6868140	-0.8528100
H	2.6841540	-1.8819670	0.1570790

S5. Cartesian coordinates of the most stable isomers of Cy·$(MeOH)_{1-3}$ microsolvated clusters displayed in Figure 5

(1) keto-Cy·MeOH_A

Cartesian coordinate (G4MP2)

	X	Y	Z
C	0.6411981	1.6313268	-0.1119103
C	1.9444182	1.2878678	0.0543193
C	2.2177605	-0.1175112	0.1251447
C	-0.0142524	-0.6994387	-0.1336171
H	0.3046603	2.6598784	-0.1803196
H	2.7230593	2.0333622	0.1343963
N	1.2897604	-1.0519797	0.0323702
N	-0.3105047	0.6807374	-0.1997602
N	3.4936622	-0.5396047	0.3246579
H	3.6638374	-1.5283844	0.2367626
H	4.2664308	0.0893962	0.1978076
O	-0.9381773	-1.5050591	-0.2325298
H	-1.3032715	0.9010748	-0.3247406
C	-3.9212832	0.1145288	0.5930081
H	-4.4771895	1.0561866	0.6339059
H	-4.6465862	-0.7057625	0.5020357
O	-3.0504608	0.1716942	-0.5221266

H	-2.4872505	-0.6335988	-0.5092218
H	-3.3813092	-0.0102270	1.5428046

(2) keto-Cy·$(MeOH)_2$_AA

Cartesian coordinate (G4MP2)

	X	Y	Z
C	1.3843520	1.4471011	-0.5756237
C	2.6830011	1.0503019	-0.5506949
C	2.9179508	-0.2778340	-0.0711781
C	0.6588689	-0.6867603	0.2821794
H	1.0705208	2.4283306	-0.9141568
H	3.4835836	1.6987554	-0.8780287
N	1.9573180	-1.0925297	0.3251406
N	0.3993569	0.6188172	-0.1717476
N	4.1866429	-0.7641707	-0.0358581
H	4.3210989	-1.6462592	0.4312251
H	4.9732150	-0.1447428	-0.1170932
O	-0.2795020	-1.4067822	0.6267667
H	-0.5800825	0.9465078	-0.1928662
C	-2.7725244	2.3086817	0.7821547
H	-2.3033908	3.2964589	0.7398192
H	-3.8595122	2.4439937	0.7032426
O	-2.2663036	1.5358072	-0.2935933
H	-2.6552918	0.6305931	-0.2215605
C	-3.2996679	-1.9876772	-0.7154000
H	-4.3172677	-1.7456485	-1.0360106
H	-2.6548715	-2.0216449	-1.6046086
O	-2.8868268	-1.0014342	0.2138627
H	-1.9480889	-1.1855598	0.4583619
H	-3.3099910	-2.9868099	-0.2601088
H	-2.5516387	1.8609358	1.7608121

(3) keto-Cy·$(MeOH)_3$_AAB

Cartesian coordinate (G4MP2)

	X	Y	Z
C	0.1108210	-2.3057870	-0.3184930
C	-1.2319810	-2.4623680	-0.4367350
C	-2.0204710	-1.2718250	-0.3235880

C	-0.1274860	0.0706220	-0.0099590
H	0.8101030	-3.1316830	-0.3868240
H	-1.6791470	-3.4318940	-0.6057010
N	-1.4751950	-0.0735150	-0.1226460
N	0.6561340	-1.0889690	-0.1056020
N	-3.3617580	-1.3281160	-0.4146410
H	-3.8848280	-0.4541820	-0.3565710
H	-3.8270730	-2.1953710	-0.6106150
O	0.4110210	1.1637100	0.1710950
H	1.6818840	-0.9992870	-0.0145650
C	4.0904830	-1.1502790	1.3188810
H	4.0405670	-2.2288990	1.4963340
H	5.1482800	-0.8562040	1.3011790
O	3.4565160	-0.8798520	0.0792810
H	3.4691870	0.0981670	-0.0583900
C	3.1509390	2.5861070	-1.1664500
H	4.2177020	2.7003790	-1.3798280
H	2.6613120	2.1695790	-2.0575770
O	3.0190130	1.7436720	-0.0344590
H	2.0573170	1.5942290	0.1244030
H	2.7287460	3.5814080	-0.9752050
H	3.6039790	-0.6368140	2.1595130
C	-4.1165030	2.0708340	1.1100280
H	-5.1986550	2.2286310	1.1489920
H	-3.8298600	1.4358780	1.9611600
O	-3.8102160	1.4767410	-0.1377580
H	-2.8546210	1.2563120	-0.1439810
H	-3.6246580	3.0459720	1.2305190

S6. Cartesian coordinates of low-energy isomers of Cy·THF displayed in Figure 7

(1) keto-Cy·THF_A

Cartesian coordinate (G4MP2)

	X	Y	Z
C	1.6198665	1.5469621	0.2246638
C	2.9208439	1.1563425	0.2356473
C	3.1580331	-0.2303046	-0.0405731
C	0.8954955	-0.7071357	-0.3101205
H	1.3077532	2.5677113	0.4182872

H	3.7223885	1.8495406	0.4490027
N	2.2058259	-1.1027048	-0.3013494
N	0.6391082	0.6598167	-0.0335557
N	4.4358246	-0.7057177	-0.0061946
H	4.5695806	-1.6386730	-0.3627700
H	5.2086453	-0.0667876	-0.0757236
O	-0.0497749	-1.4442966	-0.5458145
H	-0.3484083	0.9403880	-0.0418232
C	-2.6817194	0.5470407	1.1734142
O	-2.1689505	1.1483743	-0.0276273
C	-2.6993525	0.4563121	-1.1832358
C	-3.7181968	-0.5568239	-0.6493359
C	-3.1810074	-0.8367831	0.7626956
H	-1.8741210	0.5208665	1.9116286
H	-3.4945550	1.1723267	1.5709339
H	-3.1373974	1.1996791	-1.8572969
H	-1.8698827	-0.0530100	-1.6831159
H	-4.7196268	-0.1148898	-0.6015294
H	-3.7697799	-1.4511495	-1.2736972
H	-3.9353429	-1.2335005	1.4464145
H	-2.3370359	-1.5289497	0.7081003

(2) keto-Cy·THF_B

Cartesian coordinate (G4MP2)

	X	Y	Z
C	-3.5089817	-0.2366566	-0.0942174
C	-2.7162057	-1.3340431	-0.0487140
C	-1.2971856	-1.0951954	0.0276331
C	-1.5590452	1.2295985	0.0166925
H	-4.5903677	-0.2894793	-0.1537929
H	-3.1309080	-2.3322335	-0.0697409
N	-0.7696374	0.1182530	0.0558240
N	-2.9618584	1.0009352	-0.0657467
N	-0.4435156	-2.1364528	0.0751329
H	0.5598133	-1.9446532	0.1128256
H	-0.7816837	-3.0808926	0.0474463
O	-1.1591812	2.3792468	0.0466799
H	-3.5321711	1.8320820	-0.0947292

C	2.3746702	-0.2173262	1.2192846
O	2.2778853	-1.1535651	0.1253301
C	2.4925239	-0.4687988	-1.1205152
C	3.1777949	0.8496727	-0.7611089
C	2.5312936	1.1732510	0.5952364
H	1.4707550	-0.2985620	1.8293367
H	3.2438217	-0.4984704	1.8293282
H	3.0950840	-1.1197765	-1.7624736
H	1.5239990	-0.2842464	-1.6020678
H	4.2588337	0.7034582	-0.6564743
H	3.0090732	1.6238168	-1.5132433
H	3.1398936	1.8375941	1.2137768
H	1.5485959	1.6285389	0.4475809

(3) enol-Cy·THF_A

Cartesian coordinate (G4MP2)

	X	Y	Z
C	-0.6864646	1.3055776	0.2391218
C	-2.0587696	1.4322230	0.2047124
C	-2.7803463	0.2355255	0.0229930
C	-0.8346962	-0.9317418	-0.0595012
H	-0.0583127	2.1837426	0.3753845
H	-2.5502919	2.3905009	0.3157671
N	-2.1668922	-0.9422387	-0.1129742
N	-0.0420817	0.1382805	0.1133612
N	-4.1475939	0.2108448	0.0136930
H	-4.5631826	-0.6437067	-0.3224969
H	-4.6451465	1.0621247	-0.1848927
O	-0.2570553	-2.1178611	-0.1996786
H	0.7248460	-2.0190318	-0.1561364
C	2.6115875	-2.2220316	1.5582260
O	2.4290934	-2.0780289	0.1411069
C	3.1698055	-0.9329430	-0.3367882
C	3.9105725	-0.3589913	0.8796301
C	3.0438533	-0.8433933	2.0531261
H	1.6666866	-2.5727635	1.9818330
H	3.3844120	-2.9800882	1.7512646
H	3.8449593	-1.2635138	-1.1329451

H	2.4469015	-0.2190310	-0.7416764
H	4.9199592	-0.7777844	0.9528606
H	4.0007984	0.7284016	0.8298823
H	3.5809925	-0.8829406	3.0037289
H	2.1659600	-0.2009737	2.1662211

(4) enol-Cy·THF_B

Cartesian coordinate (G4MP2)

	X	Y	Z
C	-3.5393360	-0.2278282	-0.0808457
C	-2.7373427	-1.3455135	-0.0330534
C	-1.3416668	-1.1205285	0.0225277
C	-1.7362406	1.1111399	-0.0221966
H	-4.6214655	-0.3278601	-0.1250466
H	-3.1517379	-2.3459368	-0.0372273
N	-0.8472945	0.1303859	0.0263305
N	-3.0654953	1.0291522	-0.0765950
N	-0.4445003	-2.1261972	0.0764534
H	0.5515120	-1.9083007	0.0981155
H	-0.7520408	-3.0812164	0.0639922
O	-1.2115715	2.3515355	-0.0142323
H	-1.9681957	2.9525525	-0.0491042
C	2.5192583	-0.4564974	-1.1286731
O	2.2914407	-1.1547991	0.1070341
C	2.4103679	-0.2409360	1.2152037
C	2.5744018	1.1575202	0.6115605
C	3.2191452	0.8485893	-0.7487374
H	3.1162931	-1.1049317	-1.7778690
H	1.5548525	-0.2555432	-1.6123319
H	1.5139006	-0.3259510	1.8361191
H	3.2837835	-0.5377179	1.8114780
H	1.5926501	1.6157927	0.4682439
H	3.1819712	1.8131552	1.2399729
H	3.0624261	1.6359698	-1.4896508
H	4.2978634	0.6888993	-0.6425000

S5. Fitting Procedure

The transients were fitted to a model function convoluted with a ~0.2 ps (FWHM) Gaussian response function. The model function used in this work consists of a delta function at time zero and a bi-exponential decay function. The delta function represents the "initial spike" (see main text) that arises from the enhancement of non-resonant multiphoton ionization occurring at time zero. The fitting was carried out using a home-made nonlinear least-square fitting computer program based on the Levenberg-Marquardt method.[1] The fitting results and the best-fit time constants are given in Figure 2, 3, 5, 6. The given uncertainty represents an estimated range of time constants within which the chi-square (χ^2) are no greater than 5% off from the best-fit value.

Reference

1. Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes*, second edition; Cambridge University Press: New York, 1992