

## Supporting Information for

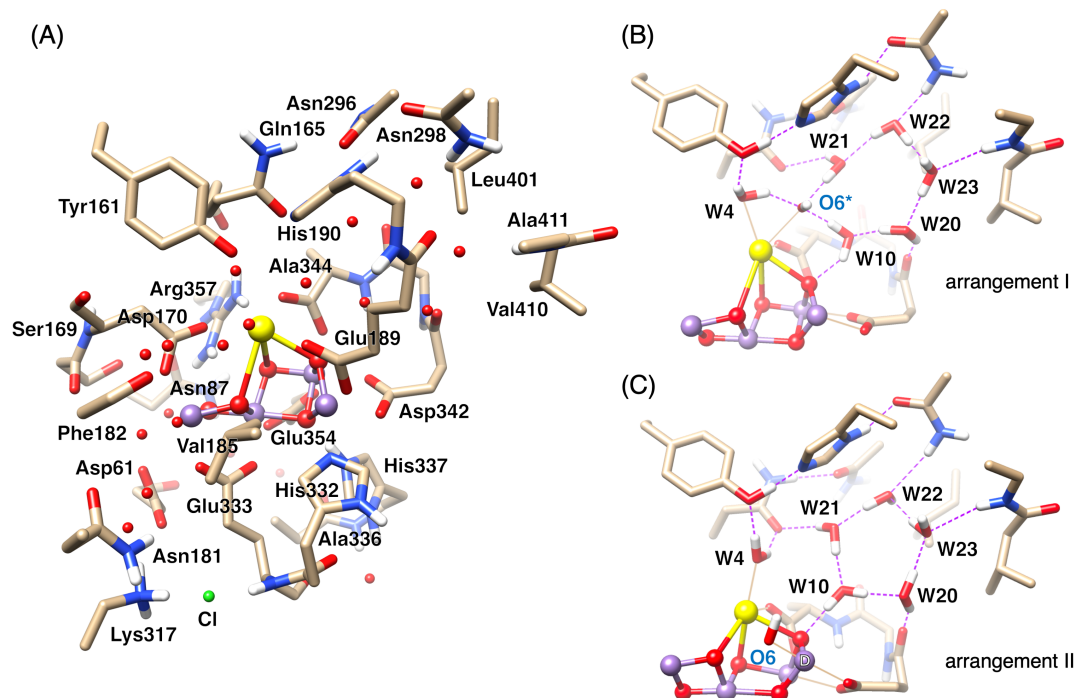
### **Conformational Flexibility of D1-Glu189: A Crucial Determinant in Substrate Water Selection, Positioning, and Stabilization within the Oxygen-Evolving Complex of Photosystem II**

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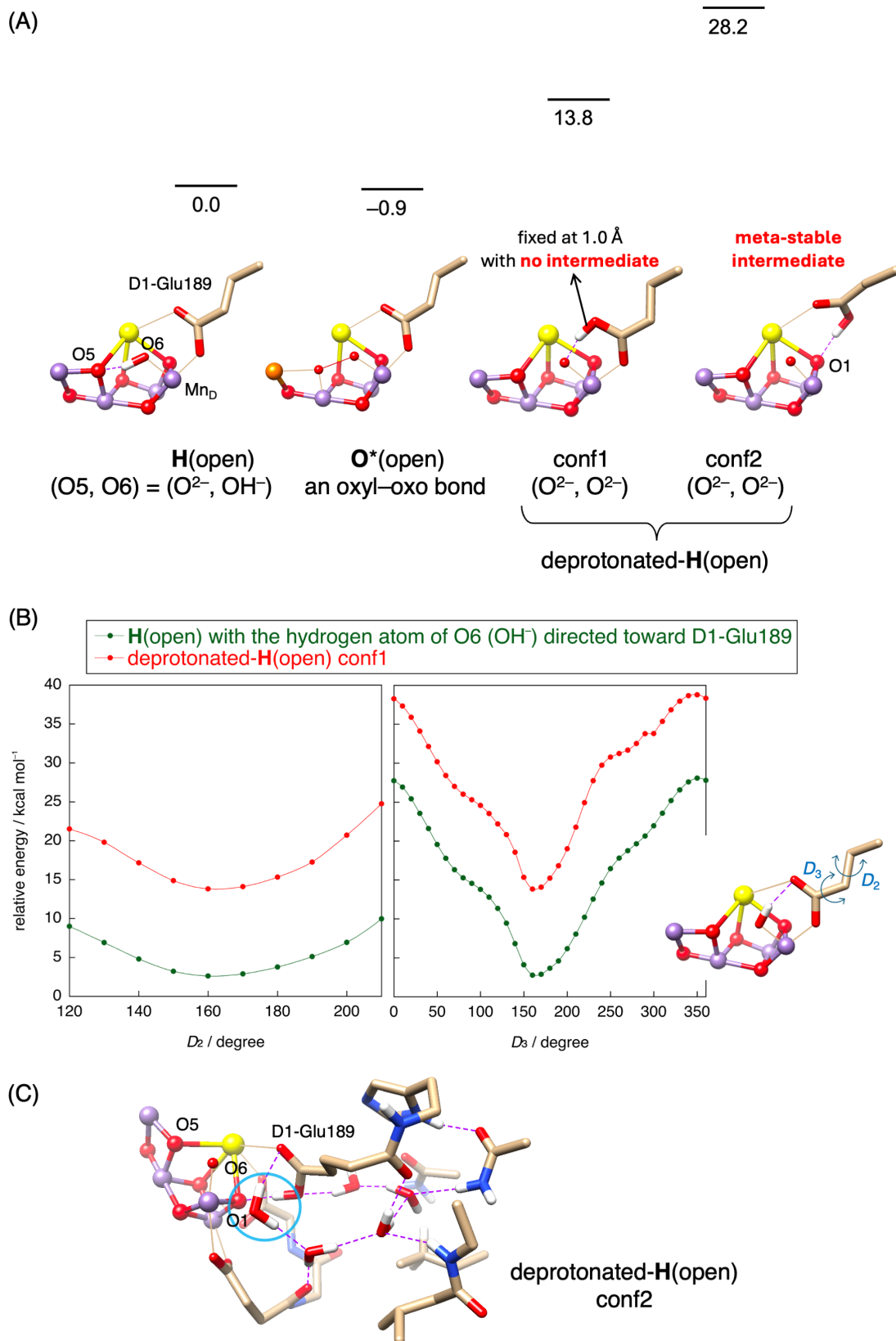
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**Figure S1.** (A) An overall view of the OEC model used in this study, with hydrogen atoms bonded to elements other than nitrogen omitted for clarity. (B) Hydrogen-bond network arrangement I, composed of five water molecules W10, W20, W21, W22, and W23, applied to stabilize O6\* (OH<sup>-</sup>) coordinated with the Ca ion. (C) Hydrogen-bond network arrangement II, employed to stabilize O6 coordinated with Mn<sub>D</sub>.



**Figure S2.** (A) Energy profiles of several intermediates in the S<sub>3</sub> state [**H(open)**]: hydroxo-oxo,

**O\***(open): oxyl–oxo, deprotonated-**H**(open): oxo–oxo with D1-Glu189 being protonated], calculated at the IEFPCM-B3LYP\*-D3(BJ)/BS2//B3LYP-D3(BJ)/BS1 level. Relative energies are given in kcal mol<sup>-1</sup> with reference to **H**(open). Protonation states of O5 and O6 are indicated below the labels. (B) Variations in relative energies for **H**(open) and deprotonated-**H**(open) conf1, with the distance between Glu189–O<sup>-</sup> and H<sup>+</sup> fixed at 1.0 Å, plotted as a function of the dihedral angles  $D_2$  and  $D_3$  of D1-Glu189. Relative energies are given in kcal mol<sup>-1</sup> with reference to **H**(open). (C) Graphical representation of deprotonated-**H**(open) conf2, highlighting the local protein environment. The following color codes are used: yellow, calcium; gold, carbon; red, oxygen; blue, nitrogen; white, hydrogen; purple, Mn<sup>IV</sup>; orange, Mn<sup>III</sup>.

Two intermediates on the left side of Figure S2A, **H**(open) and **O\***(open), represent the normal hydroxo-oxo and oxyl-oxo species in the S<sub>3</sub> state, as widely reported in the literature. In **O\***(open), a half-bond forms between O5 and O6, contributing to its stability comparable to **H**(open). On the other hand, two intermediates on the right, deprotonated-**H**(open) conf1 and conf2, are unusual oxo-oxo species rarely discussed in the literature. These states may form when the proton on O6 (OH<sup>-</sup>) of **H**(open) is transferred to the adjacent carboxylate oxygen of D1-Glu189. The conf1 deprotonated-**H**(open) has been reported to be highly unstable [s1,s2]. In response to a reviewer's request for this paper, we carried out geometry optimizations of deprotonated-**H**(open) conf1. This led to a spontaneous proton transfer, accompanied by a stabilization of about 14 kcal mol<sup>-1</sup>, reverting it to the normal hydroxo-oxo species **H**(open). Even when varying the dihedral angles  $D_2$  and  $D_3$  of the D1-Glu189 side chain, the energy difference between **H**(open) and deprotonated-**H**(open) conf1, with the distance between Glu189–O<sup>-</sup> and H<sup>+</sup> fixed at 1.0 Å, remained largely unchanged (Figure S2B). It has been reported that protonated D1-Glu189 can completely detach from Mn<sub>D</sub> and form a hydrogen bond with the O1 bridging oxo of the Mn cluster, resulting in the formation of the metastable deprotonated-**H**(open) conf2 [s3,s4]. This transient state could potentially facilitate proton release through D1-Glu189, prompting us to assess the stability of deprotonated-**H**(open) conf2 as well. Our results indicate that deprotonated-**H**(open) conf2 is even less stable than conf1, by an additional 14.4 kcal mol<sup>-1</sup> (Figure S2A), suggesting that this dihedral adjustment does not sufficiently lower the energy barrier to make the deprotonation process energetically accessible. Moreover, it was found that in conf2, a water molecule enclosed by a cyan circle intrudes between D1-Glu189 and O6 due to spatial limitations (Figure S2C). However, the specific arrangement or movement of this water molecule has not yet been experimentally validated [s5,s6]. Based on these findings, we infer that the protonation of D1-Glu189 [deprotonated-**H**(open) conf1] and the proton

release via D1-Glu189 [deprotonated-H(open) conf2] are unlikely to be linked to vital functions of the OEC.

## References

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### Cartesian coordinates for two selected structures in Figure 3A

All structures were optimized using the B3LYP-D3(BJ)/BS1 level of theory.

Spherical-harmonic angular functions (keywords 5D and 7F in Gaussian 16) were used.

#### A meta-stable structure with O6\* bound to Ca

B3LYP-D3(BJ)/BS1: -10463.3102026 a.u.

Grimme-D3(BJ): -0.9901947994 a.u.

IEFPCM-B3LYP\*/BS2: -10461.8480680 a.u.

Ca	27.704386	-36.787233	-59.232782
Mn	27.394941	-33.110006	-57.344588
Mn	27.293968	-33.165289	-60.071933
Mn	27.306099	-34.981285	-62.177044
Mn	24.828259	-35.359972	-61.029409
O	26.387037	-36.259365	-61.262183
O	28.273783	-34.542755	-60.739867
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H	24.449234	-28.135093	-53.156952
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H	23.515867	-27.113985	-55.504270
C	21.493918	-36.937582	-55.413941
C	22.661435	-35.934528	-55.451891
C	23.289823	-35.862115	-56.845963
C	22.223330	-34.537854	-54.990958
H	23.431483	-36.287547	-54.754425
H	23.574054	-36.850016	-57.210058
H	22.570996	-35.443022	-57.561832
H	24.188718	-35.235045	-56.849966
H	21.827071	-34.557072	-53.967117
H	21.432749	-34.138347	-55.642124
H	23.061078	-33.832556	-55.013907
H	20.906077	-36.795945	-54.498154
H	21.841901	-37.976458	-55.431489
H	20.820220	-36.793447	-56.270494
C	24.041019	-36.051475	-50.719057
C	23.149637	-37.272334	-50.955107
O	23.249234	-37.933847	-52.005526
H	23.648256	-35.395058	-49.938249
H	25.031118	-36.404770	-50.401110
H	24.166848	-35.500957	-51.655815
H	22.428176	-37.570690	-50.173357
C	34.536919	-29.067067	-58.887963
C	33.270480	-29.081849	-59.750772
C	33.145985	-30.381215	-60.529102
N	32.528480	-30.334904	-61.721584
O	33.599720	-31.435891	-60.049804
H	33.206482	-28.222908	-60.425355
H	32.384726	-29.049599	-59.104723
H	31.984524	-29.521546	-62.049653
H	32.364281	-31.215481	-62.193450
H	34.513862	-28.256699	-58.151728
H	35.440324	-28.949618	-59.495860

H	34.600071	-30.023896	-58.363252
C	23.583066	-48.236060	-60.183056
C	24.553046	-47.107097	-60.534906
N	24.365938	-46.509907	-61.704121
O	25.468004	-46.792577	-59.766771
H	24.128432	-49.014224	-59.646097
H	22.811298	-47.839017	-59.513632
H	23.093884	-48.667349	-61.061081
H	23.516445	-46.659831	-62.229922
H	24.828656	-45.621726	-61.862812
C	28.923577	-45.922965	-62.050082
C	29.571381	-44.560525	-61.826481
O	29.149918	-43.784058	-60.961076
N	30.618866	-44.279797	-62.579226
H	28.991869	-46.500747	-61.123222
H	27.861265	-45.749902	-62.246915
H	29.370950	-46.491779	-62.869042
H	30.803007	-44.811221	-63.418263
H	30.933732	-43.316000	-62.587734
C	27.711410	-46.613872	-65.570589
C	27.047272	-45.250011	-65.760805
C	27.635919	-43.947814	-65.187555
C	28.852992	-43.482374	-65.973515
C	26.552421	-42.874424	-65.155665
H	28.742795	-46.635469	-65.948663
H	27.147975	-47.382324	-66.111096
H	27.738513	-46.902721	-64.514247
H	26.901925	-45.088661	-66.841408
H	26.028414	-45.344521	-65.356531
H	27.931323	-44.126680	-64.144734
H	29.662272	-44.226486	-65.951425
H	29.246661	-42.534253	-65.590333
H	28.589753	-43.327519	-67.029663

H	26.919919	-41.951917	-64.690765
H	25.678557	-43.204724	-64.591019
H	26.223758	-42.629525	-66.175876
C	22.389562	-43.960227	-65.587867
C	21.210067	-44.727983	-65.001096
O	20.511098	-45.449933	-65.727992
C	22.032116	-42.468822	-65.752996
C	23.092196	-41.761950	-66.600954
C	20.673111	-42.314037	-66.405030
N	20.993082	-44.580032	-63.696875
C	19.982017	-45.351955	-62.985035
C	20.003989	-44.998992	-61.490025
H	22.584197	-44.408105	-66.566602
H	18.997533	-45.146222	-63.420631
H	23.278880	-44.044648	-64.958217
H	22.022756	-42.015264	-64.756594
H	24.084678	-41.839444	-66.146402
H	22.860518	-40.694910	-66.713610
H	23.142225	-42.202447	-67.605428
H	19.865204	-42.723396	-65.789791
H	20.637835	-42.837345	-67.368584
H	20.445928	-41.255594	-66.589579
H	21.650402	-44.012593	-63.169594
H	20.166023	-46.424148	-63.134876
H	20.992376	-45.191236	-61.058731
H	19.262816	-45.592359	-60.944962
H	19.774882	-43.938169	-61.336160
Cl	21.364618	-29.922573	-56.087811
O	25.388072	-37.648062	-53.881705
O	30.661908	-28.422511	-62.544653
O	30.167411	-27.510648	-65.224850
O	27.338178	-35.940360	-54.494212
O	25.825020	-29.267803	-55.149866



O	24.820956	-31.790678	-54.694118
O	30.488148	-30.848674	-58.623521
O	28.765184	-38.590443	-58.026179
O	26.698041	-36.762222	-57.038833
O	24.876714	-38.848510	-56.340172
O	27.514097	-41.543092	-61.244242
O	27.181125	-39.131623	-59.979974
O	28.250995	-31.657218	-56.115256
O	22.494046	-28.408678	-64.720627
O	29.094743	-29.619168	-60.721658
O	26.582278	-38.743843	-62.469459
O	23.864353	-42.579450	-63.066556
O	24.307511	-39.881991	-63.292257
O	26.053672	-43.964295	-62.022768
H	28.153878	-38.869794	-57.321198
H	28.393870	-30.735481	-56.492965
H	29.024348	-31.903791	-55.567720
H	24.684982	-38.760489	-57.298684
H	25.677307	-39.419060	-56.278647
H	26.595769	-36.495042	-54.125279
H	28.154256	-36.231171	-54.047937
H	26.341417	-29.122441	-55.984823
H	25.594272	-30.230817	-55.064764
H	24.872320	-32.123973	-53.773084
H	25.314091	-32.457861	-55.233939
H	30.021135	-30.175566	-58.052684
H	29.788347	-31.554128	-58.687329
H	28.469604	-41.701229	-61.178426
H	27.403948	-40.680215	-60.755603
H	26.325007	-39.318647	-59.566053
H	26.774729	-34.353788	-55.439810
H	22.638067	-28.162339	-63.774218
H	21.638984	-28.034013	-64.978881

H	28.428807	-39.131740	-58.808033
H	25.959342	-37.356976	-56.797685
H	27.040046	-36.415807	-56.184911
H	24.651386	-37.686293	-53.240789
H	25.031952	-37.993611	-54.728007
H	30.821876	-27.564781	-62.113229
H	29.990968	-28.841717	-61.940449
H	29.228811	-27.734097	-65.353015
H	30.358661	-27.871390	-64.338597
H	29.709962	-30.009833	-60.059662
H	28.547467	-30.381860	-61.005330
H	26.326414	-37.810220	-62.382950
H	26.850750	-38.959278	-61.511751
H	23.543919	-42.719805	-62.151773
H	24.072234	-41.610267	-63.152156
H	24.492135	-39.699173	-64.230715
H	25.167282	-39.559894	-62.886120
H	26.649856	-43.254844	-61.696982
H	25.358112	-43.453142	-62.497464

**A structure with the angle O6\*...Ca...O–D1-Glu189 fixed at approximately 140°**

B3LYP-D3(BJ)/BS1: -10463.2873766 a.u.

Grimme-D3(BJ): -0.9900846814 a.u.

IEFPCM-B3LYP\*/BS2: -10461.8278085 a.u.

Ca	27.891492	-36.497677	-59.151455
Mn	27.429410	-33.059305	-57.346837
Mn	27.269329	-33.159546	-60.084211
Mn	27.256958	-34.997249	-62.182077
Mn	24.828438	-35.487305	-60.956355
O	26.427715	-36.302832	-61.277589
O	28.259141	-34.520059	-60.762584
O	25.908609	-33.927811	-61.434812
O	28.394872	-32.476257	-58.890408

O	26.691707	-34.118299	-58.654762
O	26.371538	-33.630076	-55.993773
C	32.871406	-41.754037	-53.560295
C	31.549387	-41.348301	-52.889734
C	30.413705	-40.999969	-53.833875
C	30.034757	-41.855454	-54.877290
C	29.648027	-39.840937	-53.642632
C	28.930618	-41.586719	-55.682742
C	28.526811	-39.561086	-54.424169
C	28.147553	-40.446156	-55.441359
O	27.036394	-40.182046	-56.172060
H	31.735191	-40.488195	-52.234094
H	31.231816	-42.165227	-52.224360
H	30.601569	-42.766688	-55.059092
H	29.920113	-39.142602	-52.855231
H	28.653384	-42.259733	-56.485820
H	27.919135	-38.681580	-54.232575
H	26.864883	-40.926838	-56.849743
H	33.646656	-41.940360	-52.807442
H	33.224867	-40.953291	-54.221049
H	32.769806	-42.661895	-54.164947
N	22.229787	-43.493153	-58.589783
C	22.644761	-44.870115	-58.346945
C	22.140149	-41.425597	-59.917010
C	22.529024	-42.903699	-59.745236
O	23.081266	-43.510889	-60.666924
C	23.782064	-45.034061	-57.318457
C	24.905689	-44.090861	-57.549782
C	25.235363	-42.938335	-56.882177
N	25.772903	-44.149011	-58.626663
C	26.576491	-43.053591	-58.572229
N	26.271167	-42.304755	-57.523002
C	23.370619	-40.500230	-59.968261

C	23.015118	-39.103155	-60.527184
C	23.461598	-37.975408	-59.614400
O	23.450211	-38.169138	-58.390808
O	23.731645	-36.831337	-60.173319
H	24.116753	-46.077667	-57.370954
H	23.398832	-44.864344	-56.305171
H	24.796017	-42.530272	-55.981717
H	27.363046	-42.844215	-59.281744
H	23.806684	-40.405321	-58.971838
H	24.127158	-40.961943	-60.608561
H	21.922062	-38.993764	-60.600976
H	23.406515	-38.963255	-61.534193
H	25.808392	-44.915606	-59.305137
H	21.790308	-45.469621	-58.011922
H	21.409874	-41.103247	-59.162722
H	21.824081	-42.956159	-57.837290
H	22.986989	-45.244654	-59.310008
H	21.662055	-41.356468	-60.899680
C	30.206949	-27.056298	-58.221100
C	31.051463	-26.378182	-59.299225
O	30.890851	-26.645049	-60.490011
C	28.737758	-27.309617	-58.568146
C	28.118338	-28.383385	-57.656572
O	28.902298	-29.287921	-57.199027
O	26.891810	-28.306095	-57.427757
H	28.670251	-27.691071	-59.592234
H	28.132743	-26.401507	-58.497999
H	30.321500	-26.532135	-57.265615
H	30.626759	-28.055845	-58.075306
H	31.841992	-25.665809	-58.987180
C	33.360147	-39.662948	-59.276022
C	34.284784	-38.551962	-59.789129
O	33.864114	-37.685064	-60.557922

C	32.184061	-39.076042	-58.491921
C	31.225082	-40.139745	-58.004232
C	30.666610	-40.970395	-59.146383
N	30.959798	-42.277175	-59.141046
O	29.991606	-40.445316	-60.031498
H	33.930288	-40.374264	-58.666861
H	32.985163	-40.194566	-60.159814
H	35.339488	-38.534208	-59.457093
H	32.547629	-38.504201	-57.630007
H	31.644800	-38.374091	-59.135686
H	30.373330	-39.655934	-57.516222
H	31.695941	-40.776336	-57.246193
H	31.424167	-42.712482	-58.358668
H	30.576558	-42.869632	-59.866441
N	31.861085	-33.865155	-54.797203
C	30.754819	-34.809169	-54.634228
C	30.847133	-35.632107	-53.351764
O	30.048666	-36.547155	-53.142523
C	32.921202	-31.674966	-54.669887
C	31.693012	-32.568480	-54.538543
O	30.608675	-32.091461	-54.197393
C	30.551573	-35.664109	-55.904107
C	29.722660	-34.971070	-56.997190
O	29.859568	-35.314264	-58.184175
O	28.861612	-34.121814	-56.563345
C	32.768443	-30.847059	-55.953768
O	32.683491	-31.730197	-57.055593
H	31.500954	-35.982553	-56.344831
H	30.001354	-36.577784	-55.650991
H	31.860543	-30.235213	-55.859291
H	33.627533	-30.166430	-56.058194
H	31.993379	-31.405573	-57.673366
H	33.836702	-32.279580	-54.687594

H	32.742255	-34.187366	-55.170829
H	29.842312	-34.209635	-54.562921
H	31.635510	-35.378102	-52.618729
H	32.961520	-31.018611	-53.796424
C	20.066148	-31.360437	-59.210071
C	21.173946	-30.598156	-59.932929
O	21.455008	-30.848990	-61.104135
N	21.790964	-29.658972	-59.210956
C	22.847899	-28.811283	-59.758961
C	22.427294	-28.167960	-61.088065
O	23.121802	-28.287297	-62.101818
C	20.593490	-32.696944	-58.634220
C	21.489240	-33.423682	-59.568294
C	22.841483	-33.636059	-59.552191
N	21.049111	-33.964893	-60.768042
C	22.104787	-34.479544	-61.432385
N	23.200796	-34.294116	-60.710227
C	24.173392	-29.576235	-59.886132
C	24.602325	-30.163500	-58.544562
C	25.638622	-31.252662	-58.674038
O	25.935958	-31.701547	-59.815233
O	26.119536	-31.669337	-57.574492
H	21.154796	-32.471053	-57.722210
H	19.744616	-33.323217	-58.332849
H	23.564495	-33.409755	-58.784181
H	22.069807	-35.013148	-62.368534
H	24.952822	-28.912940	-60.269249
H	24.047837	-30.374620	-60.615709
H	25.037958	-29.404230	-57.891051
H	23.759239	-30.606745	-57.999841
H	20.106364	-33.903946	-61.123415
H	19.254613	-31.479205	-59.935521
H	19.683405	-30.807726	-58.348072

H	21.628144	-29.637953	-58.203328
H	22.997810	-27.995224	-59.038660
H	21.472456	-27.609213	-61.093837
C	26.167959	-27.319946	-63.863110
C	26.356019	-28.187614	-65.123239
O	27.490567	-28.430113	-65.531590
N	25.270783	-28.652050	-65.739174
C	25.400060	-29.535125	-66.909651
C	26.542939	-28.132845	-62.613366
C	24.515888	-30.797002	-66.715474
C	24.541082	-31.352988	-65.313754
C	25.333480	-32.266899	-64.662259
N	23.613313	-30.933549	-64.364774
C	23.833558	-31.550560	-63.194979
N	24.872954	-32.366598	-63.359153
H	23.473437	-30.564082	-66.964519
H	24.836571	-31.569771	-67.421956
H	26.178191	-32.853524	-64.987208
H	23.240705	-31.414480	-62.299289
H	22.954734	-30.156564	-64.503818
H	25.279637	-32.980218	-62.594696
H	27.587264	-28.448476	-62.669767
H	25.911982	-29.021236	-62.507742
H	26.427395	-27.528959	-61.707736
H	25.144049	-26.931636	-63.796016
H	25.162727	-28.999027	-67.835620
H	26.862469	-26.480631	-63.959520
H	24.349043	-28.333539	-65.471825
H	26.450830	-29.822847	-66.941372
C	25.287787	-36.661907	-66.406837
C	26.207966	-37.841745	-66.090202
O	25.791614	-38.795382	-65.435605
N	27.453167	-37.786145	-66.567410

C	28.319067	-38.972979	-66.568966
C	29.161088	-39.119203	-65.302946
O	29.793025	-40.154019	-65.087038
N	29.169964	-38.084647	-64.471821
C	29.793337	-38.160192	-63.151753
C	24.328939	-36.390447	-65.249472
C	24.945529	-35.830509	-63.961533
O	26.169266	-35.479923	-63.939100
O	24.147397	-35.743686	-62.988480
C	29.178518	-37.103160	-62.255455
O	29.294339	-37.198378	-61.024349
C	31.322340	-38.043025	-63.212787
O	28.575042	-36.157074	-62.896148
H	23.547612	-35.684946	-65.557584
H	23.824822	-37.317715	-64.961609
H	31.699237	-38.814400	-63.887940
H	31.625286	-37.057624	-63.583144
H	31.751377	-38.204131	-62.220760
H	24.739748	-36.922484	-67.321863
H	28.983656	-38.927558	-67.435492
H	25.872933	-35.761269	-66.621245
H	27.726088	-36.986720	-67.121133
H	27.697691	-39.866466	-66.648588
H	28.533124	-37.310411	-64.615250
H	29.539055	-39.122114	-62.698470
C	30.993758	-30.838021	-65.204788
C	29.946059	-31.873091	-64.754771
C	29.083483	-31.327805	-63.607721
C	28.288608	-32.340096	-62.798334
O	28.005424	-33.467607	-63.302972
O	27.925468	-31.971292	-61.631564
H	29.303907	-32.165837	-65.594763
H	30.446292	-32.792297	-64.422905



H	28.382758	-30.571240	-63.989201
H	29.710533	-30.797054	-62.888442
H	30.553318	-29.885880	-65.525920
H	31.616688	-31.222393	-66.020130
H	31.656551	-30.596670	-64.367599
C	36.822943	-32.169973	-62.941950
C	35.873138	-32.938470	-62.025787
C	34.963878	-33.904436	-62.790683
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