

Product Distribution Control for Glucosamine Condensation: Nuclear Magnetic Resonance (NMR) Investigation Substantiated by Density Functional Calculations

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Taiyuan 030051, China

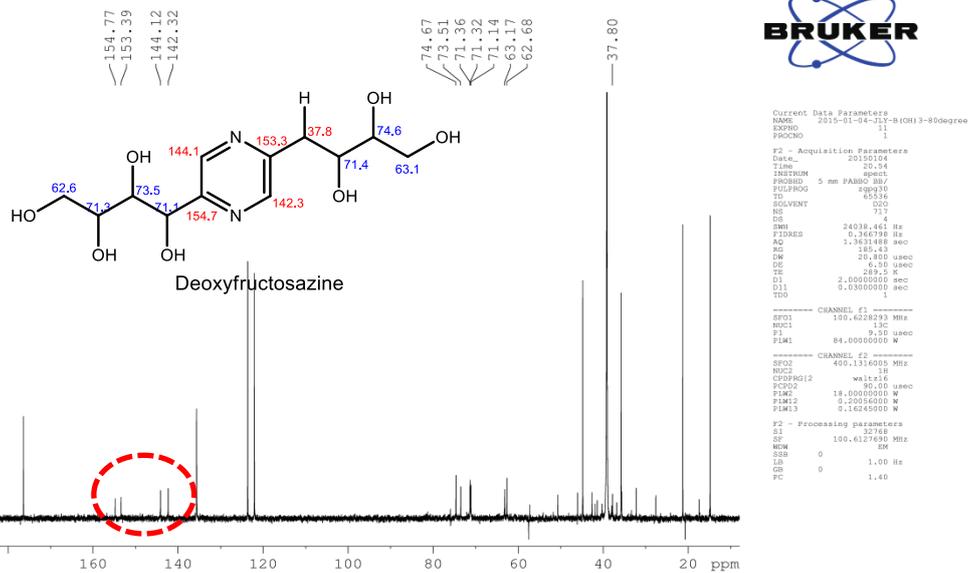


Figure S1. ¹³C NMR spectrum for the condensation of GlcNH₂ catalyzed by [C₂C₁Im][OAc] in DMSO-d₆ in the presence of 0.5 mmol boric acid. Reaction condition: 179.2 mg of GlcNH₂ and 170.2 mg of [C₂C₁Im][OAc] in 2 ml DMSO at 90 °C for 180 min. The low field signals of DOF are labeled with a red ellipse.

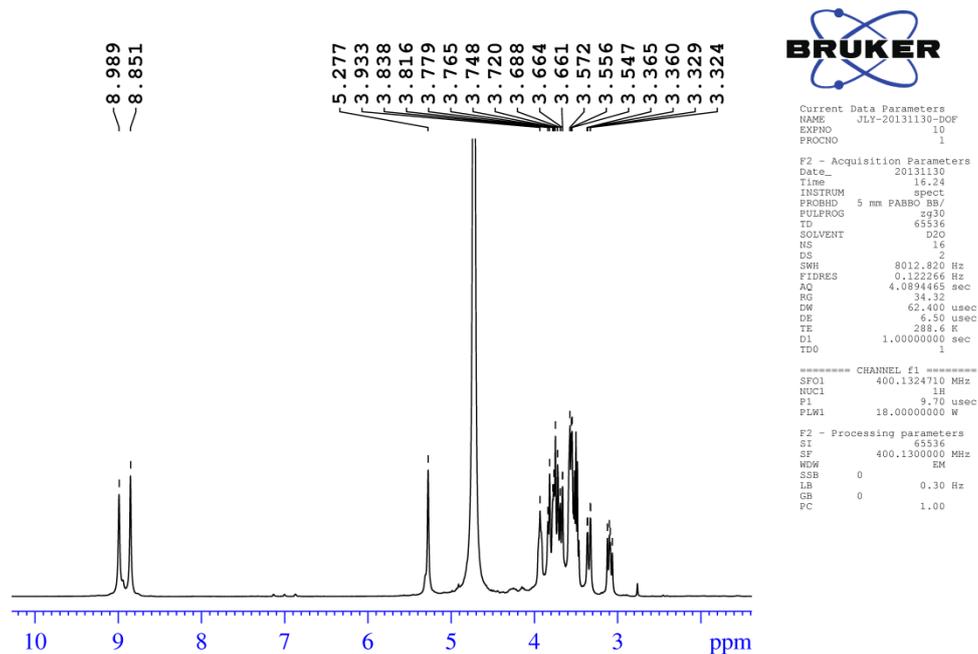


Figure S2. The ¹H NMR spectrum of DOF. Note: The changes of the chemical shifts (ppm) of protons of the DOF may be due to recrystallization leading to different chemical environments.

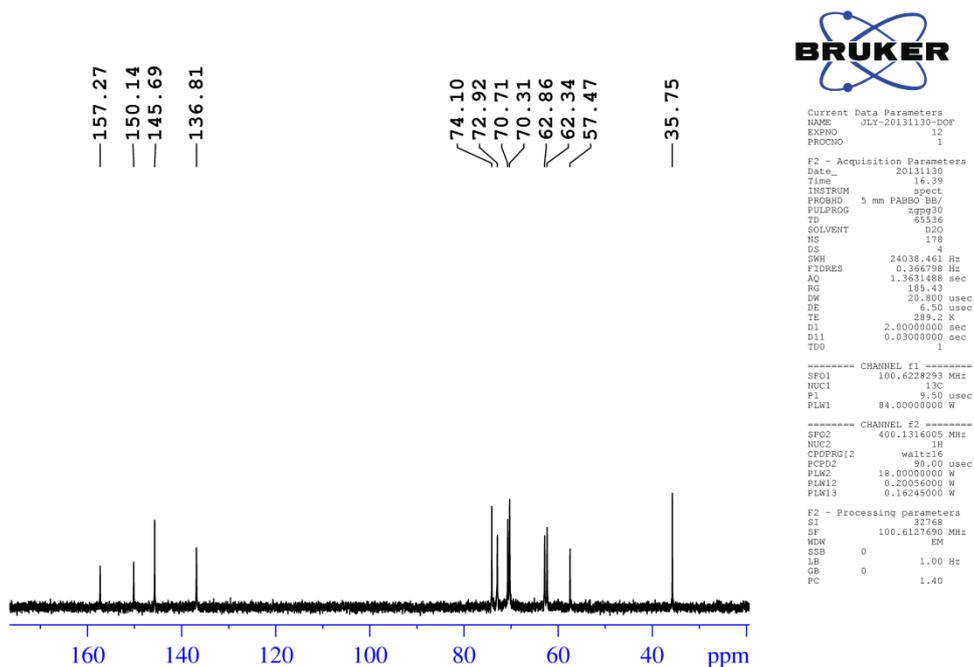
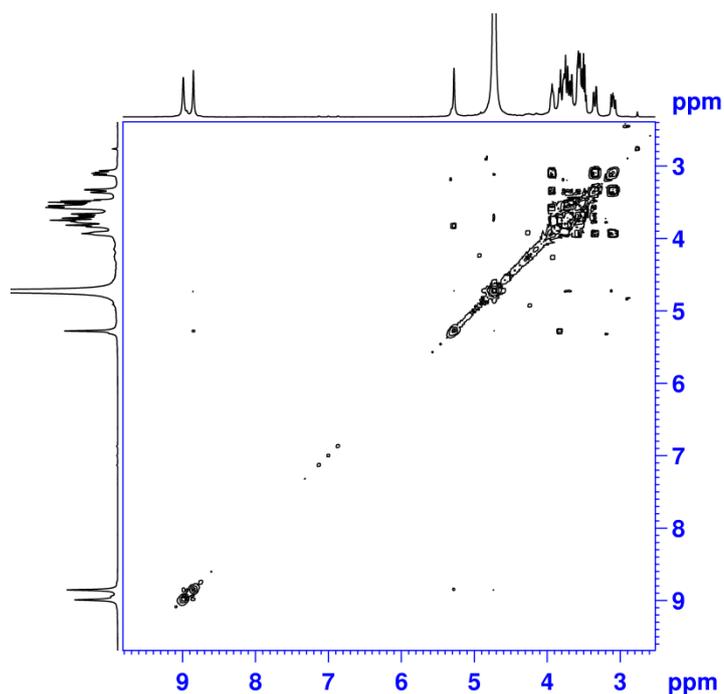


Figure S3. The ^{13}C NMR spectrum of DOF. Note: The changes of the chemical shifts (ppm) of carbons of the DOF may be due to recrystallization leading to different chemical environments.



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PROCNO   1

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PULPROG  coesypppgpr
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DS        3
SWH       4098.361 Hz
FIDRES   2.001153 Hz
AQ        0.249950 sec
RG        11.42
DSW       122.000 usec
DE        6.50 usec
TE        299.1 K
D0        0.0000300 sec
D1        1.8418586 sec
D11       0.03000000 sec
D12       0.0002000 sec
D13       0.0000400 sec
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TD0       0.0024600 sec

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P1        9.70 usec
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PL1       18.0000000 W
PL12      2.50539994 W

----- GRADIENT CHANNEL -----
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GF1      10.00 s
P16      1000.00 usec

F1 - Acquisition parameters
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FIDRES   32.018664 Hz
SW        10.243 ppm
FREQ0DE  QF

F2 - Processing parameters
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SSB       0
LB        0 Hz
GB        0
PC        1.40

F1 - Processing parameters
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SF        400.1300000 MHz
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Figure S4. The ^1H - ^1H COSY spectrum of DOF.

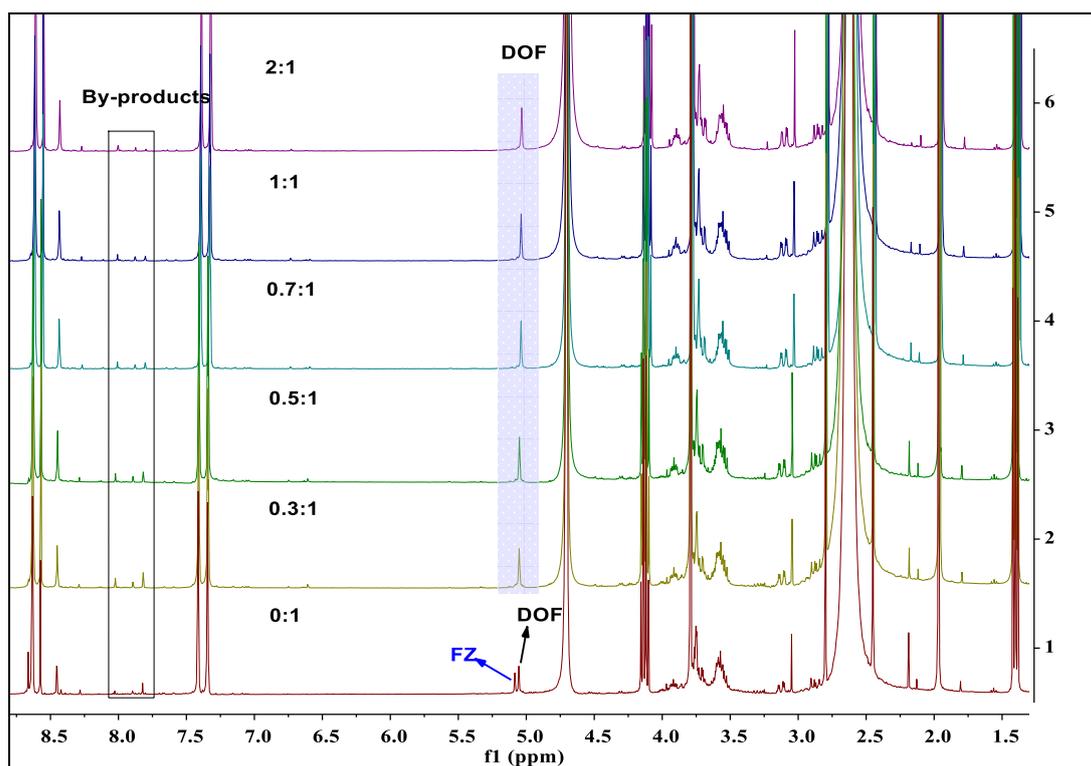


Figure S6. Stacked ^1H NMR spectra for the condensation of GlcNH_2 catalyzed by $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ in DMSO in the presence of different molar ratio of boric acid (molar ratio of $\text{GlcNH}_2/\text{B}(\text{OH})_3 = 0:1, 0.3:1, 0.5:1, 0.7:1, 1:1,$ and $2:1$) at $90\text{ }^\circ\text{C}$ (molar ratio of $\text{GlcNH}_2/[\text{C}_2\text{C}_1\text{Im}][\text{OAc}] = 1:1$). Note: peaks of DOF (light-blue frame) and FZ are indicated by black arrows; signals of possible by-products are presented by the black dash line.

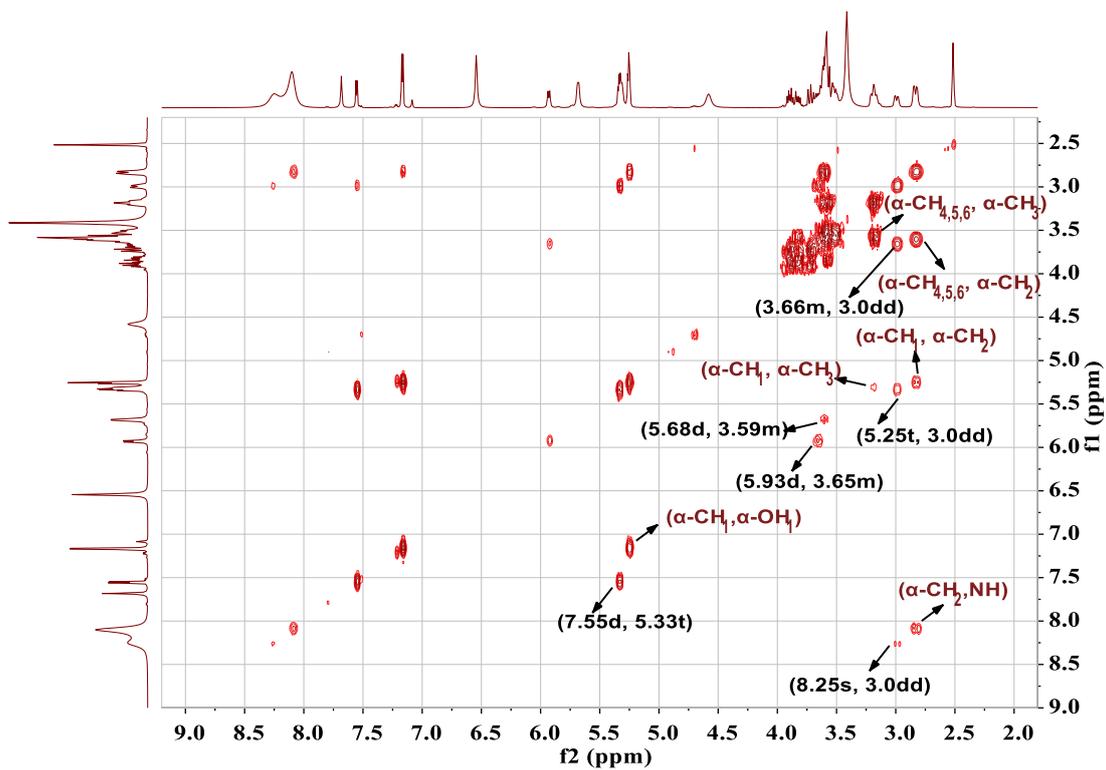


Figure S8. ^1H - ^1H COSY NMR spectrum of GlcNH_2 with 0.5 mmol B(OH)_3 . Notes: s, d, t and m represent singlet, double, triple and multi-peaks, respectively.

Table S1 Summary of peaks diffusion coefficients of free GlcNH₂ and boron complex
D (the diffusion coefficient) is given in m² s⁻¹. Note: The peak at 2.511 ppm was the solvent DMSO-d₆ (4.74e-10 m² s⁻¹)

Complex						average
δ(¹ H, ppm)	8.216	5.317	3.955~3.647	3.132	2.995	
D (m ² s ⁻¹)	1.33e ⁻¹⁰	1.32e ⁻¹⁰	1.30e ⁻¹⁰	1.32e ⁻¹⁰	1.33e ⁻¹⁰	1.32e⁻¹⁰
error	2.293e ⁻¹³	3.405e ⁻¹³	2.572e ⁻¹³	8.423e ⁻¹³	2.710e ⁻¹³	
SD	2.014e ⁻⁴	1.617e ⁻⁴	4.808e ⁻⁴	1.449e ⁻⁴	1.449e ⁻⁴	
GlcNH₂						average
δ(¹ H, ppm)	8.051	5.237	3.633~3.158	2.840	2.831	
D (m ² s ⁻¹)	1.35e ⁻¹⁰	1.35e ⁻¹⁰	1.36e ⁻¹⁰	1.35e ⁻¹⁰	1.36e ⁻¹⁰	1.35e⁻¹⁰
error	3.694e ⁻¹³	3.149e ⁻¹³	1.997e ⁻¹³	3.502e ⁻¹³	3.788e ⁻¹³	
SD	2.706e ⁻⁴	1.946e ⁻⁴	4.732e ⁻⁴	3.456e ⁻⁴	2.596e ⁻⁴	

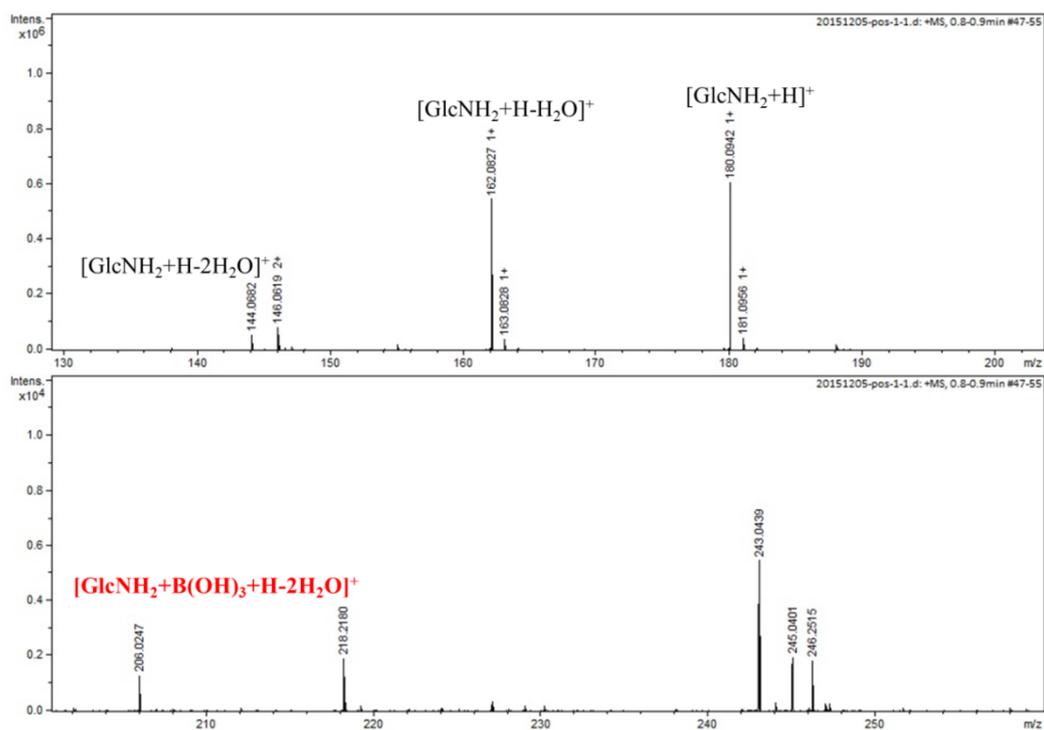


Figure S9. Positive-ion ESI Mass of GlcNH₂ with equimolar ratio of B(OH)₃ in DMSO-d₆ solution at room temperature.

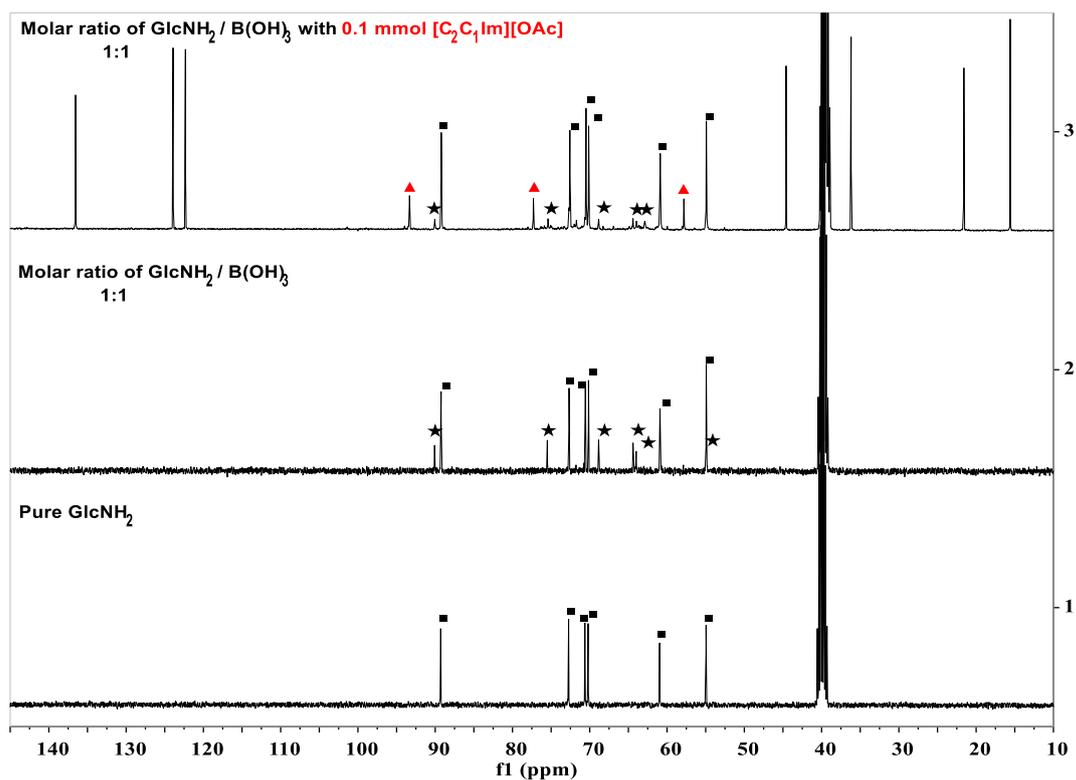
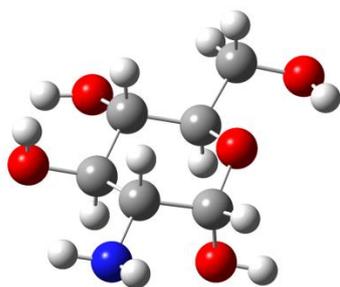


Figure S10. ^{13}C NMR of GlcNH_2 in the presence of equimolar amount of B(OH)_3 with catalytic amount of $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ at room temperature. ■ denotes the peaks of α -anomer; ▲ denotes the peaks of β -anomer; ★ denotes the peaks assigned to boron complex of the α -anomer; Note: several peaks of anomer and boron complex are not split, which may not be obviously seen in the figure.

Computational section

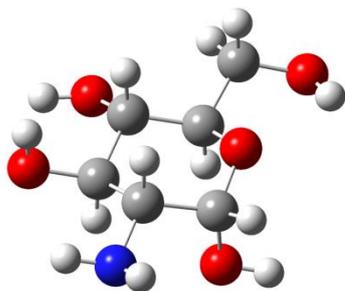


1A

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

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C	0.47326	-1.58703	-0.18210
C	-1.20993	0.10818	0.14672
C	-0.20460	1.22763	-0.13348
H	0.60310	-2.47866	-0.80566
H	1.44654	-0.36198	-1.60187
H	1.31499	0.63082	1.27539
H	-1.23598	-0.08578	1.22347
H	-0.24934	1.47359	-1.20871
O	-0.80764	-1.09007	-0.54898
O	0.54424	-1.90843	1.18089
O	2.15569	1.81471	-0.11767
O	-0.57781	2.36130	0.63663
C	-2.61534	0.42696	-0.34200
H	-2.98282	1.31464	0.17270
H	-2.58454	0.63642	-1.42066
O	-3.52494	-0.62617	-0.05687
H	-3.16209	-1.42730	-0.45136
H	0.18330	2.95369	0.67033
H	2.13456	1.96982	-1.07057
H	-0.06770	-2.63167	1.35656
N	2.88729	-0.99024	-0.14130
H	3.23312	-1.71211	-0.76341
H	3.54068	-0.21475	-0.15803

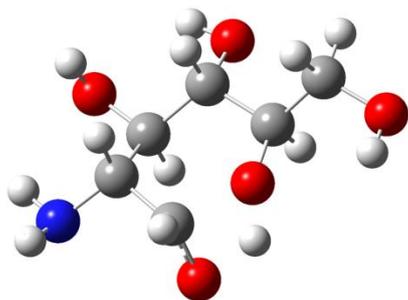


1A'

Symbolic Z-matrix:

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C	1.21329	0.05334	-0.16854
C	0.26976	1.20311	0.18420
H	-0.72894	-2.31497	1.09027
H	-1.54563	-0.18959	1.58158
H	-1.19140	0.67767	-1.31559
H	1.24678	-0.07545	-1.25652
H	0.28692	1.33674	1.27966
O	0.75148	-1.16219	0.46275
O	-0.82701	-2.17556	-0.95855
O	-2.02888	1.95479	-0.00648
O	0.72103	2.39114	-0.44570
C	2.61715	0.31194	0.36767
H	2.97568	1.26043	-0.03235
H	2.56118	0.39477	1.46218
O	3.56139	-0.67511	-0.01713
H	3.24631	-1.52382	0.31257
H	-0.04322	2.97433	-0.53710
H	-2.07523	2.12075	0.94402
H	-0.18894	-2.89306	-1.05430
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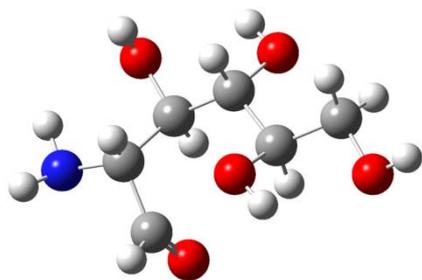


TS1

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C	1.30649	0.09410	-0.22722
C	0.28916	1.15832	0.18268
H	-0.75439	-2.28489	1.21216
H	-1.64262	-0.17404	1.58482
H	-1.17426	0.61496	-1.32345
H	1.38583	0.10062	-1.31936
H	0.30165	1.26478	1.28197
O	0.86930	-1.22305	0.18739
O	-0.76757	-2.27590	-0.84684
O	-1.98711	1.94511	-0.04743
O	0.70588	2.37404	-0.41988
C	2.68633	0.34075	0.37590
H	3.07046	1.29843	0.02341
H	2.59681	0.38165	1.47097
O	3.61972	-0.65064	-0.02090
H	3.27749	-1.50377	0.27001
H	-0.07313	2.94127	-0.49129
H	-2.05712	2.11723	0.90081
H	0.42740	-1.93423	-0.70673
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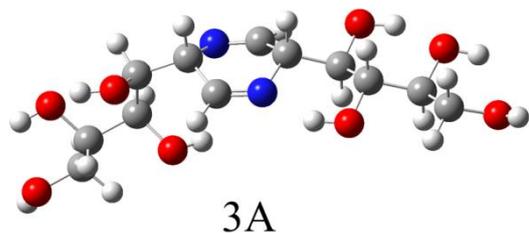


2A

Symbolic Z-matrix:

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C	-1.15387	-1.83985	0.23416
C	1.40807	0.14103	-0.20790
C	0.31046	1.12609	0.20483
H	-0.93415	-2.42856	1.14648
H	-1.66573	-0.26803	1.59160
H	-1.15942	0.56291	-1.30619
H	1.45121	0.10695	-1.30065
H	0.31644	1.21928	1.30536
O	1.10685	-1.16545	0.31293
O	-1.03056	-2.32587	-0.86274
O	-1.95587	1.90686	-0.02843
O	0.67338	2.37009	-0.38471
C	2.79181	0.48108	0.34204
H	3.17714	1.39995	-0.09726
H	2.72256	0.61289	1.43113
O	3.70041	-0.56162	0.01515
H	3.35928	-1.36397	0.42743
H	-0.13196	2.90007	-0.45319
H	-2.00885	2.08433	0.92021
H	1.07300	-1.79017	-0.41883
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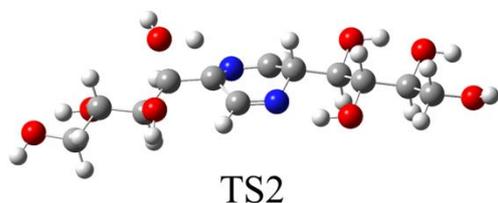


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C	0.23679	1.53536	-0.92262
N	-1.00450	1.64150	-0.67650
H	-1.06409	-0.57634	1.89046
H	0.59733	1.79040	-1.91673
C	2.51327	0.49518	-0.60598
C	3.54400	-0.08105	0.39386
H	2.23077	-0.31419	-1.29512
C	4.81578	-0.57531	-0.30406
H	3.81881	0.71641	1.10063
C	5.80921	-1.18832	0.66966
H	4.53277	-1.33334	-1.04586
H	6.07137	-0.45365	1.43879
H	5.37730	-2.07184	1.14274
C	-2.93311	1.00180	0.70112
C	-3.36323	-0.02532	-0.36703
H	-3.44220	1.94046	0.46207
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H	-3.37488	0.49871	-1.32678
C	-5.39751	-1.20110	-1.30740
H	-4.61959	-1.40187	0.67468
H	-5.54545	-0.41595	-2.05679
H	-4.75691	-1.98338	-1.72471
O	3.02863	1.60864	-1.33072
H	3.96052	1.42301	-1.53611
O	3.02035	-1.21066	1.08245
H	2.07893	-1.00429	1.27603
O	6.96430	-1.53176	-0.11097
H	7.70298	-1.70432	0.48139
O	5.43221	0.53577	-0.97302

H	6.29739	0.23596	-1.28274
O	-2.47476	-1.14668	-0.44496
H	-1.81093	-0.96464	-1.11840
O	-5.57371	0.42812	0.47657
H	-6.47556	0.08174	0.49649
O	-6.65978	-1.73510	-0.88565
H	-7.20295	-1.90599	-1.66173
O	-3.25840	0.60078	2.03083
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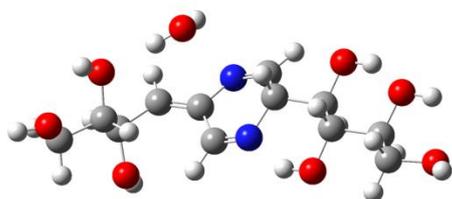


Symbolic Z-matrix:

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C	1.36002	0.77469	0.07959
C	0.53494	1.87354	-0.54285
N	-0.74168	1.84564	-0.48013
H	-1.07526	-1.47749	-0.17507
H	1.02583	2.69432	-1.05903
C	2.82479	0.79968	-0.37582
C	3.64857	-0.38238	0.18562
H	2.85721	0.73363	-1.47361
C	5.11097	-0.34623	-0.27019
H	3.62279	-0.32532	1.28475
C	5.90876	-1.53498	0.23959
H	5.13201	-0.35084	-1.36789
H	5.86886	-1.56347	1.33397
H	5.50076	-2.46356	-0.16340
C	-2.81891	0.72398	0.16036
C	-3.67089	-0.49951	-0.10732

H	-3.21487	1.58522	-0.36865
C	-5.16605	-0.18113	0.03575
H	-3.47351	-0.77766	-1.15012
C	-6.04601	-1.36838	-0.32733
H	-5.36310	0.09846	1.07866
H	-5.81564	-1.70273	-1.34521
H	-5.88342	-2.19324	0.37207
O	3.33180	2.06255	0.05695
H	4.30155	2.00948	0.04560
O	3.13118	-1.62780	-0.26860
H	2.14749	-1.52611	-0.27819
O	7.25795	-1.32589	-0.20724
H	7.84454	-1.91173	0.28162
O	5.71172	0.86764	0.20906
H	6.66008	0.80234	0.03440
O	-3.29562	-1.54921	0.78126
H	-3.43869	-2.39759	0.34898
O	-5.45198	0.91933	-0.82702
H	-6.41389	0.95220	-0.91796
O	-7.39730	-0.89759	-0.24885
H	-7.97530	-1.52718	-0.69182
O	-2.95037	1.05951	1.69719
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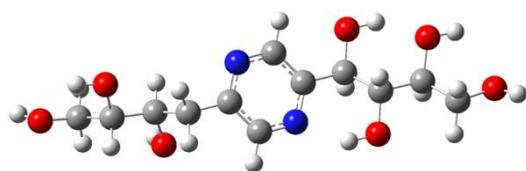
4A

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C	-0.89179	-0.92437	0.09232

C	-0.29433	-2.30873	0.05327
N	0.91797	-2.55218	-0.26733
H	1.51615	0.42636	-1.79732
H	-0.93770	-3.14271	0.32357
C	-2.42175	-0.94251	-0.13458
C	-3.05516	0.46786	-0.02899
H	-2.62922	-1.32474	-1.14650
C	-4.57871	0.44286	-0.21840
H	-2.83558	0.86108	0.97635
C	-5.18597	1.83819	-0.16990
H	-4.80038	0.00258	-1.20005
H	-4.91660	2.32494	0.77539
H	-4.81738	2.43405	-1.00683
C	3.05212	-1.53940	-0.50391
C	4.07695	-0.47496	-0.81040
H	3.42863	-2.46951	-0.09031
C	4.01622	0.73736	0.13398
H	5.06921	-0.92999	-0.69666
C	5.18677	1.68794	-0.08946
H	3.08124	1.28104	-0.04929
H	6.13097	1.13210	-0.02342
H	5.10577	2.15101	-1.07588
O	-2.91900	-1.83782	0.85093
H	-3.86112	-1.65060	0.98887
O	-2.57298	1.34305	-1.03774
H	-1.61812	1.16334	-1.14548
O	-6.60825	1.64432	-0.24748
H	-7.05344	2.48162	-0.09211
O	-5.16208	-0.36692	0.81161
H	-6.11654	-0.22123	0.77968
O	3.95332	0.07659	-2.13298
H	3.92856	-0.65304	-2.76131
O	4.03275	0.25593	1.48066
H	4.31682	1.00321	2.02693
O	5.10572	2.66300	0.95817
H	5.87325	3.24073	0.92373
O	1.37009	-0.29017	2.57790
H	2.27132	-0.21611	2.22079
H	-0.71795	-0.53465	1.10777
H	1.40074	-1.03519	3.18524



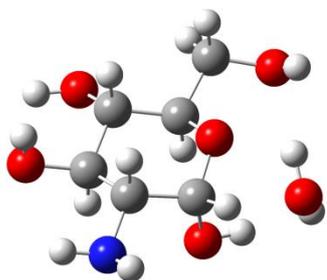
5A

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.41382	-0.53979	0.29469
C	0.64336	-0.66276	1.45383
N	-0.61840	-0.23434	1.52492
C	-1.13332	0.33212	0.42838
C	-0.36423	0.46376	-0.73179
N	0.89484	0.03263	-0.80078
H	1.06173	-1.11780	2.34536
H	-0.78223	0.93144	-1.61527
C	-2.57243	0.78722	0.47228
C	-3.50784	-0.28538	-0.15166
H	-2.85166	0.91267	1.52519
C	-4.98790	0.04348	0.05594
H	-3.29610	-0.33453	-1.22767
C	-5.90871	-0.96613	-0.61086
H	-5.19205	0.05401	1.13442
H	-5.68224	-1.02029	-1.68111
H	-5.77611	-1.95217	-0.16119
C	2.83597	-1.01807	0.22670
C	3.82703	0.14181	0.12571
H	2.95957	-1.65598	-0.65010
H	3.07774	-1.61040	1.11309
C	5.25292	-0.35981	-0.12537
H	3.53031	0.79043	-0.70536
C	6.25717	0.77757	-0.24235
H	5.54976	-1.00630	0.71248
H	5.94130	1.46840	-1.03252
H	6.33309	1.31967	0.70431
O	-2.66030	2.02043	-0.23583
H	-3.60480	2.19136	-0.38628
O	-3.32035	-1.55784	0.46128
H	-2.43017	-1.87355	0.27046
O	-7.24179	-0.47740	-0.40360
H	-7.84003	-0.93261	-1.00469

O	-5.23395	1.34716	-0.48633
H	-6.19216	1.47242	-0.50659
O	3.76784	0.86699	1.36180
H	3.93935	1.79867	1.19315
O	5.23851	-1.11617	-1.33820
H	6.16146	-1.20934	-1.61007
O	7.51321	0.17258	-0.58062
H	8.11775	0.85583	-0.88761



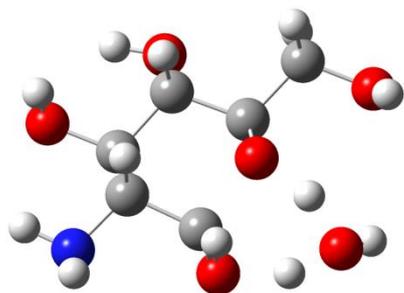
1B

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-1.71595	0.35420	-0.32038
C	-1.60855	-0.89428	0.56425
C	-0.15709	-1.41934	0.54897
C	0.72747	0.74374	0.02605
C	-0.65187	1.39931	0.03311
H	-0.01657	-2.17539	1.33191
H	-1.78024	-0.57358	1.60889
H	-1.59518	0.05698	-1.36383
H	0.93281	0.37837	-0.98508
H	-0.85176	1.78009	1.04925
O	0.71736	-0.35730	0.94539
O	0.16550	-1.91451	-0.70989
O	-3.02430	0.94618	-0.25830
O	-0.65128	2.47498	-0.89575
C	1.87463	1.64280	0.46139
H	2.02615	2.43715	-0.26808
H	1.66063	2.09667	1.43611
O	3.09552	0.89133	0.52795
H	2.99908	0.28178	1.27011
H	-1.57157	2.68757	-1.09443

H	-3.20540	1.19202	0.65767
H	1.13069	-2.05161	-0.74999
N	-2.55735	-1.90126	0.10981
H	-2.59173	-2.69858	0.73528
H	-3.48924	-1.50770	0.03941
O	3.02694	-1.66248	-0.87198
H	3.18864	-0.74013	-0.60388
H	3.61539	-1.83909	-1.61174



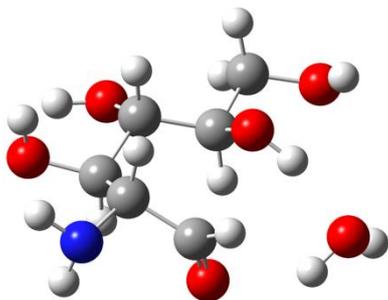
TS3

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.55393	-0.60958	-0.26605
C	1.67238	0.68037	0.55175
C	0.47916	1.60596	0.29249
C	-0.97899	-0.64043	-0.07558
C	0.31598	-1.43036	0.10547
H	0.26418	2.28252	1.13199
H	1.62754	0.40890	1.62104
H	1.52715	-0.36046	-1.32861
H	-1.07033	-0.36020	-1.13288
H	0.39871	-1.71851	1.16807
O	-0.92010	0.54411	0.73335
O	0.24801	2.03025	-0.89328
O	2.72318	-1.43408	-0.11297
O	0.22775	-2.59476	-0.70484
C	-2.21288	-1.44829	0.32623
H	-2.30023	-2.31468	-0.32877
H	-2.10175	-1.80204	1.35860
O	-3.41309	-0.69175	0.17653
H	-3.49126	-0.09749	0.92960
H	1.12534	-2.92886	-0.82738
H	2.81647	-1.66556	0.82019
H	-0.96898	2.37987	-0.83255

N	2.90105	1.38161	0.18765
H	3.14231	2.10001	0.86062
H	3.67371	0.72872	0.11804
O	-2.05728	2.31013	-0.40434
H	-1.69216	1.35720	0.24138
H	-2.70328	2.06212	-1.07431



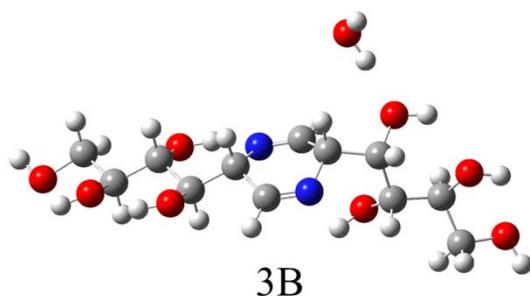
2B

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.46296	-0.70308	-0.27095
C	1.84676	0.54891	0.54687
C	0.99822	1.77401	0.22745
C	-1.12811	-0.56439	-0.03544
C	0.14447	-1.40062	0.11999
H	0.79256	2.44398	1.07855
H	1.72934	0.33621	1.61486
H	1.42542	-0.44363	-1.33178
H	-1.14721	-0.11172	-1.03410
H	0.21736	-1.69144	1.18330
O	-1.09149	0.46254	0.96169
O	0.67125	2.07370	-0.90303
O	2.51187	-1.68903	-0.17893
O	-0.01877	-2.56172	-0.68883
C	-2.39166	-1.41407	0.14255
H	-2.47863	-2.13069	-0.67209
H	-2.32942	-1.96893	1.08787
O	-3.56538	-0.60664	0.10832
H	-3.56942	-0.06264	0.90316
H	0.85832	-2.94697	-0.81140
H	2.60114	-1.95791	0.74457
H	-1.17692	2.85238	-0.82978
N	3.21671	1.03213	0.34111
H	3.89608	0.34112	0.63874

H	3.38253	1.21430	-0.64465
O	-2.01012	2.75622	-0.33892
H	-1.57736	1.23555	0.61294
H	-2.71563	2.74029	-0.99312

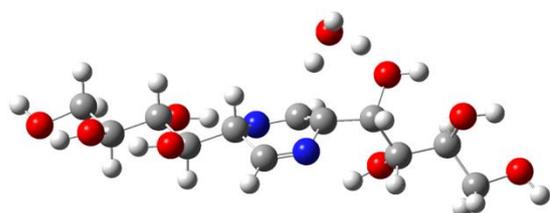


Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.34041	0.92685	0.79723
C	0.50889	0.87150	-0.46150
N	-0.73469	0.61549	-0.44170
C	-1.34831	0.38219	0.87174
C	-0.36828	-0.27104	1.81803
N	0.88223	-0.05086	1.79097
H	0.99228	1.05602	-1.41534
H	-0.75754	-0.99069	2.53481
C	-2.64808	-0.43450	0.75091
C	-3.65051	0.17593	-0.25662
H	-2.40038	-1.44732	0.40056
C	-4.95495	-0.62477	-0.33459
H	-3.88583	1.19989	0.07057
C	-5.92097	-0.06425	-1.36562
H	-4.71135	-1.66055	-0.60467
H	-6.14695	0.98126	-1.12922
H	-5.48475	-0.12505	-2.36414
C	2.84445	0.75356	0.56399
C	3.23034	-0.69518	0.20373
H	3.35849	1.00196	1.49643
C	4.61031	-0.77258	-0.45589
H	3.22883	-1.26343	1.13797
C	5.23649	-2.14700	-0.32125
H	4.48013	-0.54496	-1.52075
H	5.38243	-2.38125	0.73876
H	4.58134	-2.89886	-0.77097

O	-3.17199	-0.48026	2.07530
H	-4.11488	-0.70904	2.01386
O	-3.11998	0.17456	-1.57675
H	-2.17112	0.41576	-1.49280
O	-7.10661	-0.86854	-1.26902
H	-7.82910	-0.41736	-1.71698
O	-5.57911	-0.60646	0.95865
H	-6.45910	-0.99278	0.85484
O	2.32022	-1.29525	-0.72399
H	1.64161	-1.76469	-0.22745
O	5.45952	0.22086	0.13808
H	6.35655	0.04211	-0.17400
O	6.49762	-2.08460	-0.99979
H	7.02918	-2.84568	-0.74532
O	3.22045	1.69365	-0.45074
H	4.19000	1.69002	-0.47651
H	-1.62280	1.35980	1.29403
H	1.19658	1.93102	1.21974
O	1.98699	4.21098	-0.54409
H	2.31121	4.72513	0.20257
H	2.46688	3.36250	-0.49310



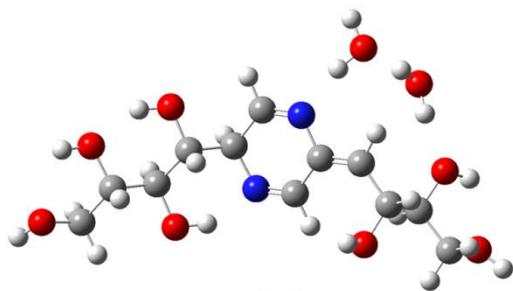
TS4

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.24050	0.63844	0.18395
C	0.45483	-0.15998	-0.70173
N	-0.81431	-0.39125	-0.50529
C	-1.39869	0.45372	0.54586
C	-0.45871	0.48994	1.72315
N	0.79944	0.65757	1.52366
H	0.92974	-0.64366	-1.55280
H	-0.83239	0.37936	2.73742
C	-2.81874	0.01162	0.91384
C	-3.74539	-0.09488	-0.31935
H	-2.77182	-0.98331	1.38134

C	-5.16253	-0.54872	0.04527
H	-3.80738	0.90201	-0.78345
C	-6.05706	-0.69620	-1.17408
H	-5.09613	-1.51911	0.55460
H	-6.10454	0.25640	-1.71322
H	-5.66557	-1.46962	-1.83719
C	2.74616	0.70003	0.06413
C	3.51462	-0.61714	0.30231
H	3.10890	1.40779	0.81157
C	4.97007	-0.56496	-0.18496
H	3.48873	-0.76536	1.38849
C	5.88591	-1.45331	0.63283
H	4.97761	-0.90786	-1.22581
H	5.90068	-1.10797	1.67202
H	5.52242	-2.48499	0.60025
O	-3.29112	0.97595	1.85745
H	-4.25786	0.89601	1.89841
O	-3.25200	-1.05455	-1.24636
H	-2.26154	-0.97491	-1.21533
O	-7.35544	-1.05303	-0.67316
H	-8.00531	-0.92882	-1.37205
O	-5.73833	0.41672	0.94060
H	-6.67204	0.18839	1.04087
O	2.95278	-1.75265	-0.34842
H	2.12965	-1.98353	0.09660
O	5.43366	0.79660	-0.13987
H	6.38438	0.77680	-0.31345
O	7.18847	-1.34155	0.04685
H	7.84085	-1.69575	0.65984
O	3.10014	1.25125	-1.26524
H	4.05869	1.44795	-1.22721
H	-1.46908	1.48832	0.14887
H	0.92018	2.20671	-0.70282
O	1.33590	2.85117	-1.40743
H	1.47124	3.72443	-1.00718
H	2.29641	2.25593	-1.47090



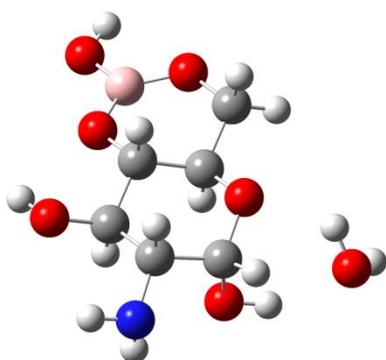
4B

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.20394	0.43524	0.27440
C	0.45468	-0.60433	-0.44098
N	-0.70528	-0.43594	-0.94955
C	-1.37649	0.84748	-0.78085
C	-0.50178	1.92855	-0.21566
N	0.66622	1.74674	0.26840
H	0.92198	-1.57610	-0.55277
H	-0.89191	2.94237	-0.23360
C	-2.66438	0.67073	0.07382
C	-3.66393	-0.31365	-0.57808
H	-2.37334	0.27115	1.05530
C	-4.92428	-0.50086	0.27362
H	-3.95732	0.10204	-1.55350
C	-5.89931	-1.49090	-0.34296
H	-4.62464	-0.86750	1.26383
H	-6.17595	-1.15737	-1.34900
H	-5.44538	-2.48176	-0.40037
C	2.37570	0.24659	0.91217
C	3.17571	-1.01848	1.07339
H	2.82253	1.12234	1.37025
C	4.23143	-1.15212	-0.03620
H	3.71332	-0.94707	2.02643
C	5.12732	-2.36497	0.17486
H	3.71791	-1.24143	-1.00167
H	5.55267	-2.33873	1.18389
H	4.55376	-3.28466	0.04723
O	-3.21140	1.97646	0.20309
H	-4.14390	1.87924	0.46234
O	-3.10622	-1.61344	-0.72971
H	-2.17305	-1.49742	-1.00745
O	-7.04792	-1.49682	0.51808

H	-7.78469	-1.90884	0.05582
O	-5.56837	0.77415	0.41429
H	-6.42880	0.61580	0.82523
O	2.41149	-2.22325	1.03668
H	1.85403	-2.25675	1.82248
O	5.02699	0.03682	-0.02462
H	5.86004	-0.19841	-0.46017
O	6.16649	-2.26106	-0.80896
H	6.88885	-2.84991	-0.56761
O	4.37686	2.60951	-1.12061
H	4.52543	1.72940	-0.73546
H	-1.72045	1.17930	-1.76934
H	1.78453	3.13664	0.59325
O	2.53078	3.77861	0.68616
H	2.16506	4.64433	0.47508
H	3.77135	3.06024	-0.50254



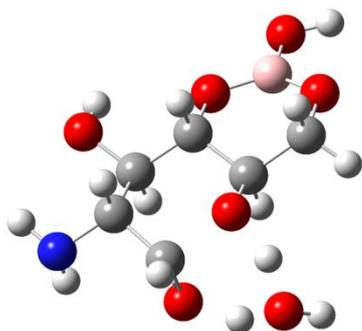
1C

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.55549	-1.53826	-0.15314
C	1.88307	-1.09531	0.48765
C	2.07706	0.41774	0.32007
C	-0.29211	0.78038	0.15609
C	-0.57181	-0.69492	0.41906
H	2.89292	0.7706	0.95576
H	1.80473	-1.28786	1.56228
H	0.60069	-1.3846	-1.2388
H	-0.21377	0.94384	-0.92522
H	-0.63282	-0.86781	1.50007
O	0.92945	1.15336	0.79836
O	2.32606	0.68228	-1.03381
O	0.37742	-2.92279	0.13807

O	-1.81788	-1.07742	-0.17611
C	-1.42505	1.6287	0.71263
H	-1.4371	1.57091	1.80459
H	-1.32171	2.67249	0.41396
O	-2.6797	1.15284	0.19681
H	-0.44959	-3.20729	-0.269
H	2.43535	1.64716	-1.12885
N	3.06641	-1.79398	-0.00742
H	2.93825	-2.79438	0.109
H	3.17403	-1.62018	-1.00296
O	1.98906	3.41259	-0.5272
H	1.42058	3.00688	0.14725
H	1.40662	3.96567	-1.0597
B	-2.82825	-0.14793	-0.21496
O	-4.03049	-0.57423	-0.70825
H	-4.69139	0.12597	-0.72954



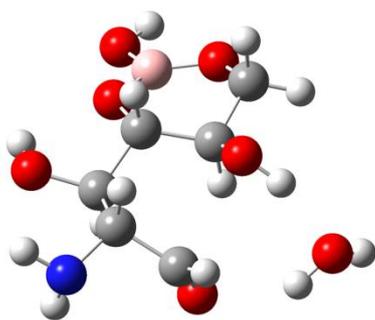
TS5

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.71449	-1.46870	-0.28972
C	2.00235	-1.17753	0.48694
C	2.43134	0.28396	0.34265
C	-0.08344	0.88387	0.01608
C	-0.42358	-0.58955	0.20979
H	3.07253	0.60179	1.17611
H	1.79985	-1.36347	1.54637
H	0.87539	-1.27063	-1.35816
H	0.11402	1.07599	-1.04418
H	-0.55214	-0.77173	1.28916
O	1.11127	1.19840	0.78387
O	2.80673	0.66885	-0.85899
O	0.39238	-2.85119	-0.10231

O	-1.60413	-0.90825	-0.48800
C	-1.24899	1.75166	0.49094
H	-1.36204	1.61616	1.57749
H	-1.03537	2.80992	0.30425
O	-2.41745	1.38416	-0.20696
H	-0.52903	-2.94628	-0.38003
H	2.70581	1.95012	-0.77184
N	3.15467	-1.99844	0.10110
H	2.90299	-2.97930	0.17810
H	3.37402	-1.82380	-0.87649
O	2.30771	2.94275	-0.32089
H	1.54010	2.20676	0.36138
H	1.83375	3.45600	-0.98540
B	-2.78787	-0.06884	-0.12404
O	-3.86617	-0.31259	-1.07451
H	-3.61454	0.03919	-1.93346



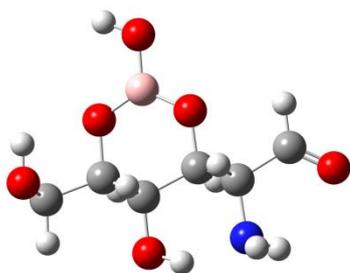
2C

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.58901	-1.42371	-0.15773
C	1.98518	-1.12462	0.42670
C	2.55470	0.22701	0.02916
C	-0.37278	0.92897	0.25495
C	-0.53405	-0.57685	0.45960
H	3.16420	0.73168	0.79386
H	1.92736	-1.16993	1.51682
H	0.60369	-1.24750	-1.24097
H	-0.19611	1.12792	-0.80945
H	-0.57720	-0.78775	1.53447
O	0.72989	1.36680	1.03888
O	2.49932	0.64851	-1.11521
O	0.34644	-2.80775	0.11016

O	-1.77174	-1.02041	-0.13492
C	-1.61845	1.67345	0.72747
H	-1.68315	1.59932	1.81703
H	-1.55243	2.72726	0.45189
O	-2.81369	1.14330	0.14511
H	-0.53410	-3.01942	-0.22368
H	2.29158	2.55816	-1.04062
N	3.04324	-2.04720	-0.00495
H	2.83062	-2.98829	0.30969
H	3.08553	-2.07327	-1.02057
O	1.91236	3.27633	-0.50284
H	1.05335	2.20768	0.65022
H	1.43113	3.84569	-1.11355
B	-2.84937	-0.17270	-0.22822
O	-4.00875	-0.69196	-0.73766
H	-4.71271	-0.03608	-0.78112



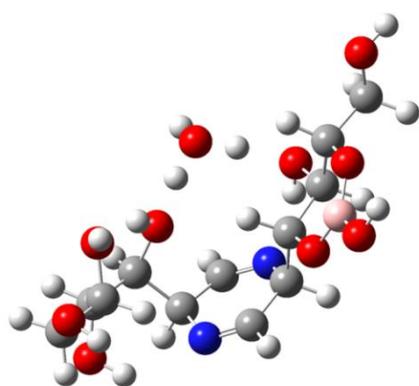
2C'

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.90746	-1.36786	-0.32459
C	-1.68114	-0.53356	-0.71904
H	-3.74149	-1.09602	-0.98995
H	-2.69934	-2.43397	-0.43562
C	-0.37243	-1.06765	-0.12762
H	-1.58895	-0.56431	-1.81911
C	0.78944	-0.15981	-0.59827
H	-0.46003	-1.02542	0.96435
H	1.13020	-0.57723	-1.55894
C	1.98079	-0.24354	0.41901
C	3.14651	0.53109	-0.12626
H	2.89608	1.54567	-0.47728
O	4.27750	0.08755	-0.21630
O	0.41558	1.17113	-0.79592
O	-0.15526	-2.41968	-0.54778

O	-3.26865	-1.12071	1.03086
O	-1.91449	0.77842	-0.25732
N	2.34560	-1.63530	0.73670
H	3.32822	-1.77326	0.50701
H	0.73662	-2.62891	-0.22468
H	-3.03668	-0.18390	1.15167
H	2.24303	-1.81295	1.72905
H	1.61389	0.30194	1.29811
B	-0.71969	1.67299	0.02358
O	-1.08491	3.03016	-0.33115
H	-1.65480	2.99146	-1.10257



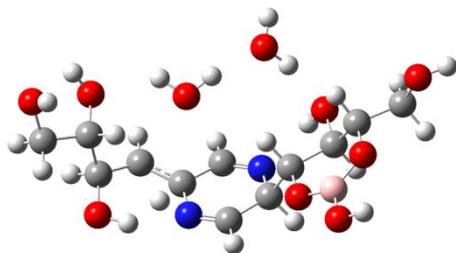
3C

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	-1.91276	-0.87369	-1.80706
C	-0.78149	-0.11660	-2.46594
N	0.43925	-0.30052	-2.20587
C	0.83454	-1.29414	-1.20981
C	-0.30056	-2.03681	-0.56204
N	-1.53269	-1.86706	-0.81264
H	-1.06114	0.63879	-3.19941
H	-0.03488	-2.77176	0.19368
C	1.71301	-0.60752	-0.13245
C	2.91775	0.13514	-0.74051
H	1.10246	0.11485	0.42125
C	3.84494	0.61874	0.37832
H	3.46738	-0.55536	-1.39383
C	5.12267	1.22037	-0.17329
H	3.32081	1.37963	0.96738
H	5.73186	0.41976	-0.60980
H	4.86222	1.93731	-0.95773

C	-2.95657	0.03450	-1.28855
C	-4.04591	-0.42722	-0.38901
H	-3.19341	0.90821	-1.88263
C	-4.27829	0.56872	0.77409
H	-4.91795	-0.32771	-1.06761
C	-5.54384	0.25237	1.56066
H	-3.41263	0.47965	1.43953
H	-6.41430	0.28176	0.90164
H	-5.46873	-0.73696	2.01520
O	2.13659	-1.63703	0.75474
O	2.50158	1.28611	-1.47385
H	1.85587	0.96799	-2.13702
O	5.81048	1.86409	0.90157
H	6.63871	2.22039	0.56330
O	4.18505	-0.47104	1.25018
O	-4.00656	-1.73698	0.10199
H	-3.10119	-2.10200	-0.03331
O	-4.33816	1.87840	0.21199
H	-4.78578	2.44688	0.85568
O	-5.73954	1.28126	2.53442
H	-5.14643	1.12891	3.27977
O	-1.71349	1.38293	-0.13559
H	-2.38624	2.06645	0.03713
H	1.47728	-2.02837	-1.71060
H	-2.47013	-1.39101	-2.61856
H	-0.86535	1.84865	-0.33112
O	0.73776	2.85422	-0.01022
H	0.71472	3.79188	-0.23164
H	1.46436	2.46802	-0.54021
B	3.33126	-1.52324	1.42394
O	3.64402	-2.53962	2.27986
H	4.49353	-2.41041	2.71509



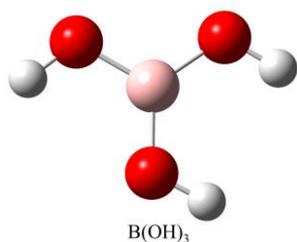
TS6

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	-1.61316	1.63325	0.78498
C	-0.44077	1.64863	1.71451
N	0.73685	1.82883	1.29265
C	0.97720	2.02290	-0.12911
C	-0.25147	2.30200	-0.93435
N	-1.45030	2.13184	-0.52420
H	-0.62115	1.48151	2.77300
H	-0.11606	2.67597	-1.94419
C	1.73816	0.79169	-0.71628
C	3.09550	0.55945	-0.01206
H	1.10641	-0.09321	-0.56973
C	3.84636	-0.64173	-0.59706
H	3.71212	1.45847	-0.13494
C	5.16173	-0.91136	0.11772
H	3.20983	-1.53225	-0.51593
H	5.79062	-0.01553	0.08334
H	4.97933	-1.18694	1.15819
C	-2.71840	0.81131	1.06872
C	-3.87970	0.55091	0.16906
H	-2.75450	0.37077	2.05894
C	-3.75353	-0.91541	-0.35065
H	-4.78084	0.58950	0.79104
C	-5.01282	-1.30011	-1.13098
H	-2.87566	-0.97592	-1.00387
H	-5.89754	-1.10869	-0.52055
H	-5.08064	-0.72400	-2.05398
O	1.91692	1.06680	-2.10166
O	2.92302	0.26718	1.37775
H	2.32035	0.94090	1.74854
O	5.77674	-1.98815	-0.60173
H	6.70857	-2.03248	-0.36478
O	4.08998	-0.36036	-1.98400
O	-4.05251	1.44906	-0.89502
H	-3.18180	1.79105	-1.17791
O	-3.58676	-1.77935	0.76987
H	-3.92385	-2.64742	0.49945
O	-4.99591	-2.70652	-1.37712
H	-4.42329	-2.88954	-2.13162
O	-0.84179	-1.20502	0.84613
H	-1.59822	-1.78916	1.00248
H	1.65029	2.88065	-0.24072

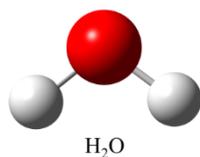
H	-2.53484	2.26143	1.39112
H	-0.08645	-1.57299	1.34832
O	1.50182	-2.06045	2.06979
H	1.54291	-2.22574	3.01806
H	2.08631	-1.29200	1.90703
B	2.96512	0.25441	-2.40737
O	3.35042	0.69127	-3.72430
H	3.41829	-0.06868	-4.30694



Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

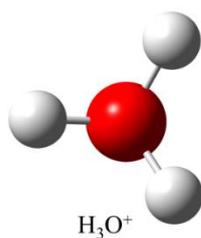
B	-1.68860	-1.69591	0.00000
O	-2.45860	-0.36223	0.00000
O	-0.14860	-1.69591	0.00000
O	-2.45860	-3.02959	0.00000
H	0.17140	-0.79081	0.00000
H	-1.83476	0.36745	0.00000
H	-1.83476	-3.75926	0.00000



Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

O	0.00000	0.00000	0.11797
H	0.00000	0.76212	-0.47188
H	0.00000	-0.76212	-0.47188

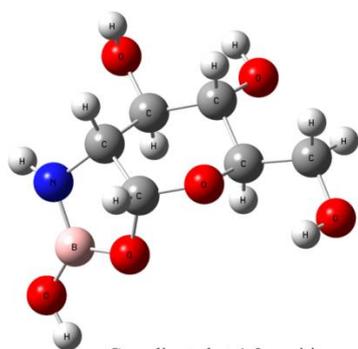


Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

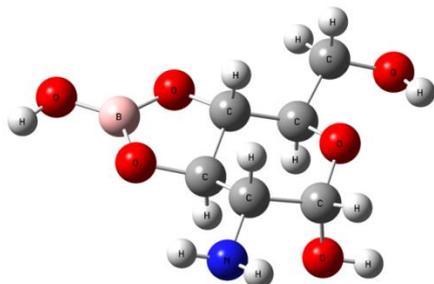
H	-0.89570	0.24997	0.22221
O	-0.00002	0.00002	-0.08331
H	0.66462	0.65008	0.22216
H	0.23124	-0.90020	0.22213

Figure S11. Optimized structures of reactants and products for the dehydration processes.



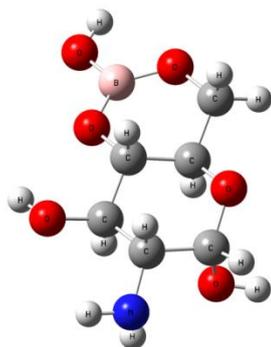
Coordinated at 1,2 positions

Free Energies = -767.043563 (Hartree/Particle)



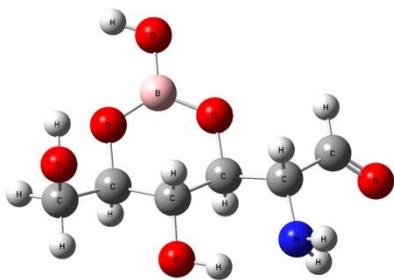
Coordinated at 3,4 positions

Free Energies = -767.040931 (Hartree/Particle)



Coordinated at 4,6 positions

Free Energies = -767.057976 (Hartree/Particle)



Coordinated at 3,5 positions

Free Energies = -767.061252 (Hartree/Particle)

Figure S12. Optimized structures of possible boron complexes.

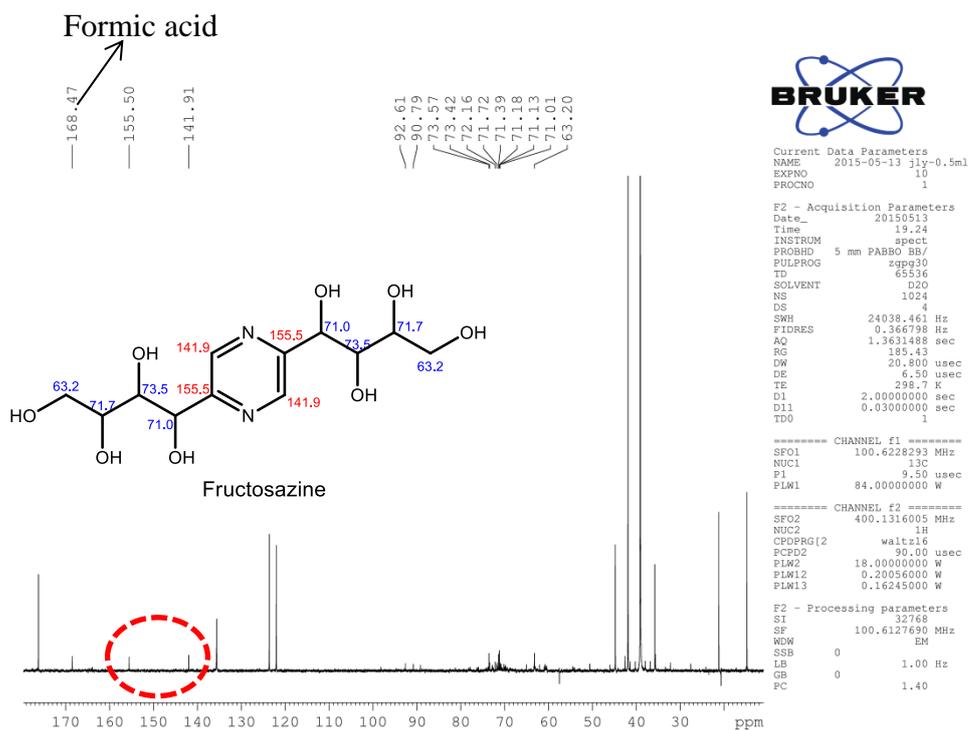


Figure S13. ^{13}C NMR spectrum for the condensation of GlcNH_2 catalyzed by $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ in DMSO in the presence of 0.5 ml H_2O_2 . Reaction condition: 90.0 mg of GlcNH_2 and 85.5 mg of $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ in 1 ml DMSO at 80°C for 180 min. Note: The low field signals of FZ are labeled with a red ellipse; peak at 168.4 ppm was assigned to the formation of formic acid as the main side-product.

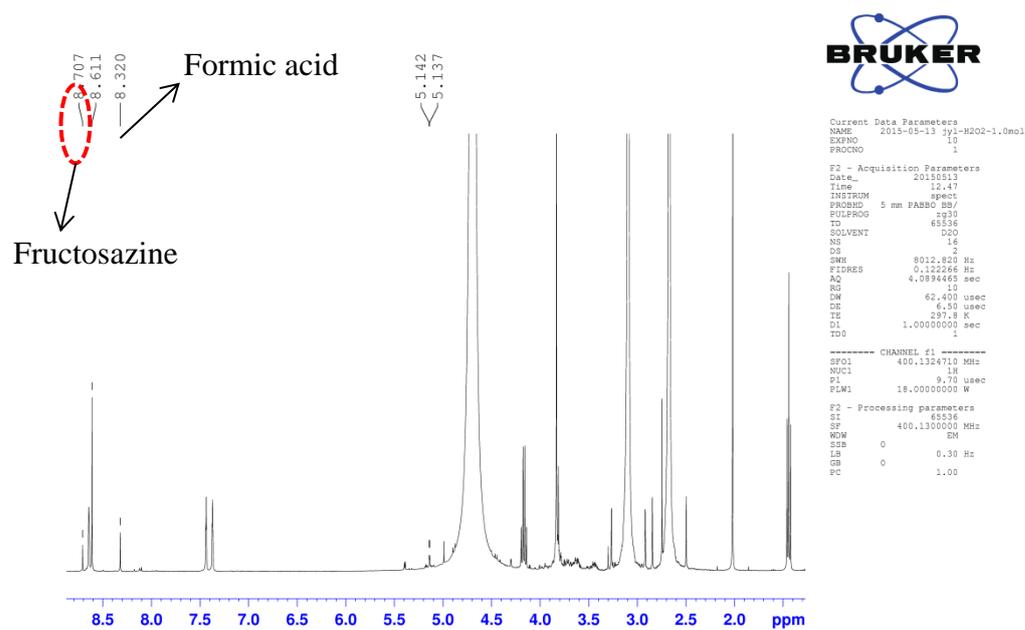


Figure S14. ^1H NMR spectrum for the condensation of GlcNH_2 catalyzed by $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ in DMSO in the presence of 1 ml H_2O_2 . Reaction condition: 89.5 mg of GlcNH_2 and 85.4 mg of $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ in 1 ml DMSO at 80°C for 180 min. Note: peak at 8.6 ppm was assigned to the signal of internal standard pyrazine.

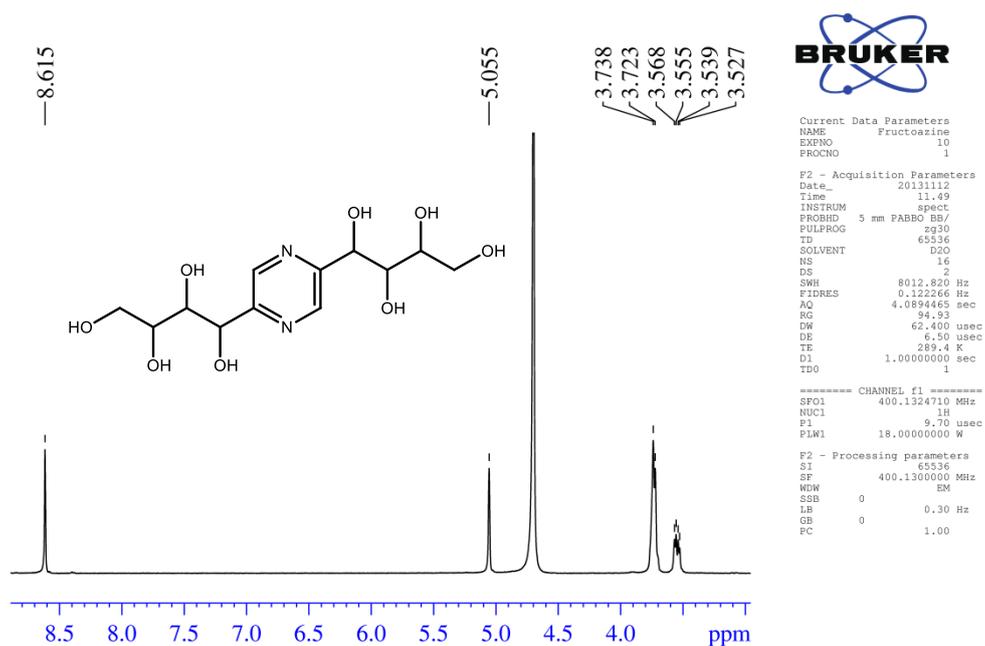
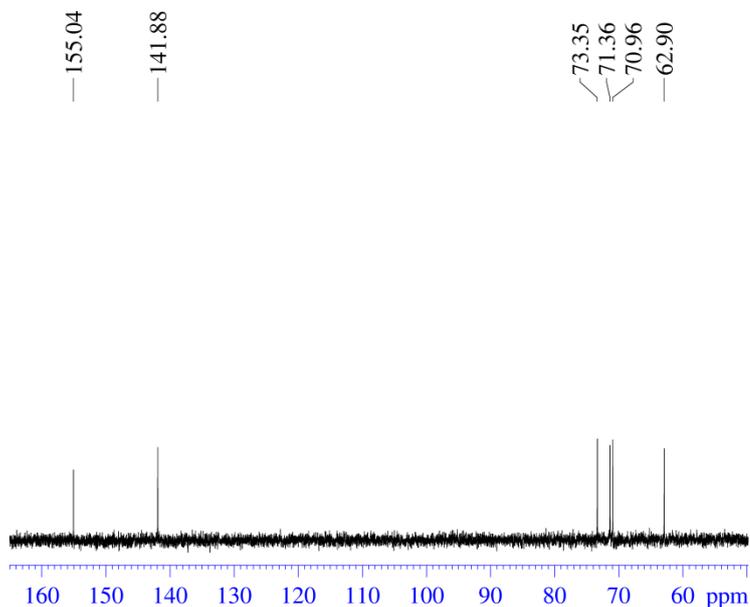


Figure S15. The ¹H NMR spectrum of FZ. Note: The changes of the chemical shifts (ppm) of protons of the FZ may be due to recrystallization leading to different chemical environments.



```

Current Data Parameters
NAME      Fructoazine
EXPNO    13
PROCNO   1

F2 - Acquisition Parameters
Date_    20131112
Time     21.30
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg30
TD       65536
SOLVENT  D2O
NS       1036
DS       4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.3631488 sec
RG       137.42
DM       20.800 usec
DE       6.50 usec
TE       290.7 K
D1       2.0000000 sec
D11      0.0300000 sec
TDO      1

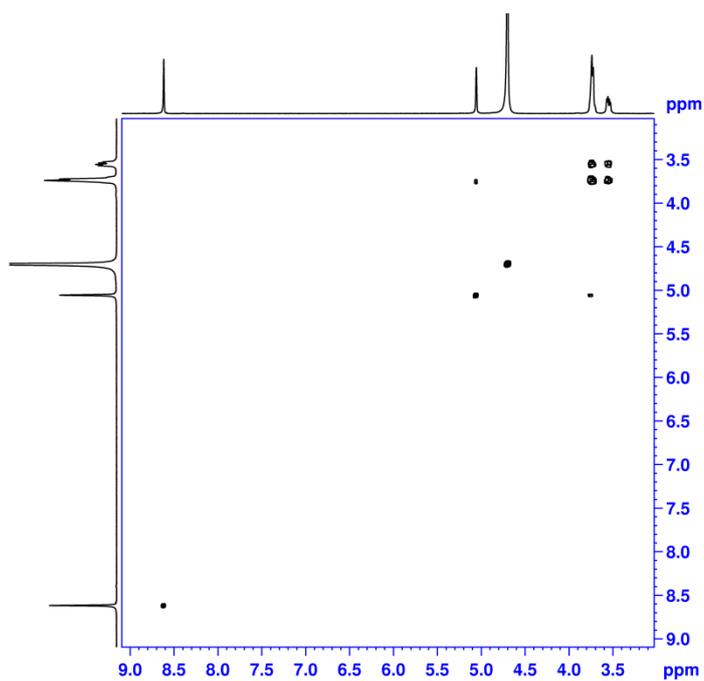
***** CHANNEL f1 *****
SFO1     100.6228293 MHz
NUC1     13C
P1       9.50 usec
PLW1     84.0000000 W

***** CHANNEL f2 *****
SFO2     400.1316005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2     18.0000000 W
PLW12    0.20045000 W
PLW13    0.16245000 W

F2 - Processing parameters
SI       32768
SF       100.6127690 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40

```

Figure S16. The ^{13}C NMR spectrum of FZ. Note: The changes of the chemical shifts (ppm) of carbons of the FZ may be due to recrystallization leading to different chemical environments.



```

Current Data Parameters
NAME      Fructoazine
EXPNO    11
PROCNO   1

F2 - Acquisition Parameters
Date_    20111112
Time     11:50
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  cosygpgpgc
TD        65536
SOLVENT  D2O
NS        1
DS        4
SWH       2427.185 Hz
FIDRES   1.185149 Hz
AQ        0.4218860 sec
RG        60.71
RW        206.000 usec
DE        6.50 usec
TE        299.4 K
D0        0.00000000 sec
D1        1.74980495 sec
D11       0.03000000 sec
D12       0.00000000 sec
D13       0.00000000 sec
D16       0.00020000 sec
TNO       0.00041200 sec

----- CHANNEL f1 -----
SFO1     400.1324258 MHz
NUC1     1H
P0        9.70 usec
P1        9.70 usec
P17       2500.00 usec
PLM1     18.0000000 W
PLM10    2.00539994 W

----- GRADIENT CHANNEL -----
GPMAM11  SMSQ10.100
GFA1     10.00 %
P16      1000.00 usec

F1 - Acquisition parameters
TD        65536
SFO1     400.1324 MHz
FIDRES   18.962379 Hz
SW        6.066 ppm
PRMODE   QF

F2 - Processing parameters
SI        1024
SF        400.1300000 MHz
WDW       QSI3NE
SSB       0
LB        0 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
SF        400.1300000 MHz
WDW       QSI3NE
SSB       0
LB        0 Hz
GB        0

```

Figure S17. The ^1H - ^1H COSY spectrum of FZ.

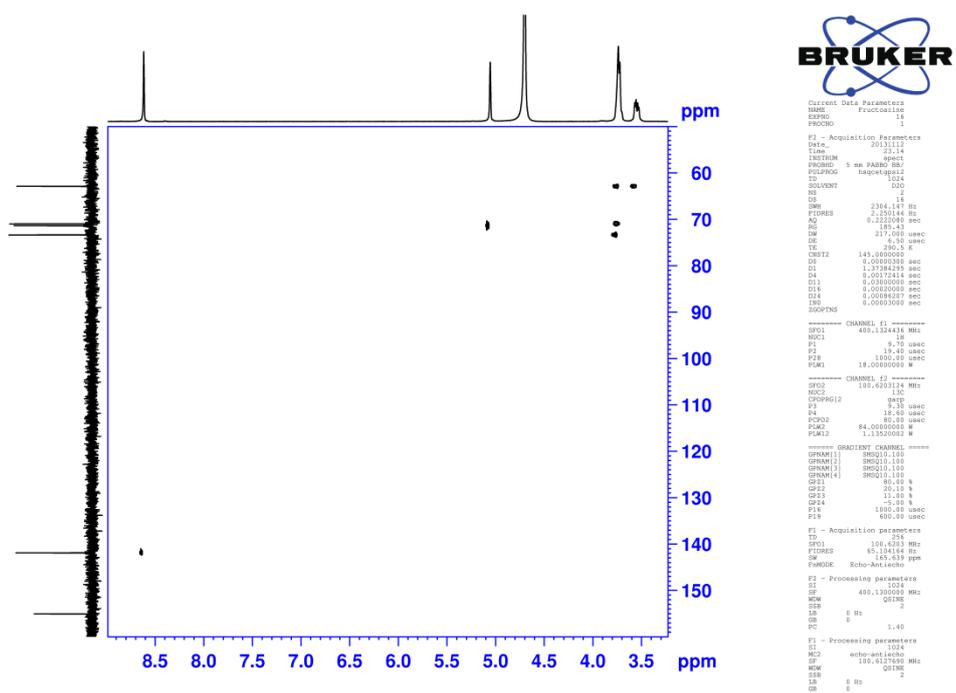


Figure S18. The ^1H - ^{13}C HSQC spectrum of FZ.