Electronic Supplementary Information for

Glucosamine condensation catalyzed by 1-ethyl-3-methylimidazolium acetate: mechanistic insight from NMR spectroscopy

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Supporting Figures and Tables

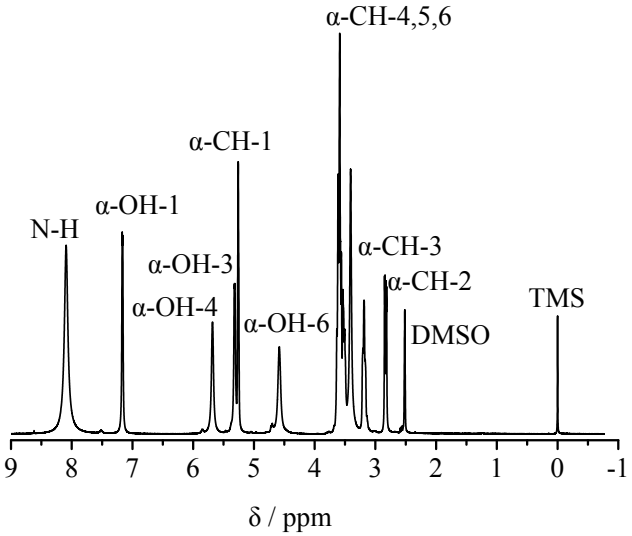

Figure S1 The ^{1}H NMR spectra of pure **GlcNH$_2$** in DMSO-d$_6$ solution.

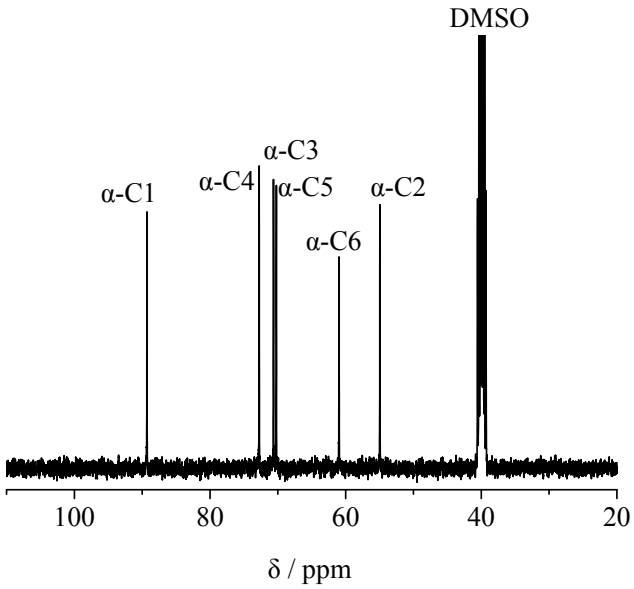

Figure S2 The ^{13}C NMR spectra of pure **GlcNH$_2$** in DMSO-d$_6$ solution.

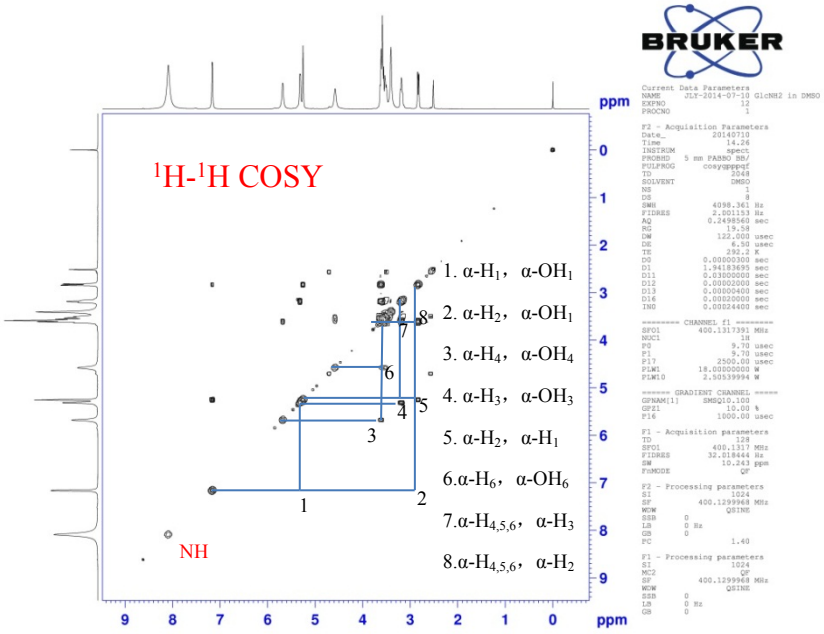

Figure S3 The ^{1}H-^{1}H COSY spectrum of **GlcNH$_2$** in DMSO-d$_6$ at room temperature.

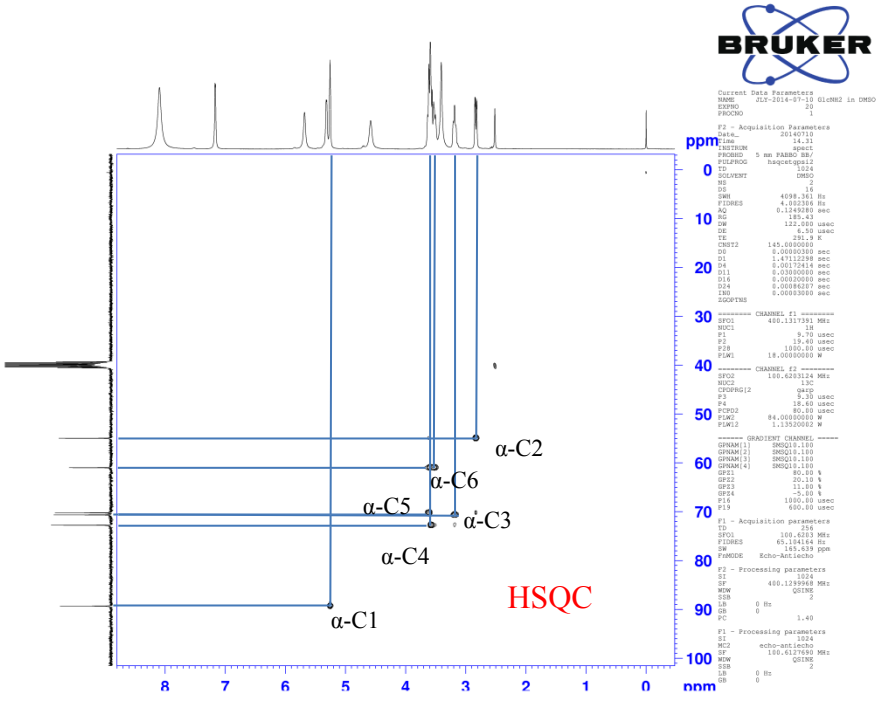

Figure S4 The HSQC spectrum of **GlcNH$_2$** in DMSO-d$_6$ at room temperature.

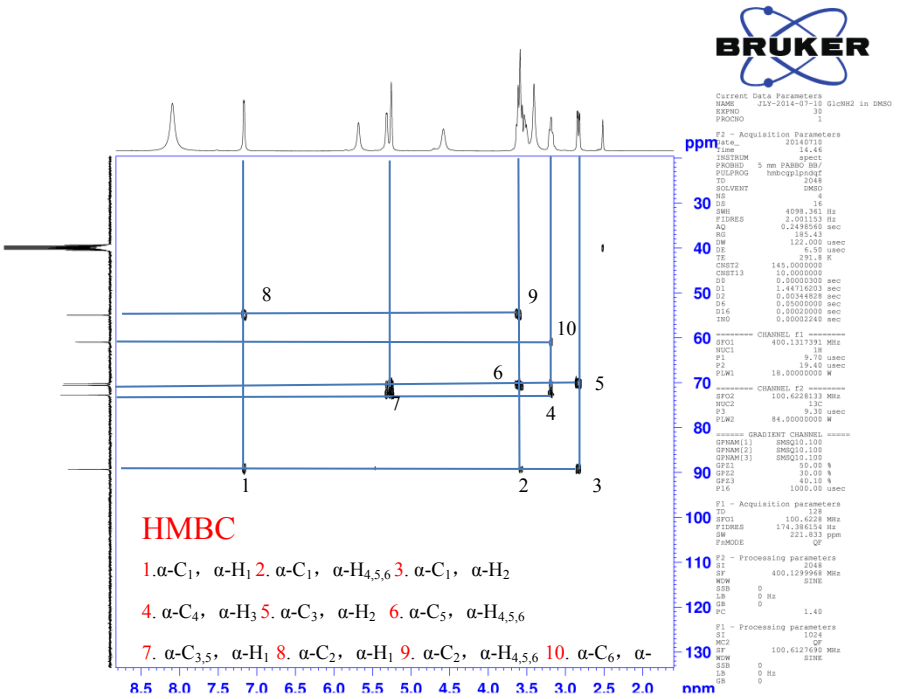

Figure S5 The HMBC spectrum of **$GlcNH_2$** in DMSO-d_6 at room temperature.

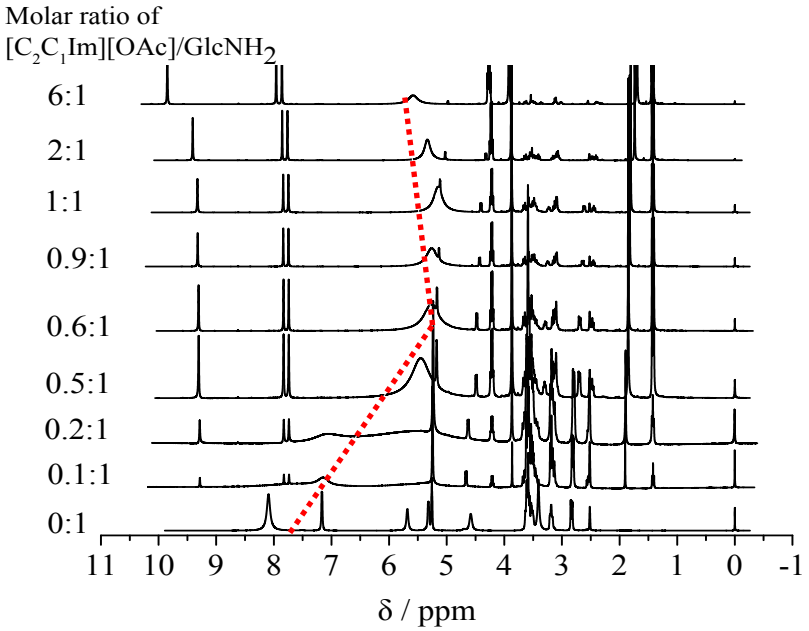

Figure S6 The effect of molar ratios of $[C_2C_1Im][OAc]/GlcNH_2$ on the ^{1}HNMR spectra for $GlcNH_2$ in DMSO-d_6 solution.

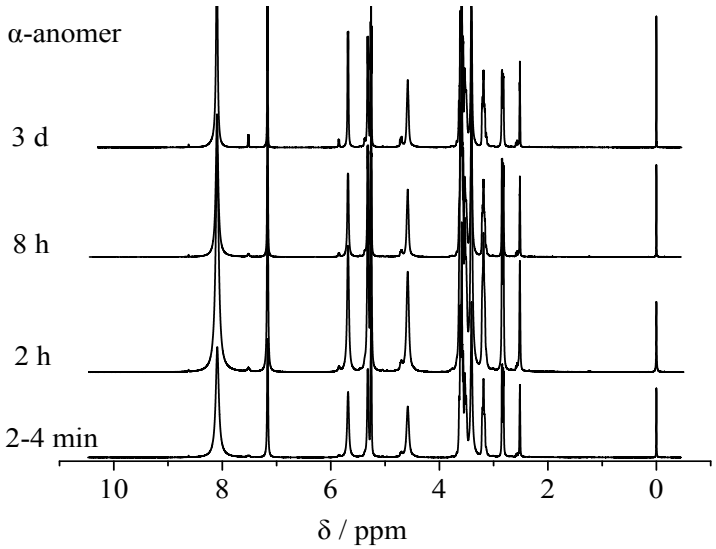

Figure S7 A time progression in ^{1}H NMR spectra of $GlcNH_2$ in DMSO-d_6.

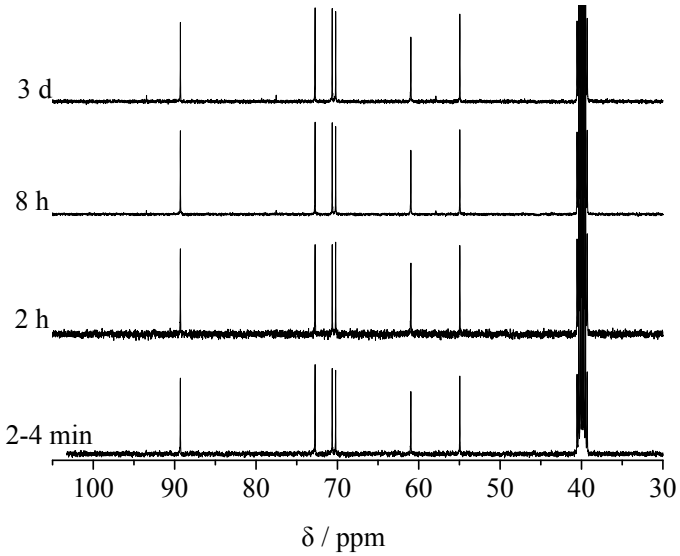

Figure S8 A time progression in ^{13}C NMR spectra of $GlcNH_2$ in DMSO-d_6.

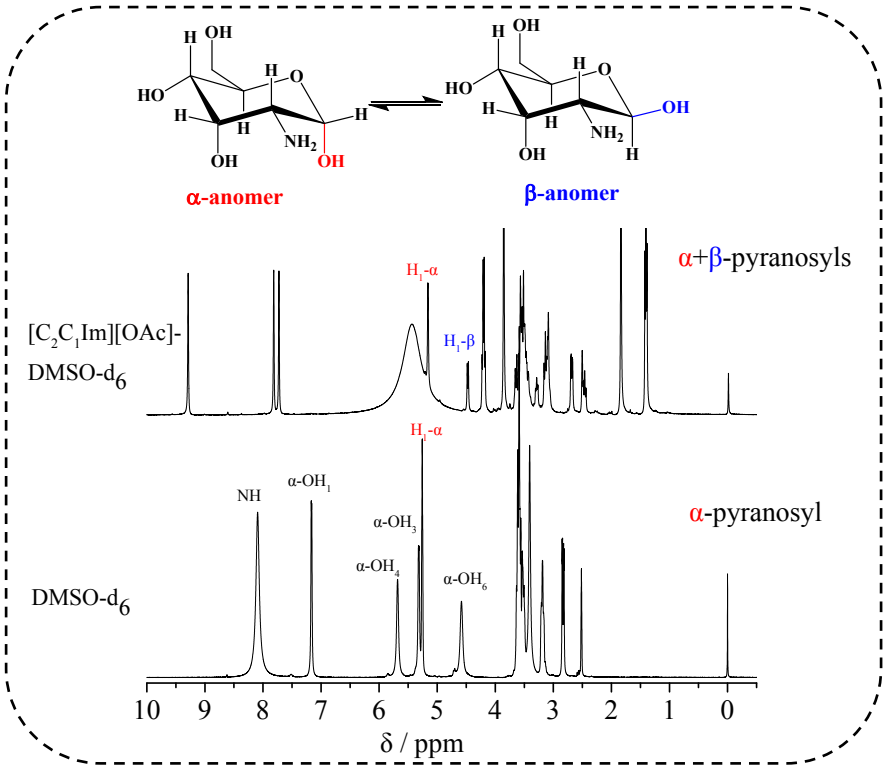

Figure S9 An equilibrium mixture of anomers with 0.5 equivalent of $[C_2C_1Im][OAc]$.

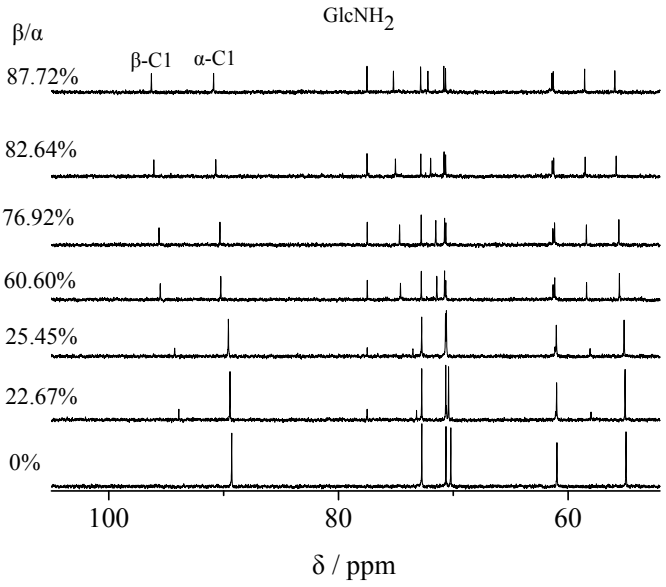

Figure S10 The changes of β/α anomeric composition of $GlcNH_2$ in an enlarged format calculated according to the integral area of β-H1/α-H2 in the ^1H NMR spectra (molar ratio of $[C_2C_1Im][OAc]/GlcNH_2$ = 0:1, 0.1:1, 0.2:1, 0.5:1, 0.6:1, 0.9:1, 1:1 from below to top).

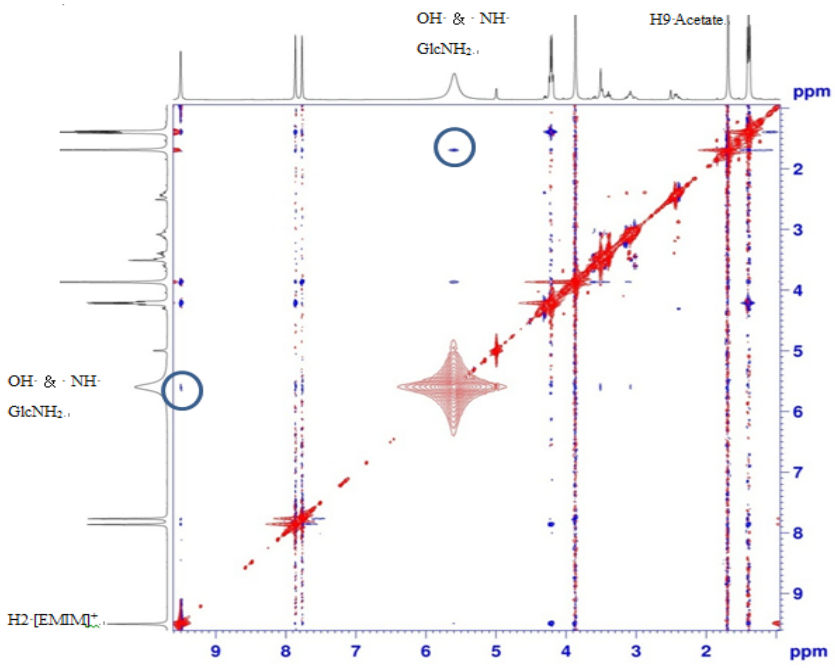

Figure S11 NOESY spectrum of 5:2 (molar ratio) mixture of $[C_2C_1Im][OAc]$-$GlcNH_2$ in DMSO-d_6. The mixing time employed was 500 ms.

Table S1 Changes in ^{13}C chemical shifts (Δδ) for pyranose tautomers of $GlcNH_2$ (α- and β-anomers) with different molar ratio of $[C_2C_1Im][OAc]$ in DMSO-d_6 ionic liquid $[C_2C_1Im][OAc]$ solutions.

entry	α-C1/Δδ	α-C2/Δδ	α-C3/Δδ	α-C4/Δδ	α-C5/Δδ	α-C6/Δδ
0:1 (δ_0)	89.3	54.9	70.2	72.7	70.6	60.9
0.1:1 (δ_1)	89.4/0.1	55.0/0.1	70.4/0.2	72.7/0	70.7/0.1	61.0/0.1
0.2:1 (δ_2)	89.6/0.3	55.1/0.2	70.6/0.4	72.8/0.1	70.7/0.1	61.0/0.1
0.5:1 (δ_3)	90.2/0.9	55.5/0.6	70.7/0.5	72.8/0.1	70.8/0.2	61.2/0.3
0.6:1 (δ_4)	90.3/1.0	55.6/0.6	70.7/0.4	72.8/0.1	70.8/0.2	61.2/0.3
0.9:1 (δ_5)	90.7/1.4	55.8/0.8	70.7/0.4	72.8/0.1	70.8/0.2	61.3/0.4
1:1 (δ_6)	90.9/1.6	55.9/0.9	70.7/0.5	72.8/0.1	70.8/0.2	61.3/0.4
2:1 (δ_7)	91.8/2.5	56.5/1.6	70.7/0.5	73.33/0.6	70.9/0.3	61.5/0.6
6:1 (δ_8)	92.4/3.1	57.1/2.2	70.8/0.6	74.3/1.6	71.1/0.4	61.5/0.6

entry	β-C1/Δδ	β-C2/Δδ	β-C3/Δδ	β-C4/Δδ	β-C5/Δδ	β-C6/Δδ
0:1(δ_0)	93.5	57.9	70.6	77.5	72.7	60.9
0.1:1 (δ_1)	93.9/0.4	58.0/0.1	70.6/0	77.6/0.1	73.2/0.5	61.1/0.2
0.2:1 (δ_2)	94.3/0.8	58.1/0.2	70.7/0.1	77.5/0	73.5/0.8	61.1/0.2
0.5:1 (δ_3)	95.5/2.0	58.4/0.5	71.4/0.8	77.5/0	74.6/1.9	61.3/0.4
0.6:1 (δ_4)	95.6/2.1	58.4/0.5	71.5/0.9	77.5/0	74.7/2.0	61.3/0.4
0.9:1 (δ_5)	96.1/2.6	58.5/0.6	71.9/1.3	77.5/0	75.0/2.3	61.4/0.5
1:1 (δ_6)	96.3/2.8	58.6/0.7	72.2/1.6	77.5/0	75.2/2.5	61.4/0.5
2:1 (δ_7)	97.1/3.6	58.8/0.9	72.9/2.3	77.6/0.1	75.8/3.1	61.5/0.6
6:1 (δ_8)	97.9/4.4	58.9/1.0	73.1/2.5	77.9/0.4	76.4/3.7	61.5/0.6

[a] ^{13}C Chemical Shifts (ppm) of $GlcNH_2$ and Δδ values (ppm) were obtained by comparing with the chemical shift of $GlcNH_2$ in DMSO-d_6 with TMS as internal standard.

Table S2. ^{1}H Chemical Shifts for the ionic liquid $[C_2C_1Im][OAc]$ and Changes in ^{1}H NMR Chemical Shifts (Δδ) of Each Carbon with Different Molar Ratio of $GlcNH_2$.

entry	H_2/Δδ	H_5/Δδ	H_4/Δδ	H_7/Δδ	H_6/Δδ	H_9/Δδ	H_8/Δδ
0:1	9.87	7.85	7.76	4.22	3.88	1.58	1.41
0.1:1	9.74/-0.13	7.85/0	7.76/0	4.21/-0.01	3.87/-0.01	1.62/0.04	1.41/0
0.2:1	9.59/-0.28	7.84/-0.01	7.75/-0.01	4.22/0	3.87/-0.01	1.65/0.07	1.41/0
0.3:1	9.46/-0.41	7.83/-0.02	7.74/-0.02	4.21/-0.01	3.86/-0.02	1.68/0.1	1.42/0.1
0.5:1	9.37/-0.5	7.83/-0.02	7.74/-0.02	4.22/0	3.87/-0.01	1.73/0.15	1.42/0.1

[a] ^{1}H Chemical Shifts (ppm) of $[C_2C_1Im][OAc]$ were referenced to TMS as internal standard. [b] Δδ values (ppm) were obtained by comparing with the chemical shift of $[C_2C_1Im][OAc]$ in DMSO-d_6. [c] The chemical shifts and Δδ values (ppm) of H_5, H_4, H_7, H_8 were the average values.

Table S3. ^{13}C Chemical Shifts for the ionic liquid $[C_2C_1Im][OAc]$ and Changes in ^{13}C NMR Chemical Shifts (Δδ) of Each Carbon with Different $GlcNH_2$ Concentrations.

entry	C_{10}/Δδ	C_2/Δδ	C_4/Δδ	C_5/Δδ	C_7/Δδ	C_6/Δδ	C_9/Δδ	C_8/Δδ
0:1	173.5	137.7	123.9	122.3	44.4	35.9	26.4	15.6
0.1:1	173.8/0.3	137.5/-0.2	123.9/0	122.3/0	44.4/0	36.0/0.1	25.9/-0.5	15.6/0
0.2:1	173.9/0.4	137.3/-0.4	123.9/0	122.3/0	44.5/0.1	36.0/0.1	25.3/-1.1	15.6/0
0.3:1	174.1/0.6	137.1/-0.6	123.9/0	122.4/0.1	44.5/0.1	36.1/0.2	24.9/-1.5	15.6/0
0.5:1	174.2/0.7	136.9/-0.8	124.0/0.1	122.4/0.1	44.5/0.1	36.1/0.2	24.2/-2.2	15.6/0

[a] ^{13}C Chemical Shifts (ppm) of $[C_2C_1Im][OAc]$ and Δδ values (ppm) were obtained by comparing with the chemical shift of $[C_2C_1Im][OAc]$ in DMSO-d_6 with TMS as internal standard.

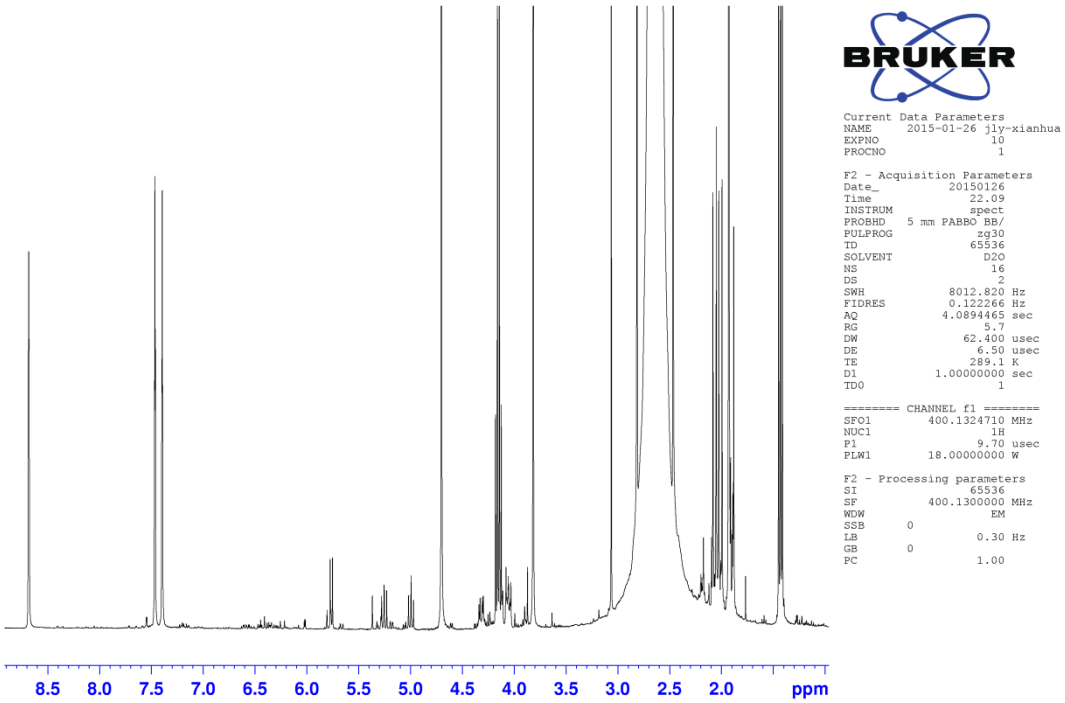

Figure S12 The D-glucosamine pentaacetate conversion in the presence of $[C_2C_1Im][OAc]$ at 80°C for 2 h. Reaction conditions: 97.5 mg D-glucosamine pentaacetate (0.25 mmol), 85.1 mg $[C_2C_1Im][OAc]$ (0.5 mmol), 2 ml DMSO

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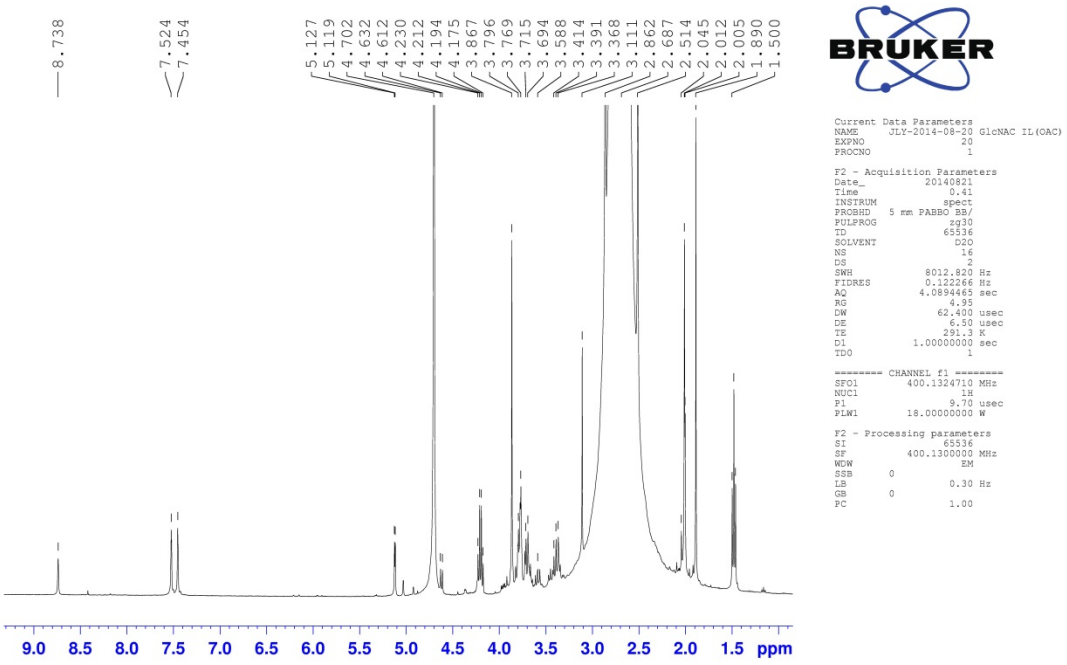


Figure S13 The direct conversion of N-acetyl-D-glucosamine in the presence of $[C_2C_1Im][OAc]$ at 80°C for 3 h. Reaction conditions: 20.1 mg N-acetyl-D-glucosamine (0.09 mmol), 10.1 mg $[C_2C_1Im][OAc]$ (0.06 mmol), 1 ml DMSO.

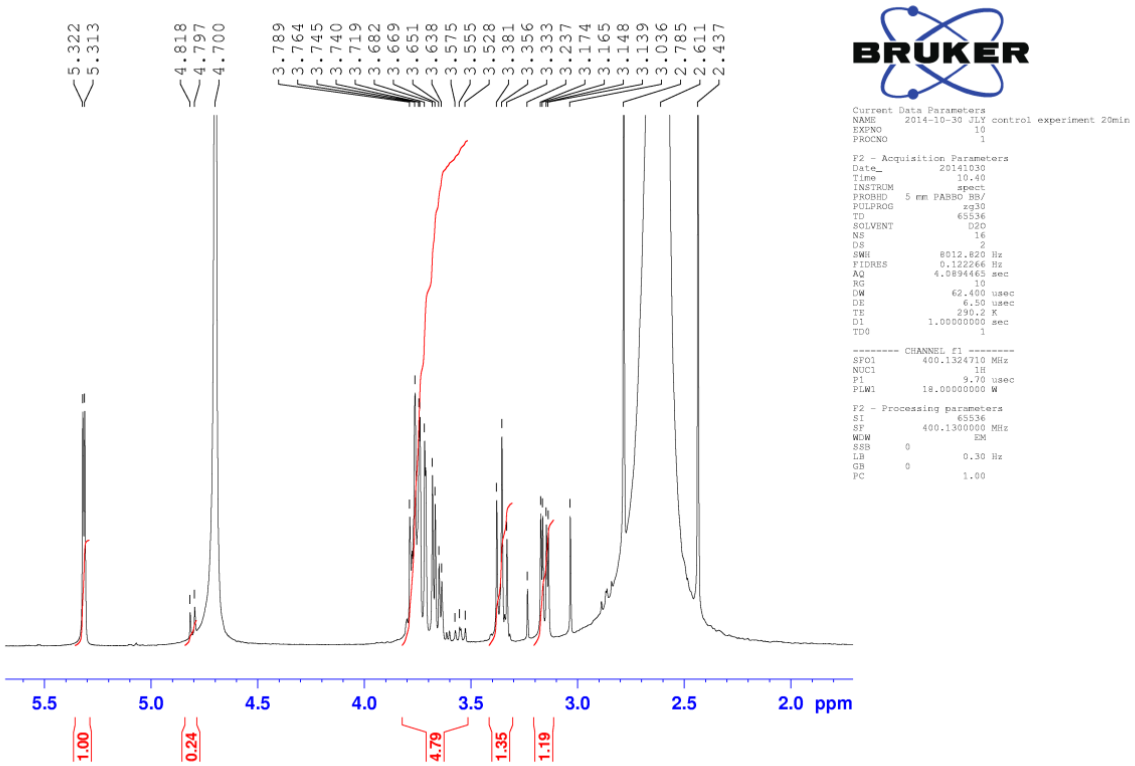


Figure S14 The blank experiment of $GlcNH_2$ conversion in the absence of $[C_2C_1Im][OAc]$ at 80 °C for 20 min as an example. Reaction conditions: 179.2 mg $GlcNH_2$, without $[C_2C_1Im][OAc]$, 2 ml DMSO at 80 °C for 20, 60, and 120 min, respectively.

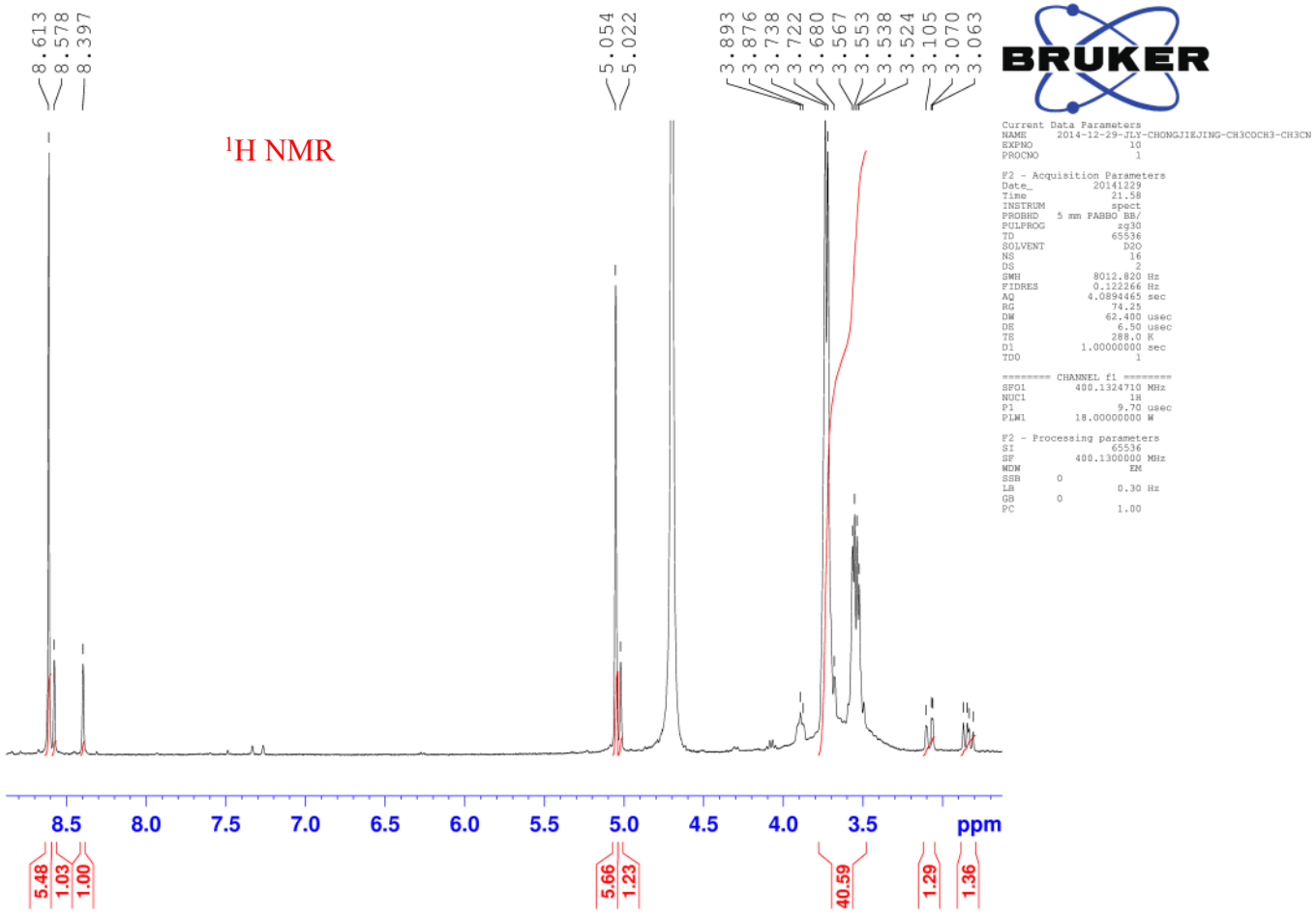


Figure S15 The ^{1}H NMR spectrum of DOF and FZ.

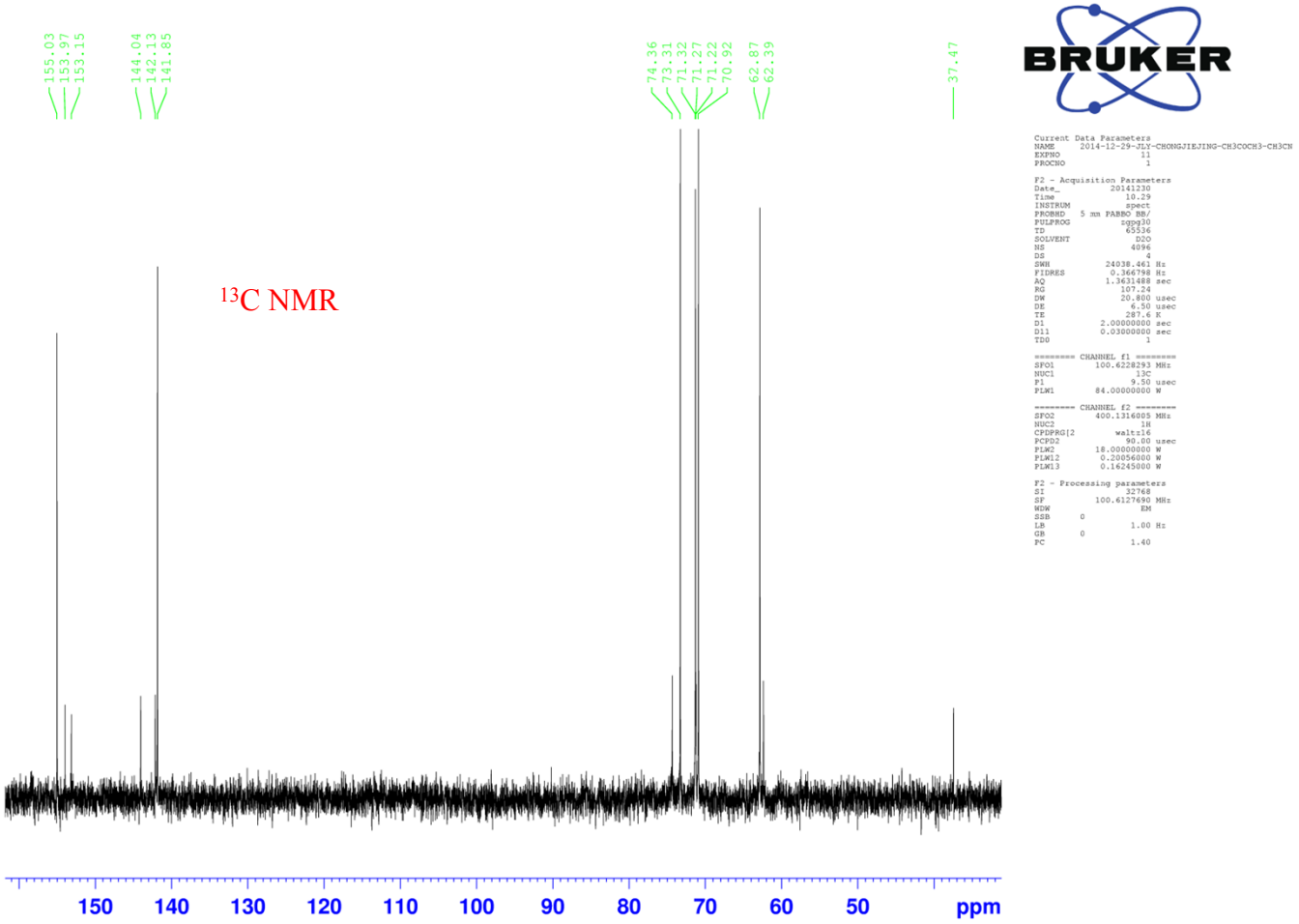


Figure S16 The ^{13}C NMR spectrum of DOF and FZ.

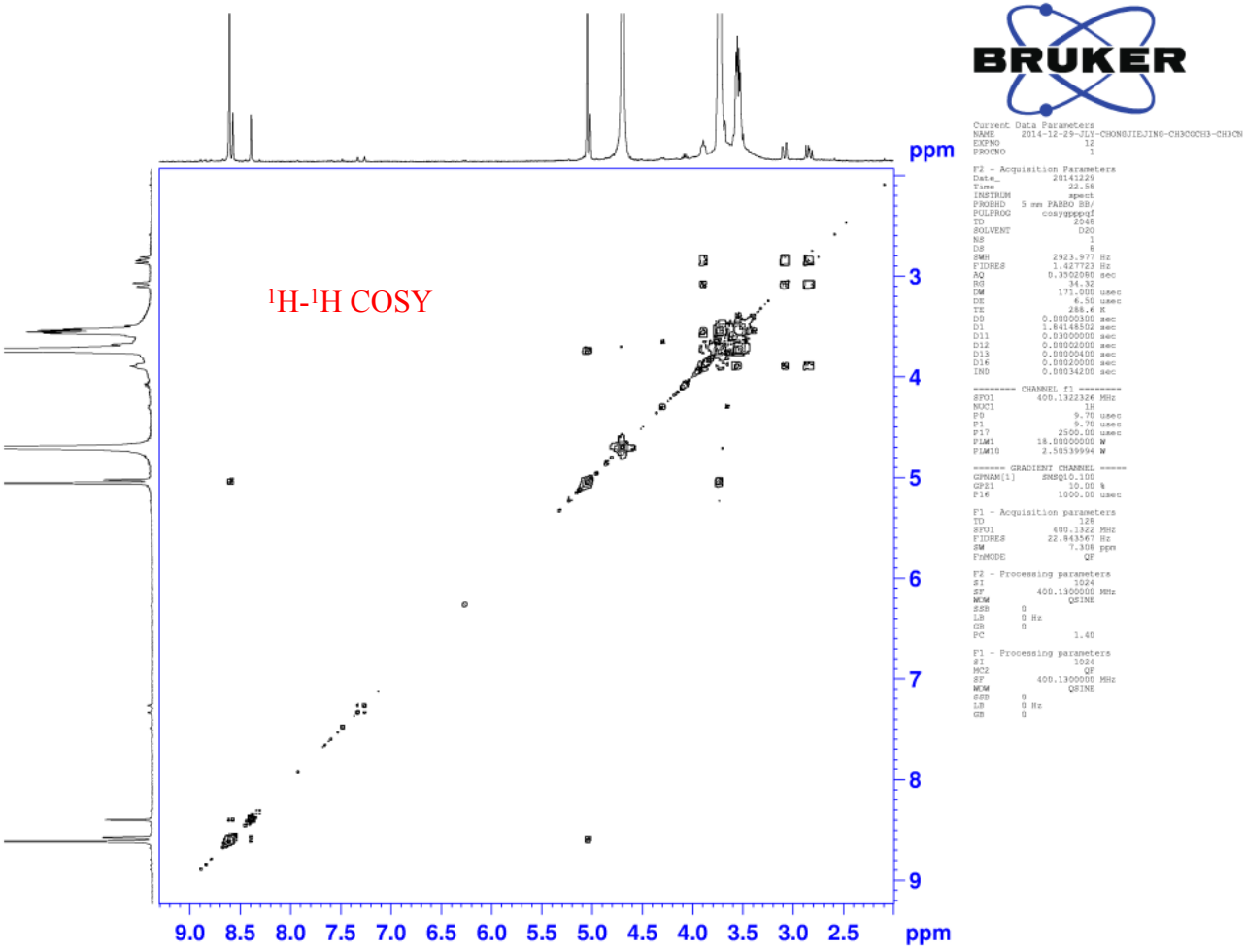


Figure S17 The ^{1}H-^{1}H COSY spectrum of DOF and **FZ**.

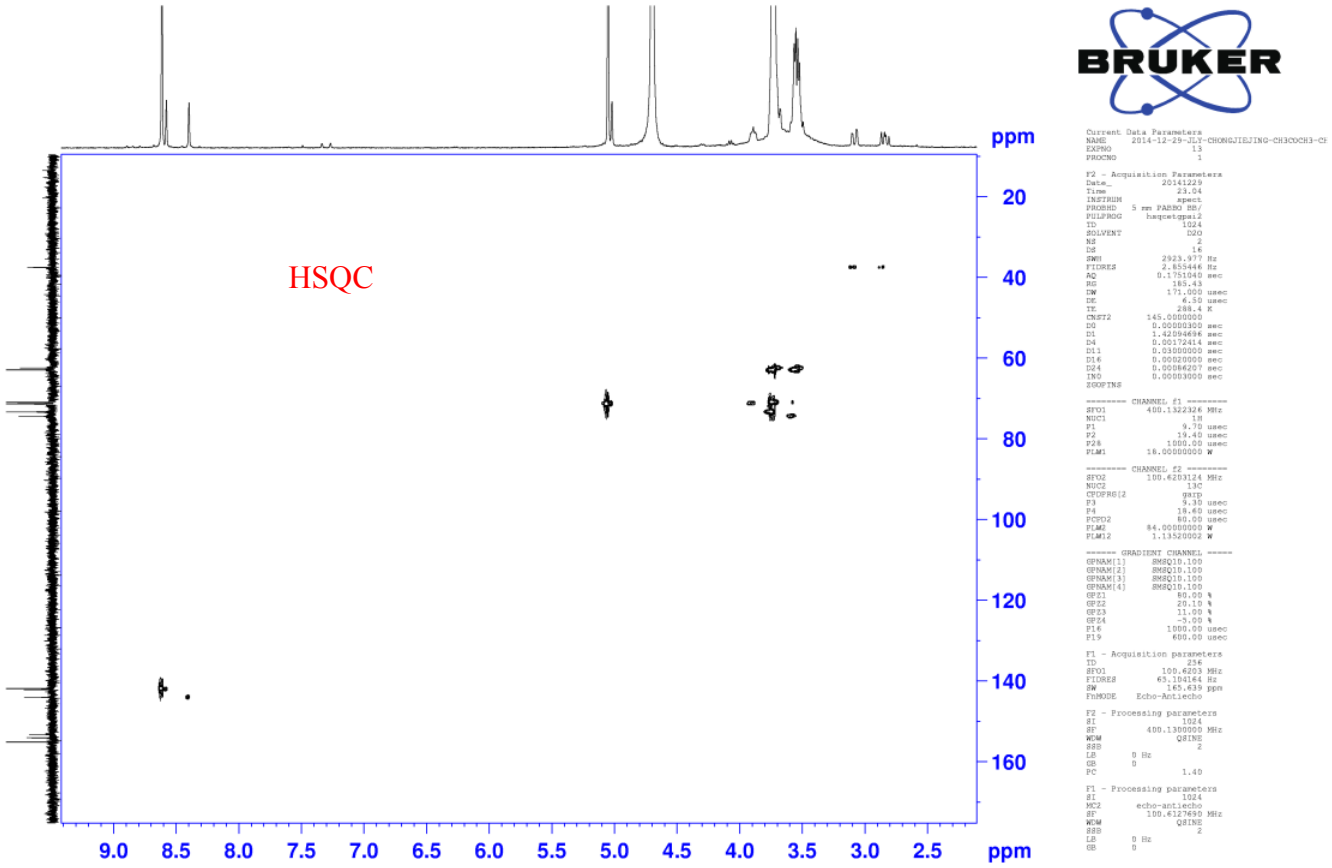


Figure S18 The HSQC spectrum of DOF and FZ.

NMR data:

Fructosazine:

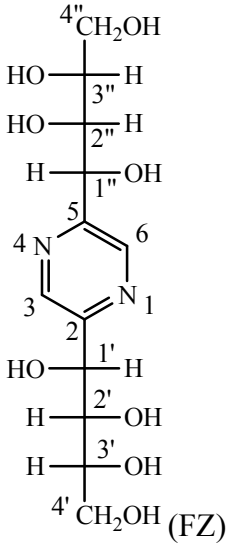
δ_H (400.13 MHz; DMSO-d_6; Me_4Si) 8.6 (2H, s, pyrazine ring protons), 5.1 [2 H, d, C(1' and 1")-H], 3.9-3.8 [2 H, m, C(2' and 2")-H], 3.9-3.8 [2 H, m, C(3' and 3")-H] and 3.9-3.5 [4 H, m, C(4' and 4")-H].

δ_C (100.6 MHz; DMSO-d_6; Me_4Si); 155.03 (C2 and C5), 141.85 (C3 and C6), 73.31 (C2' and C2"), 71.32 (C1' and C1"), 70.92 (C3' and C3"), 62.87 (C4' and C4").

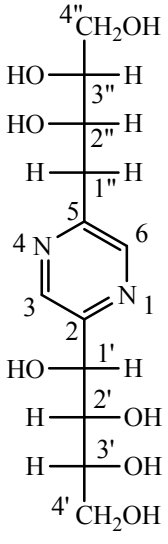
Deoxyfructosazine:

δ_H (400.13 MHz; DMSO-d_6; Me_4Si) 8.57 [1 H, d, pyrazine ring C(3)-H], 8.39 [1 H, d, pyrazine ring C(6)-H], 5.02 [1 H, d, C(1')-H], 3.10-2.81 [2 H, m, C(1")-methylene H], 3.9-3.5-4.03 [1 H, m, C(2")-H], 3.9-3.7 [1 H, m, C(2')-H], 3.9-3.7 [1 H, m, C(3')-H], 3.7-3.6 [1 H, m, C(3")-H], 3.9-3.5 [4 H, m, C(4'and 4")-H].

δ_C (100.6 MHz; DMSO-d_6; Me_4Si); 153.97 and 153.14 (C2 and C5), 142.13 and 144.04 (C3 and C6), 74.36 (C3"), 73.31 (C2'), 71.32 (C1'), 71.27 (C2"), 71.22 (C3') 62.39 (C4' and C4"), 37.47 (C1").



(FZ)



(DOF)

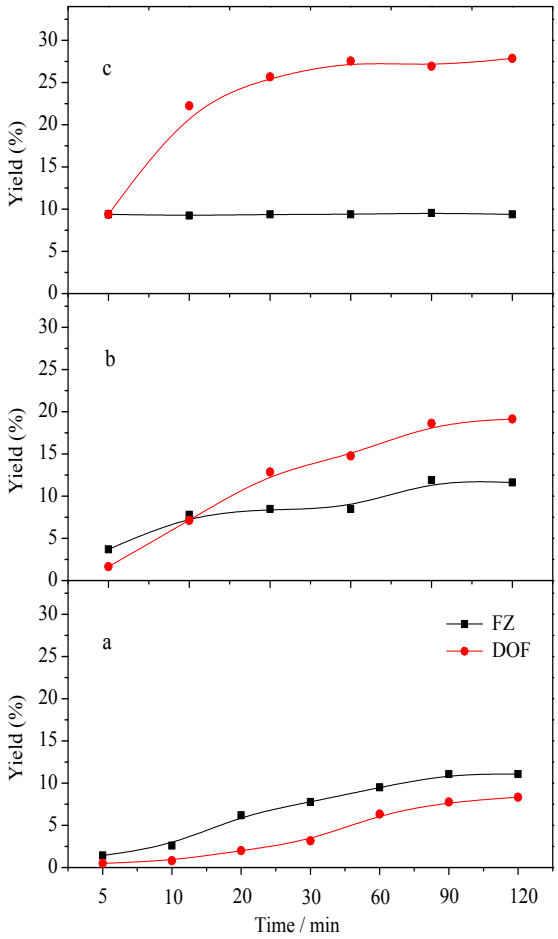


Figure S19 The effect of reaction temperature on the isolated yield of DOF and FZ was investigated at 60, 80, and 100 °C (from a to c). Reaction conditions: 179.2 mg $GlcNH_2$, 170.2 mg $[C_2C_1Im][OAc]$ (molar ratio of $GlcNH_2$/$[C_2C_1Im][OAc]$ = 1:1), 2 ml DMSO.

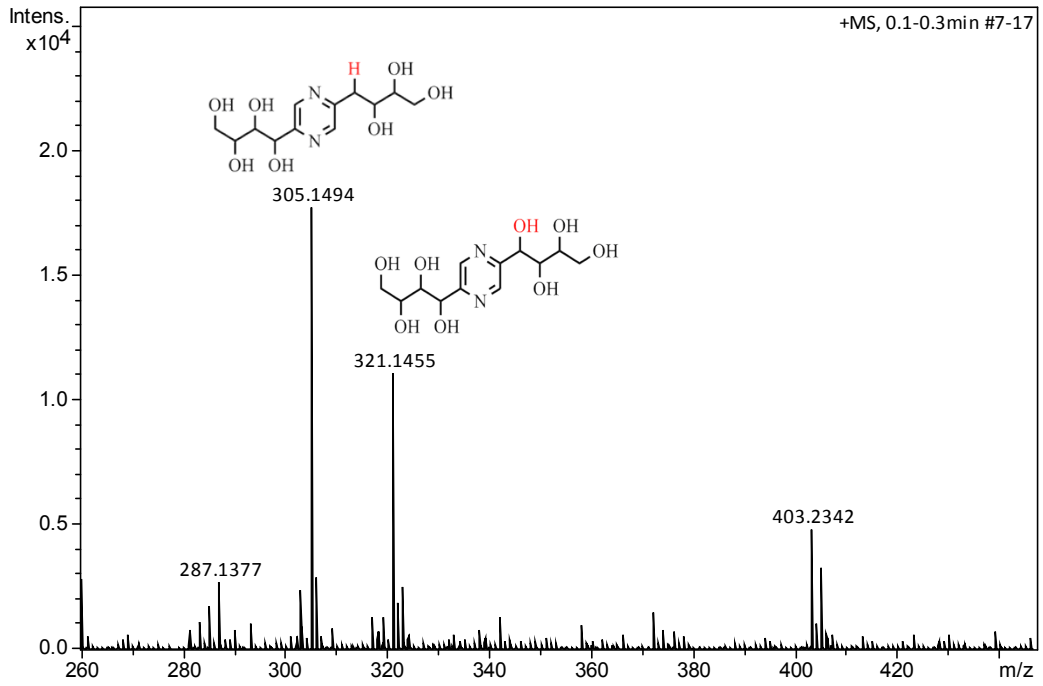


Figure S20 Qualitative identification of the DOF and FZ by using positive-ion ESI Mass Spectrum.

Mass spectrometry data:

FZ: ESI-MS m/z: 321.1455 [(M+ H)$^+$, $C_{12}H_{21}N_2O_8$], Anal. Calcd for $C_{12}H_{20}N_2O_8$: 320.1220.

DOF: ESI-MS m/z: 305.1494 [(M+ H)$^+$, $C_{12}H_{21}N_2O_7$], Anal. Calcd for $C_{12}H_{20}N_2O_7$: 304.1271.

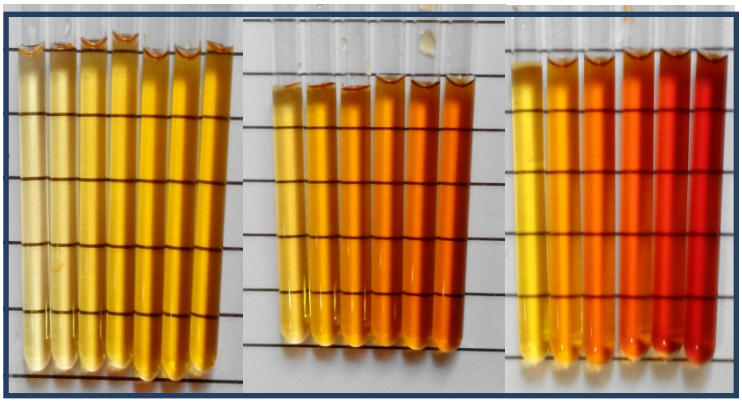


Figure S21 Changes of solution color as the increasing of reaction time at different temperature from 60 to 100 °C (from left to right).