Supplementary Information

One-step Synthesis of *N*-heterocyclic Compounds from Carbohydrates over Tungsten-based Catalysts

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Supporting information includes 10 pages, 8 figures and 3 tables.

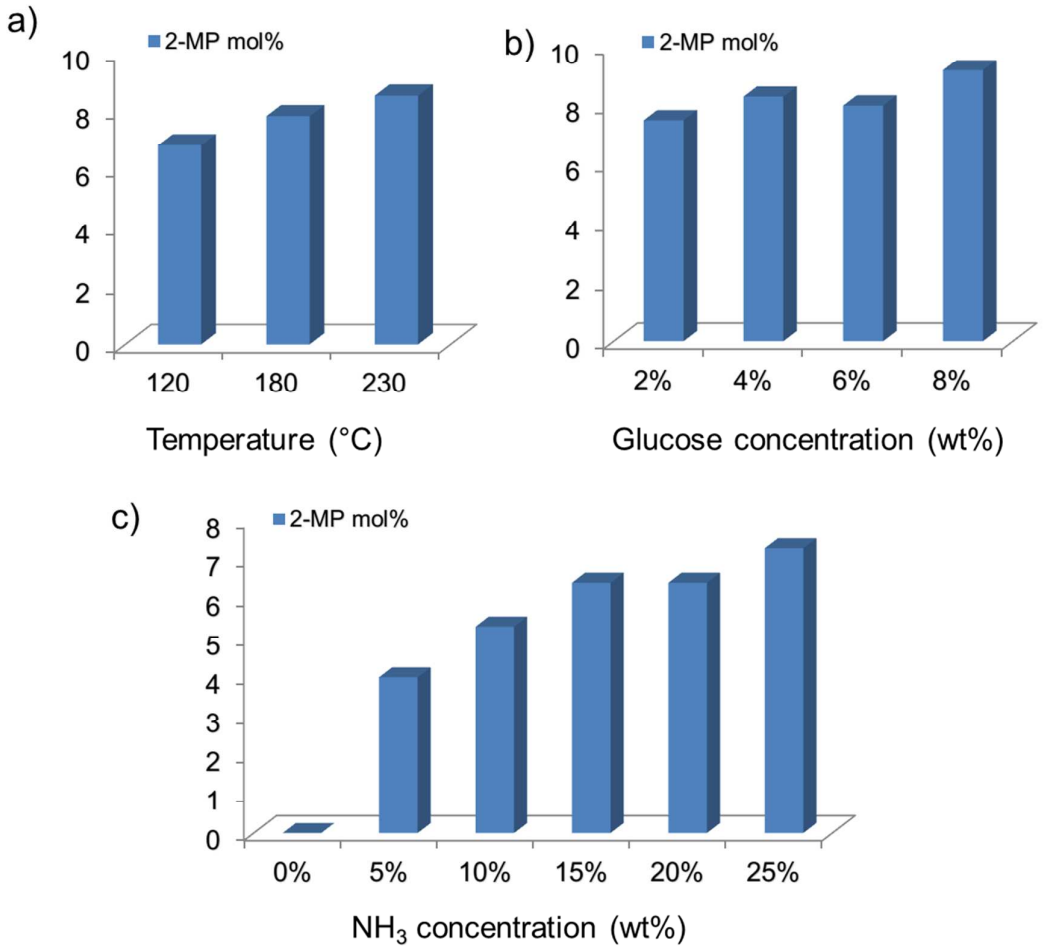

Figure S1 Optimization data of glucose reaction in ammonia solution without catalyst. 2-MP yields with different a) reaction temperatures; b) glucose concentrations; and c) ammonia concentrations. General conditions: 2% glucose concentration, 5 mL 25% ammonia solution, 15 min.

Table S1 Other minor pyrazine products shown and quantified by GC

Product	Yield without AMT (%)	Yield with AMT (%)
Pyrazine	0.8	0.8
Dimethyl pyrazines[a]	1.1	3.9
2,3,5-trimethyl pyrazine	0.2	0.1
2-ethyl-3,5(6)-dimethyl-pyrazine	2.0	3.0
2-(hydroxymethyl)-5-methyl pyrazine	1.4	3.2
2-methyl pyrrole	0.2	0.2

[a]The dimethyl pyrazines include 2,3-, 2,5- and 2,6-dimethyl pyrazine whose peaks were overlapped on GC-FID.

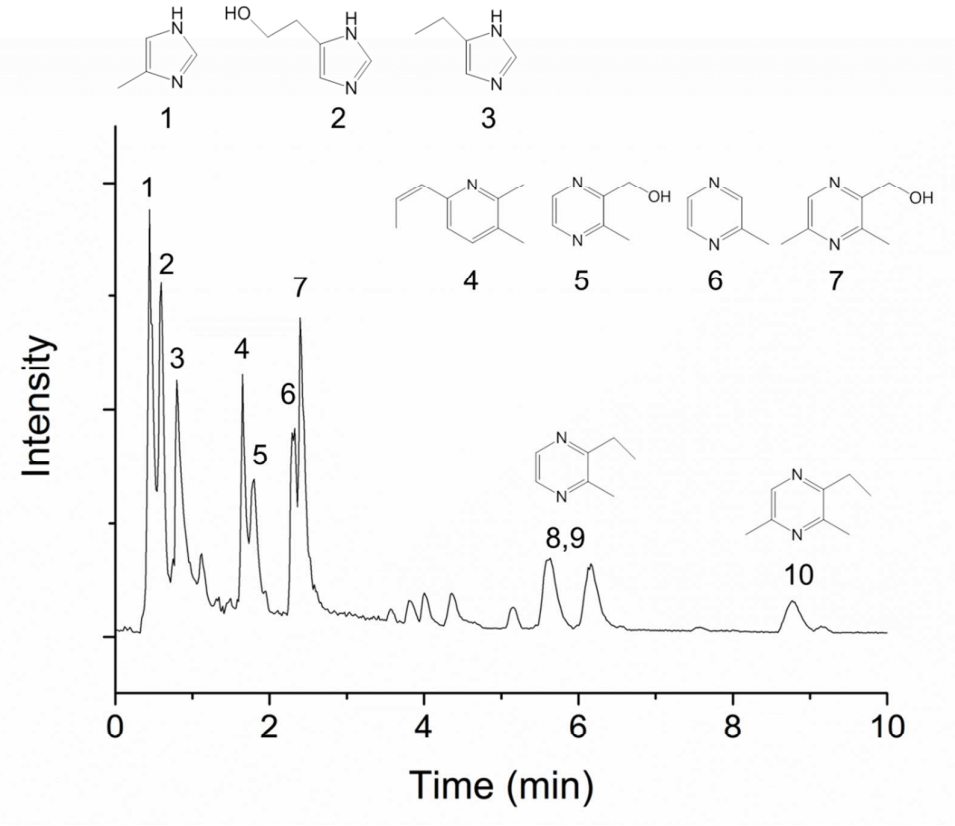

Figure S2 UPLC-ESI-MS spectrum of the reaction solution. Reaction conditions: 100 mg glucose, 100 mg AMT, 5 mL 25% ammonia solution, 180 °C, 15 min.

Table S2 2-MP yield by using the co-additives of AMT with metal salts[a]

Entry	Co-additive	2-MP mol%
1	$ZnCl_2$	18.2
2	$CuCl_2$	15.8
3	$FeCl_3$	15.9
4	$SnCl_2$	10
5	CuO	8.8
6	H_2O_2	19.9

[a]Reaction conditions: 100 mg glucose, 100 mg AMT, 20 mg co-additive, 5 mL 25% ammonia solution, 180 °C, 15 min.

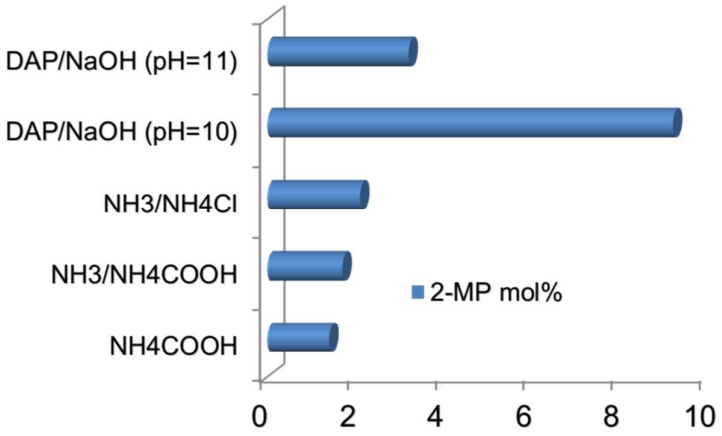

Figure S3 The effect of different ammonia sources. Reaction conditions: 100 mg glucose, 100 mg AMT, 5 mL different ammonium solutions, 180 °C, 15 min. The concentration of NH_3/NH_4^+ was 6 M and NH_3:NH_4^+ was 0.5. The addition of NaOH was to increase the basicity since ammonia solution has a pH of 11.

Table S3 the yields of 2-MP by using tungstic salts, sodium salts and the mixtures of metal salts and/or tungsten catalysts.

Entry	Catalyst/additive	Catalyst to glucose ratio	2-MP %
1	NaCl	1	8.0
2	$NaNO_3$	0.2	7.4
3	NaCl and H_2WO_4	0.2	13.0
4	NaCl and WO_3	1	21.2
5	WO_3	1	22.1
6	Li_2WO_4	0.2	8.1
7	$MgWO_4$	0.2	8.0
8	$CaWO_4$	0.2	8.3
9	$MgCl_2$ and AMT	1	10.2

Reaction conditions: 100 mg glucose, 5 mL 25% ammonia solution, 180 °C, 15 min.

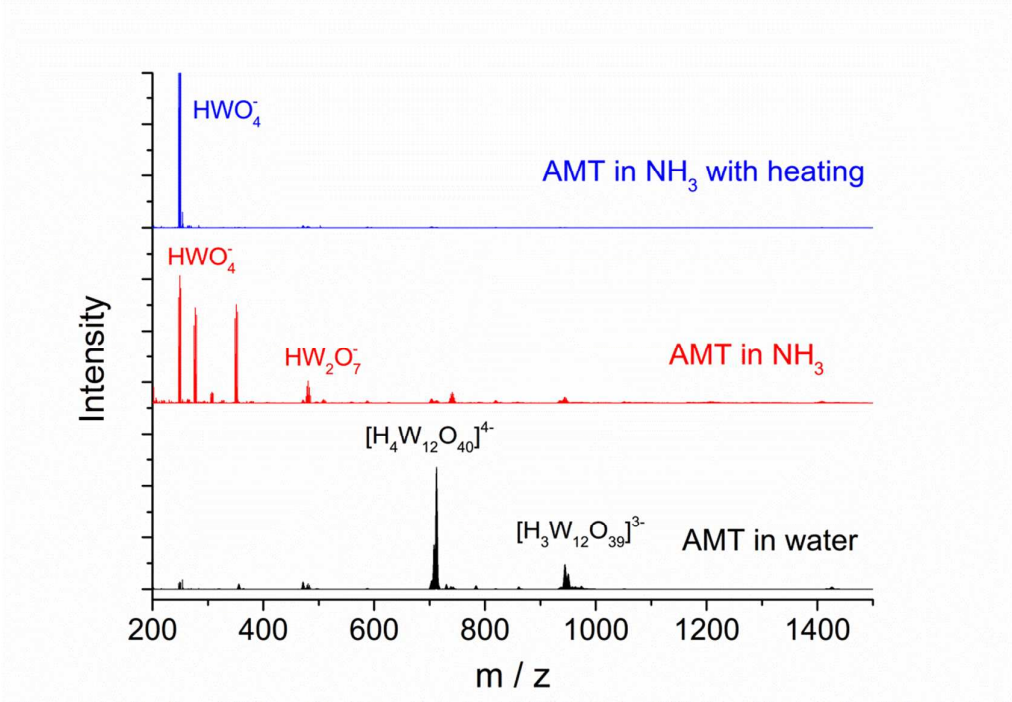

Figure S4 ESI signals (negative mode) of AMT in water, ammonia solution without and with heating (180 °C for 5 min) in the absence of glucose. It can be seen that the integrity of AMT was remained in neutral water and decomposed into small clusters in ammonia solution. Upon heating, further decomposition happened and HWO_4^- species was dominant.

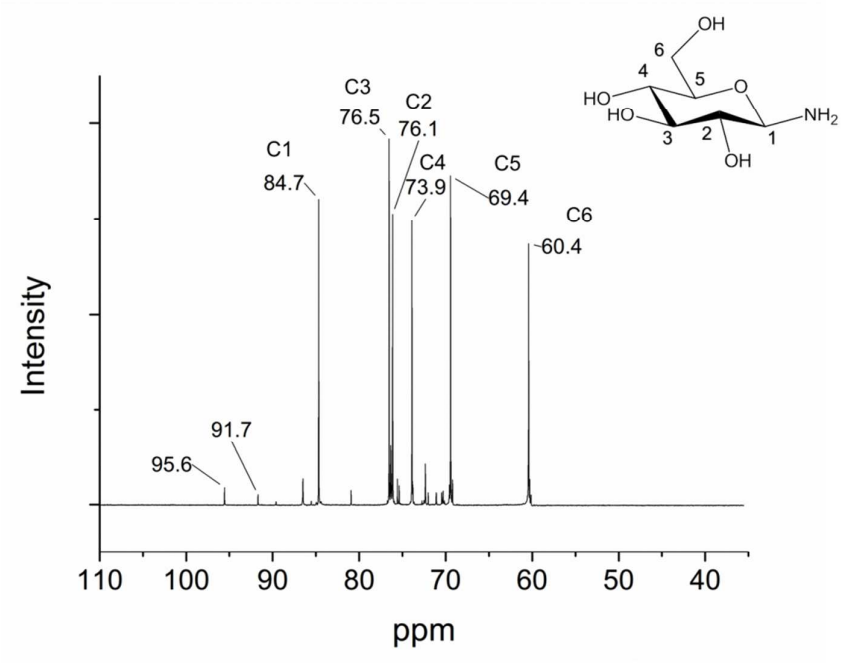

Figure S5 ^{13}C NMR of the reaction solution of glucose and AMT in ammonia deuterium water. Reaction conditions: 20 mg glucose, 20 mg AMT, 1 mL ammonia deuterium water, 180 ℃, 3 min. The peaks of β-D-glucopyranosylamine were assigned at ppm 84.7, 76.5, 76.1, 73.9, 69.4, 60.4. The minor peaks such as at 95.6 and 91.7 ppm were ascribed to α- and β-anomeric glucose.

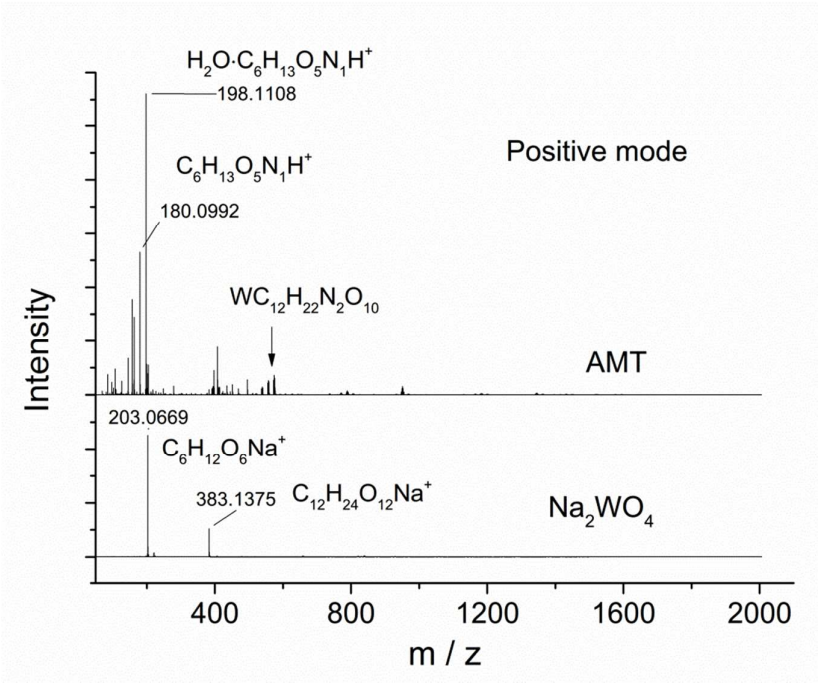

Figure S6 ESI signals (positive mode) of glucose in ammonia solution with AMT (top line) and Na_2WO_4 (bottom line). The signals of glucosylamine can be obviously found with the presence of AMT but was absent with the addition of Na_2WO_4.

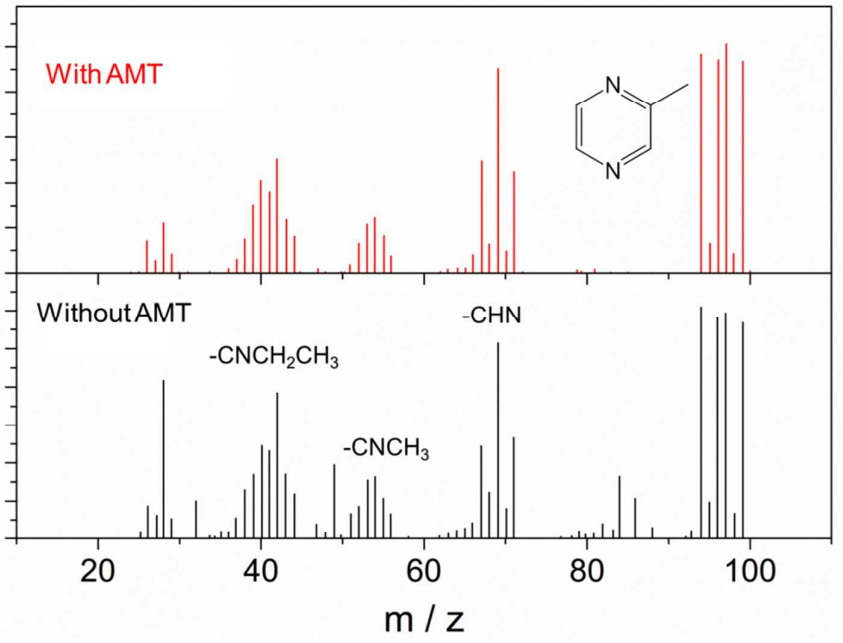

Figure S7 Isotope-labelling tests by using a mixture of unlabeled glucose and $^{13}C_6$-glucose. Reaction conditions: 50 mg unlabeled glucose, 50 mg $^{13}C_6$-glucose, 100 mg AMT, 5 mL ammonia solution, 180 °C for 15 min.

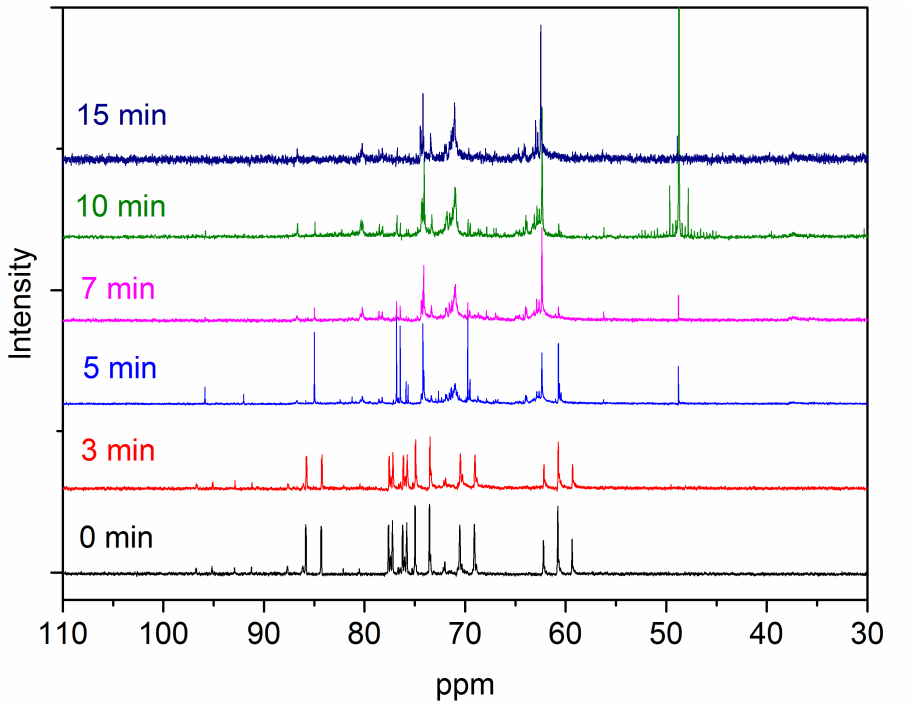

Figure S8 ^{13}C NMR of the reaction solution of glucose and AMT in ammonia deuterium water. Reaction conditions: 20 mg glucose, 20 mg AMT, 1 mL ammonia deuterium water, 180 °C, reaction time from 0 to 15 min. The spectra at 0 and 3 min were similar, containing six groups of C peaks, which were accordingly ascribed as C1, C3, C2, C4, C5 and C6 of glucose (from left to right).Significant change was observed from 5 min, which demonstrated the full glucose conversion.