

Electronic Supplementary Information for:

A New Method for Green Production of 2-Aminomethylpiperidine from Bio-renewable 2,5-Bis(aminomethyl)furan

Shuxing Zhang, Xiaoshu Ding*, and Yanji Wang *

Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, Hebei University of Technology, Tianjin 300130, China

*yjwang@hebut.edu.cn

Lists

1 Materials

2 Catalysts characterization

3 Density functional theory (DFT) calculation

Fig.S1 a. GC-MS(EI) spectrum of BAMTHF b. GC-MS spectrum of AMP c. GC-MS spectrum of 2-HHMDA d. GC-MS spectrum of OABCO

Fig.S2 a. GC-MS(CI) spectrum of BAMTHF b. GC-MS spectrum of AMP c. GC-MS spectrum of 2-HHMDA d. GC-MS spectrum of OABCO

Fig.S3 ESI-HRMS spectrum of product mixture

Fig.S4 a. TEM image of Pt/ γ -Al₂O₃(NaBH₄) b. TEM image of Pt/ γ -Al₂O₃(250)

Table S1 Physical properties of catalysts prepared by different preparation methods

Table S2 Effect of different catalyst preparation methods on the reaction

Table S3 Effect of different Pt loading on the reaction

Fig.S5 TEM images of catalysts with different reduction temperatures

Table S4 Effect of temperature on the hydrogenolysis of BAMF

Table S5 Effect of H₂ pressure on the hydrogenolysis of BAMF

Table S6 Effect of different ratios of methanol and water on the hydrogenolysis of BAMF

Table S7 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃(350) versus reaction time in 20 mL of water

Table S8 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃(350) versus reaction time in 15 mL methanol and 5 mL water

Table S9 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃(350) versus reaction time in 20 mL methanol

Table S10 Catalyst recycling performance

Scheme S1 BAMTHF and 5-AP reactivity test

Fig.S6 (a) Calculated free energy barriers for cyclization dehydration of 2-hydroxy-2,4-diene-1,6-hexanediamine in aqueous solvent at 140°C (b) Calculated free energy barriers for cyclization dehydration of 2-HHMDA in aqueous solvent at 140°C

1 Materials

ZrO₂ (99.99%, ≤100 nm) was purchased from Shanghai Aladdin Biotechnology Co., Ltd. γ-Al₂O₃ (99.99%, γ, 20 nm) was purchased from Shanghai Macklin Biochemical Co., Ltd. TiO₂ (5-10 nm, anatase) was purchased from Shanghai Yien Chemical Technology Co., Ltd. H-ZSM-5 (Si/Al=25, 2.0 μm) was obtained from Nankai University Catalyst Factory. BAMF, OABCO, 5-AP were obtained from Shanghai Bide Pharmaceutical Technology Co., Ltd. BAMTHF was obtained from Shanghai Haohong Biomedical Technology Co., Ltd. 5% Ru/C and 5% Pt/C were obtained from Shanghai Yien Chemical Technology Co., Ltd. 5% Rh/C was obtained from Shanghai Aladdin Biotechnology Co., Ltd. 5% Pd/C was obtained from Shanghai Macklin Biochemical Co., Ltd.

2 Catalysts characterization

The X-ray powder diffractometer (Bruker D8 FOCUS) was used to obtain XRD patterns using Cu Kα radiation ($\lambda = 0.15418$ nm). Data were collected at a scanning rate of 6°/min from 5° to 90°.

To investigate the textural properties of the catalysts, N₂ adsorption desorption analysis was performed at the liquid nitrogen by using the instrument (ASAP2020M+C, Micromeritics, USA) and the Brunauer Emmet Teller (BET) method. The samples were first degassed at 200 °C for 2 h and then further analyzed.

NH₃-TPD tests were performed on the catalysts to determine distribution of acidic sites using Micromeritics AutoChem II-2920 chemisorbent analyzer from Micromeritics, USA. 100 mg of the sample was treated at 200°C for 1 h using helium as the carrier gas (flow rate: 60 mL/min), then cool to 100°C. After that, a constant NH₃ flow (30 mL/min) was used for 20 min, and the physically adsorbed NH₃ were removed by using helium to purge 30 min. Finally, the temperature of sample was heated to 700°C in helium flow (flow rate: 60 mL/min) with ramping rate of 10 °C/min. A thermal conductivity detector (TCD) was used to record the signal.

X-ray photoelectron spectroscopy (XPS) were obtained on Escalab 250Xi spectrometer from Thermo Scientific, USA. Measurements were conducted at 14.6 kV and 200 W, respectively. The C1s peak at 284.8 eV was used to calibrate all binding energies.

Talos F200S field emission high-resolution electron microscope from FEI, USA was used to observe the microscopic morphology of the catalyst samples. Measurement of the particle size of 100 Pt particles was performed. The surface averaged particle diameter (d_s) of Pt particles including their standard deviations were calculated using:

$$d_s \pm \sigma_{ds} = \frac{\sum_{i=1}^N d_i^3}{\sum_{i=1}^N d_i^2} \pm \sqrt{\frac{1}{N} \sum_{i=1}^N (d_i - d_s)^2}$$

ICP-MS was used to determine the actual Pt loading using an Agilent 7850 ICP-MS. The catalyst after reduction was cooled to 25 °C and saturated with pulses of CO (CO/He = 10/90 as vol %) on Micromeritics AutoChem II 2920 system.

In-situ FTIR tests were performed on an in situ FTIR spectrometer (6700, Nicolet) equipped with a Mercury-Cadmium-Telluride detector (using liquid nitrogen cooling) and a stainless steel in-situ cell (CaF₂ windows). For FTIR measurement, transmission mode is used. The sample was treated at 350 °C with a feed of 10% H₂ (30 mL/min), then the samples were cooled down to 140 °C. After cooling down to 140 °C, the background spectrum was collected. Then BAMF was introduced into the cell through the bubbling device and the sample was exposed to BAMF vapor for 20 min. After the physical adsorption, Ar were introduced and maintained for 60 min (140 °C). The IR spectrum were collected every 10 min.

3 Density functional theory (DFT) calculation

To further investigate the reaction mechanism for the preparation of AMP by hydrogenolysis of BAMF, we have used DFT calculations to compute the transition states at key steps. DFT calculations were performed using Gaussian 09. Geometry optimization, frequency analysis and transition state search were performed using density functional theory (DFT)/M06-2X function with 6-311g(d,p) basis set. The single-point energy for each optimized geometric configuration was calculated using the def2-TZVP basis set. Each transition state had only one negative frequency. Intrinsic reaction coordinate (IRC) analysis was carried out to confirm that all stationary states were smoothly connected to each other. The solvent effect of water is included using the PCM model.

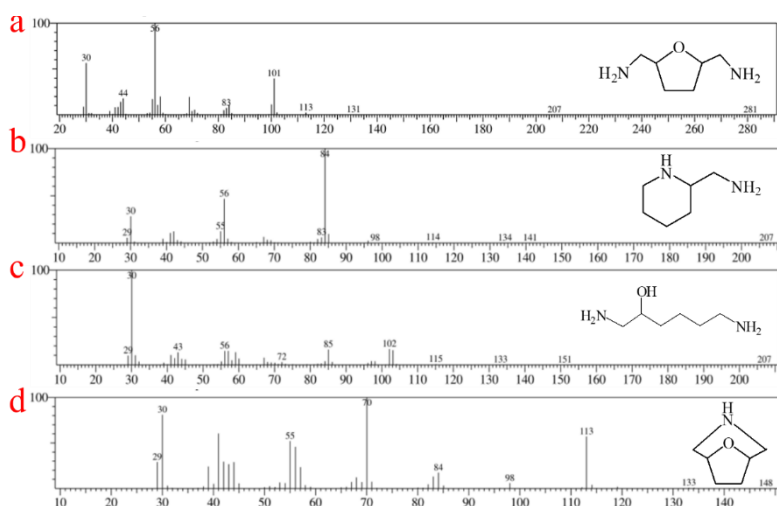


Fig.S1 a. GC-MS(EI) spectrum of BAMTHF b. GC-MS (EI) spectrum of AMP
c. GC-MS (EI) spectrum of 2-HHMDA d. GC-MS(EI) spectrum of OABCO

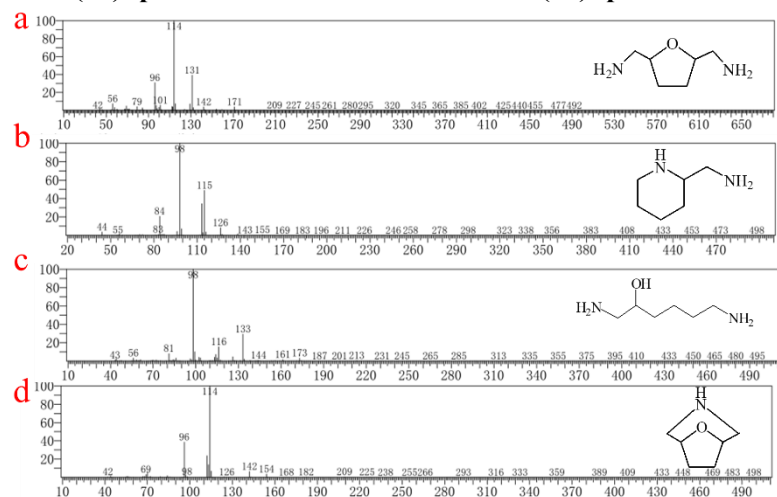


Fig.S2 a. GC-MS(CI) spectrum of BAMTHF b. GC-MS(CI) spectrum of AMP
c. GC-MS (CI) spectrum of 2-HHMDA d. GC-MS (CI) spectrum of OABCO

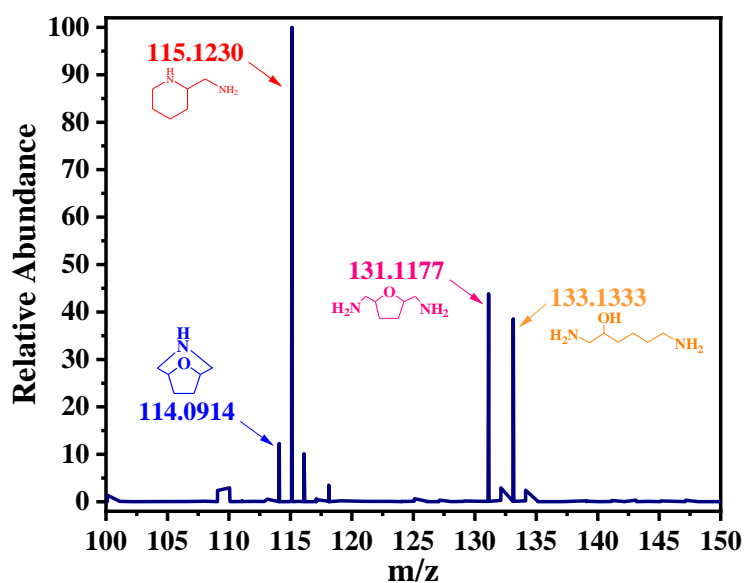


Fig.S3 ESI-HRMS spectrum of product mixture

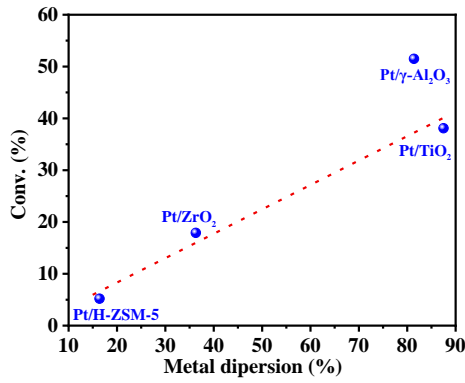


Fig.S4 The relationship between metal dispersion and conversion

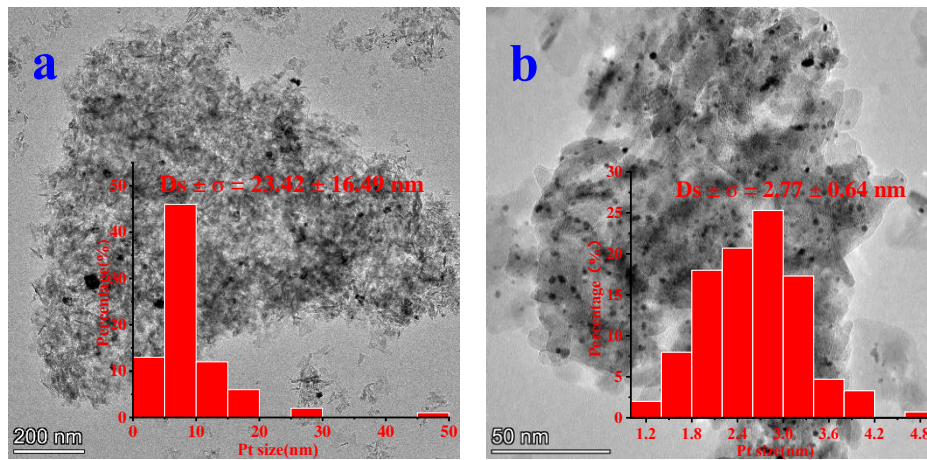


Fig.S5 a. TEM image of Pt/ γ -Al₂O₃(NaBH₄) b. TEM image of Pt/ γ -Al₂O₃(250)

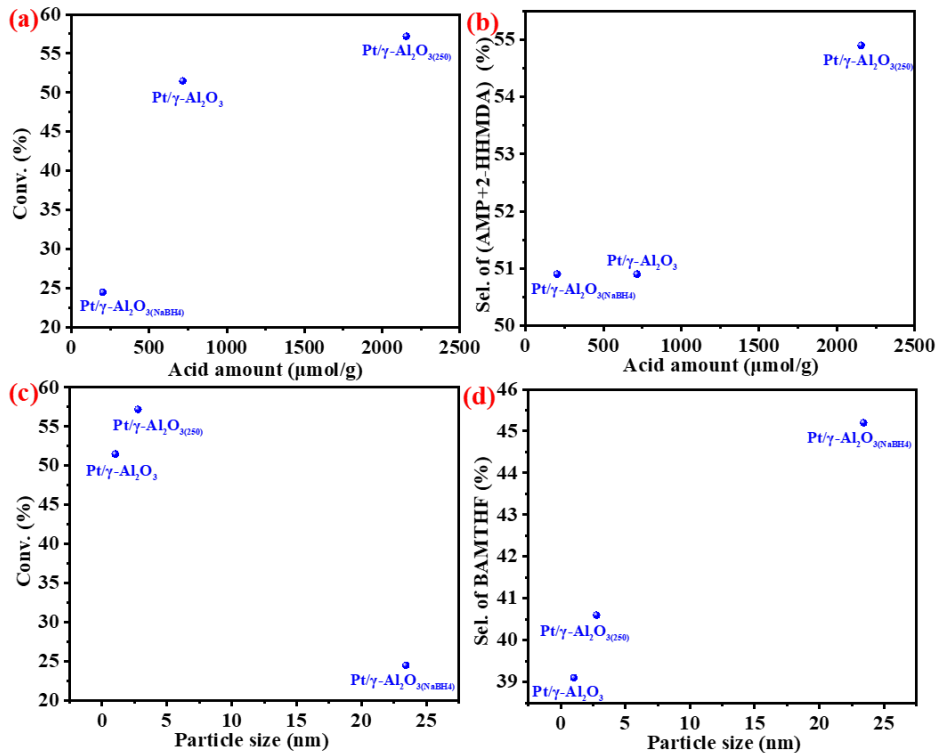


Fig.S6 The relationship between acid amount and conversion b. The relationship between

acid amount and selectivity of hydrogenolysis product c. The relationship between particle size and conversion d. The relationship between particle size and selectivity of BAMTHF

Table S1 Physical properties of catalysts prepared by different preparation methods

Catalyst	ABET ^a (m ² /g)	D _{pore} ^b (nm)	Pt loading ^c (%)	Surface averaged particle size ^d (nm)	Acid amount ^e (μmol/g)
Pt/γ-Al ₂ O ₃	135.4	19.7	2.8	1.03 ± 0.49	716.1
Pt/γ-Al ₂ O ₃ (250)	137.8	22.3	3.0	2.77 ± 0.64	2155.4
Pt/γ-Al ₂ O ₃ (NaBH ₄)	139.0	19.3	2.9	23.42 ± 16.49	202.5

a Surface area calculated by BET, b Desorption mean pore size calculated by BJH method, c Pt loading measured by ICP-MS, d Measured from TEM images, e Surface acid amount measured by NH₃-TPD.

Table S2 Effect of different catalyst preparation methods on the reaction

Entry	Catalyst	Conv. (%)	Sel. (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	Pt/γ-Al ₂ O ₃ (NaBH ₄)	24.5	27.9	23	45.2	3.9
2	Pt/γ-Al ₂ O ₃	51.5	24.5	26.4	39.1	10.1
3	Pt/γ-Al ₂ O ₃ (250)	57.2	26.1	28.8	40.6	4.5

Reaction condition: 2 mmol BAMF, 20 mL methanol, 80 °C, 2 MPa H₂, 4 h, 0.1 g catalysts. Others are polymers.

Table S3 Effect of different Pt loading on the reaction

Entry	Catalyst	Conv. (%)	Sel. (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	0.7% Pt/γ-Al ₂ O ₃ (250)	9.2	25.7	43.8	30.5	-
2	1% Pt/γ-Al ₂ O ₃ (250)	51.2	30.2	27.9	36.3	5.7
3	2% Pt/γ-Al ₂ O ₃ (250)	58.8	27.4	30.8	37.7	4.1
4	3% Pt/γ-Al ₂ O ₃ (250)	51.5	24.5	26.4	39.1	10.1

Reaction condition: 2 mmol BAMF, 20 mL methanol, 80 °C, 2 MPa H₂, 4 h, 0.1g catalysts. Others are polymers.

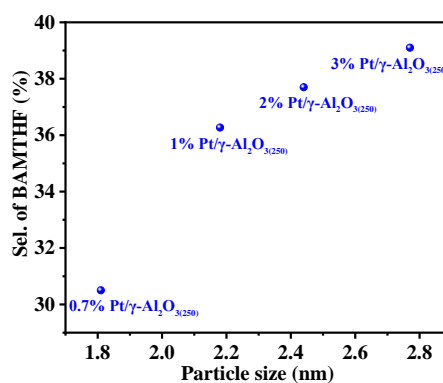


Fig.S7 The relationship between particle size and selectivity of BAMTHF

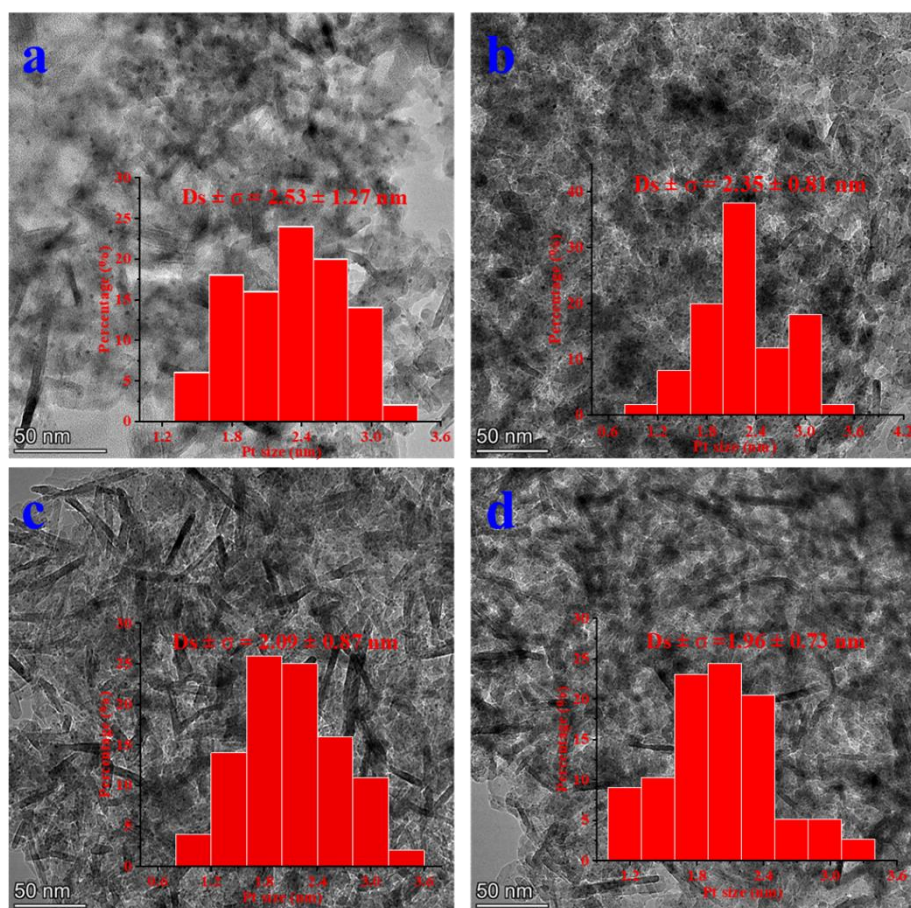


Fig.S8 TEM images of catalysts with different reduction temperatures a. 150°C b. 250°C c. 350°C d. 450°C

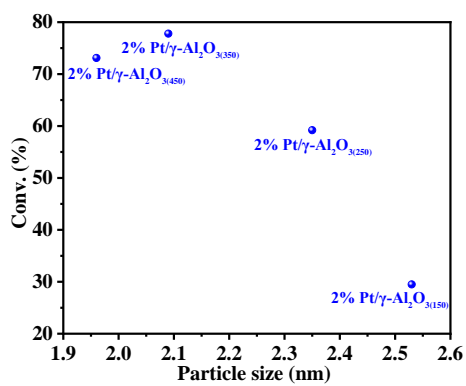


Fig.S9 Effect of particle size of catalyst on conversion

Table S4 Effect of temperature on the hydrogenolysis of BAMF

Entry	Temperature (°C)	Conv. (%)	Sel. (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	80	84.6	17.4	37.5	33.1	12.0
2	100	100	38.8	34.7	21.6	4.7
3	120	100	57.8	17.9	18.5	5.6
4	140	100	60.2	14.8	17.6	7.4
5	160	100	68.1	0	15.2	16.6
6	180	100	44.2	0	25.2	30.5
7	200	100	7.5	0	9.3	83.2

Reaction condition 2 mmol BAMF, 15 mL methanol + 5 mL water, 2 MPa H₂, 0.1g 2% Pt/ γ -Al₂O₃(350), 4h. Others are polymers.

Table S5 Effect of H₂ pressure on the hydrogenolysis of BAMF

Entry	H ₂ Pressure (MPa)	Conv. (%)	Sel. (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	0.3	45.2	40.0	23.9	19.5	16.7
2	0.5	100	44.8	18.7	15.3	21.3
3	1	100	63.2	12.9	16.6	7.3
4	2	100	60.2	14.8	17.3	7.7
5	3	100	39.2	24.6	28.3	7.9
6	4	100	34.0	26.2	33.4	6.4

Reaction condition 2 mmol BAMF, 15 mL methanol + 5 mL water, 140°C, 0.1g 2% Pt/ γ -Al₂O₃(350), 4h. Others are polymers.

Table S6 Effect of different ratios of methanol and water on the hydrogenolysis of BAMF

Entry	Solvent	Conv. (%)	Sel. (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	20 mL MeOH	93.7	40.2	25.9	30.3	3.6
2	15 mL MeOH+5 mL H ₂ O	100	63.2	12.9	16.6	7.3
3	10 mL MeOH+10 mL H ₂ O	100	67.9	0	19.0	13.1
4	5 mL MeOH+15 mL H ₂ O	100	64.9	0	20.8	14.3
5	20 mL H ₂ O	100	72.0	0	16.5	11.5

Reaction condition 2 mmol BAMF, 140°C, 0.1g 2% Pt/ γ -Al₂O₃(350), 1 MPa H₂, 4h. Others are polymers.

Table S7 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃₍₃₅₀₎ versus reaction time in 20 mL of water

Entry	Time (min)	Conv. (%)	Yield (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	0	0	0	0	0	0
2	30	28.5	15.3	5.3	8.0	0
3	60	36.7	17.4	10.6	8.7	0
4	90	56.4	25.0	15.3	9.8	6.3
5	120	84.1	37.6	22.2	13.1	11.1
6	150	100	45.2	25.1	17.5	12.2
7	180	100	56.3	16.0	16.4	11.3
8	210	100	62.0	8.0	17.0	13.0
9	240	100	65.0	4.1	16.1	14.8
10	270	100	69.5	0	17.0	13.5

Reaction condition 2 mmol BAMF, 20 mL water, 140°C, 0.1g 2% Pt/ γ -Al₂O₃₍₃₅₀₎, 140°C, 1 MPa H₂. Others are polymers.

Table S8 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃₍₃₅₀₎ versus reaction time in 15 mL methanol and 5 mL water

Entry	Time (min)	Conv. (%)	Yield (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	0	0	0	0	0	0
2	30	25.3	9.3	6.7	5.1	4.2
3	60	41.8	18.3	11.7	10.3	1.5
4	90	78.2	33.2	26.1	16.8	2.0
5	120	95.4	41.7	33.2	19.2	1.3
6	150	100	44.0	30.7	22.2	3.0
7	180	100	45.7	28.3	22.7	3.4
8	210	100	48.8	23.2	23.9	4.1
9	240	100	52.6	18.5	24.0	4.8
10	360	100	67.4	0.0	25.2	7.4

Reaction condition 2 mmol BAMF, 15 mL methanol + 5 mL water, 140°C, 0.1g 2% Pt/ γ -Al₂O₃₍₃₅₀₎, 140°C, 1 MPa H₂. Others are polymers.

Table S9 Product distributions for the hydrogenation/hydrogenolysis of BAMF over 2% Pt/ γ -Al₂O₃(350) versus reaction time in 20 mL methanol

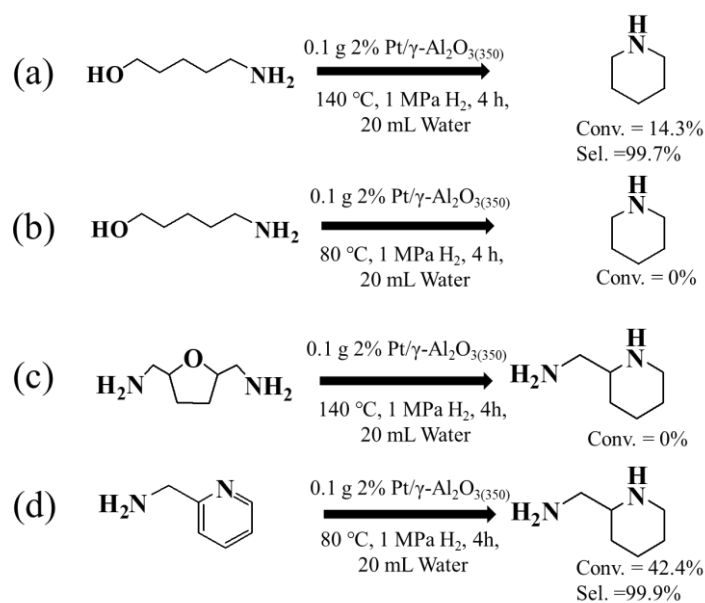
Entry	Time (min)	Conv. (%)	Yield (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	0	0	0	0	0	0
2	30	28.5	16.6	0	11.9	0
3	90	46.7	21.3	8.6	16.8	0
4	150	82.3	31.7	24.0	25.3	1.3
5	210	92.9	35.4	30.6	26.3	0.6
6	270	100	37.3	32.1	28.6	2.0
7	330	100	37.0	32.0	28.2	2.8
8	390	100	37.6	31.9	28.2	2.2
9	510	100	37.7	31.1	28.4	2.9

Reaction condition 2 mmol BAMF, 20 mL methanol, 140 °C, 0.1 g 2% Pt/ γ -Al₂O₃(350), 140 °C, 1 MPa H₂. Others are polymers.

Table S10 Catalyst recycling performance

Entry	No. of cycle	Conv. (%)	Yield (%)			
			AMP	2-HHMDA	BAMTHF	Others
1	1	100	72.0	0	16.5	11.5
2	2	100	68.1	0	18.0	13.9
3	3	100	69.3	0	15.9	14.8
4	4	100	67.6	0	17.0	15.4
5	5	100	63.3	0	23.5	13.2

Reaction condition 2 mmol BAMF, 20 mL Water, 140 °C, 0.1 g 2% Pt/ γ -Al₂O₃(350), 140 °C, 1 MPa H₂, 4h. Others are polymers.



Scheme S1 BAMTHF, 2-aminomethylpyridine and 5-AP reactivity test

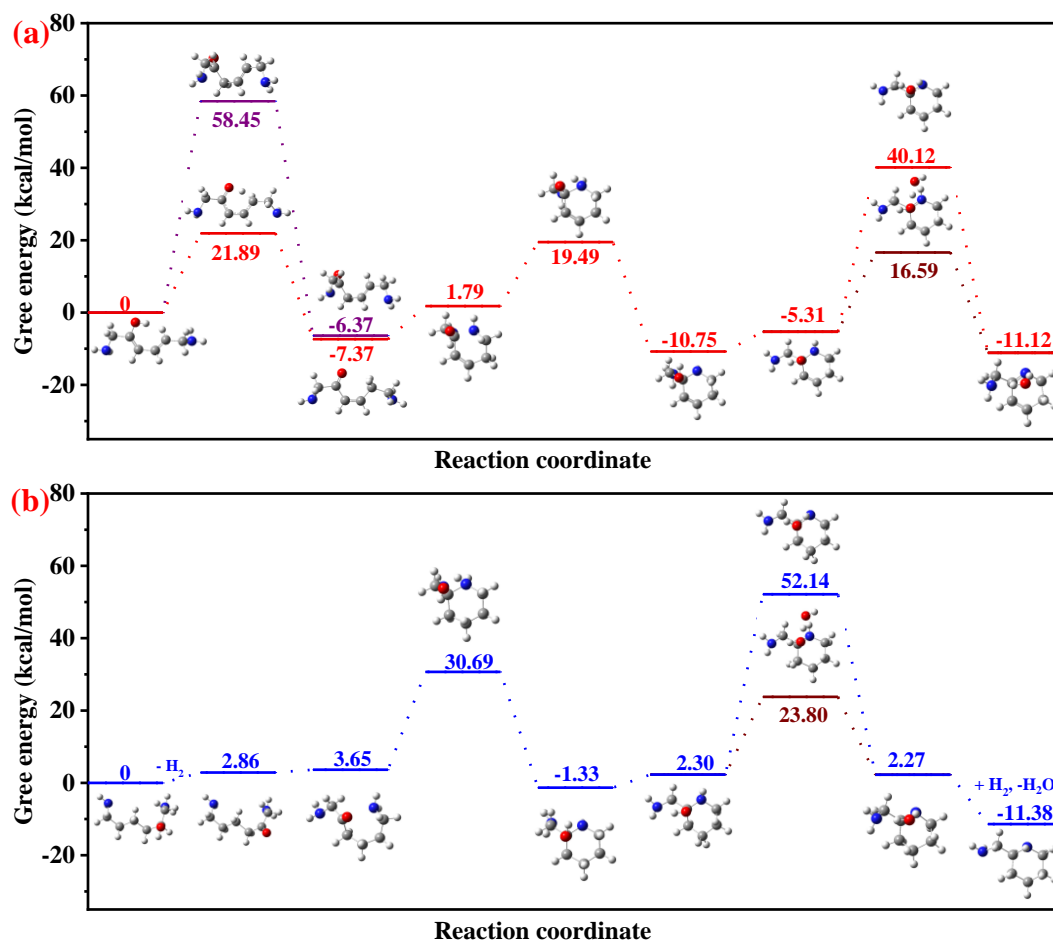


Fig.S10 (a) Calculated free energy barriers for cyclization dehydration of 2-hydroxy-2,4-diene-1,6-hexanediamine in aqueous solvent at 140°C (b) Calculated free energy barriers for cyclization dehydration of 2-HHMDA in aqueous solvent at 140°C