

Electronic Supplementary Information (ESI) for:

Electronic Ni-N interaction enhanced reductive amination on N-doping porous carbon supported Ni catalyst

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Filtration and leaching test.

In order to confirm the heterogeneous nature of the catalyst system, we carried out a hot filtration test. After the reaction for 3 h, the autoclave was allowed to cool to room temperature and the excess gas was released, the catalyst was separated by filtration using PTFE membrane filter. 44.2% yield of furfuryl amine was achieved after analysing the reaction mixture by GC. Then, the catalytic reaction was continued for another 3 h with the filtrate under identical conditions. No noticeable improvement in furfuryl amine yield beyond 45.7% was observed.

After the filtration experiment, the filtrate was evaporated through rotary evaporator. The obtained product was dissolved and digested with HNO_3 solution and H_2O_2 solution. The resulting solution was cooled to room temperature followed by sonication. The solution was transferred into a 50 mL volumetric flask, diluted with deionized water, and the amount of Ni was measured by ICP-MS analysis. The ICP-MS analysis confirmed no obvious leaching of Ni took place in the filtrate, indicating the heterogeneous nature of this catalyst system.

Table S1 Application of heterogeneous catalysts in catalytic ammonification.

Type of C-O bond	Catalysts	Conditions	aminating agent	Yield (%)	References
C=O	30 mg 6 mol % Ni@SiO ₂ -800	0.5 mmol 2-bromobenzaldehyde, 3 mL t-BuOH, 120 °C, 15 h	0.5-0.7 MPa NH ₃ , 2 MPa H ₂	96 %	1
	25 mg Co-Co ₃ O ₄ @C [3.5 mol % Co]	0.5 mmol aldehyde, 3 mL t-BuOH, 120 °C, 15 h	0.5-0.7 MPa NH ₃ , 4 MPa H ₂	80~95 %	2
	3.5 wt. % Ni/γ-Al ₂ O ₃	0.5 mmol benzaldehyde, 2.0 mL H ₂ O, 80 °C, 20 h	0.5 mL NH ₃ ·H ₂ O 25 %, 1 MPa H ₂	78 %	3
	0.2 mol % 5wt % RuTiP	1 mmol cyclohexanone, 2 mL methanol; 30 °C, 6 h, IS: n-butanol	0.6 MPa NH ₃ , 1.4 MPa H ₂	96 % cyclohexylamine	4
	0.1 mol % 2 wt. % Pt/P-TiO ₂	1 mmol LA, 1 mmol n-octylamine, 2 mL methanol, 1 h, rt	hydrogen balloon	61 % Pyrrolidone	5
	0.02 g 1wt. % RuNb ₂ O ₅	0.5 mmol furfural, 5mL MeOH, 90 °C, 4 h. IS: PhCl	0.1MPa NH ₃ , 4 MPa H ₂	99 % furfuryl amine	6
	50 mg 5wt. % Ru/Al ₂ O ₃	6.6 mmol heptaldehyde, 0.58 mmol n-dodecane, MeOH (20 mL), 80 °C, 2 h	0.4 MPa NH ₃ , 3 MPa H ₂	75 % furfuryl amine	7
	0.5 g 1 wt. % Ru/Nb ₂ O ₅ ·nH ₂ O	15 mmol furfural, 80 mL MeOH, 70 °C, 6 h	0.1 MPa NH ₃ , 3 MPa H ₂ ,	89 % furfuryl amine	8
	0.1 g 5 wt. % Ru/ZrO ₂	2 mmol glycolaldehyde, cat., 75 °C, 3 MPa H ₂ , 12 h	2.0 mL 25 wt.% NH ₃ ·H ₂ O	93 % ethanolamine	9
C_{Ar}-O-C_{Ar}	Pd (OH) ₂ /C	0.2 mmol diphenyl ether, 20 mol % cat. 1 equiv HCO ₂ Na, 1 mL m-xylene, 5ul H ₂ O, 160 °C, Ar, 24 h	0.5 mmol Pyrrolidine	42 % 1-cyclohexylpyrrole 18 % 1-phenylpyrrolidine	10
	Pd (OH) ₂ /C	0.2 mmol diphenyl ether, 20 mol % cat. 1 equiv NaBH ₄ , 1 mL m-xylene, 160 °C, Ar, 24 h	5 equiv NH ₃ ·H ₂ O	83 % N-cyclohexyl aniline	11
C_{Ar}-OH	Pd/C	0.2 mmol Phenol, 10 mol % cat. 50 mol % NaBH ₄ , 40 mol % LiOH, 2 mL 1,4-dioxane, 4 Å molecular sieves, 170 °C, Ar, 12 h	0.6 mmol N ₂ H ₄ ·H ₂ O	71 % aniline	12
	Pd/C	0.2 mmol phenol, 7 mol % cat. 6 equiv HCO ₂ Na, 0.8 mL toluene, 100 °C, Ar, 24 h	0.2 mmol p-toluidine	95 % N-cyclohexyl-4-methylaniline	13
	Pd/C	0.2 mmol phenol, 0.28 mmol cat. (10 mol %), 1.5 equiv HCO ₂ Na, 0.5 equiv TFA, 1 mL toluene, 140 °C, Ar, 12 h	0.2 mmol octylamine	86 % N-octyl aniline	14

C-OH	3 wt. % Ru/CNT	0.5 mmol lactic acid, 50 mg cat., 1 MPa H ₂ , 220 °C, 2 h	2.5 mL NH ₃ ·H ₂ O (25 wt. %)	62 % alanine	15
	10 wt. % Ni/θ-Al ₂ O ₃	4 g o-xylene, 3.0 mmol alcohol, 0.5 mmol n-dodecane, 160 °C, 4 h	0.4 MPa NH ₃	66.4 % 2-octylamine	16
	1 % Pt, 1 % Co/CeO ₂	5 mL p-xylene, 2 mmol cyclopentanol, 50 mg cat. 160 °C, 4 h	0.35 MPa NH ₃	67.4 % Cyclopentylamine	17
	2.2 wt. % Ru(OH)x/TiO ₂	2.5 mmol benzyl alcohol, Ru: 0.015 mmol, 0.5 mL mesitylene, 141 °C, 12 h, 1 atm Ar	0.25 mmol urea	93 % tribenzylamine	18
	65 wt. % Ni/Al ₂ O ₃ -SiO ₂ (200 mg)	alcohol (0.5 mmol), t-amyl alcohol (3 mL), 160 °C, 18 h. IS: Dodecane	aq. NH ₃ (25 wt. %, 0.4 mL)	58 %	19

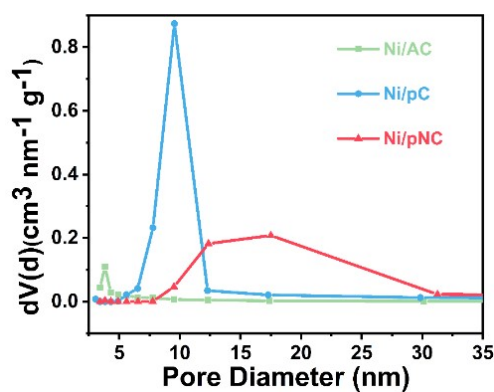


Fig. S1 Pore size distribution of Ni/AC, Ni/pC and Ni/pNC.

Procedure for isolation and identification of products

A small amount of sample points were dipped into the TLC plate with a capillary tube, and the TLC plate was put into the prepared developing solvent (PE:EA= 2:1) for TLC detection, so that various components in the mixture moved to the corresponding position with the developing solvent, as shown in Fig. S2. The TLC plate was irradiated under an ultraviolet lamp to determine the product point in the desired sample. After determining the sample point, the mixture sample was spread on the PTLC plate at a position higher than the eluent liquid surface, and a horizontal sample band was formed under the irradiation of UV lamp. After drying, each ribbon carrying different compounds was scraped off the plate and extracted and washed with ethyl acetate to obtain filtrate, and then the solvent was removed to obtain pure compounds. The yield and purity of the products obtained were shown in the Table S2. Finally, the compound was dissolved in DMSO- d_6 and loaded into nuclear magnetic tube for nuclear magnetic testing, the ^1H NMR spectra were showed in Fig. S3-Fig. S5.

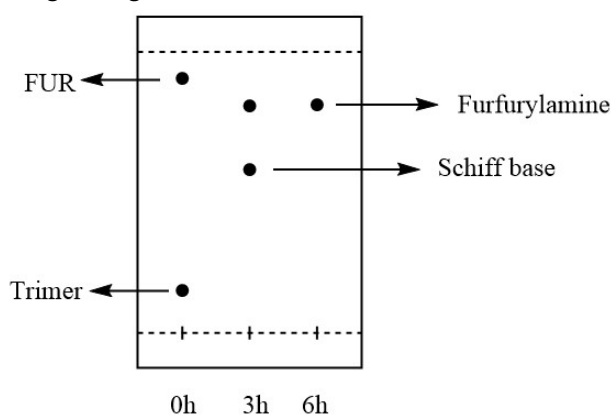


Fig. S2 TLC detection of mixed sample solution at different reaction time.

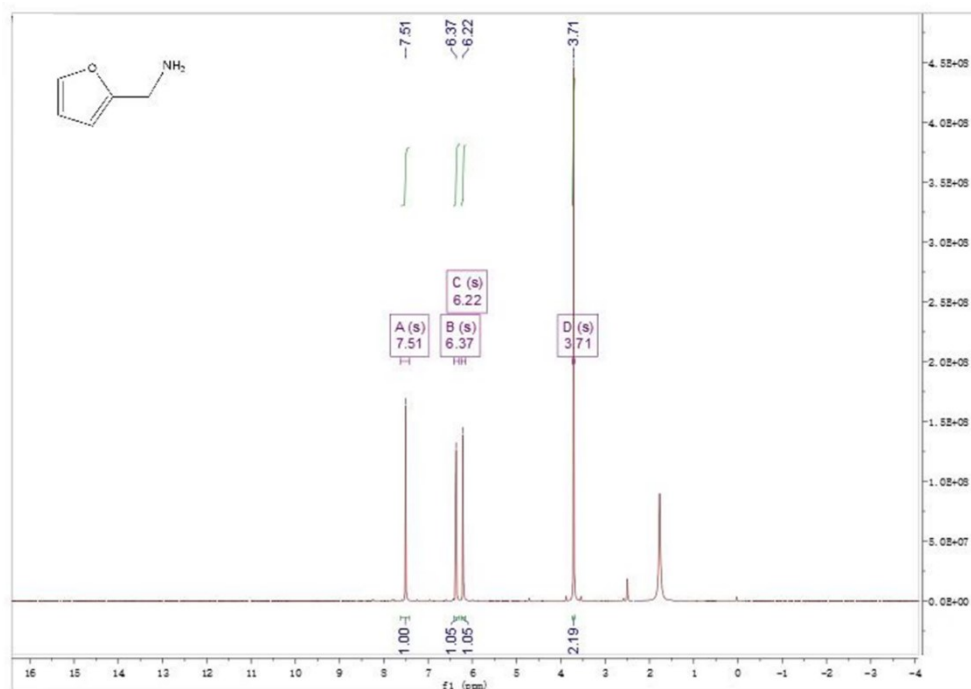


Fig. S3 ^1H NMR spectrum (400 MHz, DMSO- d_6) of isolated furfuryl amine (96 % yield at 6 h). δ 7.51 (s, 1H, 2-furan), 6.37 (s, 1H, 2-furan), 6.22 (s, 1H, 2-furan), 3.71 (s, 2H, methylene).

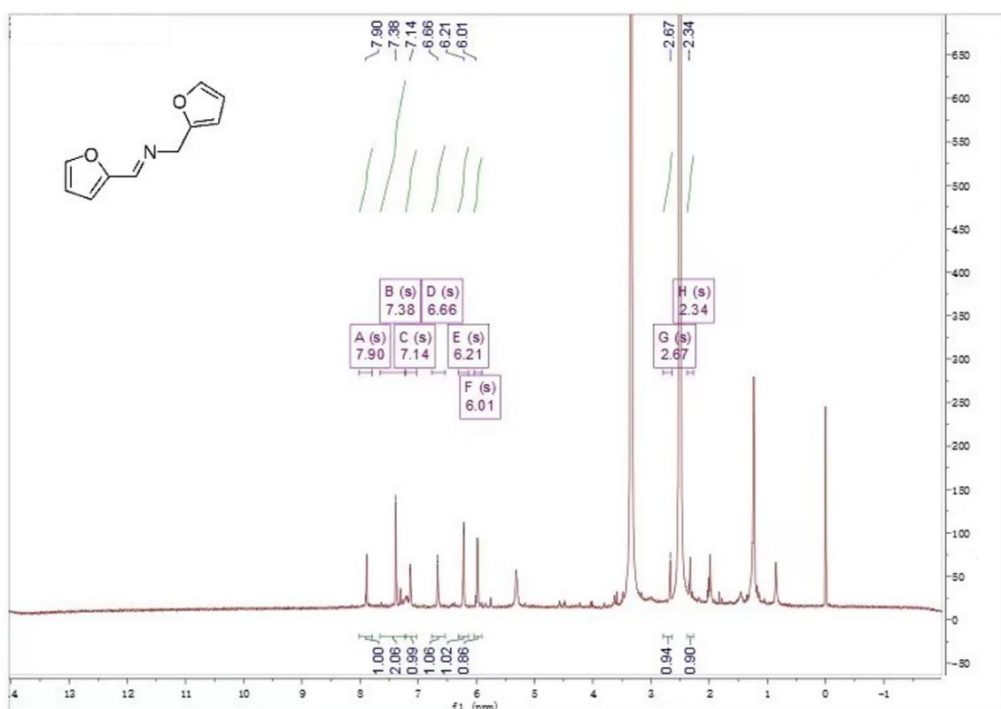


Fig. S4 ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$) of isolated Schiff base (60 % yield at 3 h). δ 7.90 (s, 1H, 2-furan), 7.38 (s, 2H, 2-furan), 7.14 (s, 1H, 2-furan), 6.66 (s, 1H, 2-furan), 6.21 (s, 1H, 2-furan), 6.01 (s, 1H, 2-furan), 2.67 (s, 1H, aldimine), 2.34 (s, 1H, methylene).

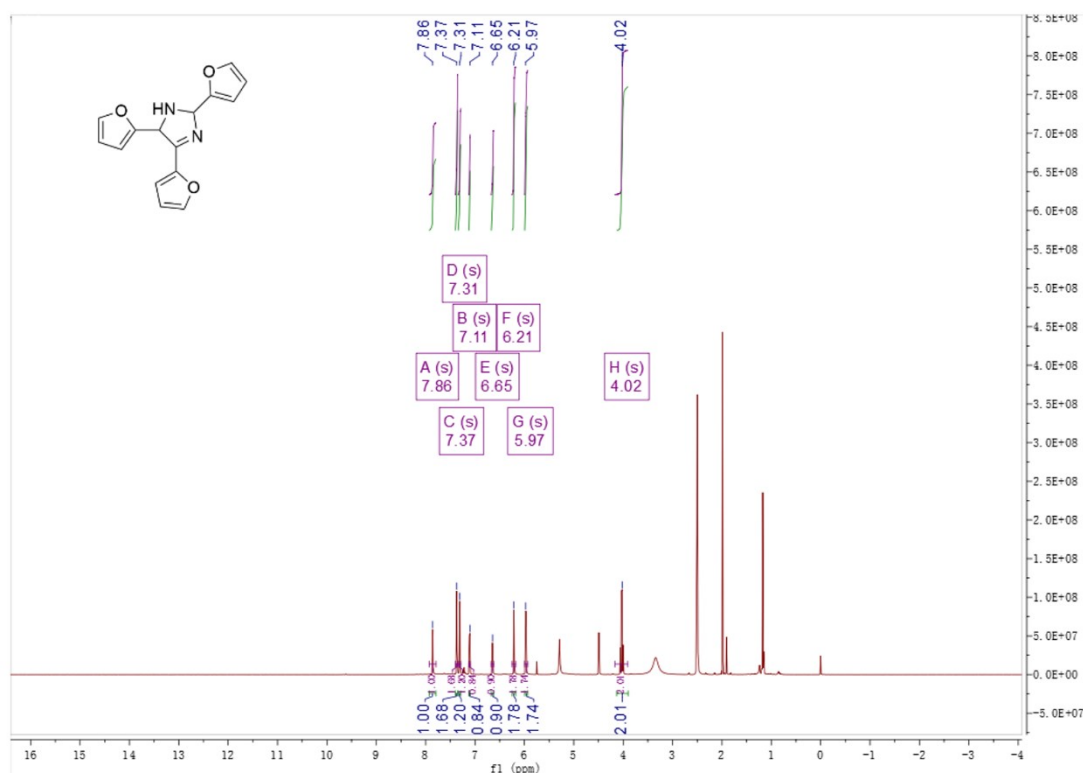
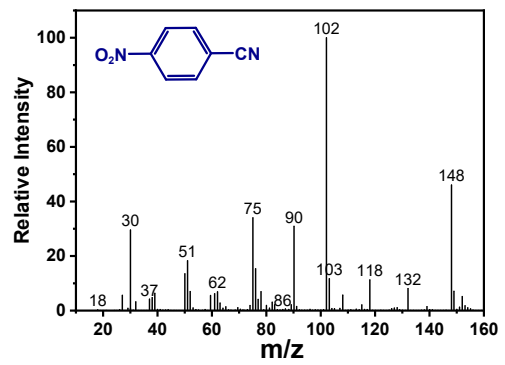
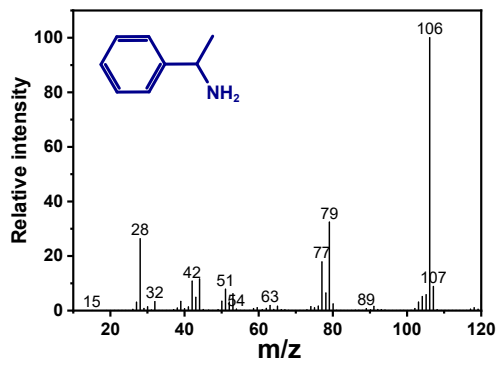
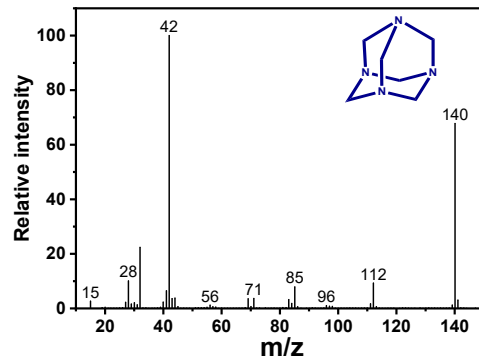
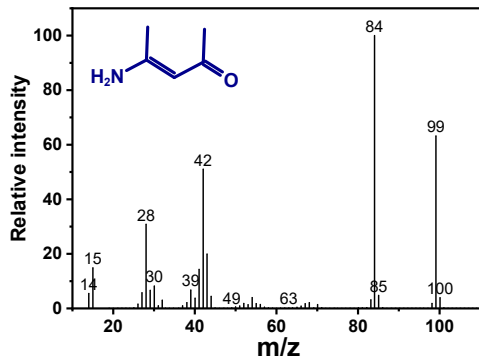
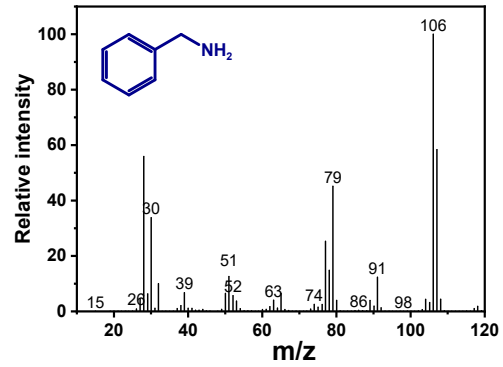
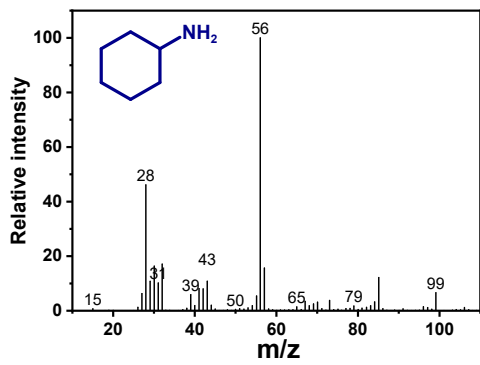
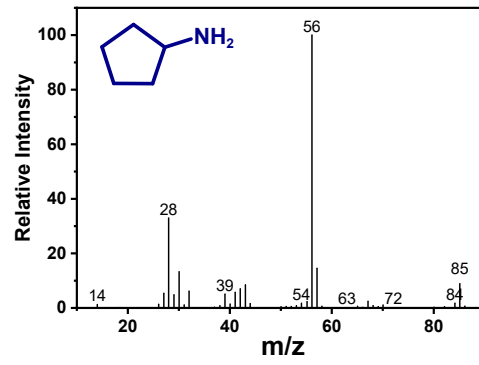
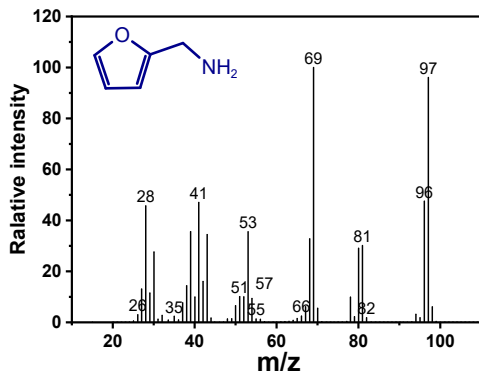


Fig. S5 ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$) of isolated trimer (72 % yield at 0 h). δ 7.86 (s, 1H, amine), 7.37 (s, 2H, 2-furan), 7.31 (s, 1H, 2-furan), 7.11 (s, 1H, 2-furan), 6.65 (s, 1H, 2-furan), 6.21 (s, 2H, 2-furan), 5.97 (s, 2H, 2-furan), 4.02 (s, 2H, methine).



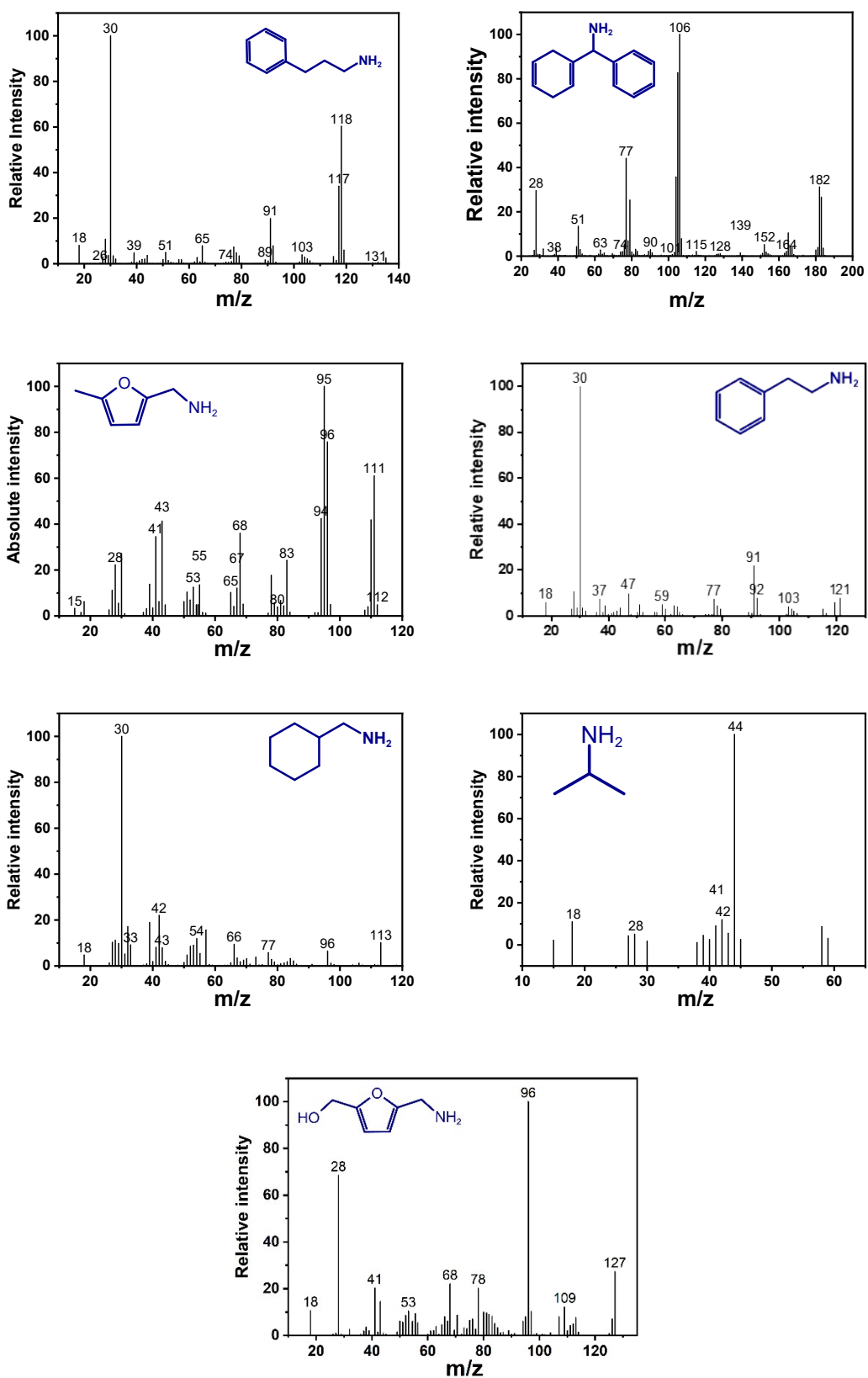


Fig. S6 MS spectra of the products for the reductive amination of various aldehydes and ketones catalyzed by Ni/pNC catalyst.

Notes and references

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