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Electronic Supplementary Information (ESI) for

Modulating trans-imination and hydrogenation towards the highly selective production of primary diamines from dialdehydes

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Experimental Procedures

Methods

Catalyst preparation. All catalysts were prepared by incipient wetness impregnation. As an example, for the preparation of Co/ZrO_2 catalyst, 209 mg $Co(OAc)_2{\cdot}4H_2O$ was added to 1.5 g water and sonicated for 10 min, followed by addition of 1 g ZrO_2. Then the mixture was evaporated to dryness at 333 K. The obtained solid was ground to powder and then transferred to a quartz boat in the tube furnace and fluxed with air for 30 min. The tube furnace was then heated to 673 K in air atmosphere at a ramp of 5 K/min and was held at that temperature for 2 h. After cooling to room temperature, the gas was switched to hydrogen atmosphere and the tube was fluxed with hydrogen for 30 min. The tube furnace was then heated to 623 K in hydrogen atmosphere at a ramp of 2 K /min and was held at that temperature for 2 h. After being cooled to room temperature, the catalyst was passivated with 1 % (v/v) O_2/N_2 for 4 h at room temperature. The other ZrO_2-supported metal catalysts were prepared with the similar procedure, except that the metal precusors were changed to the corresponding metal salts and the reduction temperature was adjusted to the suitable temperature (For Ni, Cu, Ru, Pd, Pt, Ir and Rh, the reduction temperature were 623 K, 673 K, 523 K, 523 K, 523 K, 573 K and 573 K, respectively).

Reaction tests. In the typical reaction for reductive amination of dialdehydes, 0.25 mmol 2,5-diformylfuran (DFF) (Bidepharm), 0.75 mmol butylamine, 30 mg catalyst, and 3 g methanol were put into an autoclave (Parr reactor with a volume of 50 mL). The autoclave was purged with NH_3 for three times, and charged with 0.6 MPa NH_3 and 2 MPa H_2 at room temperature. After sealing the autoclave, the reaction mixture was stirred at a rate of 800 r/min and heated at 373 K for 10 h with continuous stirring. After the reaction, the liquid-phase products were analyzed with a GC system (Agilent 7890A) equipped with a HP-5 column (30 m × 0.25 um × 0.25 mm i.d) and a FID detector by using dodecane as an internal standard.

The conversion of DFF (X_{DFF}) and the yield of BAMF (Y_{BAMF}) were calculated using the following equations:

$$\mathbf{X_{DFF}\ (\%)} = (\mathrm{mol}_{\mathrm{DFF\ consumed}})/\ (\mathrm{mol}_{\mathrm{DFF\ fed}}) * 100$$

$$\mathbf{Y_{BAMF}\ (\%)} = (\mathrm{mol}_{\mathrm{BAMF\ produced}})/\ (\mathrm{mol}_{\mathrm{DFF\ fed}}) * 100$$

The purification process of 2,5-bis(aminomethyl)furan (BAMF): After the typical reaction, the Co/ZrO_2 catalyst was removed by centrifugation, and the upper liquid was distilled by rotatory evaporator. Then, 5 ml CH_2Cl_2 and 5 ml H_2O were add to the residue, and the BAMF was extracted in H_2O phase. The pure BAMF solid was obtained by recrystallization.

H_2-TPR was carried out with a Micromeritics AutoChem II 2920 System. 0.10 g of the calcined sample was loaded in a quartz reactor, heated in Ar flow at 573 K for 1 h with a ramp of 10 K/min, and then cooled down to 323 K. The reactor was flushed with 10% H_2/Ar to reach a stable background. Then the sample was heated to 1073 K at a rate of 10 K/min in 10 vol% H_2/Ar with a flow rate of 30 mL/min.

Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) experiments were performed on a JEOL JEM-2100F microscope operated at 200 kV, equipped with an Oxford Instruments

ISIS/INCA energy-dispersive X-ray spectroscopy (EDS) system with an Oxford Pentafet Ultrathin Window (UTW) Detector. Before observation, the catalyst sample was ultrasonically dispersed in ethanol and then a drop of the suspension was put onto a copper TEM grid coated with a thin holey carbon film for STEM observation.

In-situ X-ray diffraction (XRD) analysis was carried out on a PANalytical X'pert diffractometer using Cu Kα radiation source (λ = 0.15432 nm) with a scanning angle (2θ) of 10^o- 80^o, operated at 40 kV and 40 mA. The Co/ZrO_2 catalyst was transferred to the chamber with H_2 flow of 20 mL/min, and the XRD spectra were collected with elevating the temperature.

H_2 and NH_3-microcalorimetric measurements were performed by a BT2.15 heat-flux calorimeter, which was connected to a gas handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement. The ultimate dynamic vacuum of the microcalorimetric system was 10^{-7} Torr. First, the fresh sample was reduced at 623 K for Co/ZrO_2 and 523 K for Pd/ZrO_2 in a special glass cell. After that, the glass cell was placed into the the high vacuum system and stabilized for 12 h. And the H_2-microcalorimetric data and NH_3-microcalorimetric data were collected by sequentially introducing small doses (10^{-6} mol) of H_2 and NH_3 into the system until it became saturated (5-6 Torr). The H_2 and NH_3-microcalorimetric adsorption was conducted under 313 K and 353 K, respectively. Simultaneously, the differential heat versus adsorbate coverage plots and adsorption isothermals can be obtained.

NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz Bruker DRX-400 NMR spectrometers.

Results and Discussion

Figure S1

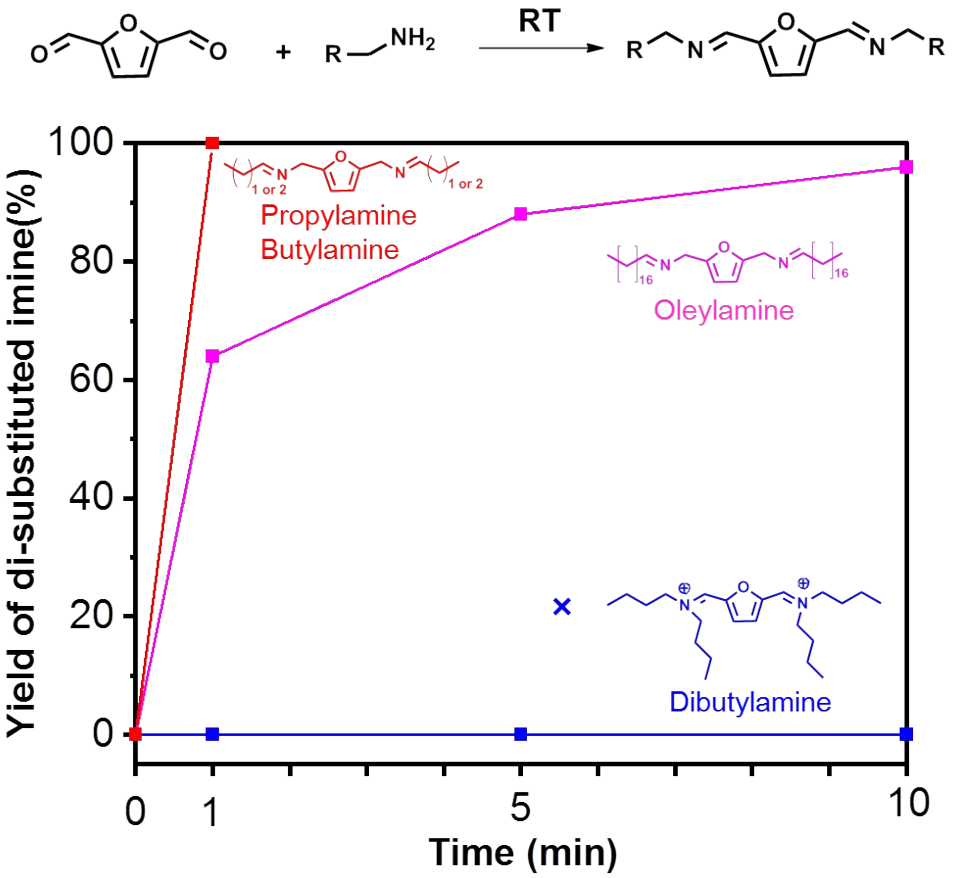


Figure S1. Reactivity of DFF with various alkylamines.

Reaction condition: 0.5 mmol DFF, 1.5 mmol alkylamines, 5 g methanol, room temperature.

Figure S2

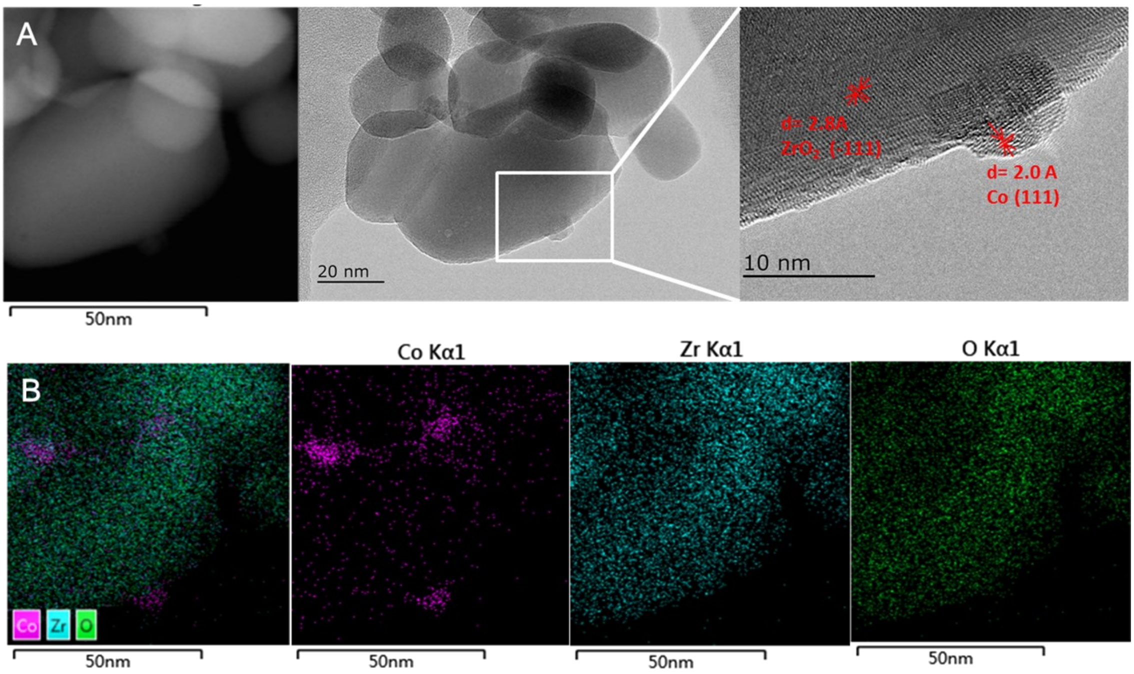


Figure S2. HAADF-STEM (A) and EDS-Mapping (B) of the Co/ZrO_2 catalyst.

Figure S3

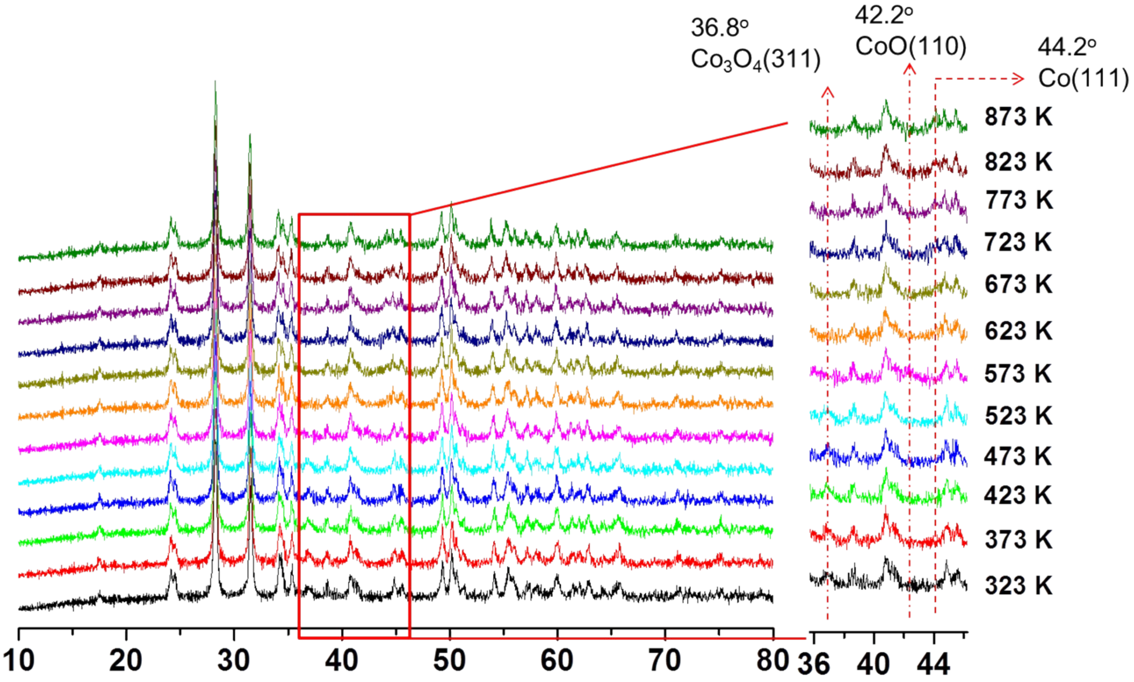


Figure S3. In-situ XRD patterns of Co/ZrO_2 catalyst.

The peak at 36.8° for Co_3O_4 (311) disappeared at 573 K and above; the peak at 42.2° for CoO (110) appeared only at 573 K, and then disappeared due to transformation into metallic Co^0. [S1]

Figure S4

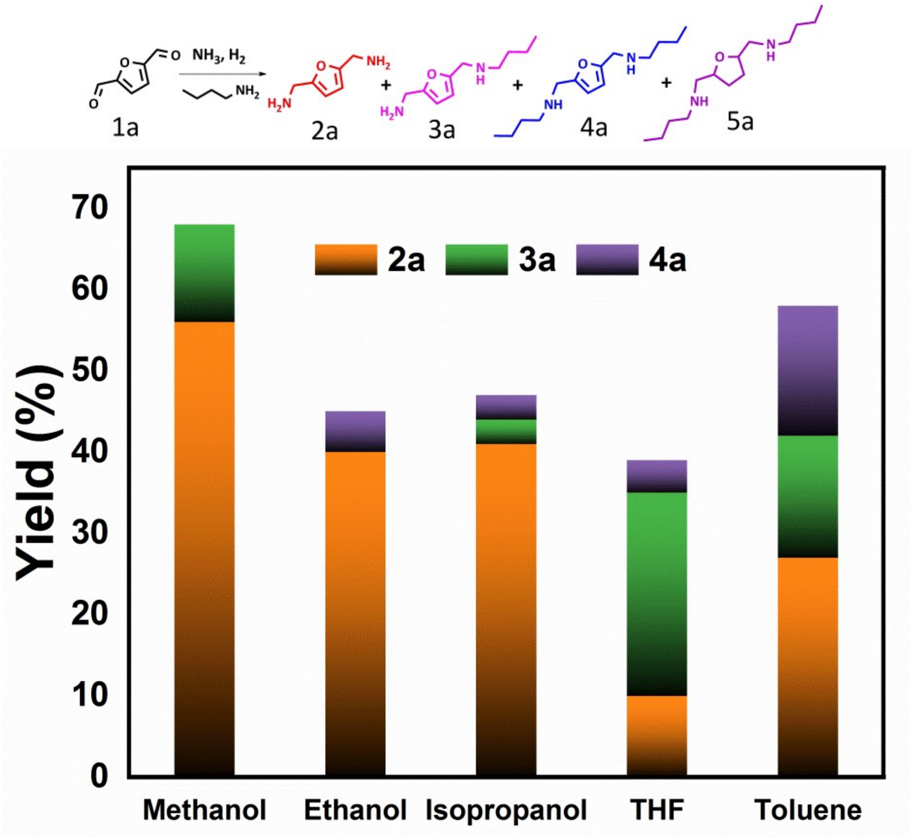


Figure S4. Solvents optimization over the Ru/ZrO$_2$ catalyst.

Reaction conditions: 30 mg Ru/ZrO$_2$ catalyst, 0.25 mmol DFF, 0.75 mmol butylamine, 3 g solvent, 0.6 MPa NH$_3$, 2 MPa H$_2$, 373 K, 10 h, dodecane as internal standard.

Figure S5

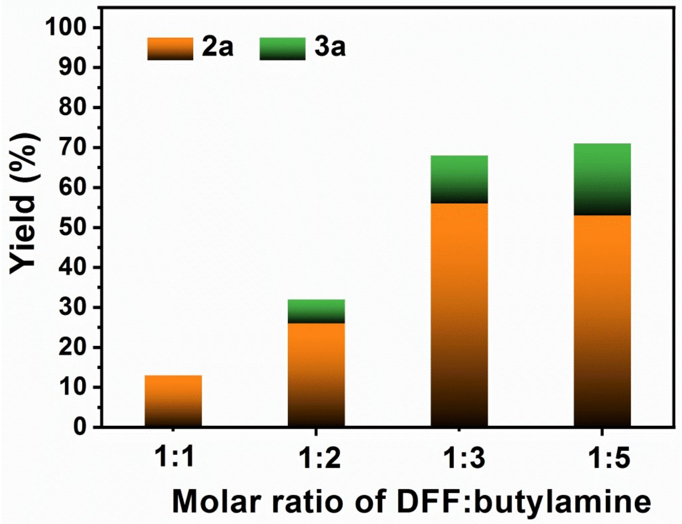


Figure S5. The effect of butylamine amount on the product yield over Ru/ZrO_2 catalyst.

Reaction conditions: 30 mg Ru/ZrO_2 catalyst, 0.25 mmol DFF, defined amount of butylamine, 3 g methanol, 0.6 MPa NH_3, 2 MPa H_2, 373 K, 10 h, dodecane as internal standard.

Figure S6

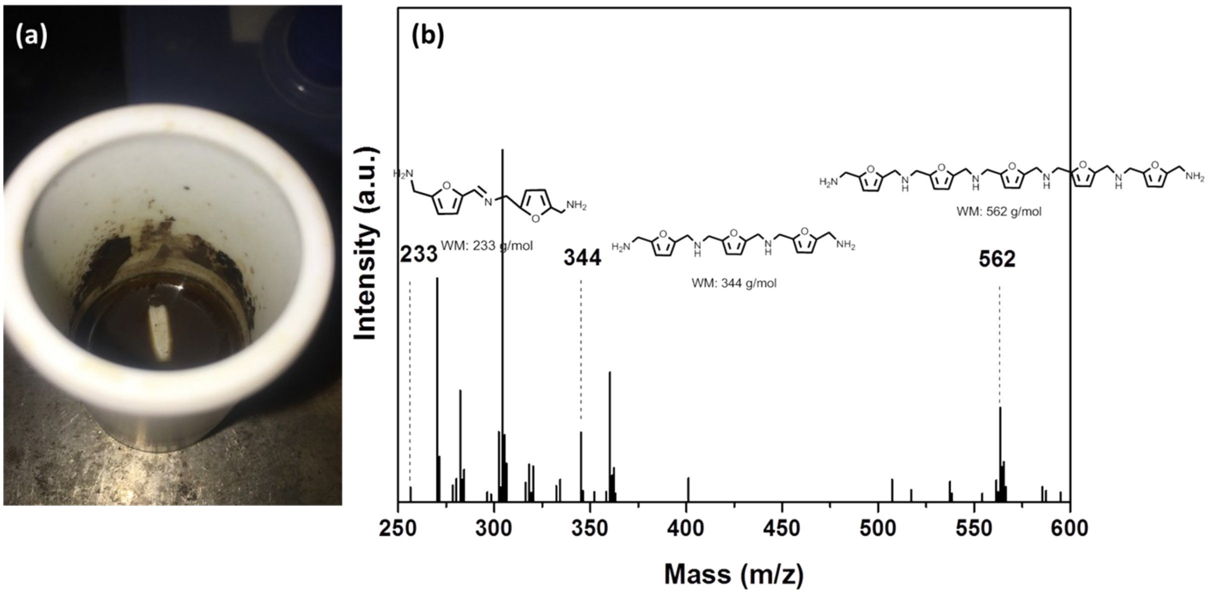


Figure S6. (a) Photograph of reduction amination of DFF over Co/ZrO$_2$ catalyst in the absence of alkylamine. (b) MALDI-TOF mass spectrum of (a) and the identification of some oligomers (m/z = MW +1 (H$^+$) or + 23 (Na$^+$).

Figure S7

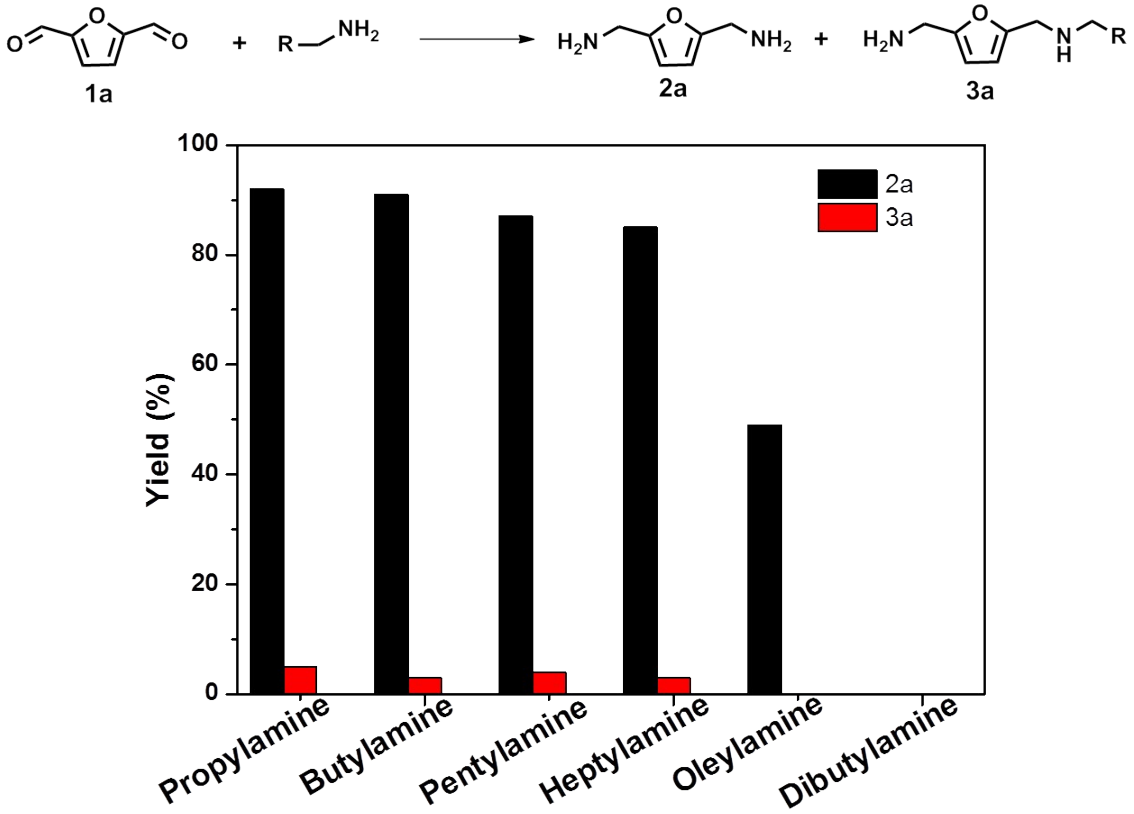


Figure S7. Effect of different alkylamines on the yield of BAMF over Co/ZrO_2 catalyst.

Reaction conditions: 30 mg Co/ZrO_2 catalyst, 0.25 mmol DFF, 0.75 mmol alkylamine, 3 g methanol, 0.6 MPa NH_3, 2 MPa H_2, 373 K, 10 h, dodecane as internal standard.

Figure S8

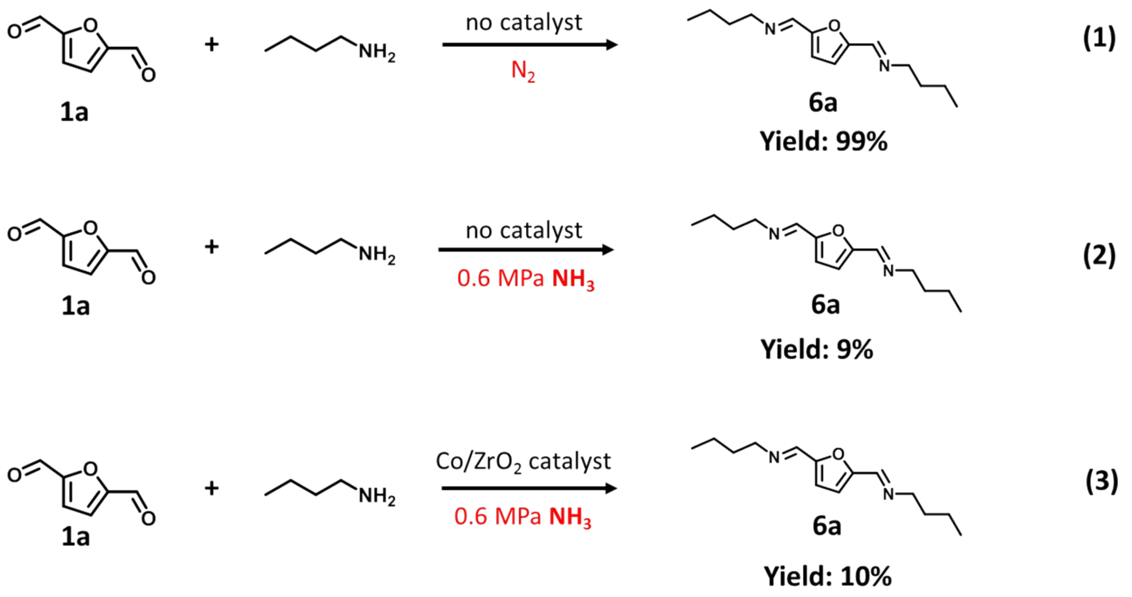


Figure S8. Reaction of DFF and butylamine under different atmosphere with or without catalyst.

(1) Without catalyst, 2MPa N_2; (2) Without catalyst, 0.6 MPa NH_3, 2 MPa N_2; (3) 30 mg Co/ZrO_2 catalyst, 0.6 MPa NH_3; 2 MPa N_2. Reaction conditions: 0.25 mmol DFF, 0.75 mmol butylamine, 3 g methanol, 373 K, 10 h, dodecane as internal standard.

Figure S9

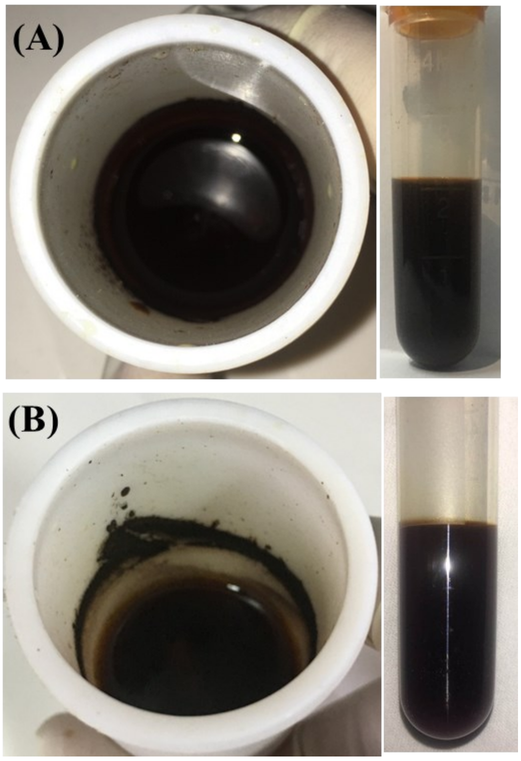


Figure S9. Photographs of reaction solutions under different conditions.

(A) Without catalyst, 0.6 MPa NH_3, 2 MPa N_2; (B) 30 mg Co/ZrO_2 catalyst, 0.6 MPa NH_3; 2 MPa N_2. (Reaction conditions: 0.25 mmol DFF, 0.75 mmol butylamine, 3 g methanol, 373 K, 10 h, dodecane as internal standard).

Figure S10

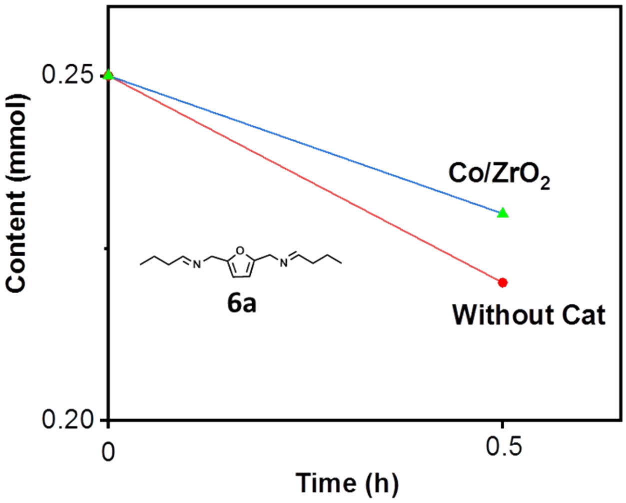


Figure S10. Reaction of 6a with NH_3 with or without catalyst.

Reaction conditions: 30 mg catalyst, 0.25 mmol 6a, 3 g methanol, 0.6 MPa NH_3, 2 MPa N_2, 373 K, 0.5 h, dodecane as internal standard.

Table S1. Differential adsorption heat of H_2 and NH_3 on Co/ZrO_2, Pd/ZrO_2 and ZrO_2 catalysts.

Entry	Catalyst	H_2		NH_3		H_2 adsorption after pre-adsorption of NH_3	
		Heat (kJ/mol)	Coverage (µmol/g)	Heat (kJ/mol)	Coverage (µmol/g)	Heat (kJ/mol)	Coverage (µmol/g)
1	Co/ZrO_2	99.7	8.7	168.5	138.1	n.d.	n.d.
2	Pd/ZrO_2	108.1	25.1	172.5	157.3	87.9	18.7
3	ZrO_2	n.d.	n.d.	198.9	123.2	n.d.	n.d.

Figure S11

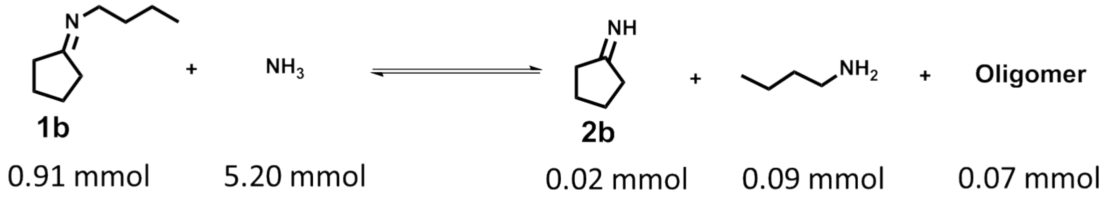


Figure S11. Trans-imination between secondary imine and NH_3 over Co/ZrO_2 catalyst.

Reaction condition: 1 mmol secondary imine (**1b**), 30 mg Co/ZrO_2, 3 g methanol, 0.6 MPa NH_3, 2 MPa N_2, 100℃, 30min.

Figure S12

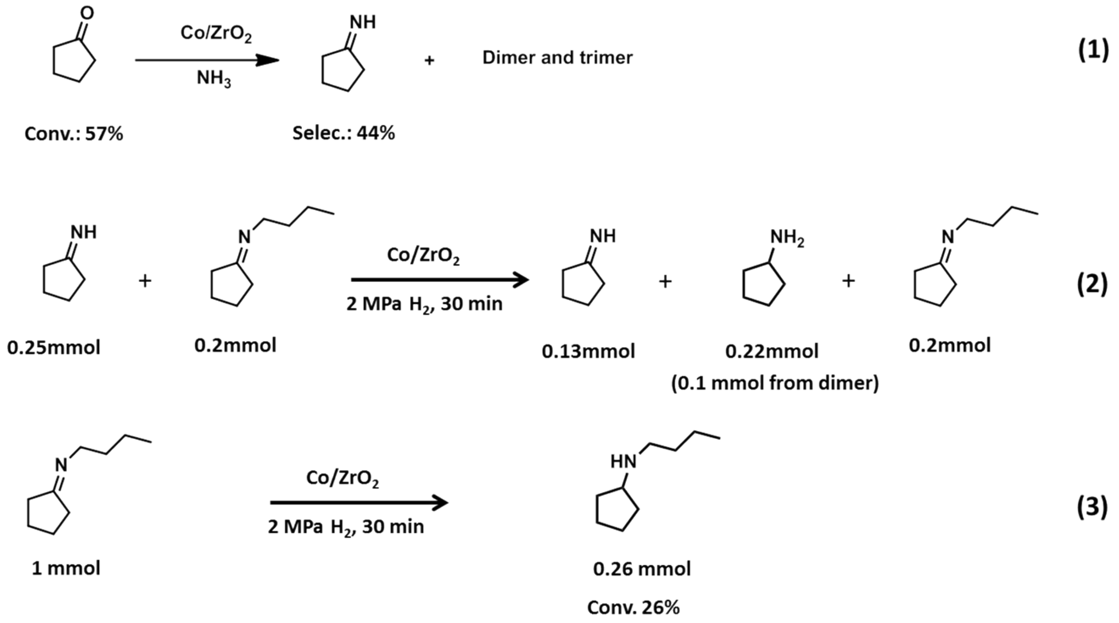


Figure S12. Competitive hydrogenation of primary and secondary imines over Co/ZrO$_2$ catalyst.

Reaction conditions: (1) 1 mmol cyclopentanone, 30 mg Co/ZrO$_2$, 3 g methanol, 0.6 MPa NH$_3$, 2 MPa N$_2$, 373 K, 30min; (2) Add 0.2 mmol secondary imine to the solution after reaction (1), 30 mg Co/ZrO$_2$, 2 MPa H$_2$, 373 K, 30min; (3) 1 mmol secondary imine, 30 mg Co/ZrO$_2$, 3 g methanol, 2 MPa H$_2$, 373 K, 30min.

Figure S13

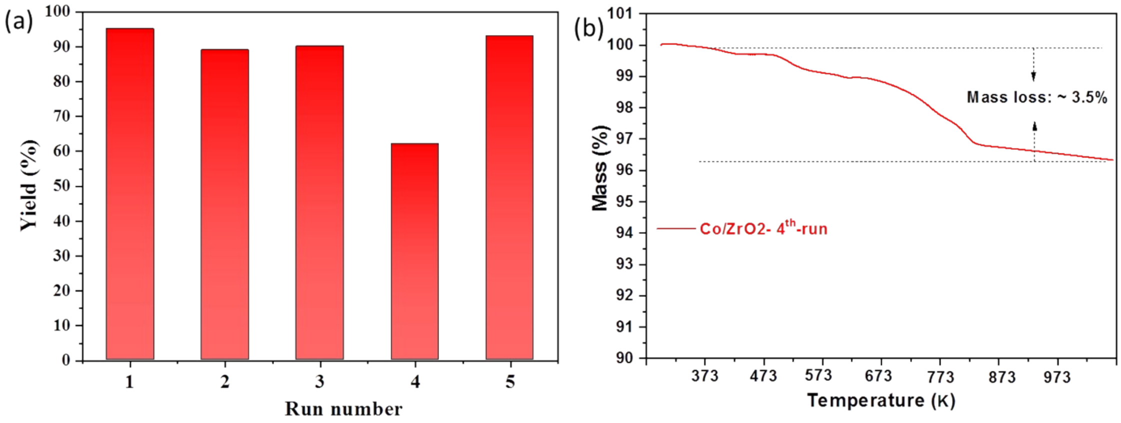
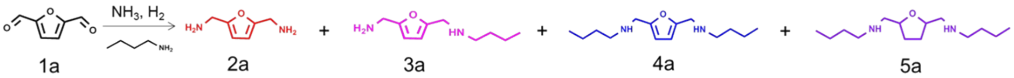


Figure S13. (a)Reuse test of Co/ZrO$_2$ catalyst and (b) TG result of used Co/ZrO$_2$ catalyst after the 4th run.

Reaction conditions: 30 mg Co/ZrO$_2$ catalyst, 0.25 mmol DFF, 0.75 mmol butylamine, 3 g methanol, 0.6 MPa NH$_3$, 2 MPa H$_2$, 373 K, 10 h, dodecane as internal standard. After each reaction, the catalyst was recovered by centrifugation and washing three times by ethanol. After the fourth reaction, the catalyst was calcined at 673 K and reduced at 623 K and then submitted to the fifth reaction.

Table S2. The Reductive amination of 10wt% DFF over Co/ZrO$_2$ catalyst[a]



Entry	Catalyst	DFF Concentration (wt%)	Yield (%)			
			2a	3a	4a	5a
1	Co/ZrO$_2$	10	71	4	16	n.d.

[a] Reaction condition: 200 mg Co/ZrO$_2$ catalyst, 2.5 mmol DFF, 7.5 mmol butyamine, 3 g methanol, 1.5 MPa NH$_3$, 4 MPa H$_2$, 373 K, 10h, dodecane as internal standard.

Figure S14

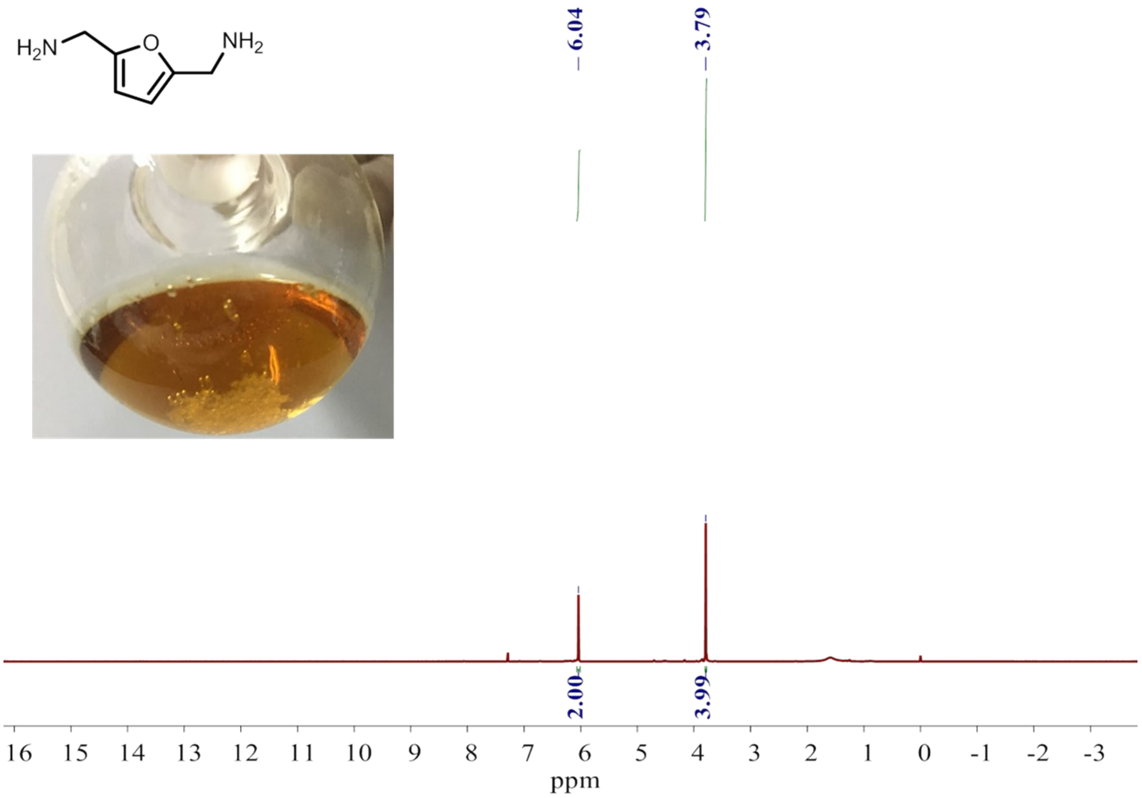


Figure S14. ^{1}H NMR spectrum ($CDCl_3$-*d*, 400 MHz) of isolated BAMF

δ6.04 (s, 2H, -C=CH-CH=C-), 3.79 (s, 4H, -CH_2-N)

Figure S15

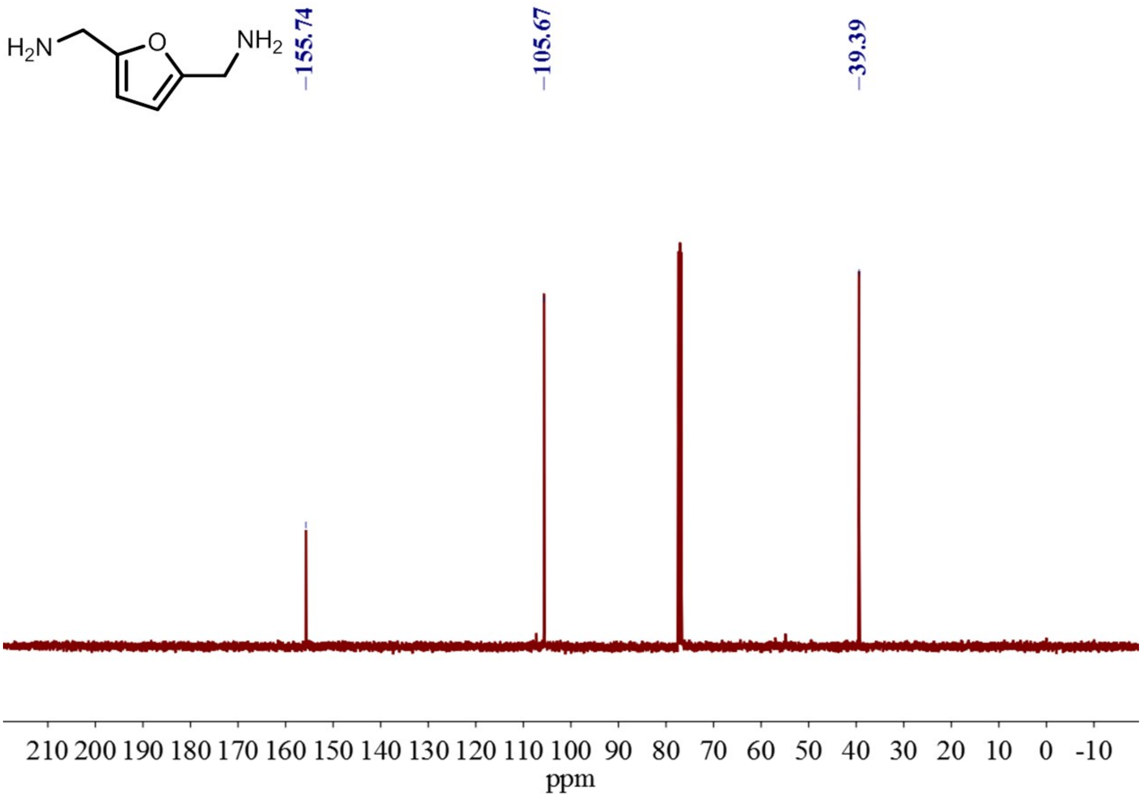


Figure 15. ^{13}C NMR spectrum (CDCl$_3$-*d*, 101 MHz) of isolated BAMF

δ155.74, 105.67, 39.39

Figure S16

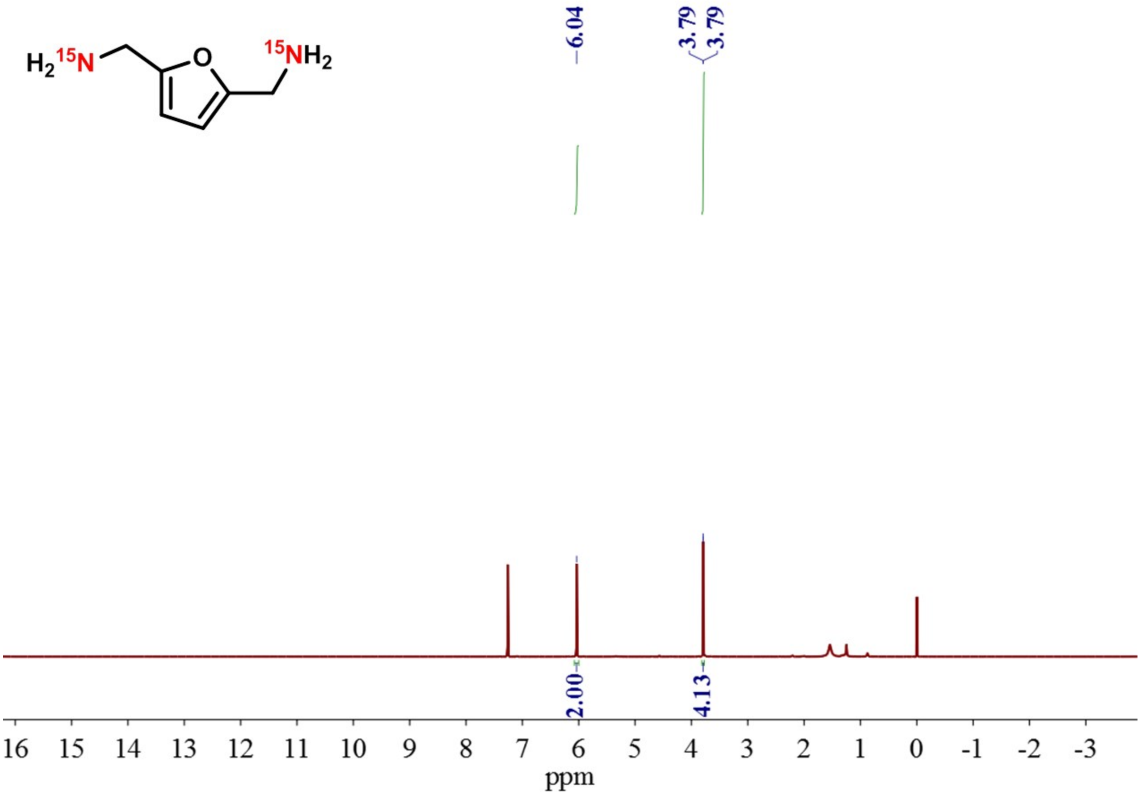


Figure S16. ^1H NMR spectrum ($CDCl_3$-*d*, 700 MHz) of isolated ^{15}N-substituted BAMF

(The ^{15}N-substituted BAMF was synthesised using $^{15}NH_3$ as amination agent)

δ6.04 (s, 2H, -C=CH-CH=C-), 3.79 (d, 4H, $-CH_2-N$)

Figure S17

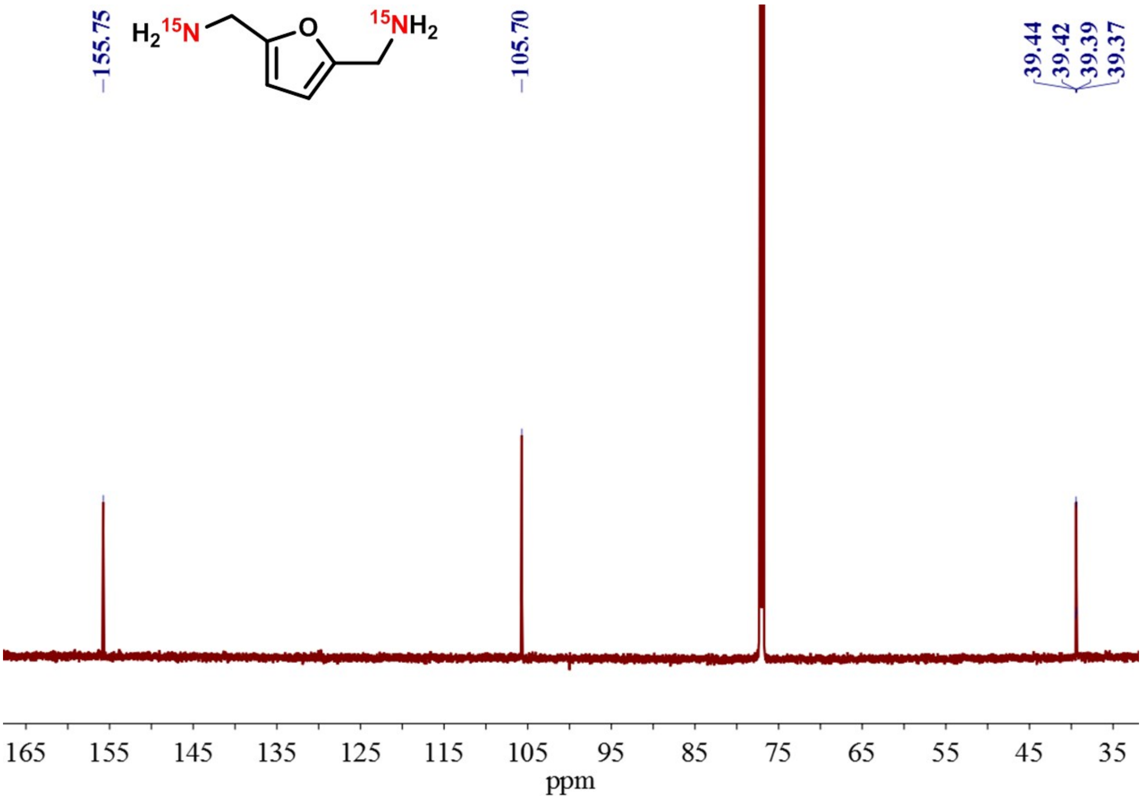


Figure S17. **^{13}C NMR spectrum (CDCl$_3$-*d*, 176 MHz) of isolated ^{15}N-substituted BAMF**

(The ^{15}N-substituted BAMF was synthesised using $^{15}NH_3$ as amination agent)

δ155.74, 105.67, 39.39(q, -^{15}N-C)

Figure S18

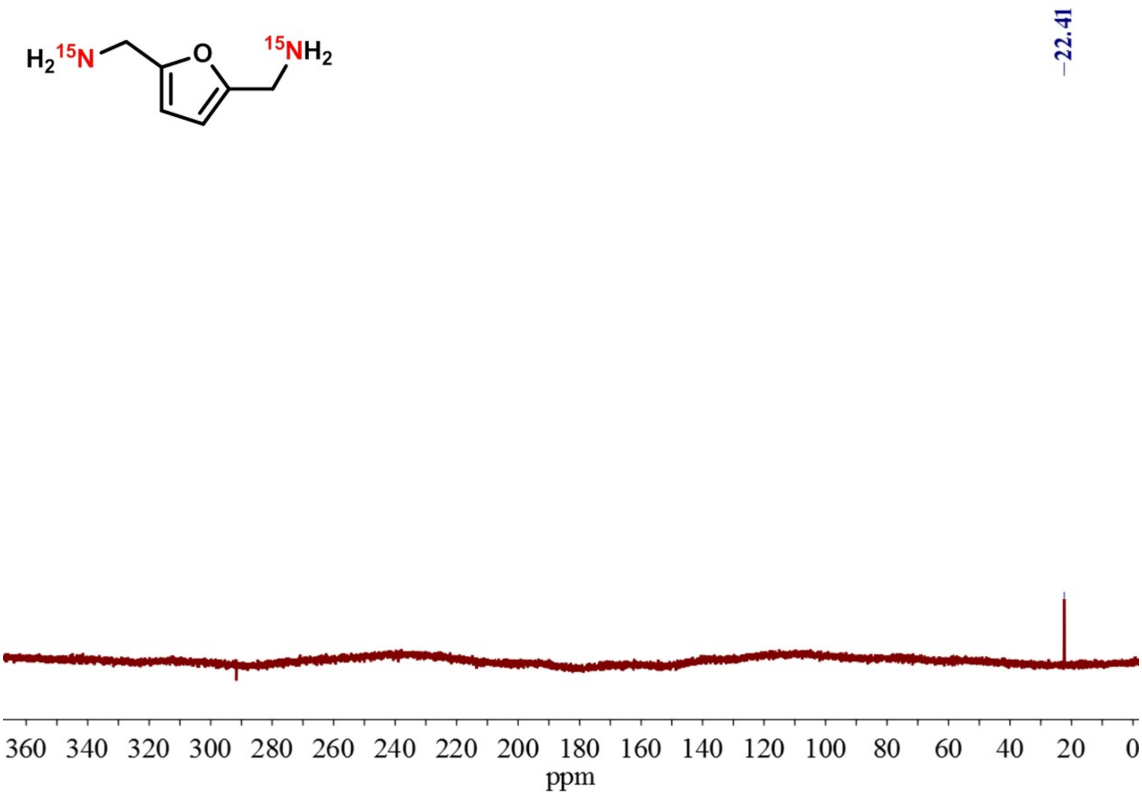


Figure S18. ^{15}N NMR spectrum (CDCl$_3$-*d*, 71 MHz) of isolated ^{15}N-substituted BAMF

(The ^{15}N-substituted BAMF was synthesised using $^{15}NH_3$ as amination agent)

δ22.41

Figure S19

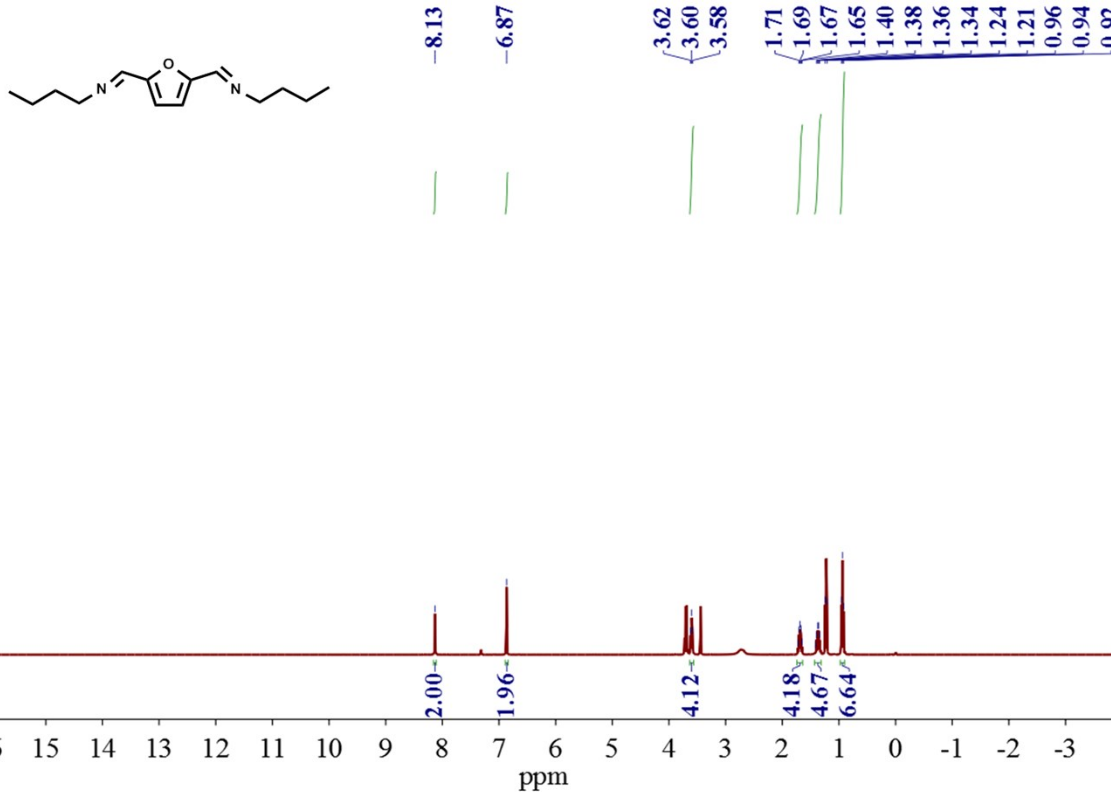


Figure S19. ^{1}H NMR spectrum (CDCl$_3$-*d*, 400 MHz) of isolated N$_1$,N$_2$-di-substituted imine (Schiff base 6a) δ8.13 (s, 2H, -CH=N-), 6.87 (s, 2H, -C=CH-CH=C-), 3.60 (t, *J* = 7.6 Hz, 4H, -N-CH$_2$-), 1.69 (m, 4H, -N-C-CH$_2$-), 1.38 (m, 4H, -N-C-C-CH$_2$-), 0.94 (t, *J* = 7.5 Hz, 6H, -N-C-C-C-CH$_3$)

Figure S20

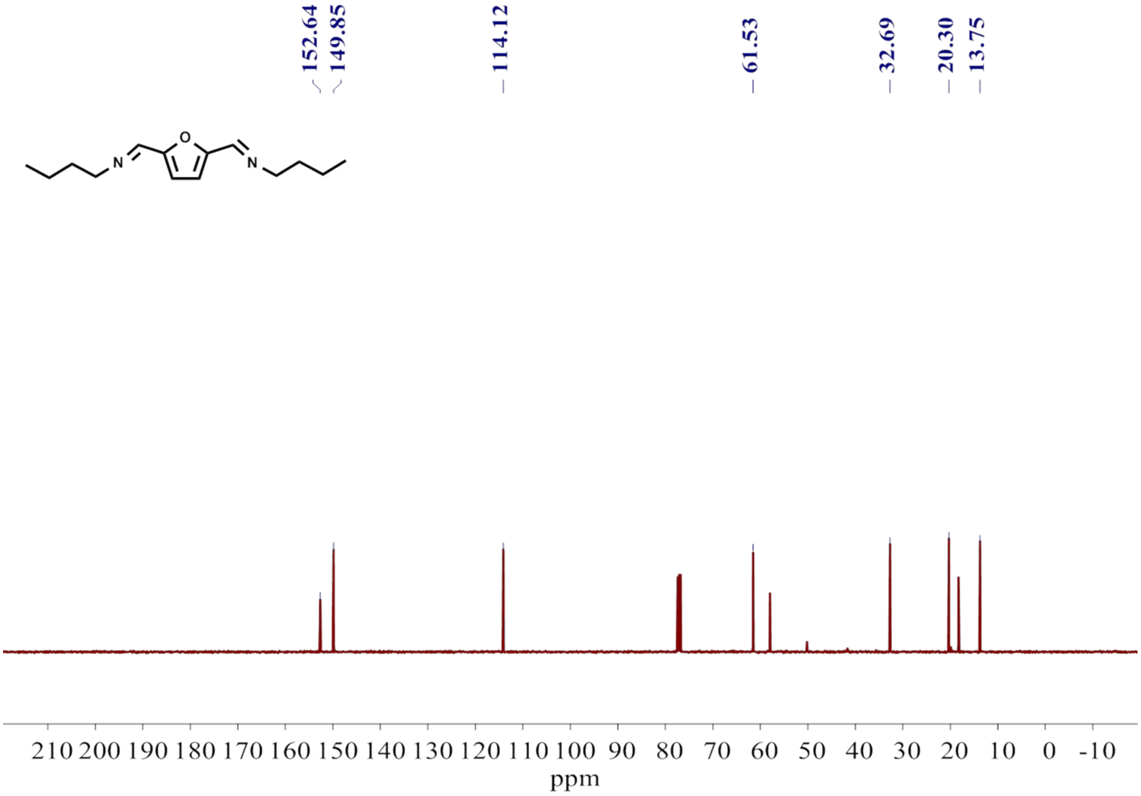


Figure S20. **^{13}C NMR spectrum (CDCl$_3$-*d*, 101 MHz) of isolated N$_1$,N$_2$-di-substituted imine (Schiff base 6a)**

δ152.64, 149.85, 114.12, 61.53, 32.69, 20.30, 13.75

Figure S21

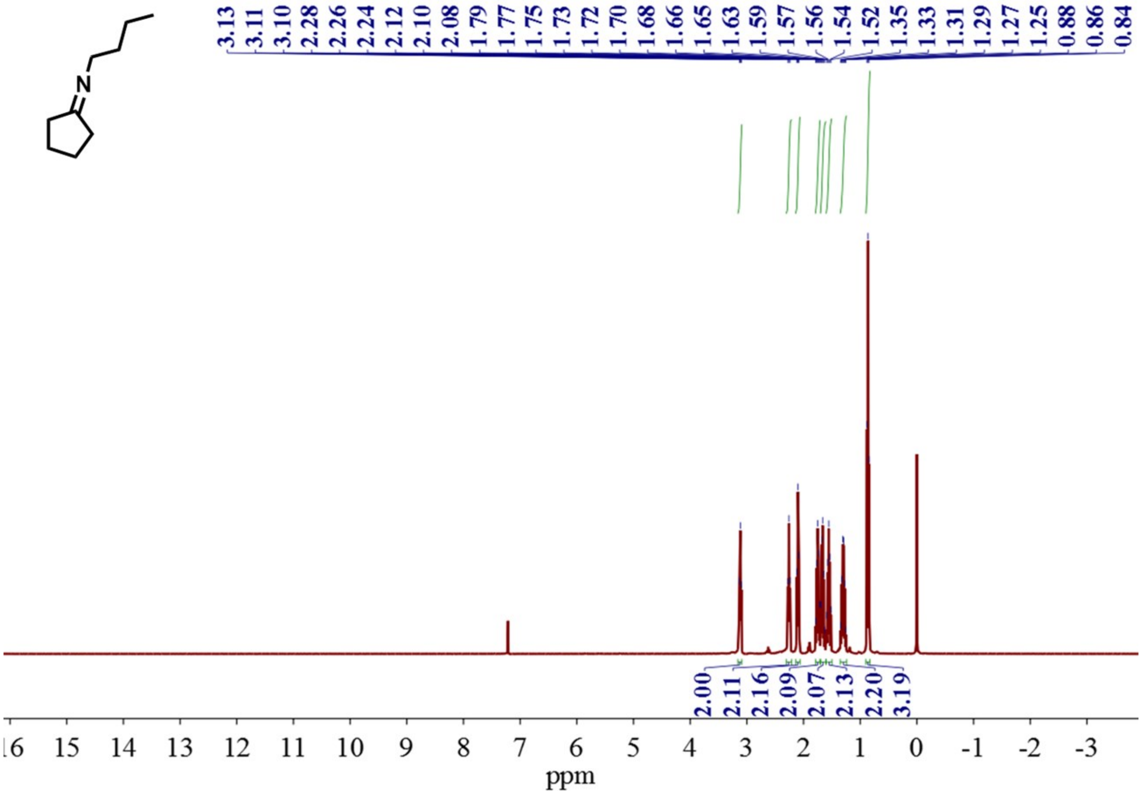


Figure S21. ^{1}H NMR spectrum ($CDCl_3$-*d*, 400 MHz) of isolated butyl-substituted Schiff base derived from cyclopentanone

δ3.11 (t, *J* = 7.1 Hz, 2H, =N-CH_2-), 2.28 (t, *J* = 7.3 Hz, 2H, -N=C-CH_2-), 2.16 (t, *J* = 7.5 Hz, 2H, -N=C-CH_2-), 1.75 (m, 2H, -N=C-CH_2-), 1.66 (m, 2H, -N=C-CH_2-), 1.56 (m, 2H, =N-C-CH_2-), 1.31(m, 2H, =N-C-C-CH_2-), 0.86 (t, *J* = 7.4 Hz, 3H, =N-C-C-C-CH_3)

Figure S22

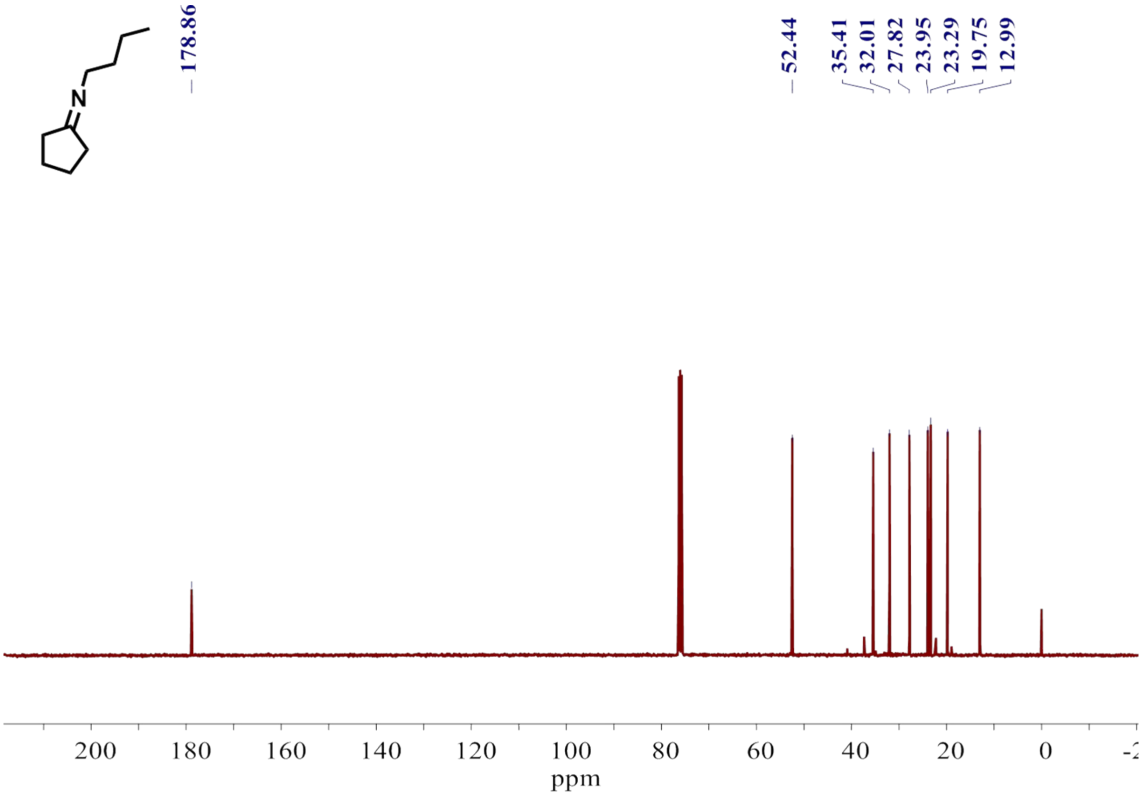


Figure S22. ^{13}C NMR spectrum (CDCl$_3$-*d*, 101 MHz) of isolated butyl-substituted Schiff base derived from cyclopentanone

δ178.86, 52.44, 35.41, 32.01, 27.82, 23.95, 23.29, 19.75, 12.99

Reference

S1. W. Li, X. Nie, X. Jiang, A. Zhang, F. Ding, M. Liu, Z. Liu, X. Guo and C. Song, *Applied Catalysis B: Environmental*, 2018, **220**, 397-408.