[*Supporting Information*]

Selective synthesis of 2,5-bis(aminomethyl)furan *via* enhancing catalytic dehydration-hydrogenation of 2,5-diformylfuran dioxime

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1. Experimental Section

1.1 Materials: 2,5-diformylfuran dioxime (**1**) was synthesized from 2,5-diformylfuran according to our previous report and purified by recrystallization before use. Raney Ni, Ru/C, Rh/C $RhCl_3 \cdot 3H_2O$ and γ-Al_2O_3 were purchased from Aladdin Chemistry Co. Ltd. MeOH, 28% aqueous ammonia and N,N-dimethylformamide (DMF) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Deionized water was purified by a Milli-Q system (Millipore). MCM-41, NaY (SiO_2/Al_2O_3 ratio is 5.1), NaZSM-5 (SiO_2/Al_2O_3 ratio is 25), HZSM-5 (SiO_2/Al_2O_3 ratio is 20, 60, 120, 200, 300, 500), Hβ (SiO_2/Al_2O_3 ratio is 25) were from Catalyst Plant of Nankai University. MCM-41, NaY, γ-Al_2O_3, NaZSM-5, HZSM-5, and Hβ were calcined at 550 °C for 5 h under air conditions before use. All chemicals were of analytical grade and used as received unless otherwise stated.

1.2 Catalyst preparation: Supported Rh catalysts were prepared by an impregnation method. In the case of the Rh/HZSM-5 catalyst, HZSM-5 (0.5 g) was added into aqueous $RhCl_3$ solution (0.5 g) with stirring. After treatment with ultrasound for 15 min, the mixture was kept for 24 h at room temperature. Then the mixture was dried at 110 ^{o}C for 12 h. The recovered solid powder was grinded and pretreated under H_2 flow (30 mL min^{-1}) at 200 ^{o}C for 3 h before the catalytic reactions. Other supported Rh catalysts were also prepared according to this method by changing the support materials.

1.3 Procedure for pyridine FT-IR measurements: The acid amount of Rh/HZSM-5 was estimated using pyridine FT-IR measurements. The sample was pressed into self-supporting disks (13 mm diameter, ca. 20 mg) and placed in an IR cell attached to a closed glass-circulation system. Prior to pyridine adsorption, the sample was dehydrated by heating at 500 °C for 1 h under vacuum. Then the sample was heated at 200 ^{o}C for 1 h to remove the physical adsorbed pyridine. FT-IR spectrum was scanned and the integrated area of absorption peaks at 1546 cm^{-1} (pyridinium ions formed by Brønsted acid sites) and 1454 cm^{-1} (pyridine coordinatively bonded to Lewis acid sites) was related to the amount of Brønsted and Lewis acid sites on the samples, respectively. The amount of the acid sites was calculated by the equation (C. A. Emeis, *Journal of catalysis*, **1993**, *141*, 347-354):

$$C\ (\text{pyridine on B sites}) = 1.88 \times IA(B)R^2/W;$$

$$C\ (\text{pyridine on L sites}) = 1.42 \times IA(L)R^2/W,$$

where C is the concentration of pyridine adsorbed on the Brønsted or Lewis acid sites in mmol g^{-1}, respectively, IA(B,L) is the integrated area of peaks around 1546 cm^{-1} or 1454 cm^{-1}, R is the radius of the sample disc in cm, W is the weight of the disc in milligram.

1.4 Procedure for transmission electron microscopy (TEM): The microstructure of Rh/HZSM-5 was examined by TEM on a JEOL JEM-2100EX electron microscopy. Before TEM investigation, the samples were dispersed by ultrasonication in anhydrous ethanol, then the solution was dropped onto a carbon film supported on a copper grid. The distribution of particle size was obtained by measuring 100-200 particles in TEM images.

1.5 Typical procedure for conversion of 1 to 2,5-bis(aminomethyl)furan (2): The conversion of **1** to **2** was conducted in a 15 mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. 1.0 mmol **1** (154 mg), 100 μL 28% aqueous ammonia, 30 mg Rh/HZSM-5 (SiO_2/Al_2O_3 ratio is 20), 7.0 mL MeOH were loaded into the reactor. Then the reactor was sealed and purged with H_2 for 3 times to exclude air. 2.0 MPa H_2 was charged into the reactor when the autoclave was heated to 130 ^oC under stirring. After reaction all products in the liquid phase were analyzed using gas chromatography-mass spectrometer (GC-MS), high performance liquid chromatography (HPLC) and nuclear magnetic resonance (NMR). The catalyst was recovered by centrifugation, washed with DMF (25 mL × 3), dried at 110 ^oC under vacuum, and then utilized for reuse experiments.

1.6 Procedure for identification and isolation of 2: When the reaction of **1** to **2** was completed, the reaction mixture in the liquid phase was evaporated to remove MeOH. **2** was purified by silica gel chromatography and identified by NMR. ^1H NMR

($CDCl_3$, 400 MHz): δ = 2.76 (4H), 3.63 (4H), 6.06 ppm (2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 38.20, 103.85, 155.69 ppm (See Fig. S9-10).

1.7 Product analysis: HPLC was conducted on a WATERS 600 with a Zorbax 80Å Extend-C18 column (4.6 × 150 mm, 5 μm, Agilent Technologies) attached to a UV/Vis detector. A mixture of CH_3OH and H_2O (v: v = 10: 90) (mobile phase) was run through the column (maintained at 35 °C) at a flow rate of 1.0 $mL min^{-1}$. External standard method was utilized for calculation of the conversions and product yields. The conversion of substrate (mol%) and yield of products (mol%) were calculated according to the following formula:

$$\text{Conversion (\%)} = \left(1 - \frac{\text{Moles of Substrate after reaction}}{\text{Moles of Substrate loaded initially}}\right) \times 100\%$$

$$\text{Yield (\%)} = \left(\frac{\text{Moles of product}}{\text{Moles of Substrate loaded initially}}\right) \times 100\%$$

2. Additional results

Fig. S1 Image of reaction solution of **1** over Rh/NaY catalyst (Table 1, entry 5 in the main text).

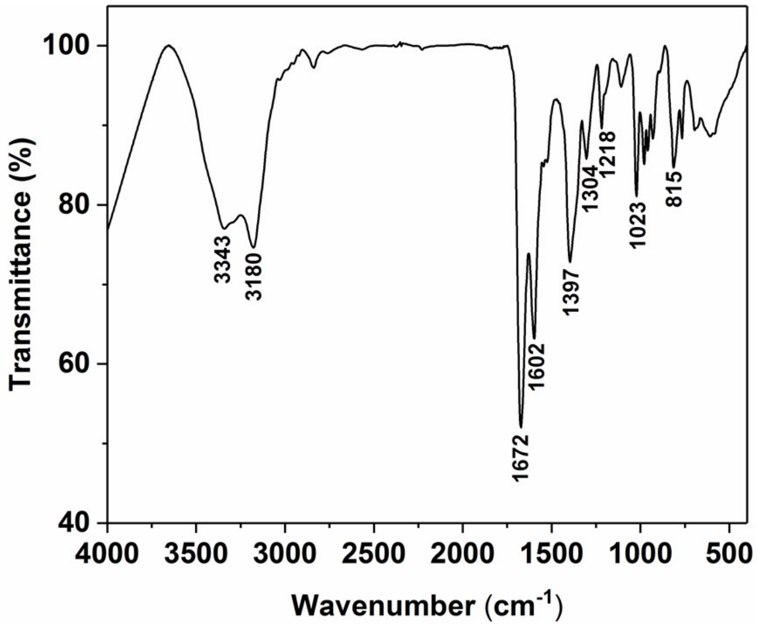


Fig. S2 IR spectrum of reaction solution of **1** over Rh/NaY catalyst (Table 1, entry 5 in the main text). The peaks at 3343 cm^{-1} and 3180 cm^{-1} were attributed to the N-H stretching vibrations of amide by-products. The peak at 1672 cm^{-1} was attributed to the C=O stretching vibrations of amide. The peak at 1218 cm^{-1} was attributed to the C-N stretching vibrations of amine by-products.

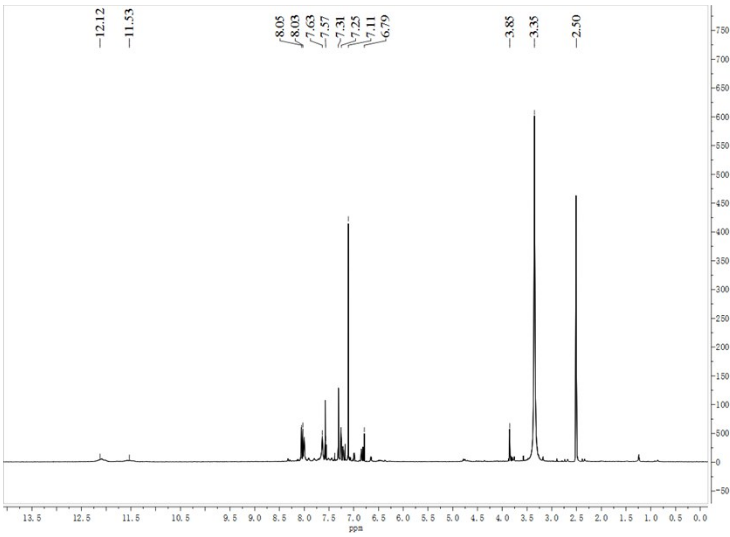


Fig. S3 ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of reaction solution of **1** over Rh/NaY catalyst (Table 1, entry 5 in the main text). δ (ppm) 8.05 (amide); 7.63 (amide); 7.11 (furan); 3.85 (CH_2).

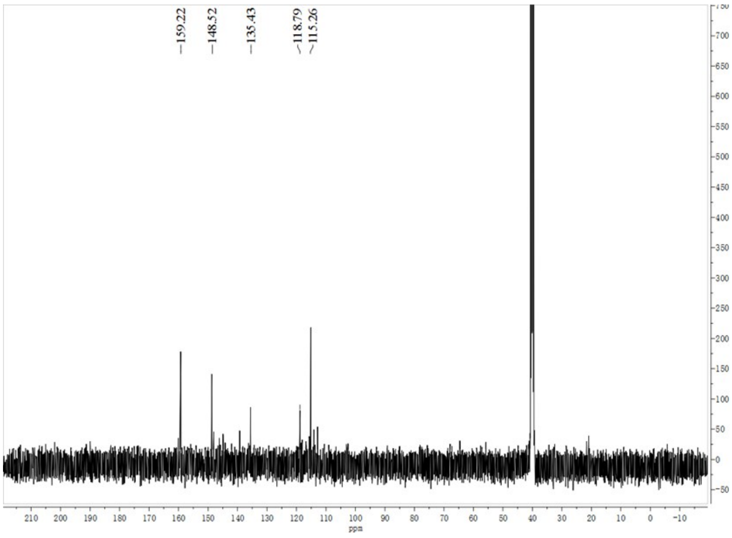
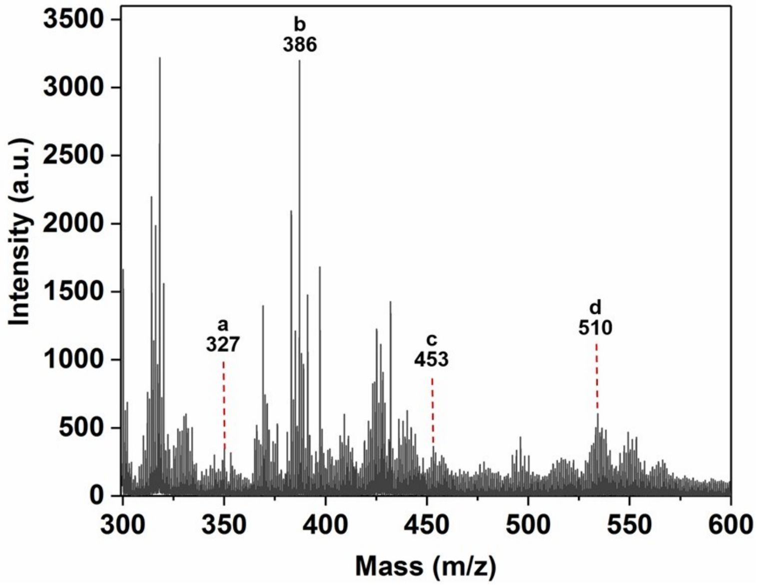
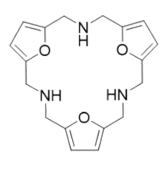
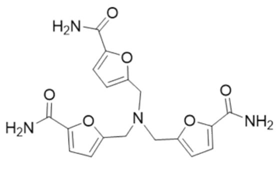


Fig. S4 ^{13}C NMR (DMSO-d_6, 101 MHz) spectrum of reaction solution of **1** over Rh/NaY catalyst (Table 1, entry 5 in the main text). δ (ppm) 159.22 (amide); 148.52 (furan); 115.26 (furan).

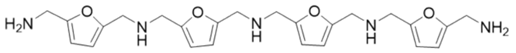




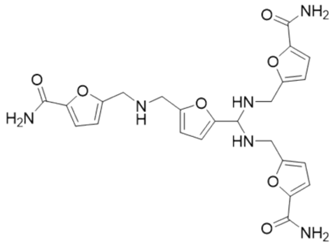
a (MW = 327)



b (MW = 386)



c (MW = 453)



d (MW = 510)

Fig. S5 MALDI-TOF mass spectrum of reaction solution of **1** over Rh/NaY catalyst (Table 1, entry 5 in the main text) and proposed structure of oligomers (m/z = MW + 1 (H^+) or + 23 (Na^+)).

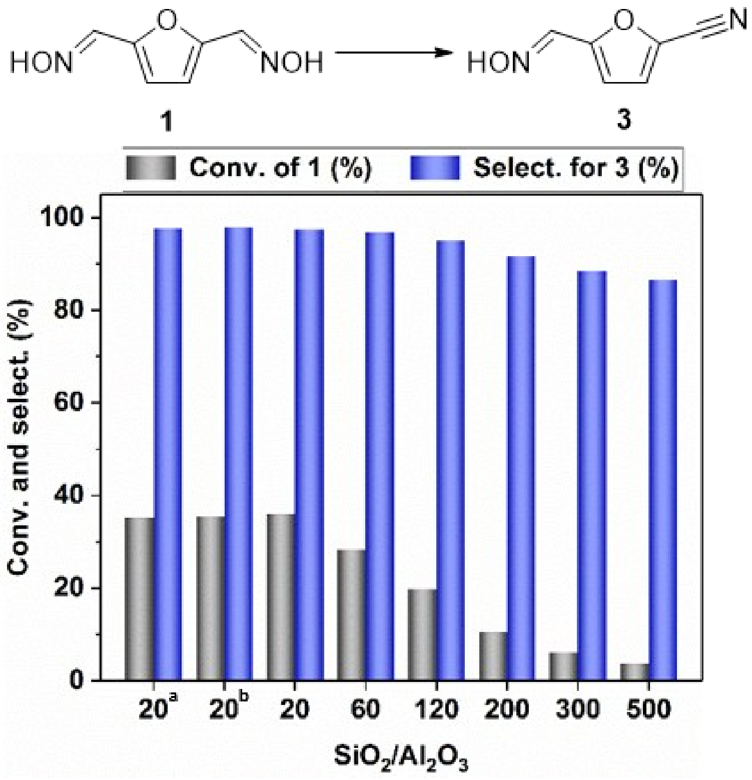


Fig. S6 Dehydration of **1** catalyzed by Rh/HZSM-5 with different SiO_2/Al_2O_3 ratio. Reaction conditions: 1.0 mmol **1** (154 mg), 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa N_2, 90 °C, 30 min. [a]HZSM-5 substituting for Rh/HZSM-5 and 100 μL 28% aqueous ammonia was added. [b]HZSM-5 substituting for Rh/HZSM-5.

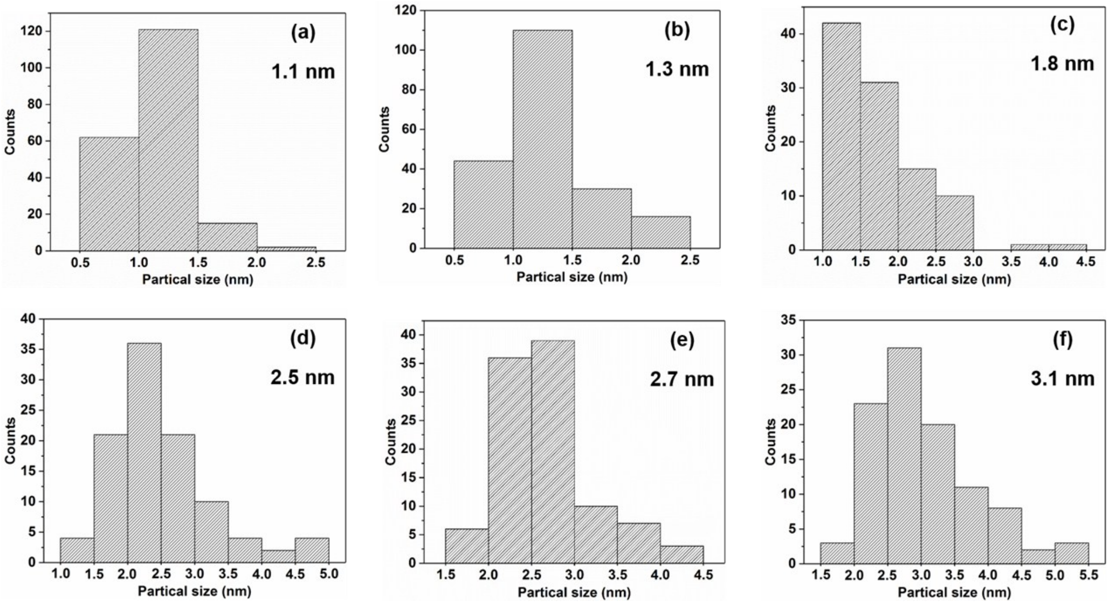


Fig. S7 Particle size distribution of Rh/HZSM-5 with different SiO_2/Al_2O_3 ratio. The SiO_2/Al_2O_3 ratio of (a)-(f) is 20, 60, 120, 200, 300, 500, respectively.

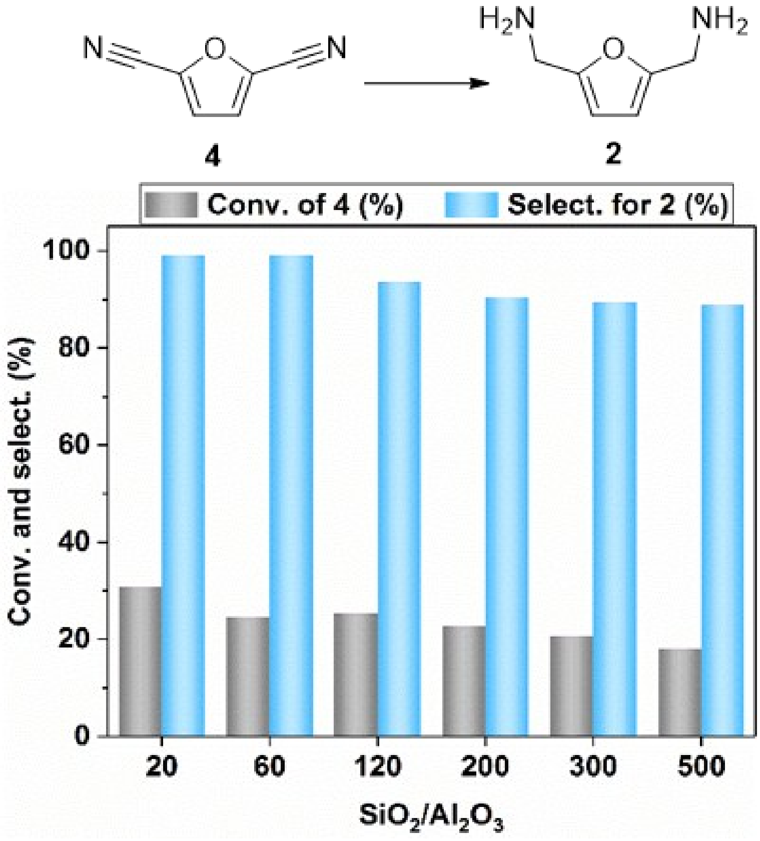


Fig. S8 Hydrogenation of **4** catalyzed by Rh/HZSM-5 with different SiO_2/Al_2O_3 ratio. Reaction conditions: 1.0 mmol **4** (118 mg), 100 μL 28% aqueous ammonia, 30 mg Rh/HZSM-5, 7.0 mL MeOH, 2.0 MPa H_2, 90 °C, 30min.

Table S1 Rh content of Rh/HZSM-5 with different SiO_2/Al_2O_3 ratio.

SiO_2/Al_2O_3 ratio	Rh Content (wt%)	
	Calculated results	ICP-OES results
20	4.95	4.14
60	4.90	3.86
120	4.93	4.00
200	5.01	4.31
300	4.94	4.01
500	4.95	4.20

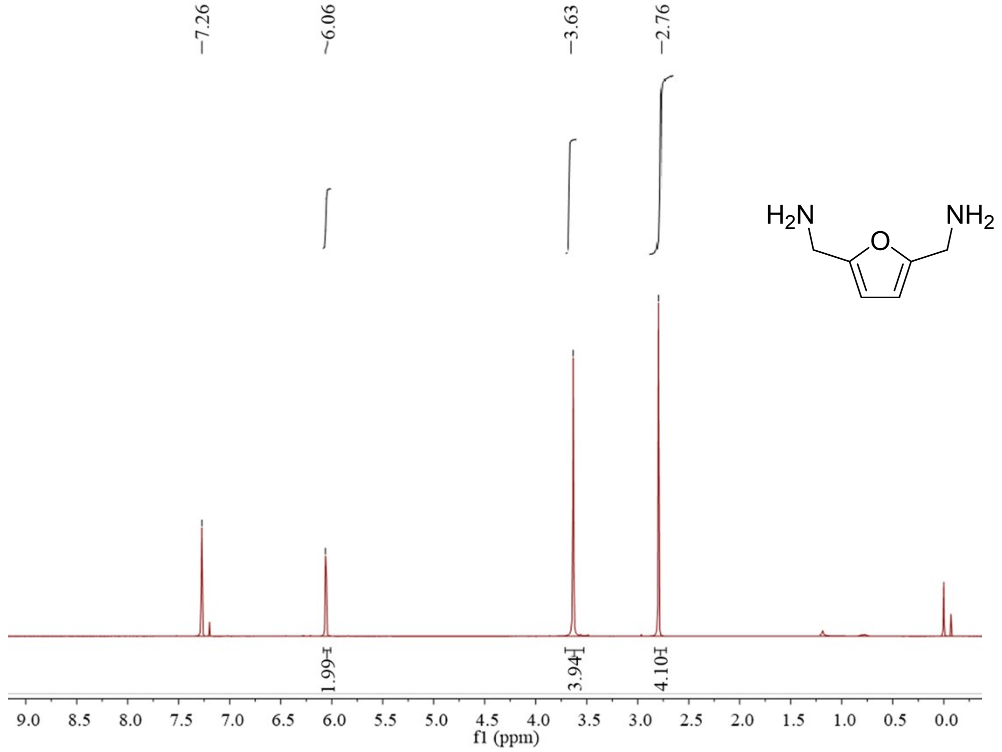


Fig. S9 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of isolated **2**.

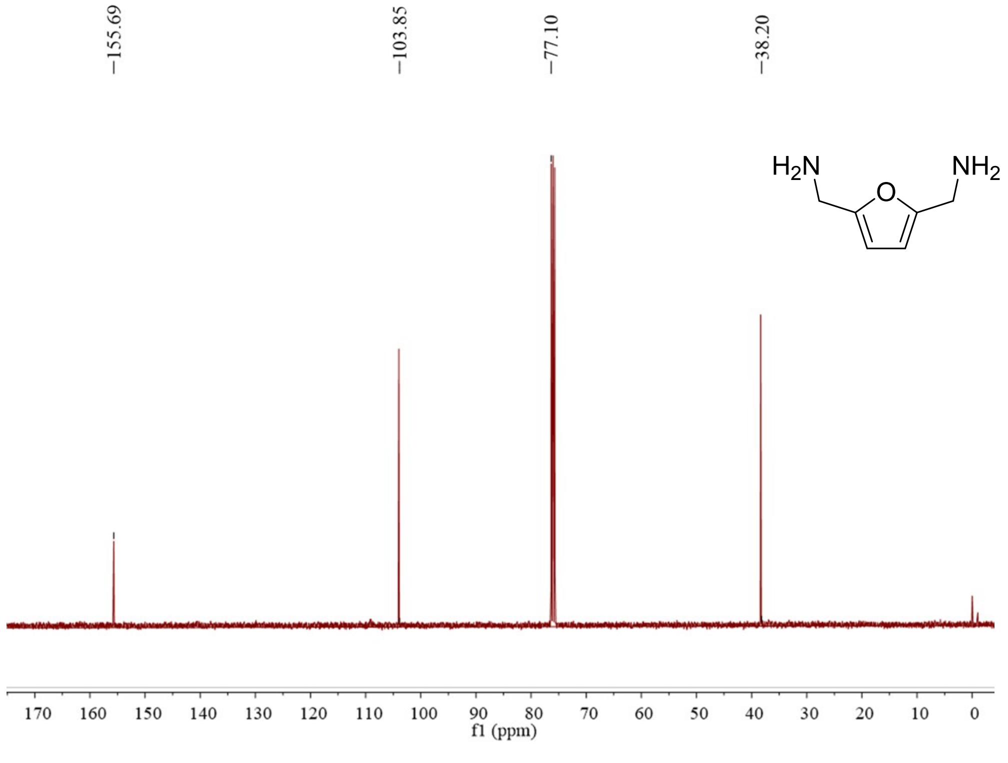


Fig. S10 ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of isolated **2**.