Electronic Supplementary Information (ESI) for

An efficient approach to synthesizing 2,5-bis(*N*-methyl-aminomethyl)furan from 5-hydroxymethylfurfural *via* 2,5-bis(*N*-methyl-iminomethyl)furan using a two-step reaction in one pot

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Number of pages: 30

Number of figures: 19

Number of tables: 5

EXPERIMENTAL SECTION

2.1. Materials. HMF (99%) was obtained from Shanghai Energy Chemical Industrial Co. Ltd (Shanghai, China). CuO, ZnO, Fe_2O_3, V_2O_5, $VOSO_4$, MoO_3, Mn_2O_3, Mn_3O_4, MnO, manganese chloride tetrahydrate, ammonium persulfate, methanol, H_2SO_4, $NaHCO_3$, Ru/C, Pt/C, Pd/C, Raney-Ni, Raney-Co, aniline, furfurylamine, alkylamines and hexadecane were supplied by Aladdin Chemical Technology Co. Ltd (Shanghai, China). MIFA (99%), 30 wt% methylamine methanol solution, potassium permanganate, and other reagents were purchased in Xiamen Green Reagent Glass Instrument Co., Ltd. No further treatment was conducted for all reagents before use.

2.2. Catalysts preparation. α-, β-, and γ-MnO_2 were prepared according to previous work.[1]

Synthesis of α-MnO_2, $KMnO_4$ (2.496 g, AR) and $MnCl_2 \cdot 4H_2O$ (1.227 g, AR) were mixed in 80 mL de-ionized water and treated in a Teflon-sealed autoclave at 160 ℃ for 12 h. After the treatment, the resulting solid was collected by filtration, then washed repeatedly with ultrapure water to pH≈7 and dried at 80 ℃ for 10 h. Finally, the samples were calcinated at 400 ℃ for 4 h.

Synthesis of β-MnO_2, $MnCl_2 \cdot 4H_2O$ (3.404 g, AR) and $(NH_4)_2S_2O_8$ (3.898 g) were mixed in 80 mL de-ionized water and treated in a Teflon-sealed autoclave at 160 ℃ for 12 h. After the reaction, the precipitate was collected by filtration, then washed repeatedly with ultrapure water to pH≈7 and dried at 80 ℃ for 10 h. Finally, the samples were calcinated at 400 ℃ for 4 h.

Synthesis of γ-MnO_2, $MnCl_2 \cdot 4H_2O$ (1.583 g, AR) and $(NH_4)_2S_2O_8$ (1.801 g, AR) were mixed in 80 mL de-ionized water and treated in a round-bottomed flask at 90 ℃ for 24 h under the normal pressure. After the treatment, the resulting solid was collected by filtration, then washed repeatedly with ultrapure water to pH≈7 and dried at 80 ℃ for 10 h. Finally, the samples were calcinated at 300 ℃ for 4 h.

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[1] F. Gao, X. Tang, H. Yi, C. Chu, N. Li, J. Li and S. Zhao, *Chem. Eng. J.*, 2017, **322**, 525-537.

2.3. Catalysts Characterization. The X-ray diffraction (XRD) patterns of the catalysts were obtained by using a Rigaku Ultima IV diffractometer with a Cu Kα radiation source (detection parameters: 30 mA, 40 kV, and 2θ from 10° to 90° at a scanning speed of 10°/min).

The morphology of the catalyst was inspected by a scanning electron microscopy (SEM) by using a Hitachi S-4800 microscope at 20 kV. The infrared (IR) spectra of samples were recorded on the Thermo Scientific Nicolet iS5 Fourier transform infrared (FT-IR) spectrometer using the KBr pellet method.

The N_2 adsorption-desorption analysis was performed for determining the specific surface area and pore distribution of the catalysts by using Micromeritics ASAP 2020 HD88. Prior to the measurement of adsorption, the samples were degassed under vacuum at 373 K for 4 h. The specific surface area, pore volume, and pore diameter of the samples were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The X-ray photoelectron spectroscopy (XPS) analysis was performed by using a Thermo Scientific ESCALAB 250Xi electron spectrometer under a base pressure less than 2×10^{-9} mbar. A monochromatic Al Kα ($h\nu$ = 1486.6 eV) excitation energy source was adopted. The binding energies were calibrated by assuming the biding energy of the C 1s line to be 284.8 eV.

O_2 temperature-programmed desorption (O_2-TPD), O_2 temperature-programmed oxidation (O_2-TPO), and H_2 temperature-programmed reduction (H_2-TPR) were measured by using an automated multiuse adsorption instrument (Micromeritics AutoChem II 2920), furnished with a thermal conductivity detector (TCD). The detailed programs are described as follows:

For O_2-TPD analysis, 30 mg of sample was preheated with He stream at 200 °C for 0.5 h and then cooled down to 50 °C. The sample was swept by a flow of 3% O_2/He at a rate of 30 mL min^{-1} for 0.5 h and further purged with He (30 mL min^{-1}) for another 0.5 h. The O_2-TPD signals were collected when the reactor was heated to 800 °C with a ramp of 10 °C min^{-1} in the He stream. For O_2-TPO there was no adsorption step while run in 3% O_2/He from 50 to 800 °C.

Before H_2-TPR analysis, 30 mg of catalyst was loaded and preheated in the same way as O_2-TPD. After that, the sample was swept by a flow of 10% H_2/Ar at a rate of 30 mL min^{-1} until a stable baseline was obtained. Then, the H_2-TPR signals were recorded when the temperature increased from 50 to 800 °C at a rate of 10 °C min^{-1}.

2.4. General Reactions. The typical selective amination-oxidation-amination of HMF was conducted in a 25 mL stainless steel reactor with mechanical stirring as follows: HMF (63 mg, 0.5 mmol), catalyst (22 mg, 35 wt% to HMF) and 30 wt% methylamine methanol solution (5.0 mL) were added to the reactor. The reactor was purged with air three times at atmospheric conditions, followed by keeping Air pressure at 1.0 MPa. The reaction was then heated in an automatic heating to target temperature. After running the reaction for the desired duration, the reactor was rapidly cooled to room temperature. Next, the liquid products and solid catalyst were separated by centrifugation, followed by rotary evaporation of the solvent under vacuum at 45 ℃ and further sampled for analyses.

A representative reduction procedure for production BMAF from BMIF: The liquid products and solid catalyst were separated by centrifugation after the AOA reaction. Then the liquid products, 1.0 mL of 30 wt% methylamine methanol solution and 45 mg catalyst were added to original stainless autoclave. The reactor was purged with H_2 three times at atmospheric conditions, followed by keeping H_2 pressure at 2.0 MPa, and then brought to the desired temperature by external heating with stirring at 800 rpm. After running the reaction for the desired duration, the reactor was rapidly cooled to room temperature. Next, the liquid products and solid catalyst were separated by centrifugation, followed by rotary evaporation of the solvent under vacuum at 45 ℃ and further sampled for analyses.

2.4. Product analysis. The qualitative analyses of samples were determined by thermo-Fisher Trace 1300 & ISQ LT GC-MS instrument equipped with a TR-5MS column (15.0 m × 250 μm × 0.25 μm). The following programmed temperature was applied: 40 ºC (2 min)-10 ºC/min - 260 ºC (2 min). The carrier gas was He with a flow rate of 1.2 mLmin^{-1} and split ratio was 1:50. The mass spectra were obtained by electron impact ionization (EI), at an electron energy of 70 eV and with a 25 μA emission current.

HMF, BMIF, BMAF and other products were analyzed quantitatively by Agilent 7890 series GC equipped with a DB-WAXETR column (30 m × 0.25 mm × 0.25 µm, Agilent) and a flame ionization detector (FID) operating at 270 ºC. Carrier gas was N_2, with a flow rate of 1.0 mL/min. The following programmed temperature was applied: 40 ºC (4 min) - 15 ºC/min - 250 ºC (5 min). HMF, BMIF, DFF and BMAF were quantitative analyzed using the external standard. Typically, the conversion (conv., %) of HMF and yield (yield, %) of BMIF, DFF and BMAF were calculated according to the following equations:

$$HMF\ Conv.\ (mol\%) = \left(1 - \frac{\text{Mol of } HMF \text{ in products}}{\text{Initial mole of HMF}}\right) \times 100\%$$

$$\text{BMIF Yield (mol\%)} = \frac{\text{Mol of BMIF in productions}}{\text{Initial mole of HMF}} \times 100\%$$

$$DFF\ Yield\ (mol\%) = \frac{\text{Mol of } DFF \text{ in productions}}{\text{Initial mole of HMF}} \times 100\%$$

$$BMAF\ Yield\ (mol\%) = \frac{\text{Mol of } BMAF \text{ in productions}}{\text{Initial mole of HMF}} \times 100\%$$

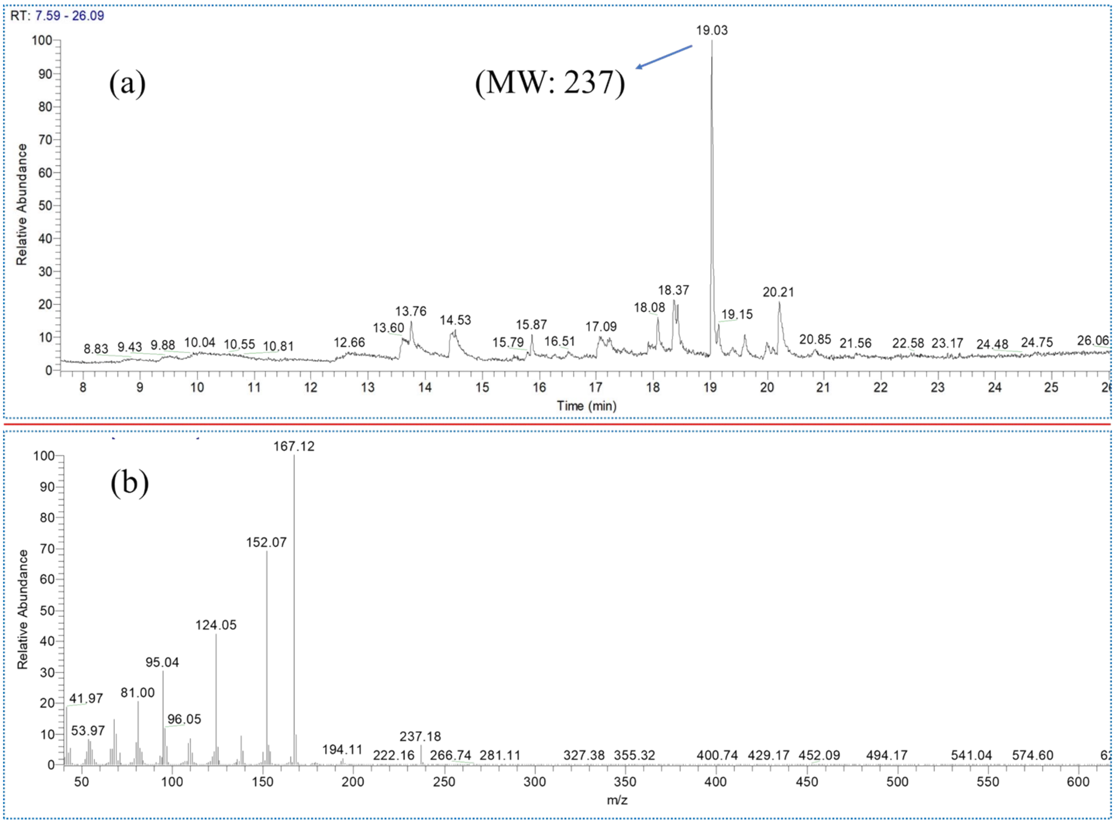


Figure S1. GC spectrum of the reaction catalyzed by V_2O_5 (a) and MS spectrum of unknow compound MW237 (b).

Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of V_2O_5, 1.0 MPa Air, 90 ℃, 3 h.

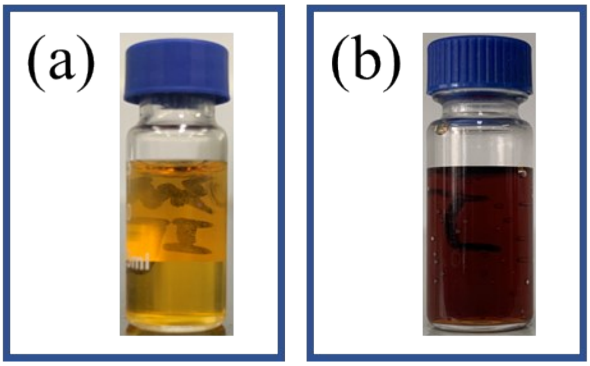


Figure S2. The liquid products from the reaction catalyzed by α-MnO_2 (a) and V_2O_5 (b).

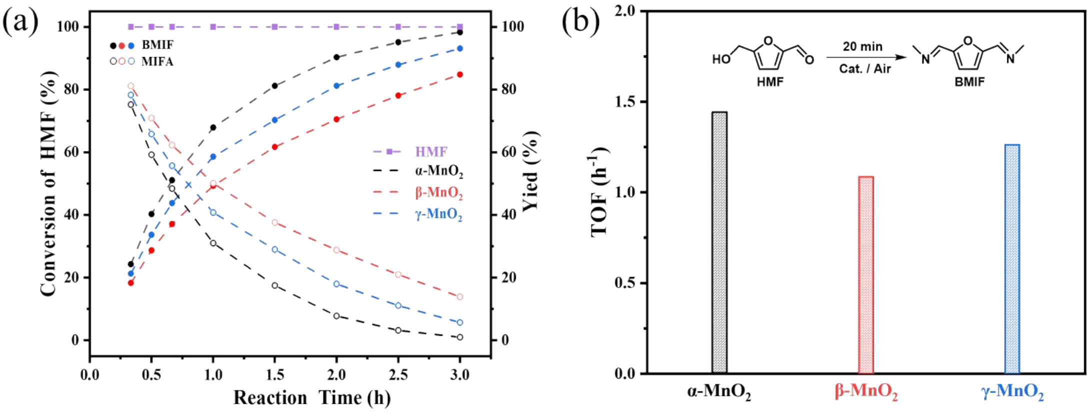


Figure S3. Profiles of BMIF yield and MIFA yield vs reaction time (a) and TOF value catalyzed by α-MnO_2, β-MnO_2, and γ-MnO_2 at 20 min (b).

Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of catalysts, 1.0 MPa Air, 90 ℃.

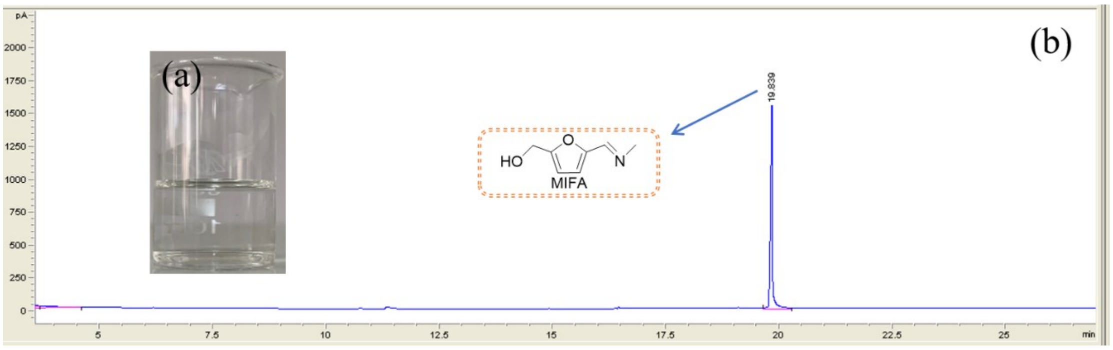


Figure S4. MIFA formed within 10 min at room temperature without catalyst. Liquid products (a) and GC spectrum (b).

Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, room temperature, air, 10 min.

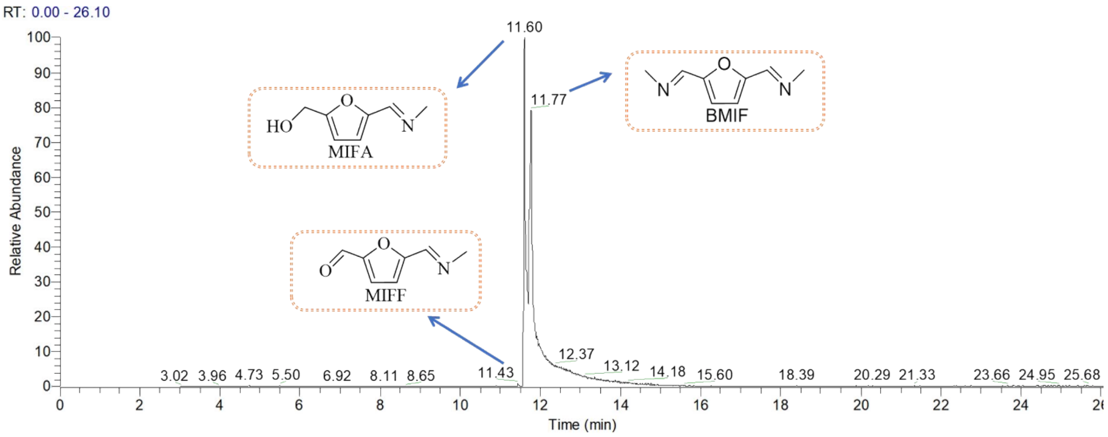


Figure S5. GC spectrum of the typical AOA reaction for 30 min.

Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of α-MnO_2, 1.0 MPa Air, 90 ℃, 30 min.

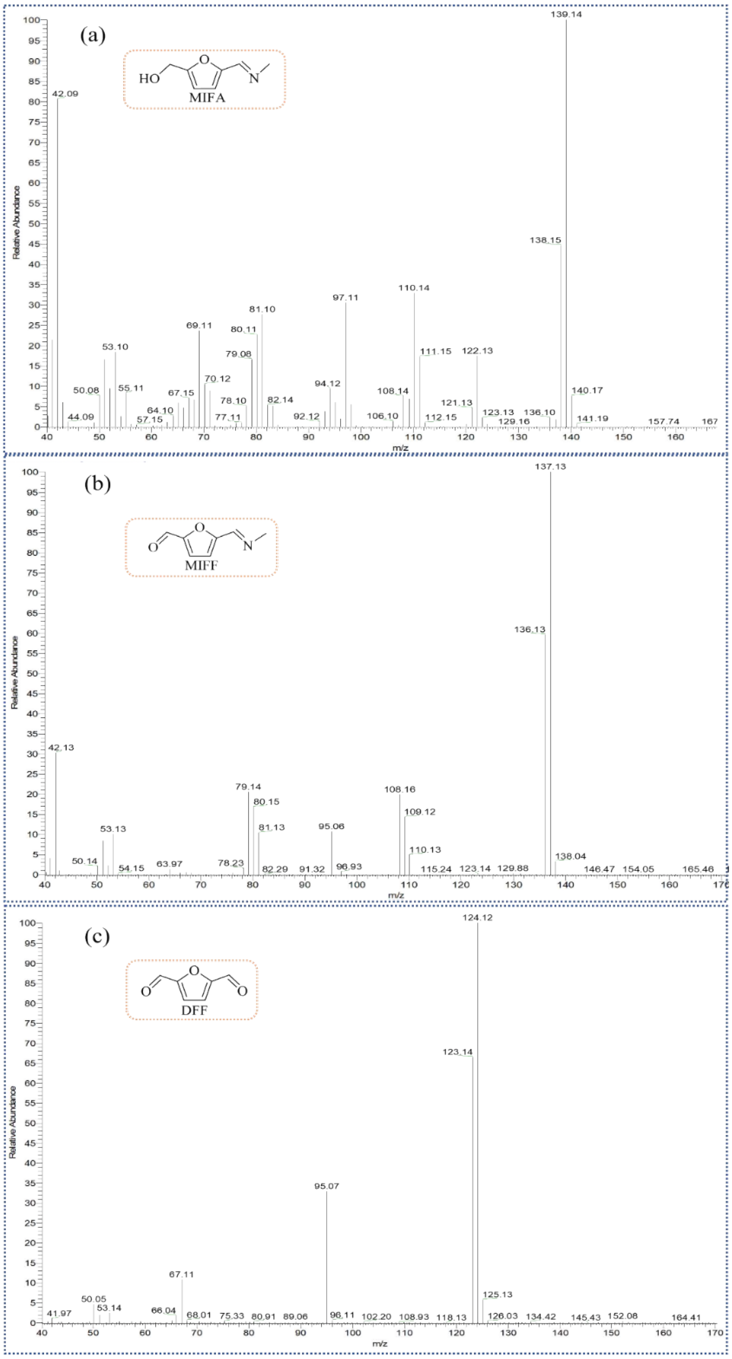


Figure S6. MS spectra of MIFA (a), MIFF (b) and DFF (c).

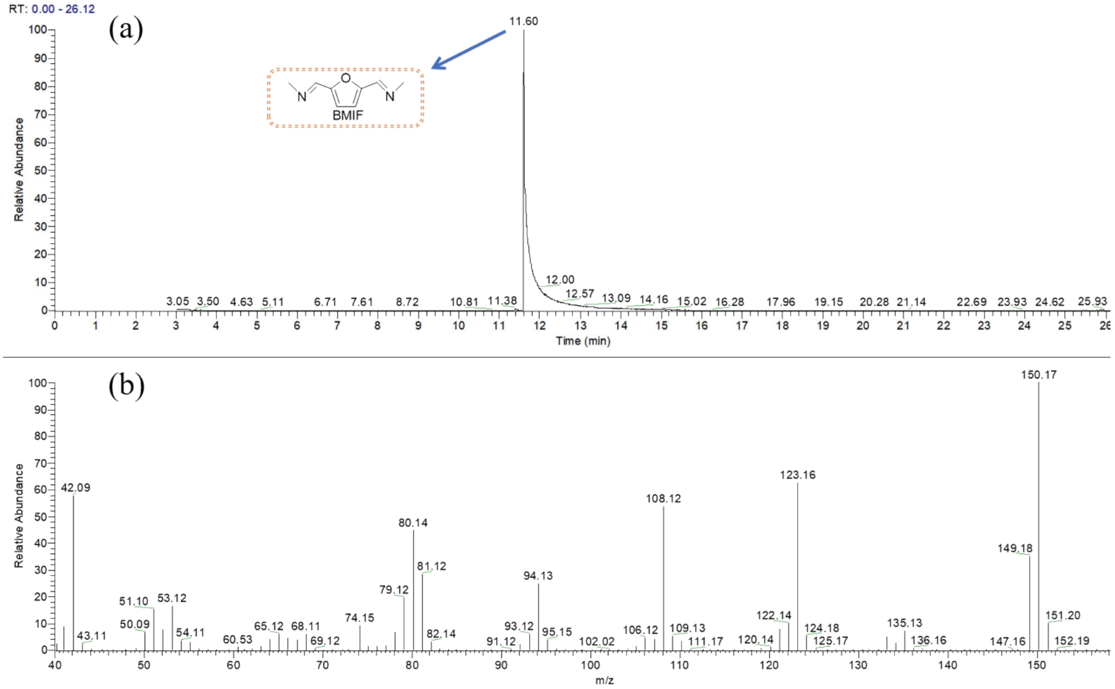


Figure S7. GC spectrum of the typical AOA reaction for 3h (a) and MS spectrum of BMIF (b).

Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of α-MnO_2, 1.0 MPa Air, 90 ℃, 3 h.

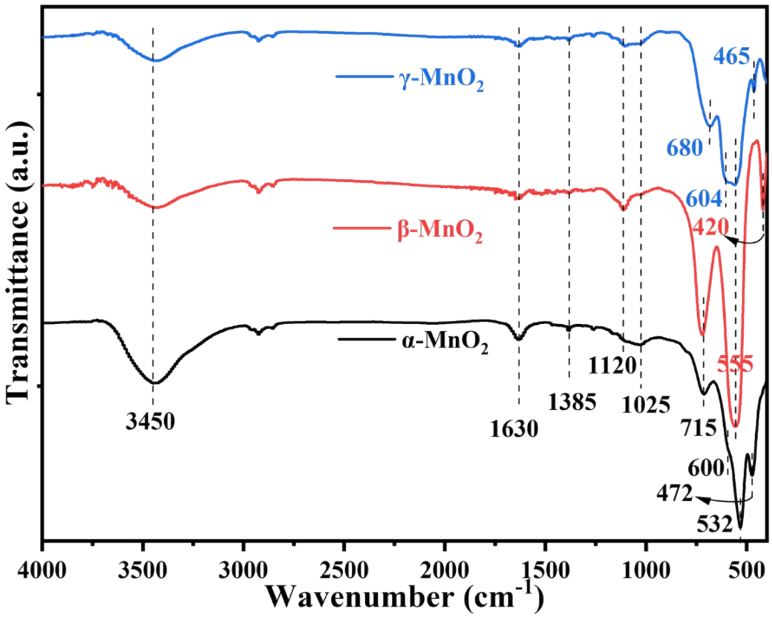


Figure S8. FT-IR spectra of *α*-MnO_2, *β*-MnO_2, and *γ*-MnO_2.

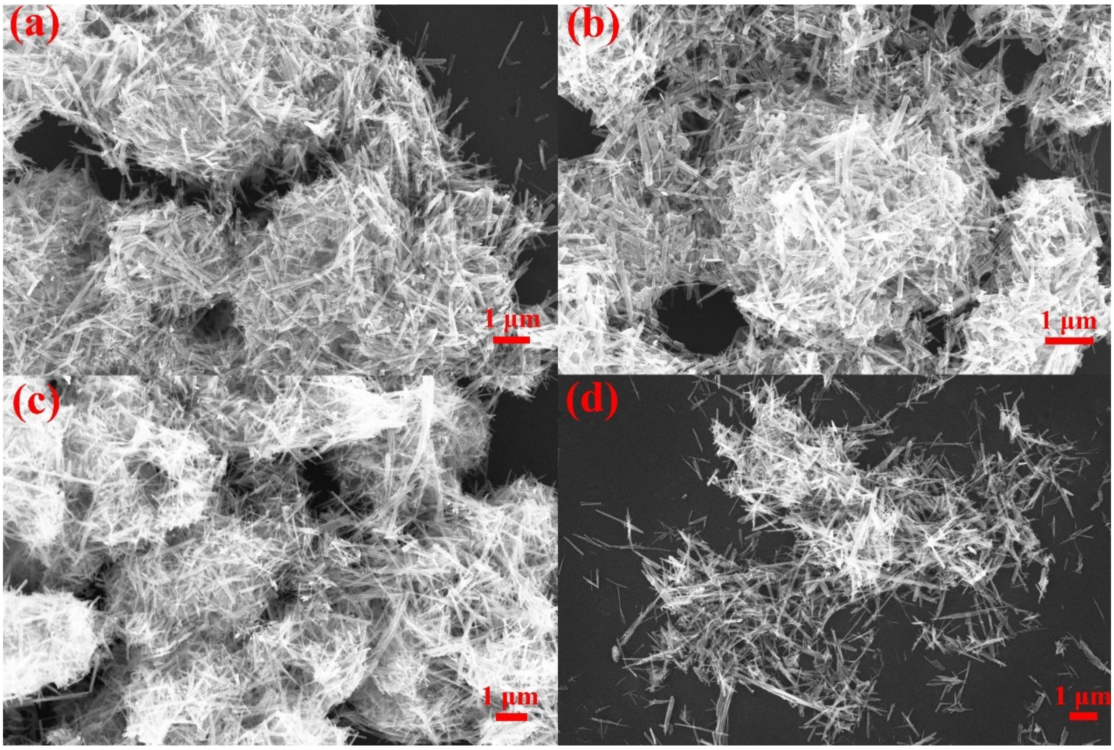


Figure S9. SEM images of α-MnO_2 (a), the recovered α-MnO_2 after the first cycle (b), the recovered α-MnO_2 after the third cycle (c), the recovered α-MnO_2 after the fifth cycle (d).

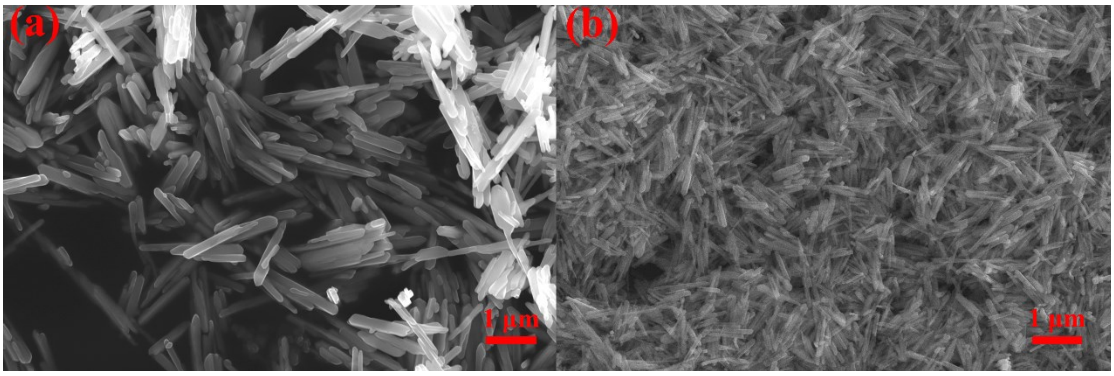


Figure S10. SEM images of *β*-MnO_2 (a), the recovered *β*-MnO_2 after the first cycle (b).

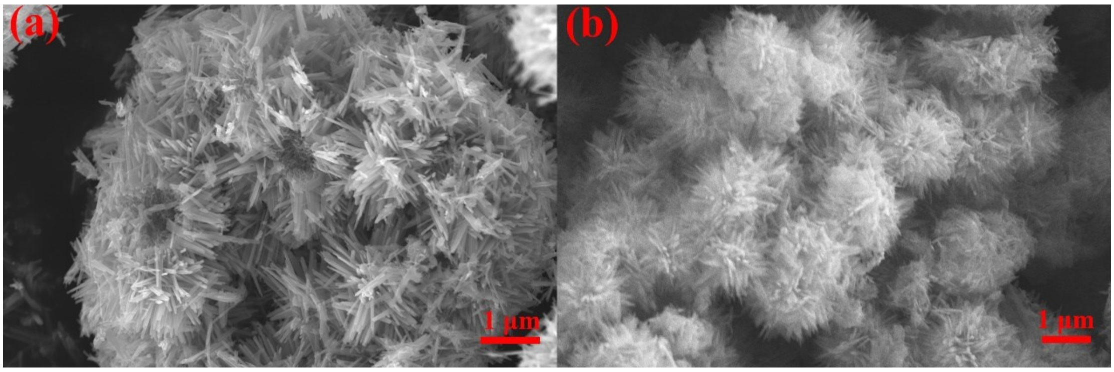


Figure S11. SEM images of γ-MnO_2 (a), the recovered γ-MnO_2 after the first cycle (b).

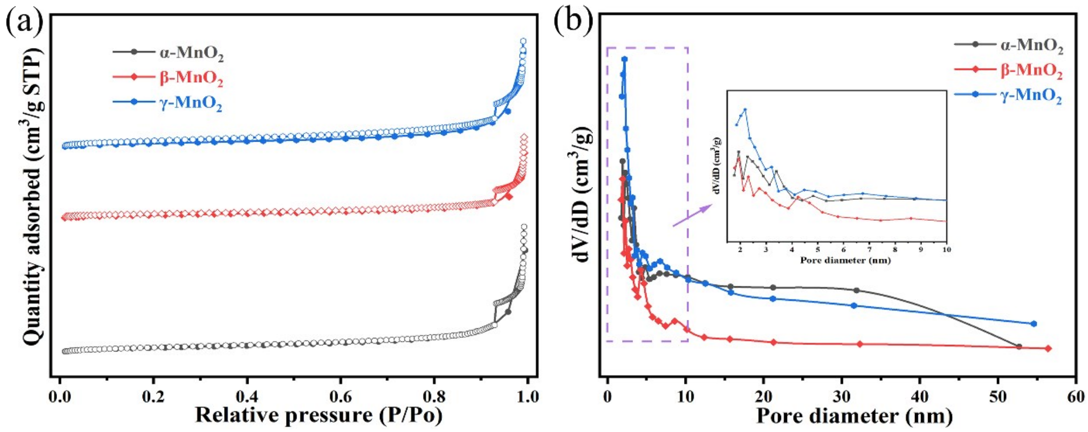


Figure S12. N_2 adsorption/desorption isotherms (a) and pore size distribution (b) for α-MnO$_2$, β-MnO$_2$, and γ-MnO$_2$.

Figure S13. The recovered MnO_2 after H_2-TPR

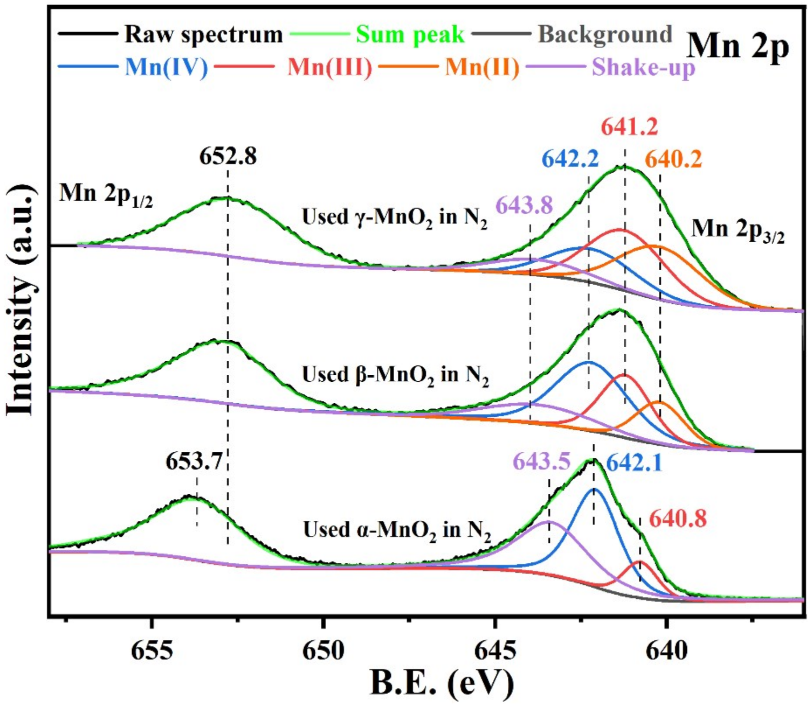


Figure S14. XPS spectra of Mn 2p of recovered α-MnO_2, β-MnO_2, γ-MnO_2 by reaction under N_2-atmosphere.

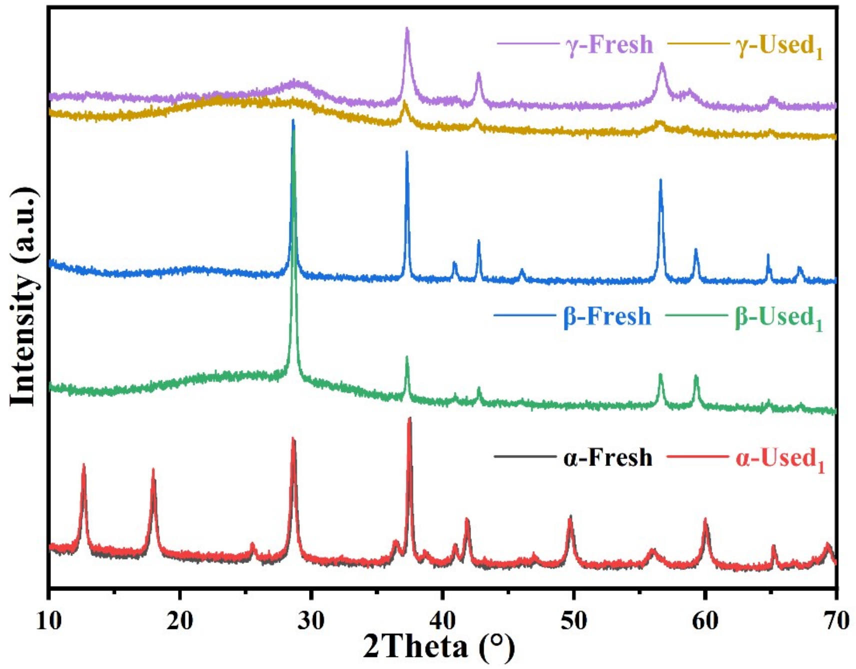


Figure S15. XRD patterns of the fresh and recovered α-MnO_2, β-MnO_2 and γ-MnO_2 after the first cycle.

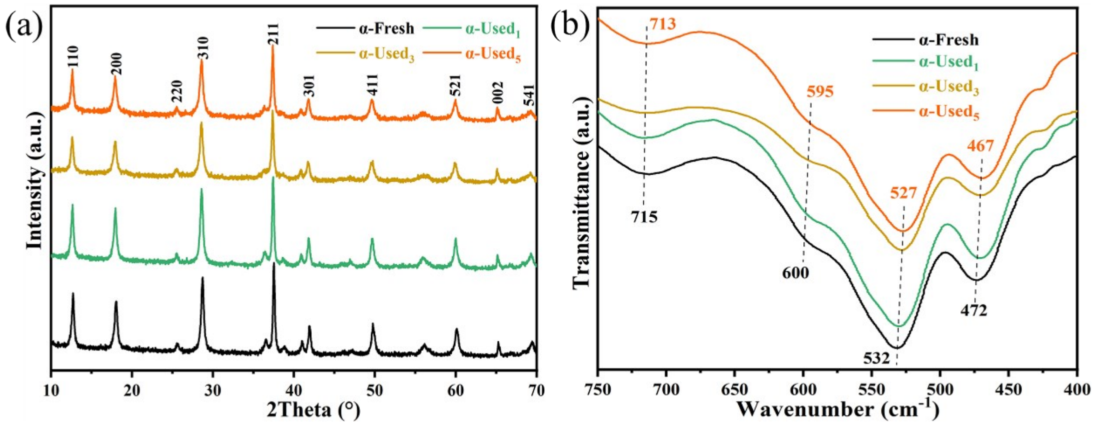


Figure S16. XRD patterns (a) and FT-IR spectra (b) of the fresh *α*-MnO_2 and the recovered catalyst after the first, third, and fifth cycle.

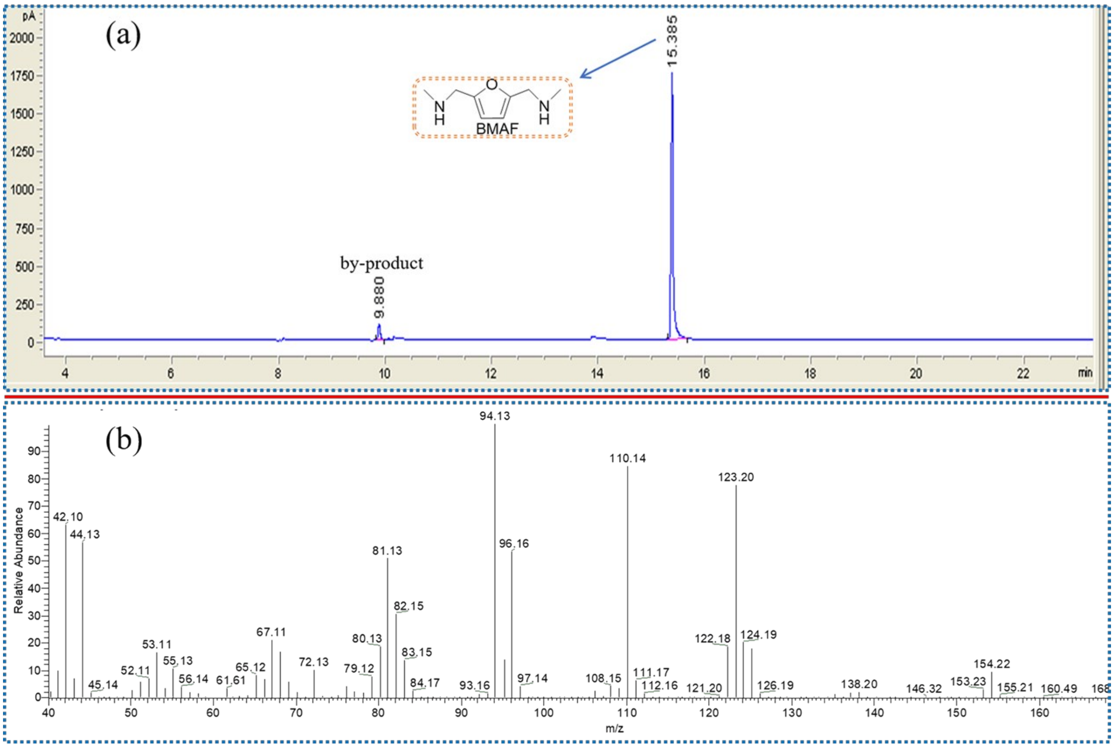


Figure S17. GC spectrum (a) and MS spectrum (b) of BMAF from the reduction of BMIF by Ru/C.

Reaction conditions: 5.0 mL of liquid products from the AOA reaction by α-MnO_2, 1.0 mL of 30 wt% methylamine methanol solution, 45 mg of Ru/C, 2.0 MPa H_2, 130 ℃, 3 h.

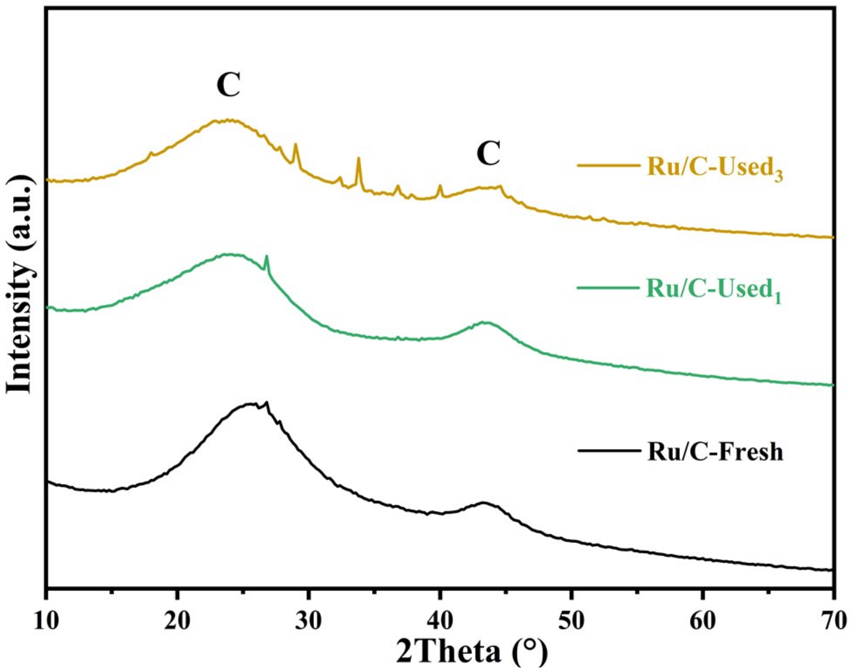


Figure S18. XRD patterns of the fresh Ru/C and the recovered catalyst after the first and third cycle.

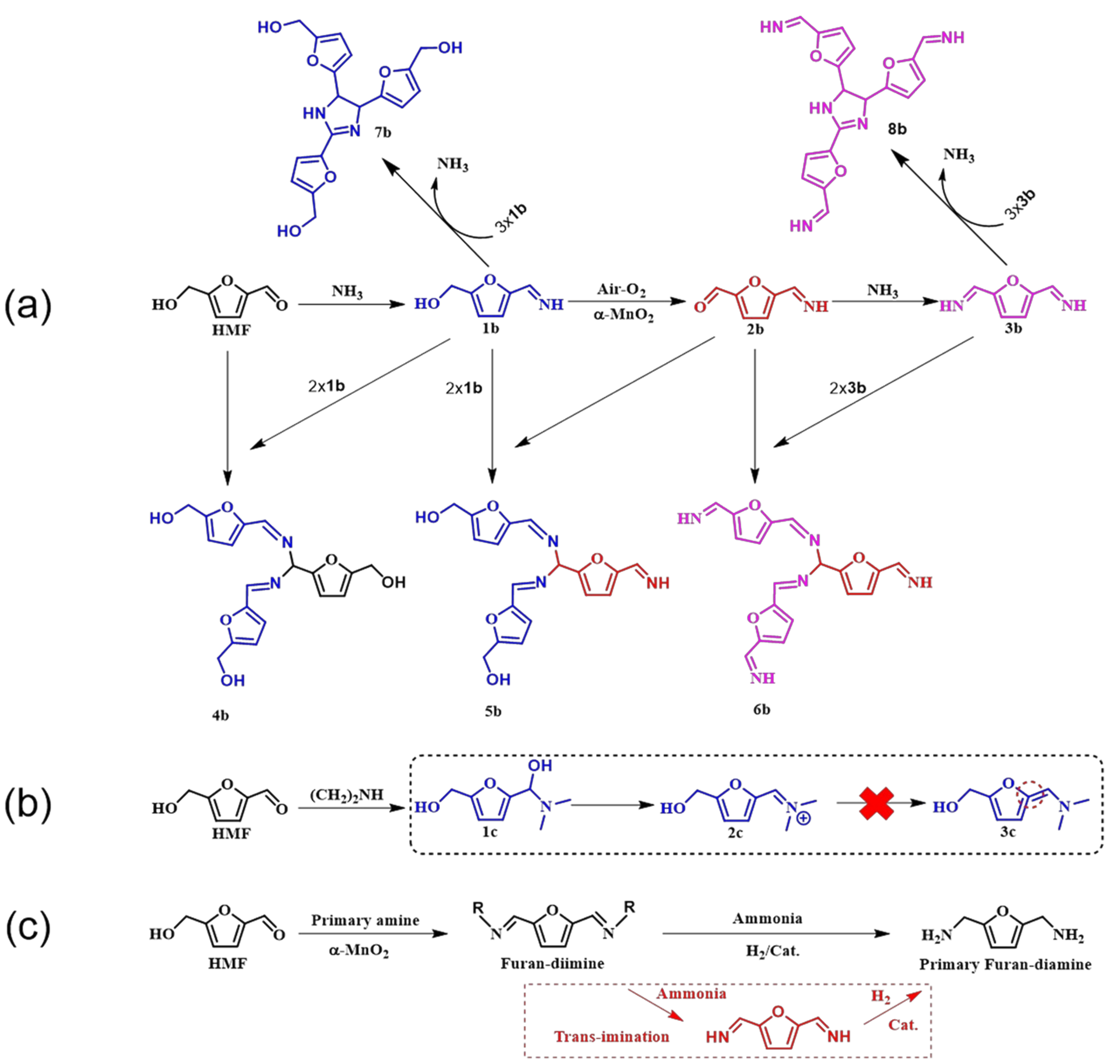


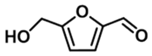
Fig. S19 Plausible reactions for HMF reacted with ammonia (a), dimethylamine (b), and primary amine (c).

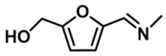
Table S1. Catalytic conversion of HMF[a]

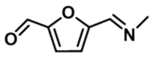
Entry	Catalyst	Time (h)	Conv. (%)	Yield (%)		
				MIFA	BMIF	MW237
1	V_2O_5	0.5	100	57.3	0	15.1
2	V_2O_5	1.5	100	12.2	0	39.3
3	V_2O_5	3.0	100	0	0	46.3
4	$VOSO_4$	3.0	100	0	0	47.8
5	MoO_3	3.0	100	0	0	48.2

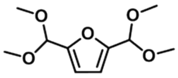
[a] Reaction conditions: 0.5 mmol HMF, 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of catalyst, 1.0 MPa Air, 90 °C.

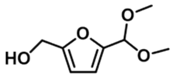
Table S2. Other products formed during the oxidation process in Table 2[a]

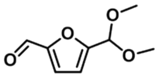

HMF

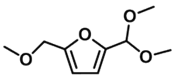

MIFA


MIFF


4a


1a

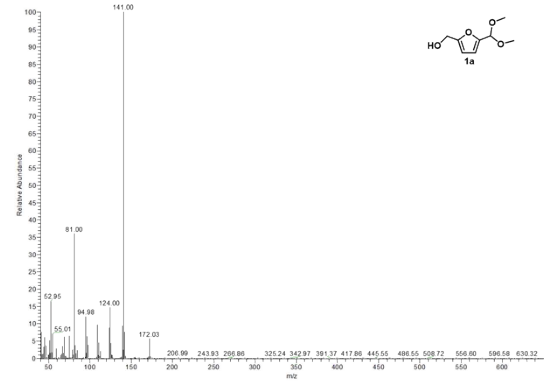

2a

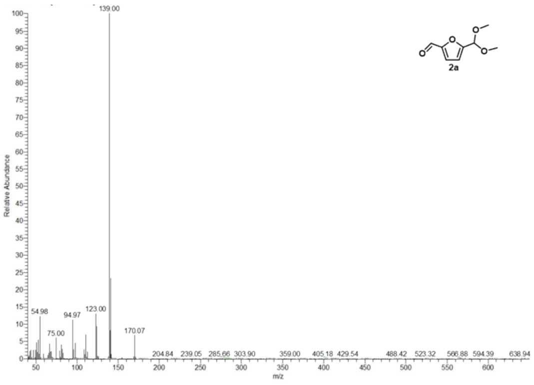

3a

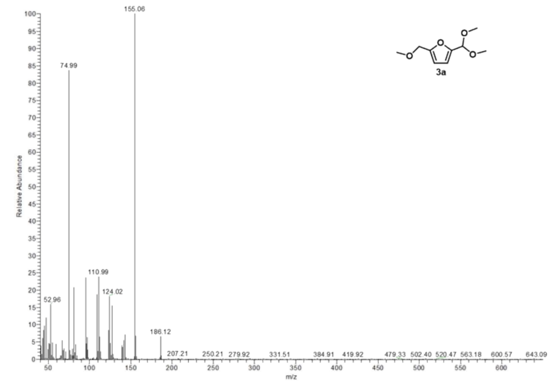
Entry	Substrate	Conversion and Yield (%)						
		HMF	MIFA	MIFF	**1a**	**2a**	**3a**	**4a**
1	MIFA	-	100	-	-	-	-	-
2	MIFA	19.7	60.2	12.3	<1	-	-	-
3[b]	HMF	100	40.3	-	-	-	-	-
4	HMF	37.2	-	-	11.7	<1	<1	<1
5[c]	HMF	68.1	-	-	5.5	2.8	<1	29.3
6[d]	HMF	40.3	-	-	23.8	<1	<1	1.9
7[e]	HMF	71.1	-	-	20.6	<1	46.4	2.3
8[f]	HMF	62.5	-	-	5.1	2.3	<1	19.2
9[df]	HMF	43.8	-	-	30.1	<1	2.7	<1
10[ef]	HMF	80.3	-	-	75.3	<1	<1	2.1
11[g]	HMF	78.8	-	-	0	0	0	0

[a] Reaction conditions: 0.5 mmol substrate, 5.0 mL MeOH, 22 mg of α-MnO_2, 1.0 MPa Air, 90 °C, 3 h. [b] 20 mg of H_2SO_4 (pH=4), 40 mmol methylamine. [c] 8 h. [d] pH=6. [e] pH=4. [f] 1.0 MPa O_2. [g] 20 mg of $NaHCO_3$.

MS spectra for 1a-4a.







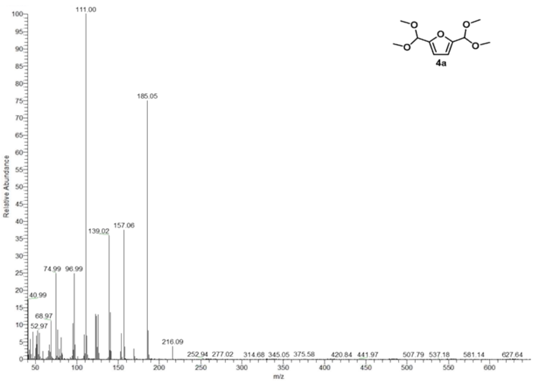


Table S3. Lattice oxygen ratio of the fresh and the recovered α-MnO_2, β-MnO_2, γ-MnO_2[a]

Entry	Catalyst	Binding energy of O 1s (eV)			$O_L/(O_A+O_L)$
		O_L	O_A	O_w	(%)
1	α-MnO_2	529.6 (72.7%)	531.1 (21.3%)	533.1 (6.0%)	77.3
2	β-MnO_2	529.4 (60.2%)	531.5 (34.3%)	533.7 (5.5%)	63.7
3	γ-MnO_2	529.6 (64.4%)	531.3 (29.1%)	533.2 (6.5%)	68.9
4	α-MnO_2[b]	529.5 (59.1%)	530.8 (34.8%)	533.1 (6.1%)	62.9
5	α-MnO_2[c]	529.6 (70.6%)	531.1 (23.4%)	533.1 (6.0%)	75.1

[a] Values in parentheses are the percentages of each oxygen species. [b] Recovered α-MnO_2 (reaction under 1.0 MPa N_2). [c] Recovered α-MnO_2 (reaction under 1.0 MPa Air)

Table S4. $R_{Mn^{4+}}$ ratio of the fresh and recovered α-MnO_2[a]

Entry	Catalyst	Binding energy of Mn 2p (eV)		$R_{Mn^{4+}}$ (%)
		Mn^{3+}	Mn^{4+}	
1	α-MnO_2	640.9 (7%)	642.2 (93%)	93.0
2	α-MnO_2[b]	640.9 (21%)	642.1 (79%)	79.0
3	α-MnO_2[c]	640.9 (8%)	642.2 (92%)	92.0

[a] Values in parentheses are peak percentages. [b] Recovered α-MnO_2 (reaction under 1.0 MPa N_2). [c] Recovered α-MnO_2 (reaction under 1.0 MPa Air).

Table S5. Preparation of BMIF from HMF[a]

Entry	Catalyst	Atmosphere	Conv. (%)	Yield of BMIF (%)
1	α-MnO_2	Air	100	41.7
2	α-MnO_2	N_2 (1 MPa)	100	3.1
3	β-MnO_2	N_2 (1 MPa)	100	3.7
4	γ-MnO_2	N_2 (1 MPa)	100	6.3

[a] Reaction conditions: 0.5 mmol HMF (63 mg), 5.0 mL of 30 wt% methylamine methanol solution, 22 mg of catalyst, 90 ℃, 3 h.