Electronic Supplementary Information for

Alkali α-MnO_2/Na_xMnO_2 collaboratively catalyzed ammoxidation-Pinner tandem reaction of aldehydes

Xiuquan Jia, Jiping Ma,* Min Wang, Xiaofang Li, Jin Gao, and Jie Xu*

Contents:

1. Additional Results

Preparation of α-MnO_2. α-MnO_2 was prepared according to the literature procedure (see below).[S1] A 100 mL aqueous solution containing 40 mmol $KMnO_4$ was added into another 100 mL aqueous solution containing 60 mmol $Mn(NO_3)_2$. After stirring at room temperature for 4 h, the resulting solid was collected by filtration, washed repeatedly with distilled water, and finally dried overnight in air at 60 °C and then calcined in air at 250 °C for 4 h.

Preparation of β-MnO_2. β-MnO_2 was prepared according to the literature procedure (see below).[S2] A 60 mL aqueous solution containing stoichiometric amount of $MnSO_4$ (18 mmol) and $KMnO_4$ (3 mmol) was loaded in a 100 mL Teflon-lined autoclave, which was sealed and maintained at 140 °C for 12 h. After naturally cooling to room temperature, the resulting solid was collected by centrifugation, washed repeatedly with distilled water, and finally dried overnight in air at 80 °C.

Preparation of δ-MnO_2. δ-MnO_2 was prepared according to the literature procedure (see below).[S3] An aqueous solution (A) was prepared by dissolving 0.04 mol of $KMnO_4$ and 1.2 mol of NaOH in 400 mL of water. Afterward, another aqueous solution (B) was prepared by dissolving 0.112 mol of $MnCl_2 \cdot 4H_2O$ in 400 mL of water. Solution B was added dropwise to solution A with vigorous stirring in an ice bath. The resulting precipitate was statically aged at room temperature for 1 day and then washed and dried at 90 °C.

Preparation of OMS-2. OMS-2 was prepared according to the literature procedure (see below).[S4] $KMnO_4$ (5.89 g) in water (100 mL) was added to a solution of $MnSO_4 \cdot H_2O$ (8.8 g) in water (30 mL) and conc. HNO_3 (3 mL). The solution was refluxed at 100 °C for 24 h. Then, the dark brown solid was filtered off, washed with a large amount of water (ca. 3 L), and dried at 120 °C to afford 8.2 g of OMS-2.

Preparation of Na_xMnO_2. Na_xMnO_2 was prepared according to the literature procedure with some modification (see below).[S5] A mixture of 10 mmol Na_2CO_3 and 30 mmol $MnCO_3$ was heated at 1000 ^oC for 15 h, followed by naturally cooling to room temperature.

[S1] E. Schleitzer (Ed.), Gmelin Handbook of Inorganic Chemistry 8th Edition (Manganese), Verlag Chemie GmbH, Weinheim/Bergstrasse, 1973.

[S2] F. Y. Cheng, T.R. Zhang, Y. Zhang, J. Du, X. P. Han, J. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 2474.

[S3] O. Ghodbane, J.-L. Pascal, and F. Favier, *ACS Appl. Mater. Interfaces.* **2009**, *1*, 1130.

[S4] R. N. DeGuzman, Y.-F. Shen, E. J. Neth, S. L. Suib, C.-L. O'Young, S. Levine, J. M. Newsam, *Chem. Mater*. **1994**, *6*, 815.

[S5] R. Stoyanova, D. Carlier, M. Sendova-Vassileva, M. Yoncheva, E. Zhecheva, D. Nihtianova, C. Delmas, *J. Solid State Chem*. **2010**, *183,* 1372.

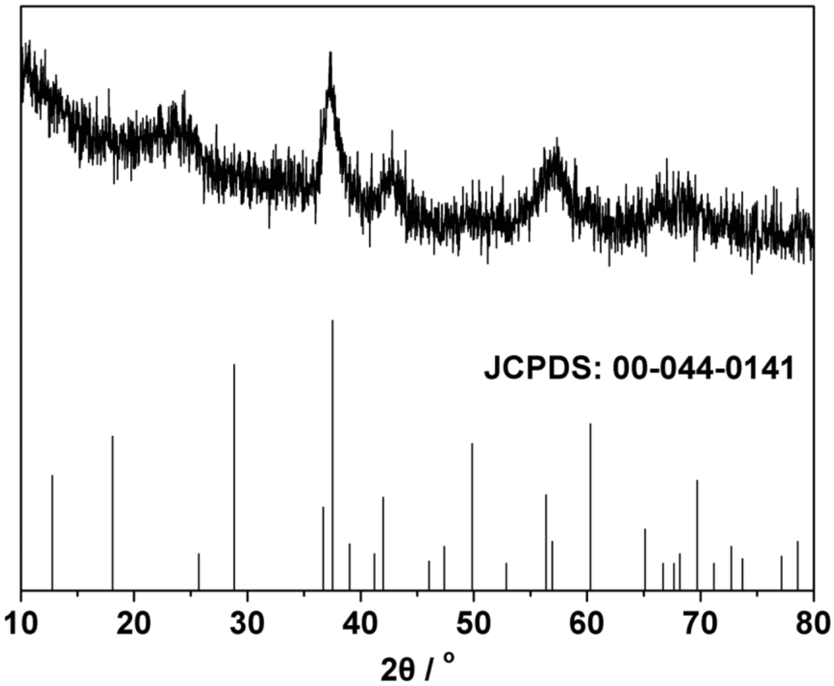


Figure S1 XRD patterns of α-MnO_2.

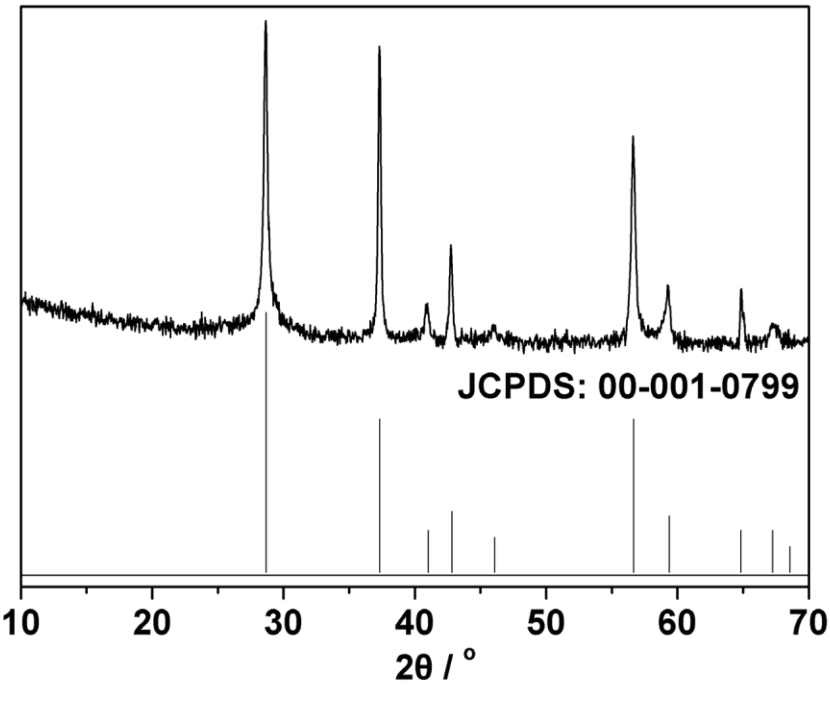


Figure S2 XRD patterns of β-MnO_2.

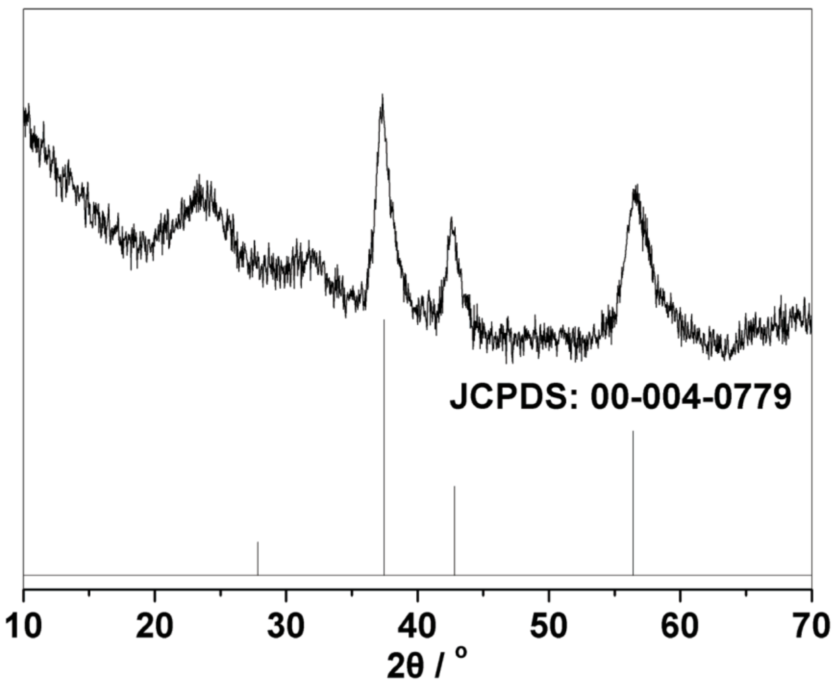


Figure S3 XRD patterns of γ-MnO_2.

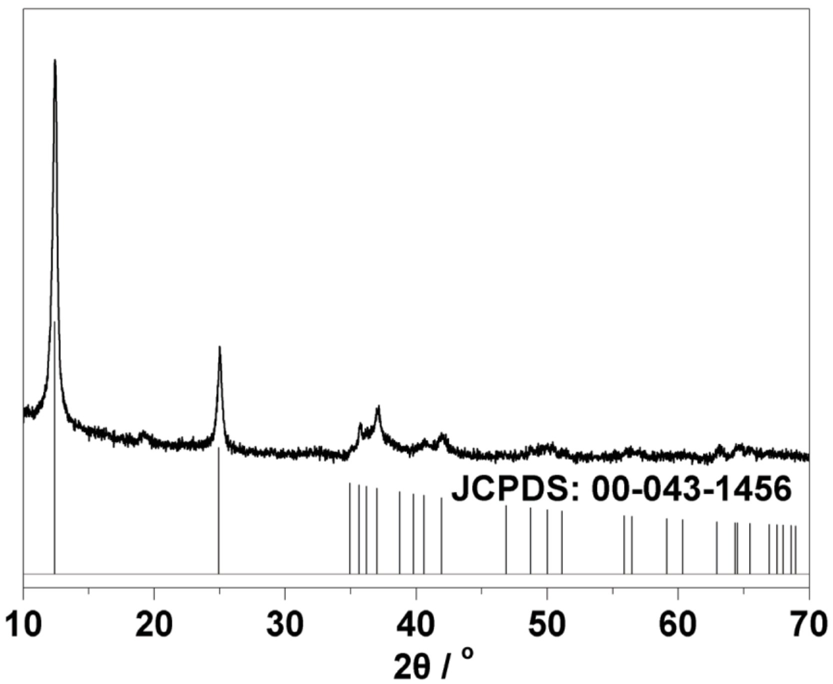


Figure S4 XRD patterns of δ-MnO_2.

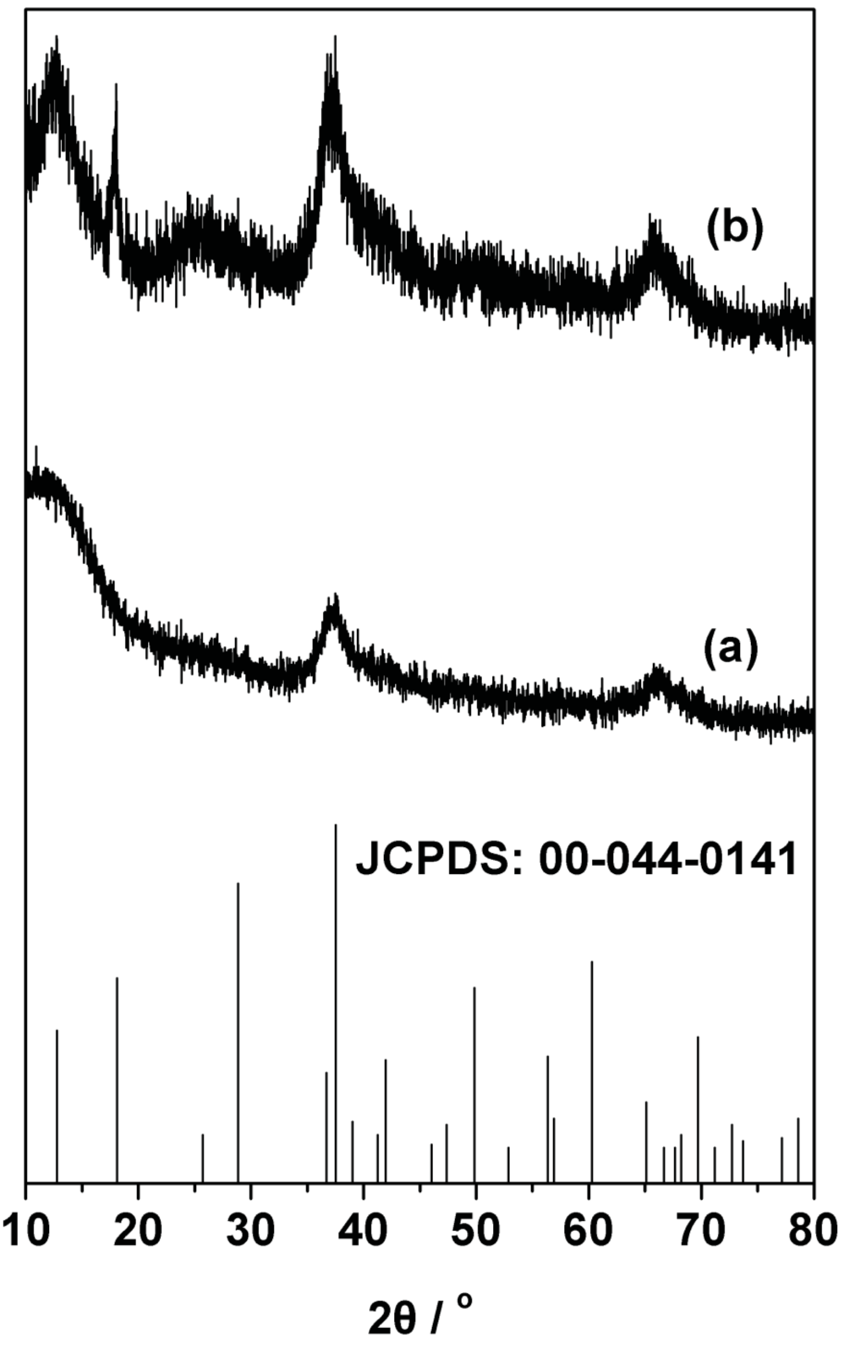


Figure S5 XRD patterns of (a) fresh and (b) used α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^oC.

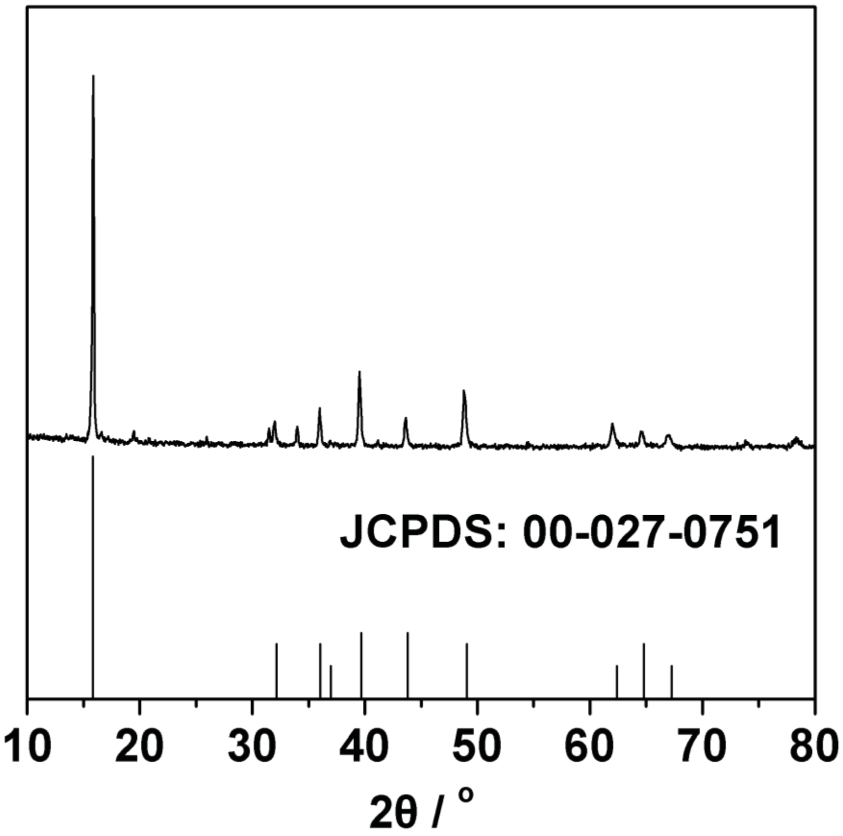


Figure S6 XRD patterns of Na_xMnO_2.

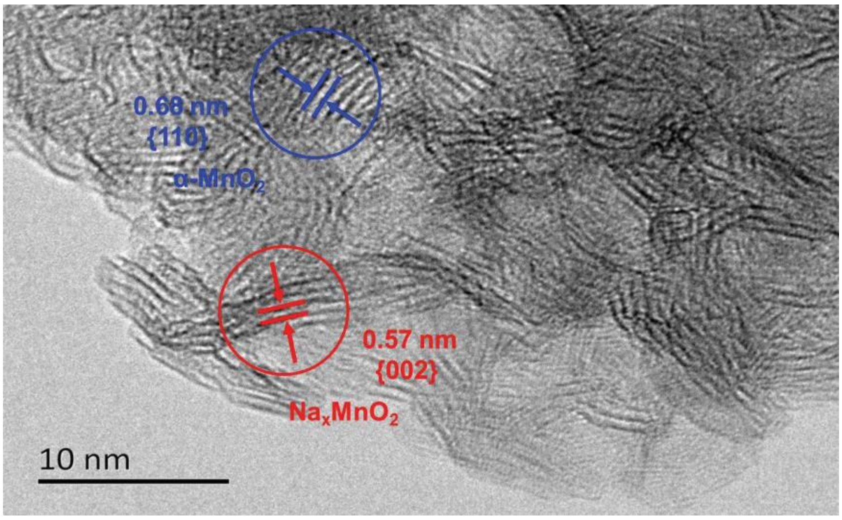


Figure S7 HRTEM image of α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C.

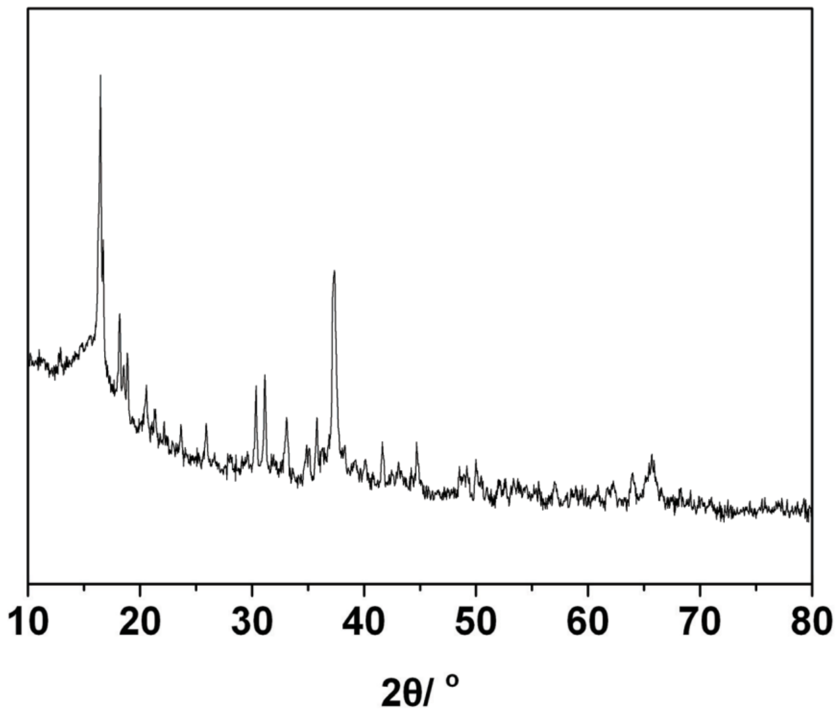


Figure S8 XRD pattern of manganese oxide calcined at 500 ^{O}C with NaOH/Mn molar ratio of 1.2 and substituting NaMnO4 for KMnO4

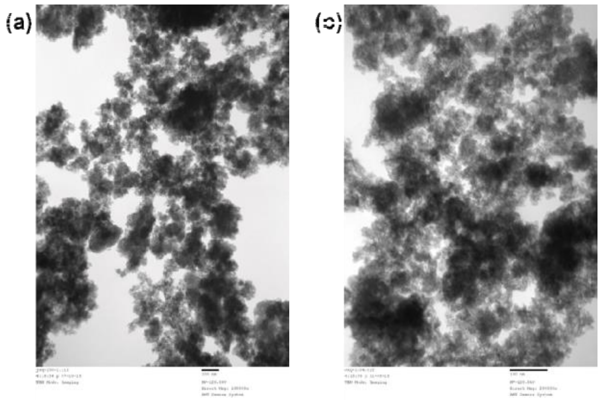


Figure S9 TEM images of (a) fresh and (b) used α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C.

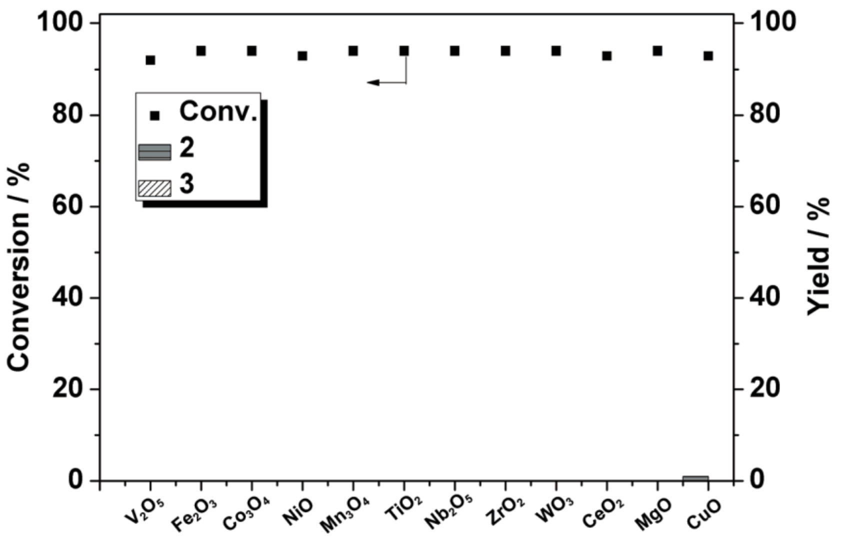
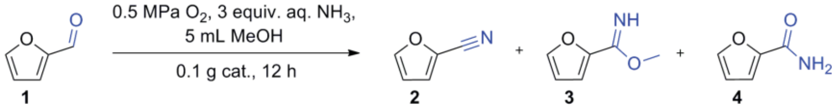


Figure S10 Catalytic conversion of furfural to methyl furan-2-carboximidate over different metal oxides. Reaction conditions: 0.5 mmol furfural, 0.1 g catalyst, 120 μL aq. NH_3 (3 equiv.), 5 mL MeOH, 0.5 MPa O_2, 30 °C, 12 h.

Table S1. Catalytic conversion of furfural at different temperatures.[a]



Entry	T (°C)	Conv. (%)	Yield (%)		
			2	**3**	**4**
1	30	> 99	11	89	-
2	90	> 99	3	24	32
3	120	> 99	-	2	62

[a] Reaction conditions: 0.5 mmol furfural, 0.1 g α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 °C, 120 μL aq. NH_3 (3 equiv.), 5 mL MeOH, 0.5 MPa O_2, 12 h.

Table S2. ICP elemental analysis of α-MnO_2/Na_xMnO_2.

Element	Weight%	Atomic%
O	42.9	70.7
Na	1.49	1.71
K	4.69	3.17
Mn	50.9	24.4

Table S3. EDS elemental analysis of α-MnO_2/Na_xMnO_2.

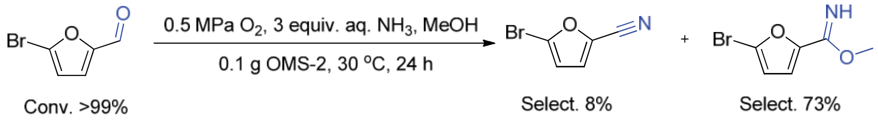
Element	Weight%	Atomic%
O	39.75	67.29
Na	2.67	3.15
K	5.83	4.04
Mn	51.75	25.52

Table S4. ICP elemental analysis of manganese oxide prepared with $KMnO_4$ + KOH.

Element	Weight%	Atomic%
O	33.3	63.7
K	7.38	3.30
Mn	59.3	33.0

Table S5. ICP elemental analysis of manganese oxide prepared with $NaMnO_4$ + NaOH.

Element	Weight%	Atomic%
O	52.6	75.2
Na	8.47	8.46
Mn	39.0	16.3



Scheme S1. Catalytic conversion of 5- bromofurfural over OMS-2.

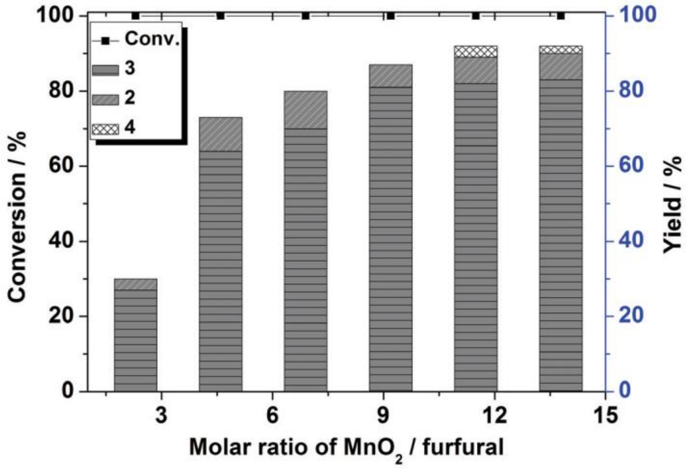


Figure S11. α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C oxidized synthesis of methyl furan-2-carboximidate from furfural. Reaction conditions: 0.5 mmol furfural, 120 µL aq. NH_3 (3 equiv.), 5 mL MeOH, 0.5 MPa N_2, 30 ^{o}C, 12 h. Note: The molar mass of α-MnO_2/Na_xMnO_2 was approximate to that of MnO_2.

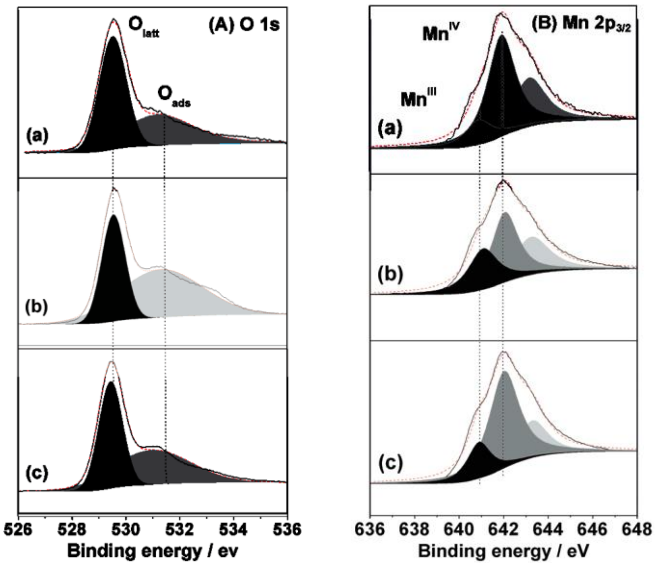


Figure S12. XPS spectra of (a) fresh α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C, (b) α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C was treated with furfural and ammonia in MeOH at 30 ^{o}C under N_2 atmosphere for 48 h, (c) α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C in (b) was treated at 30 ^{o}C under O_2 atmosphere for 12 h.

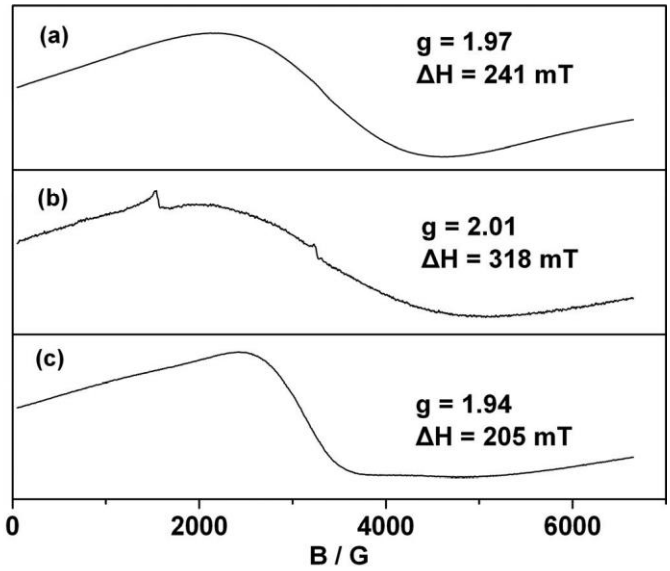


Figure S13. EPR spectra of (a) fresh α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C, (b) α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C was treated with furfural and ammonia in MeOH at 30 ^{o}C under N_2 atmosphere for 48 h, (c) α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 ^{o}C in (b) was treated at 30 ^{o}C under O_2 atmosphere for 12 h.

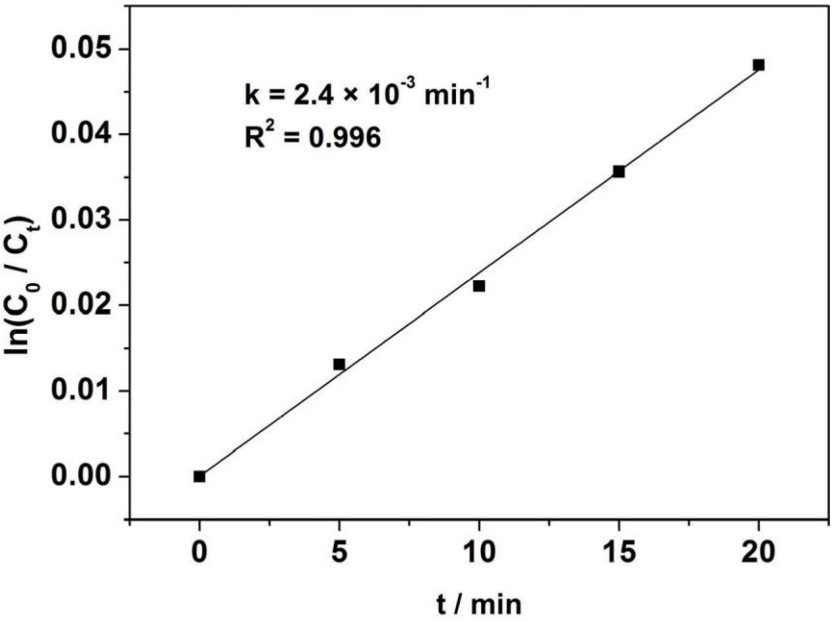


Figure S14. Relationship of ln(C_0/C_t) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 250 °C.

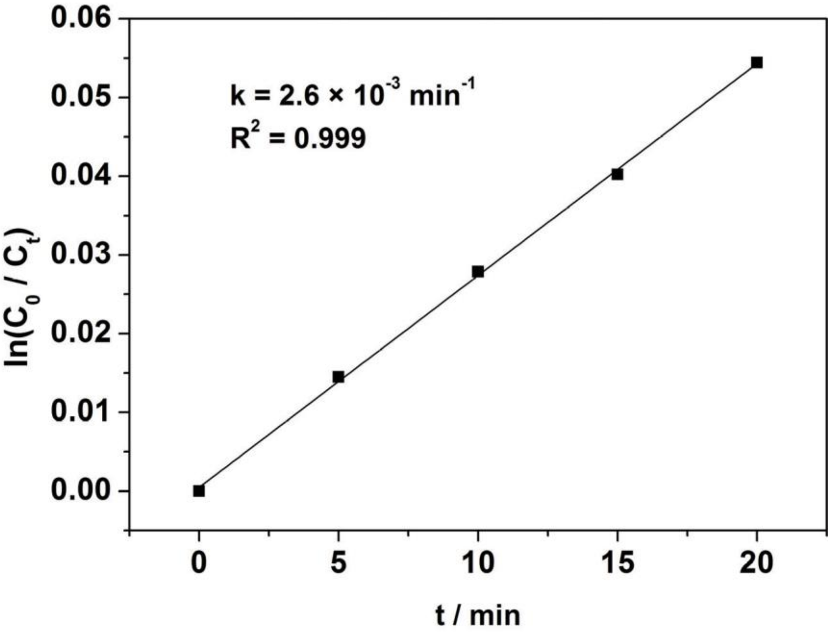


Figure S15. Relationship of ln(C_0/C_t) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 400 °C.

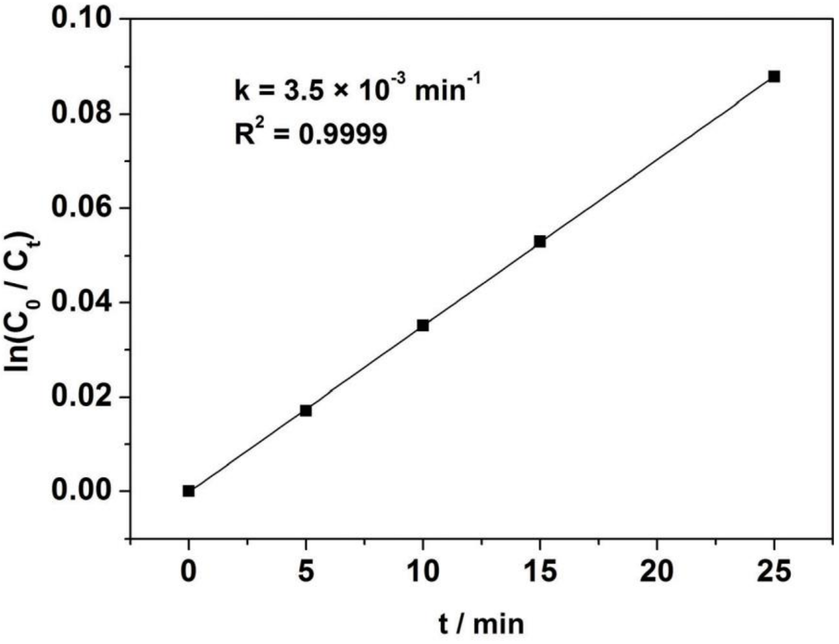


Figure S16. Relationship of ln(C_0/C_t) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 420 °C.

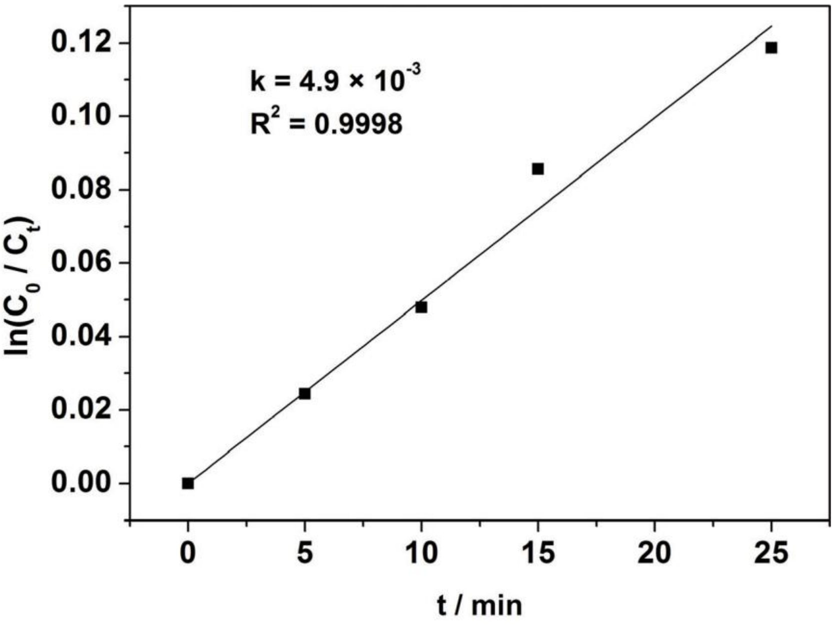


Figure S17. Relationship of ln(C_0/C_t) and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 450 °C.

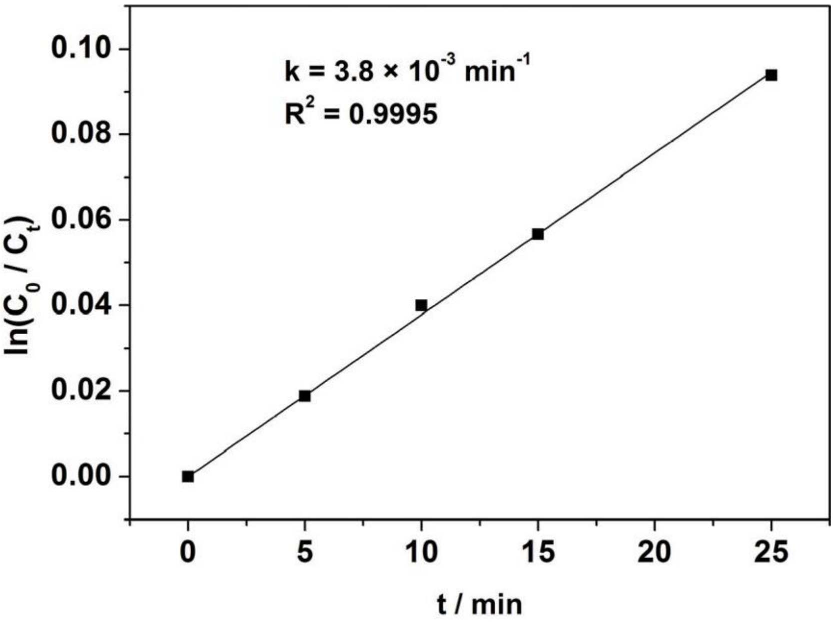


Figure S18. Relationship of $\ln(C_0/C_t)$ and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over α-MnO_2/Na_xMnO_2 with NaOH/Mn molar ratio of 1.2 calcined at 500 ^oC.

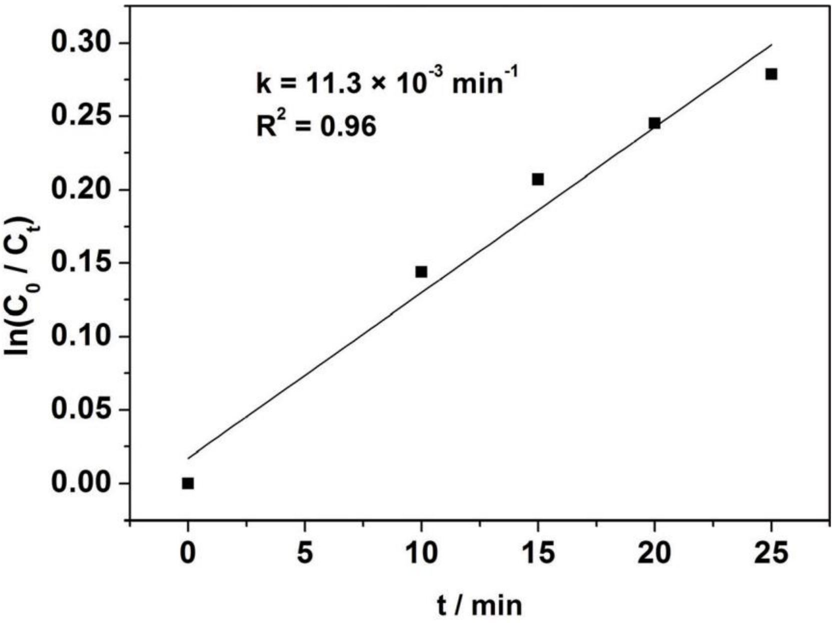


Figure S19. Relationship of $\ln(C_0/C_t)$ and reaction time t of 2-furonitrile conversion to methyl furan-2-carboximidate over Na_xMnO_2.

2. GC, MS and NMR Traces

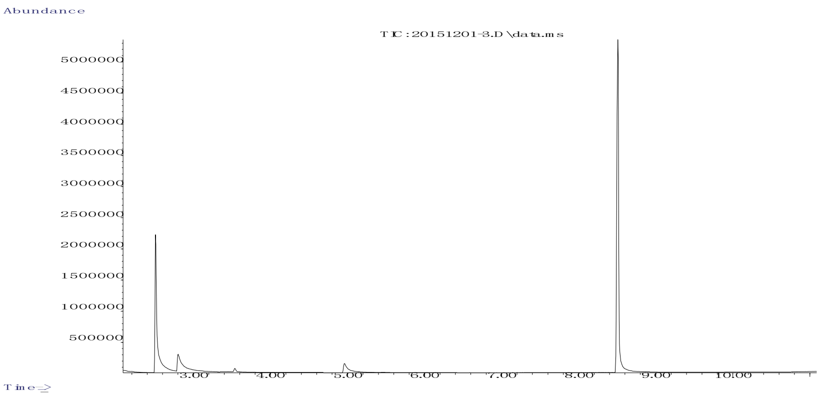


Figure S20 GC spectrum of products from furfural (**Figure 7 0.5 h** in the main text).

MS: m/z (%):95 (100) [M+], 64 (13), 44 (15), 39 (48), 32 (52)

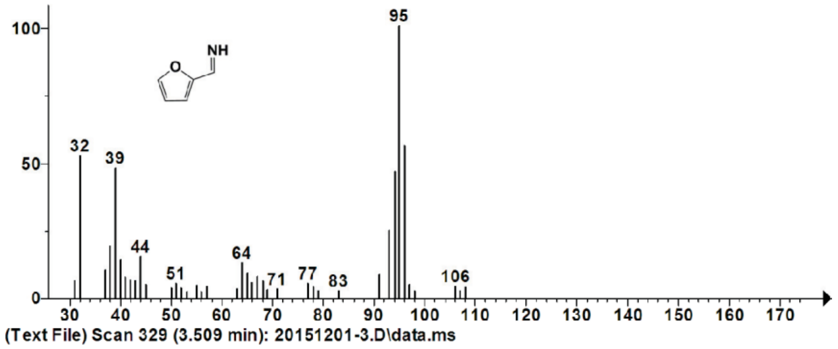


Figure S21 Mass spectrum of **aldimine**.

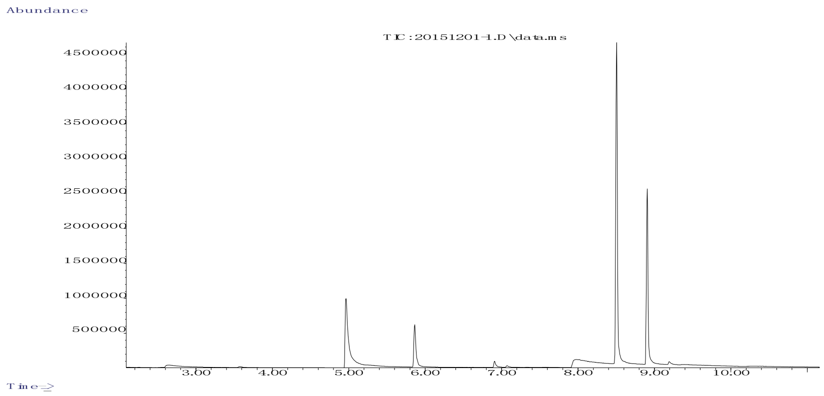


Figure S22 GC spectrum of **Table S1, entry 2**.

MS: m/z (%):111 (100) [M+], 95 (96), 44 (14), 39 (27), 32 (7)

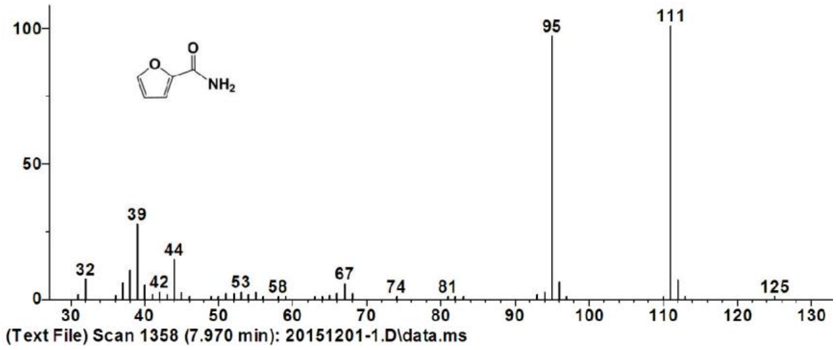


Figure S23 Mass spectrum of **4**.

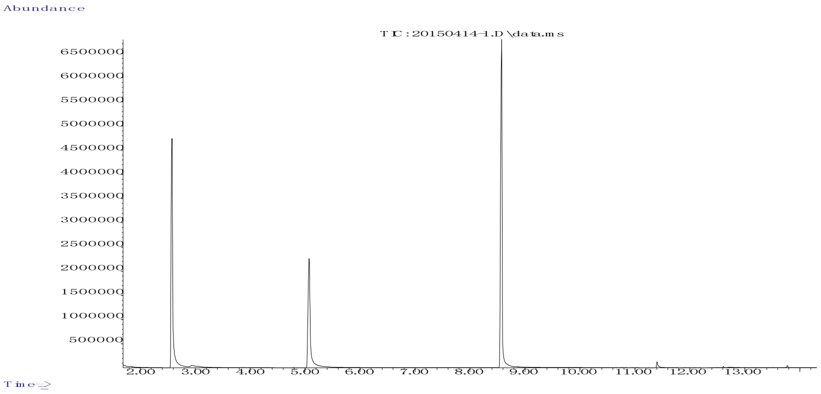


Figure S24 GC spectrum of **Table 1, entry 3** in the main text.

MS: m/z (%): 93 (100) [M+], 64 (47), 38 (23)

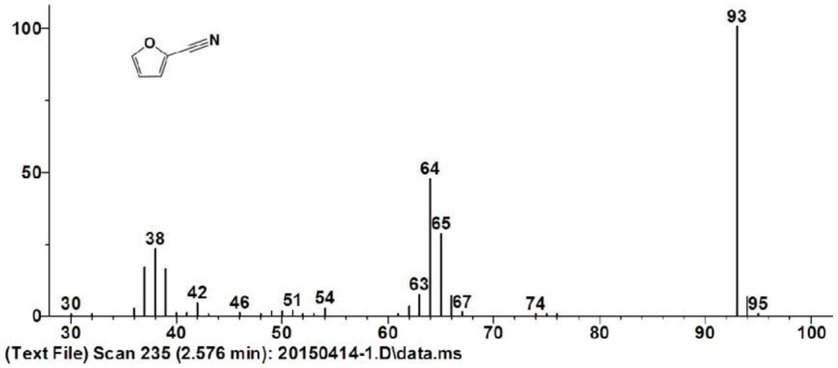


Figure S25 Mass spectrum of **2**.

MS: m/z (%): 125 (41) [M+], 94 (100), 81 (41), 67 (57), 39 (41)

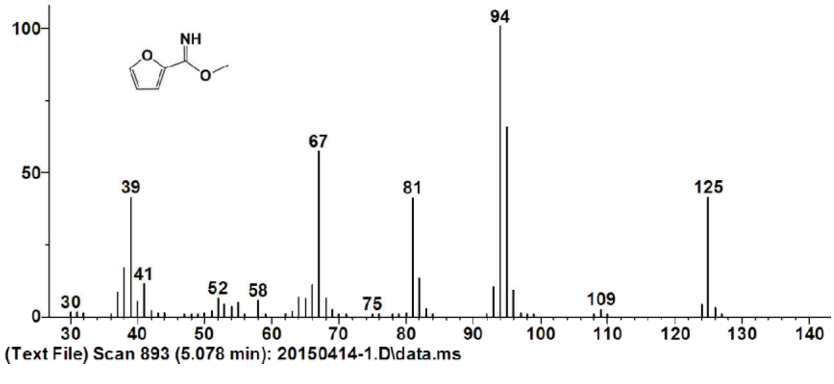


Figure S26 Mass spectrum of **3**.

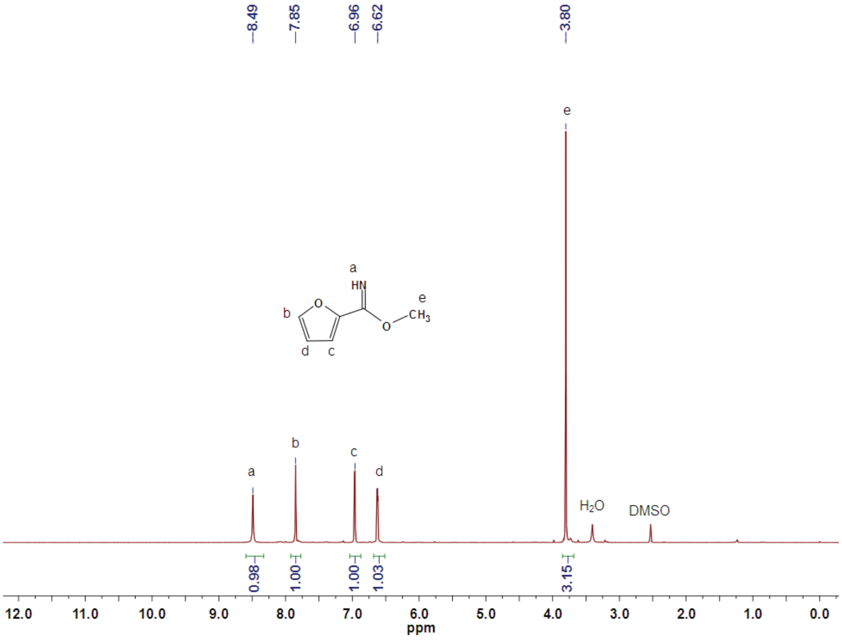


Figure S27 ^{1}H NMR (DMSO-d$_6$) of isolated **methyl furan-2-carbox Imidate**.

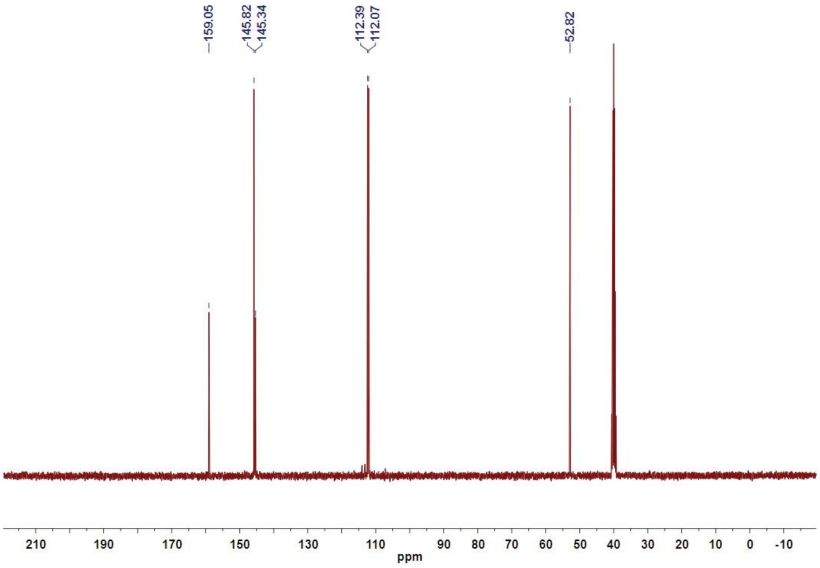


Figure S28 ^{13}C NMR (DMSO-d$_6$) of isolated **methyl furan-2-carbox imidate**.

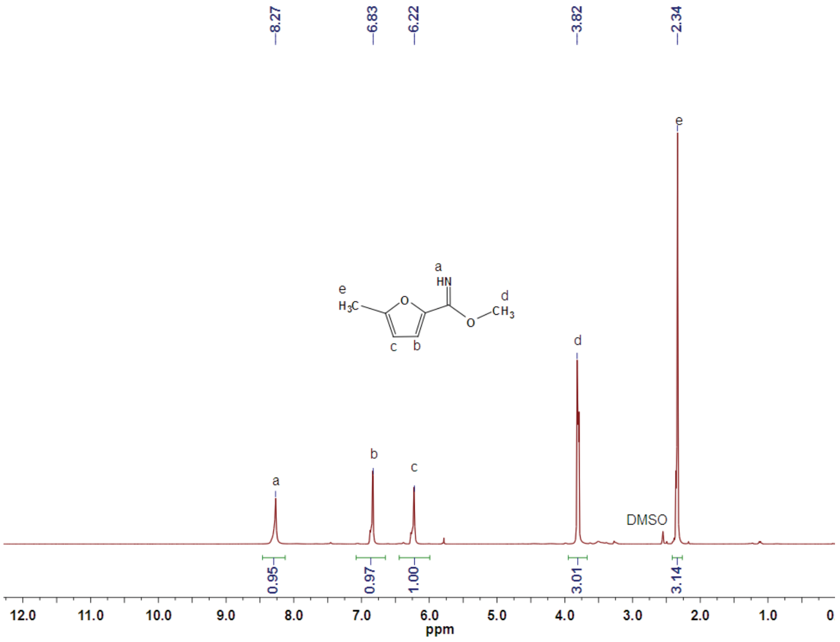


Figure S29 ^{1}H NMR (DMSO-d$_6$) of isolated **methyl 5-methylfuran-2-carbox Imidate** (Fig.6 entry 1).

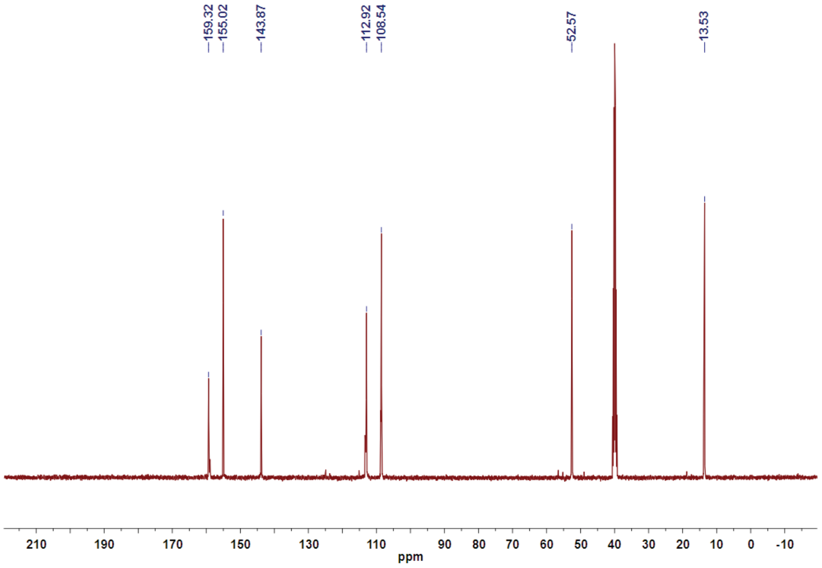


Figure S30 ^{13}C NMR (DMSO-d$_6$) of isolated **methyl 5-methylfuran-2-carbox imidate**.

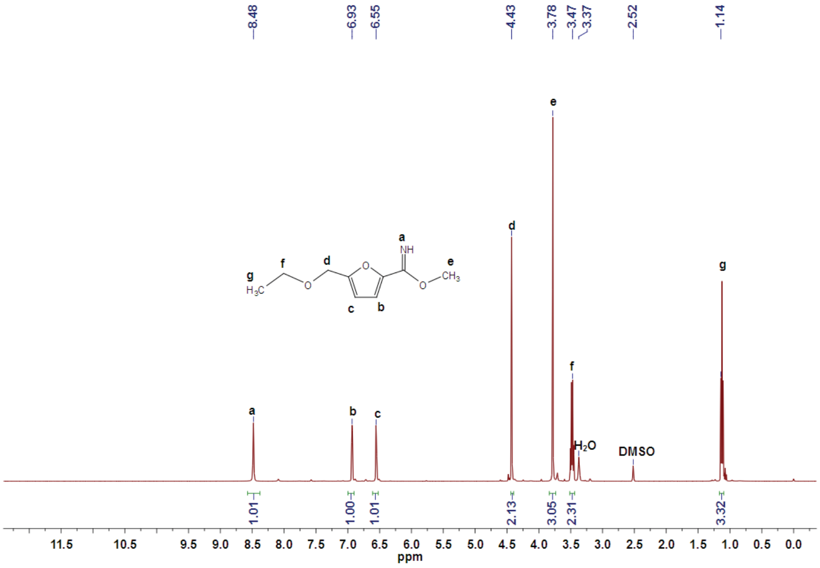


Figure S31 ^{1}H NMR (DMSO-d$_6$) of isolated **methyl 5-ethoxymethylfuran -2-carboxinidate** (Fig.6 entry 4).

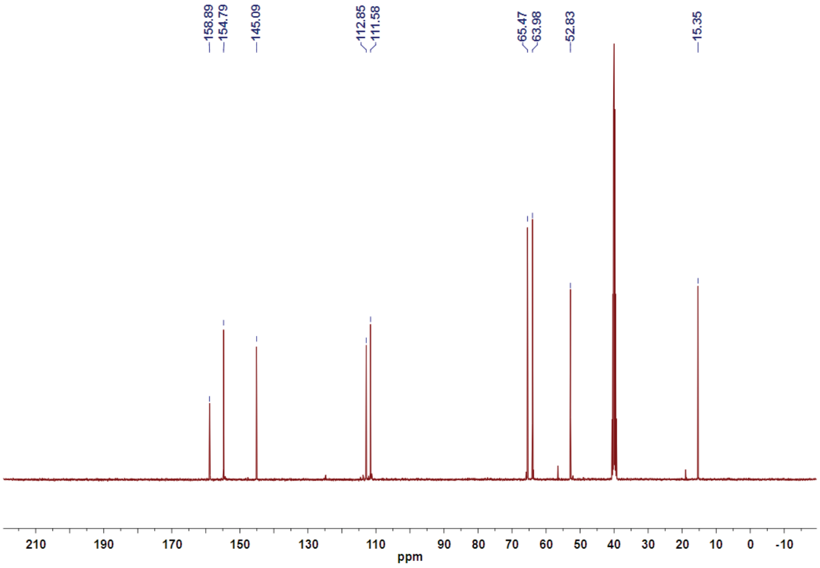


Figure S32 ^{13}C NMR (DMSO-d$_6$) of isolated **methyl 5-ethoxymethylfuran -2-carboximidate**.

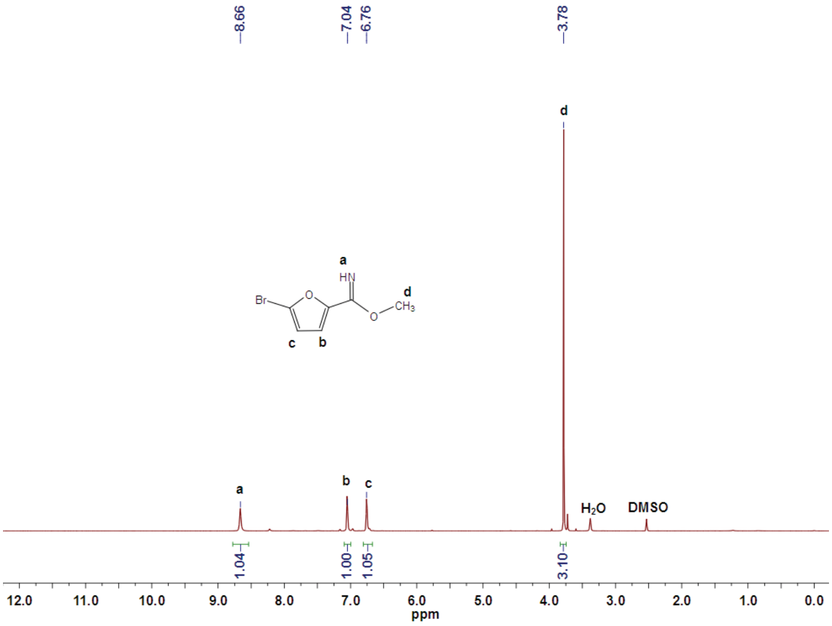


Figure S33 ^{1}H NMR (DMSO-d_6) of isolated **methyl 5-bromofuran-2-carbox-Imidate** (Fig.6 entry 5).

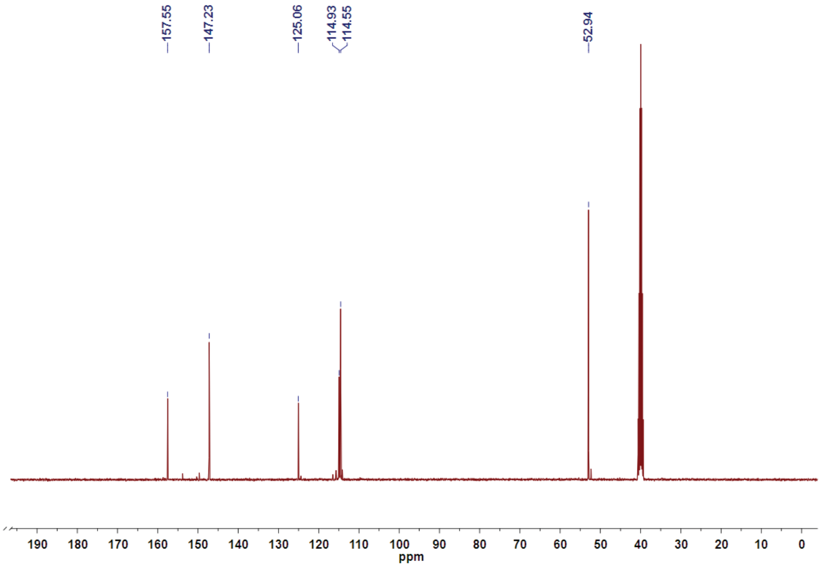


Figure S34 ^{13}C NMR (DMSO-d_6) of isolated **methyl 5-bromofuran-2-carbox-imidate**.

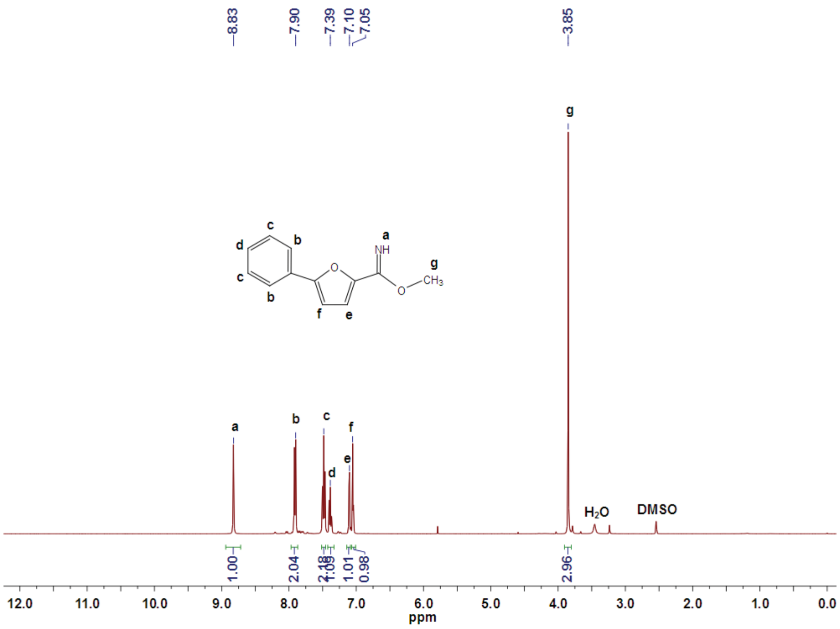


Figure S35 ^{1}H NMR (DMSO-d_6) of isolated **methyl 5-phenylfuran-2-carbox-Imidate** (Fig.6 entry 7).

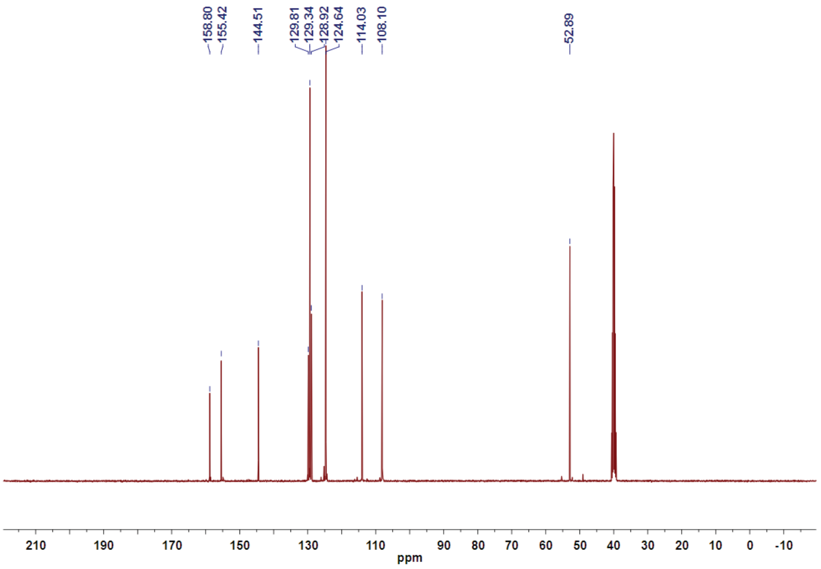


Figure S36 ^{13}C NMR (DMSO-d_6) of isolated **methyl 5-phenylfuran-2-carbox-imidate**.

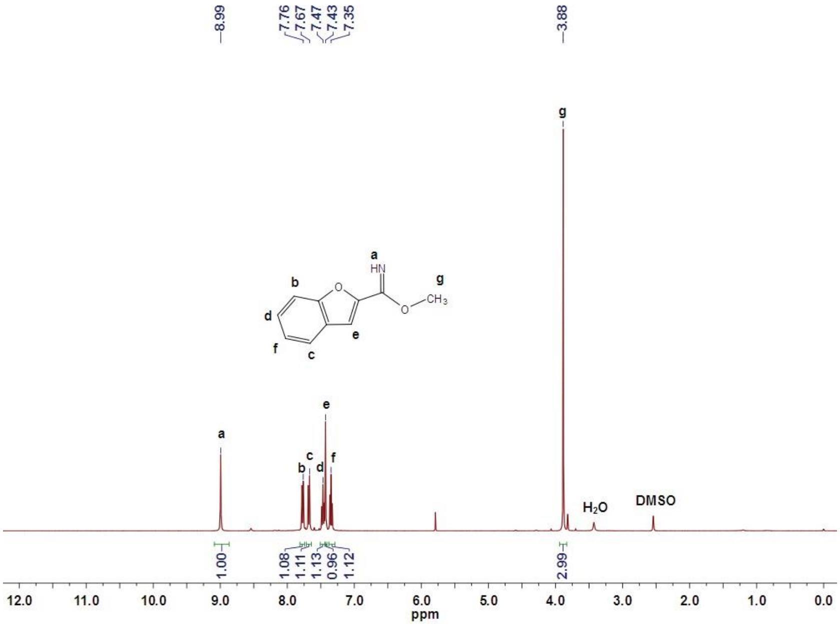


Figure S37 ^{1}H NMR (DMSO-d$_6$) of isolated **methyl benzofuran-2-carboximidate** (Fig.6 entry 8).

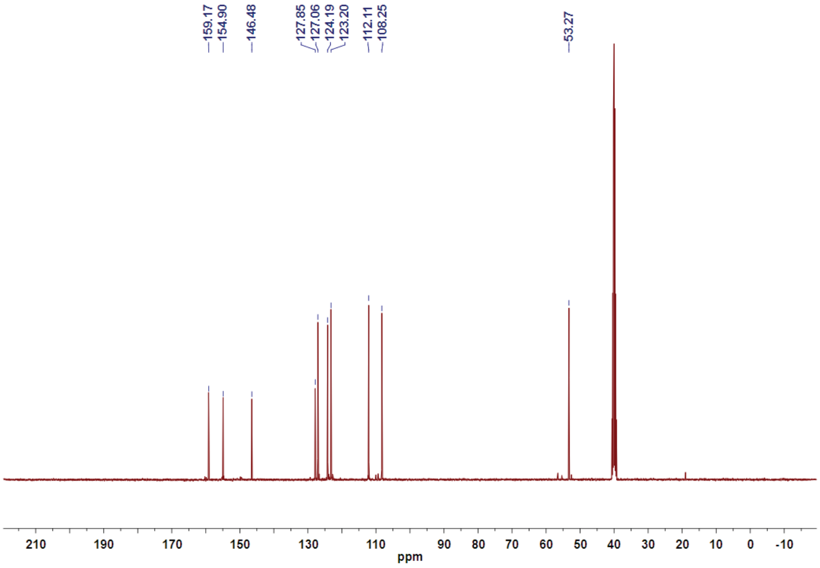


Figure S38 ^{13}C NMR (DMSO-d$_6$) of isolated **methyl benzofuran-2-carboximidate**.