

Supporting information for

Aerobic oxidative esterification of 5-hydroxymethylfurfural to dimethyl furan-2, 5-dicarboxylate by using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen

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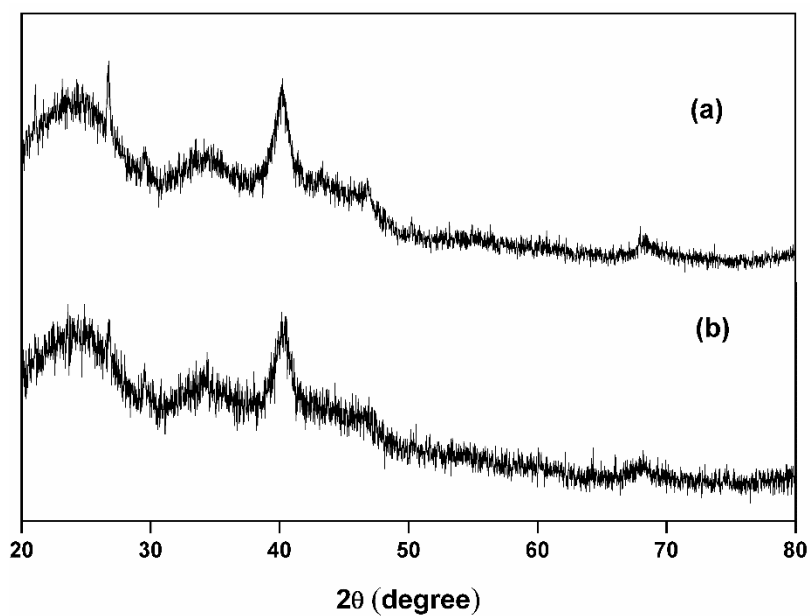


Figure S1. The XRD spectra of catalysts. (a) Fresh PdCoBi/C (1:1:1) catalyst. (b) PdCoBi/C (1:1:1) catalyst after recycling four times.

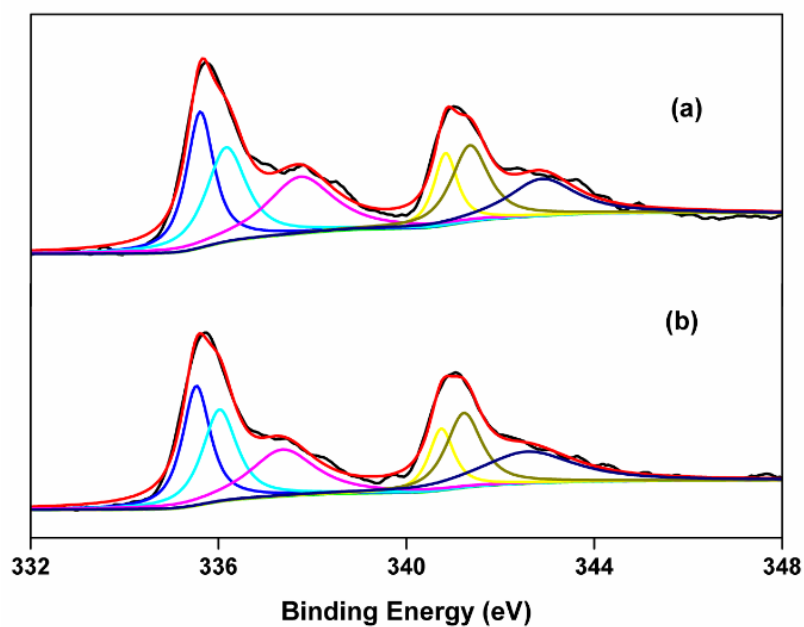


Figure S2. The Pd 3d_{5/2} XPS spectra of catalysts. (a) Fresh PdCoBi/C (1:1:1) catalyst. (b) PdCoBi/C (1:1:1) catalyst after recycling four times.

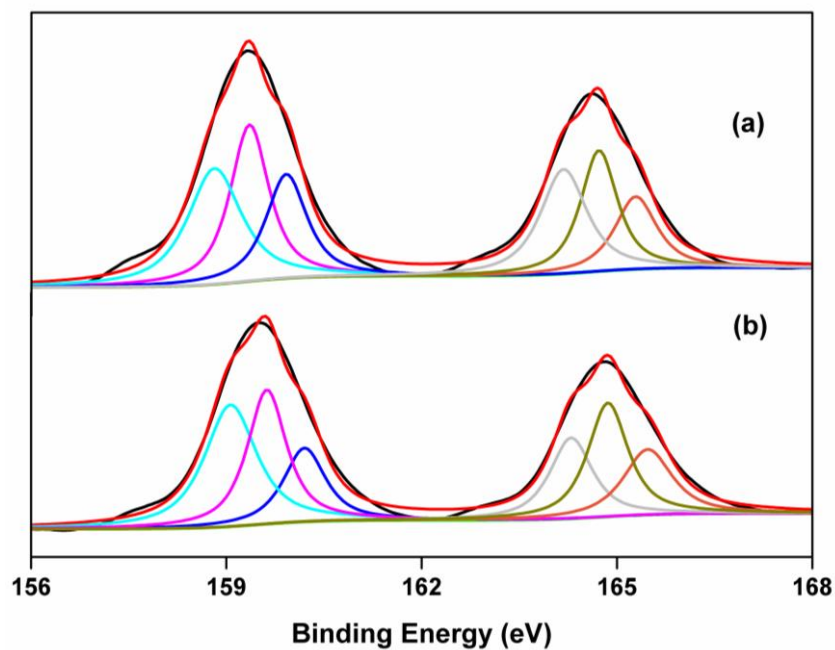


Figure S3. The Bi $4f_{7/2}$ XPS spectra of catalysts. (a) Fresh PdCoBi/C (1:1:1) catalyst. (b) PdCoBi/C (1:1:1) catalyst after recycling four times.

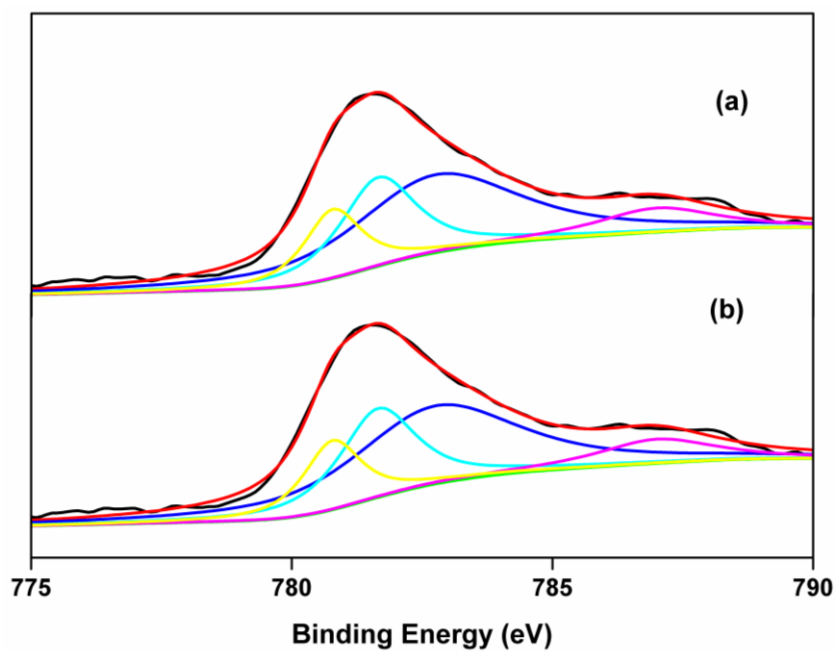


Figure S4. The Co $2p_{3/2}$ XPS spectra of catalysts. (a) Fresh PdCoBi/C (1:1:1) catalyst. (b) PdCoBi/C (1:1:1) catalyst after recycling four times.

Table S1. Effect of alkaline species on oxidative esterification of HMF ^a

Entry	Base	Conversion [%] ^b	Yield [%] ^b	TON ^c	TOF [h ⁻¹] ^d
1	NaOAc	21	7	1.40	0.10
2	NaHCO ₃	46	32	6.40	0.46
3	K ₂ CO ₃	98	93	18.60	1.33
4	KOH	44	13	2.60	0.18
5	<i>t</i> -BuOLi	98	84	16.80	1.20
6	<i>t</i> -PenONa	97	75	15.00	1.07
7	Et ₃ N	0	0	0.00	0.00
8	KH ₂ PO ₄	0	0	0.00	0.00

[a] Reactions conditions : 0.5 mmol HMF, 5 mol% Pd/C catalyst, 5 mol% Co(NO₃)₂, 5 mol% Bi(NO₃)₃, 20 mol% base, 2 mL MeOH, 1 atm O₂, 14 h, 60 °C. [b] The product yields were determined by HPLC, ethyl benzoate was used as internal standard. [c] TON = (mol of DMFDCA)/(mol of catalyst). [d] TOF = TON/ Reaction time (h).

Table S2. Effect of reaction time on oxidative esterification of HMF ^a

Entry	Time (h)	Conversion [%] ^b	Yield [%] ^b	TON ^c	TOF [h ⁻¹] ^d
1	1	80	24	4.80	4.80
2	2	90	49	9.80	4.90
3	4	93	63	12.60	3.15
4	6	95	71	14.20	2.36
5	8	96	79	15.80	1.96
6	10	97	86	17.20	1.72
7	12	97	90	18.00	1.50
8	14	98	93	18.60	1.33

[a] Reactions conditions : 0.5 mmol HMF, 5% mol Pd/C, 5% mol Co(NO₃)₂, 5%mol Bi(NO₃)₂, 20 mol% K₂CO₃ as base, 2 mL MeOH, 1atm O₂, 60 °C. [b] The yields was determined by HPLC, ethyl benzoate was used as internal standard. [c] TON = (mol of DMFDCA)/(mol of catalyst). [d] TOF = TON/ Reaction time (h).

Table S3. Effect of heterogeneous catalyst recycle numbers ^a

Entry	Circulation times	Conversion [%] ^b	Yield [%] ^b	TON ^c	TOF [h ⁻¹] ^d
1	1	99	96	9.60	0.69
2	2	95	88	8.80	0.63
3	3	95	85	8.50	0.61
4	4	86	70	7.00	0.50
5 ^c	5	96	90	9.00	0.64

[a] Reactions conditions: 0.5 mmol HMF, 20 mol% K₂CO₃, 10 mol% PdCoBi /C (1:1:1) catalyst, 2 mL MeOH, 1atm O₂, 14 h, 60 °C. [b] The yields were determined by HPLC, ethyl benzoate was used as internal standard. [c] Added fresh heterogeneous catalyst to 10 mol% after recycling 4 times. [c] TON = (mol of DMFDCA)/(mol of catalyst). [d] TOF = TON/ Reaction time (h).

Mechanistic experiments

To further study the mechanism, the $^1\text{H-NMR}$ and the Infrared Spectra (IR) analysis on 0.5 h, 8 h, and 14 h of the reaction mixture were carried out. The characteristic peaks of HMMF and FMF were obviously observed according to $^1\text{H-NMR}$ analysis. The $^1\text{H-NMR}$ characteristic peaks of HMF, HMMF, FMF, DMFDCA were successfully detected while reaction proceed at 0.5 h. The characteristic peaks of HMMF and FMF extremely decreased after 8 h. When the reaction time prolonged to 14 h, the characteristic peaks of FMF disappeared and very small amount of HMMF was observed. The results were listed in **Figure S5-Figure S7** and corresponding statements have been added and highlighted in manuscript.

According to the Infrared Spectra (**IR, Figure S8**), the obvious aldehyde peaks of FMF could be observed as the reaction was carried out for 0.5 h. This indicating that the intermediate FMF was generated during the reaction. In combination with the $^1\text{H-NMR}$ analysis, the characteristic peaks of the hydroxyl group was the overlap of HMMF and HMF. When the reaction was prolonged for 14 h, only the characteristic peaks of ester group belonged to FDCA were observed. And no significant hydroxyl peaks was observed which indicating that HMF and HMMF had been almost completely converted.

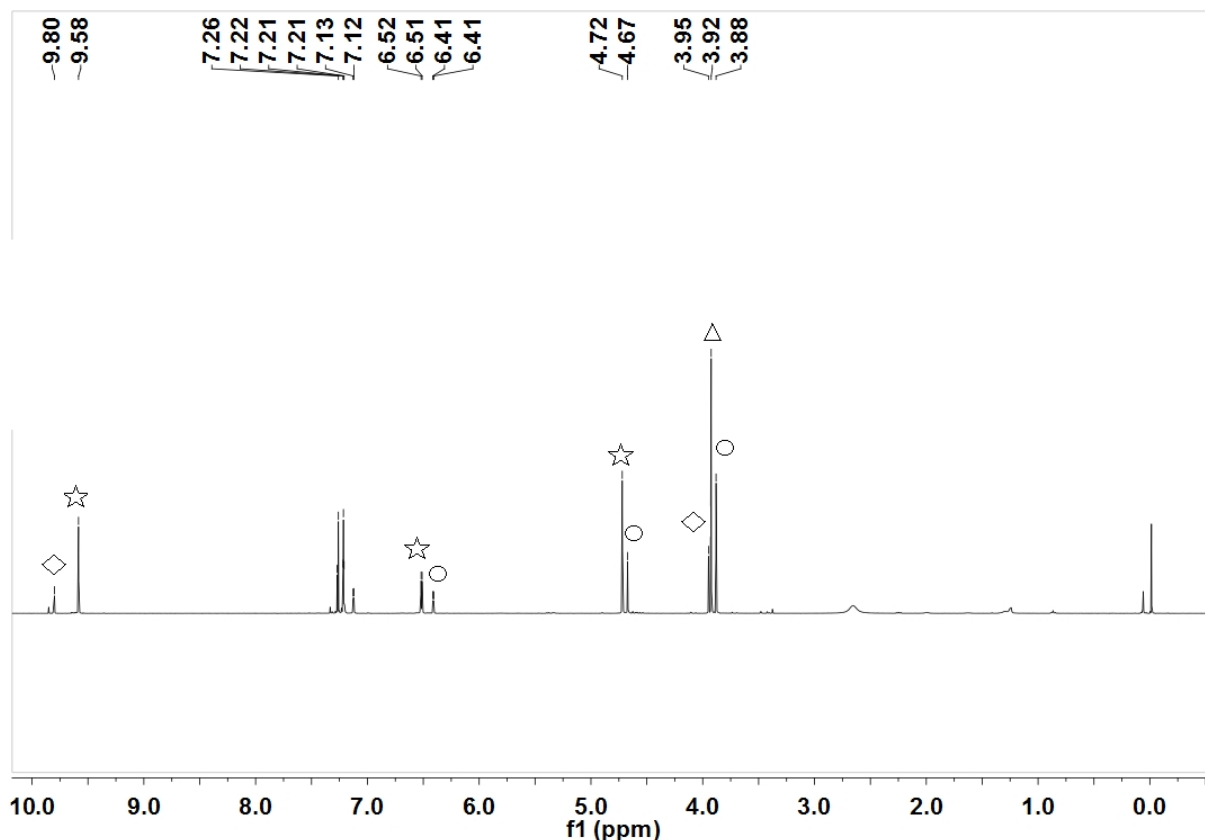


Figure S5. $^1\text{H-NMR}$ spectra of reaction mixture for 0.5 hours

- △: Dimethyl furan dicarboxylate (DMFDCA);
- : 5-hydroxymethyl-2-methyl-furoate (HMMF);
- ◇: 5-formyl-2-methyl-furoate (FMF);
- ☆: 5-Hydroxymethylfurfural (HMF)

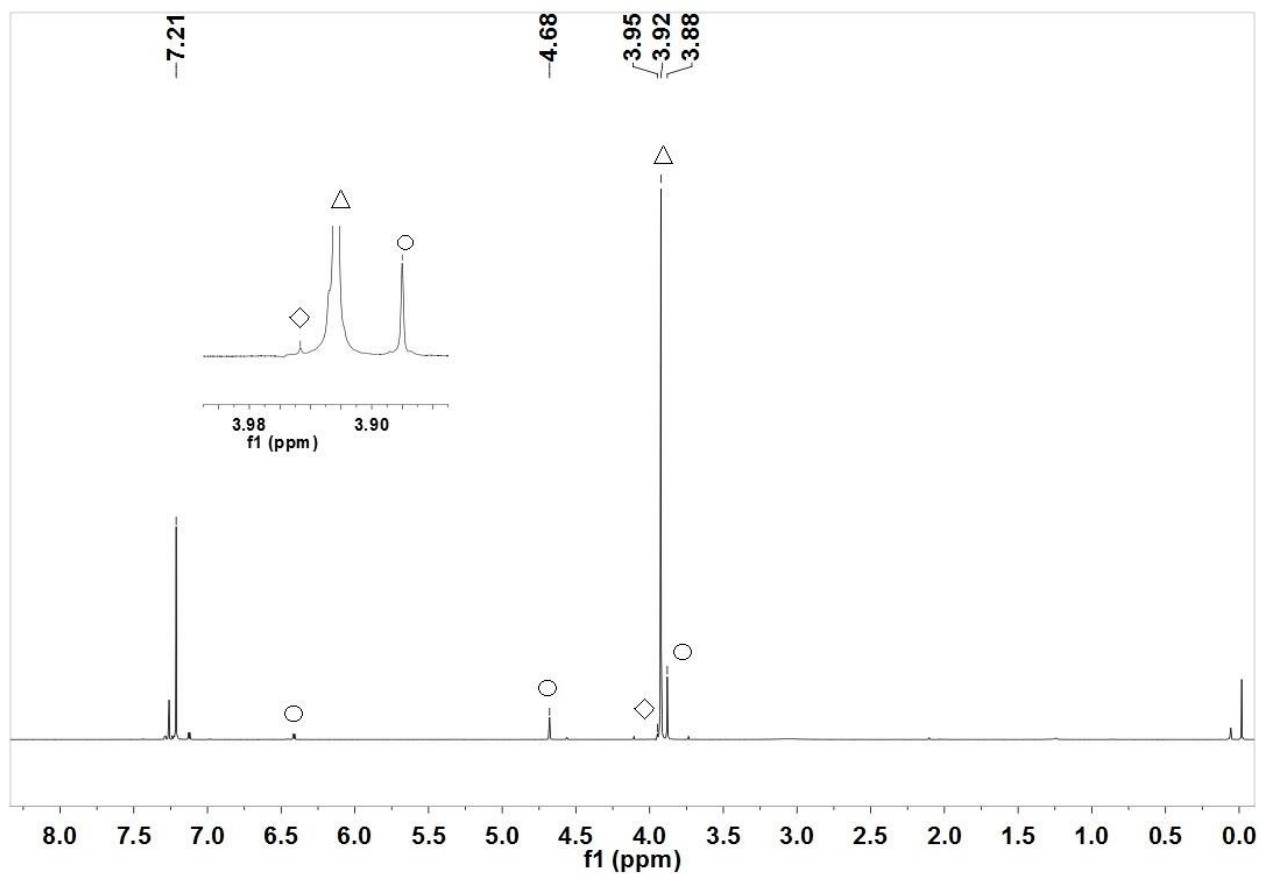


Figure S6. ¹H-NMR spectra of reaction mixture for 8 hours

- △ : Dimethyl furan dicarboxylate (DMFDCA);
- : 5-hydroxymethyl-2-methyl-furoate (HMMF);
- ◇ : 5-formyl-2-methyl-furoate (FMF);
- ☆ : 5-Hydroxymethylfurfural (HMF)

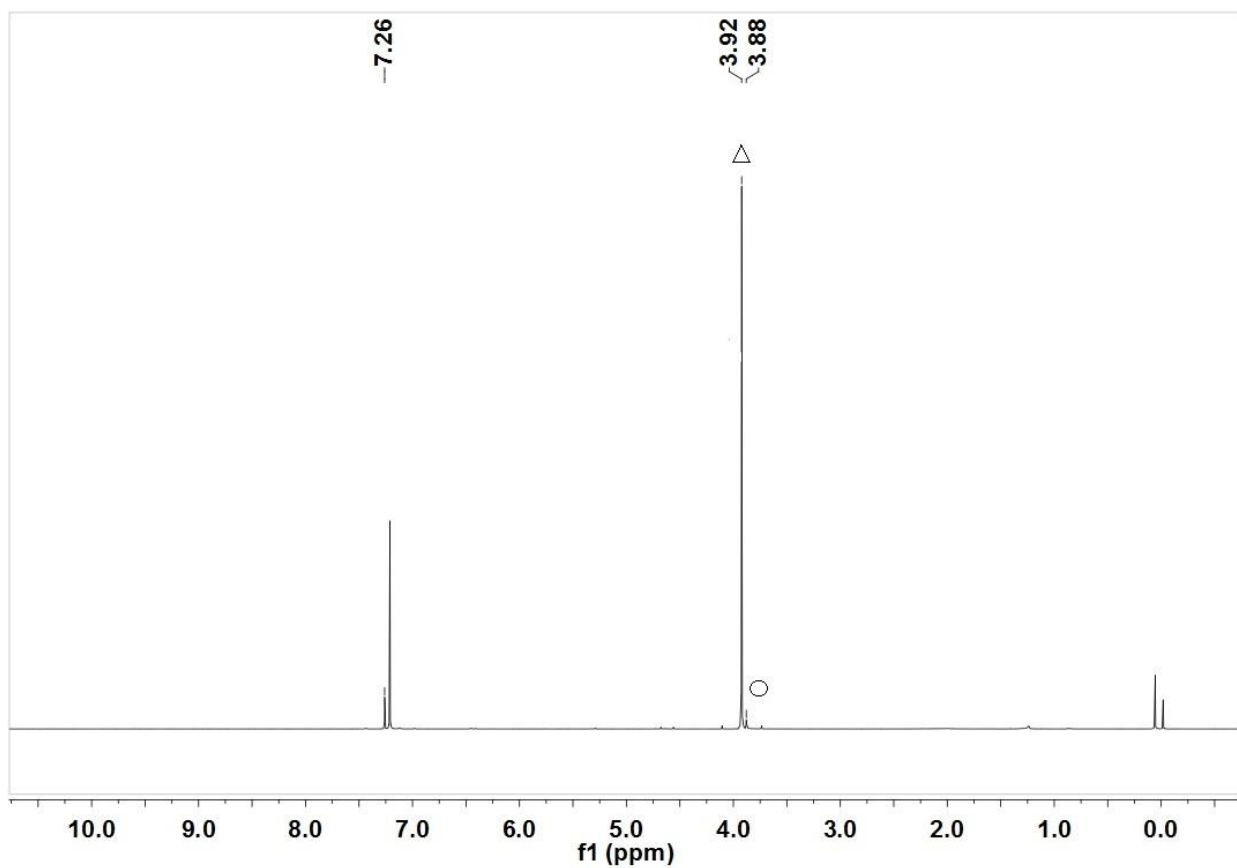


Figure S7. ^1H -NMR spectra of reaction mixture for 8 hours

- \triangle : Dimethyl furan dicarboxylate (DMFDCA);
- \circ : 5-hydroxymethyl-2-methyl-furoate (HMMF);
- \diamond : 5-formyl-2-methyl-furoate (FMF);
- \star : 5-Hydroxymethylfurfural (HMF)

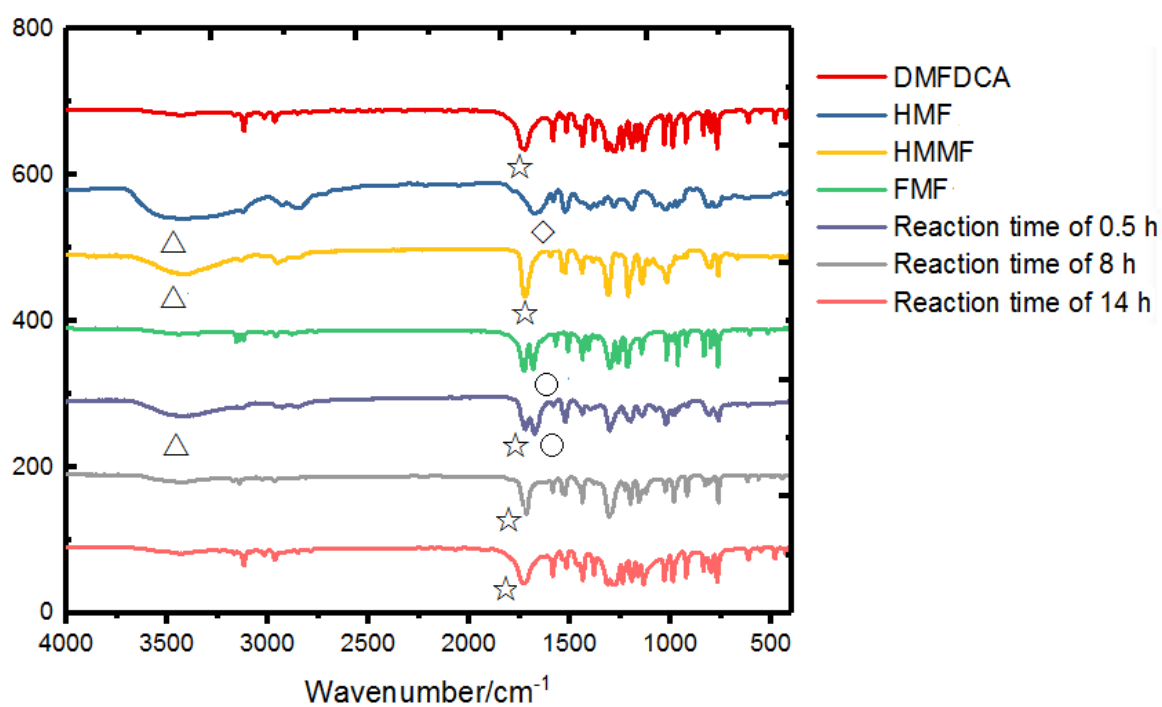
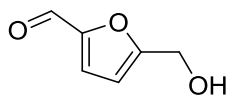


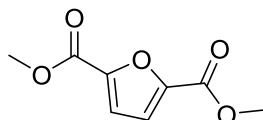
Figure S8. IR spectrum. ◇ : C=O stretching vibration absorption of HMF; ○ : C=O stretching vibration absorption of HMMF; ☆ : C=O stretching vibration absorption of DMFDCA; △ : -OH stretching vibration absorption

NMR Spectra and Analysis



¹H-NMR and of 5-Hydroxymethylfurfural

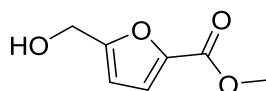
¹H-NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 4.72 (s, 2H), 4.17 (s, 1H).



¹H-NMR and ¹³C-NMR of dimethyl furan-2,5-dicarboxylate

¹H-NMR (400 MHz, CDCl₃) δ 7.21 (s, 2H), 3.92 (s, 6H).

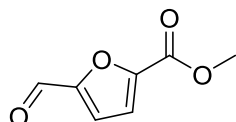
¹³C-NMR (101 MHz, CDCl₃) δ 158.57, 146.84, 118.63, 52.54.



¹H-NMR and ¹³C-NMR of methyl 5-(hydroxymethyl)furan-2-carboxylate

¹H-NMR (400 MHz, CDCl₃) δ 7.07 (d, *J* = 3.3 Hz, 1H), 6.40 (d, *J* = 3.3 Hz, 1H), 4.67 (s, 2H), 3.88 (s, 3H).

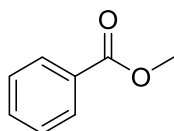
¹³C-NMR (101 MHz, CDCl₃) δ 159.37, 158.46, 144.29, 119.09, 109.73, 57.80, 52.22.



¹H-NMR and ¹³C-NMR of methyl 5-formylfuran-2-carboxylate

¹H-NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.25 (d, *J* = 6.0 Hz, 2H), 3.95 (s, 3H).

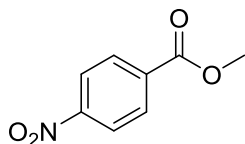
¹³C-NMR (101 MHz, CDCl₃) δ 179.25, 158.65, 154.06, 147.83, 119.07, 118.92, 52.85.



¹H-NMR and ¹³C-NMR of methyl benzoate

¹H-NMR (400 MHz, CDCl₃) δ 8.05-8.03 (m, 2H), 7.57 – 7.49 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 3.90 (s, 3H).

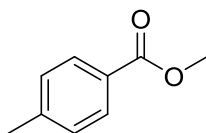
¹³C-NMR (101 MHz, CDCl₃) δ 167.06, 132.91, 130.14, 129.56, 128.35, 52.06.



¹H-NMR and ¹³C-NMR of methyl 4-nitrobenzoate

¹H-NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 8.4 Hz, 2H), 3.98 (s, 3H).

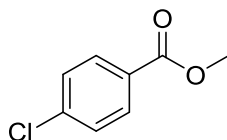
¹³C-NMR (101 MHz, CDCl₃) δ 165.40, 150.76, 135.70, 130.94, 123.78, 53.07.



¹H-NMR and ¹³C-NMR of methyl 4-methylbenzoate

¹H-NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H).

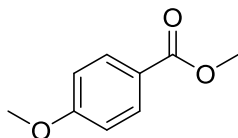
¹³C-NMR (101 MHz, CDCl₃) δ 167.09, 143.44, 129.48, 128.96, 127.29, 51.84, 21.53.



¹H-NMR and ¹³C-NMR of methyl 4-chlorobenzoate

¹H-NMR (400 MHz, CDCl₃) δ 7.99 – 7.96 (m, 2H), 7.43 – 7.40 (m, 2H), 3.92 (s, 3H).

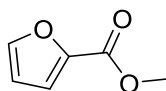
¹³C-NMR (101 MHz, CDCl₃) δ 166.77, 139.90, 131.50, 129.24, 52.81



¹H-NMR and ¹³C-NMR of methyl 4-methoxybenzoate

¹H-NMR (400 MHz, CDCl₃) δ 8.01 – 7.98 (m, 2H), 6.93 – 6.90 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H).

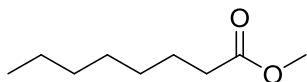
¹³C-NMR (101 MHz, CDCl₃) δ 166.78, 163.21, 131.48, 122.48, 113.49, 55.31, 51.76.



¹H-NMR and ¹³C-NMR of methyl furan-2-carboxylate

¹H-NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.12 (d, *J* = 11.4, 5.5 Hz, 1H), 6.46 (d, *J* = 1.7, 1.2 Hz, 1H), 3.84 (s, 3H).

¹³C-NMR (101 MHz, CDCl₃) δ 159.23, 146.41, 144.66, 118.04, 111.95, 51.99.



$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of methyl octanoate

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.64 (s, 3H), 2.28 (t, $J = 7.6$ Hz, 2H), 1.62 – 1.56 (m, 2H), 1.27 (dd, $J = 11.7, 6.2$ Hz, 8H), 0.85 (t, $J = 6.8$ Hz, 3H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 174.51, 51.58, 34.26, 31.82, 29.27, 29.09, 25.12, 22.76, 14.21.

