Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

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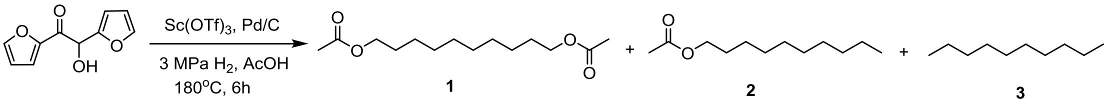
I. General

If not stated otherwise, the reagents were purchased from Sinopharm group Co., Ltd. Furfural was purified by vacuum distillation. Furion and Pd/C were purchased from Alfa Aesar Chemicals Co., Ltd. Metal triflates (Sc^{3+}, Hf^{4+}, Al^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Bi^{2+}, Zn^{2+}, Gd^{3+}, La^{3+}, Y^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Eu^{3+}, Er^{3+}, Dy^{3+}, Tm^{3+}, Ho^{3+}, Yb^{3+}, Lu^{3+}), Pt/C, Ru/C and Rh/C were purchased from Adamas Reagent Co., Ltd. Merrifield resin (Cross-linking: 1% DVB, Particle Size: 200-400mesh, Substitution: 3.5mmol/g) was purchased from Tianjin Nankai Hecheng Sci. & Tech. Co., Ltd.

If not stated otherwise, the reaction was carried out in an autoclave sponsored by Anhui Kemi Machinery Technology Co., Ltd. Usually, the initial temperature was 30℃, then heating to the required reaction temperature through intelligent temperature controller in 30min. After that the reaction was heating preservation with a certain period of time.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. NMR spectra were analysed with MestReNova software.

II. Typical experiment and product analysis



0.5 mmol furion, 3 mol % Pd/C, 4 mol % $Sc(OTf)_3$ and 10 mL acetic acid were added into a 25mL stainless steel autoclave equipped with temperature programmed controller. The autoclave was replaced with hydrogen for 5 times and pressurized the hydrogen to 3 MPa at room temperature. The reaction temperature was heated to 180 ℃ in 30min. The reaction temperature was kept at 180 ℃ for 6 hours. After the reaction was complete, cooled to room temperature and then carefully released the pressure. A certain amount of Biphenyl was added to the solution as the internal standard. Then the solution was analyzed by Gas Chromatography ((30m×0.32mm×0.25μm), SHIMADZU, GC-2010 Pulse quipped with RTX-65 capillary column). The conversion of furion and the yield of products was calculated according to the following formula:

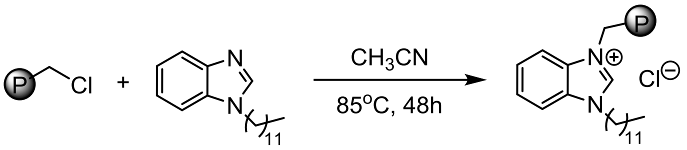
$$\mathrm{Conversion/\%} = \frac{\mathrm{n_{furion}} - \mathrm{n'_{furion}}}{\mathrm{n_{furion}}}$$

$$\text{Yield}/\% = \frac{n_{(\text{yield of produt})}}{n_{\text{furion}}} \times 100\%$$

n_{furion}: mol of furion before reaction; n'_{furion}: mol of furion after reaction

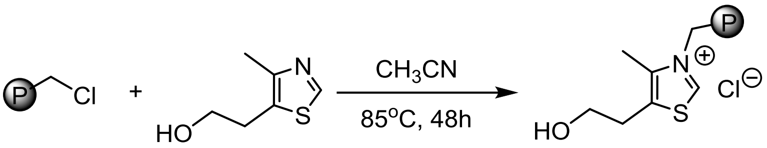
III NHC catalyst preparation

1. Imidazole-type immobilized NHC catalyst preparation



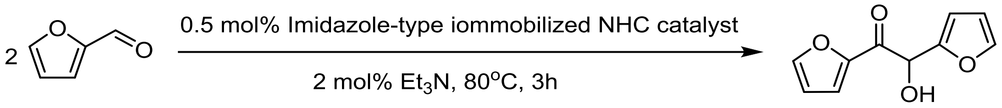
5.0 g Merrifield resin and 50 mL acetonitrile were added into a round-bottomed flask. The mixture was stirred at room temperature for 2h and then was filtered. The filter residue was dissolve in fresh acetonitrile (50 mL) and stirred at room temperature for 48h. 10.0 g 3-dodecyl benzimidazole was added to the above mixture, heating up to reflux for 48h. After the reaction, the reaction solution was cooled to room temperature and then was filtered. The filter residue was washed with acetonitrile and acetone which dried in vacuum. The light yellow solid was obtained.

2. Thiazole-type immobilized NHC catalyst preparation

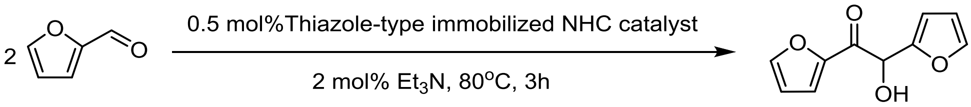


5.0 g Merrifield resin and 50 mL acetonitrile were added into a round-bottomed flask. The mixture was stirred at room temperature for 2h and then was filtered. The filter residue was dissolve in fresh acetonitrile (50 mL) and stirred at room temperature for 48h. 10.0 g 2-(4-methylthiazol-5-yl)ethan-1-ol was added to the above mixture, heating up to reflux for 48h. After the reaction, the reaction solution was cooled to room temperature and then was filtered. The filter residue was washed with acetonitrile and acetone which dried in vacuum. The light yellow solid was obtained.

IV. Benzoin condensation reaction



1.0 g fresh furfural, 0.5 mol % Imidazole-type immobilized NHC catalyst and 2 mol % (25 mg) Et_3N were added into 10 mL Schleck tube under argon atmosphere. The reaction mixture was stirred at 80 ℃ for 3h under free-solvent. After the reaction, the white solid product was obtained and then was dissolved in acetic acid. The acetic acid solution used in the next hydrodeoxygenation reactions.



1.0 g fresh furfural, 0.5 mol % Thiazole-type immobilized NHC catalyst and 2 mol % (25 mg) Et_3N were added into 10 mL Schleck tube under argon atmosphere. The reaction mixture was stirred at 80 ℃ for 3h under free-solvent. After the reaction, the white solid product was obtained and then was dissolved in acetic acid. The acetic acid solution used in the next hydrodeoxygenation reactions.

V. NHC catalyst cycle

1.0 g fresh furfural, 0.5mol% Imidazole-type immobilized NHC catalyst, and 2 mol% (25 mg) Et_3N were added into 10 mL Schleck tube under argon atmosphere. The reaction mixture was stirred at 80 ℃ for 3h under free-solvent. After the reaction, the acetic acid was added to dissolve the product, and then was filtered to obtain catalyst which dried in vacuum for the next cycle. The same method was used for the thiazole-type immobilized NHC catalyst.

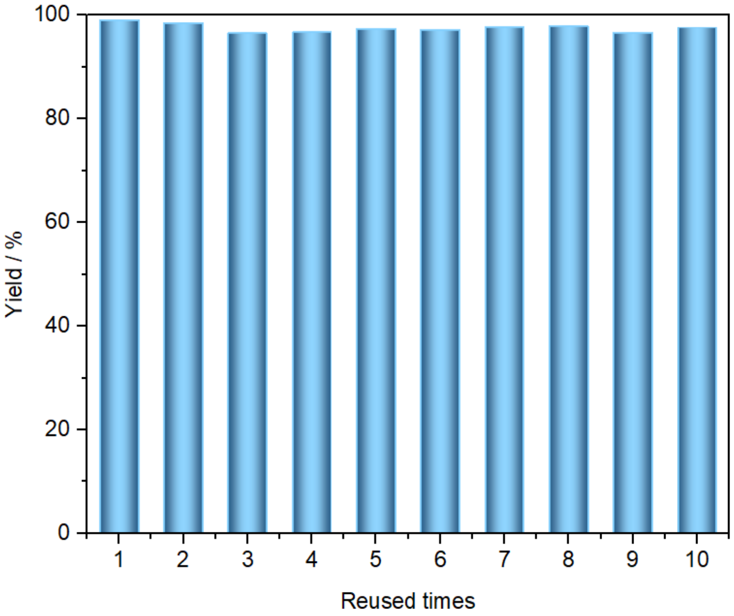


Figure S1. Imidazole-type immobilized NHC catalyst reused times.

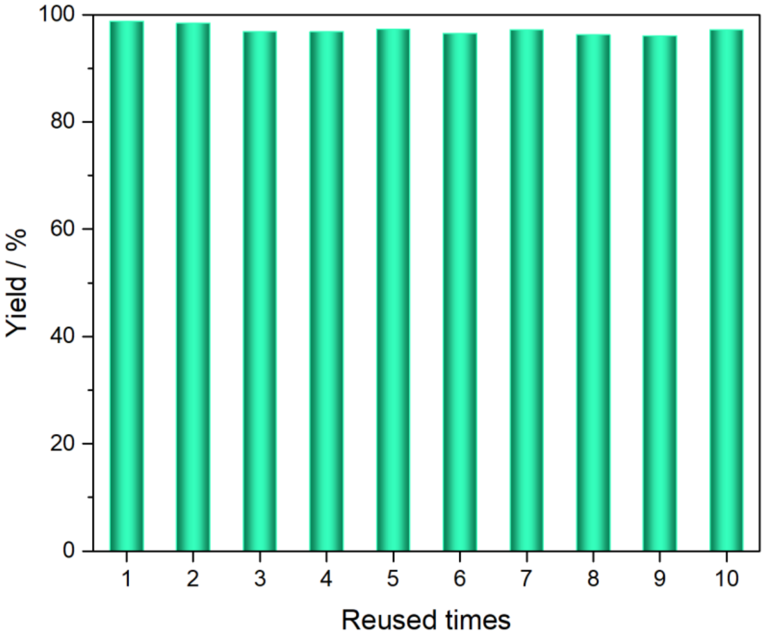
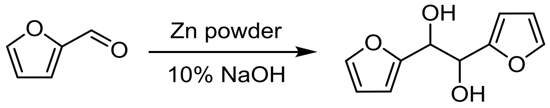


Figure S2. Thiazole-type immobilized NHC catalyst reused times.

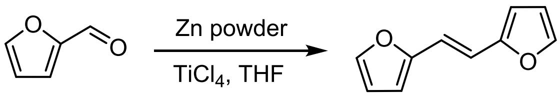
VI. Synthesis of substrates

1. 1, 2-Di-2-furanyl-1,2-enthanediol



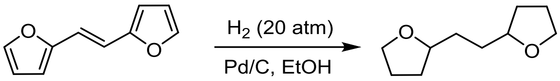
According to literature [1], 1.55 g Zn powder was added to 10 mL10 % NaOH solution in ice water bath for 5 min, then slowly was added 4.84 g (50 mmol) furfural that was purified by vacuum distillation. After addition, the reaction was carried out at room temperature for 3h. Dilute HCl was added to neutralize reaction solution and extracted with ethyl acetate (3×50 mL), The organic phase was combined, dried over Na_2SO_4, filtered and concentrated under vacuum to obtain product. ^{1}H NMR(400MHz, $CDCl_3$): δ=7.34-7.25(m, 2H), 6.39-6.11(m, 4H), 4.97-4.81(m, 2H); ^{13}C NMR(101MHz, $CDCl_3$): δ=152.91, 152.69, 142.25, 142.19, 110.37, 110.25, 108.05, 107.90, 69.94, 69.69.

2. 1, 2-Difuryl ethylene



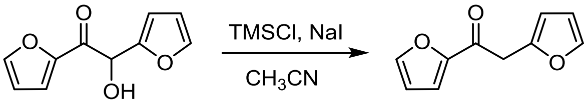
According to literature [2], 5.18 g (50 mmol) furfural and 100 mL THF were added to 500 mL four-neck round bottom flask with equipped with Constant pressure dropping funnel and stirred at -20℃ for 30 min. 11.83 g (60 mmol) $TiCl_4$ was then added dropwise to the flask over 30min at -20 ℃. Then 8.1 g (100 mmol) Zn powder was added to solution in small portions over 30min. The mixture was kept at -20 ℃ for 1h before warming up to room temperature and then refluxed for overnight. After the reaction, the reaction quench with ice cold water and was filtered, the precipitated solid was dissolved in dichloromethane and extracted with dichloromethane (2×100 mL), After removing the solvent, the crude product was purified by silica gel chromatography to give white solid product (2.53 g, 58.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.8 Hz, 2H), 6.81 (s, 2H), 6.41 (dd, *J* = 3.3, 1.8 Hz, 2H), 6.32 (dd, *J* = 3.3, 0.7 Hz, 2H). ^{13}C NMR (101MHz, $CDCl_3$): δ=153.00, 142.11, 114.97, 111.72, 108.75.

3. 1, 2-Ditetrahydrofuran ethane



According to literature [3], 2.9 g (20 mmol) 1,2-Difuryl ethylene, 25 mg of Pd/C (10%) and 5 mL of anhydrous methanol were added into a 25mL autoclave reactor. The reaction was carried out at 20 atm H_2 and 80 ℃ for 3 h. After completion of the reaction, the reaction mixture was filtered and concentrated in vacuo to afford product. ^{1}H NMR (400MHz, $CDCl_3$): δ=3.88-3.80 (m, 4H), 3.79-3.68 (m 2H), 2.03-1.81 (m, 6H), 1.73-1.41 (m, 6H); ^{13}C NMR (101MHz, $CDCl_3$): δ=79.49, 79.04, 67.88, 67.65, 32.69, 32.13, 31.43, 31.33, 25.76, 25.72.

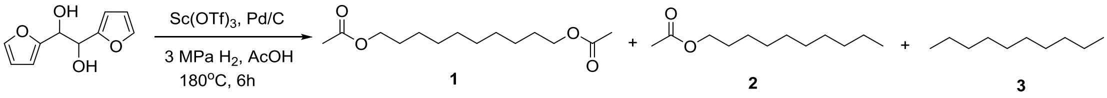
4. 1,2-Di-2-furanylethanone



According to literature [4], 1.92g (10 mmol) furion and 3.90 g (26 mmoL) NaI was added in 20 mL dry CH_3CN. 3.3 mL (25 mmol) TMSCl was added dropwise over 10 min to above solution under the argon atmosphere. The mixture was stirred at room temperature for 1h. After completion of the reaction, 50 mL 10% sodium thiosulfate solution was added to the mixture and extracted with dichloromethane (3×50 mL), The organic phase was washed with 10% sodium thiosulfate solution, water, brine, dried over Na_2SO_4, filtered and concentrated under vacuum to obtain crude product. The crude product was purified by silica gel chromatography to give target product. ^{1}H NMR (400MHz, $CDCl_3$) : δ=7.61-7.59 (m, 1H), 7.37-7.35 (m, 1H), 7.24-7.23 (m, 1H), 6.55-6.53 (m, 1H), 6.34-6.32 (m, 1H), 6.26-6.24 (m, 1H), 4.16 (s, 2H); ^{13}C NMR (101MHz, $CDCl_3$) : δ＝183.81, 151.99, 147.78, 146.86, 142.12, 118.28, 112.43, 110.89, 108.38, 38.18.

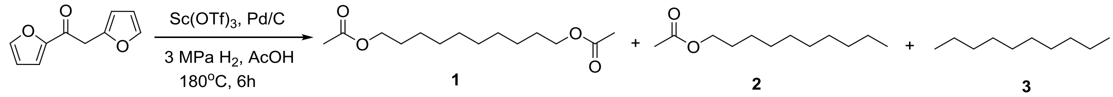
VII. Reaction mechanism

1. 1,2-di(furan-2-yl) ethane-1,2-diol as substrate



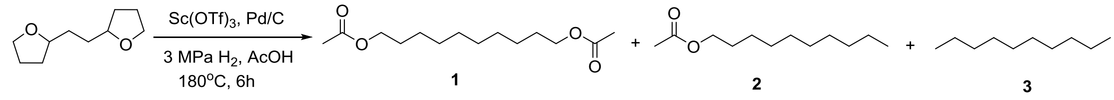
0.5 mmol 1,2-di(furan-2-yl)ethane-1,2-diol, 3 mol % Pd/C, 4 mol % $Sc(OTf)_3$ and 10 mL acetic acid were added into a 25mL stainless steel autoclave equipped with temperature programmed controller. The autoclave was replaced with hydrogen for 5 times and pressurized the hydrogen to 3 MPa at room temperature. The reaction temperature was heated to 180 ℃ in 30min. The reaction temperature was kept at 180 ℃ for 6 hours. After the reaction was complete, cooled to room temperature and then carefully released the pressure. Biphenyl was added as the internal standard to the solution. Then the solution was analyzed by Gas Chromatography.

2. 1,2-di(furan-2-yl) ethan-1-one as substrate



0.5 mmol 1,2-di(furan-2-yl) ethan-1-one, 3 mol % Pd/C, 4 mol % $Sc(OTf)_3$ and 10 mL acetic acid were added into a 25mL stainless steel autoclave equipped with temperature programmed controller. The autoclave was replaced with hydrogen for 5 times and pressurized the hydrogen to 3 MPa at room temperature. The reaction temperature was heated to 180 ℃ in 30min. The reaction temperature was kept at 180 ℃ for 6 hours. After the reaction was complete, cooled to room temperature and then carefully released the pressure. Biphenyl was added as the internal standard to the solution. Then the solution was analyzed by Gas Chromatography.

3. 1,2-bis(tetrahydrofuran-2-yl)ethane as substrate



0.5 mmol 1,2-bis(tetrahydrofuran-2-yl)ethane, 3 mol % Pd/C, 4 mol % $Sc(OTf)_3$ and 10 mL acetic acid were added into a 25mL stainless steel autoclave equipped with temperature programmed controller. The autoclave was replaced with hydrogen for 5 times and pressurized the hydrogen to 3 MPa at room temperature. The reaction temperature was heated to 180 ℃ in 30min. The reaction temperature was kept at 180 ℃ for 6 hours. After the reaction was complete, cooled to room temperature and then carefully released the pressure. Biphenyl was added as the internal standard to the solution. Then the solution was analyzed by Gas Chromatography.

Table S1 Possible intermediates as substrate were used to verify the reaction pathway.

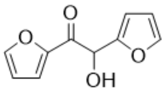
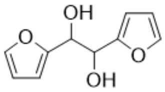
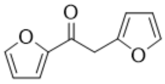
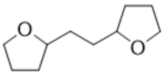
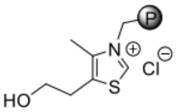
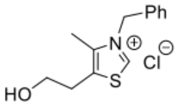
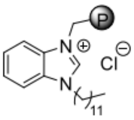
Entry	Substrate	Yield/%			
		1	**2**	**3**	**Total**
1		66	29	3	98
2		4	1	0	5
3		57	32	3	92
4		52	40	5	97

Table S2 Furoin from different sources for hydrodeoxygenation reaction [a].

Entry	NHC Catalyst	Substrate	Yield/%			
			1	**2**	**3**	**Total**
1		Furoin[b]	3	0	0	3
2		Furoin[c]	2	0	0	2
3	—	Furoin[c]	66	29	3	98
4		Furoin[b]	65	27	2	94

a. 0.5 mol% NHC catalyst (Entry 1 and 4) and 0.1 mol% NHC Catalyst (Entry 2), *b*. Furoin was prepared from furfural with NHC catalyst, *c*. Commercially available furoin

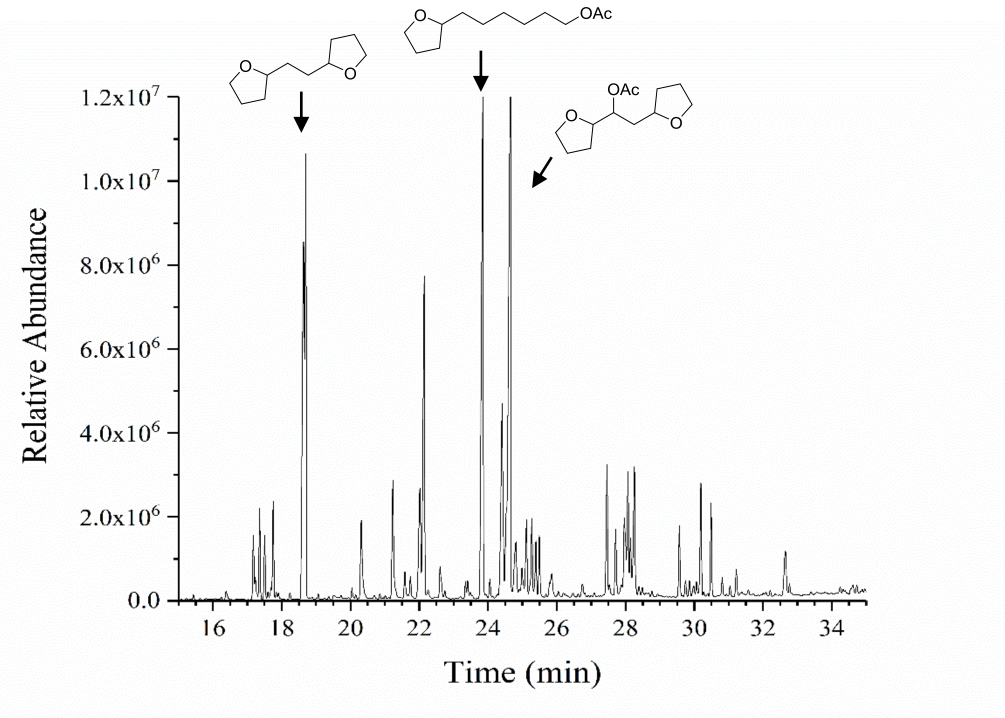


Figure S3 GC-MS of the reaction mixture of heating 10min.

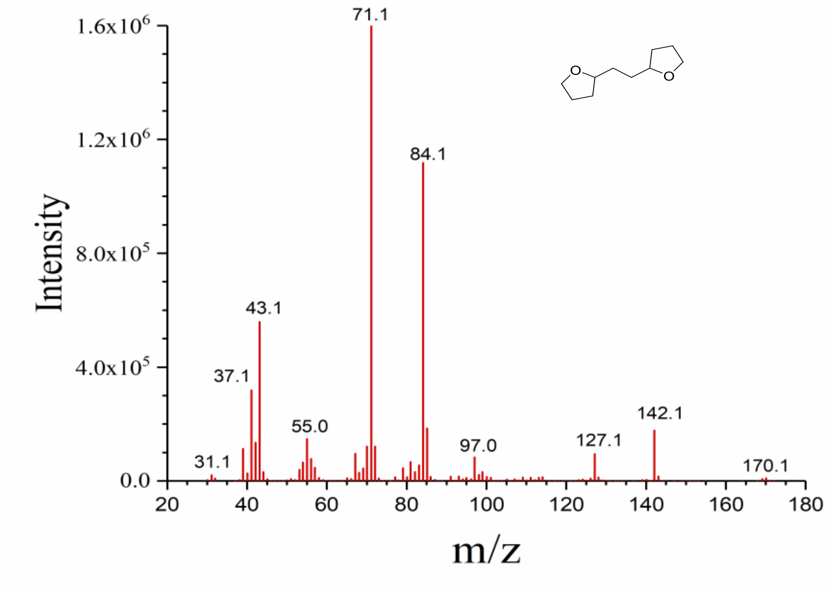


Figure S4 Mass spectrum of 1, 2-ditetrahydrofuran ethane.

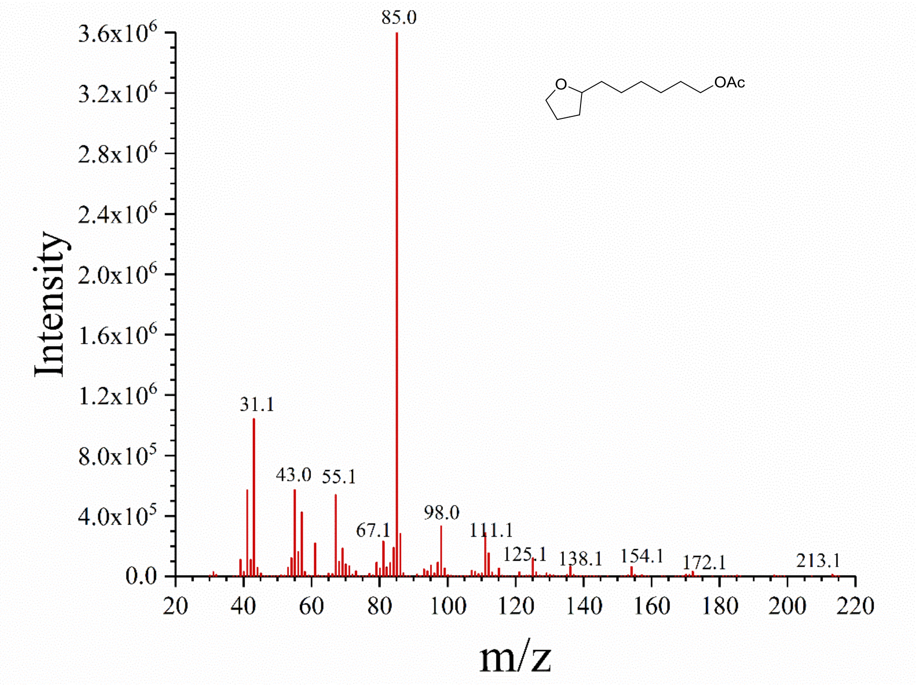


Figure S5 Mass spectrum of 6-(tetrahydrofuran-2-yl) hexyl acetate.

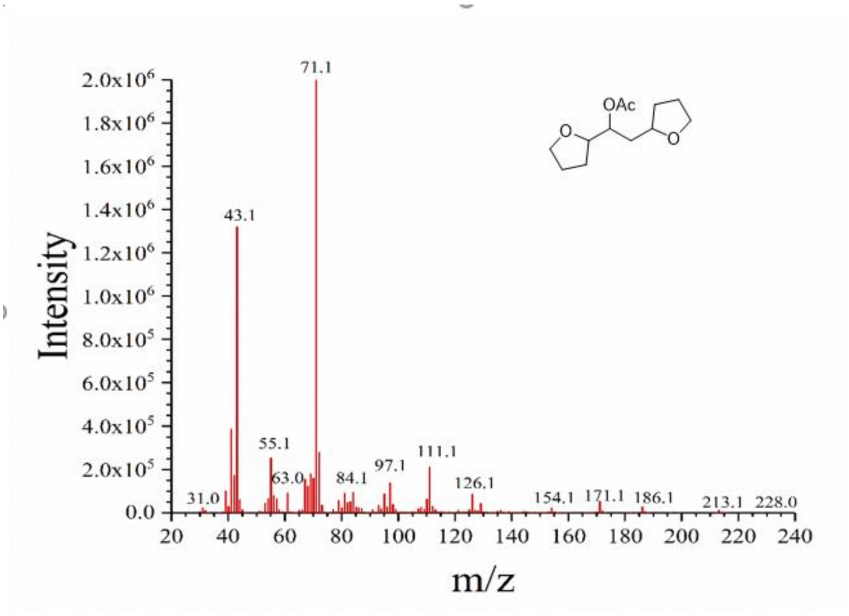


Figure S6 Mass spectrum of 1,2-bis(tetrahydrofuran-2-yl) ethyl acetate.

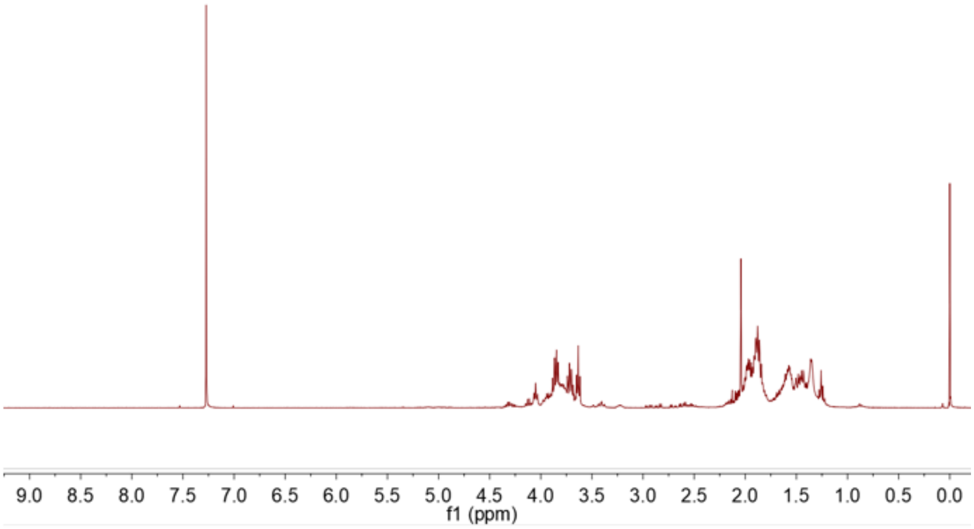


Figure S7 ^{1}H NMR of the reaction mixture of heating 10min.

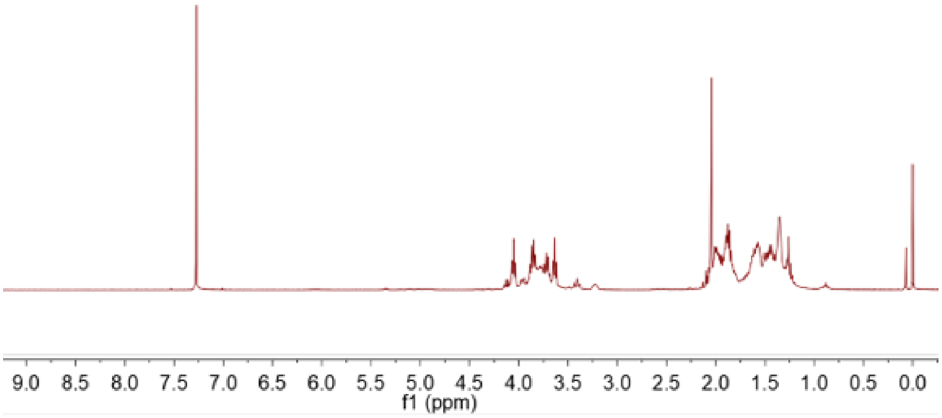


Figure S8 ^{1}H NMR of the reaction mixture of heating 20min.

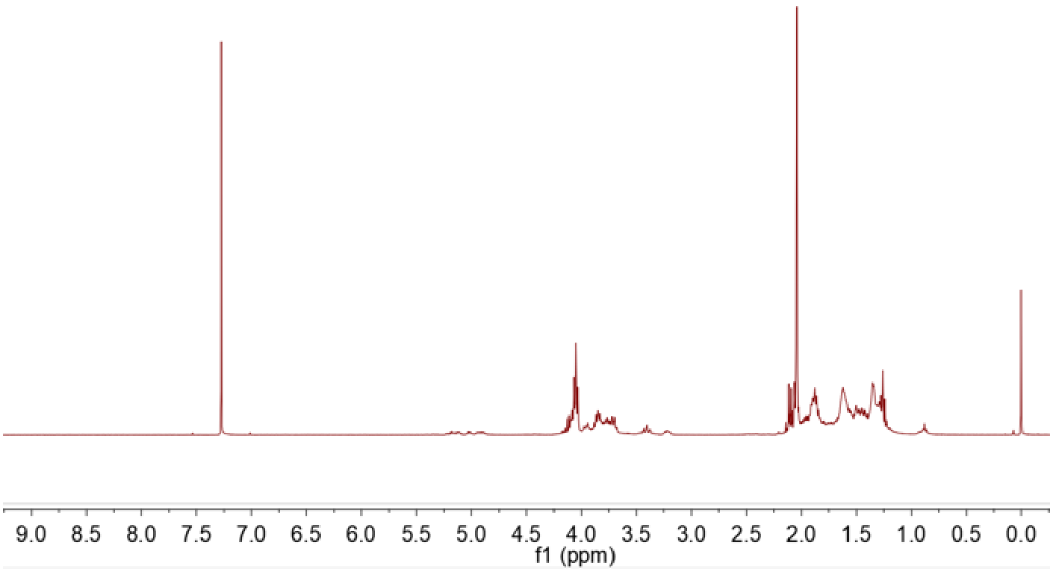


Figure S9 ^{1}H NMR of the reaction mixture of heating 30min.

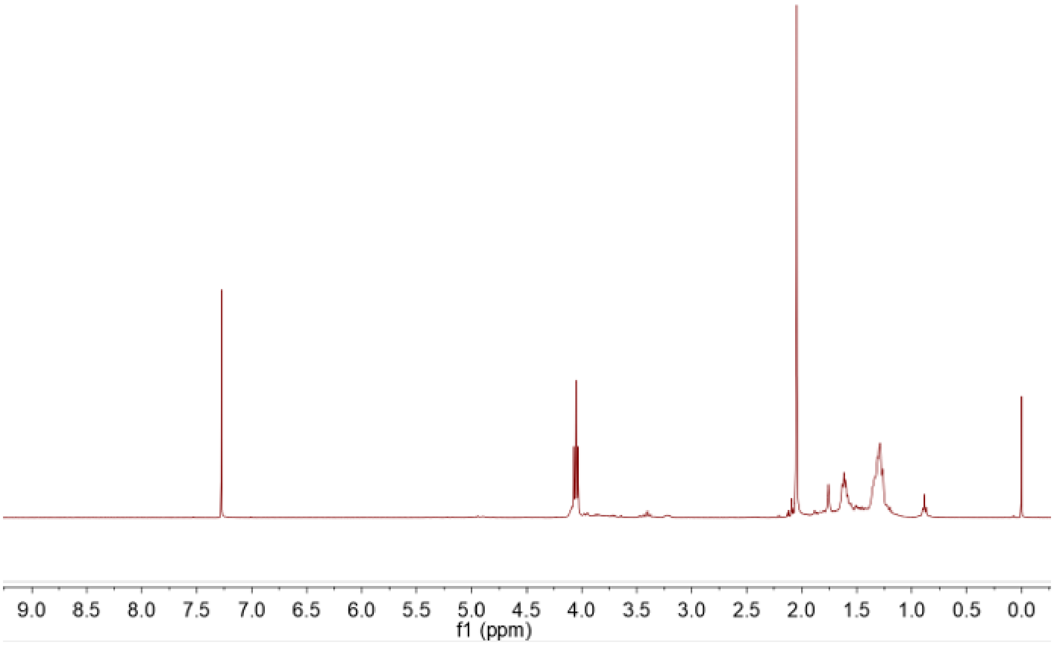


Figure S10 ^{1}H NMR of the reaction mixture of heating 30min and maintained 30min.

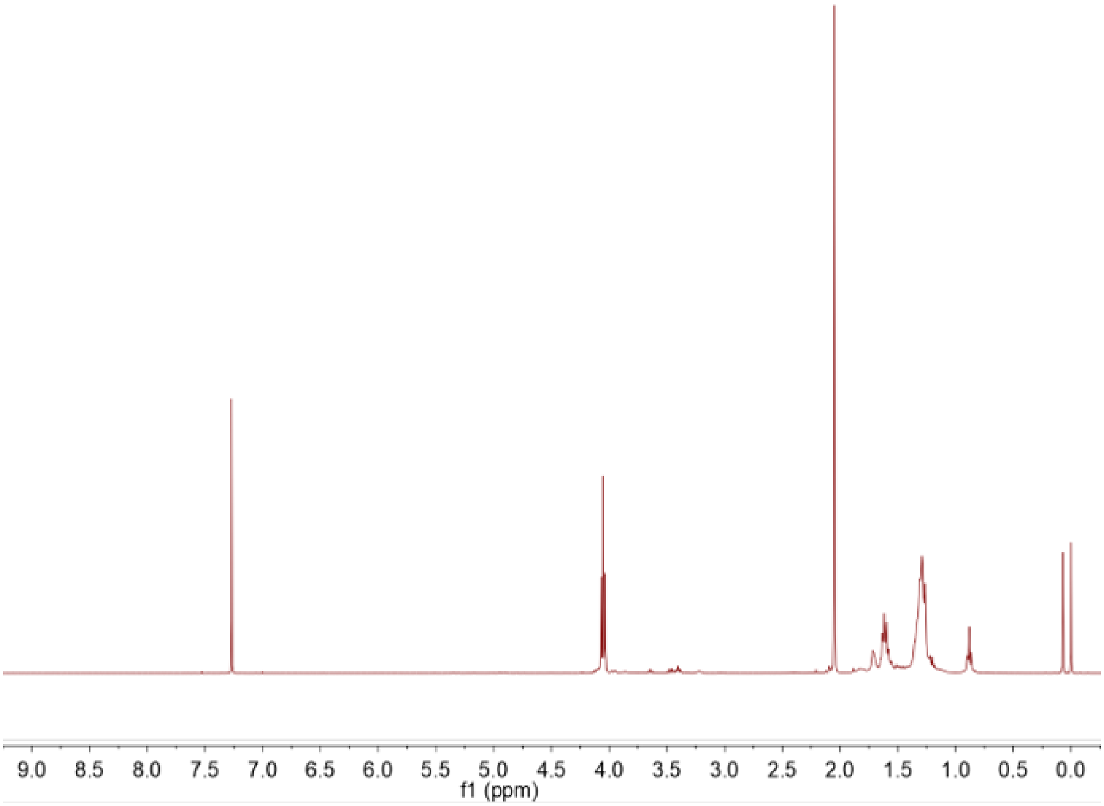


Figure S11 ^{1}H NMR of the reaction mixture of heating 30min and maintained 120min.

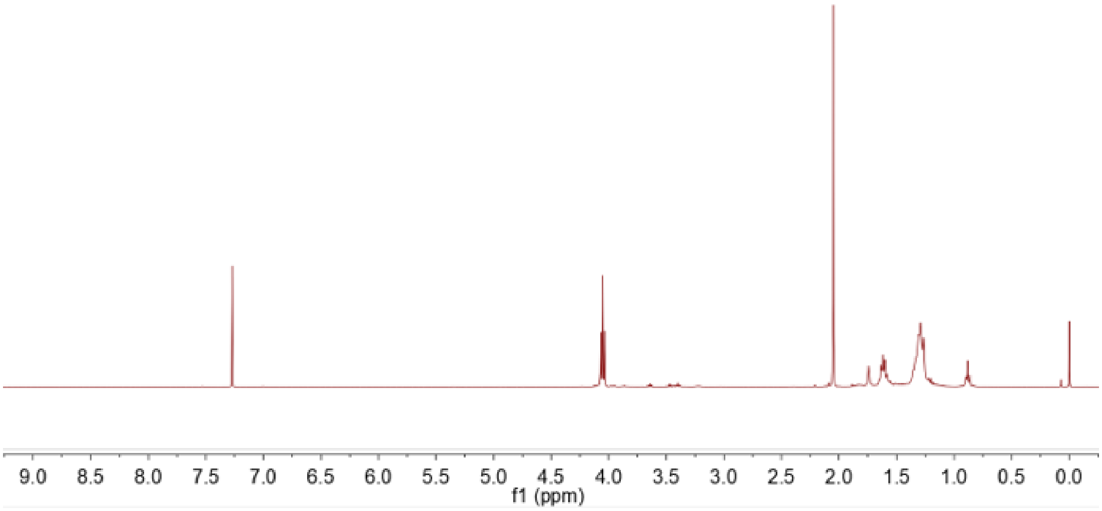


Figure S12 ^{1}H NMR of the reaction mixture of heating 30min and maintained 360min.

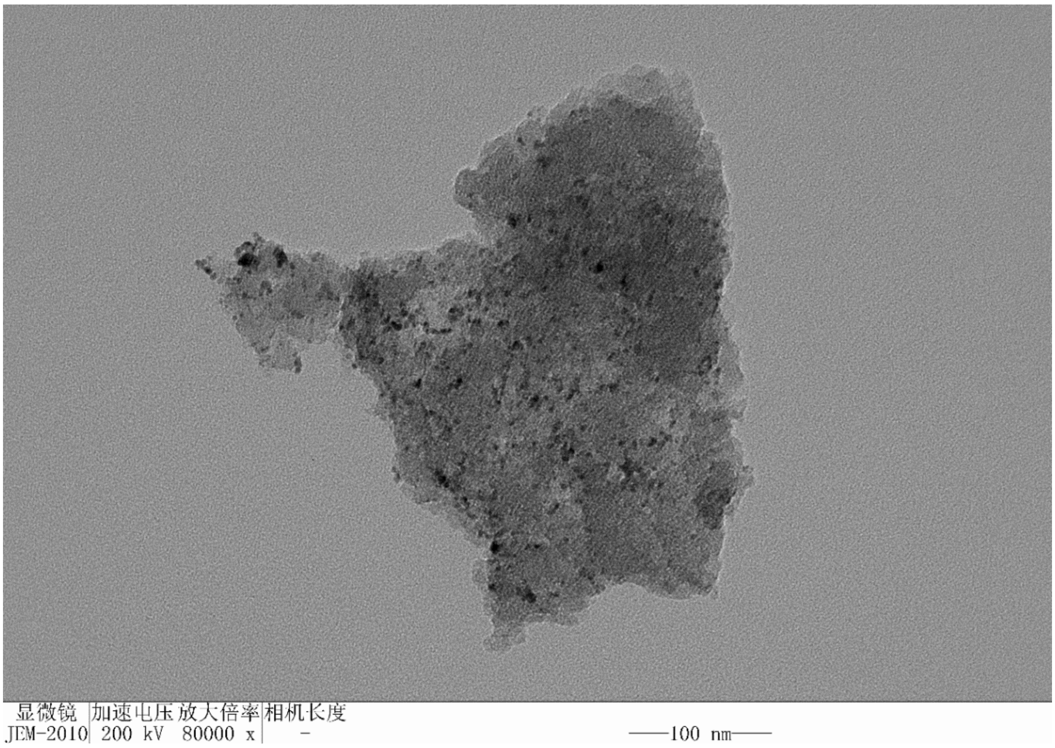


Figure S13. The TEM of fresh Pd/C catalyst

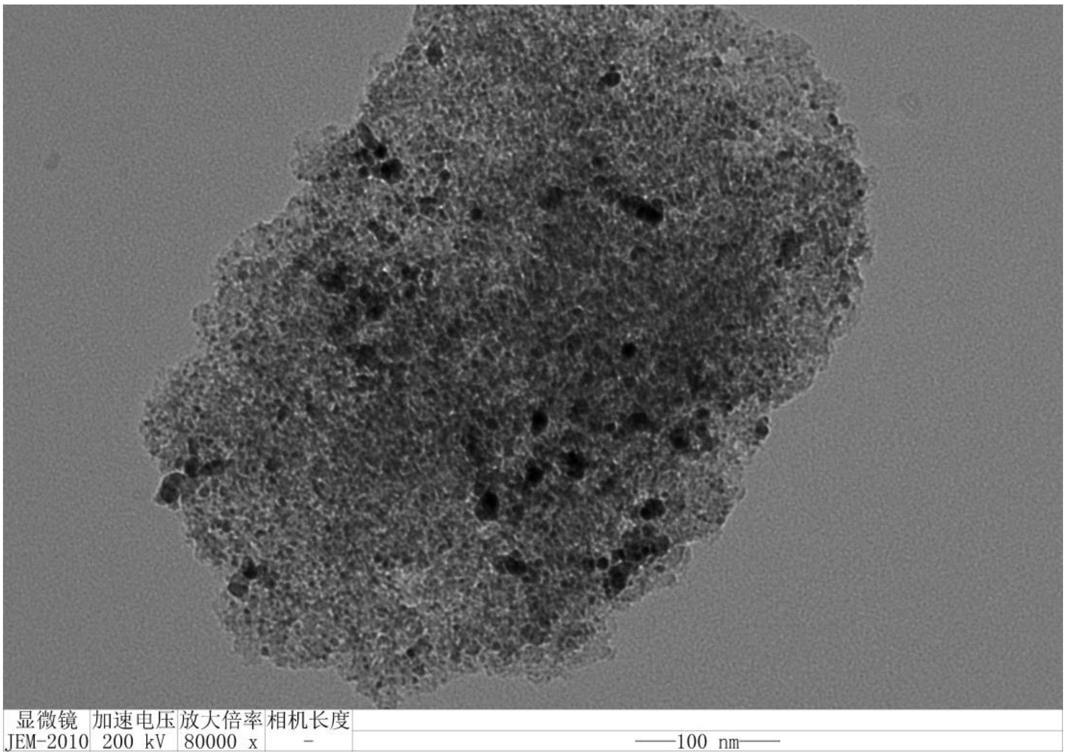
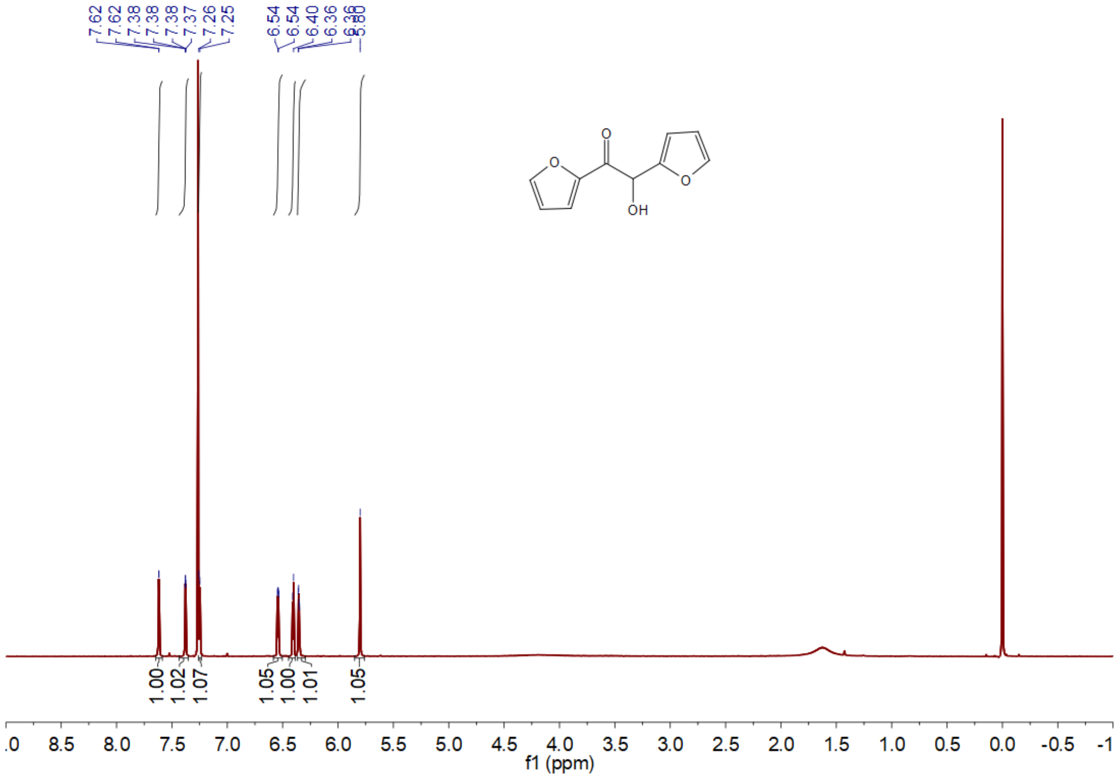
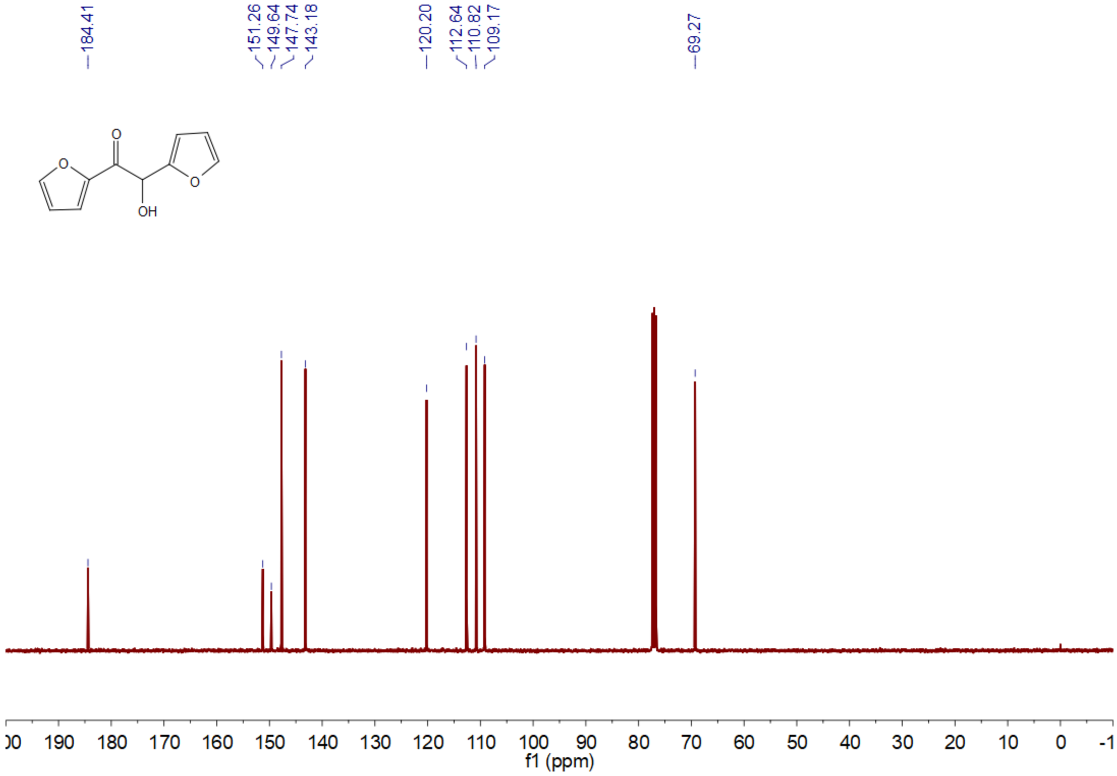
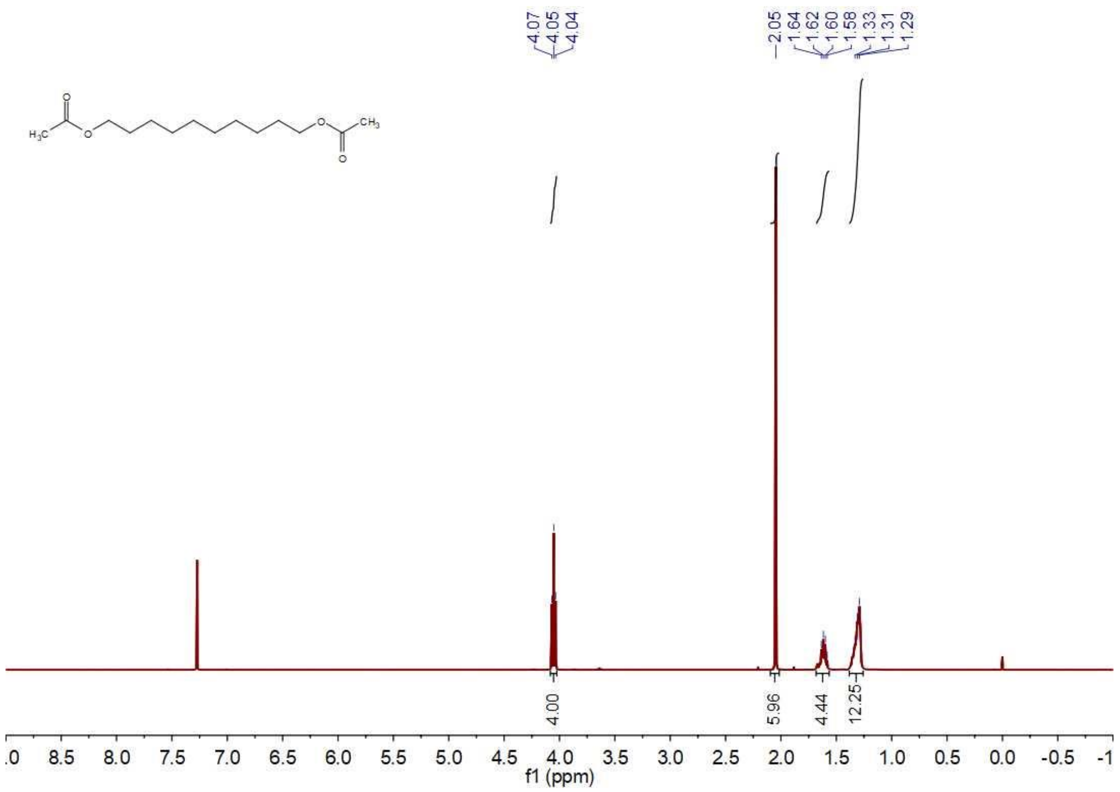


Figure S14. The TEM of Pd/C catalyst after 5 cycles

VIII. NMR spectrum data



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4.04
2.05
1.64
1.62
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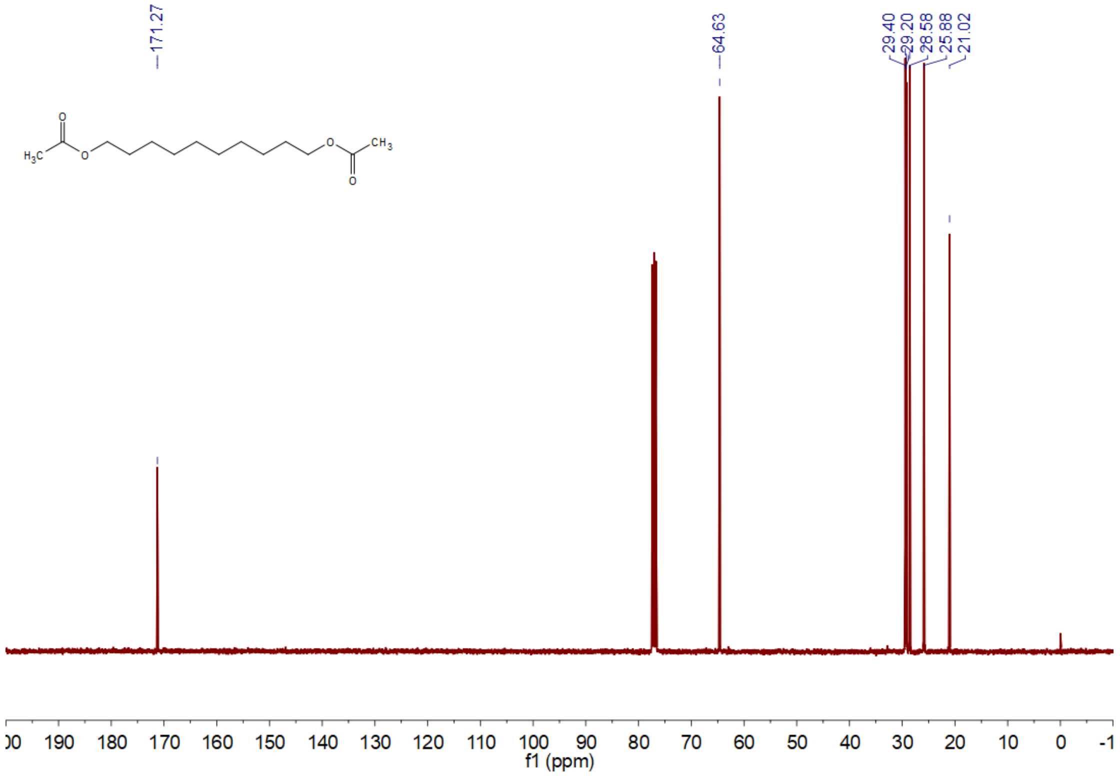
1.58
1.33
1.31
1.29
H3C
O
O
O
O
CH3
4.00
5.96
4.44
12.25
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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64.63
29.40
29.20
28.58
25.88
21.02
H3C
O
O
O
O
CH3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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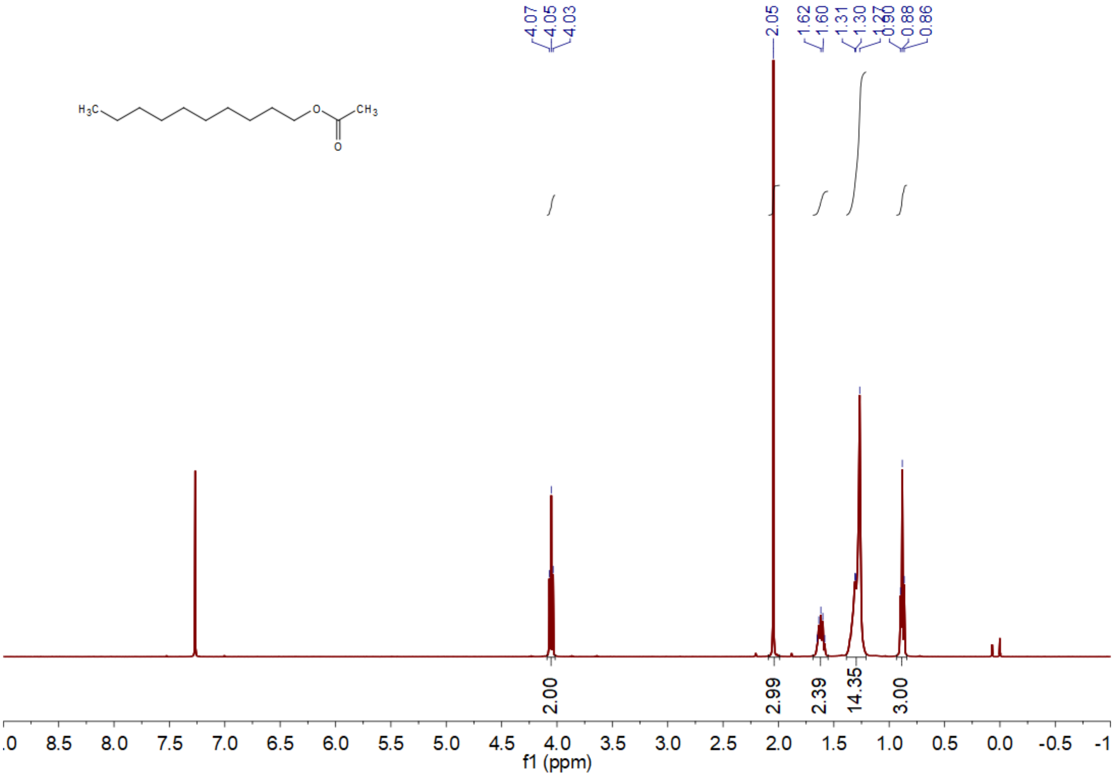
f1 (ppm)


H3C
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CH3
O
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4.05
4.03
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1.62
1.60
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1.30
1.27
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0.88
0.86
2.00
2.99
2.39
14.35
3.00
8.5
8.0
7.5
7.0
6.5
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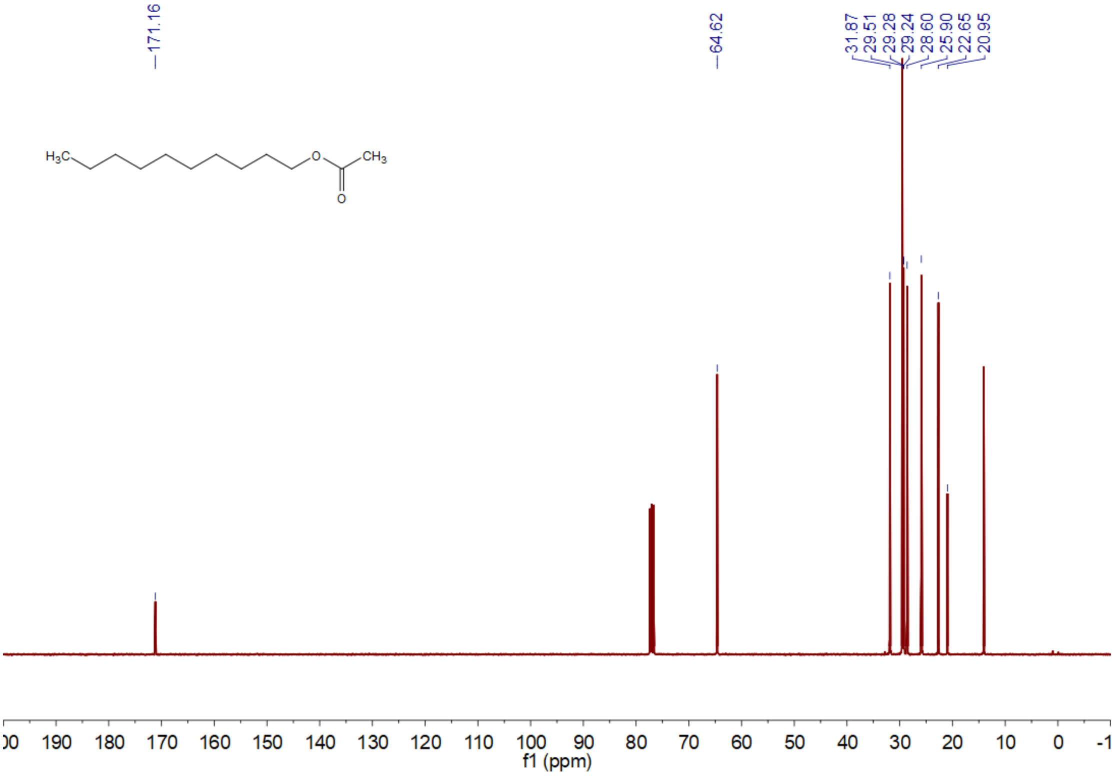
f1 (ppm)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64.62
31.87
29.51
29.28
29.24
28.60
25.90
22.65
20.95
H3C
O
CH3
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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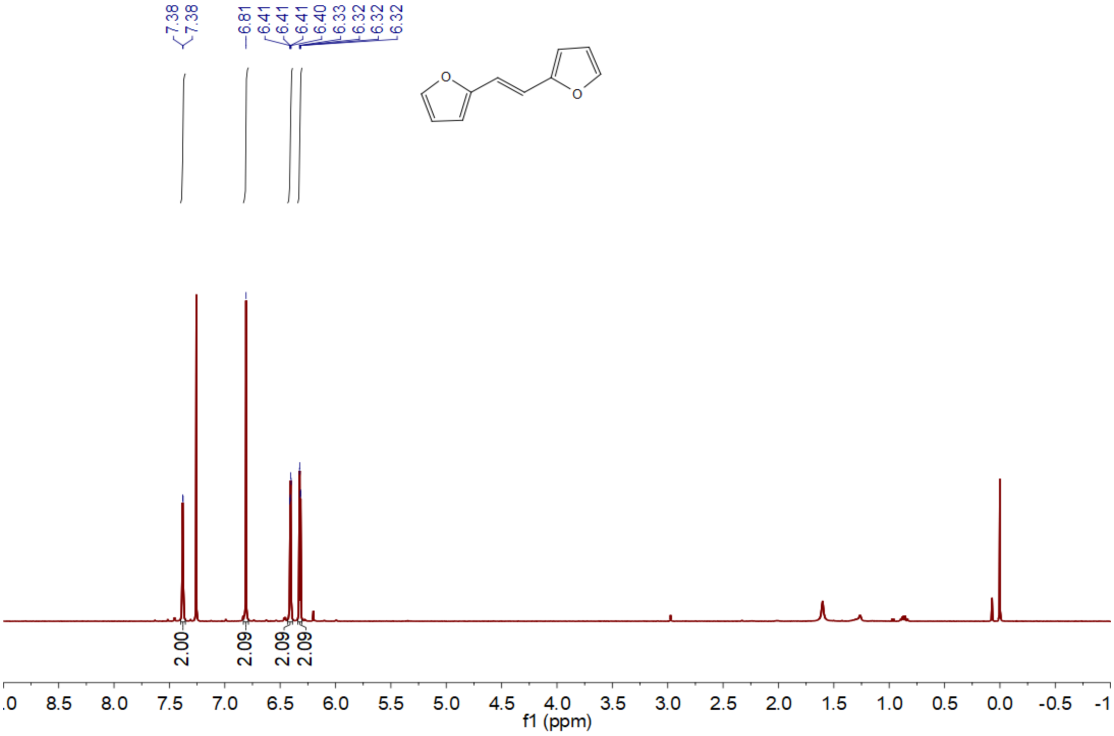
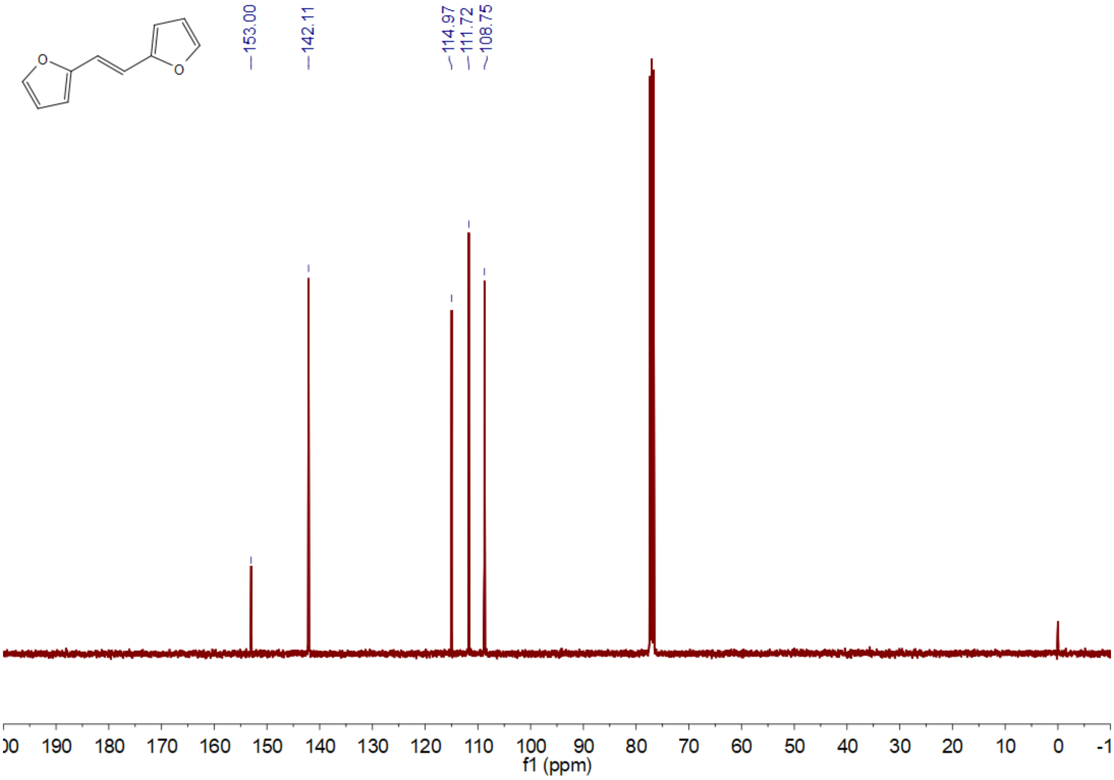
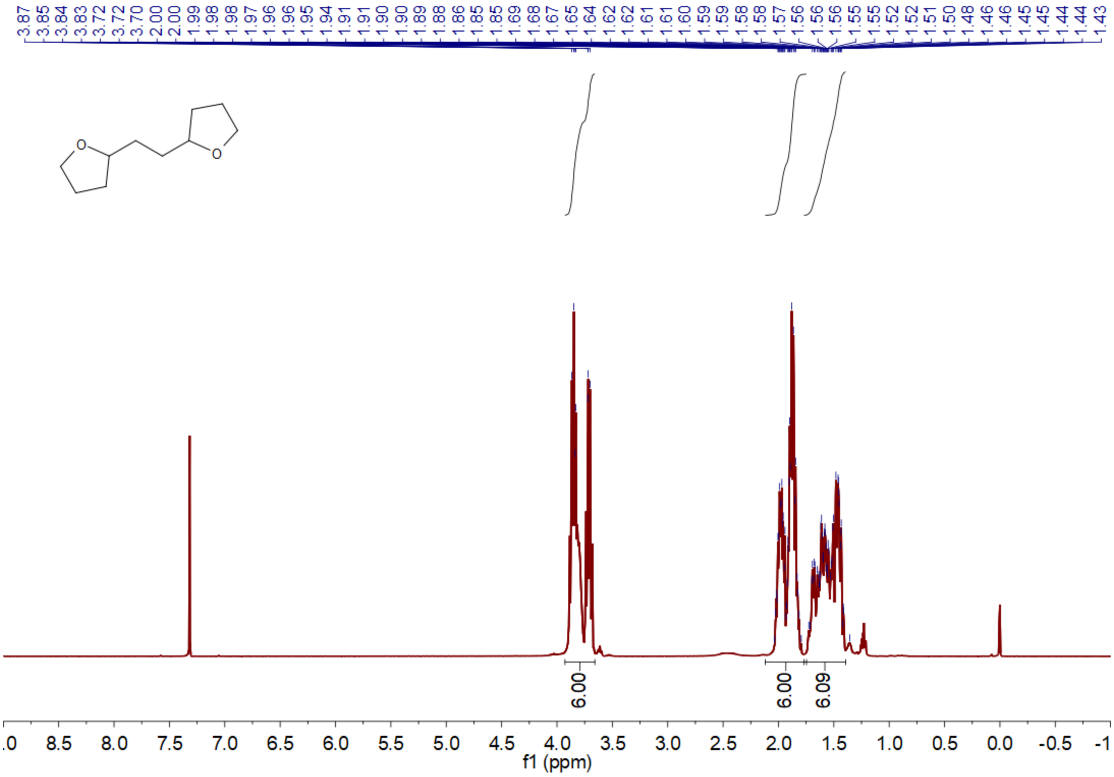
0
f1 (ppm)


7.38
7.38
6.81
6.41
6.41
6.41
6.40
6.33
6.32
6.32
6.32
6.32
O
O
2.00
2.09
2.09
2.09
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


O
O
153.00
142.11
114.97
111.72
108.75
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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3.85
3.84
3.83
3.72
3.72
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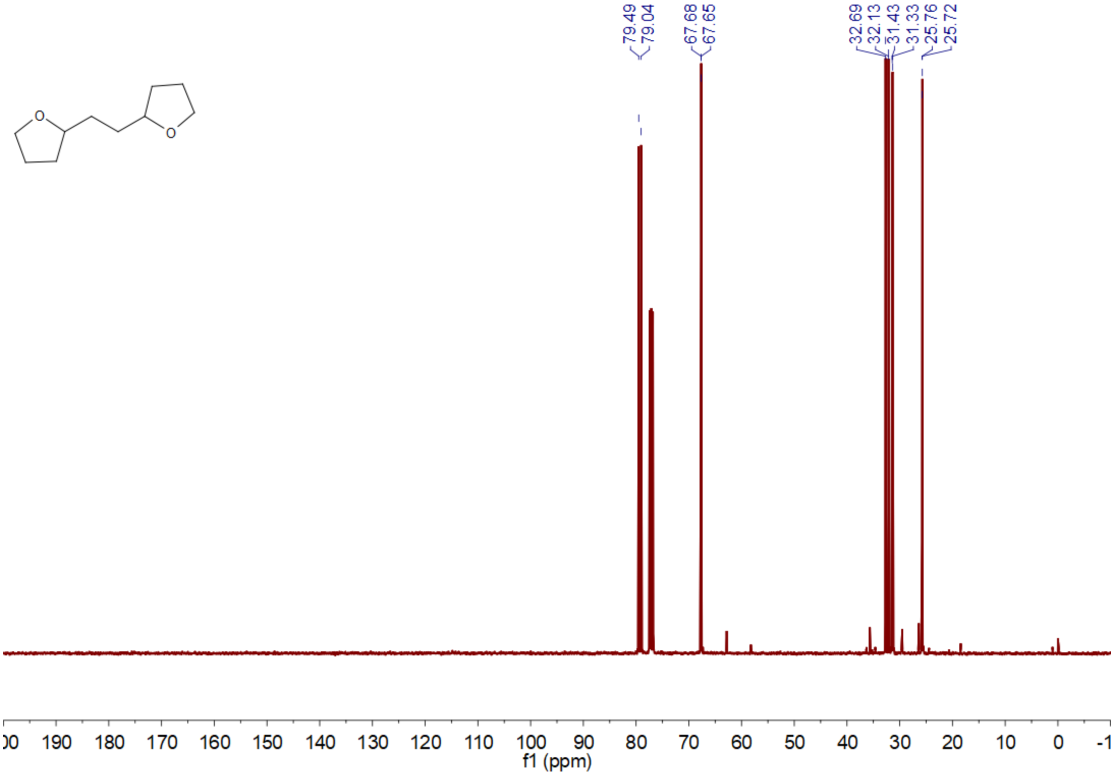
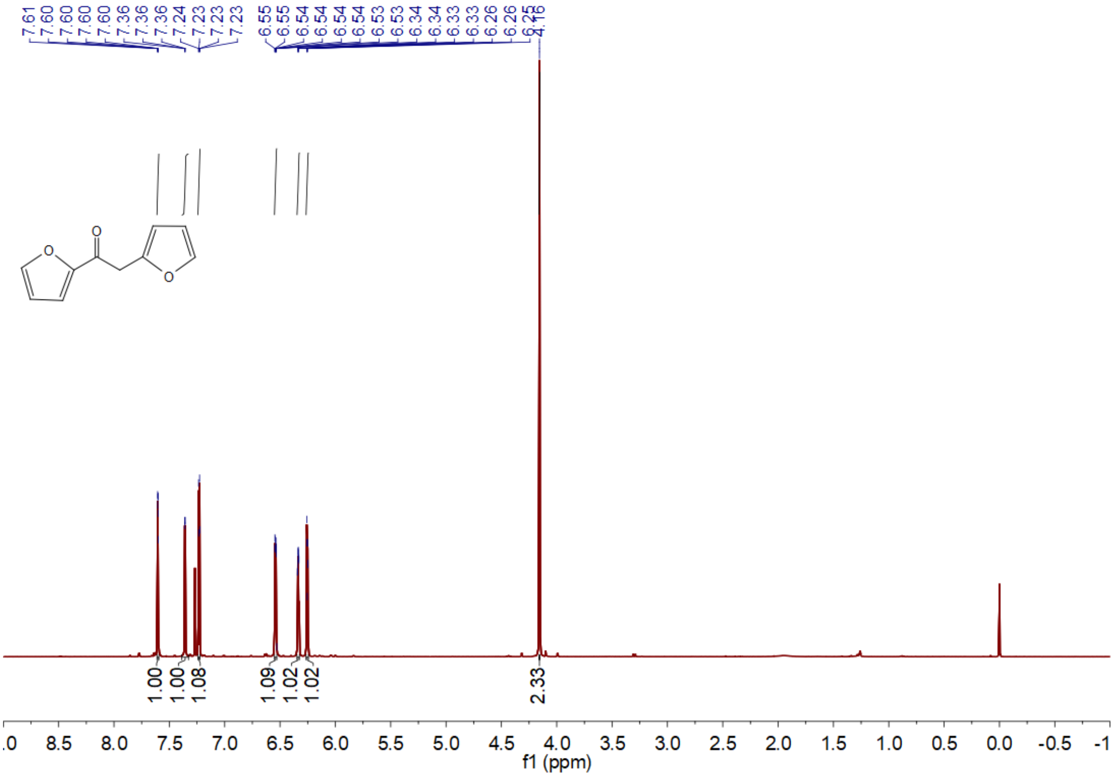
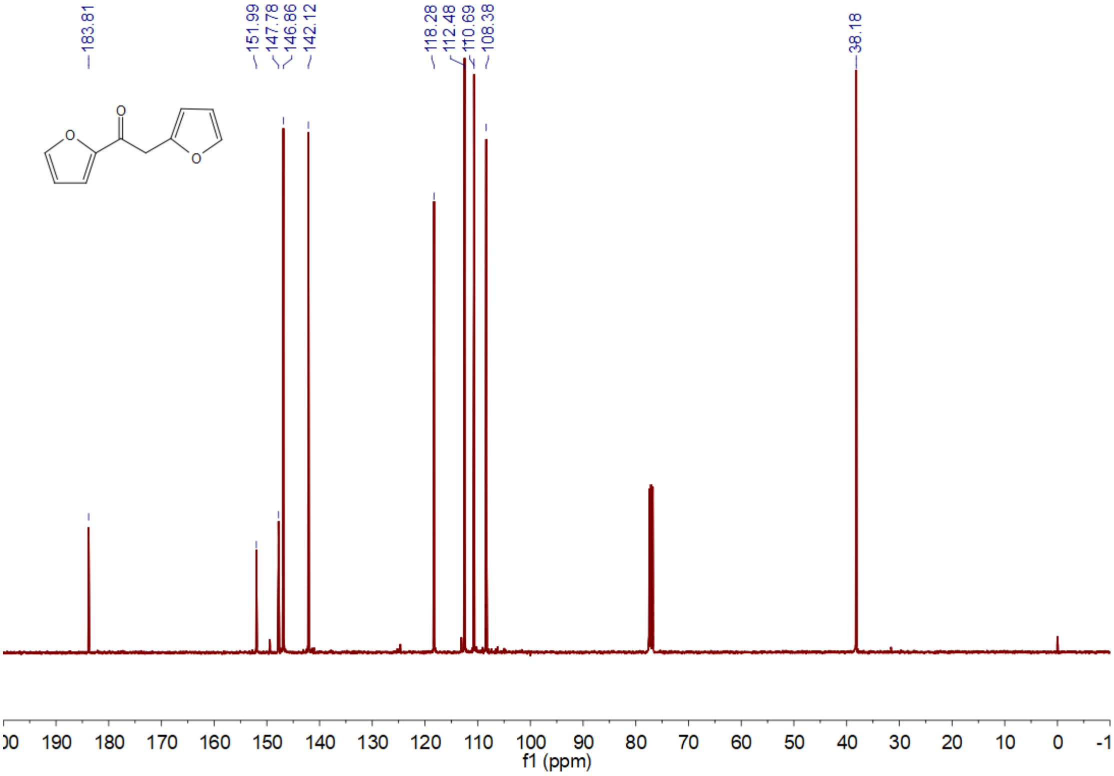
2.00
2.00
1.99
1.98
1.98
1.97
1.96
1.96
1.95
1.94
1.91
1.91
1.90
1.90
1.89
1.88
1.86
1.85
1.85
1.69
1.68
1.67
1.65
1.64
1.62
1.62
1.61
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.56
1.56
1.56
1.55
1.55
1.52
1.52
1.51
1.50
1.48
1.46
1.46
1.45
1.45
1.44
1.44
1.43
O
O
6.00
6.00
6.09
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


79.49
79.04
67.68
67.65
32.69
32.13
31.43
31.33
25.76
25.72
O
O
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.61
7.60
7.60
7.60
7.60
7.36
7.36
7.36
7.24
7.23
7.23
7.23
6.55
6.55
6.54
6.54
6.54
6.54
6.53
6.53
6.34
6.34
6.33
6.33
6.26
6.26
6.25
4.16
O
O
O
1.00
1.00
1.08
1.09
1.02
1.02
2.33
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


183.81
151.99
147.78
146.86
142.12
118.28
112.48
110.69
108.38
38.18
O
O
O
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

VIIII. references

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