Supporting Information

Hydrodeoxygenation of lignocellulose-derived oxygenates to diesel or jet fuel range alkanes under mild conditions

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Ⅰ. General information

The stainless steel autoclave was purchased from Anhui Kemi Machinery Technology Co., Ltd. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Multiplicities are described using the following abbreviations: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. NMR spectra were analysed with MestReNova software.

Ⅱ. Experiment and characterization

2.1 The HDO reaction was carried out with different catalyst/substrate ratios

Table S1 HDO of 1A with different catalyst/substrate mass ratios

Entry	Catalyst/1A ratios	Alkanes yield/%			
		C8	C9	C10	Total
1	2/1	18.6	43.8	29.5	91.9
2	1/1	12.6	27.8	20.3	60.8
3	1/2	1.1	2.6	3.8	7.7
4	1/5	0.1	0.9	0.3	1.3

Reaction conditions: 100 mg of 1A, 10 mL cyclohexane, 180 °C, 4 MPa H_2, 10 h and 600 rpm. The mass of Ru/HAP and HZSM-5 (50) are equal and the conversion are 100% in all cases. The total alkanes yield decreased with the decreasing catalyst loadings. When the catalyst/1A ratios ≤ 1/2, a small amount of alkanes were produced, and the product mainly appeared as oxygen-containing intermediates. For efficiently converting 1A to alkanes, a certain amount of catalysts is necessary.

2.2 HDO of lauraldehyde and methyl laurate over Ru/HAP+HZSM-5 catalyst

Table S2 HDO of two model compounds.

Entry	Substrates	Conv./%	Yield/%	
			n-$C_{11}H_{24}$	n-$C_{12}H_{26}$
1	Lauraldehyde	100.0	90.4	7.2
2	Methyl laurate	94.4	69.9	13.1

Reaction conditions: 100 mg of substrates, 100 mg of Ru/HAP, 100 mg of HZSM-5 (50), 10 mL cyclohexane, 160 °C, 4 MPa H_2, 4 h and 600 rpm. Undecane was produced as the main product in both cases, which indicates that the Ru/HAP+HZSM-5 catalyst has prominent decarbonylation and decarboxylation activities.

2.3 XPS full spectra

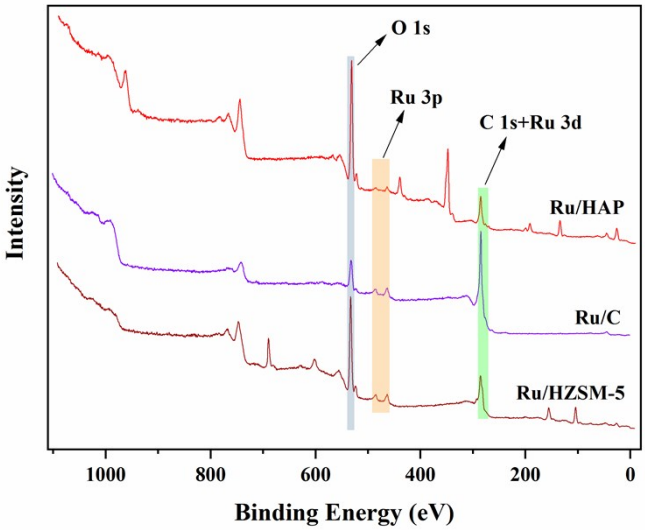


Figure S1 XPS full spectra of Ru-based catalysts.

2.4 Catalyst stability and recyclability

Table S3 Recycle of the catalyst.

Entry	Alkanes yield/%			
	C8	C9	C10	Total
*a*1	12.6	39.3	31.2	83.1
*a*2	0.4	0.8	0.3	1.5
*b*1	11.8	38.7	31.4	81.9
*b*2	10.5	36.9	27.3	74.7

Reaction conditions: 100 mg of 1A, 100 mg of Ru/HAP, 100 mg of HZSM-5 (50), 10 mL cyclohexane, 160 °C, 4 MPa H_2, 10 h and 600 rpm. *a*1, *a*2: The first cycling test, in which no additional catalyst was added; *b*1, *b*2: The second cycling test, in which 100 mg fresh HZSM-5 (50) was added to the used Ru/HAP+HZSM-5 (50) catalyst and tested for the second run. The conversion are 100% in all cases.

ICP-AES analysis: The reaction solution of *a*2 was extracted by deionized water, the extract liquor was detected by ICP-AES. The leaching of Ru was just 0.007% relative to original Ru loading.

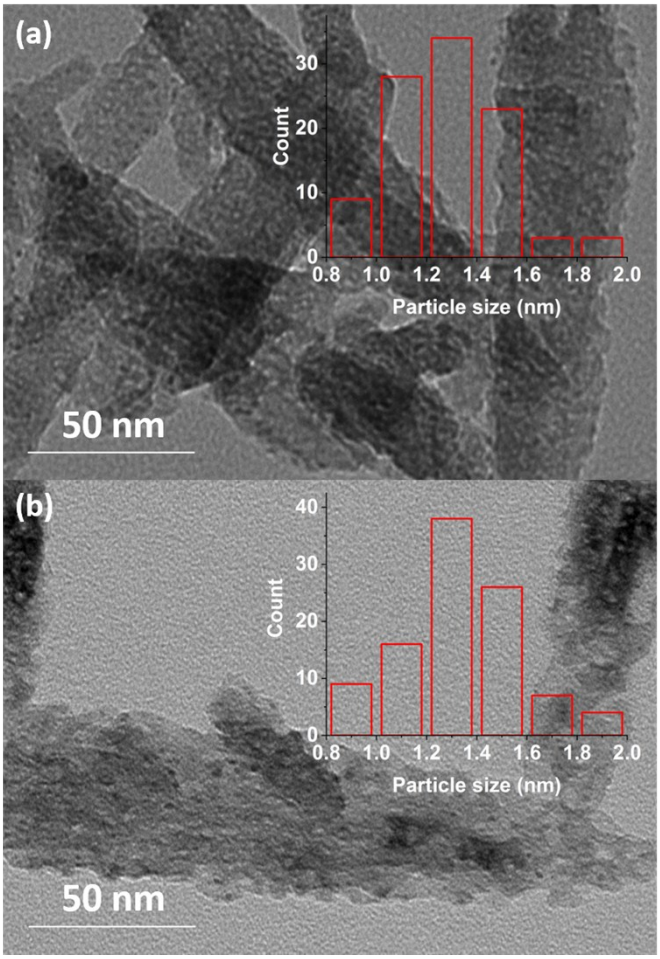


Figure S2 TEM images of Ru/HAP+HZSM-5 (50) catalyst (a) before and (b) after use.

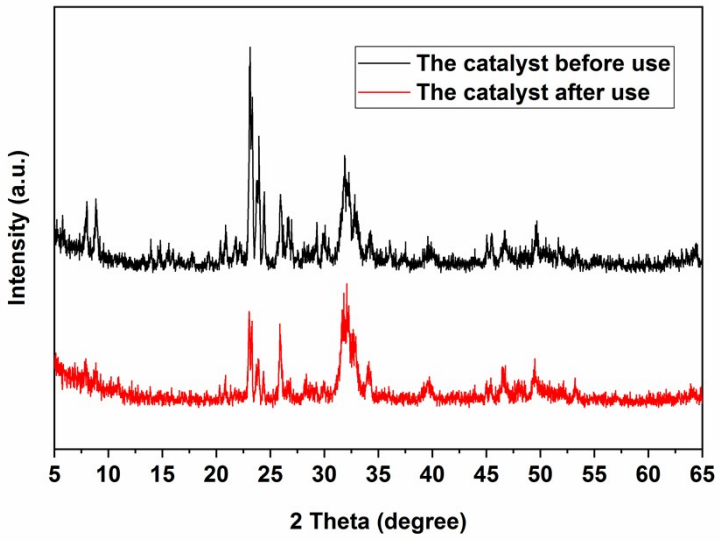


Figure S3 Powder XRD patterns of Ru/HAP+HZSM-5 (50) catalyst before and after use.

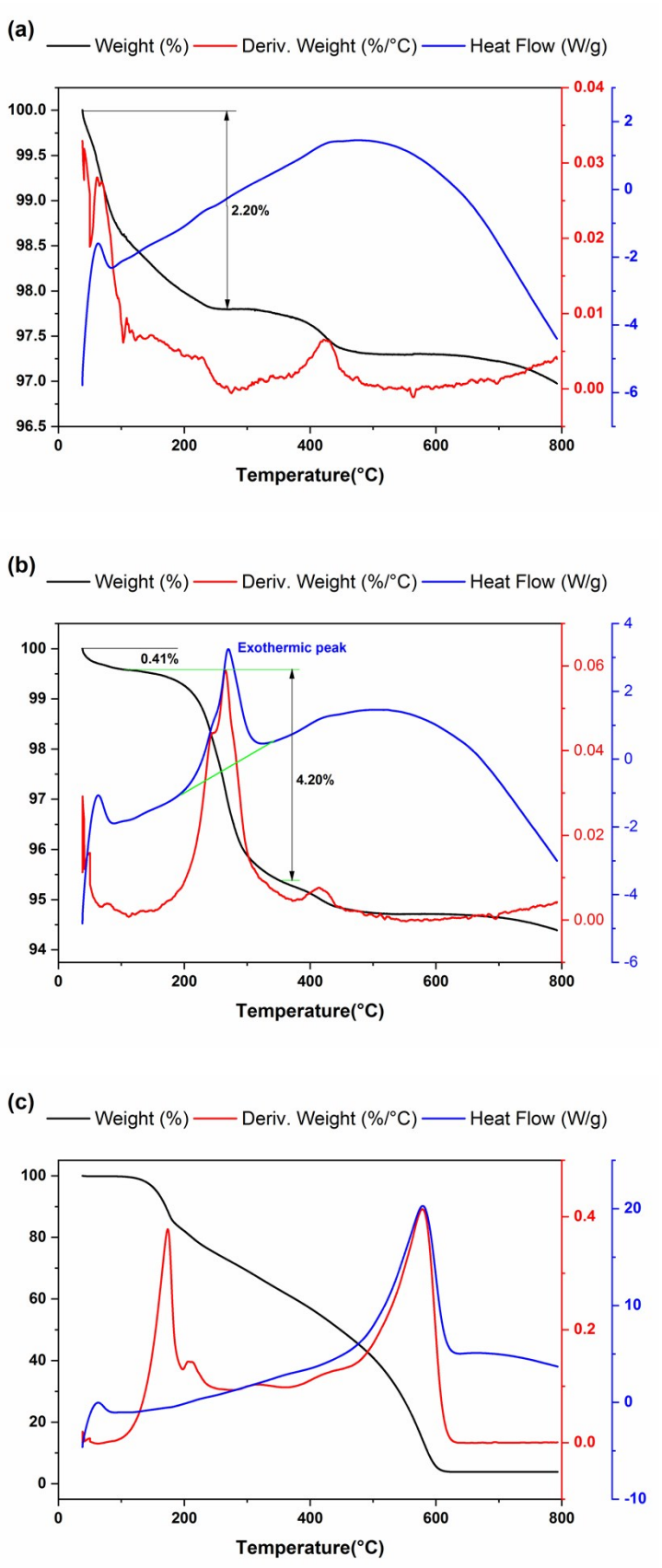
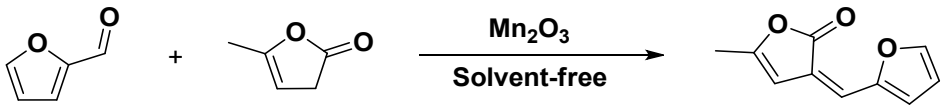


Figure S4 DSC-TGA of (a) Ru/HAP+HZSM-5 (50) catalyst before use, (b) Ru/HAP+HZSM-5 (50) catalyst after use and (c) 1A.

Ⅲ. Synthesis of substrates

3.1 Synthesis of 3-(furan-2-ylmethylene)-5-methylfuran-2(3H)-one (1A)

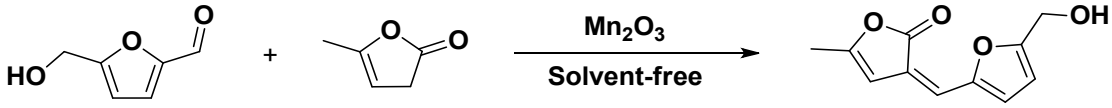


The substrate was prepared by solvent-free aldol condensation of furfural and α-angelica lactone according to the literature.[1] Furfural (10 mmol, 0.96 g), α-angelica lactone (10 mmol, 0.98 g), and Mn_2O_3 (1 mmol, 1.58 g) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 80 °C for 4 h. The reaction products were dissolved with hot methanol. Then, Mn_2O_3 catalyst was separated by filtration. Finally, an orange red crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 1.8 Hz, 1H), 6.97 (s, 1H), 6.72 (d, J = 3.5 Hz, 1H), 6.57 - 6.45 (m, 2H), 2.19 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.00, 156.80, 151.93, 145.73, 122.52, 118.67, 117.47, 112.86, 103.57, 14.74.

3.2 Synthesis of 3-((5-(hydroxymethyl)furan-2-yl)methylene)-5-methylfuran-2(3H)-one (2A)

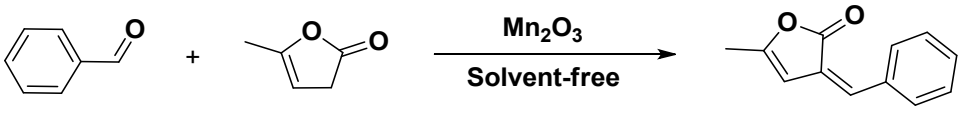


The substrate was prepared by solvent-free aldol condensation of 5-hydroxymethylfurfural and α-angelica lactone according to the literature.[1] 5-hydroxymethylfurfural (10 mmol, 1.26 g), α-angelica lactone (10 mmol, 0.98 g), and Mn_2O_3 (1 mmol, 1.58 g) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 80 °C for 6 h. The reaction products were dissolved with hot methanol. Then, Mn_2O_3 catalyst was separated by filtration. Finally, a yellow crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.93 (s, 1H), 6.67 (d, J = 3.5 Hz, 1H), 6.51 - 6.41 (m, 2H), 4.70 (s, 2H), 2.19 (t, J = 1.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.24, 157.91, 156.70, 151.67, 122.20, 118.71, 118.63, 118.61, 110.77, 103.76, 57.63, 14.67.

3.3 Synthesis of 3-benzylidene-5-methyl-3H-furan-2-one (3A)



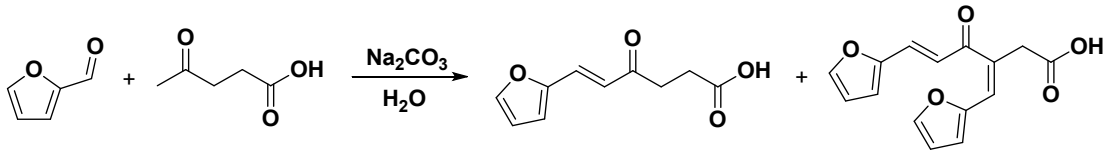
The substrate was prepared by solvent-free aldol condensation of benzaldehyde and α-angelica lactone according to the literature.[1] Benzaldehyde (10 mmol, 1.06 g), α-angelica lactone (10 mmol, 0.98 g), and Mn_2O_3 (1 mmol, 1.58 g) were added to a 25mL round-bottom flask equipped with a

reflux condenser and a magnetic stirrer. The reaction was carried out at 80 °C for 6 h. The reaction products were dissolved with hot methanol. Then, Mn_2O_3 catalyst was separated by filtration. Finally, a light yellow needle crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 - 7.51 (m, 2H), 7.49 - 7.34 (m, 3H), 7.30 (s, 1H), 6.29 (t, *J* = 1.3 Hz, 1H), 2.21 (d, *J* = 1.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.88, 158.26, 135.07, 133.96, 129.93, 129.88, 128.98, 125.40, 101.99, 14.83.

3.4 Synthesis of δ-Furfurylidenelevulinic acid (4A)

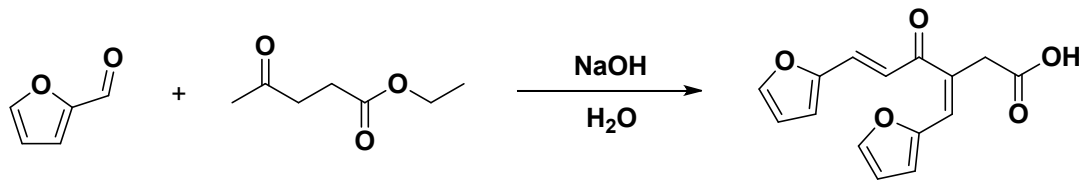


The substrate was prepared by water phase aldol condensation of furfural and levulinic acid according to the literature.[2] Levulinic acid (155.0 mmol, 18.0 g) and 100 mL deionized water was added to a 500 mL three-necked flask equipped with a reflux condenser and a constant pressure dropping funnel. Na_2CO_3 (226.0 mmol, 24.0 g) was added in portions at room temperature accompanied with CO_2 release. The reaction temperature was then heated to reflux. A solution of 7.7 mL (93.0 mmol) of furfural and 16 mL of methanol were added dropwise under vigorous stirring more than 1 h. After that, the reaction was stopped until substantially no furfural was detected by TLC (ethyl acetate: petroleum ether=1:3). Slowly pour the reaction solution into cold dilute HCl solution after rapid cooling. The insoluble solid was separated by filtration. (1) The target product (δ-Furfurylidenelevulinic acid) was obtained as a light yellow solid by recrystallization from hot water and dried at 60 °C. (2) The obtained insoluble solid was the undesired by-product (i.e., the aldol condensation product of one levulinic acid molecule with two furfural molecules). A new preparation method with high yield was used to obtain the later product. And the related experiments were listed below.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 15.8 Hz, 1H), 6.72 - 6.62 (m, 2H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.96 (t, *J* = 6.6 Hz, 2H), 2.73 (t, *J* = 6.6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 197.44, 178.24, 150.89, 145.12, 129.18, 122.73, 116.12, 112.60, 35.44, 27.98.

3.5 Synthesis of 3-furfurylidene-6-[2]furyl-4-oxo-hex-5-enoic acid (5A)



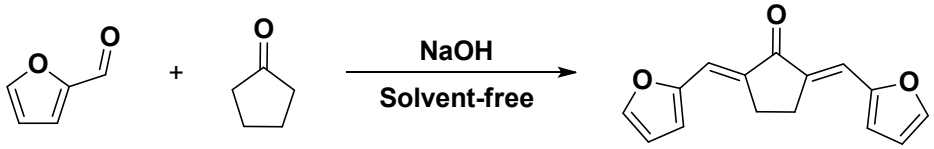
The substrate was prepared by water phase aldol condensation of furfural and ethyl levulinate according to the literature.[3] NaOH (0.06 mol, 2.40 g) was dissolved in 50 mL deionized water in a 150 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. Furfural (0.06 mol, 5.76 g) was then added. After 30 min, Ethyl levulinate (0.03 mol, 4.33 g) was introduced

dropwise through a peristaltic pump. The reaction was carried out at 50 °C for 50 min. After reaction, the reactor was cooled to ambient temperature. Aqueous HCl solution was used to adjust the reaction solution until the pH = 5 ~ 6. Finally, a tawny solid was obtained after filtration, washed with deionized water and dried at 40 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 12.28 (s, 1H), 7.97 (d, J = 1.7 Hz, 1H), 7.90 (d, J = 1.7 Hz, 1H), 7.78 (s, 1H), 7.49 (d, J = 15.3 Hz, 1H), 7.42 (d, J = 15.3 Hz, 1H), 7.04 (t, J = 2.9 Hz, 2H), 6.70 (ddd, J = 13.7, 3.4, 1.8 Hz, 2H), 3.75 (s, 2H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 189.39, 172.42, 151.71, 151.34, 146.97, 146.20, 131.30, 129.73, 127.89, 118.82, 118.50, 116.67, 113.45, 113.25, 33.06.

3.6 Synthesis of 2,5-bis(2-furylmethylidene)cyclopentanone (6A)

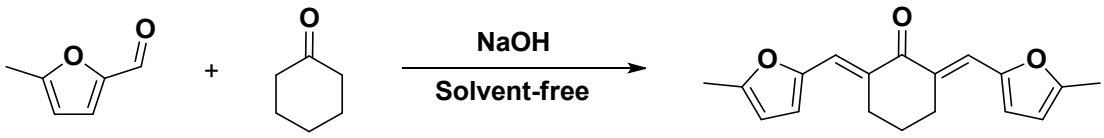


The substrate was prepared by solvent-free aldol condensation of furfural and cyclopentanone according to the literature.[4] Furfural (25 mmol, 2.40 g), cyclopentanone (10 mmol, 0.84 g), and NaOH (0.36 mmol, 14.40 mg) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 50 °C for 2 h. The reaction products were dissolved with hot methanol. The insolubles was separated by filtration. Finally, a golden yellow needle crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 1.7 Hz, 2H), 7.34 (s, 2H), 6.69 (d, J = 3.5 Hz, 2H), 6.53 (dd, J = 3.5, 1.8 Hz, 2H), 3.06 (d, J = 1.5 Hz, 4H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 195.42, 152.78, 145.04, 135.88, 119.87, 115.98, 112.63, 25.81.

3.7 Synthesis of 2,6-bis[(E)-(5-methyl-2-furyl)methylidene]cyclohexanone (7A)

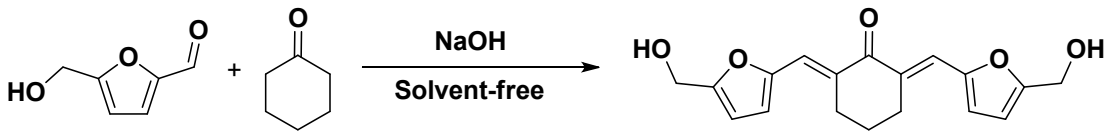


The substrate was prepared by solvent-free aldol condensation of 5-methylfurfural and cyclohexanone. 5-methylfurfural (25 mmol, 2.75 g), cyclohexanone (10 mmol, 0.98 g), and NaOH (0.36 mmol, 14.40 mg) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 70 °C for 2 h. The reaction products were dissolved with hot methanol. The insolubles was separated by filtration. Finally, a fluffy yellow crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 2H), 6.57 (d, J = 3.3 Hz, 2H), 6.12 (d, J = 3.3 Hz, 2H), 2.97 (td, J = 6.5, 1.8 Hz, 4H), 2.37 (s, 6H), 1.91 - 1.83 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 188.98, 155.10, 151.49, 131.66, 123.32, 117.68, 108.92, 28.01, 21.80, 14.05.

3.8 Synthesis of 2,6-bis((5-(hydroxymethyl)furan-2-yl)methylene)cyclohexanone (8A)

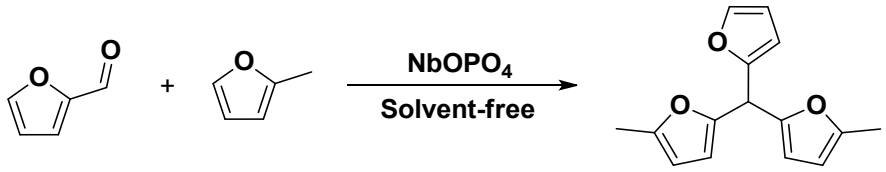


The substrate was prepared by solvent-free aldol condensation of 5-hydroxymethylfurfural and cyclohexanone according to the literature.[4] 5-hydroxymethylfurfural (25 mmol, 3.15 g), cyclohexanone (10 mmol, 0.98 g), and NaOH (0.36 mmol, 14.40 mg) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 70 °C for 2 h. The reaction products were dissolved with hot methanol. The insolubles was separated by filtration. Finally, an orange red crystal was obtained as the high purity product by recrystallization from methanol, filtration and dried at 60 °C.

^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.36 (d, J = 2.0 Hz, 2H), 6.88 (d, J = 3.5 Hz, 2H), 6.50 (d, J = 3.4 Hz, 2H), 5.40 (t, J = 5.7 Hz, 2H), 4.47 (d, J = 4.6 Hz, 4H), 2.99 - 2.88 (m, 4H), 1.81 (p, J = 6.3 Hz, 2H).

^{13}C-NMR (101 MHz, DMSO-d_6) δ = 187.67, 158.85, 151.51, 132.72, 122.92, 118.24, 110.36, 56.34, 27.96, 21.68.

3.9 Synthesis of 2-((furan-2-yl)(5-methylfuran-2-yl)methyl)-5-methylfuran (9A)



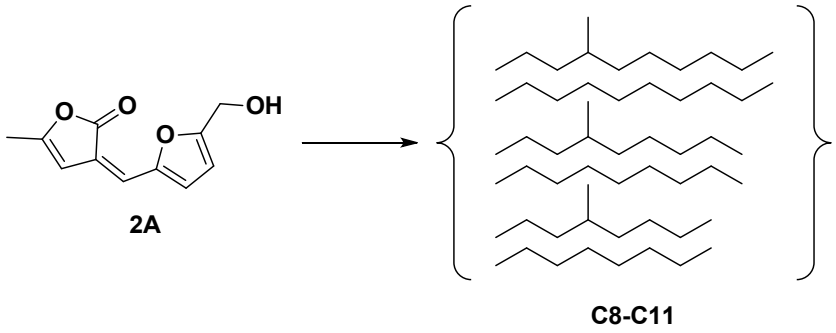
The substrate was prepared by solvent-free hydroxyalkylation/alkylation (HAA) condensation of furfural and 2-MF according to the literature.[5] Furfural (20 mmol, 1.92 g), 2-methylfuran (2-MF, 45 mmol, 3.69 g) and $NbOPO_4$ (200 mg) were added to a 25 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction was carried out at 80 °C for 5 h. Then, $NbOPO_4$ catalyst was separated by filtration and the excessive 2-MF was removed by rotary evaporation at 50 °C. In the end, a dark red liquid was obtained as the high purity HAA product.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, J = 2.7 Hz, 1H), 6.23 (t, J = 2.7 Hz, 1H), 6.03 (s, 1H), 5.89 (d, J = 3.3 Hz, 2H), 5.82 (d, J = 3.4 Hz, 2H), 5.34 (d, J = 2.9 Hz, 1H), 2.17 (d, J = 3.8 Hz, 6H).

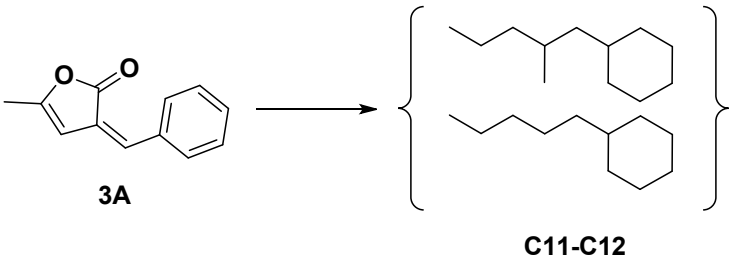
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 151.53, 150.48, 149.28, 140.79, 109.25, 106.87, 106.04, 105.20, 38.04, 12.55.

Ⅳ. Main products of HDO of lignocellulose-derived oxygenates

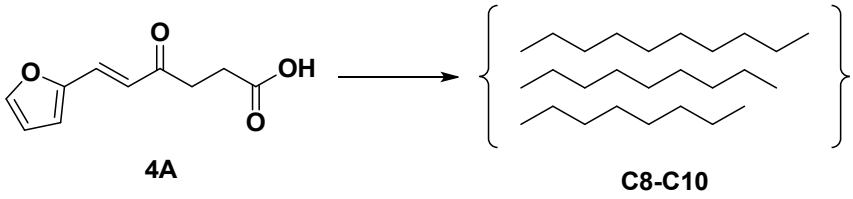
4.1 HDO of 2A



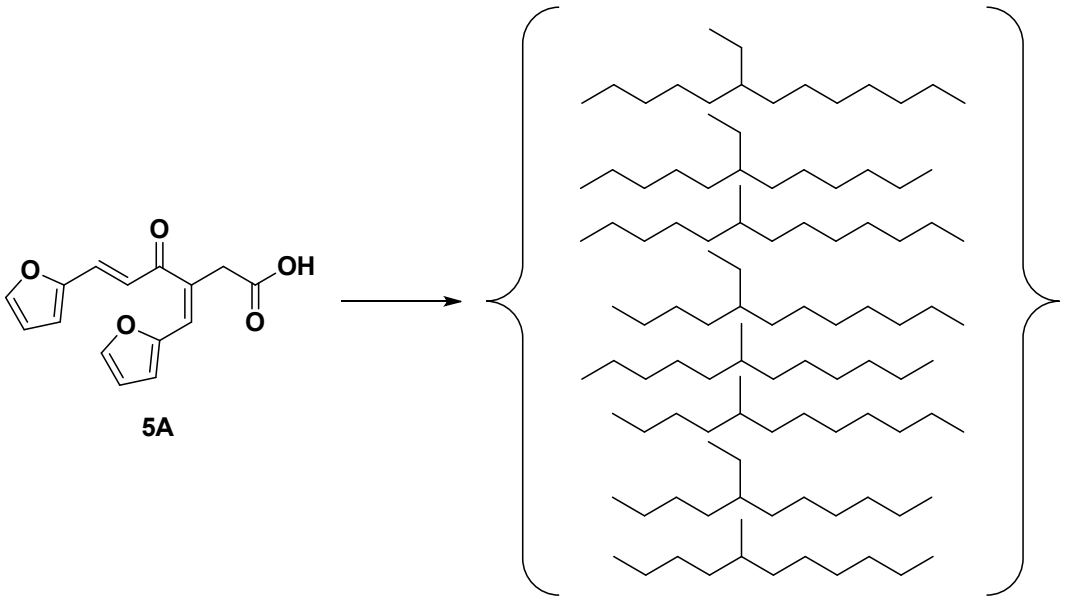
4.2 HDO of 3A



4.3 HDO of 4A



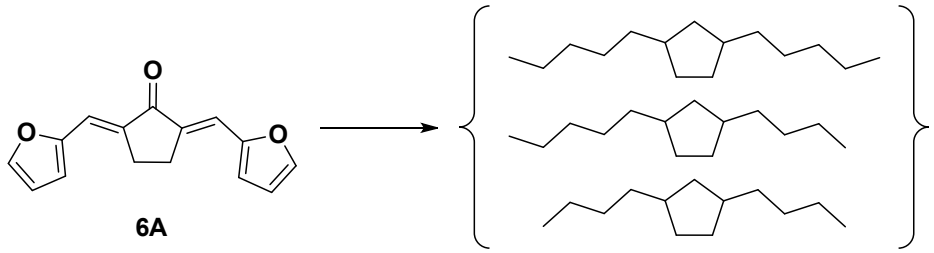
4.4 HDO of 5A



5A

C12-C15

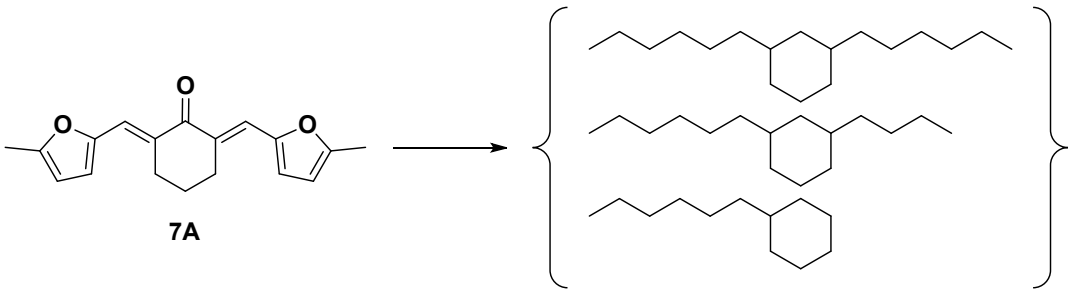
4.5 HDO of 6A



6A

C13-C15

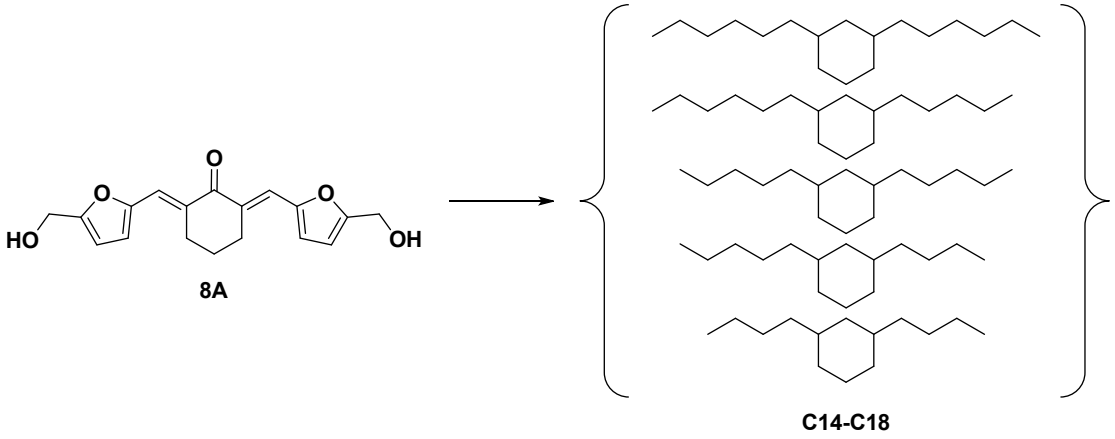
4.6 HDO of 7A



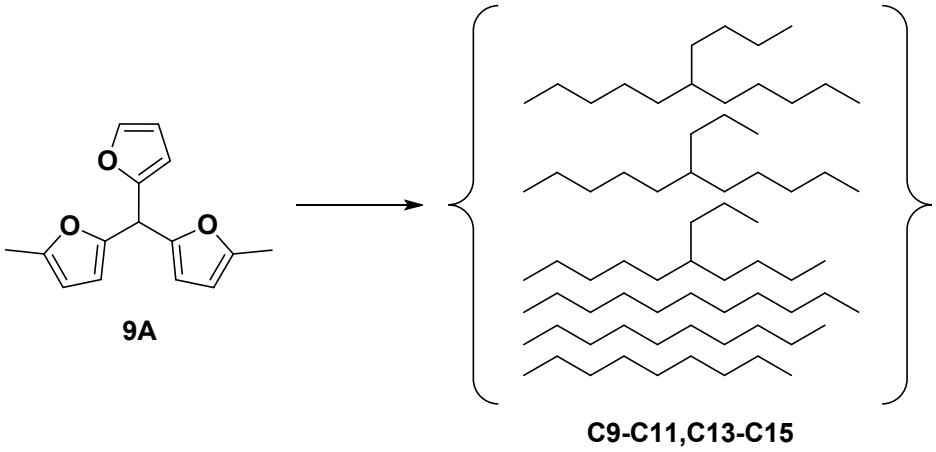
7A

C12,C16,C18

4.7 HDO of 8A



4.8 HDO of 9A



Ⅴ. Reference

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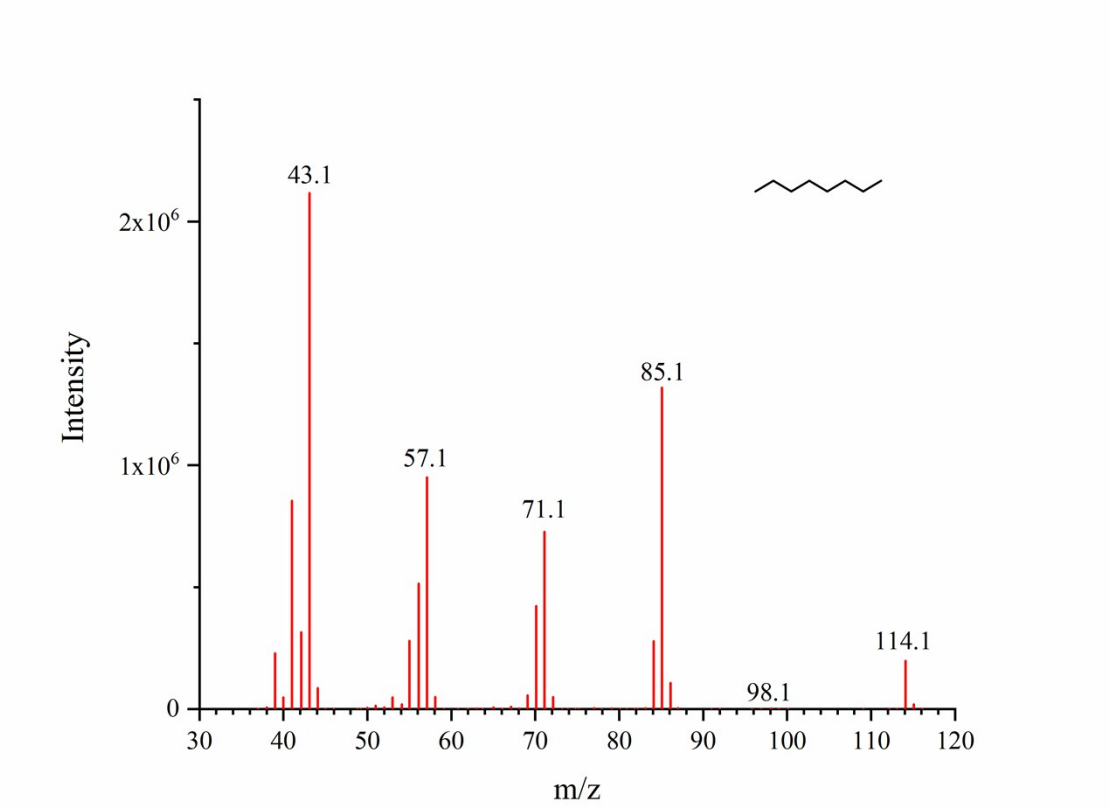
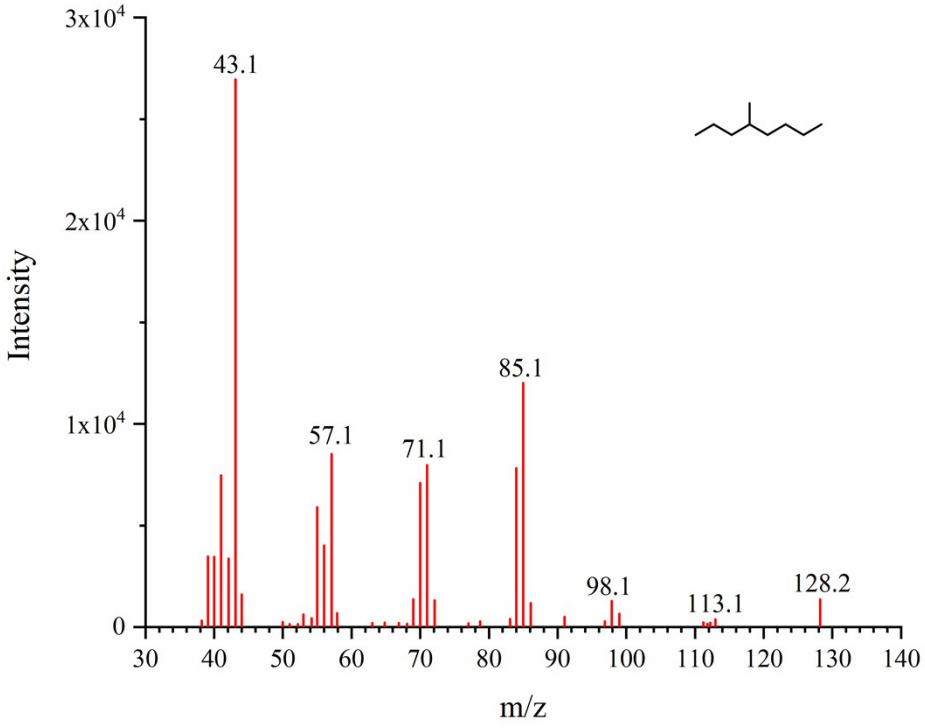
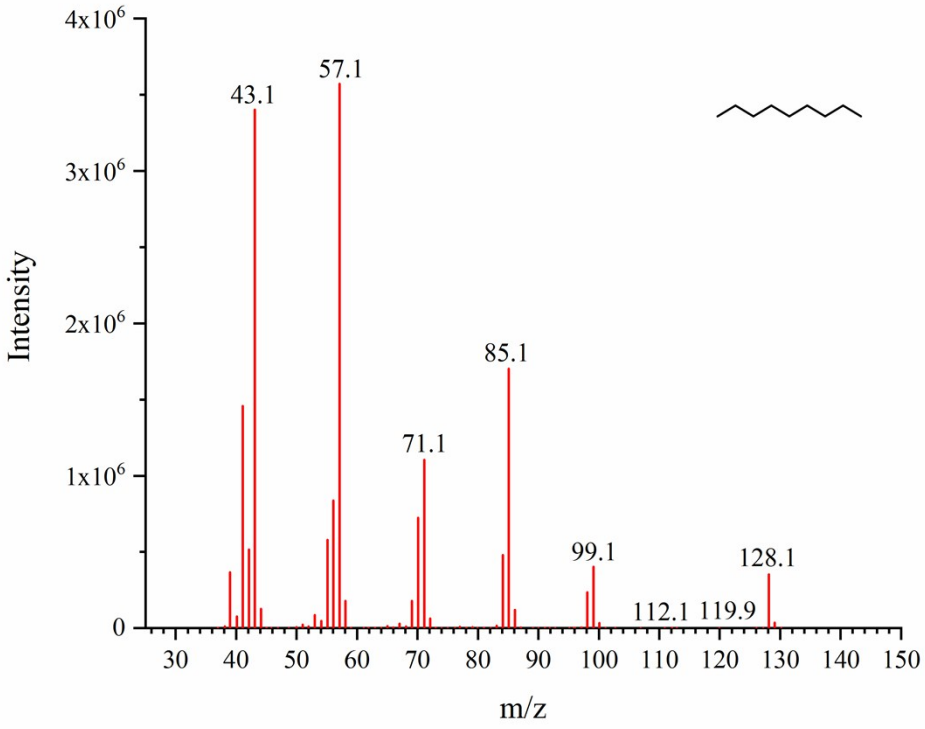
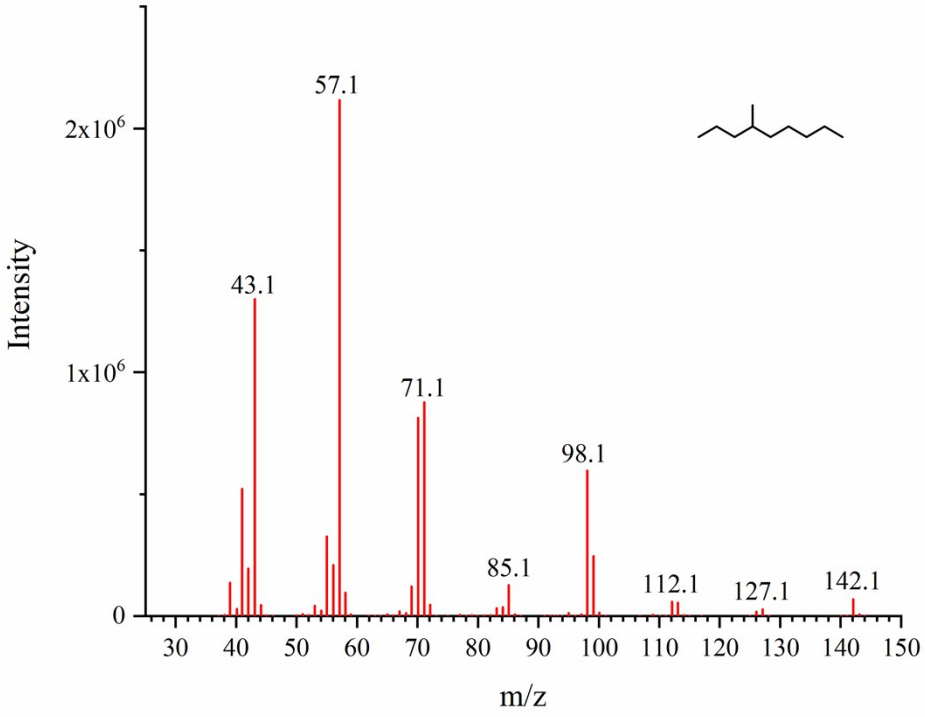
5. Q. Xia, Y. Xia, J. Xi, X. Liu, Y. Zhang, Y. Guo and Y. Wang, *ChemSusChem*, 2017, **10**, 747-753.

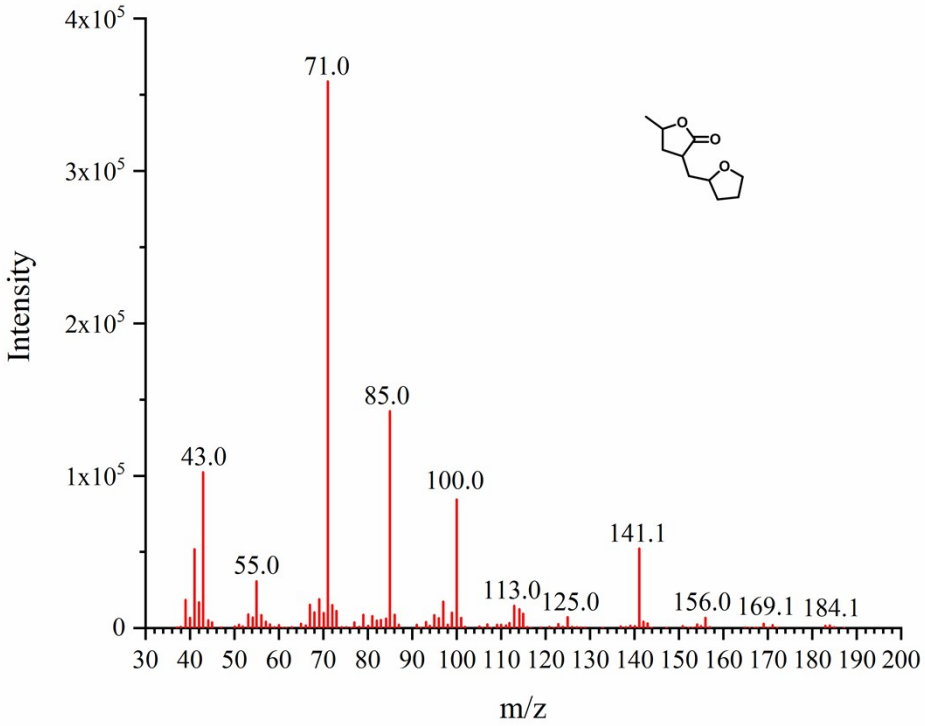
VI. GC-MS spectra

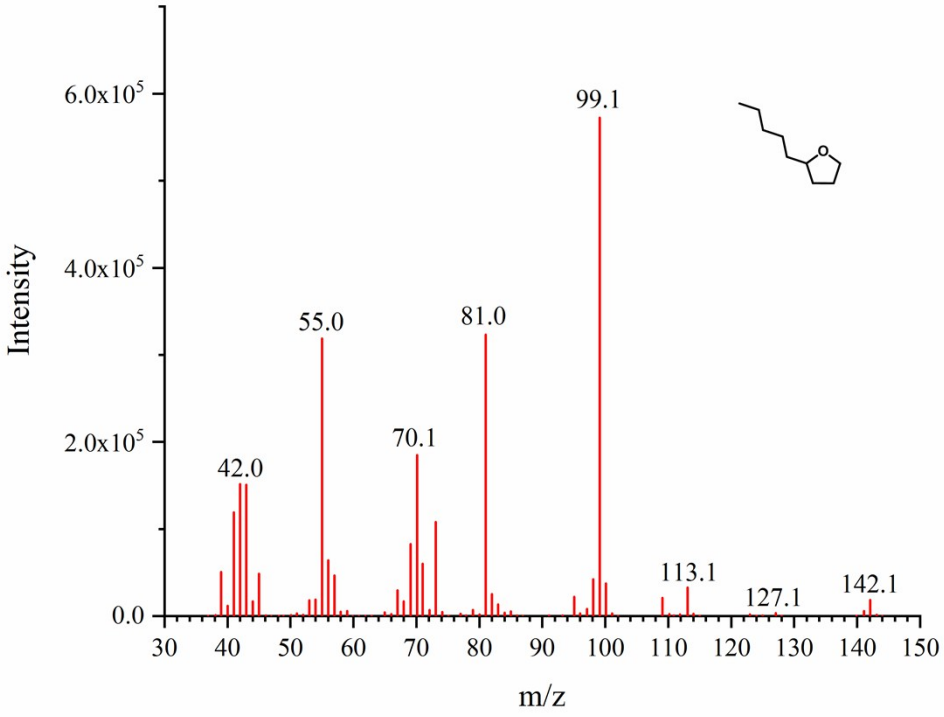


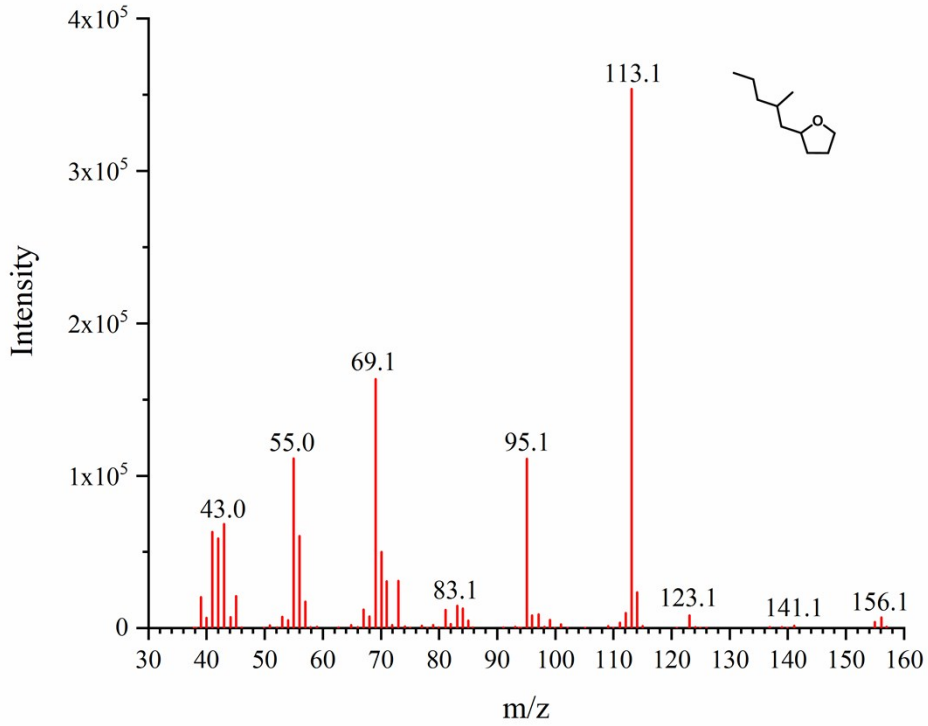

3x10^4
2x10^4
1x10^4
0
Intensity
43.1
57.1
71.1
85.1
98.1
113.1
128.2
30 40 50 60 70 80 90 100 110 120 130 140
m/z

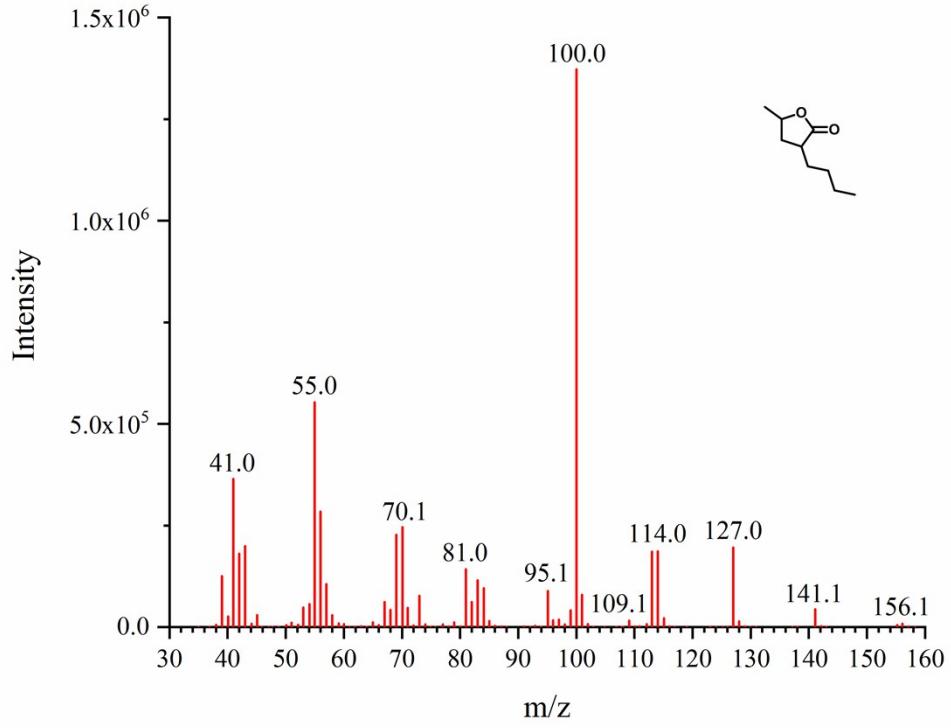

4x10^6
3x10^6
2x10^6
1x10^6
0
Intensity
43.1
57.1
71.1
85.1
99.1
112.1
119.9
128.1
30 40 50 60 70 80 90 100 110 120 130 140 150
m/z

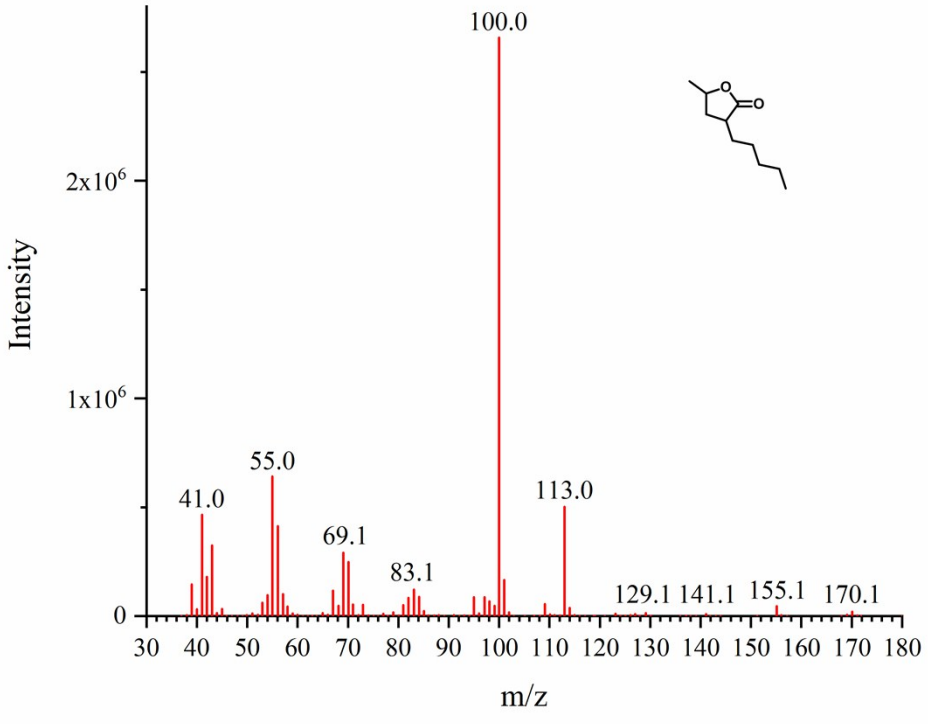

57.1
2x10^6
43.1
1x10^6
71.1
98.1
85.1
112.1
127.1
142.1
0
30 40 50 60 70 80 90 100 110 120 130 140 150
Intensity
m/z

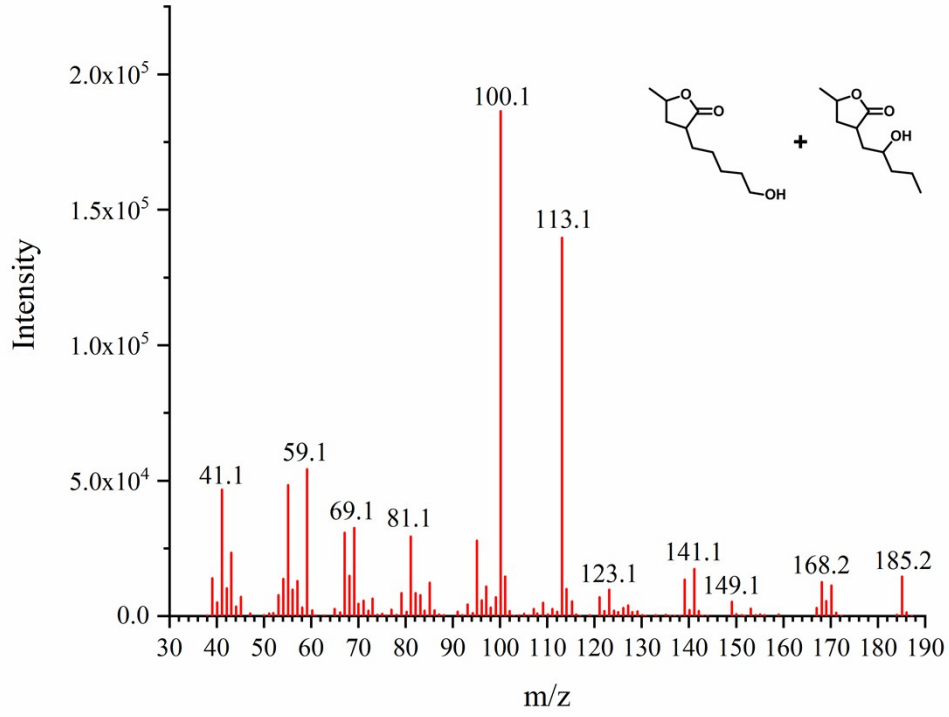

4x10^5
71.0
3x10^5
2x10^5
85.0
43.0
1x10^5
100.0
141.1
55.0
113.0
125.0
156.0
169.1
184.1
0
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Intensity
m/z

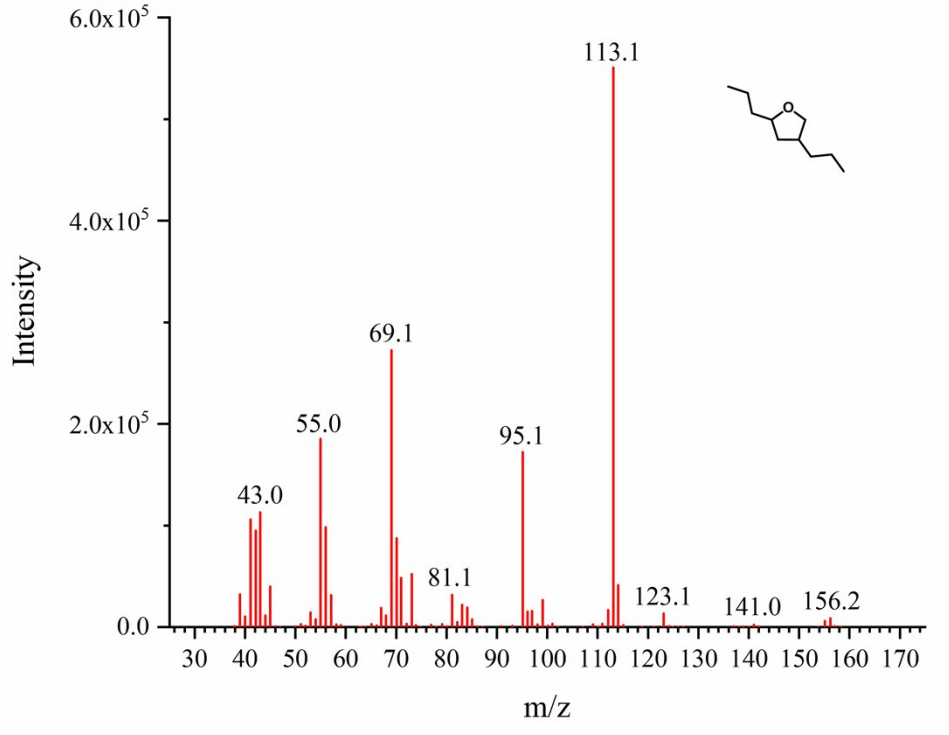

Intensity
6.0x10^5
4.0x10^5
2.0x10^5
0.0
99.1
55.0
81.0
70.1
42.0
113.1
127.1
142.1
30 40 50 60 70 80 90 100 110 120 130 140 150
m/z

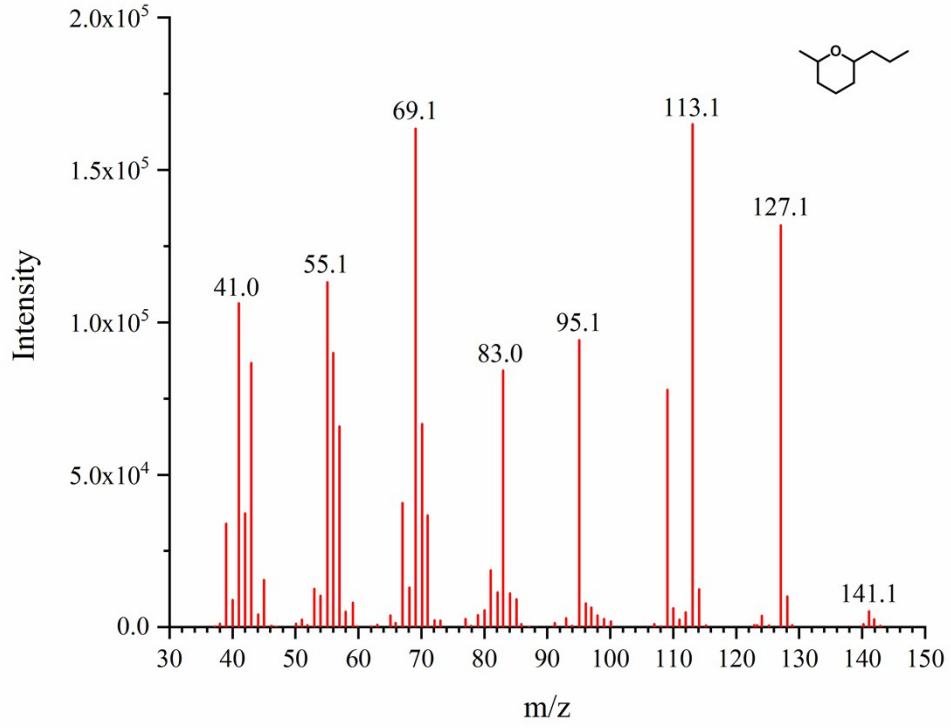

Intensity
4x10^5
3x10^5
2x10^5
1x10^5
0
113.1
69.1
55.0
95.1
43.0
83.1
123.1
141.1
156.1
30 40 50 60 70 80 90 100 110 120 130 140 150 160
m/z

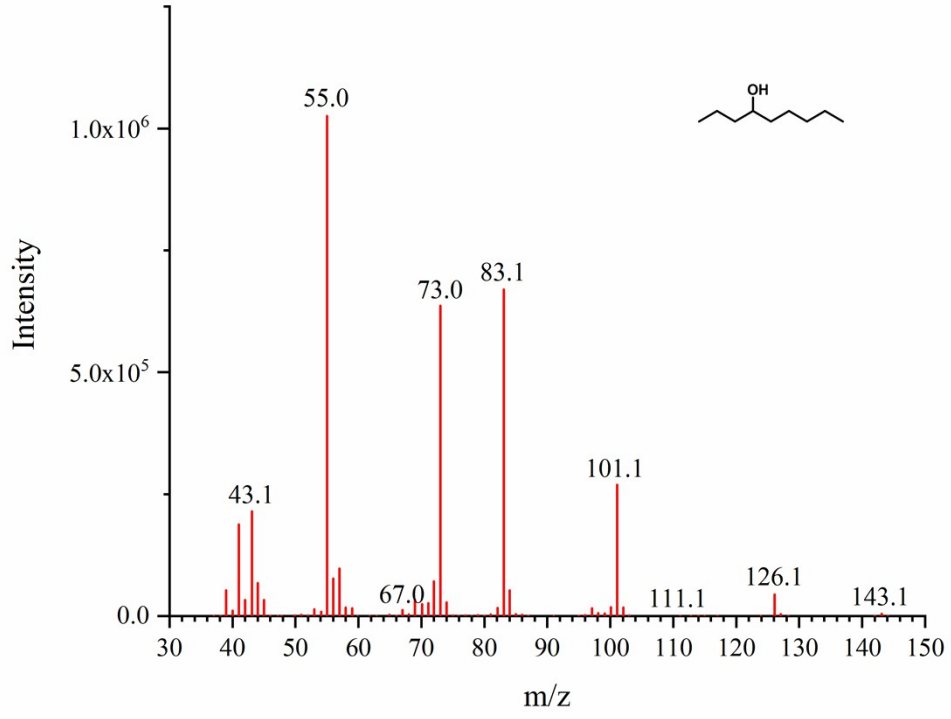

1.5x10^6
1.0x10^6
5.0x10^5
0.0
Intensity
100.0
55.0
41.0
70.1
81.0
95.1
109.1
114.0
127.0
141.1
156.1
30 40 50 60 70 80 90 100 110 120 130 140 150 160
m/z

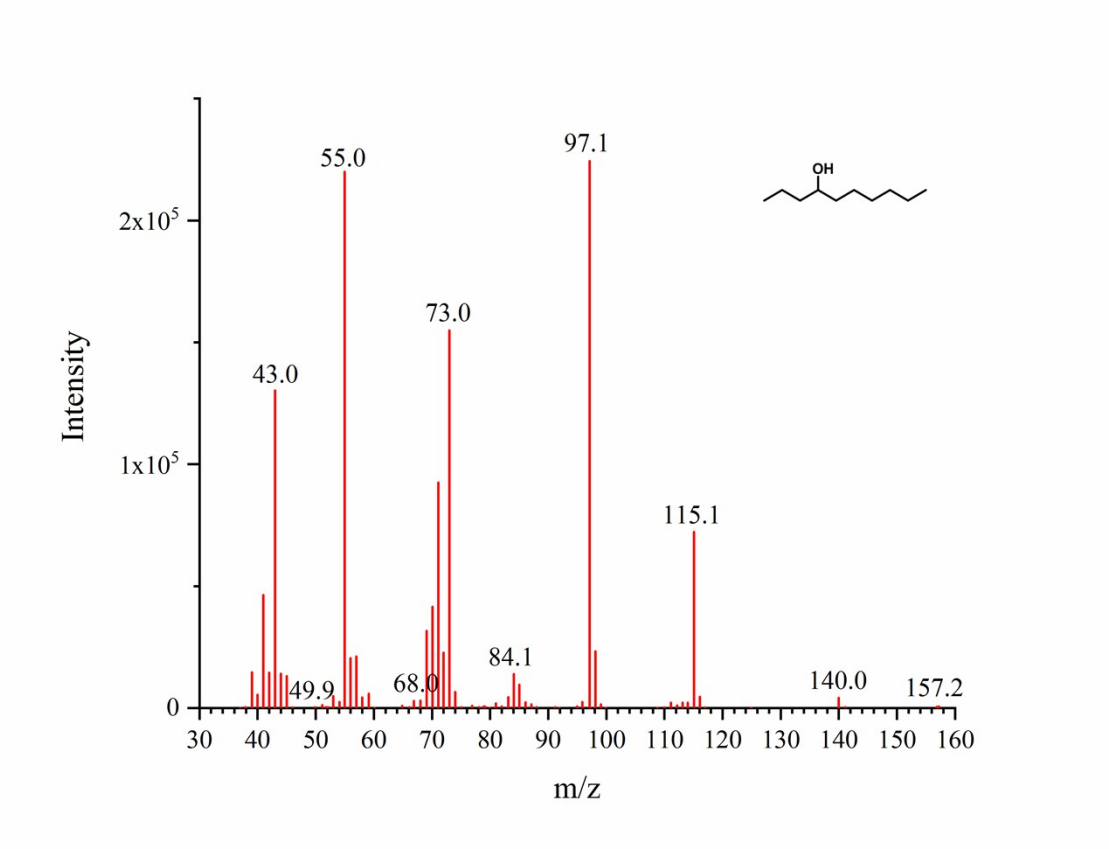

2x10^6
1x10^6
0
Intensity
100.0
55.0
41.0
69.1
83.1
113.0
129.1
141.1
155.1
170.1
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
m/z


Intensity
2.0x10^5
1.5x10^5
1.0x10^5
5.0x10^4
0.0
100.1
113.1
59.1
41.1
69.1
81.1
123.1
141.1
149.1
168.2
185.2
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190
m/z
O
O
OH
+
O
O
OH

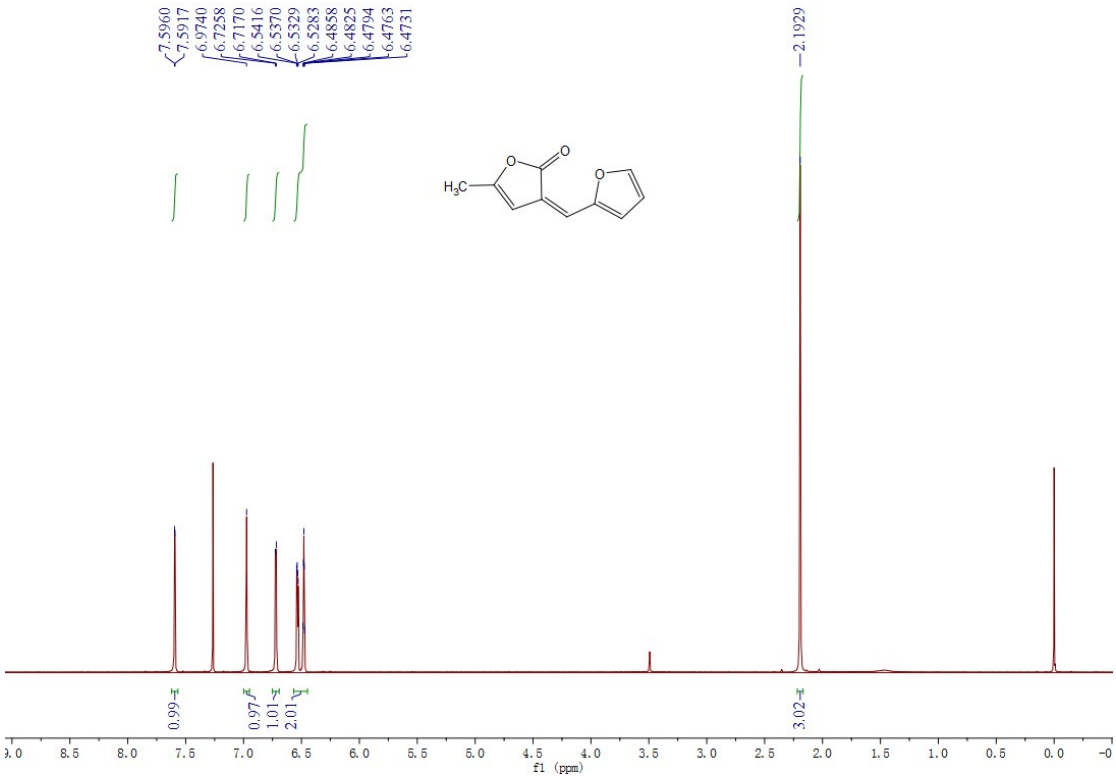

Intensity
6.0x10^5
4.0x10^5
2.0x10^5
0.0
113.1
69.1
55.0
95.1
43.0
81.1
123.1
141.0
156.2
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
m/z
O


2.0x10^5
1.5x10^5
1.0x10^5
5.0x10^4
0.0
Intensity
41.0
55.1
69.1
83.0
95.1
113.1
127.1
141.1
30 40 50 60 70 80 90 100 110 120 130 140 150
m/z
O

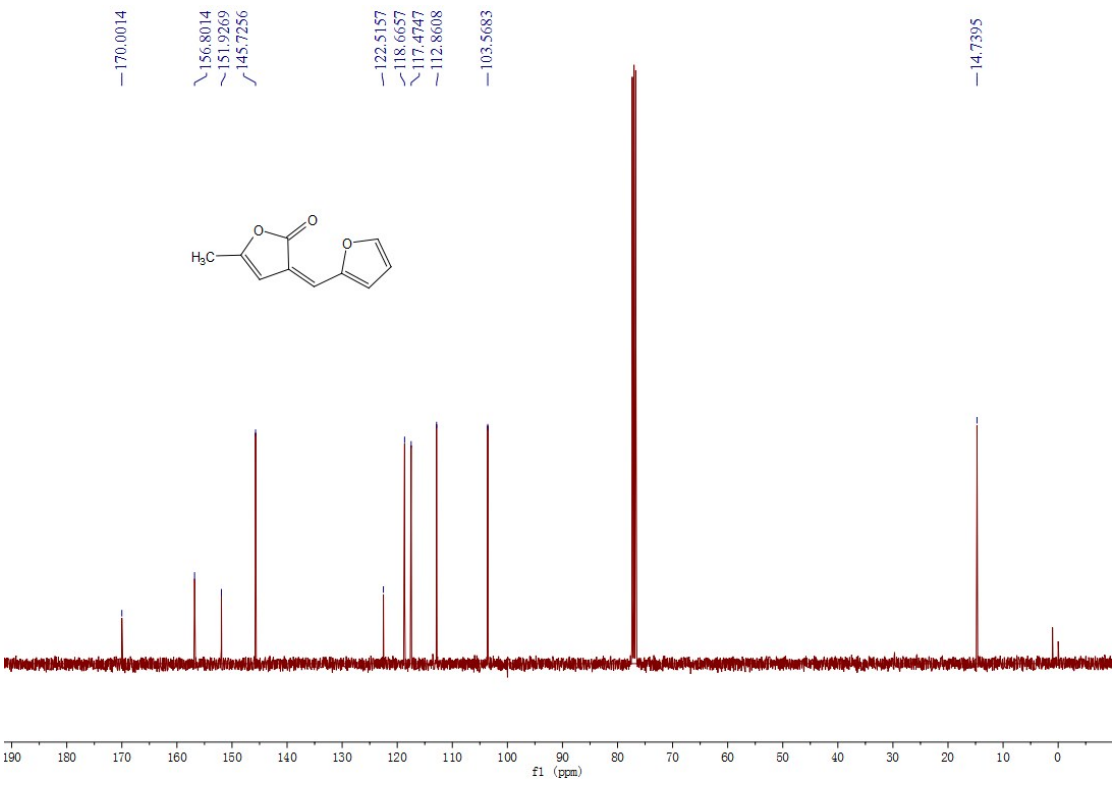

1.0x10^6
5.0x10^5
0.0
Intensity
55.0
43.1
73.0
83.1
67.0
101.1
111.1
126.1
143.1
30 40 50 60 70 80 90 100 110 120 130 140 150
m/z
OH



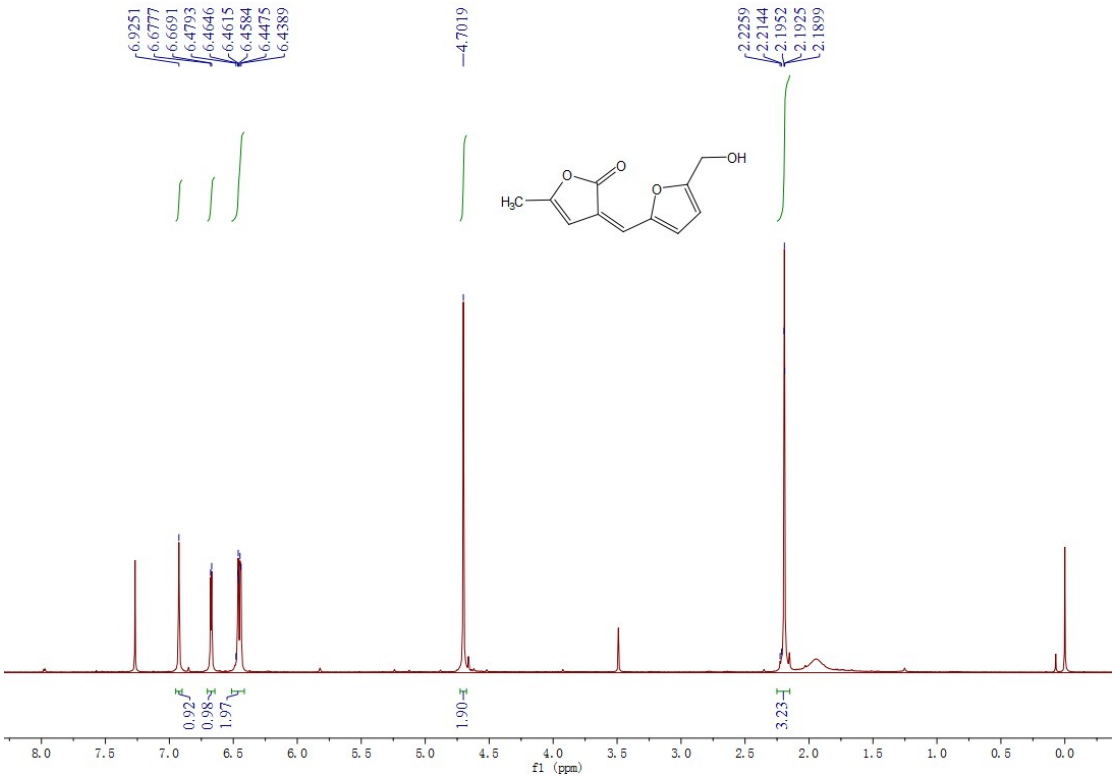
Ⅶ. NMR spectra



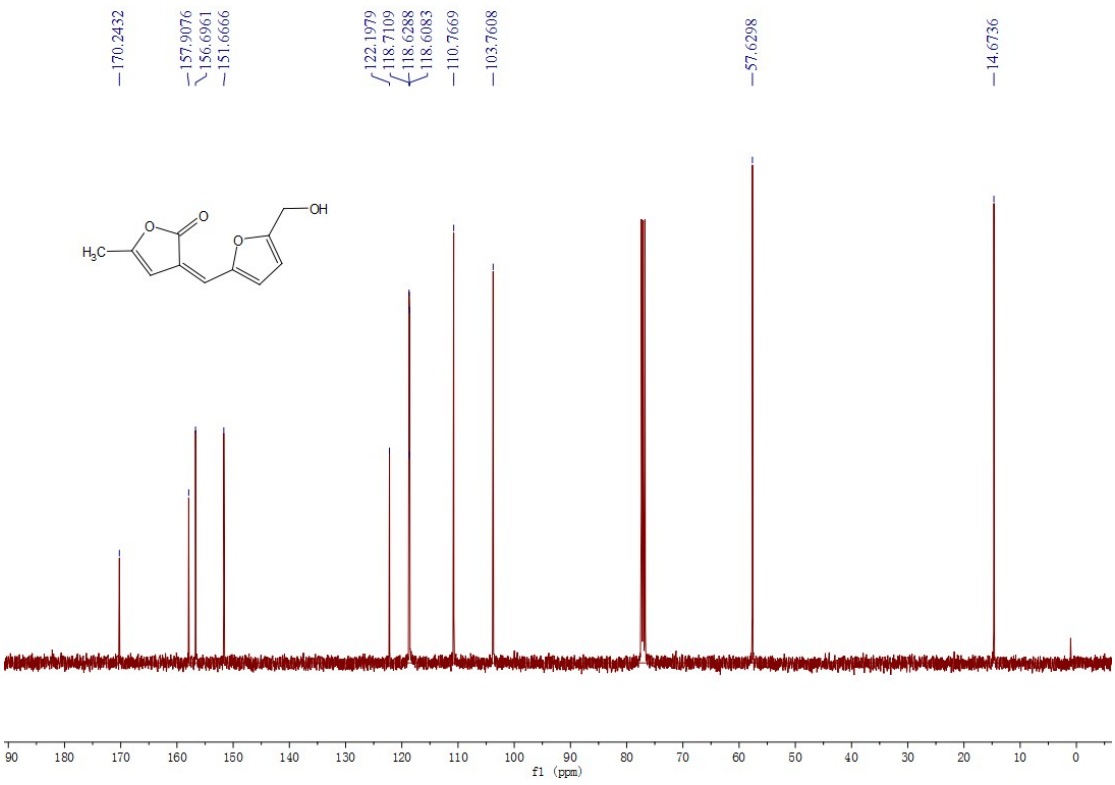
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1A**



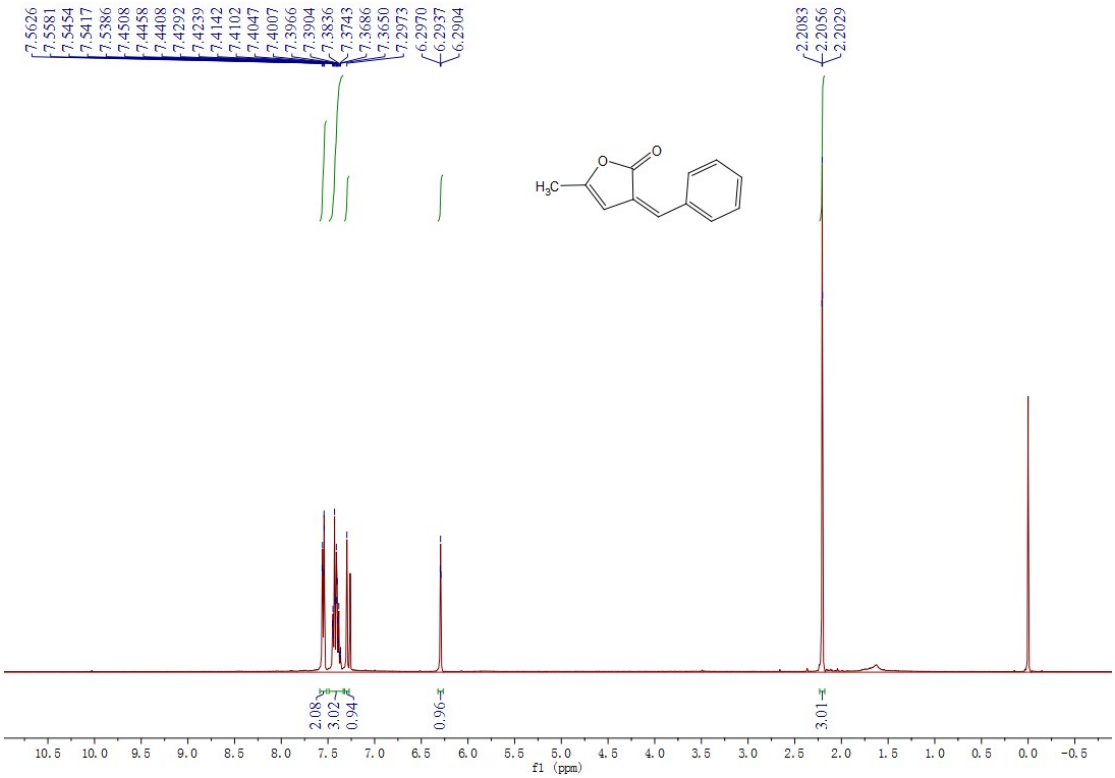
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1A**



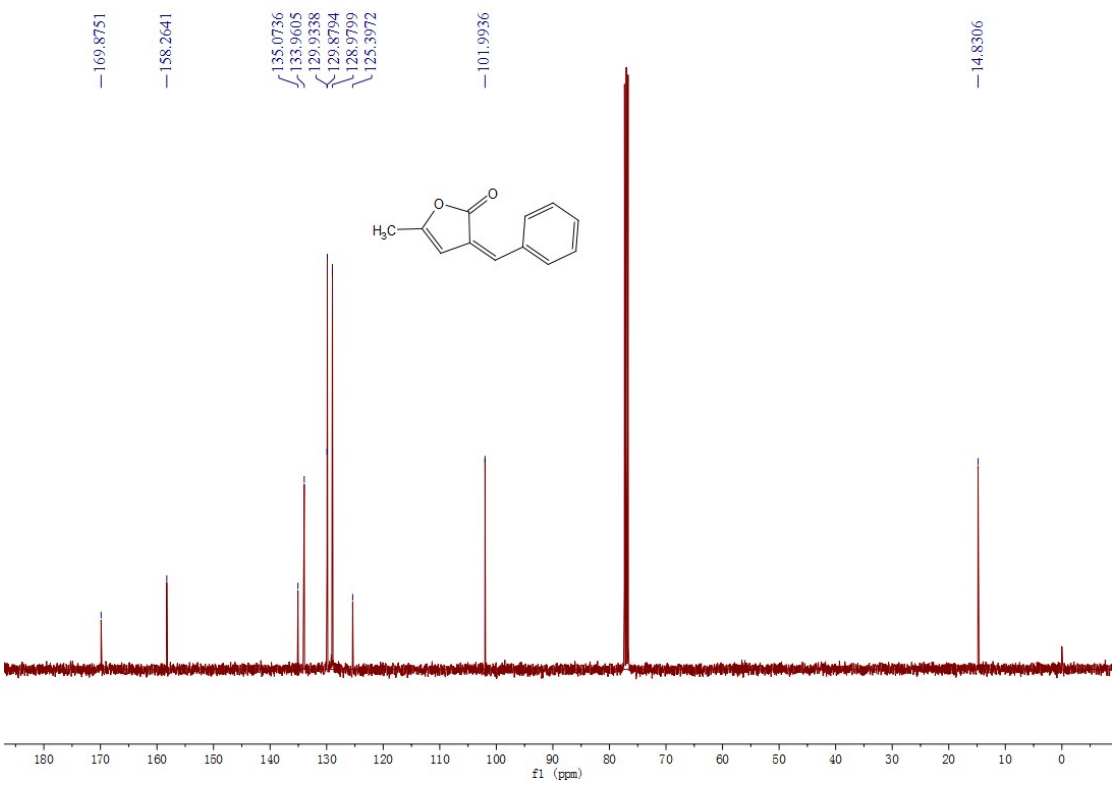
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2A**



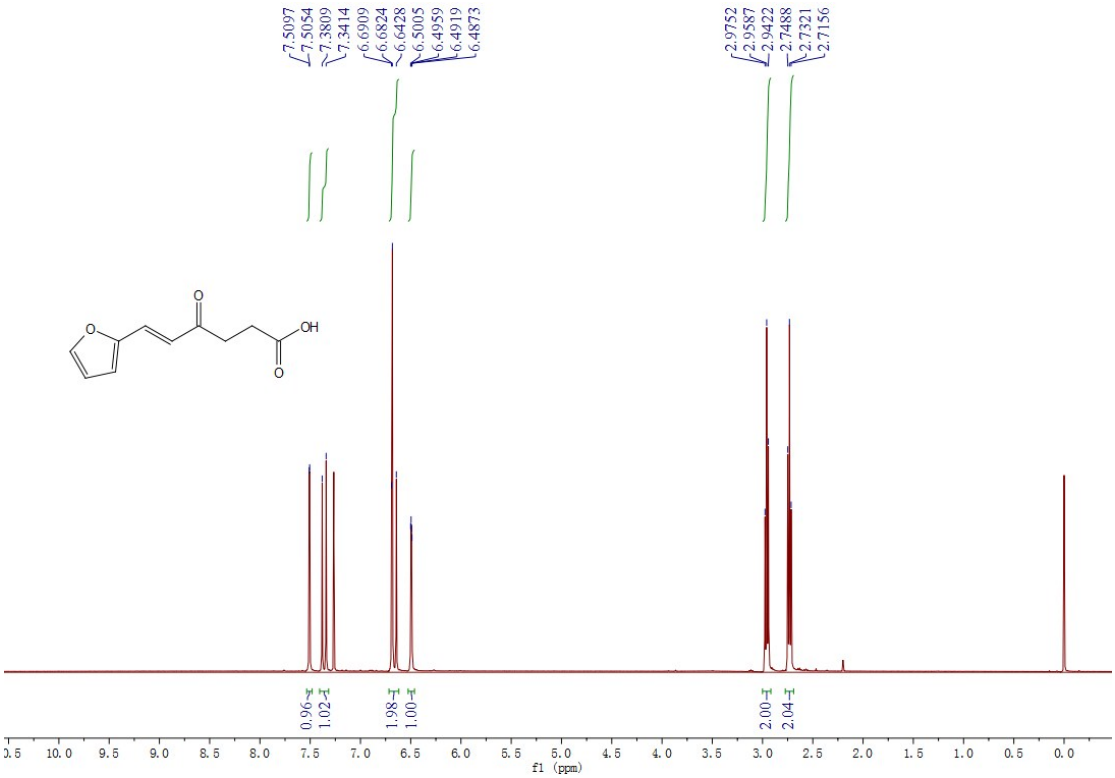
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **2A**



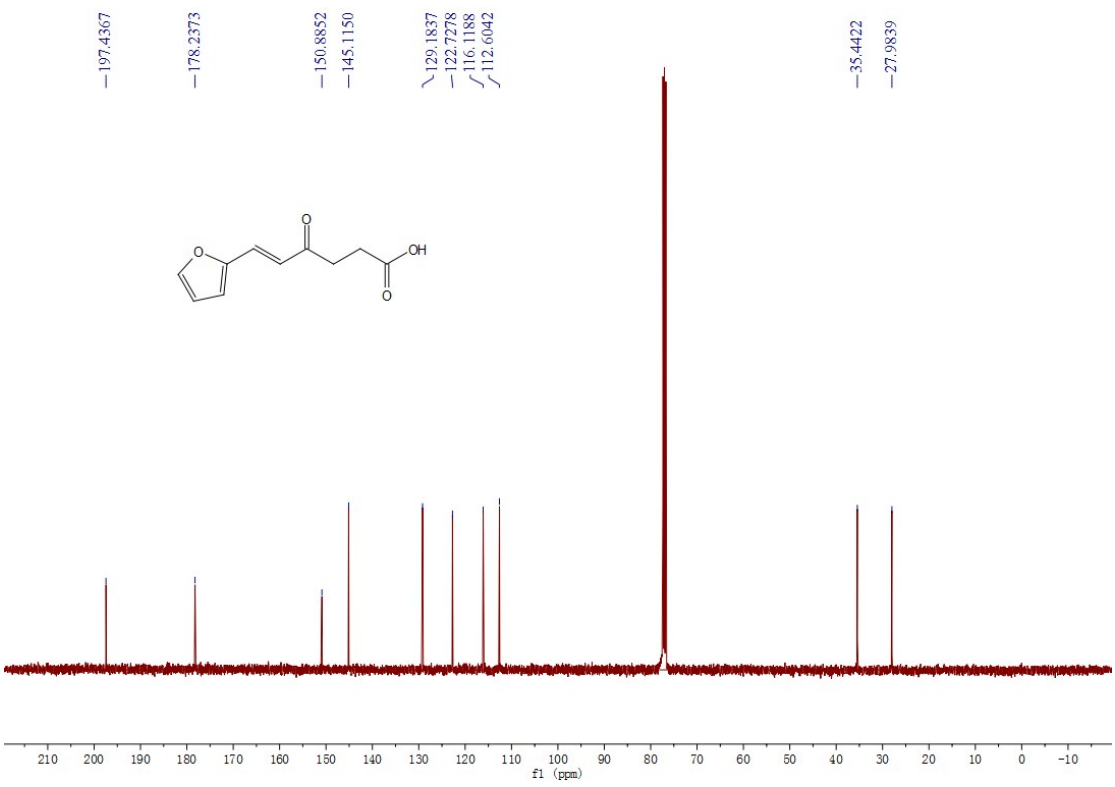
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3A**



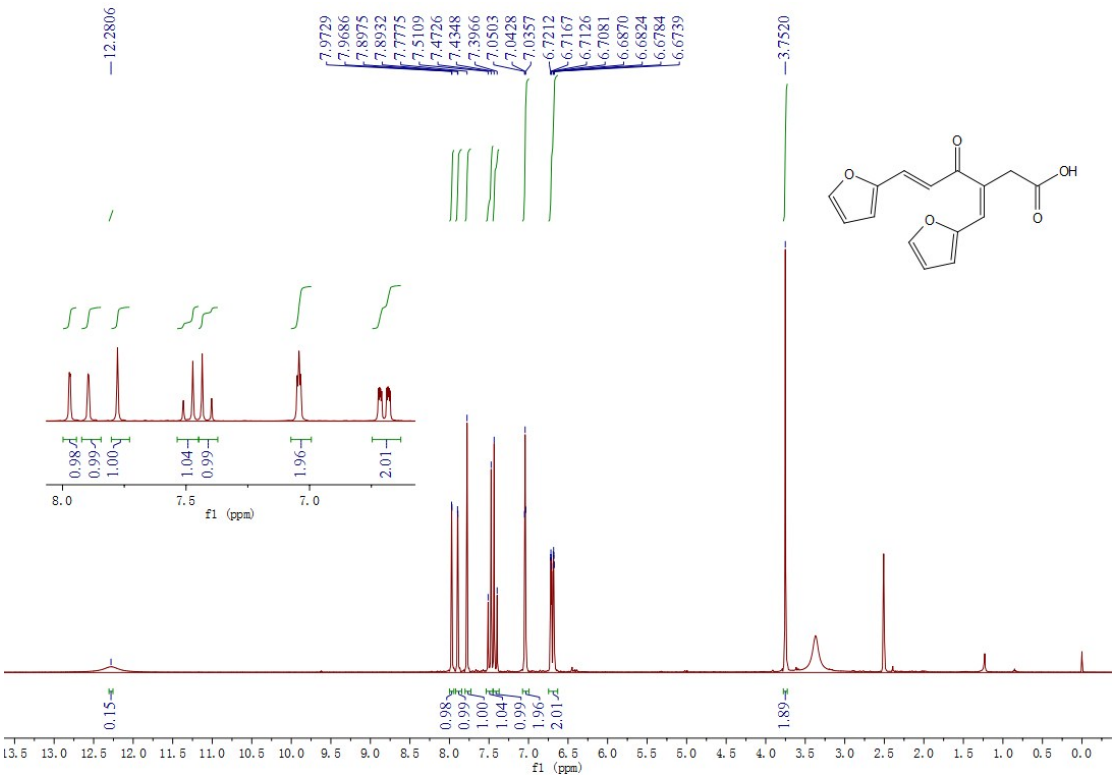
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **3A**



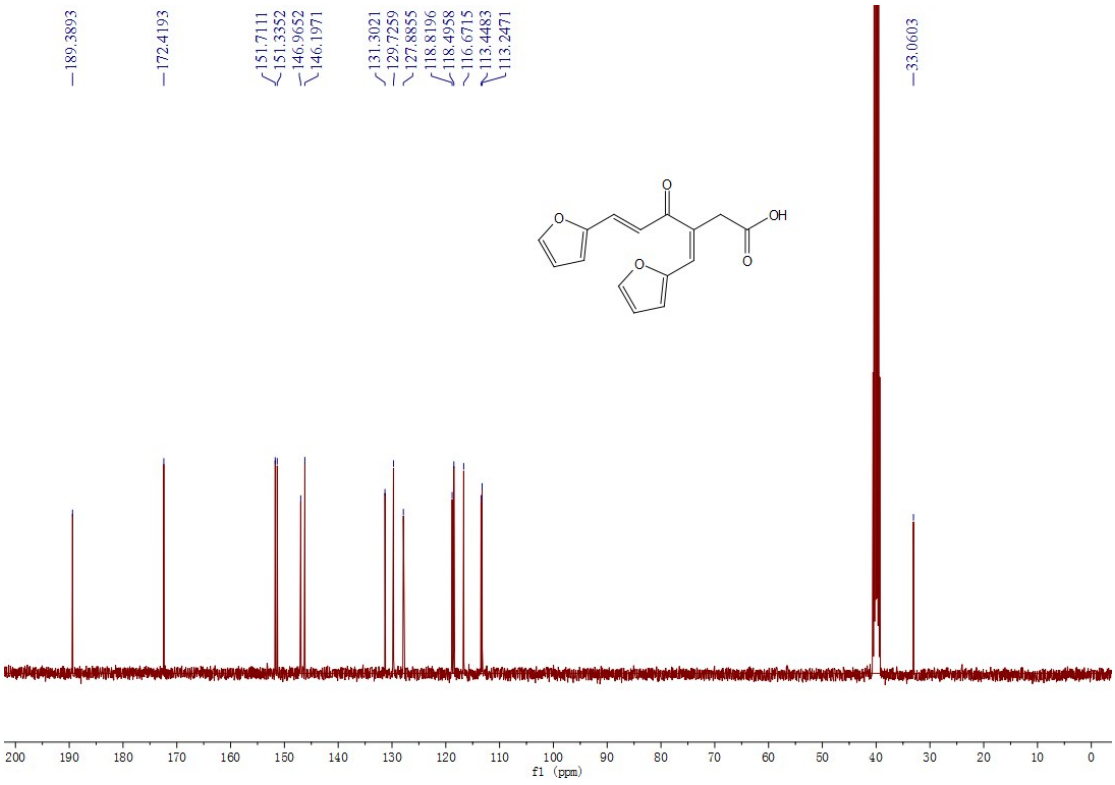
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4A**



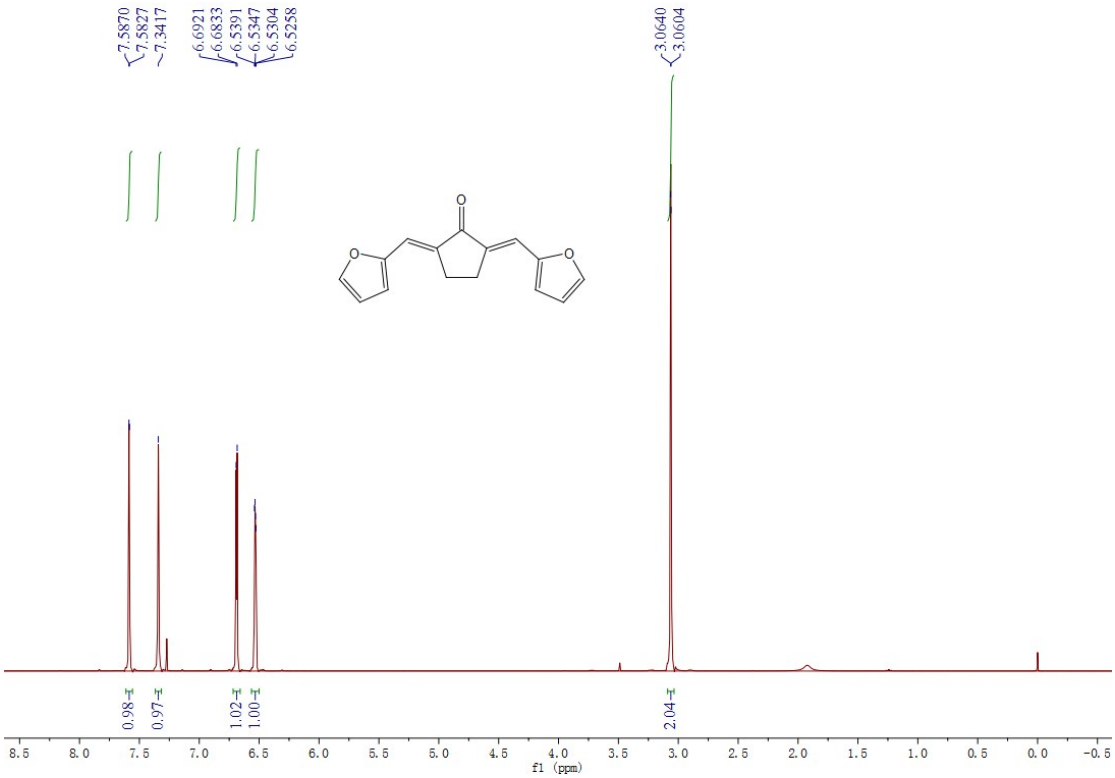
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4A**



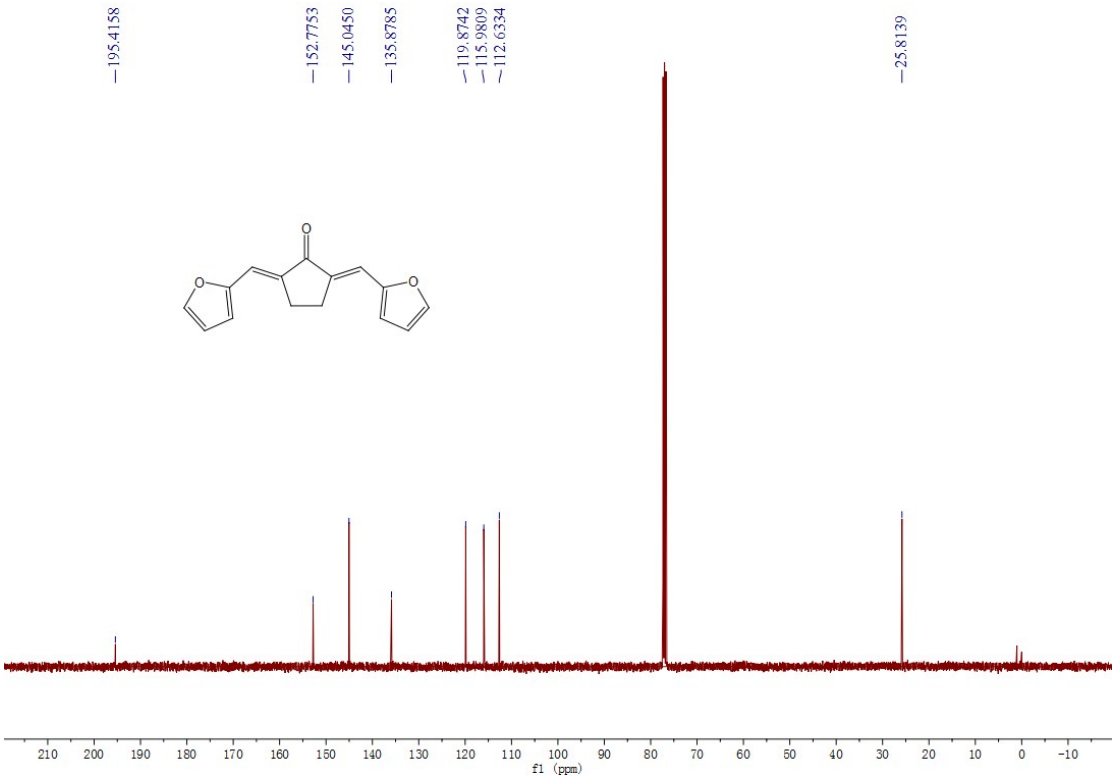
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **5A**



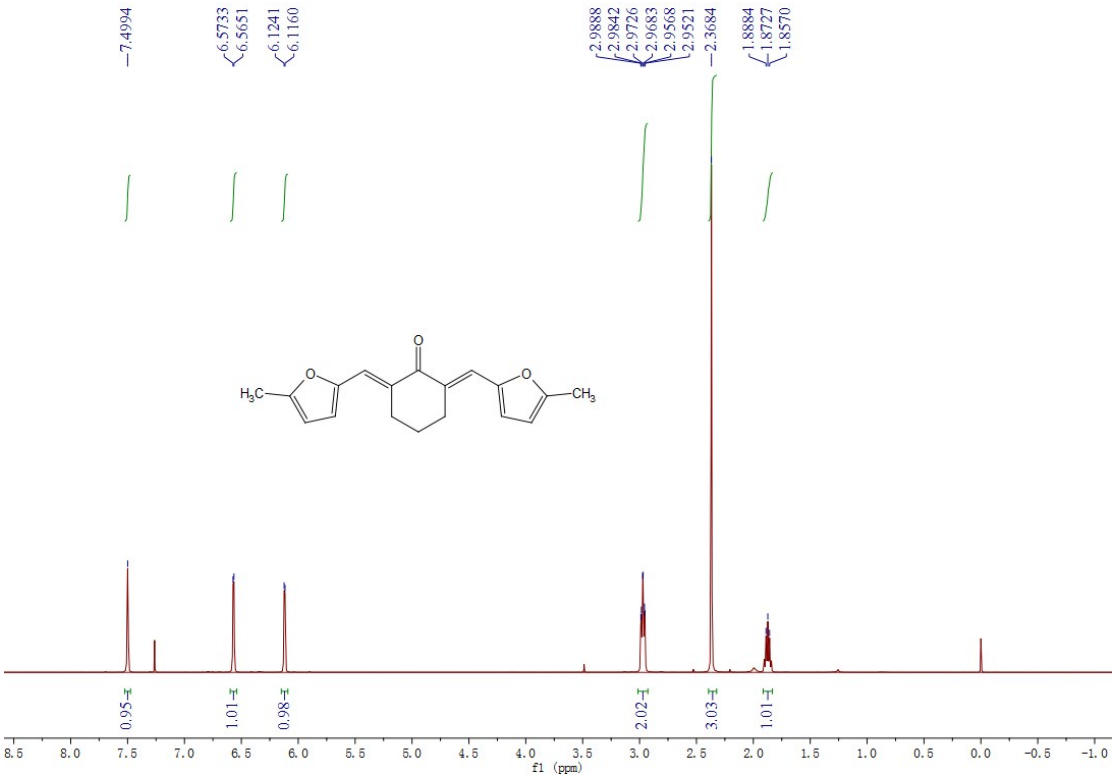
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **5A**



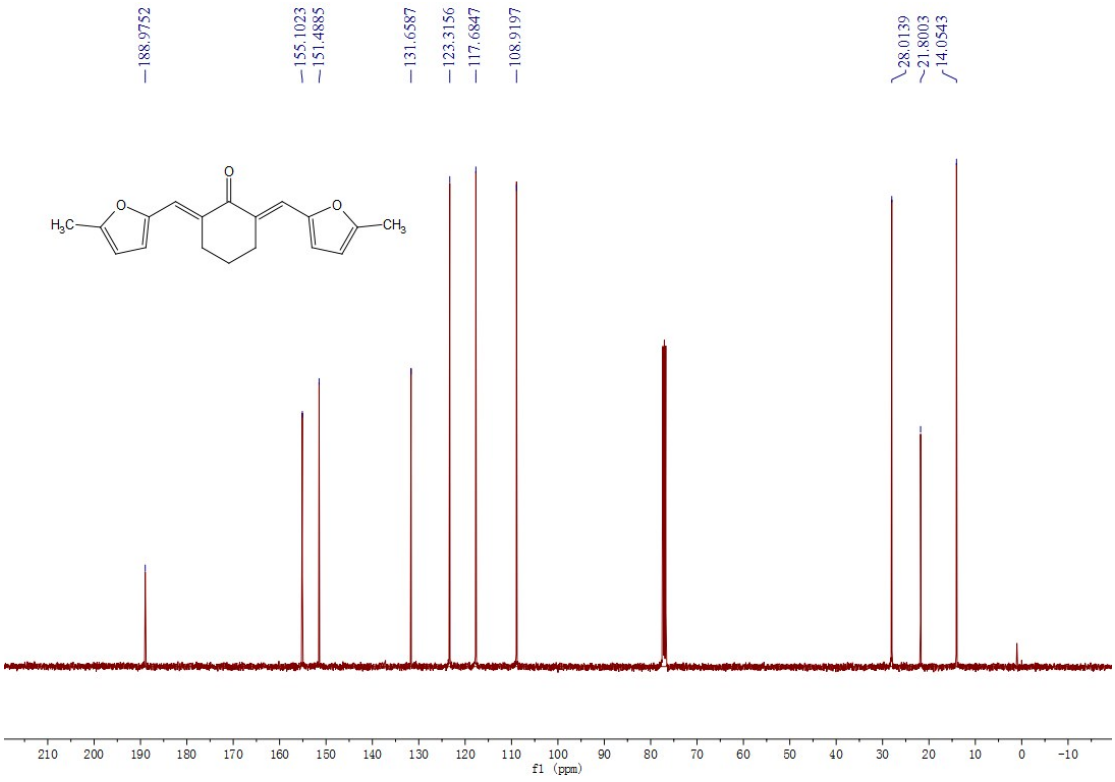
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6A**



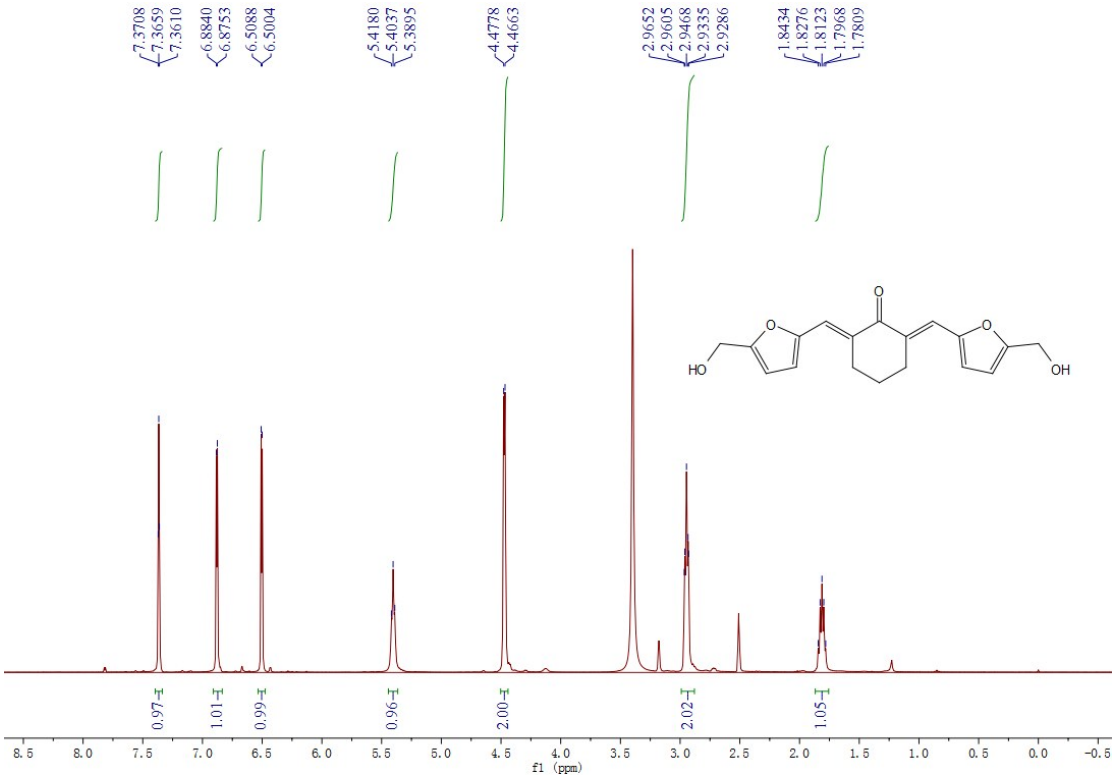
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **6A**



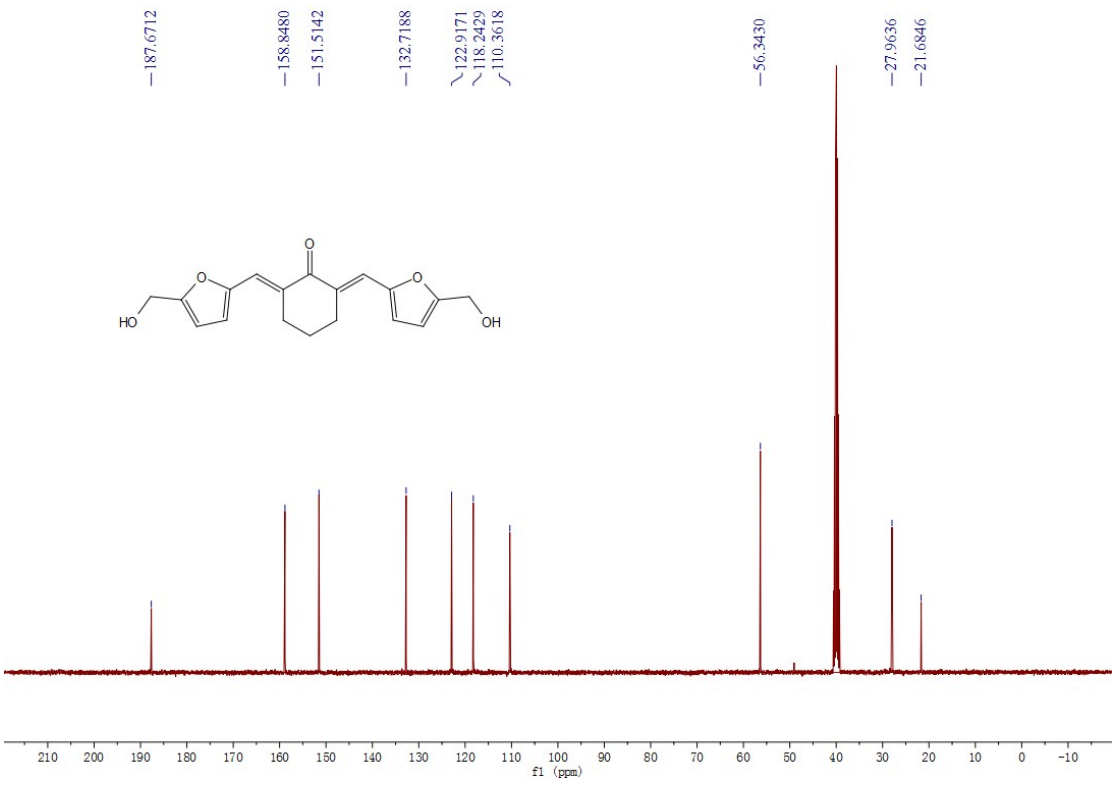
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7A**



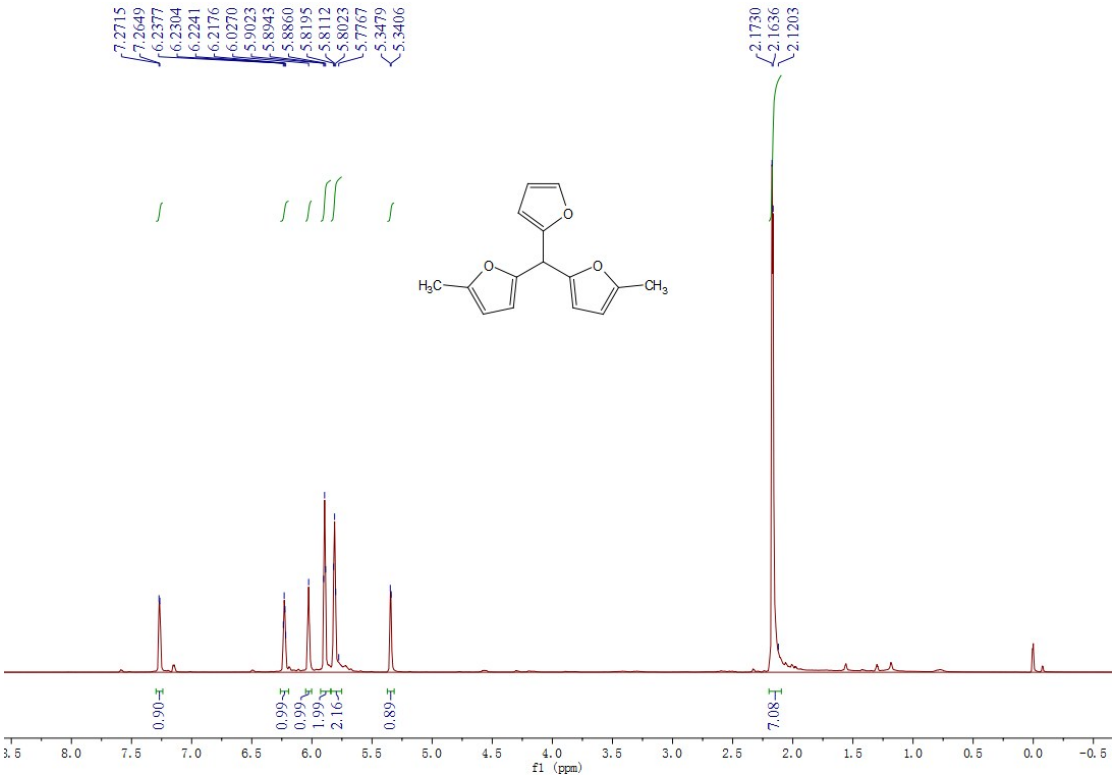
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **7A**



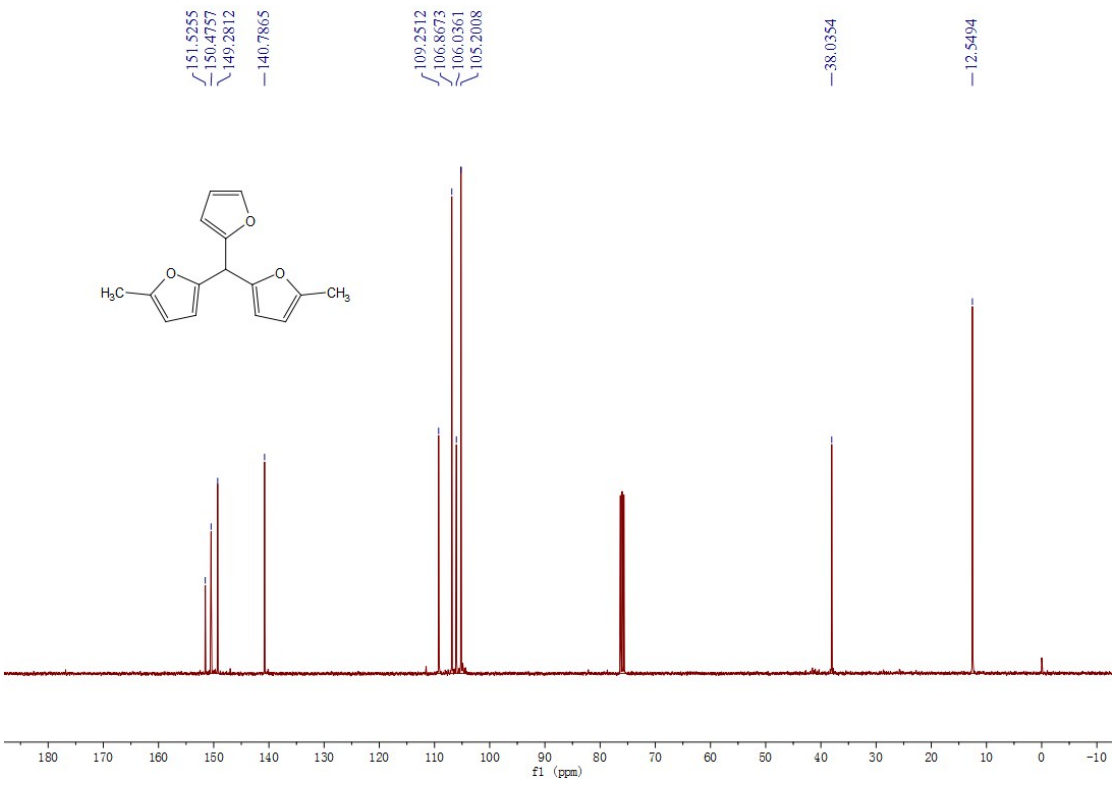
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8A**



^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8A**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9A**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **9A**