Direct Sulfhydryl Ligand Derived UiO-66 for the Removal of Aqueous Mercury and Subsequential Application as a Catalyst for Transfervinylation

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Through linear fitting, the relevant data of the kinetic pseodo-first-order and pseodo-second-order models are obtained. As shown in the Table S1, when the initial concentrations are 100 mg/L, 50 mg/L, and 25 mg/L, the correlation coefficients of the pseodo-first-order kinetic models are 0.86, 0.80, and 0.74, respectively. However, the correlation coefficients of the pseodo-second-order kinetic model are 0.99, 0.99 and 0.98, respectively.

Table S1 Pseodo-first-order kinetic model and quasi-second-order kinetic model constants for Hg(II) adsorption [a]

C_0 (mg/L)	pH	$q_{e,exp}$ (mg/g)	Pseudo-first			Pseudo-second		
			$q_{m,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{m,cal}$ (mg/g)	K_2 (g/(mg·min))	R^2
100	5	83.06	49.25	0.077	0.87	88.18	$2.49*10^{-3}$	0.99
50	5	43.08	28.22	0.157	0.80	45.16	$7.09*10^{-3}$	0.99
25	5	20.06	15.64	0.237	0.74	22.42	$5.87*10^{-3}$	0.98

[a] $q_{e,\,exp}$ is the experimental maximum adsorption capacity, $q_{m,\,cal}$ is the calculated maximum adsorption capacity

The Langmuir model and Freundlich model were fitted with the UiO-66-SH adsorbing mercury. The expressions of the models are Eq. S1 and Eq S2

Langmuir model: $q_e = q_m K_L C_e /(1+K_L C_e)$ (Eq. S1)

Freundlich model: $q_e = K_F C_e^{1/n}$ (Eq. S2)

The fittingparameters at temperatures of 293 K, 298 K and 303 K are summarized in Table S2. The correlation coefficients of the Freundlich model at 293 K, 298 K, and 303 K are 0.91, 0.91, and 0.92, respectively, and the correlation coefficients of the Langmuir model are 0.97, 0.98, and 0.98, respectively. Compared with the Freundlich model, the Langmuir model has a higher correlation coefficient. Therefore, the adsorption of mercury ions by UiO-66-SH is more in line with the Langmuir adsorption isotherm model. When the temperature increases from 293 K to 303 K, the theoretical saturated adsorption capacity increases from 603 mg/g to 630 mg/g, and the adsorption constant KL increases from 0.008 L/mg to 0.012 L/mg, which also shows that the adsorption process of UiO-66-SH for mercury ions is an endothermic reaction.

Table S2 Model constants of Langmuir adsorption isotherm and Freundlich adsorption isotherm for Hg(II) adsorption adsorption [a]

	$q_{e, exp}$ (mg/g)	Langmuir constants			Freundlich constants		
		q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
303	465.19	630.60	0.012	0.98	29.72	1.99	0.92
298	440.99	623.27	0.010	0.98	24.96	1.93	0.91
293	408.13	603.01	0.008	0.97	19.45	1.86	0.91

[a] $q_{e, exp}$ is the experimental maximum adsorption capacity, $q_{m, cal}$ is the calculated maximum adsorption capacity

Table S3 lists some adsorbents for mercury removal from water, and their removal rate and adsorption equilibrium time are shown. It can be seen that the UiO-66-SH material prepared in this work has good performance in terms of the removal rate and the contact time that are required for adsorption equilibrium.

Table S3 Comparison of the adsorption performance of different types adsorbents for mercury ions

sorbents	Removal rate (%)	Time (min)	Ref.
MIL-101-Thymine	51.27	200	45
ZIF-90-SH	22.4	60	74
SH-ePMO	64	60	75
UiO-66-SO$_3$H	55	120	55
UiO-66-SH	83.06	30	This work

Using UiO-66-SH+Hg to catalyze the reaction of benzoic acid and vinyl acetate, we optimized the conditions for catalyst dosage, reaction temperature and reaction time.

We took the UiO-66-SH+Hg that was recovered in the adsorption, which was performed at 25 °C with the adsorbent dosage of 1.0 g/L, pH = 5, the initial mercury concentration of 100 mg/L, and the contact time of 30 min. The material was washed three times and dried at 60 °C to obtain the catalyst. Subsequently, we optimized the conditions with the catalyst dosage of 0.05 g, 0.1 g, 0.2 g, 0.4 g, and the reaction temperature was explored at 25 °C, 40 °C, 60 °C, 80 °C, 120 °C, and the reaction time was 0.5 h, 1 h, 2 h, 4 h, respectively. The reactions were carried out with mixing 2 mmol benzoic acid and 8 mL vinyl acetate with the catalyst. The reactions were monitored with gas chromatography, and the results are shown in Table S4.

Table S4 UiO-66-SH+Hg as a catalyst condition optimization table for vinyl transfer

	Catalyst	Dosage of Catalyst (g)	Temperature (°C)	Time (h)	Yield (%)
1	UiO-66-SH+Hg	0.2	25	4	24
2	UiO-66-SH+Hg	0.2	40	4	33
3	UiO-66-SH+Hg	0.2	60	4	54
4	UiO-66-SH+Hg	0.2	80	4	82
5	UiO-66-SH+Hg	0.2	120	4	——
6	UiO-66-SH+Hg	0.2	80	0.5	62
7	UiO-66-SH+Hg	0.2	80	1	69
8	UiO-66-SH+Hg	0.2	80	2	78
9	UiO-66-SH+Hg	0.05	80	4	56
10	UiO-66-SH+Hg	0.1	80	4	70
11	UiO-66-SH+Hg	0.4	80	4	84
12	UiO-66	0.2	80	4	——
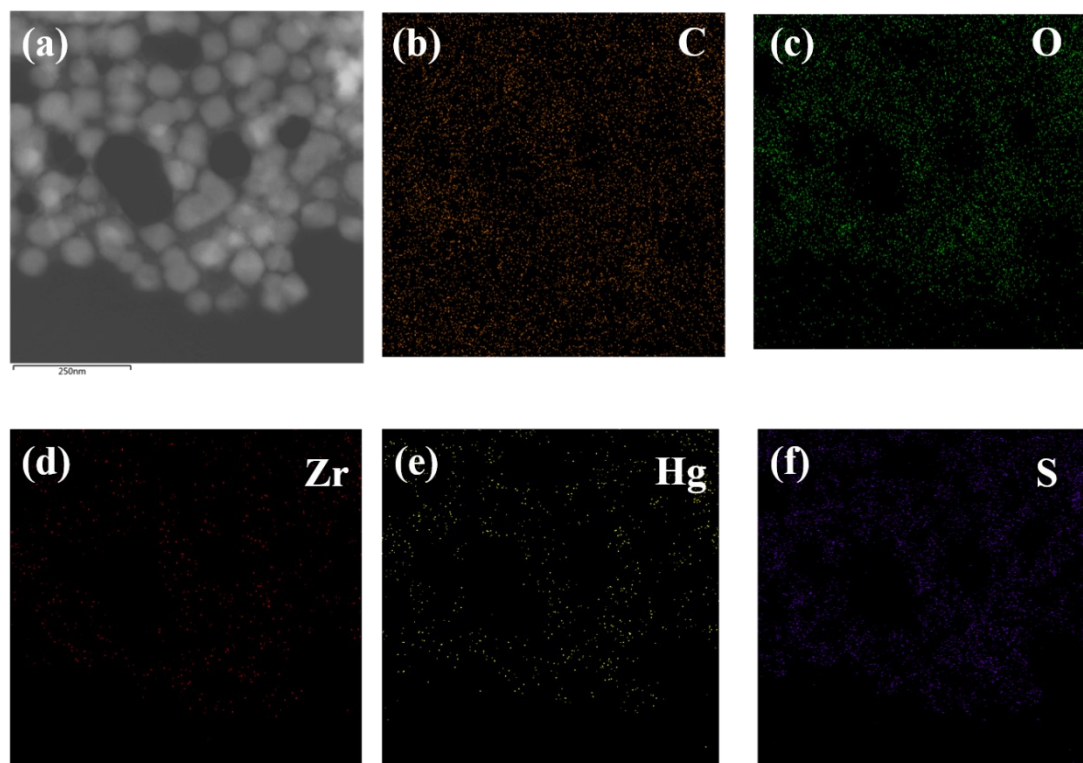
Fig. S1 EDS diagram of UiO-66-SH+Hg after reaction
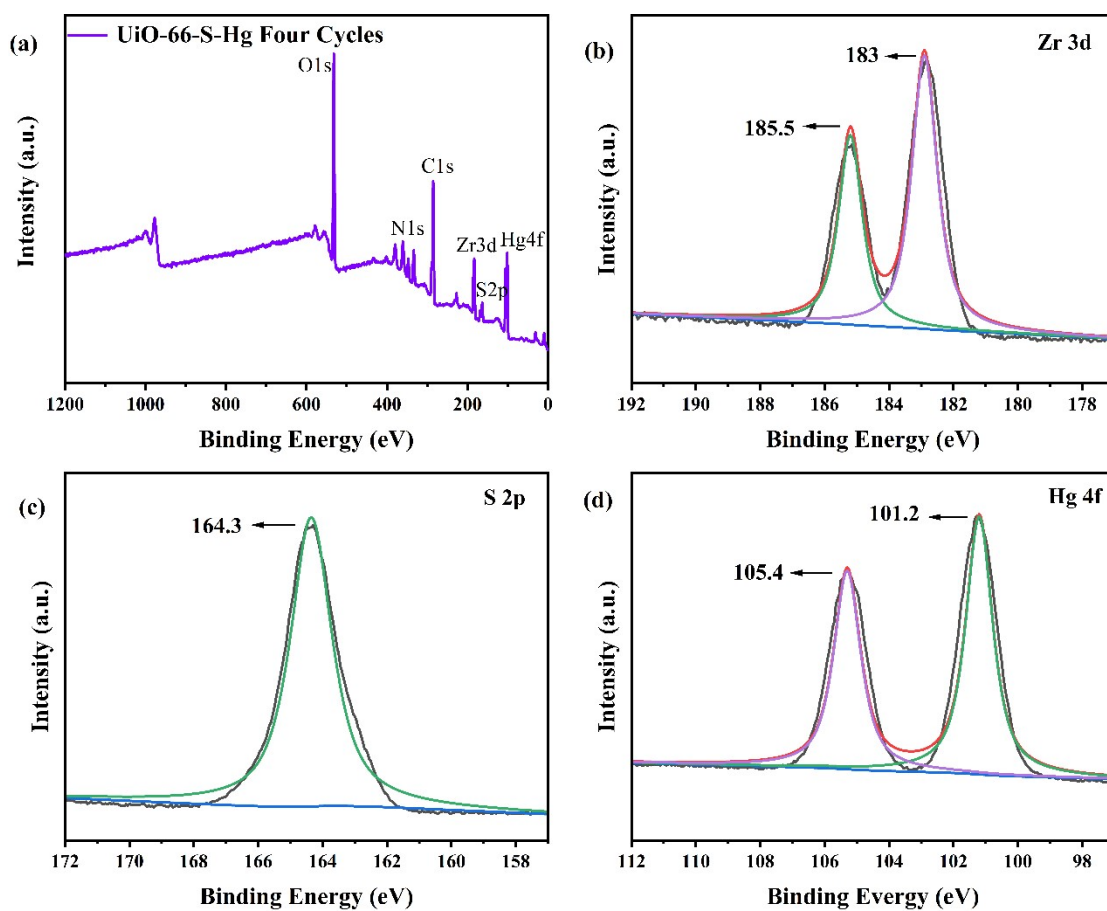
Fig. S2 XPS spectrum of UiO-66-S-Hg after 4 cycles of transfer vinylation of benzoic acid with vinyl acetate

Characterization of vinylation products

Vinyl benzoate (Table 1, entry 1)
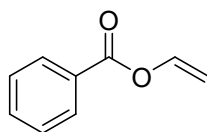
Colorless liquid (82%). ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.14 (dt, J = 8.5, 1.5 Hz, 2H), 7.62 (ddd, J = 7.2, 2.6, 1.2 Hz, 1H), 7.55 (dd, J = 13.9, 6.2 Hz, 1H), 7.52 – 7.47 (m, 2H), 5.11 (dd, J = 13.9, 1.7 Hz, 1H), 4.76 – 4.71 (m, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 163.73 (s), 141.53 (s), 133.69 (s), 130.10 (s), 129.04 (s), 128.62 (s), 98.31 (s). Physical and spectral data were consistent with those previously reported.[1]

### Vinyl 4-(tert-butyl)benzoate (Table 1, entry 2)
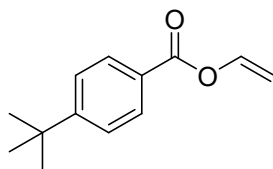
Colorless liquid (89%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 – 7.87 (m, 2H), 7.40 (ddd, J = 10.3, 8.7, 4.1 Hz, 3H), 4.96 (dd, J = 14.0, 1.6 Hz, 1H), 4.58 (dd, J = 6.3, 1.6 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.64 (s), 157.39 (s), 141.51 (s), 129.93 (s), 126.15 (s), 125.53 (s), 97.91 (s), 35.17 (s), 31.09 (s). Physical and spectral data were consistent with those previously reported.[2]

### Vinyl 4-methylbenzoate (Table 1, entry 3)
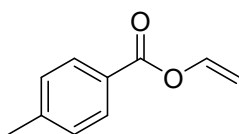
Colorless liquid (80%) ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.99 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 14.0, 6.2 Hz, 1H), 7.26 (d, J = 7.8 Hz, 2H), 5.05 (dd, J = 14.0, 1.6 Hz, 1H), 4.68 (dd, J = 6.3, 1.5 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 163.78 (s), 144.52 (s), 141.56 (s), 130.13 (s), 129.34 (s), 126.26 (s), 98.01 (s), 21.82 (s). Physical and spectral data were consistent with those previously reported.[3]

### Vinyl 2-methylbenzoate (Table 1, entry 4)
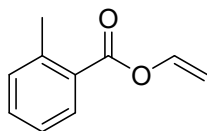
Colorless liquid (68%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (dd, J = 8.1, 1.3 Hz, 1H), 7.47 – 7.31 (m, 2H), 7.20 (ddd, J = 12.2, 8.6, 7.8 Hz, 2H), 4.95 (dd, J = 14.0, 1.6 Hz, 1H), 4.60 (dd, J = 6.3, 1.6 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.12, 164.23, 141.52, 132.74, 131.96, 131.02, 128.13, 125.90, 97.95, 21.02. Physical and spectral data were consistent with those previously reported.[3]

## Vinyl 3-methylbenzoate (Table 1, entry 5)
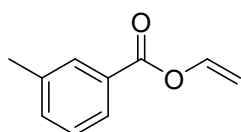
Colorless liquid (60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, J = 7.9 Hz, 2H), 7.42 (dd, J = 14.0, 6.3 Hz, 1H), 7.34 – 7.22 (m, 2H), 4.97 (dd, J = 14.0, 1.6 Hz, 1H), 4.60 (dd, J = 6.3, 1.6 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.79 (s), 141.49 (s), 138.35 (s), 134.38 (s), 130.50 (s), 128.86 (s), 128.42 (s), 127.17 (s), 98.07 (s), 77.39 (s), 77.08 (s), 76.76 (s), 21.25 (s). Physical and spectral data were consistent with those previously reported.[4]

Vinyl 4-hydroxybenzoate (Table 1, entry 6)
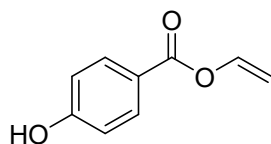
White solid (72%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 – 7.98 (m, 2H), 7.48 (dd, J = 14.0, 6.3 Hz, 1H), 6.98 – 6.85 (m, 2H), 6.08 (s, 1H), 5.05 (dd, J = 14.0, 1.6 Hz, 1H), 4.69 (dd, J = 6.3, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.74 (s), 160.63 (s), 141.41 (s), 132.51 (s), 121.18 (s), 115.49 (s), 98.10 (s). Physical and spectral data were consistent with those previously reported.[1]
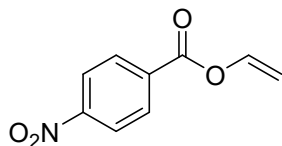
Vinyl 4-chlorobenzoate (Table 1, entry 7)
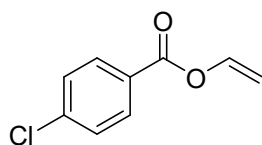
Light yellow solid (75%). ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.09 – 7.98 (m, 2H), 7.50 (dd, J = 13.9, 6.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 5.08 (dd, J = 13.9, 1.8 Hz, 1H), 4.73 (dd, J = 6.2,

1.8 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 162.81 (s), 141.37 (s), 140.22 (s), 131.42 (s), 128.99 (s), 98.57 (s). Physical and spectral data were consistent with those previously reported.[4]
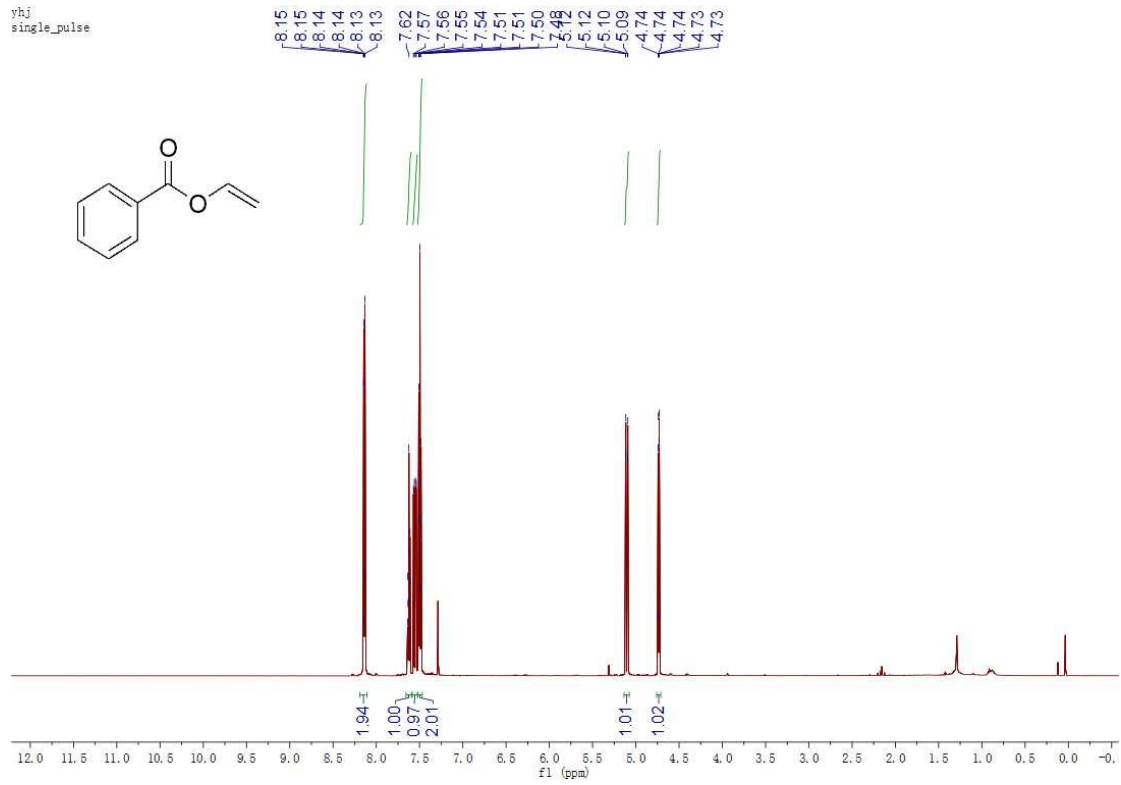
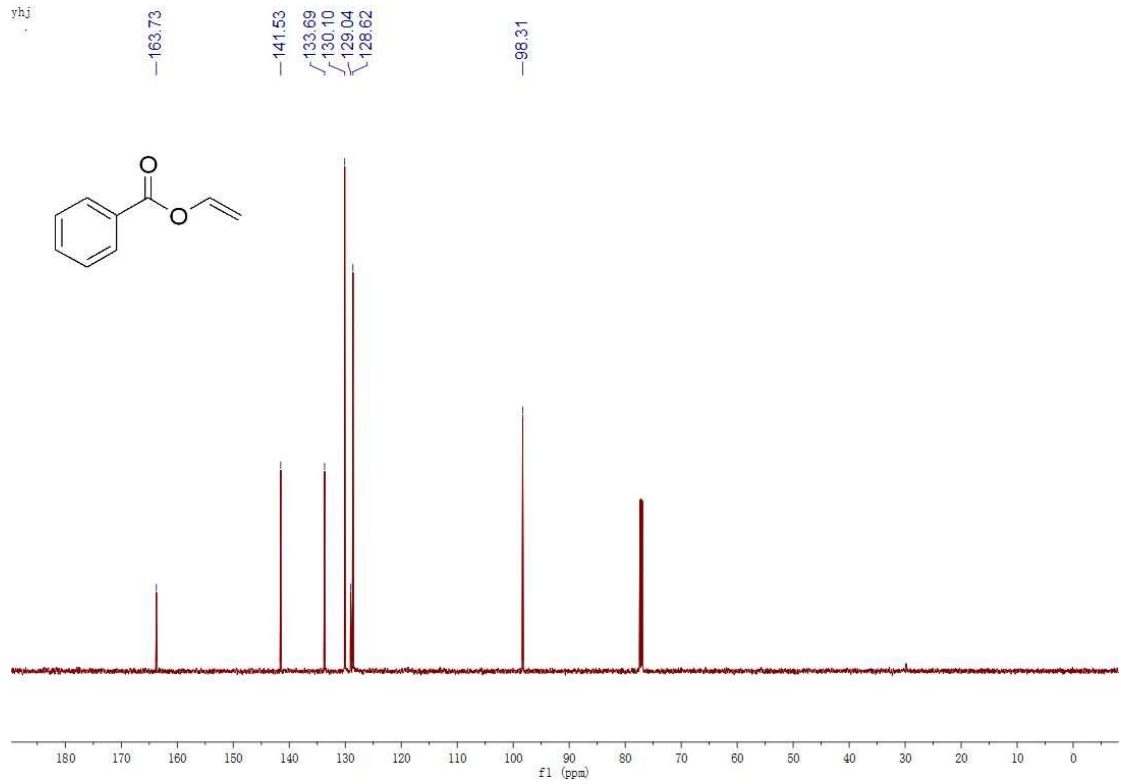**Vinyl 4-nitrobenzoate (Table 1, entry 8)**

Yellow solid (82%).   ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 8.32 (ddd, J = 24.5, 7.0, 1.9 Hz, 4H), 7.52 (dd, J = 13.9, 6.2 Hz, 1H), 5.17 (dd, J = 13.9, 2.0 Hz, 1H), 4.83 (dd, J = 6.2, 2.0 Hz, 1H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 161.92 (s), 151.01 (s), 141.23 (s), 134.46 (s), 131.23 (s), 123.81 (s), 99.63 (s). Physical and spectral data were consistent with those previously reported.[5]
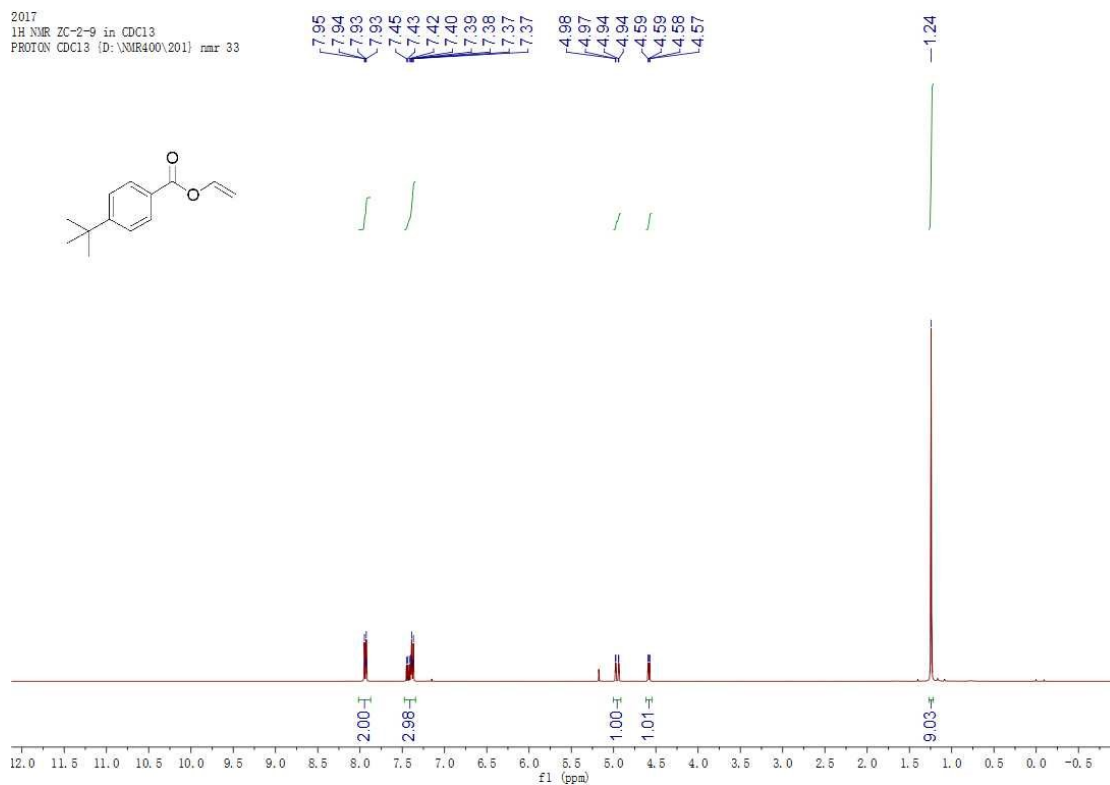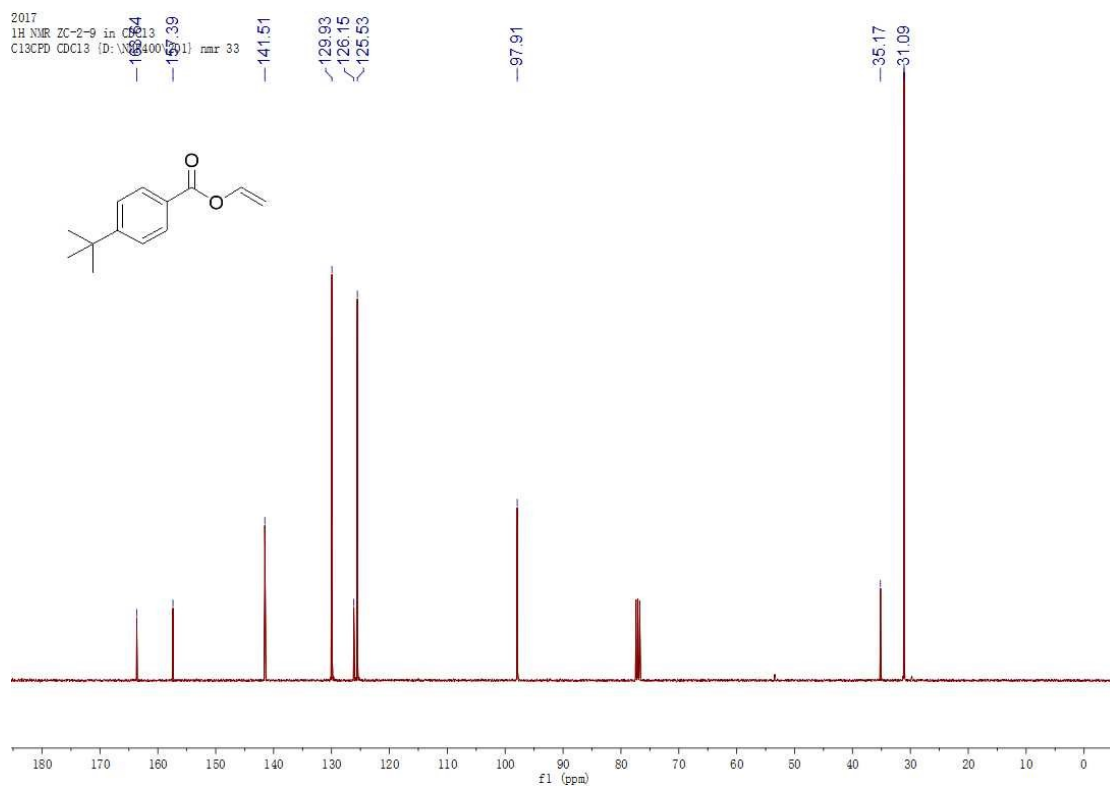
Characterization Spectrum

yhj
single_pulse

8.15
8.15
8.14
8.14
8.13
8.13
7.62
7.57
7.56
7.55
7.54
7.51
7.51
7.50
7.48
7.42
5.12
5.10
5.09
4.74
4.74
4.73
4.73

1.94
1.00
0.97
2.01
1.01
1.02

12.0 11.5 11.0 10.5 10.0 9.5 9.0 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.
f1 (ppm)

yhj

163.73
141.53
133.69
130.10
129.04
128.62
98.31

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7.95
7.94
7.93
7.45
7.43
7.42
7.40
7.39
7.38
7.37
7.37
4.98
4.97
4.94
4.94
4.59
4.58
4.57
1.24

2.00
2.98
1.00
1.01
9.03

12.0 11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

141.51
129.93
126.15
125.53
97.91
35.17
31.09

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7.99
7.98
7.52
7.51
7.50
7.49
7.26
7.25

5.06
5.06
5.04
5.03
4.68
4.68
4.67
4.67

2.41

1.97
0.94
2.10

1.00
1.00

3.03

10.5 10.0 9.5 9.0 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
f1 (ppm)

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144.52
141.56

130.13
129.34
126.26

98.01

21.82

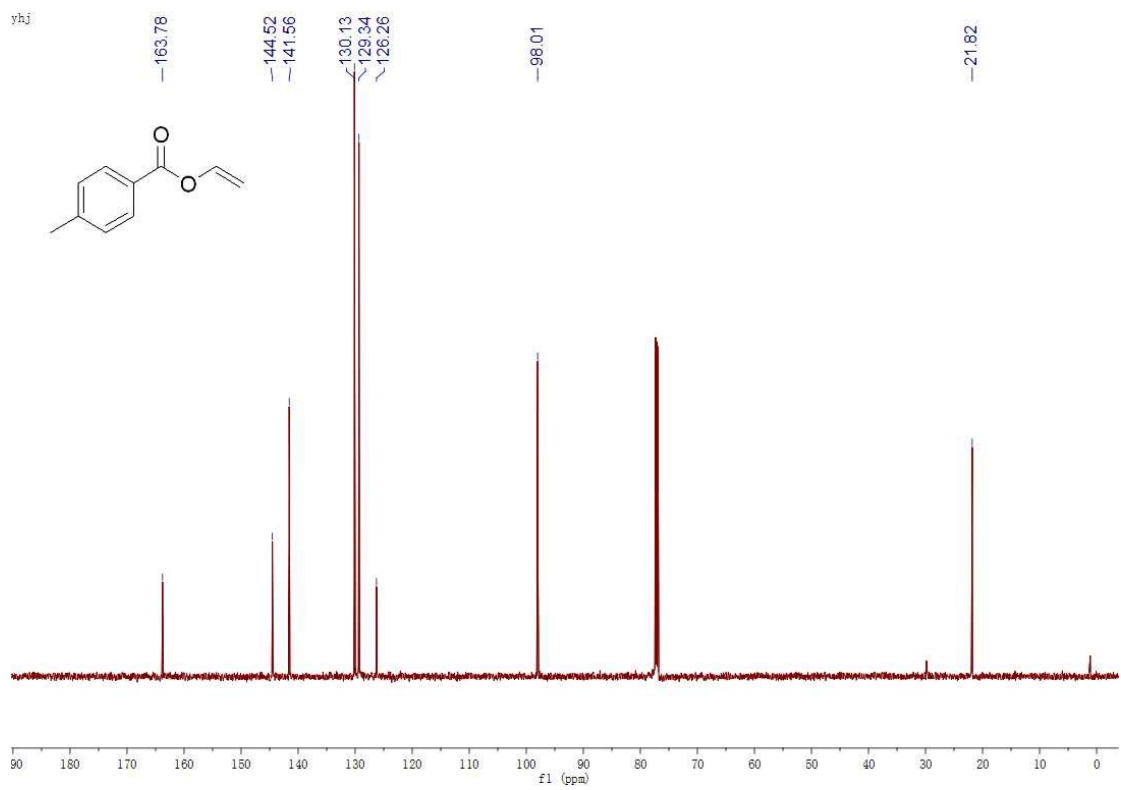90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
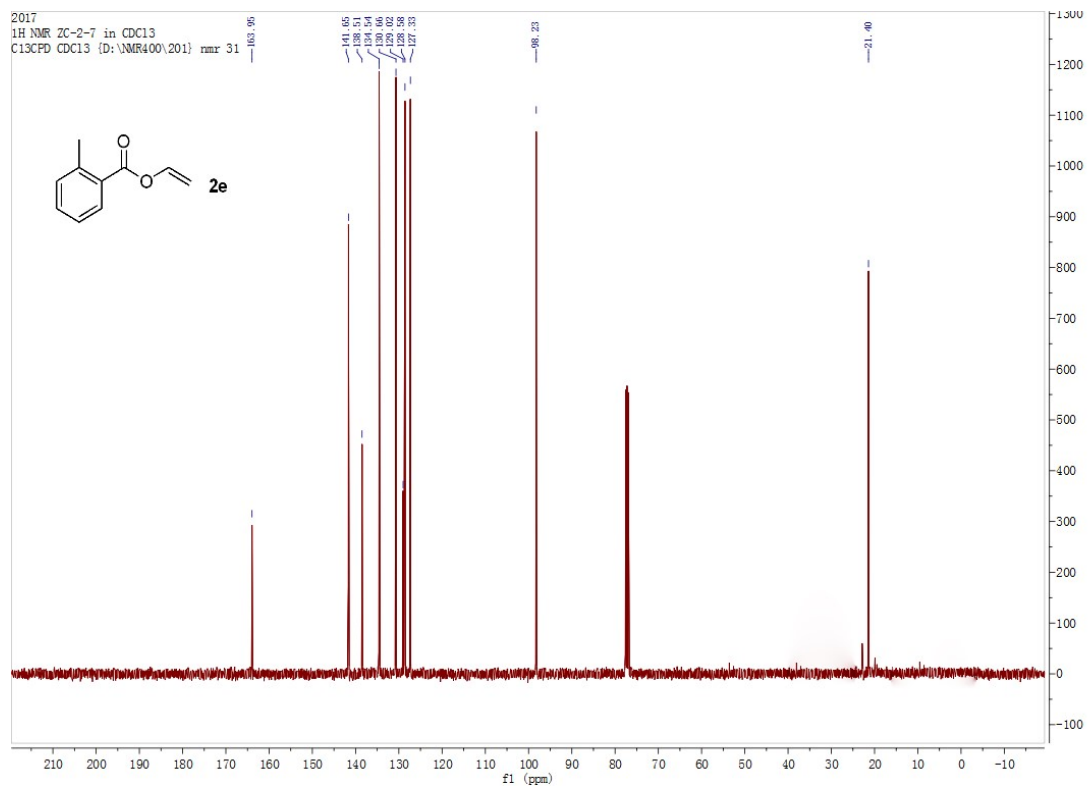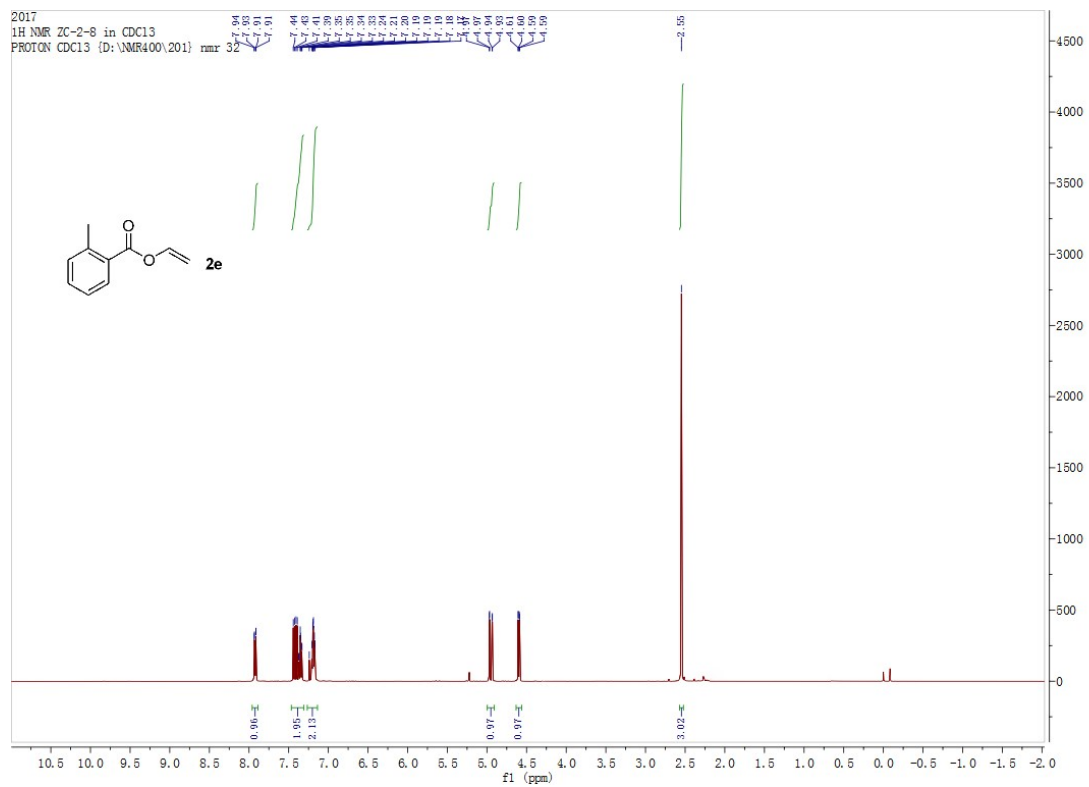f1 (ppm)

2017
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PROTON CDC13 {D:\NMR400\201} nmr 32

2e

2017
1H NMR ZC-2-7 in CDC13
C13CPD CDC13 {D:\NMR400\201} nmr 31

2e

7.82
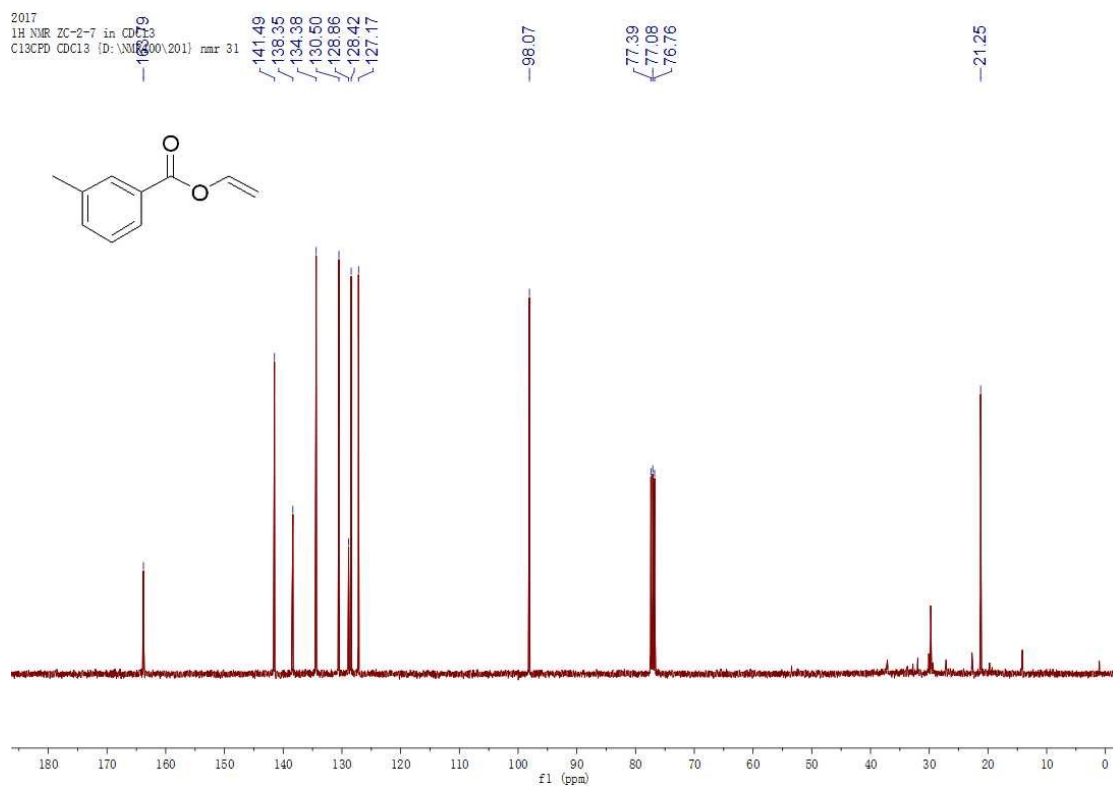7.80
7.45
7.43
7.41
7.40
7.29
7.27
7.25

4.99
4.99
4.96
4.95
4.61
4.60
4.59
4.59

2.31

1.98
1.03
2.03
1.00
0.99
2.98

12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

141.49
138.35
134.38
130.50
128.86
128.42
127.17

98.07

77.39
77.08
76.76

21.25

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
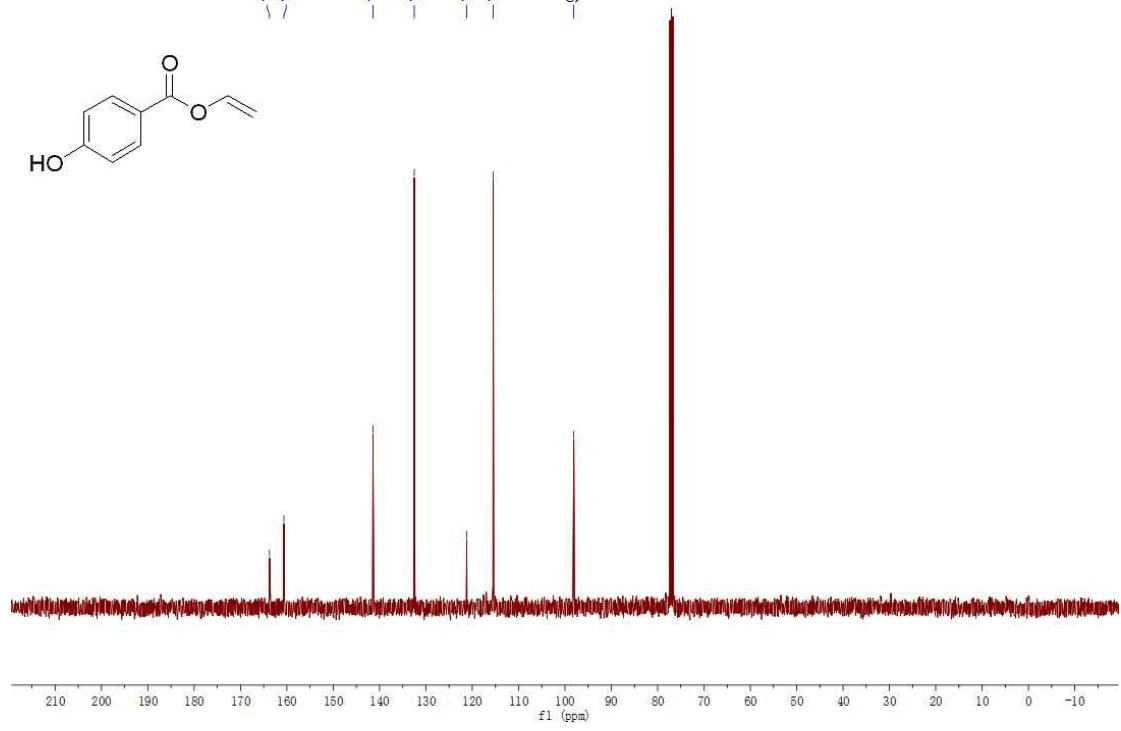f1 (ppm)

8.04 8.04 8.03 8.02 8.01 8.01 7.49 7.47 6.92 6.91 6.90 6.88 6.88 5.07 5.06 5.03 5.03 4.70 4.69 4.68 4.68

1.99 0.97 2.01 1.03 1.00 1.00

11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)
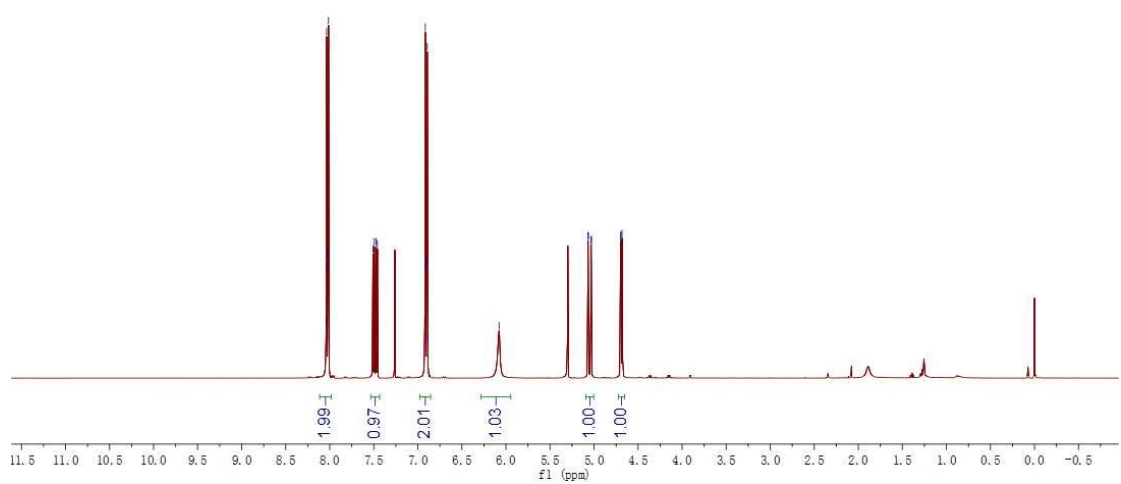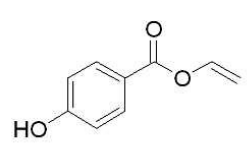
163.74 160.63 141.41 132.51 121.18 115.49 98.10

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8.04
8.04
8.04
8.03
8.03
8.02
7.52
7.51
7.49
7.48
7.45
7.44
7.44
7.43
5.09
5.09
5.07
5.07
4.73
4.73
4.72
4.72

2.00
0.94
2.00
1.02
1.03

1.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

yhj

162.81
141.37
140.22
131.42
128.99
127.64
98.57

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8.35
8.35
8.34
8.31
8.31
8.30
8.30
7.54
7.53
7.52
7.51

5.19
5.18
5.16
4.83
4.83
4.82
4.82

4.08
0.95
0.98
0.99

12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

161.92
151.01
141.23
134.46
131.23
123.81
99.63

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1.   K. Ishihara and N. Nakajima, *J. Mol. Catal. B: Enzym.*, 2003, **23**, 411-417.
2.   T. Carmona, N. Fernández-Peña, M. P. Tarazona, E. Saiz and F. Mendicuti, *Eur. Polym. J.*, 2010, **46**, 1796-1809.
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