Supporting information for

$Mn(acac)_2/Ca(OTf)_2$-catalyzed short to middle-length aliphatic aldehyde oxidations to the corresponding acids through dioxygen activation

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Content

1. Analytic method

In the present study, the corresponding aliphatic acid was employed as the solvent for aliphatic aldehyde oxidation, which caused the challenge in determining the yield of the produced acid. Accordingly, the following procedure is introduced to determine the acid yield. This method relies on mass balance and internal standard calibration by subtracting the mass of initial solvent acid from the mass of the total acid determined after reaction. A exampled analytic procedure with heptanal oxidation is described as follows:

1) Determining the mass of reaction mixtures

Before the reaction, a clean, dry 25 mL round-bottom flask equipped with a magnetic stir bar was weighed as m_{flask}. The exact mass of 8 mL of heptanoic acid as the solvent was weighed to the flask as m_{solvent}, and the exact mass of 2 mL heptanal was next weighed to the flask as m_{aldehyde}. Thus, the total initial mass (m_{initial}) is equal to m_{flask} plus m_{solvent} and m_{aldehyde}. It is worth mentioning that, herein, the weight of the catalyst is ignored in the initial mass due to its very low content (<4 mg) comparing with that of aldehyde added (~1.6 g). After the reaction, the flask was cooled down to the room temperature and weighed again as the m_{final}. The total mass of the post-reaction mixtures is calculated as:

$$m_{total\ mixture} = m_{final} - m_{flask}$$

2) Preparing the sample for GC analysis

An aliquot of 1 mL reaction mixtures was withdrawn from the above flask, and transferred into a 5 mL weighed centrifuge tube, which was weighed again to give the mass of this 1 mL reaction mixtures as m_{aliquot}. To this aliquot, 2 mL of acetone was added as the diluent, followed by adding 140.0 mg biphenyl as the internal standard. The resulting solution was analyzed GC to determine the content of aliphatic acid in this 1 mL aliquot.

3) GC analysis and quantification

GC analysis was performed on a GC9310-VI instrument equipped with a CB-WAX capillary column (30 m × 0.32 mm, 0.3 μm film thickness) and a flame ionization detector (FID). The injector and detector temperatures were set at 250 °C and 280 °C, respectively. The oven temperature was programmed: initial 130 °C held for 2 min, then ramped at 10 °C/min to 220 °C and held for 2 min. After GC analysis of the diluted aliquot, the mass of heptanoic acid in the diluted aliquot ($m_{\text{acid, aliquot}}$) is calculated according to the following equation:

$$m_{acid,\ aliquot} = \bar{f}_{acid/IS} \times \frac{A_{acid}}{A_{IS}} \times m_{IS}$$

Where A_{acid} and A_{IS} are the peak areas of heptanoic acid and biphenyl in GC graph, respectively, m_{IS} is the mass of biphenyl added to the aliquot as the internal standard, $\bar{f}_{acid/IS}$ is the mean relative correction factor of aliphatic acid. The $\bar{f}_{acid/IS}$ value was determined using the same batch of heptanoic acid as employed in the catalytic reactions, and the actual concentration of the heptanoic acid standard solution was corrected based on its certified purity (98%) prior to calibration.

Because the 1 mL aliquot was withdrawn from the whole post-reaction mixtures, accordingly, the total mass of heptanoic acid in the reaction mixtures ($m_{acid,\ total}$) is calculated as follows:

$$m_{acid,total} = m_{acid,aliquot} \times \frac{m_{total\ mixture}}{m_{aliquot}}$$

4) Correction of the initial solvent

Since the initial heptanoic acid solvent (8 mL) has a purity of 98 wt%, its mass ($m_{solvent}$) is corrected as:

$$m_{acid,intial} = m_{solvent} \times 0.98$$

Similarly, the mass of initial heptanal substrate was corrected using its purity of 97 wt%:

$$m_{aldehyde,intial} = m_{aldehyde} \times 0.97$$

Accordingly, the mass of heptanoic acid produced in heptanal oxidation is calculated as follows:

$$m_{acid,produced} = m_{acid,total} - m_{acid,initial}$$

5) Yield calculation

The theoretical maximum mass of heptanoic acid from 2 mL of heptanal is calculated as follows:

$$m_{acid,\ theoretical} = \frac{m_{aldehyde,initial}}{114.18} \times 130.18\ g$$

Where 114.18 g/mol is the molecular weight of heptanal, and 130.18 g/mol is the molecular weight of heptanoic acid.

Accordingly, the yield of heptanoic acid is calculated as follows:

$$Yield = \frac{m_{acid,\ produced}}{m_{acid,\ theoretical}} \times 100\%$$

2. Method for the determination of the viscosity

The test liquid was prepared by mixing 2 mL of aldehyde and 8 mL of the corresponding acid. The viscosity was measured at 20 °C using a Pinkevitch capillary viscometer with a constant of 0.008774 mm^2/s^2.

Before the measurement, the viscometer was thoroughly cleaned, dried, and mounted vertically in a constant-temperature water bath maintained at 20.0 °C. Exact 2 mL of aldehyde and 8 mL of the corresponding acid were transferred by pipette and mixed. An appropriate volume of the resulting mixture was introduced into the filling bulb of the viscometer, ensuring that the liquid level fell between the upper and lower filling marks. The viscometer was then equilibrated in the water bath for 15 min to allow the sample to attain a uniform temperature.

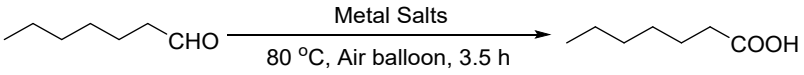
After equilibration, the liquid was drawn up the capillary arm using a rubber bulb to a position approximately 5 mm above the upper timing mark and allowed to flow freely. The efflux time required for the liquid meniscus to pass from the upper to the lower timing mark was measured with a stopwatch readable to 0.01 s. At least three replicated measurements were carried out, and the flow times were required not to differ by more than 1 s; the mean value was taken as the flow time t (unit: s).

The viscosity of the test system, v, was calculated according to Equation (1):

$$v = K \times t$$

where v is the viscosity in , K is the viscometer constant (0.008774 mm^2/s^2), and t is the average flow time in seconds.

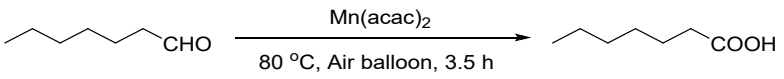
Table S1 The influence of simple metal salts on heptanal oxidation[a]



Entry	Metal Salts	Conv. (%)	Yield (%)
1	-	65	55
2	$Mn(OAc)_2$	99	70
3	$Fe(OAc)_2$	81	63
4	$Cu(OAc)_2$	68	46
5	$Co(OAc)_2$	98	62
6	$MnCl_2$	96	66
7	$FeCl_2$	73	60
8	$FeCl_3$	80	50
9	$CoCl_2$	96	59

[a]Conditions: heptanal 2 mL, metal salts 4 μmol, heptanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

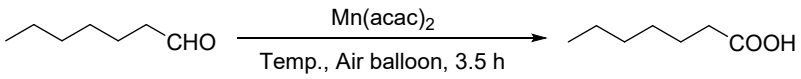
Table S2 The influence of the volume ratio of solvent on heptanal oxidation[a]



Entry	Aldehyde : Acid (mL : mL)	Conv. (%)	Yield (%)
1	1:9	99	53
2	2:8	99	82
3	4:6	77	58
4	6:4	52	35
5	8:2	44	24
6	9:1	36	23

[a]Conditions: $Mn(acac)_2$ 2 μmol per 1 mL heptanal, the total volume of heptanal and acid 10 mL, air balloon, 80 °C, 3.5 h.

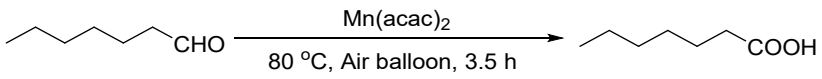
Table S3 The influence of temperature on heptanal oxidation[a]



Entry	Temp. (°C)	Conv. (%)	Yield (%)
1	60	80	62
2	70	95	71
3	80	99	82
4	90	99	78

[a]Conditions: heptanal 2 mL, $Mn(acac)_2$ 4 μmol, heptanoic acid 8 mL, air balloon, 3.5 h.

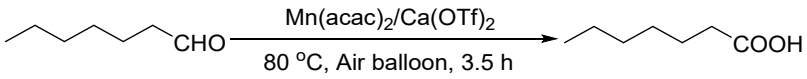
Table S4 The influence of the $Mn(acac)_2$ loading on heptanal oxidation[a]



Entry	Catalyst (μmol)	Conv. (%)	Yield (%)
1	0.2	74	58
2	0.5	80	60
3	1	96	71
4	2	99	72
5	4	>99	82
6	8	>99	80

[a]Conditions: heptanal 2 mL, heptanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

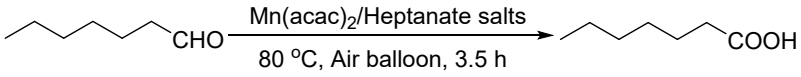
Table S5 The influence of $Ca(OTf)_2$ loading on catalytic efficiency[a]



Entry	$Ca(OTf)_2$ Content (μmol)	Conv. (%)	Yield (%)
1	2	99	72
6	4	99	80
7	8	99	85
8	16	95	78

[a]Conditions: heptanal 2 mL, $Mn(acac)_2$ 4 μmol, heptanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

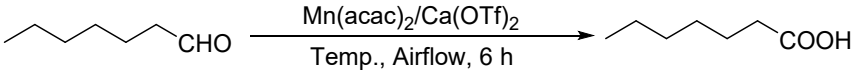
Table S6 The influence of heptanate salts on catalytic efficiency[a]



Entry	Heptanate salts	Heptanate Salts Content (μmol)	Conv. (%)	Yield (%)
1	R_6COOK	4	99	79
2	$(R_6COO)_2Ca$	4	99	87
3	R_6COOK	8	99	84
4	$(R_6COO)_2Ca$	8	98	85

[a]Conditions: heptanal 2 mL, $Mn(acac)_2$ 4 μmol, heptanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

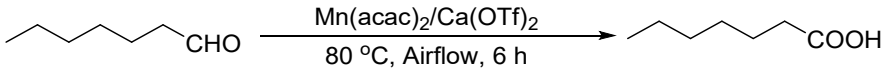
Table S7 The influence of temperature on 40 mL-level reaction[a]



Entry	Temp. (°C)	Conv. (%)	Yield (%)
1	60	35	20
2	70	98	75
3	80	99	87
4	90	99	80

[a]Conditions: heptanal 8 mL, $Mn(acac)_2$ 16 μmol, $Ca(OTf)_2$ 32 μmol, heptanoic acid 32 mL, airflow 60 mL/min at 1 atm, 6 h.

Table S8 The influence of airflow rate on 40 mL-level reaction[a]



Entry	Flow rate (mL/min)	Conv. (%)	Yield (%)
1	10	92	63
2	20	99	73
3	40	99	81
4	60	99	87
5	80	99	85
6	100	99	84

[a]Conditions: heptanal 8 mL, $Mn(acac)_2$ 16 μmol, $Ca(OTf)_2$ 32 μmol, heptanoic acid 32 mL, airflow at 1 atm, 80 °C, 6 h.

Table S9 $Mn(acac)_2/Ca(OTf)_2$-catalyzed oxidations of aliphatic aldehydes in acetic acid[a]

Entry	Aldehyde	Conv. (%)	Yield (%)
1	Pentanal	>99	86
2	Hexanal	>99	88
3	Heptaanl	>99	85
4	Octanal	>99	90
5	Nonanal	>99	86
6	Decanal	>99	89
7	Undecanal	>99	87
8	Dodecanal	>99	87

[a] Conditions: aldehyde 2 mL, $Mn(acac)_2$ 4 μmol, $Ca(OTf)_2$ 8 μmol, acetic acid 8 mL, air balloon, 80 °C, 3.5 h.

Table S10 $Mn(acac)_2/Ca(OTf)_2$-catalyzed oxidations of aliphatic aldehydes in heptanoic acid[a]

Entry	Aldehyde	Conv. (%)	Yield (%)
1	Pentanal	>99	84
2	Hexanal	>99	89
3	Heptaanl	>99	85
4	Octanal	>99	91
5	Nonanal	>99	86
6	Decanal	>99	89
7	Undecanal	>99	87
8	Dodecanal	>99	89

[a] Conditions: aldehyde 2 mL, $Mn(acac)_2$ 4 μmol, $Ca(OTf)_2$ 8 μmol, heptanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

Table S11 $Mn(acac)_2/Ca(OTf)_2$-catalyzed oxidations of aliphatic aldehydes in octanoic acid[a]

Entry	Aldehyde	Conv. (%)	Yield (%)
1	Pentanal	>99	89
2	Hexanal	>99	90
3	Heptaanl	>99	88
4	Octanal	>99	95
5	Nonanal	>99	89
6	Decanal	>99	91
7	Undecanal	>99	87
8	Dodecanal	>99	88

[a] Conditions: aldehyde 2 mL, $Mn(acac)_2$ 4 μmol, $Ca(OTf)_2$ 8 μmol, octanoic acid 8 mL, air balloon, 80 °C, 3.5 h.

Table S12 The viscosity of the initial reaction mixtures[a]

Entry	Aldehyde/Acid	Viscosity (mm^2/s)
1	Pentanal/Pentanoic acid	2.1
2	Hexanal/Hexanoic acid	2.7
3	Heptanal/Heptanoic acid	3.9
4	Octanal/Octanoic acid	4.6
5	Nonanal/Nonanoic acid	7.0

[a]The viscosity data were determined with a Pinkevitch viscometer at 20 ^oC, using 2 mL of aldehyde and 8 mL of the corresponding acid as the reaction mixtures.

Table S13 Relative contents of the by-products in heptanal oxidation based on their peak areas in GC-MS analysis

Entry	By-product	Peak area	Relative Area Ratio (%)
1	Ketone	42324	12.3
2	γ-Heptalactone	38857	11.2
3	Hexanoic acid	80526	23.2
4	Heptanoic anhydride	184917	53.3

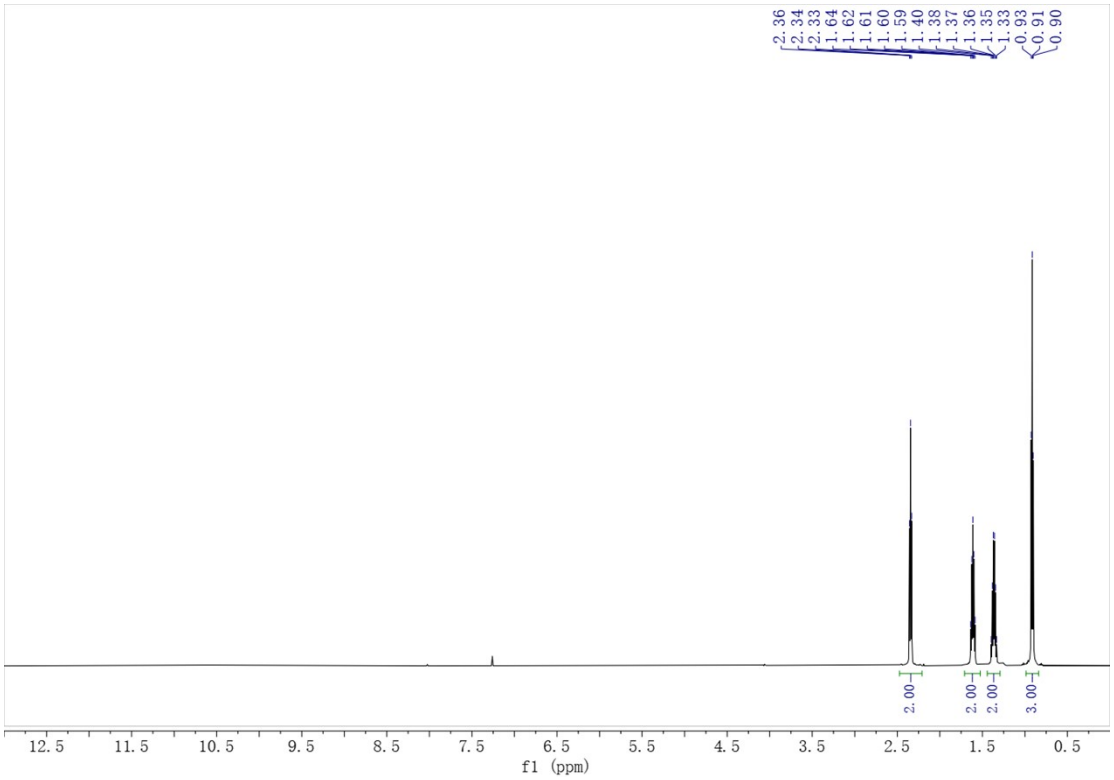


Fig. S1 ^{1}H NMR spectrum of the pentanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.6 Hz, 2H), 1.61 (p, J = 7.5 Hz, 2H), 1.36 (h, J = 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H).

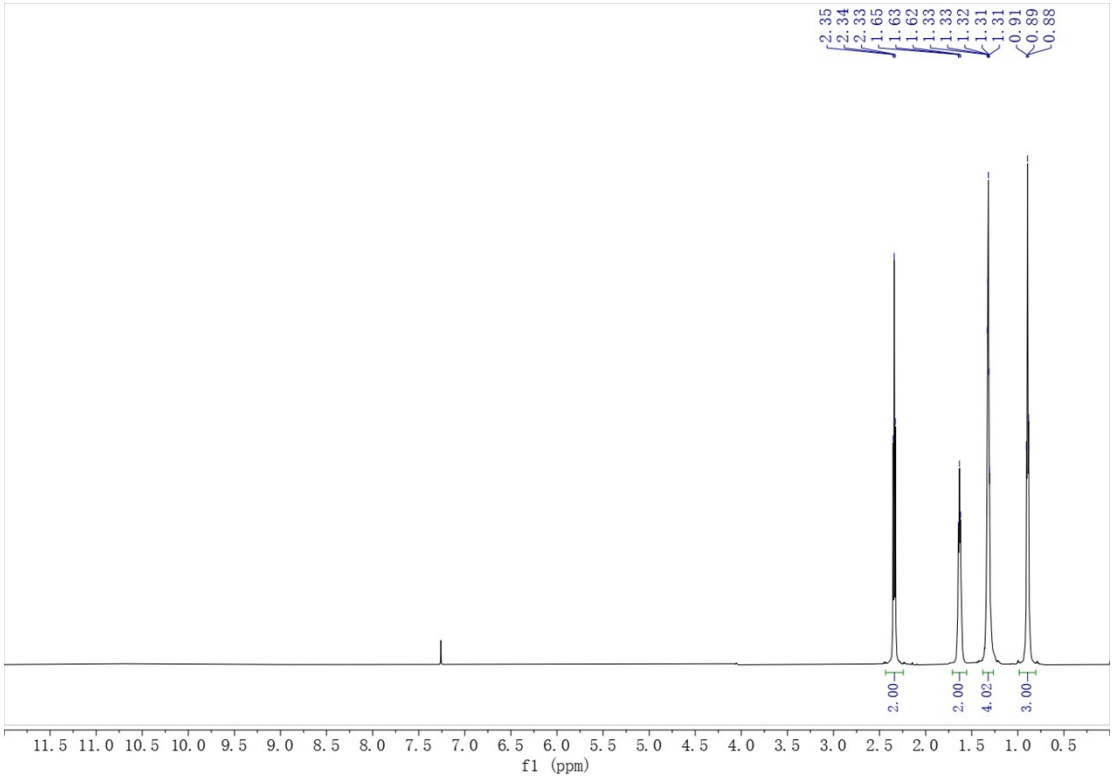


Fig. S2 ^{1}H NMR spectrum of the hexanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.6 Hz, 2H), 1.63 (t, J = 7.4 Hz, 2H), 1.32 (p, J = 3.8 Hz, 4H), 0.89 (t, J = 7.0 Hz, 3H).

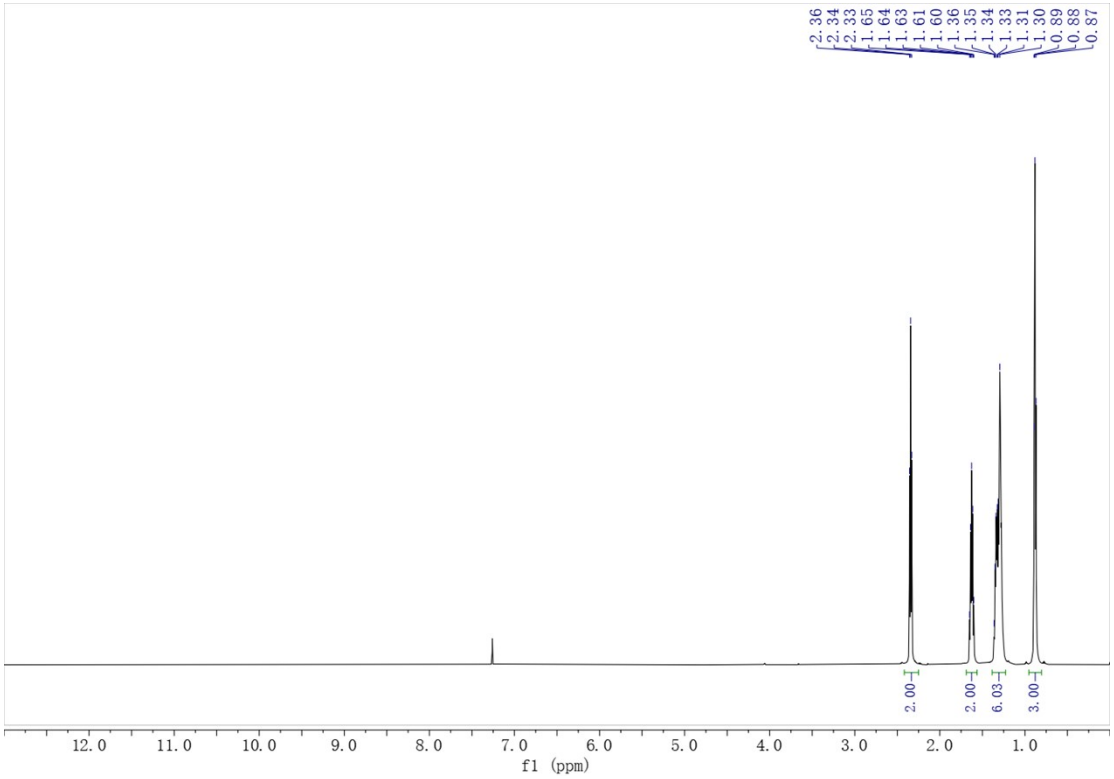


Fig. S3 ^{1}H NMR spectrum of the heptanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.5 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.39 – 1.23 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H).

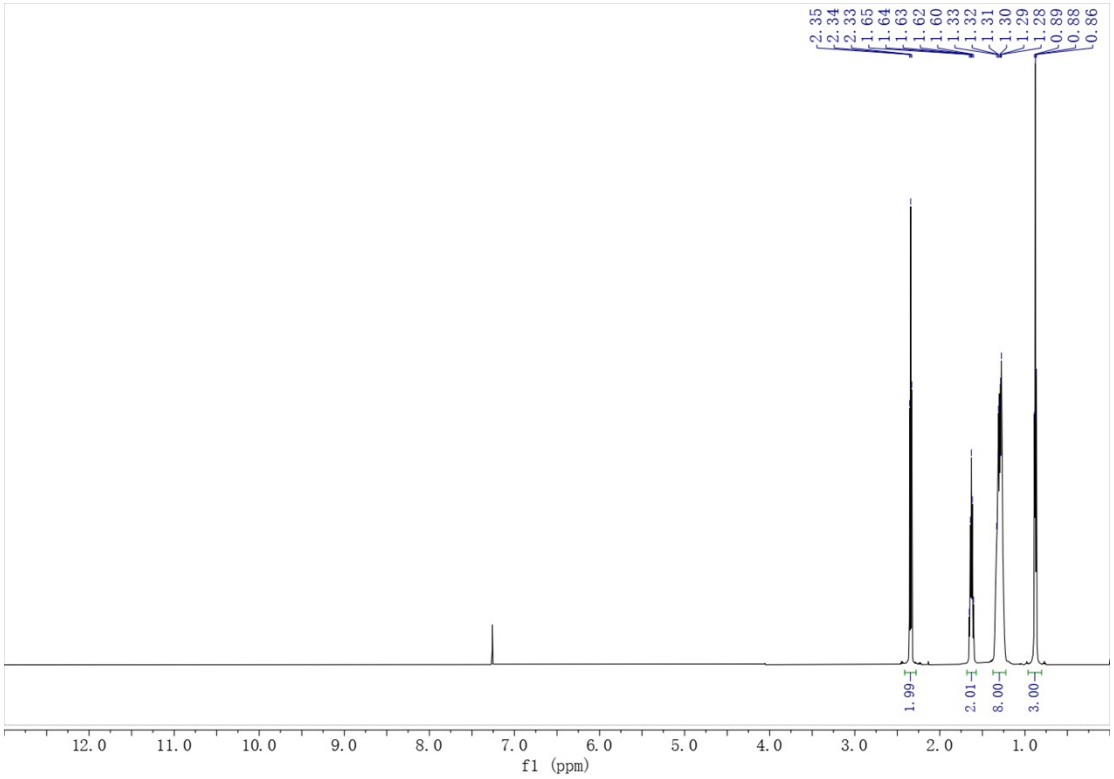


Fig. S4 ^{1}H NMR spectrum of the octanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, *J* = 7.5 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.38 – 1.22 (m, 8H), 0.96 – 0.80 (m, 3H).

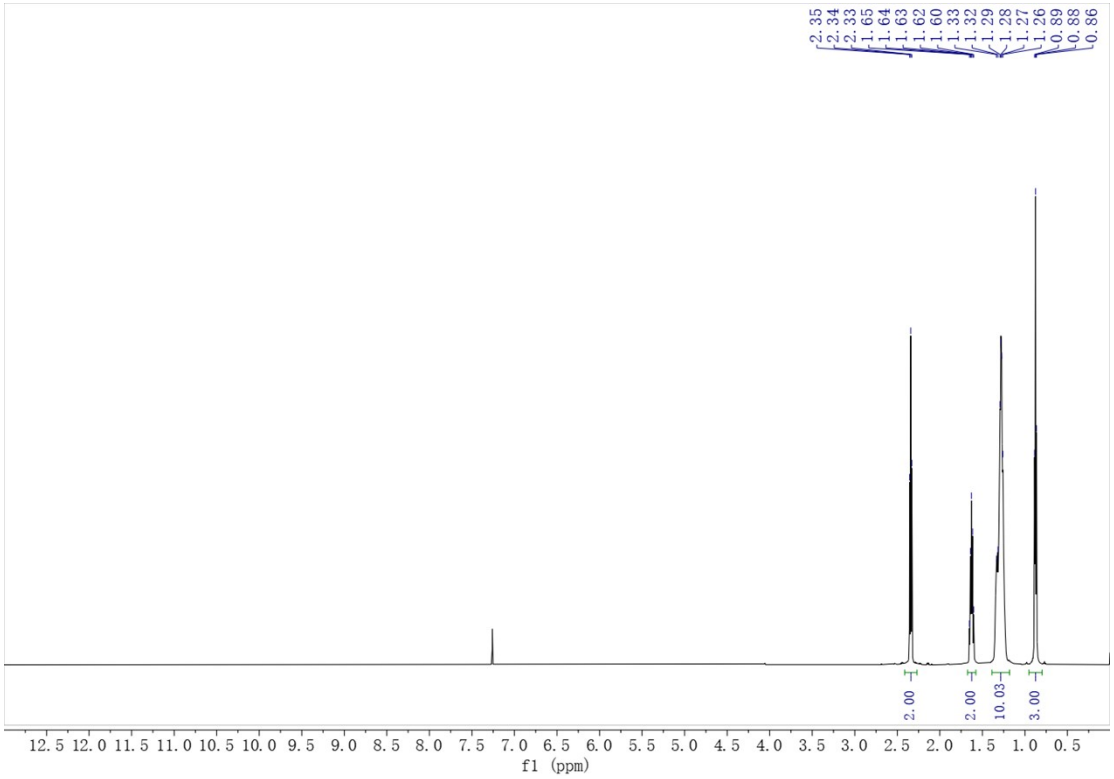


Fig. S5 ^{1}H NMR spectrum of the nonanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.6 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.39 – 1.18 (m, 10H), 0.88 (t, J = 7.1 Hz, 3H).

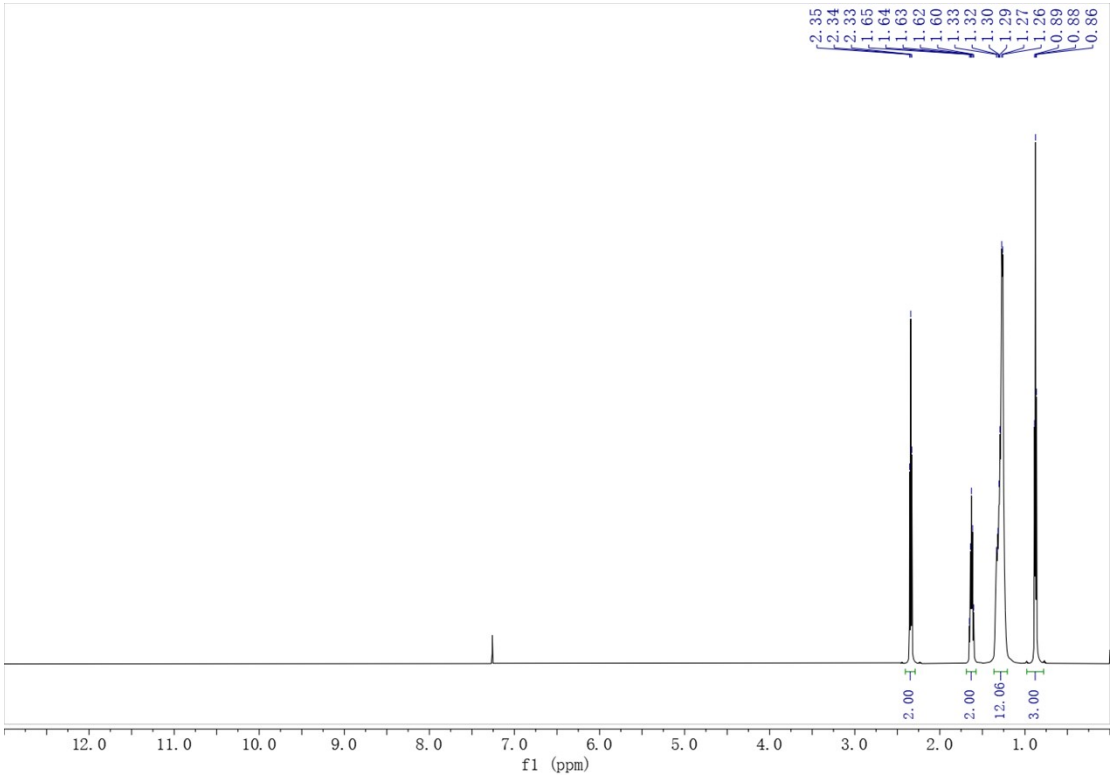


Fig. S6 ^{1}H NMR spectrum of the decanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.5 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.36 – 1.21 (m, 12H), 0.88 (t, J = 7.1 Hz, 3H).

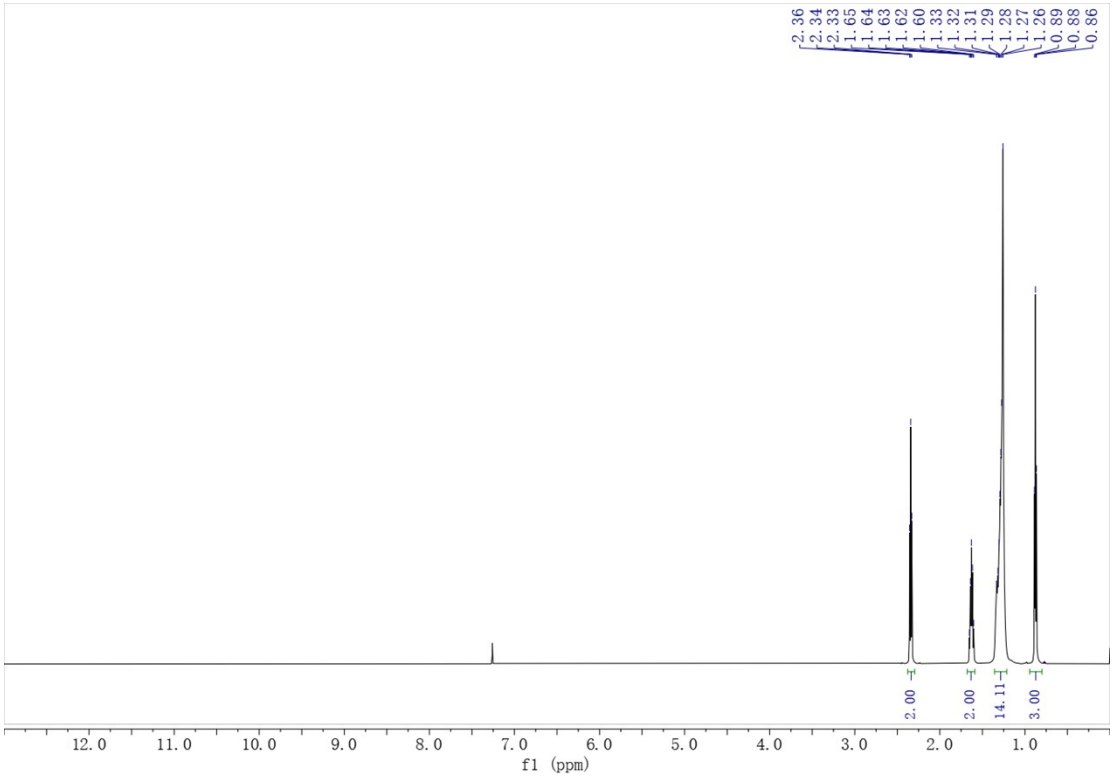


Fig. S7 ^{1}H NMR spectrum of the undecanoic acid reaction solution after oxidation in $CDCl_3$

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.6 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.36 – 1.21 (m, 14H), 0.88 (t, J = 7.1 Hz, 3H).

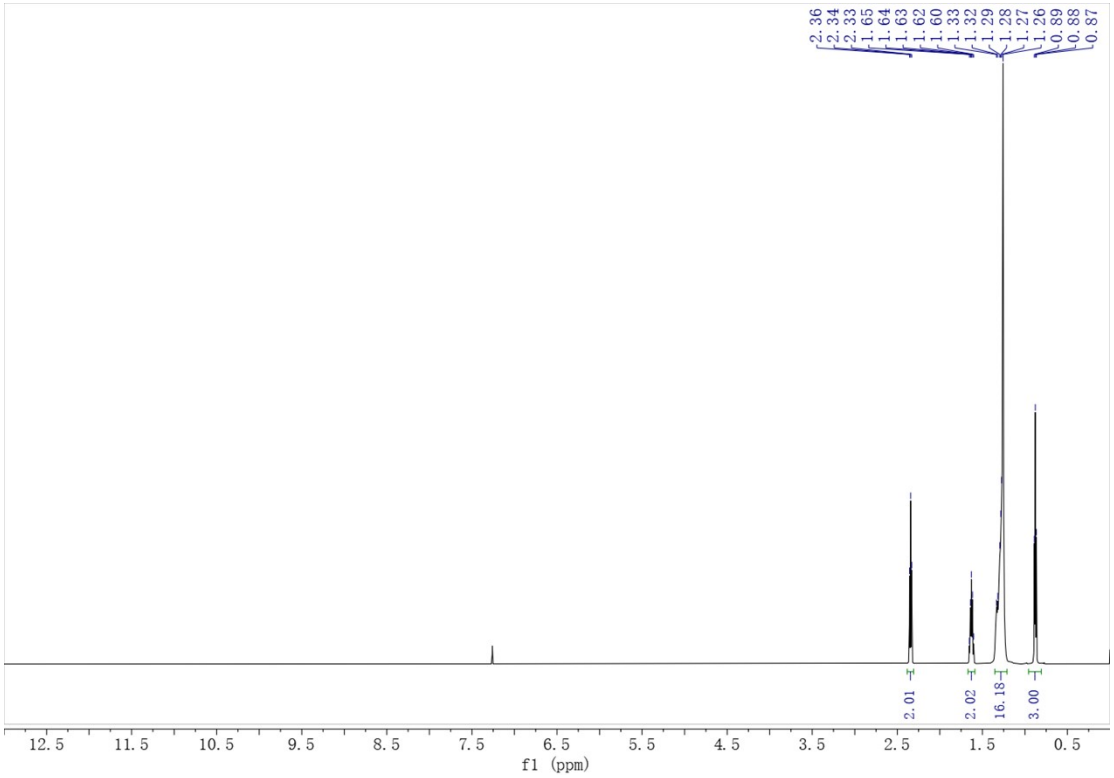
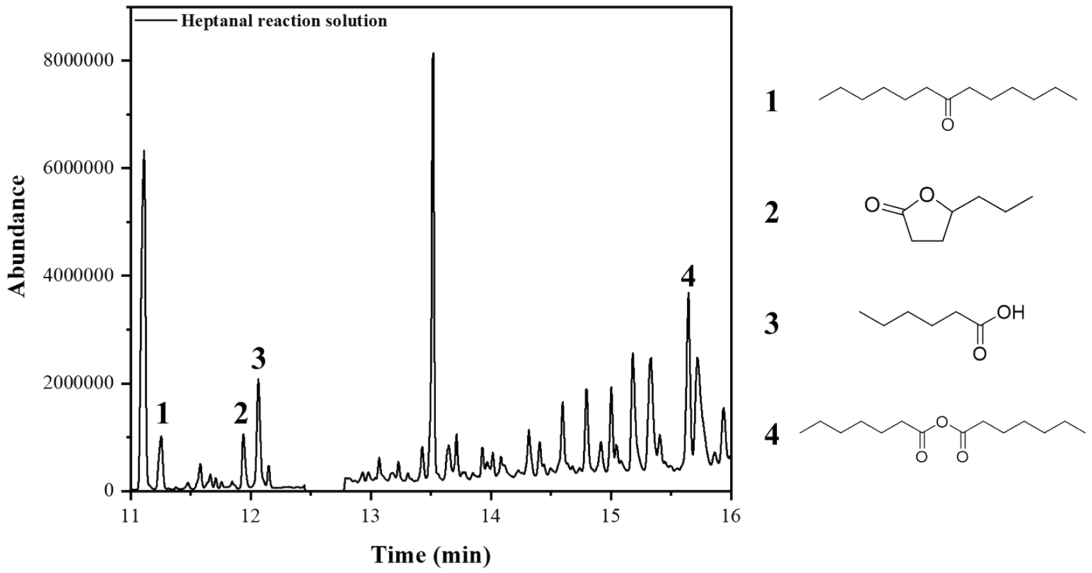


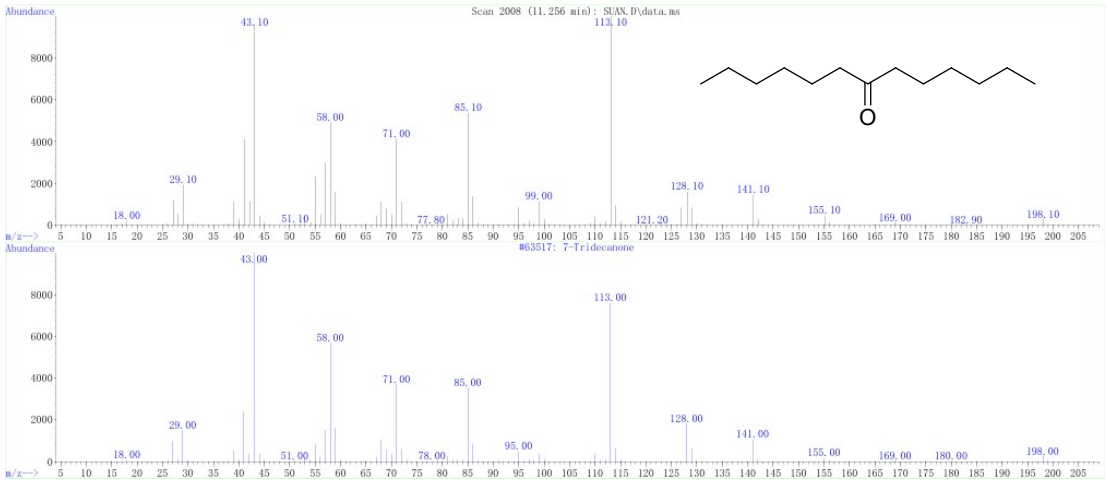
Fig. S8 ^{1}H NMR spectrum of the dodecanoic acid reaction solution after oxidation in $CDCl_3$

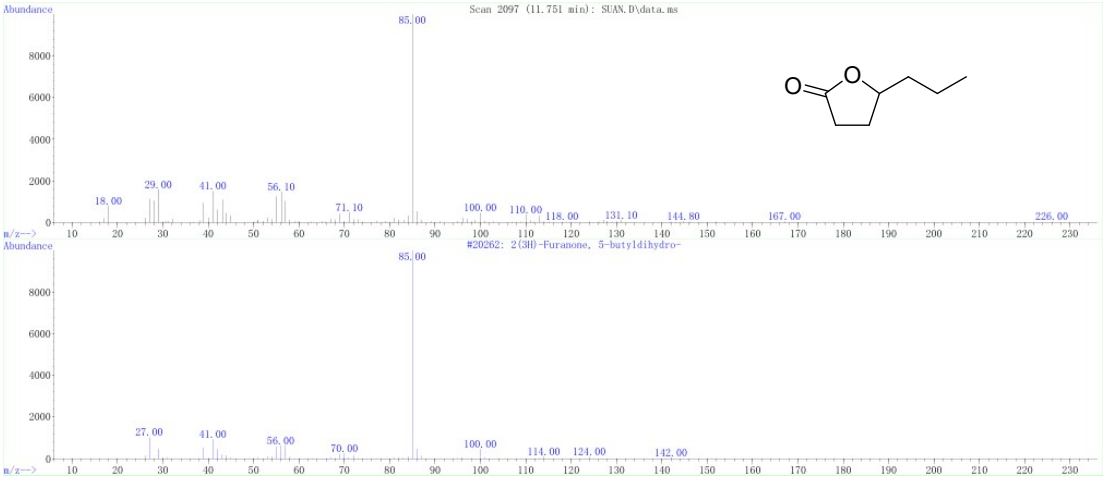
^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (t, J = 7.5 Hz, 2H), 1.63 (p, J = 7.5 Hz, 2H), 1.35 – 1.21 (m, 16H), 0.88 (t, J = 7.1 Hz, 3H).

Fig. S9 GC and GC-MS graphs of the by-products in GC-MS analysis of heptanal oxidation[a]



[a] The sample was prepared by vacuum distillation of the post-reaction mixtures of heptanal oxidation using a Claisen-type distillation head connected to a Vigreux column. Other peaks are assigned to the compounds containing heteroatoms according to the data-base of GC-MS instrument (e.g., Si), possibly due to the damage of GC-MS column in analysis.

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226.00
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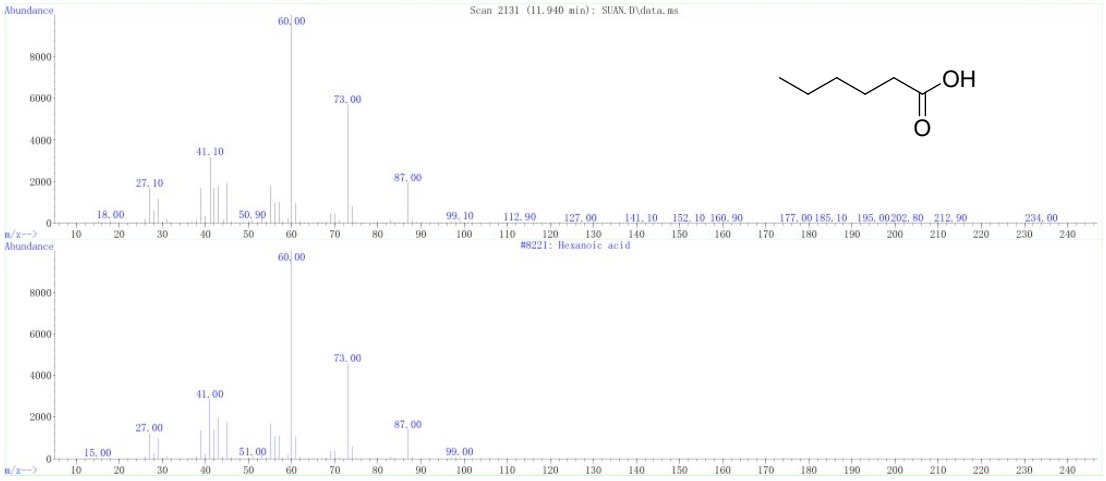
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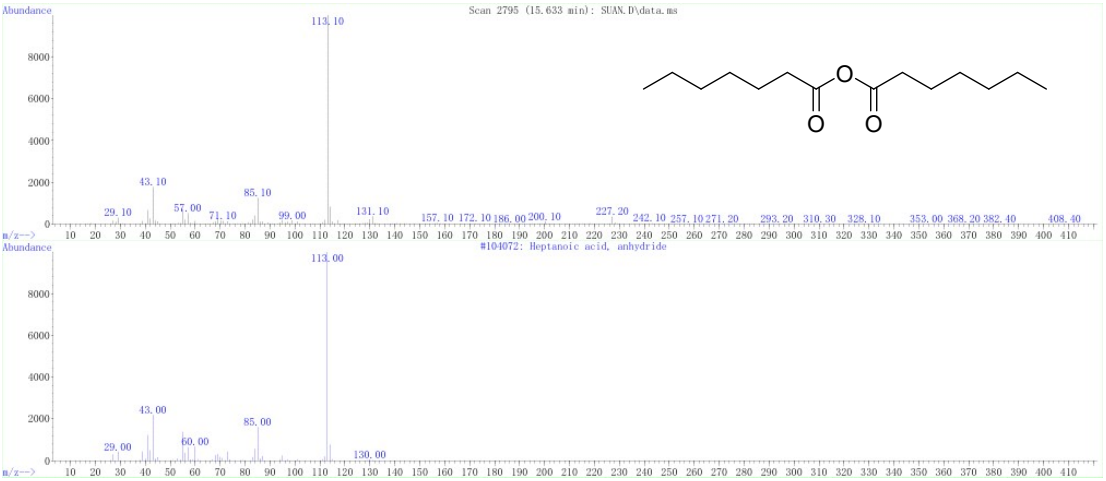
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