Electronic Supplementary Material (ESI) for Green Chemistry.
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Supporting Information

The Carbon Material Functionalized with NH_2^+ and SO_3H Groups Catalyzed Esterification with High Activity and Selectivity

Shaoqi Zhan,[a] Xiaochun Tao,*[a] Liangzhen Cai,*[a] Xiaohui Liu,[a] and Taoping Liu*[b]

[a] School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China

E-mail: xctao@ecust.edu.cn

[b] Suzhou Eleco Chemical Industry CO., Ltd. 608 Xiao Shu Road, Kunshan, Jiangsu 215341, P.R. China

1. General information

a. Chemicals and materials

D-glucose, *p*-toluenesulfonic acid monohydrate, diphenylamine, ethanol, 4-phenylbutyric acid, octanol, 2-phenylethyric acid, hexanol, benzyl alcohol, pivalic acid, 3-cyclopentenecarboxylic acid, dodecanoic acid, octadecanoic acid, benzoic acid, allyl alcohol, propargyl alcohol, cyclohexanol, dodecanol, citric acid, butanol, hexanoic acid, glycerol, cinnamic acid, trans-crotonic acid, ethyl acetate, toluene, heptane, hexane, deuterated chloroform, deuterated water, sodium hydroxide, potassium bromide were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Dimesitylammonium pentafluorobenzenesulfonate, Cyclododecanol, (-)-menthol, were purchased from TCI (Shanghai) Development Co., Ltd.. All the chemicals were of chemically pure and used as received. Highly purified nitrogen (≥ 99.99%) was supplied by East China University of Science and Technology. Deionized water was used to prepare the solutions.

b. Physical characterizations

The X-Ray diffraction (XRD) measurement was performed in the θ–2θ mode using a Bruker D8 Focus diffractometer ($CuK\alpha_1$ radiation, $\lambda = 1.5406$ Å), operated at 40 kV and 40 mA (scanning step: 0.02 ^{o} per step). A fine powder sample was grinded, then put into the glass slide and pressed to make a flat surface under the glass slide.

The scanning electron microscopy (SEM) was performed with a JEOL JSM-63602V and Hitachi S-3400N microscope operated at 5 kV or 15 kV.

The thermal gravimetry analysis (TGA) was performed at a heating rate of 10 K/min from 40 to 800 ^{o}C in flowing air by using a WCT-2 thermal analyzer.

The Fourier transform infrared spectroscopy (FT-IR) was carried out on a Nicolet Nexus 670 FT-IR spectrometer in the range of 400–4000 cm^{-1}. The samples were ground along with KBr and then pressed into thin wafers before analysis.

The X-Ray photoelectron spectra (XPS) were measured using a Thermo ESCA LAB-250 spectrometer with monochromatic Al Kα radiation.

The ^{13}C magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C MAS

NMR) was measured at room temperature using a Bruker ASX200 spectrometer at a Larmor frequency of 50.3 MHz. A Bruker MAS probe head was used with a 7 mm zirconia rotor. The spinning rate of the sample was 4.0 or 4.5 kHz. The frequency of the spectra is expressed with respect to neat tetramethylsilane.

The element analysis (EA) was carried out on a vario EL Ⅲ elemental analyzer.

Trace analysis of S and N in solution were also detected by Sulfur and Nitrogen Fluorescence Analyzer (Antek 9000).

The NMR spectra were obtained using Brüker 400 or 500 MHz Fourier-transform NMR spectrometer. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz.

High resolution mass spectrometry (HRMS) data were obtained on Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization (ESI) in positive or negative mode.

Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and were uncorrected.

2. Preparation of the catalysts

GDTCSA: In a typical synthesis, 3.6 g glucose (20.0 mmol) and 1.9 g *p*-toluenesulfonic acid monohydrate (10.0 mmol) were mixed in toluene (40 mL) in 100 ml three-neck flask, then 3.41 g diphenylammonium tosylate (10.0 mmol) prepared in advance was added in the flask. The mixture was stirred by mechanical agitation under a flow of nitrogen, the water formed during the reaction and the toluene were distilled off while heating to 180 ^{o}C slowly. After reacting for 5 hours, the product was washed with hot toluene for 5 × 25 mL (toluene and 1.3 g *p*-toluenesulfonic acid were recovered) to get a black powder GDTCSA (5.7 g). IR (KBr): 1507, 1495, 1167, 1040, 1004 cm^{-1}; ^{13}C MAS NMR (50.3 MHz): 141, 140, 139, 130, 20 ppm (see article); EA: C% = 66.77, H% = 4.91, N% = 2.31, S%= 7.78.

GDCSA: GDTCSA (1.0 g) was reacted with 0.1 N aqueous NaOH (20 mL), the reactant was filtered after stirring for 1 h. The filtered aqueous phrase was concentrated and then recrystallized by EtOH to get a white solid sodium *p*-toluenesulfonate (w.t. 32%). m.p.□300 ^{o}C (reference [1] m.p.□300 ^{o}C); ^{1}H NMR (400 MHz, D_2O): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H) ppm.[1] The filter residue was washed with distilled water and dried to get a black powder GDCSA (w.t. 67%). IR (KBr): 1504, 1147, 1111, 1028, 1001 cm^{-1}. EA: C%=73.34, H%=5.35, N%=2.54, S%=1.95.

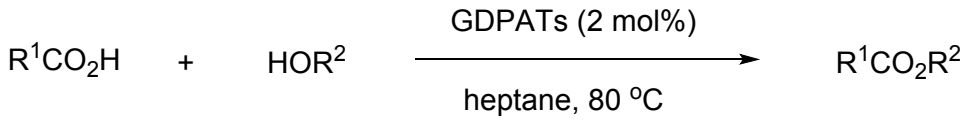
Diphenylammonium tosylate [2]**:** *p*-Toluenesulfonic acid monohydrate (3.8 g, 20.0 mmol) was added to a solution of diphenylamine (3.38 g, 20.0 mmol) in toluene (40 mL) in 100 mL flask at room temperature, and the mixture was stirred for 30 min. Evaporation of the solvent gave the crude product, which was washed with hexane (ca. 50 mL) to give a pure product diphenylammonium tosylate (6.8 g) as colorless crystals, the yield is 96%. m.p. = 130–132 ^{o}C (reference [2] m.p. = 128-130 ^{o}C); IR (KBr): 1619, 1590, 1491, 1474, 1432, 1250, 1233, 1134, 1123, 1035, 1006 cm^{-1};[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.23 (br, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.49 (m, 4H), 7.28 (s, 6H), 7.02 (d, *J* = 7.5 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 140.5, 137.5, 130.0, 129.0, 128.9, 125.9, 123.3, 21.3 ppm.[2]

GTCSA: *p*-Toluenesulfonic acid monohydrate (3.8 g, 20.0 mmol) was added to a solution of glucose (3.6 g, 20.0 mmol) in toluene (40 mL) in 100 mL three-neck flask.[4] The mixture was stirred by mechanical agitation under a flow of nitrogen. The water was formed during the reaction and the toluene was distilled off while heating to 180 ^{o}C slowly. After reacting for 5 hours, the product was washed with hot toluene for 5 times to get a black powder GTCSA (1.9 g). IR (KBr): 1156, 1114, 1031, 1004 cm^{-1}; ^{13}C MAS NMR (50.3 MHz): 137, 130, 20 ppm.[5]

3. Esterification reaction catalyzed by GDTCSA

a. Typical procedure

The reaction mixture, carboxylic acid (2.0 mmol), alcohol (2.0 mmol), 2 mol% of GDTCSA (2.43 mmol NH_2^+ and $SO_3H \cdot g^{-1}$; 16 mg, 0.04 mmol), and heptane (4 mL), was stirred at 80 °C (Scheme 1s). Then separation of GDTCSA by filtration and evaporation of heptane in vacuo gave the crude material, which was purified by column chromatography to give the desired colorless oil carboxylic ester.



Scheme 1s. Esterification reaction.

b. Cycle usage experiment

Cycle experiment of catalytic activity

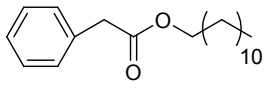
The reaction mixture, 4-phenylbutyric acid (180 mg, 1.1 mmol), 1-hexanol (102 mg, 1.0 mmol), and 5 mol% of GDTCSA (2.43 mmol NH_2^+ and $SO_3H \cdot g^{-1}$; 21 mg, 0.05 mmol) were heated in 2 mL heptane under the condition of 80 °C. The mixture was centrifuged and the solution phase was decanted to separate GDTCSA, which was washed three times with heptane. GDTCSA was recovered and reused for the next reaction with keeping same mole ratio. The leaching of S and N in first, fifth and last solution were detected by Sulfur and Nitrogen Fluorescence Analyzer, the N is about 10-15 mg/L (11-17 ppm) and S is about 80-100 mg/L (89-110 ppm), so the leaching of N is 0.36-0.54% and S is 1.1-1.3% by calculating.

Cycle experiment of selectivity

The reaction mixture, 4-phenylbutyric acid (180 mg, 1.1 mmol), cyclododecanol (184 mg, 1.0 mmol), and 5 mol% of GDTCSA (2.43 mmol NH_2^+ and $SO_3H \cdot g^{-1}$; 21 mg, 0.05 mmol) were heated in 2 mL heptane under the condition of 80 °C. The mixture was centrifuged and the solution phase was decanted to separate GDTCSA, which was washed three times with heptane. GDTCSA was recovered and reused for the next reaction with keeping same mole ratio. The selectivity of the ester was 95%-97% examined by ^1H NMR analysis.

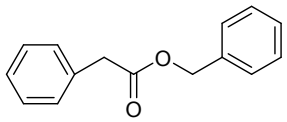
4. Characterization of carboxylic esters

Dodecyl 2-phenylacetate (1) [6]**:**



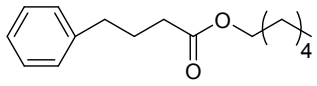
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 4.08 (t, *J* = 7.0 Hz, 2H), 3.61 (s, 2H), 1.62-1.57 (m, 2H), 1.25 (s, 18H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 134.2, 129.2, 128.5, 127.0, 65.0, 41.5, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 28.6, 25.9, 22.7, 14.1 ppm.

Benzyl 2-phenylacetate (2) [7]**:**



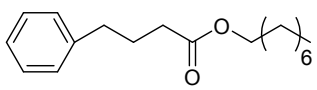
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.25 (m, 10H), 5.13 (s, 2H), 3.67 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 135.8, 133.9, 129.3, 128.6, 128.5, 128.2, 128.1, 127.1, 66.6, 41.3 ppm.

Hexyl 4-phenylbutyrate (3):



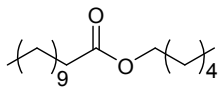
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.17 (m, 5H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.98-1.92 (m, 2H), 1.64-1.58 (m, 2H), 1.36-1.30 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 141.5, 128.5, 128.4, 126.0, 64.5, 35.2, 33.7, 31.5, 28.6, 26.6, 25.6, 22.6, 14.0 ppm; HRMS calculated for $C_{16}H_{24}O_2Na$ 271.1680, found 271.1674 $[M+Na]^+$.

Octyl 4-phenylbutyrate (4) [8]**:**



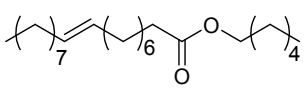
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.12 (m, 5H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.32 (d, *J* = 7.5 Hz, 2H), 1.99-1.94 (m, 2H), 1.63-1.60 (m, 2H), 1.31-1.27 (m, 10), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 141.5, 128.5, 128.4, 126.0, 64.5, 35.2, 33.7, 31.8, 29.3, 29.2, 28.7, 26.6, 26.0, 22.7, 14.1 ppm.

Hexyl dodecanoate (5) [9]**:**



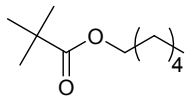
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.07 (t, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.64-1.60 (m, 4H), 1.39–1.27 (m, 26H), 0.92-0.88 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 64.4, 34.4, 31.9, 31.4, 29.6, 29.5, 29.3, 29.3, 29.2, 28.6, 25.6, 25.0, 22.7, 22.5, 14.1, 14.0 ppm.

Hexyl oleate (6) [10]**:**



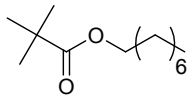
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38-5.33 (m, 2H), 4.06 (t, *J* = 7.0 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.04-1.99 (m, 2H), 1.63-1.59 (m, 4H), 1.31-1.25 (m, 28H), 0.88 (t, *J* = 6.5 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.1, 130.0, 129.8, 64.4, 34.4, 31.9, 31.4, 29.8, 29.7, 29.5, 29.3, 29.2, 29.1, 29.1, 28.6, 27.2, 27.2, 25.6, 25.0, 22.7, 22.6, 14.1, 14.0 ppm.

Hexyl pivaloate (7) [11]**:**



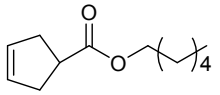
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.8 Hz, 2H), 1.65-1.58 (m, 2H), 1.39-1.28 (m, 6H), 1.20 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 64.4, 38.7, 31.4, 28.6, 27.2, 25.5, 22.5, 13.9 ppm.

Octyl pivaloate (8) [12]**:**



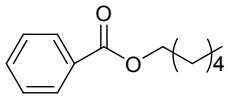
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.04 (t, *J* = 7.0 Hz, 2H), 1.64-1.55 (m, 2H), 1.30-1.27 (m, 10H), 1.19 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6, 64.4, 38.7, 31.8, 29.2, 28.6, 27.2, 25.9, 22.6, 14.0 ppm.

Hexyl 3-cyclopentene-1-carboxylate (9):



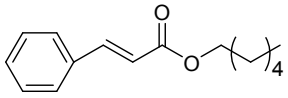
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (s, 2H), 4.09 (t, *J* = 7.0 Hz, 2H), 3.13-3.08 (m, 1H), 2.65 (d, *J* = 8.0 Hz, 4H), 1.64-1.61 (m, 2H), 1.35-1.30 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR(125 MHz, $CDCl_3$): δ 176.3, 129.0, 64.7, 41.7, 36.3, 31.4, 28.6, 25.6, 22.5, 14.0 ppm; HRMS calculated for $C_{12}H_{20}O_2Na$ 219.1362, found 219.1361 $[M+Na]^+$.

Hexyl benzoate (10) [13]**:**



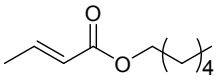
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.57-7.42 (m, 3H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.80-1.73 (m, 2H), 1.45-1.33 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 132.8, 130.5, 129.5, 128.3, 65.2, 31.5, 28.7, 25.7, 22.6, 14.0 ppm.

Hexyl cinnamate (11) [14]**:**



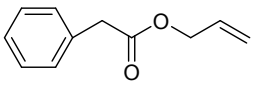
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.54-7.52 (m, 2H), 7.39-7.37 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 1.72-1.67 (m, 2H), 1.41-1.33 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.8, 31.5, 28.7, 25.7, 22.6, 14.0 ppm.

Hexyl 2-butenoate (12) [15]**:**



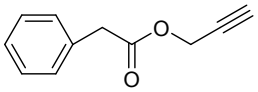
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01-6.92 (m, 1H), 5.87-5.83 (m, 1H), 4.11 (t, *J* = 6.8 Hz, 2H), 1.88 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.66-1.63 (m, 2H), 1.38-1.31 (m, 6H), 0.89 (t, *J* = 6.8 H, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 143.4, 121.8, 63.3, 30.4, 27.6, 24.6, 21.5, 16.9, 13.0 ppm.

Allyl 2-phenylacetate (13) [16]**:**



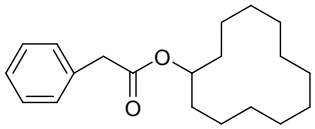
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 5.94-5.86 (m, 1H), 5.29-5.20 (m, 2H), 4.60(d, *J* = 5.5 Hz, 2H), 3.65 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 133.9, 132.0, 129.3, 128.6, 127.1, 118.3, 65.5, 41.3 ppm.

Propargyl 2-phenylacetate (14) [17]**:**



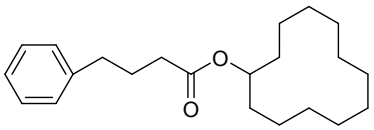
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 4.69 (s, 2H), 3.68 (s, 2H), 2.47 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 133.4, 129.3, 128.6, 127.3, 75.0, 52.3, 40.9 ppm.

Cyclododecyl phenylacetate (15):



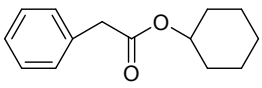
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 5.05-5.00 (m, 1H), 3.59 (s, 2H), 1.71-1.67 (m, 2H), 1.51-1.33 (m, 20H) ppm; ^{13}C NMR(125 MHz, $CDCl_3$): δ 171.4, 134.5, 129.2, 128.5, 126.9, 72.8, 41.8, 29.1, 24.1, 23.9, 23.4, 23.2, 20.9 ppm; HRMS calculated for $C_{20}H_{30}O_2Na$ 325.2141, found 325.2143 $[M+Na]^+$.

Cyclododecyl 4-phenylbutyrate (16):



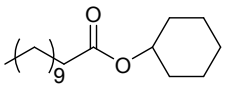
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.16 (m, 5H), 5.05-5.00 (m, 1H), 2.64(t, *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.97-1.91 (m, 2H), 1.73-1.66 (m, 2H), 1.52-1.30 (m, 20H); ^{13}C NMR(125 MHz, $CDCl_3$): δ 173.1, 141.6, 128.5, 128.4, 126.0, 72.1, 35.2, 34.1, 29.2, 26.8, 24.1, 24.0, 23.5, 23.3, 21.0 ppm; HRMS calculated for $C_{22}H_{34}O_2Na$ 353.2442, found 353.2457 $[M+Na]^+$.[3]

Cyclohexyl phenylacetate (17) [18]**:**



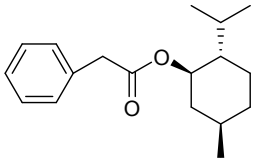
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H), 4.80-4.74 (m, 1H), 3.59 (s, 2H), 1.82-1.79 (m, 2H), 1.71-1.66 (m, 2H), 1.54-1.49 (m, 1H), 1.45-1.23 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.1, 134.4, 129.2, 128.5, 126.9, 73.0, 41.8, 31.5, 25.4, 23.6 ppm.

Cyclohexyl dodecanoate (18) [19]**:**



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77-4.74 (m, 1H), 2.27(t, *J* = 7.5 Hz, 2H), 1.84-1.81 (m, 2H), 1.73-1.70 (m, 2H), 1.62-1.56 (m, 4H), 1.39-1.26 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 72.2, 34.8, 31.9, 31.7, 29.6, 29.5, 29.3, 29.3, 29.1, 25.4, 25.1, 23.7, 22.7, 14.1 ppm.

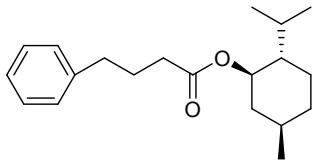
L-(−)-Menthyl phenylacetate (19) [20]**:**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 5H), 4.67 (dt, *J* = 11.2, 4.4 Hz, 1H), 3.60 (s, 2H), 1.99-1.94 (m, 1H), 1.77-1.61 (m, 3H), 1.51-1.31 (m, 2H), 1.04-0.93 (m, 2H), 0.90-0.86

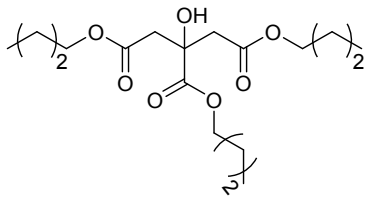
(m, 4H), 0.83 (d, J = 6.8 Hz, 3H), 0.68 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 134.4, 129.2, 128.5, 126.9, 74.7, 47.0, 41.8, 40.8, 34.2, 31.4, 26.1, 23.4, 22.0, 20.7, 16.2 ppm.

L-(−)-Menthyl 4-phenylbutyrate (20) [21]**:**



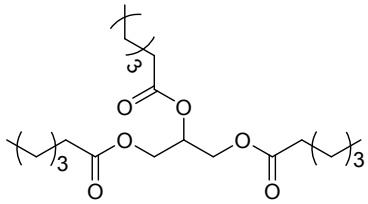
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 4.74 (dt, J = 11.0, 4.5 Hz, 1H), 2.67 (t, J =8.0 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 2.03-1.88 (m, 4H), 1.72-1.68 (m, 2H), 1.55-1.47 (m, 1H), 1.43-1.37 (m, 1H), 1.13-0.90 (m, 9H), 0.80 (d, J = 7.0 Hz, 3H); ^{13}C NMR(125 MHz, $CDCl_3$): δ 173.0, 141.5, 128.5, 128.4, 126.0, 74.0, 47.1, 41.0, 35.2, 34.3, 34.1, 31.4, 26.8, 26.3, 23.5, 22.1, 20.1, 16.3 ppm; HRMS calculated for $C_{20}H_{30}O_2Na$ 325.2141, found 325.2153 $[M+Na]^+$.

Tributyl citrate (21) [3]**:**



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (t, J = 6.5 Hz, 2H), 4.13 (br, 1H), 4.08 (t, J = 6.5 Hz, 4H), 2.88 (d, J = 15.5 Hz, 2H), 2.79 (d, J = 15.5 Hz, 2H), 1.67-1.56 (m, 6H), 1.40-1.33 (m, 6H), 0.91 (t, J= 7.0 Hz, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 169.9, 73.2, 66.2, 64.9, 43.3, 30.5, 30.4, 19.1, 13.7 ppm.

Glycerol trihexanoate (22) [22]**:**



^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29-5.25 (m, 1H), 4.30 (dd, J = 12.0, 4.0 Hz, 2H), 4.16 (dd, J = 12.0, 4.5 Hz, 2H), 2.37-2.30 (m, 6H), 1.66-1.61 (m, 6H), 1.34-1.30 (m, 18H), 0.90 (t, J = 6.5 Hz, 9H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.6, 173.4, 173.0, 68.9, 62.1, 34.2, 34.0, 34.0, 31.3, 31.2, 24.6, 24.6, 24.4, 22.3, 13.9 ppm.

5. Spectra of the catalysts

a. Spectra of GDTCSA

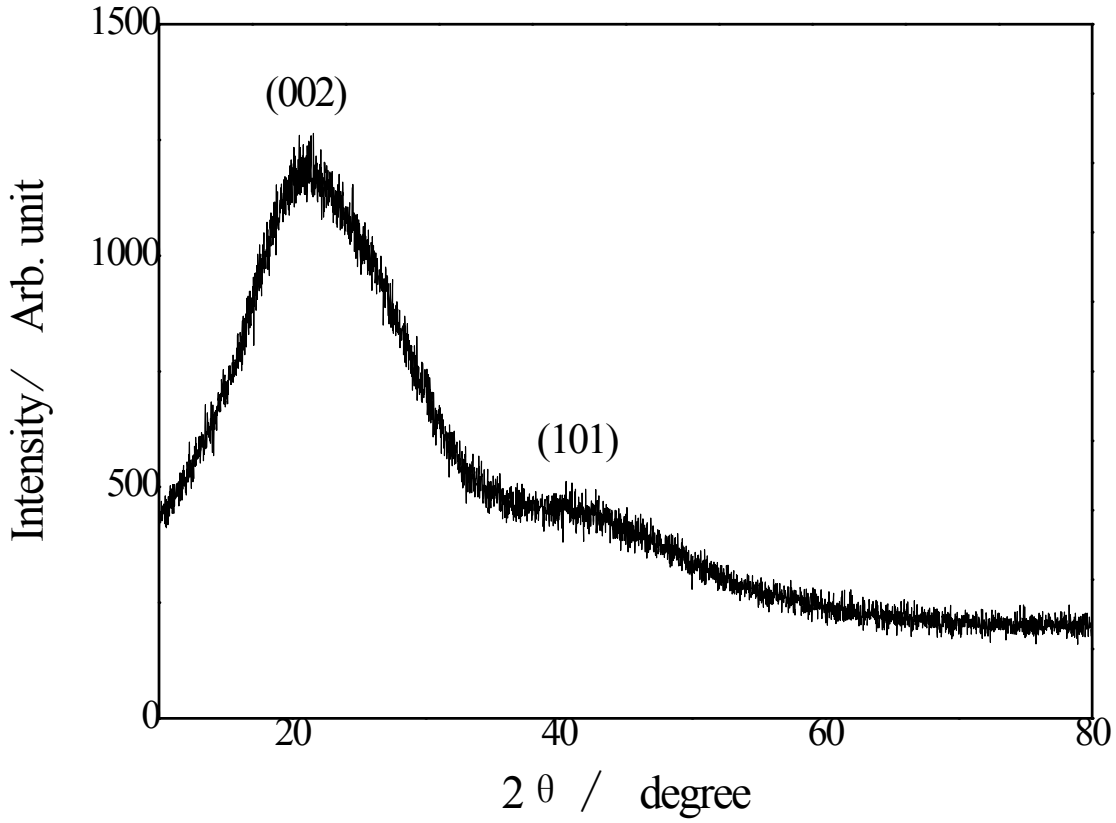


Fig. S1 The XRD pattern of GDTCSA.

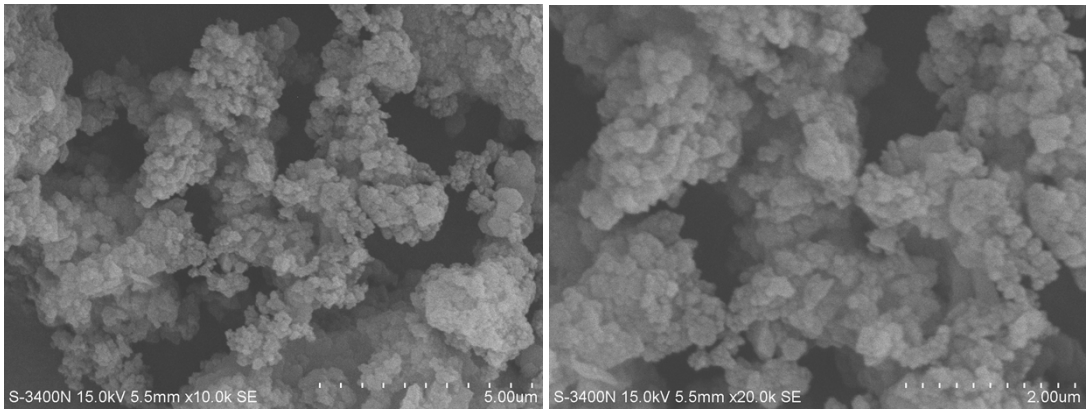


Fig. S2 The SEM image of GDTCSA.

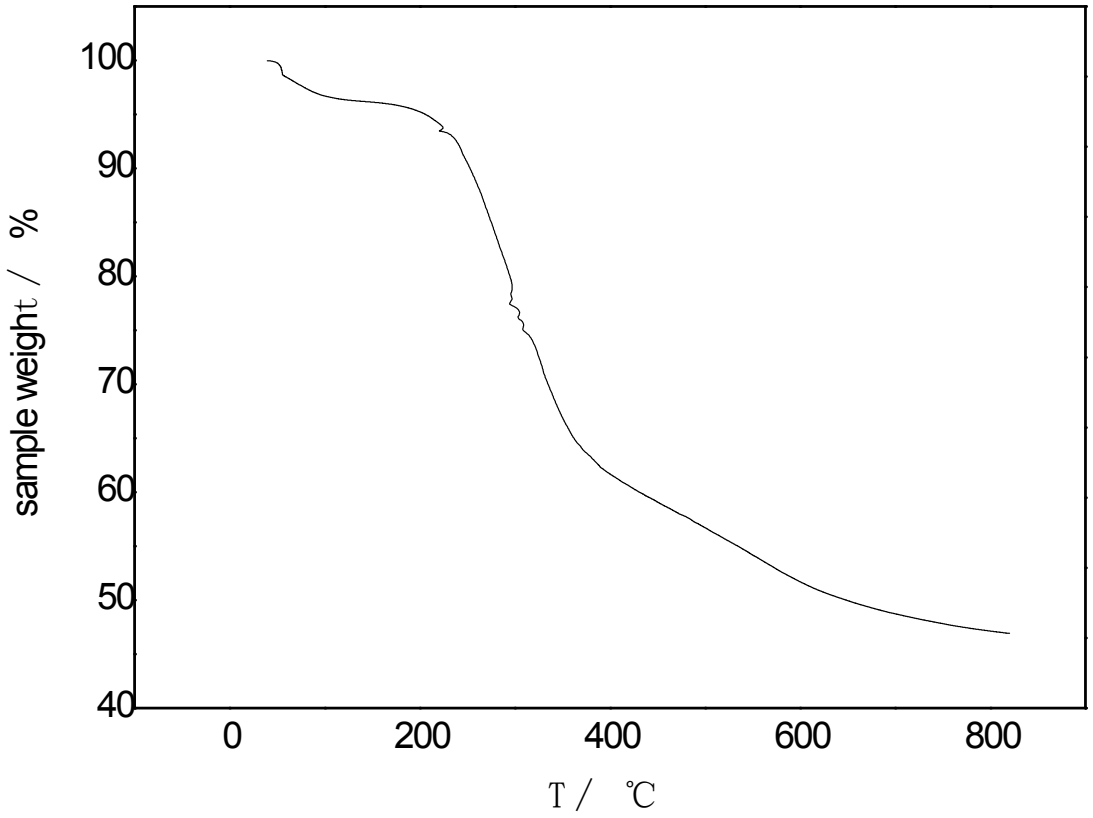


Fig. S3 The TGA pattern of GDTCSA.

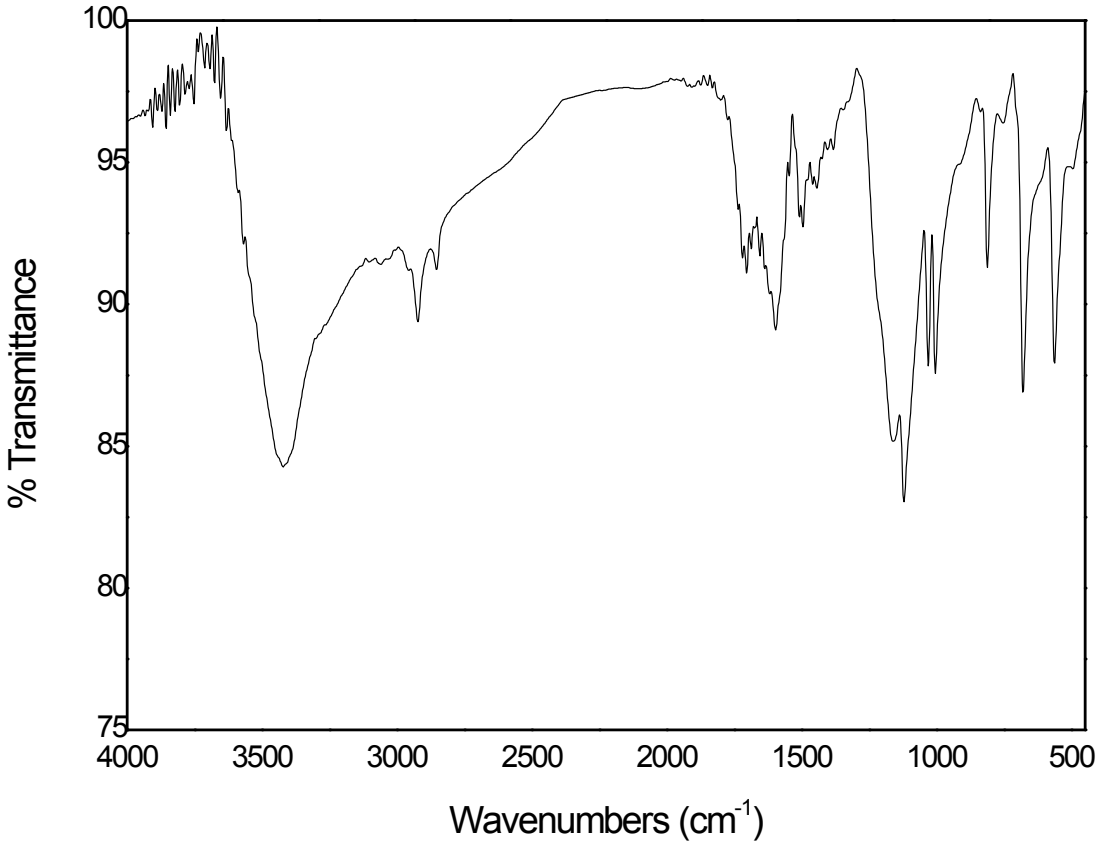


Fig. S4 The FT-IR spectrum of GDTCSA.

b. Spectrum of sodium *p*-toluenesulfonate

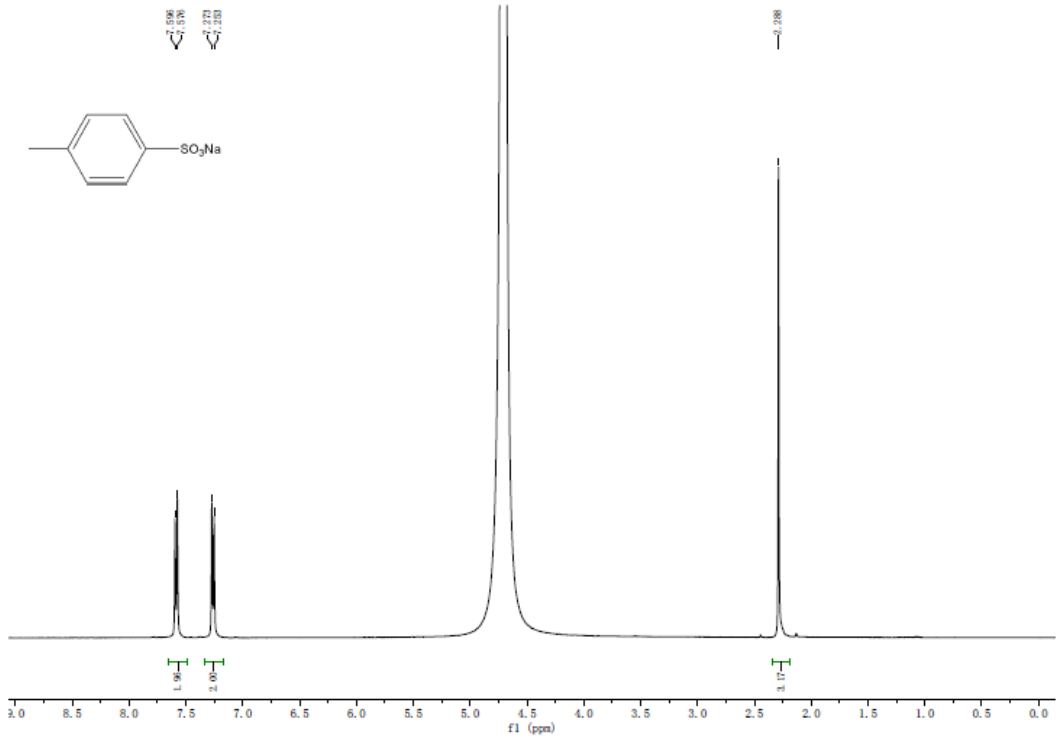


Fig. S5 The ^{1}HNMR spectrum of sodium *p*-toluenesulfonate.

c. Spectrum of GDCSA

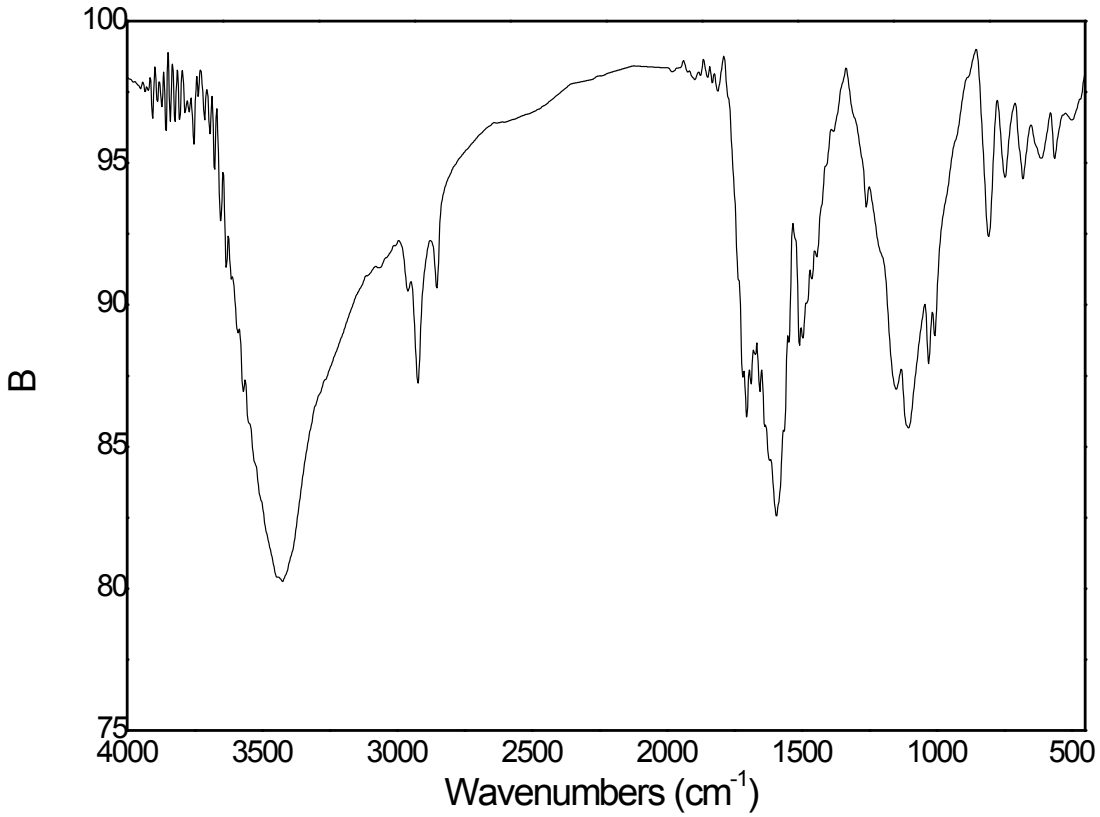


Fig. S6 The FT-IR spectrum of GDCSA.

d. Spectra of diphenylammonium tosylate

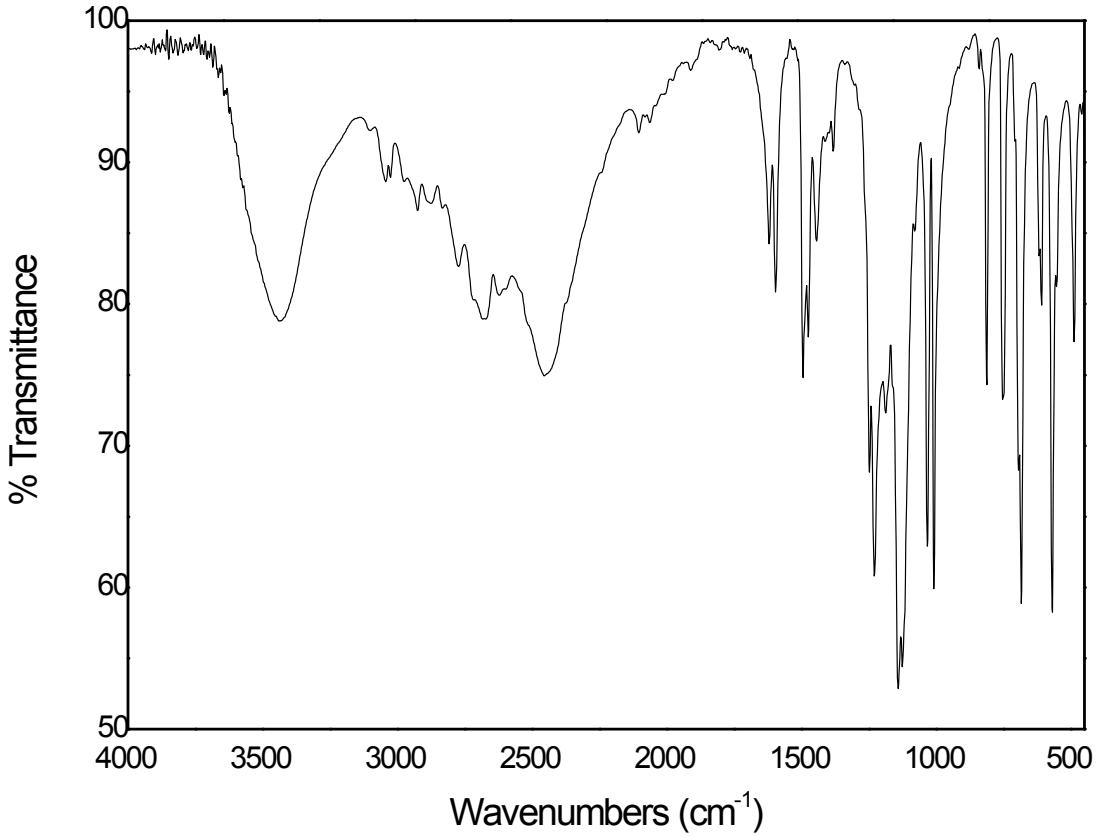


Fig. S7 The FT-IR spectrum of $[Ph_2NH_2]^+[OTs]^-$.

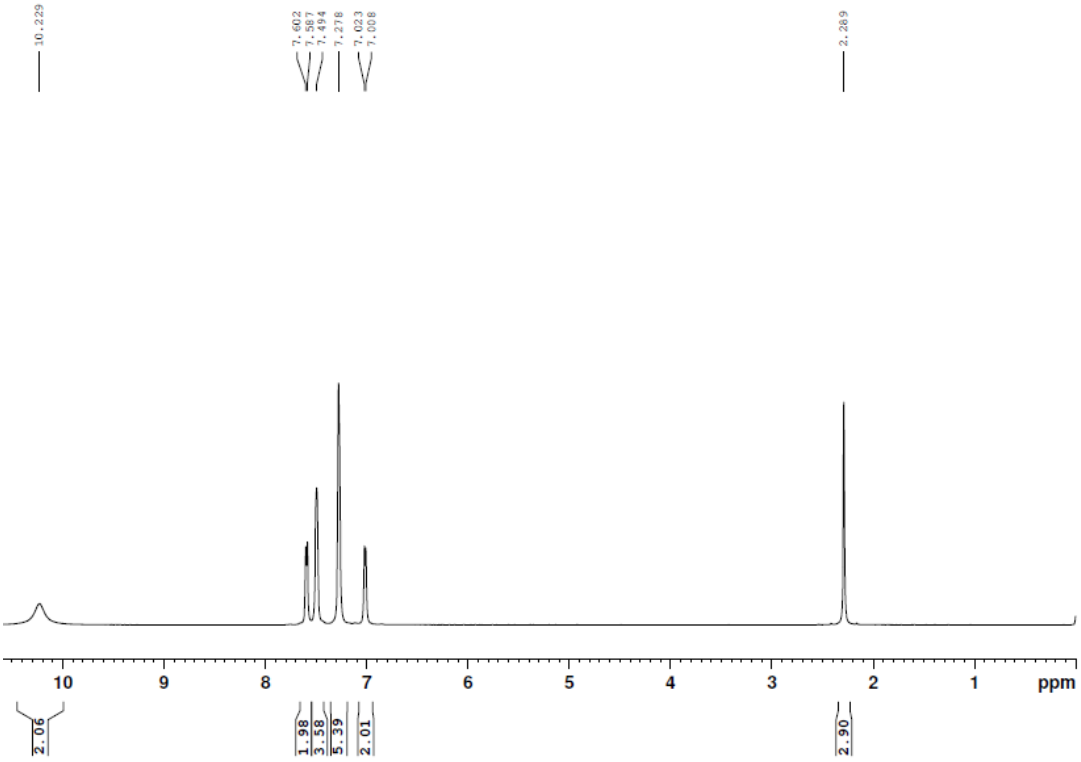


Fig. S8 The ^1H NMR spectrum of $[Ph_2NH_2]^+[OTs]^-$.

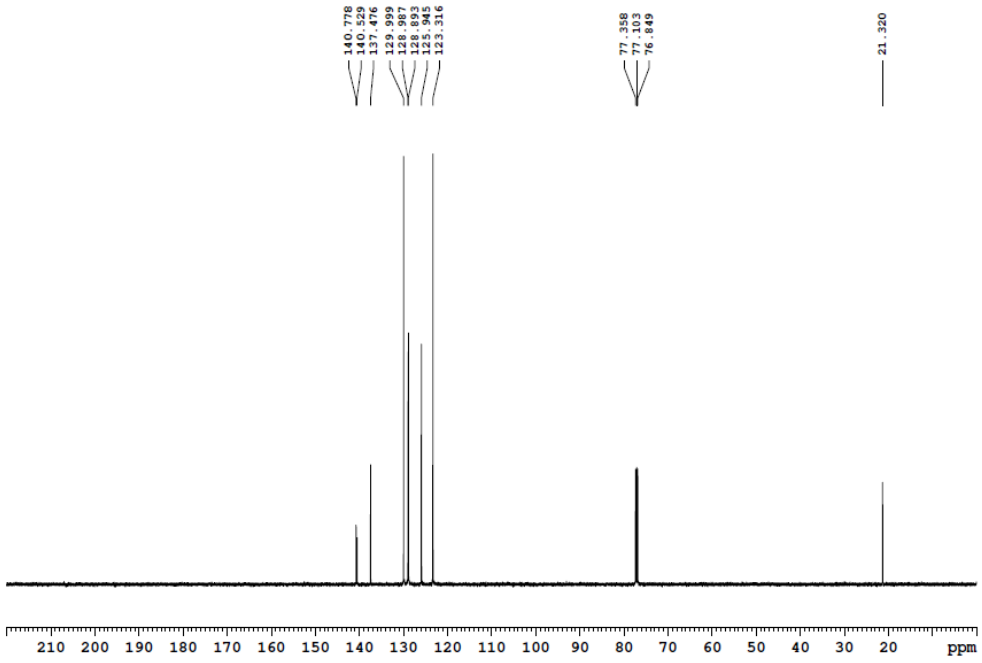


Fig. S9 The ^{13}C NMR spectrum of $[Ph_2NH_2]^+[OTs]^-$.

e. Spectra of GTCSA

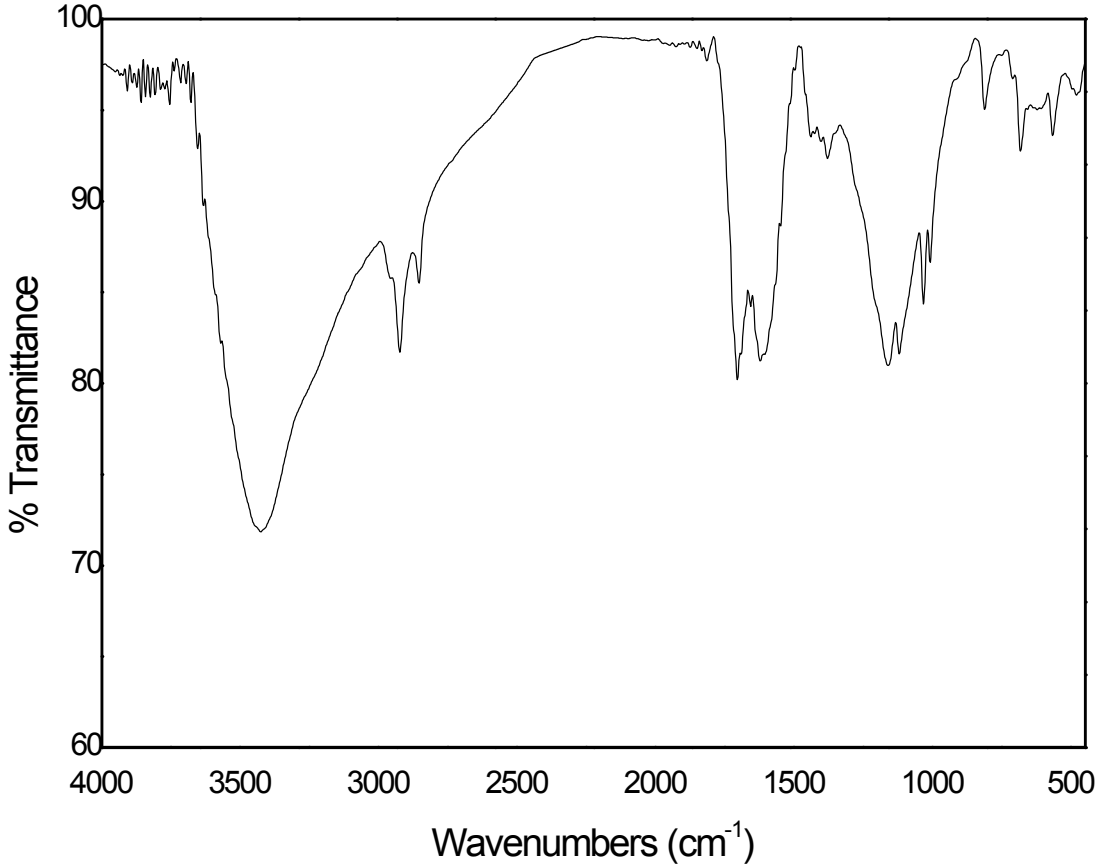


Fig. S10 The FT-IR spectrum of GTCSA.

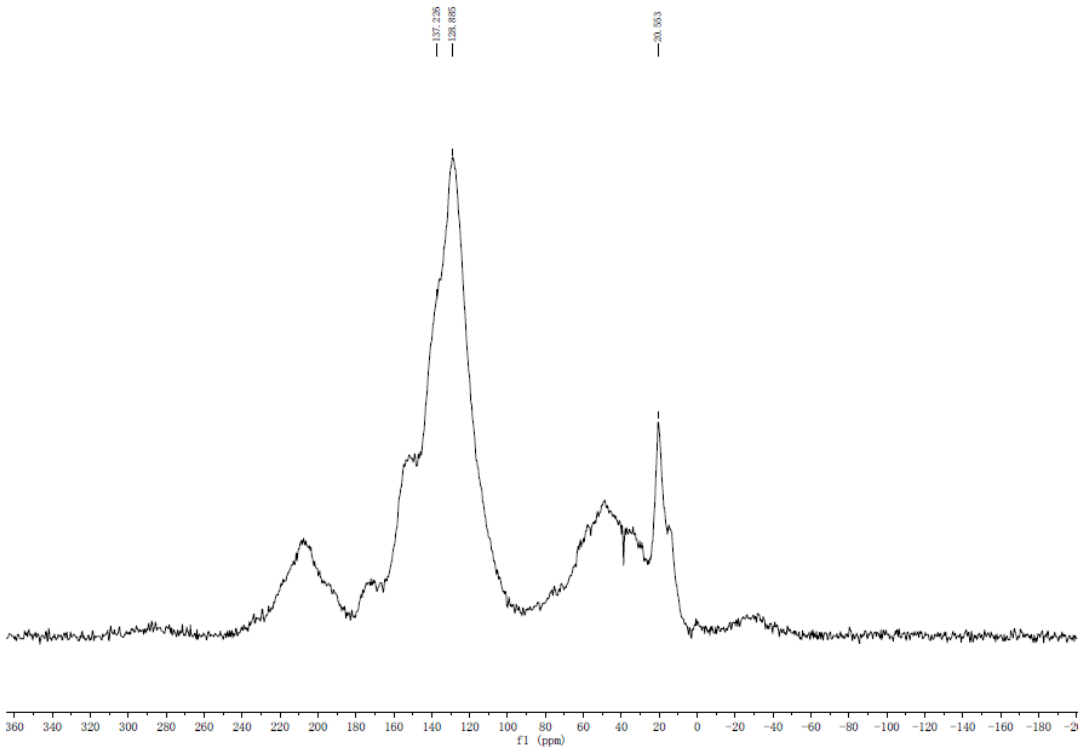


Fig. S11 The ^{13}C MAS NMR spectrum of GTCSA.

6. Spectra of carboxylic esters

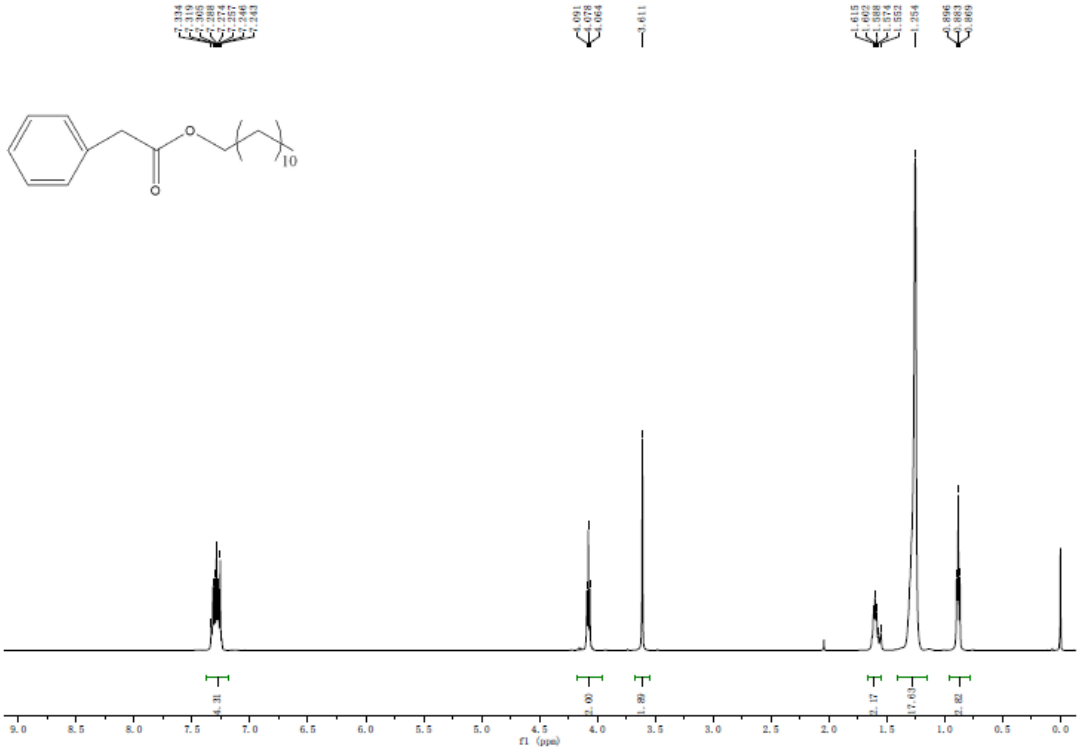


Fig. S12 The ^{1}H NMR spectrum of dodecyl 2-phenylacetate (1).

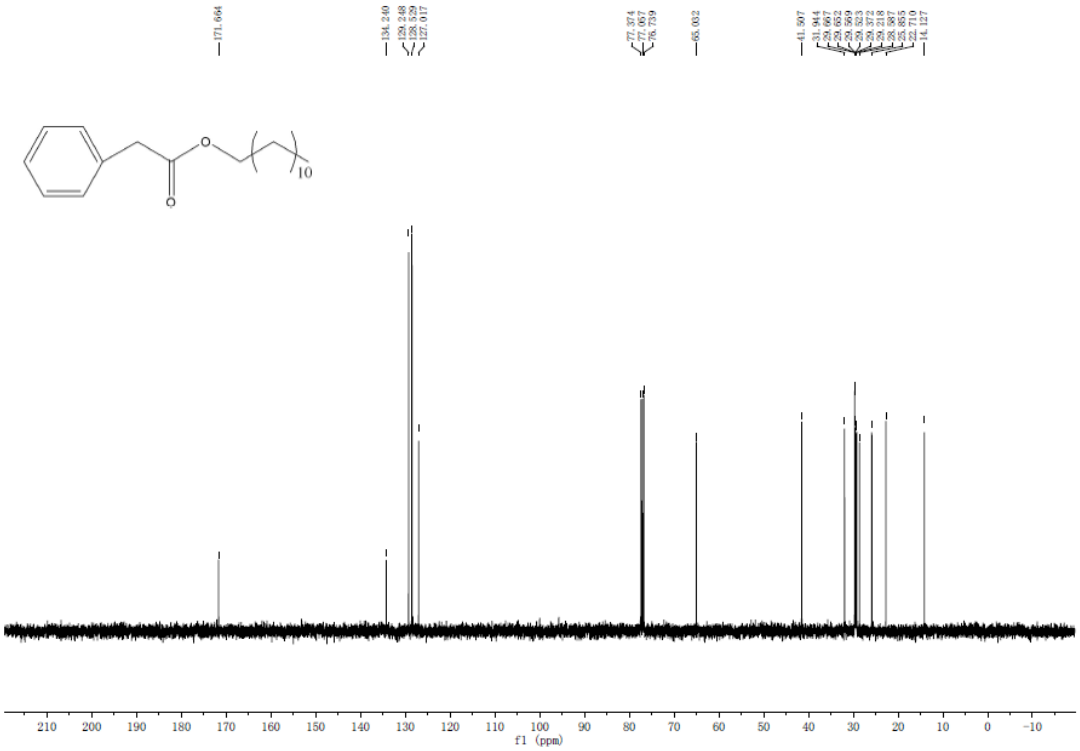


Fig. S13 The ^{13}C NMR spectrum of dodecyl 2-phenylacetate (1).

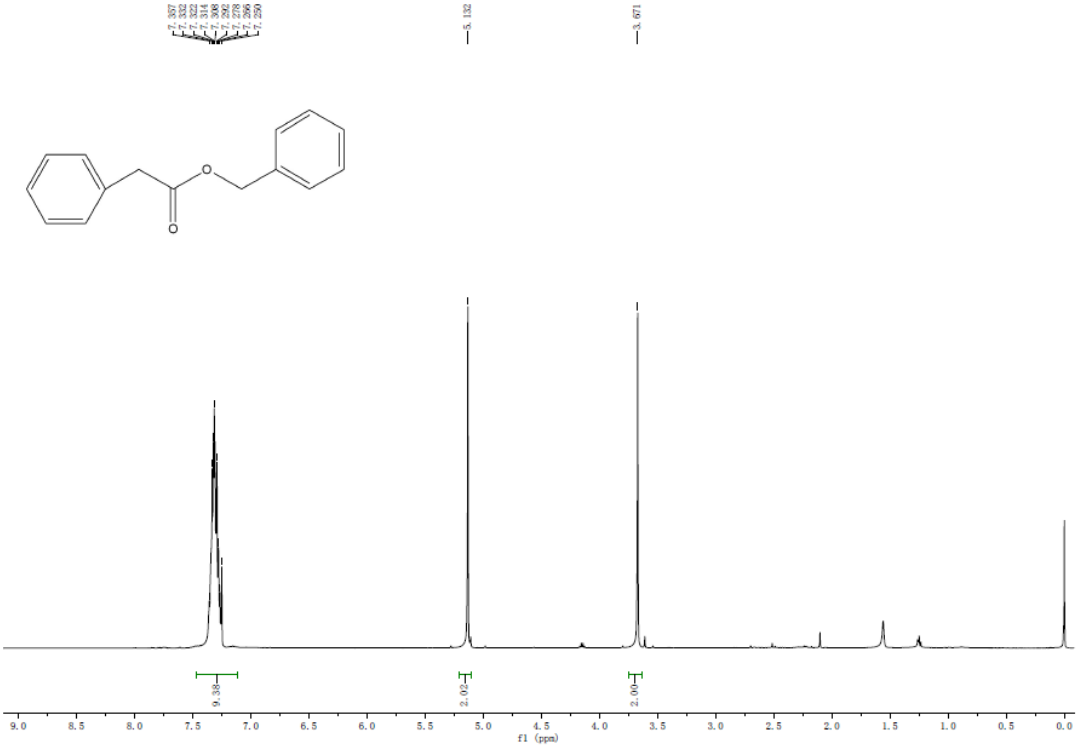


Fig. S14 The ^{1}H NMR spectrum of benzyl 2-phenylacetate (2).

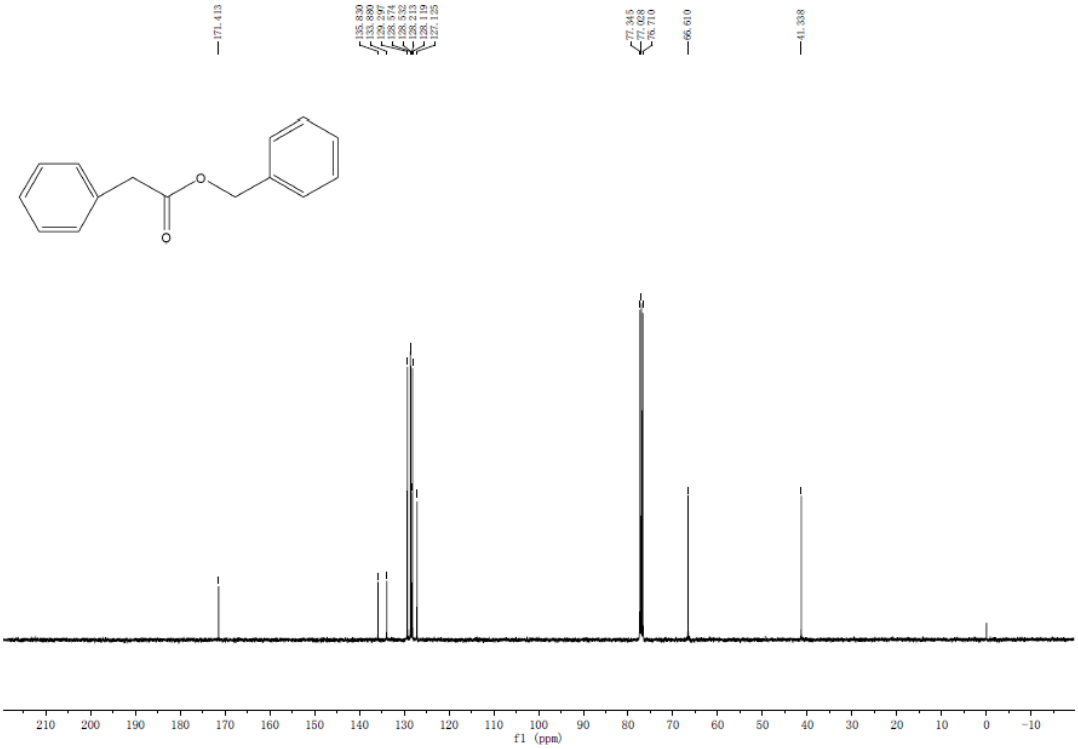


Fig. S15 The ^{13}C NMR spectrum of benzyl 2-phenylacetate (2).

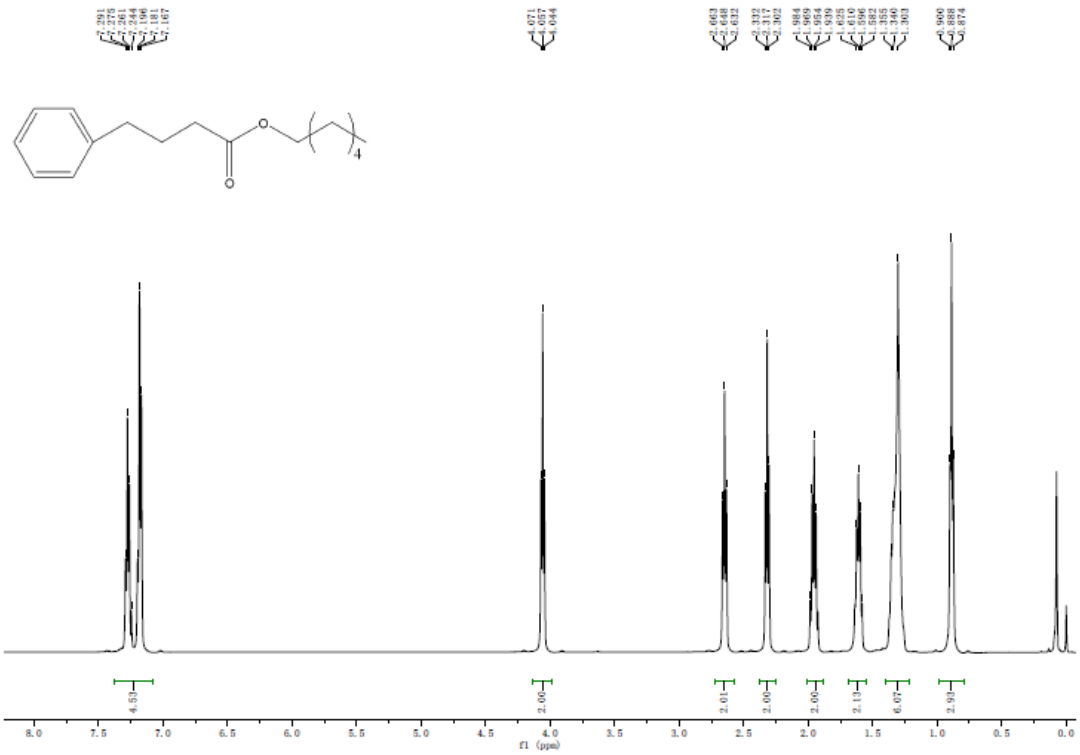


Fig. S16 The ^{1}H NMR spectrum of hexyl 4-phenylbutyrate (3).

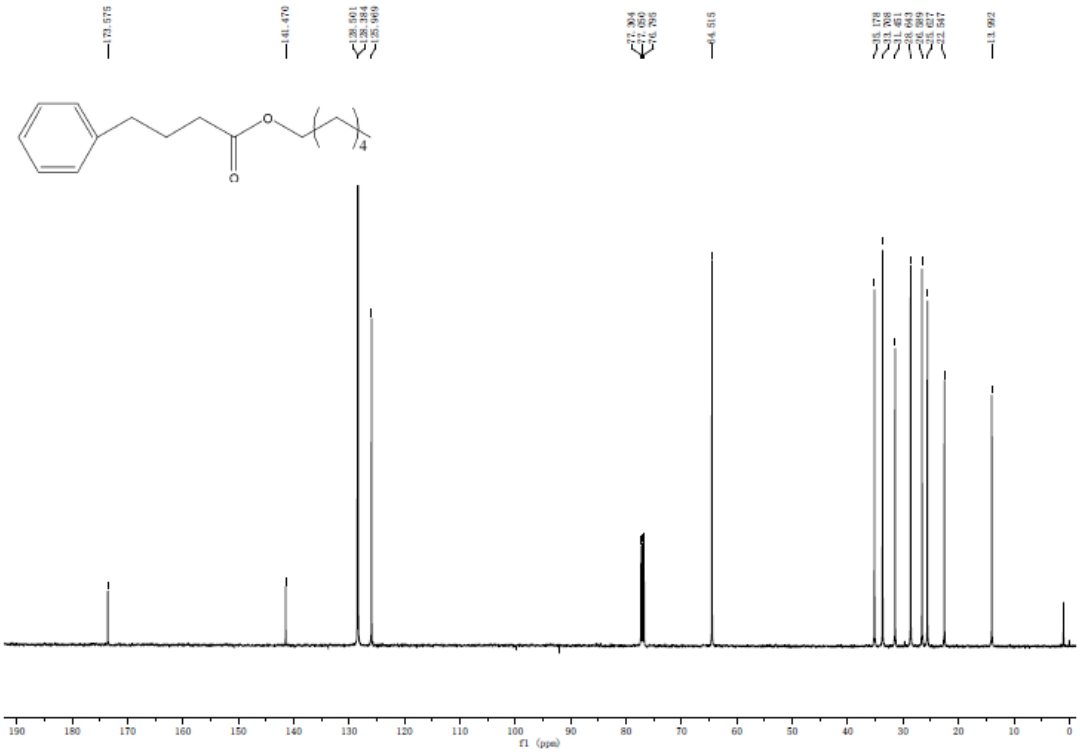


Fig. S17 The ^{13}C NMR spectrum of hexyl 4-phenylbutyrate (3).

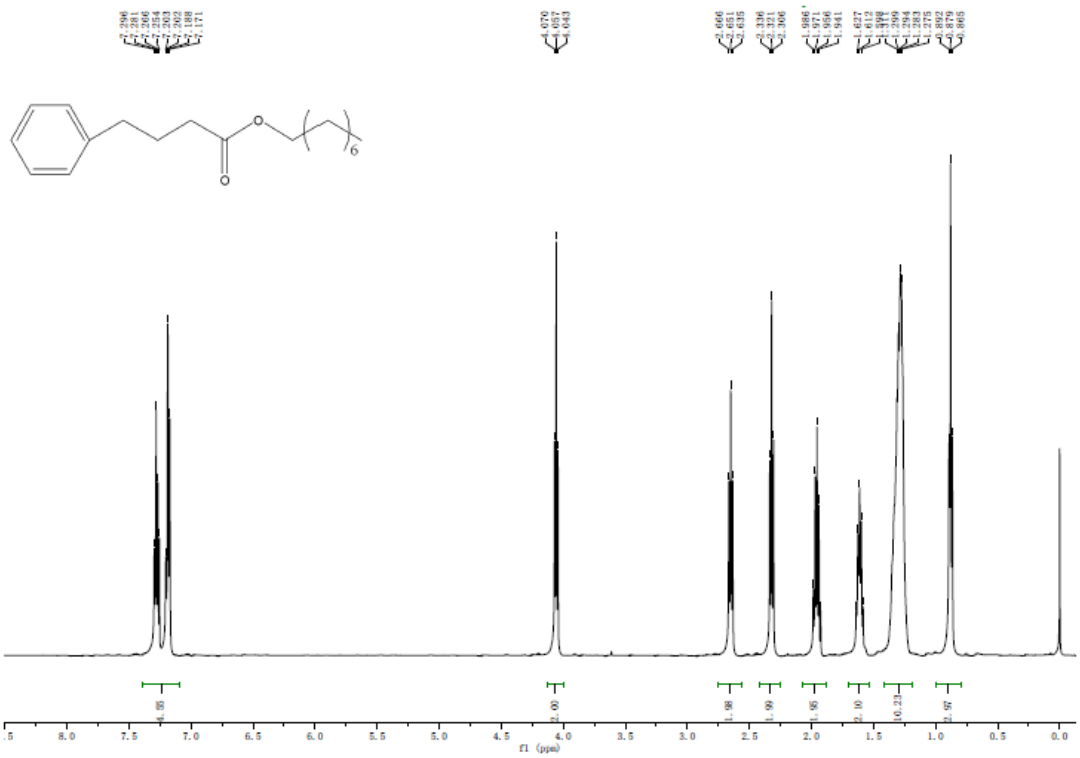


Fig. S18 The ^{1}H NMR spectrum of octyl 4-phenylbutyrate (4).

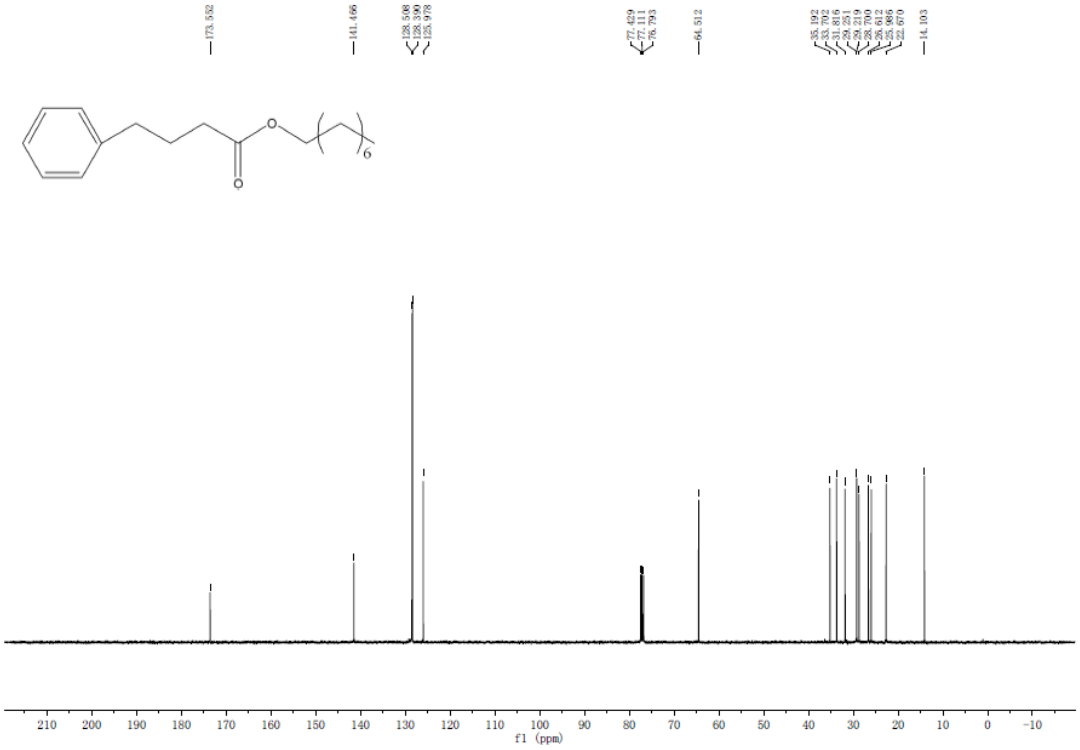


Fig. S19 The ^{13}C NMR spectrum of octyl 4-phenylbutyrate (4).

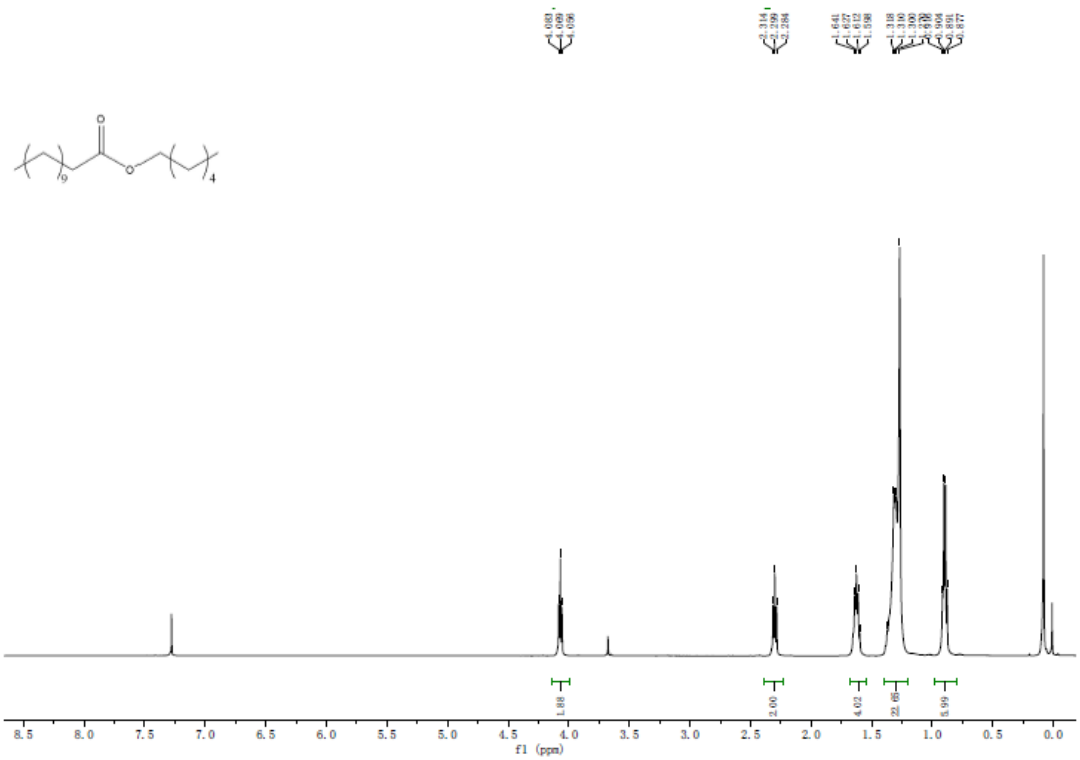


Fig. S20 The ^{1}H NMR spectrum of hexyl dodecanoate (5).

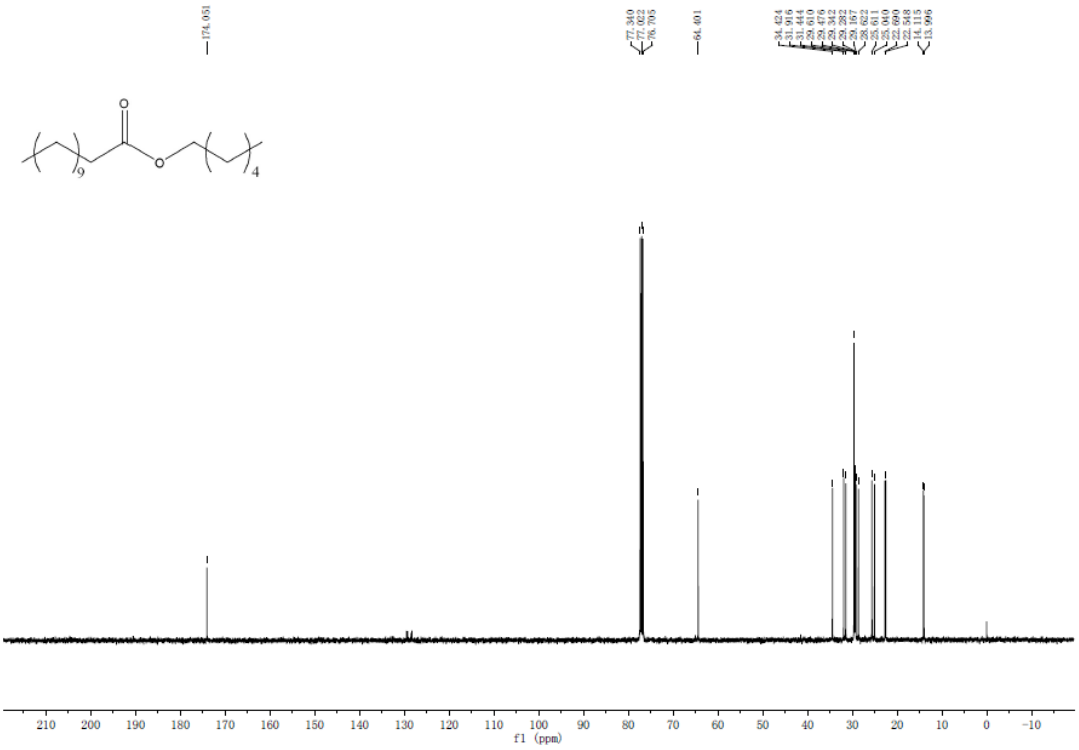


Fig. S21 The ^{13}C NMR spectrum of hexyl dodecanoate (5).

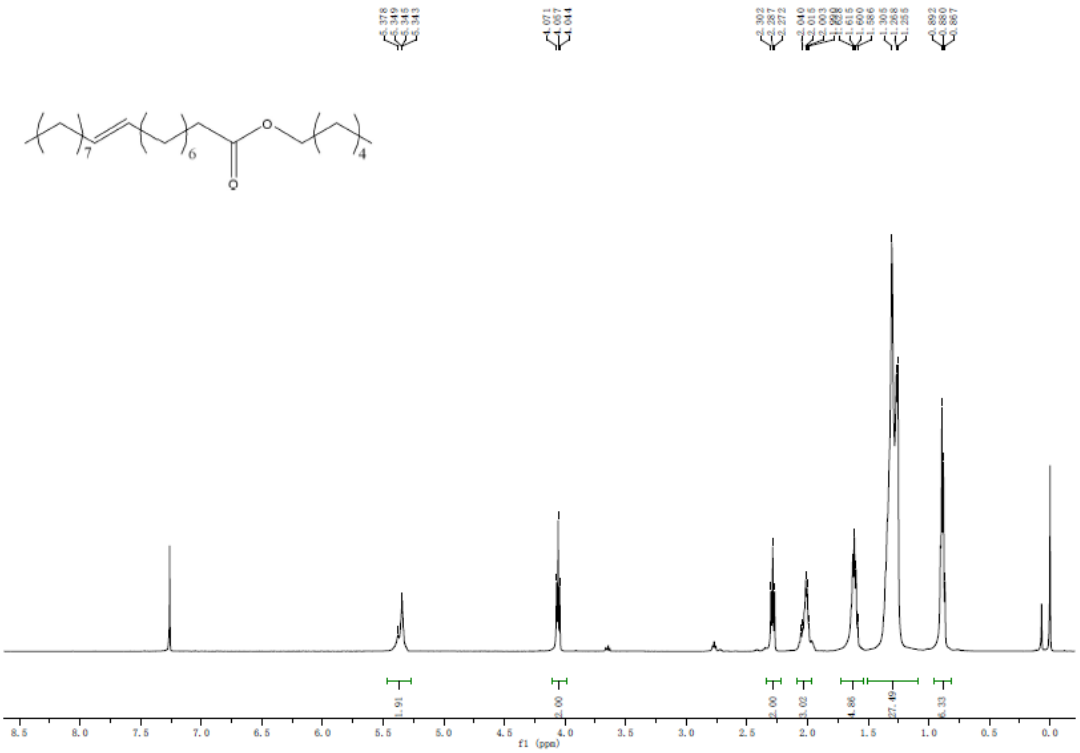


Fig. S22 The ^{1}H NMR spectrum of hexyl oleate (6).

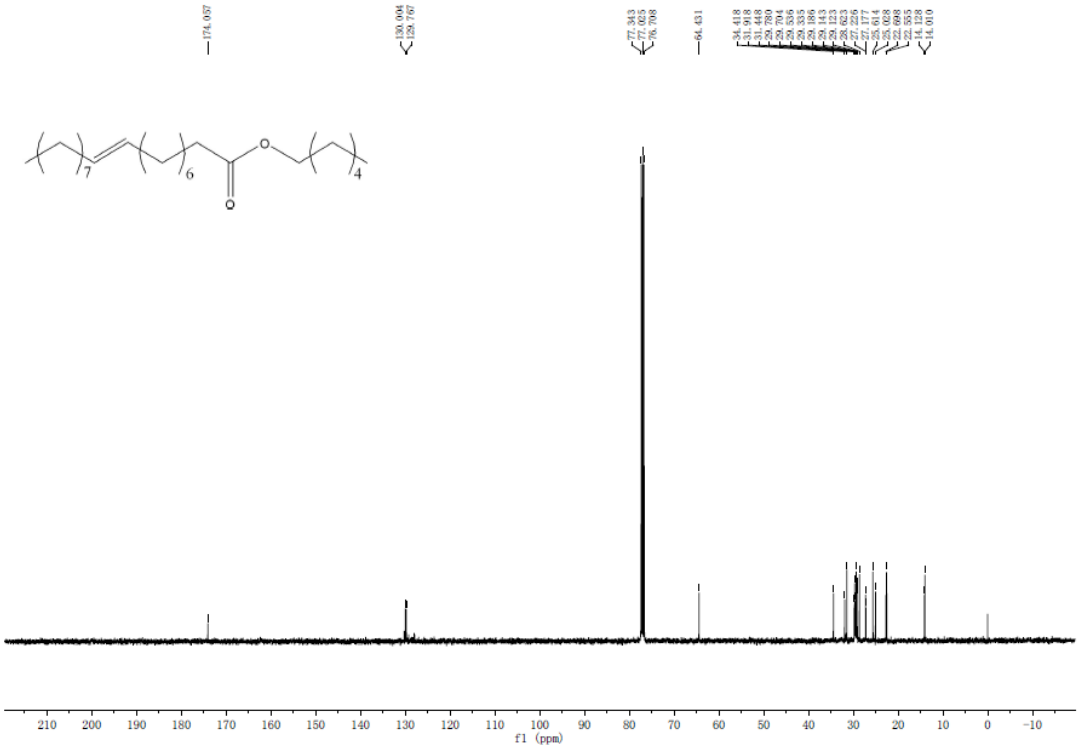


Fig. S23 The ^{13}C NMR spectrum of hexyl oleate (6).

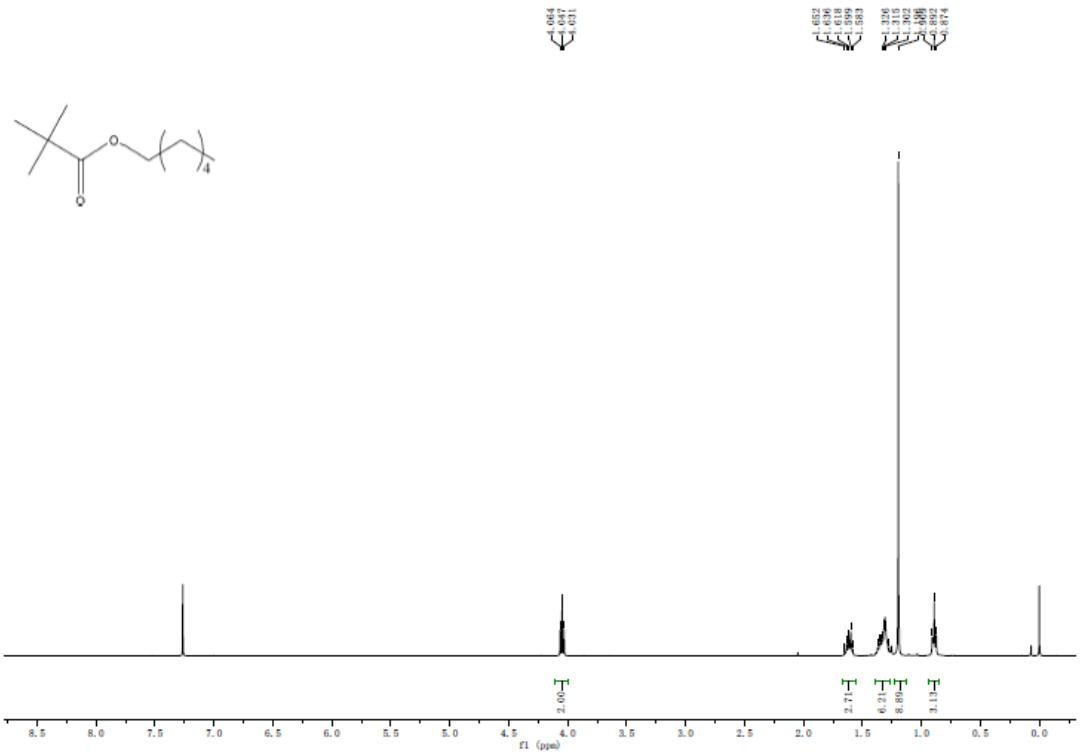


Fig. S24 The ^{1}H NMR spectrum of hexyl pivaloate (7).

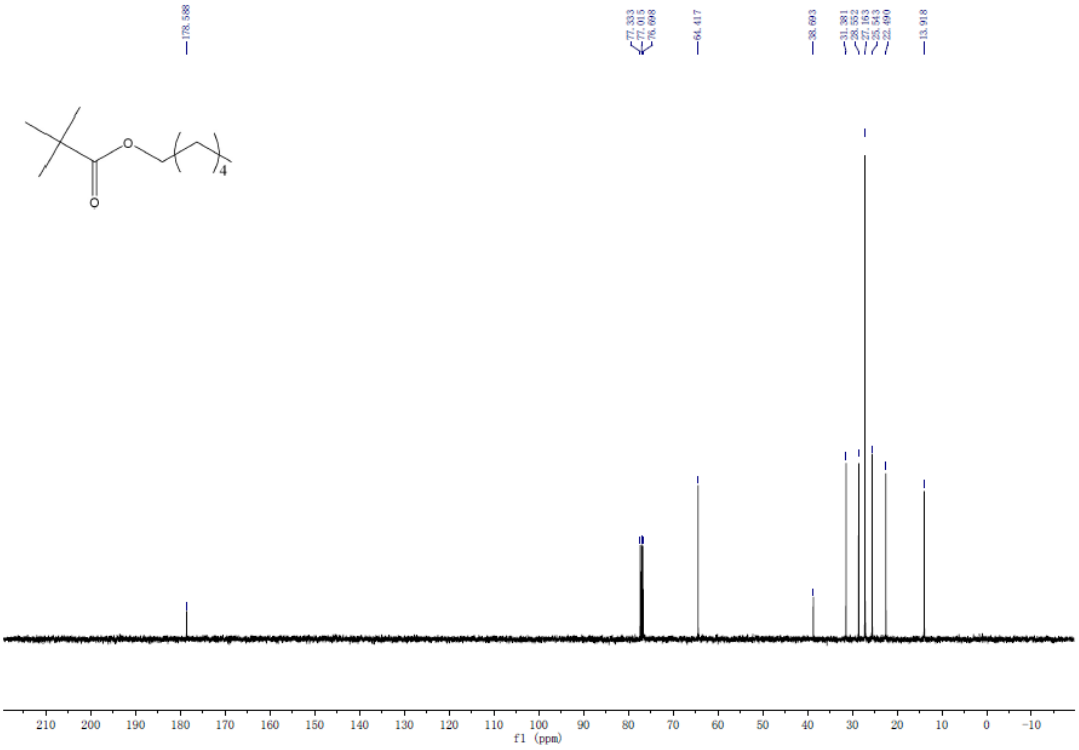


Fig. S25 The ^{13}C NMR spectrum of hexyl pivaloate (7).

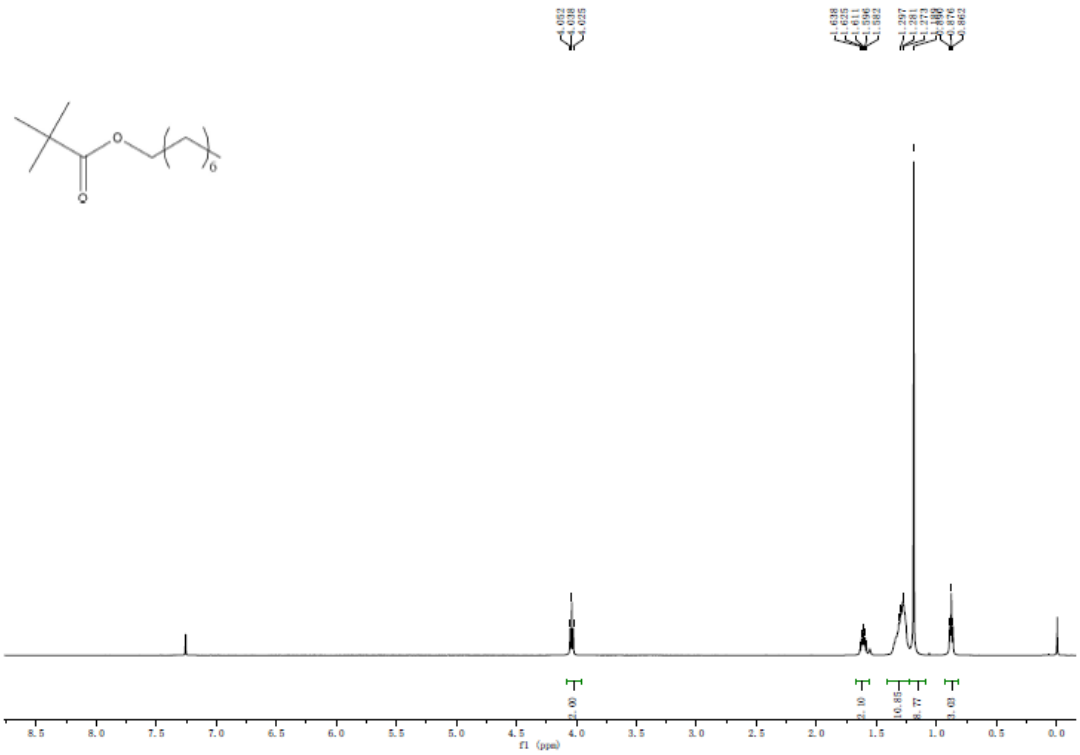


Fig. S26 The ^{1}H NMR spectrum of octyl pivaloate (8).

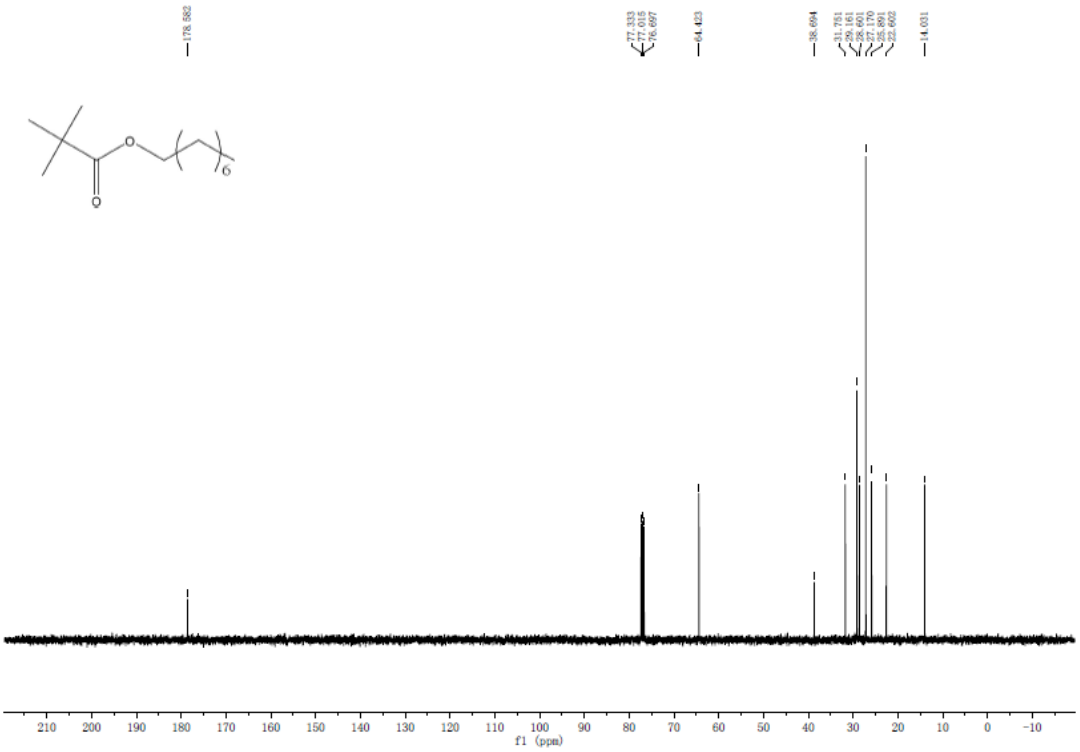


Fig. S27 The ^{13}C NMR spectrum of octyl pivaloate (8).

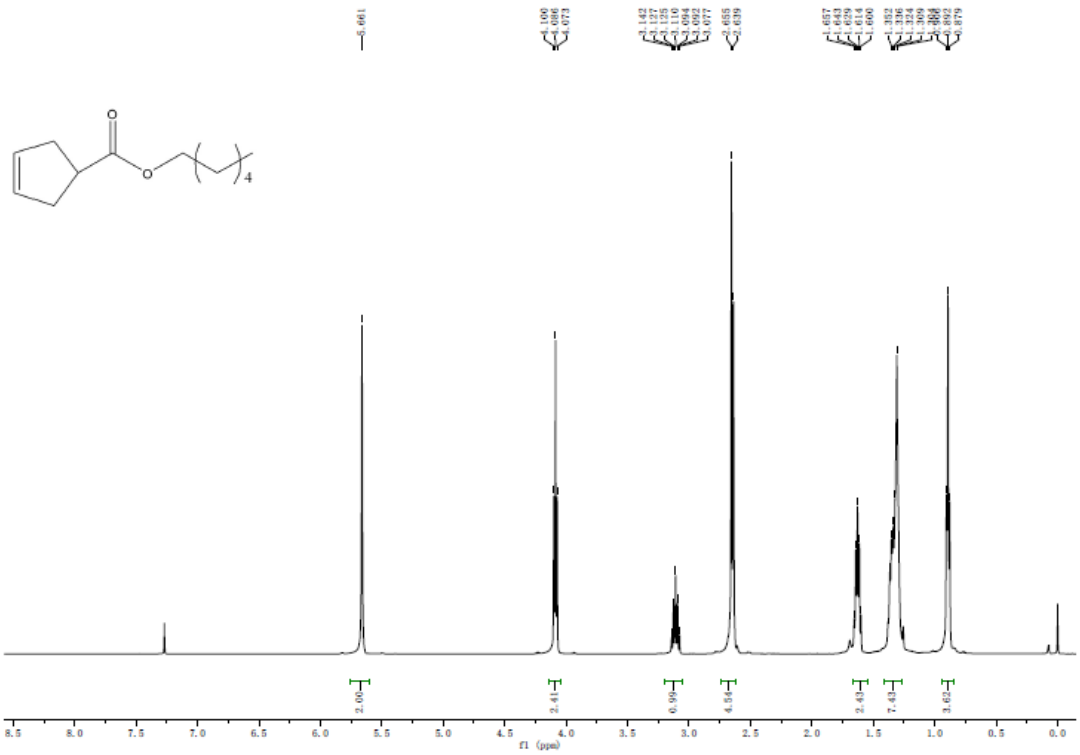


Fig. S28 The ^{1}H NMR spectrum of hexyl 3-cyclopentene-1-carboxylate (9).

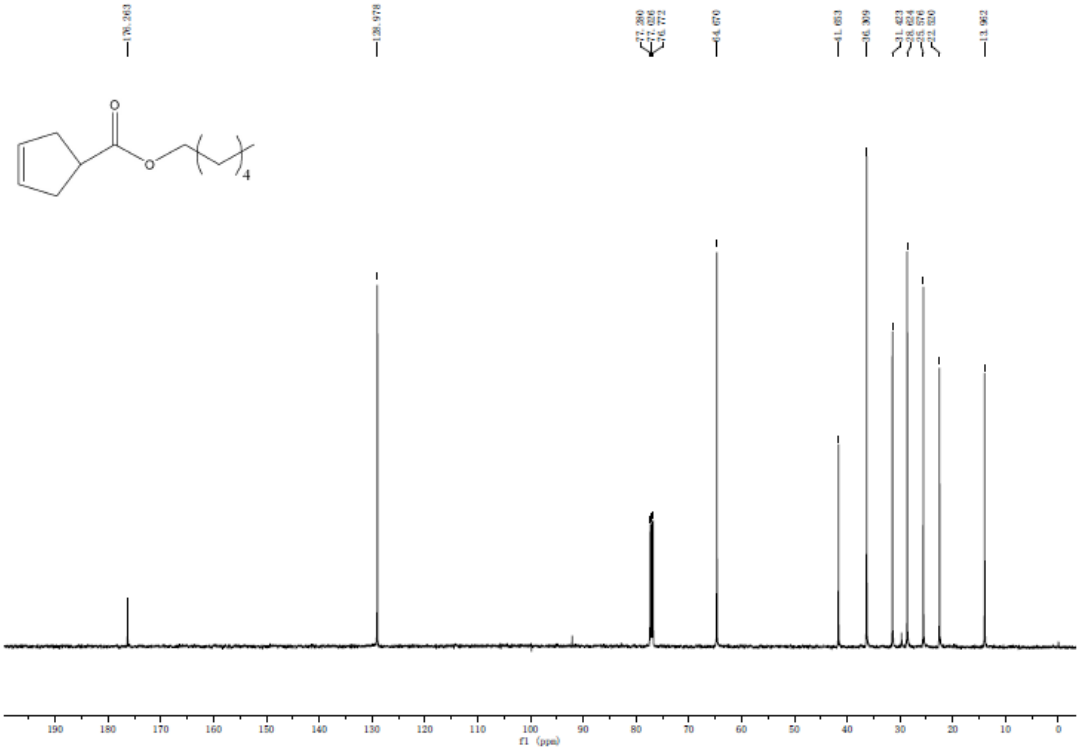


Fig. S29 The ^{13}C NMR spectrum of hexyl 3-cyclopentene-1-carboxylate (9).

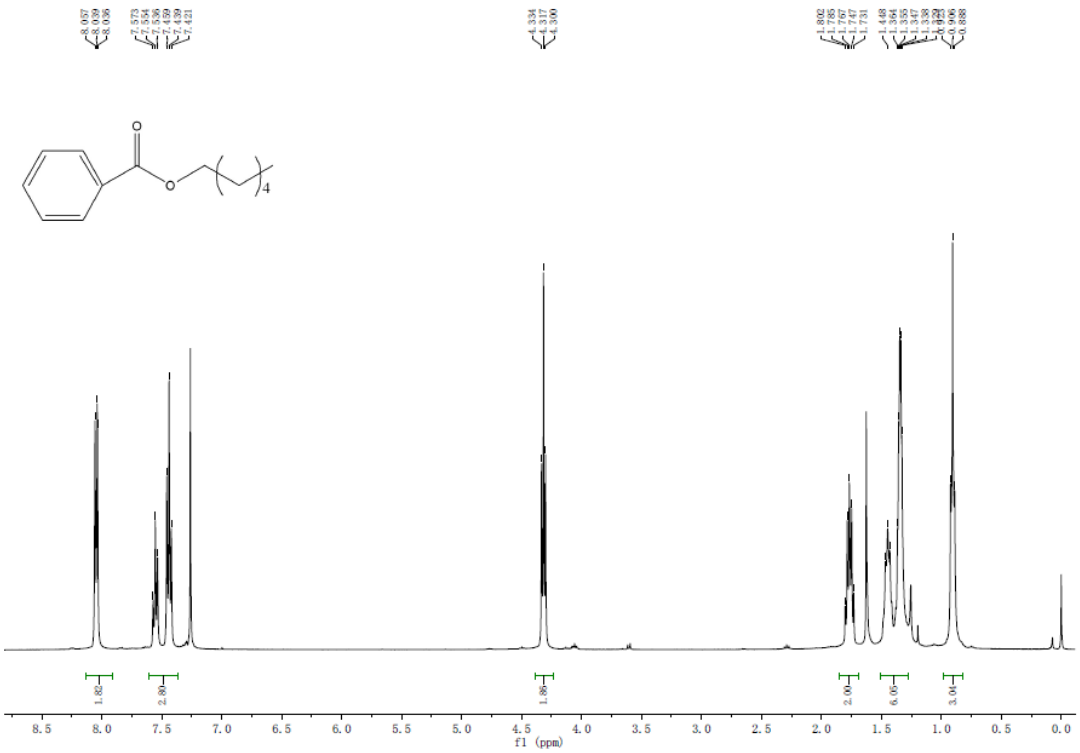


Fig. S30 The ^{1}H NMR spectrum of hexyl benzoate (10).

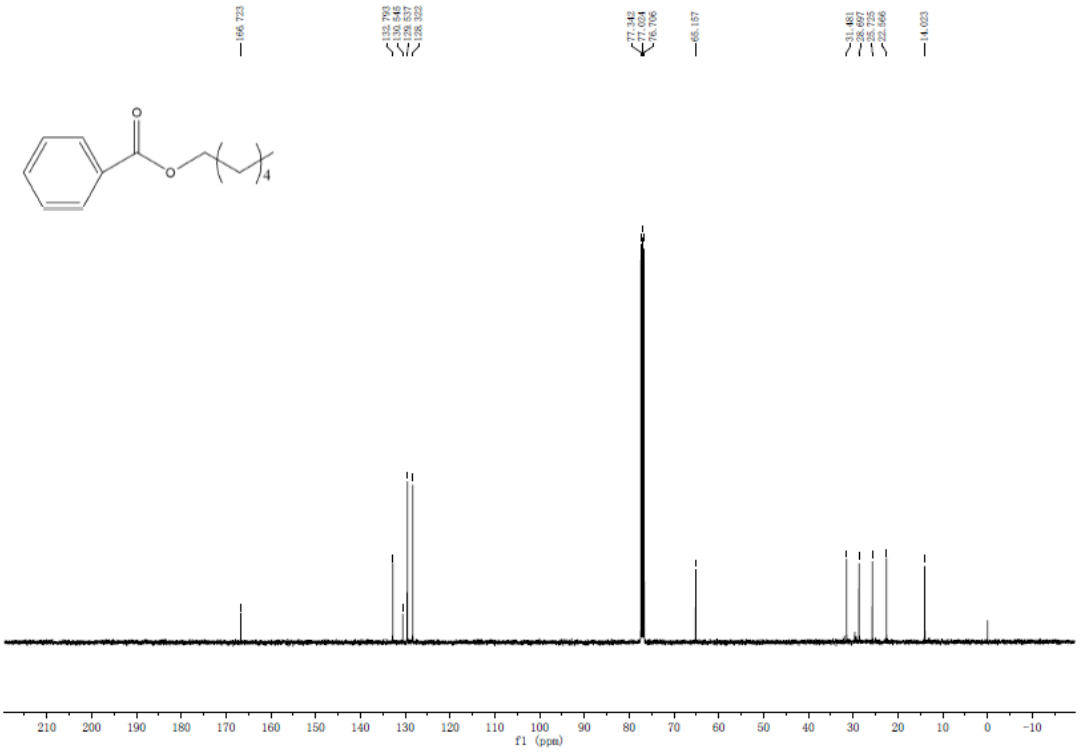


Fig. S31 The ^{13}C NMR spectrum of hexyl benzoate (10).

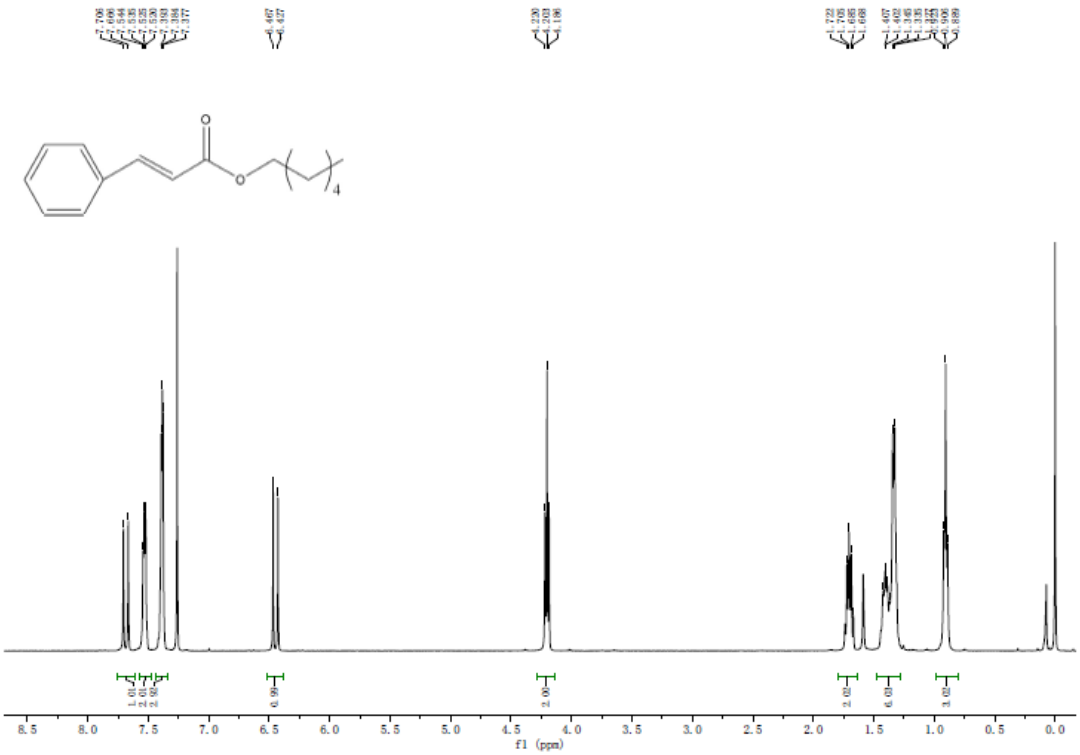


Fig. S32 The ^{1}H NMR spectrum of hexyl cinnamate (11).

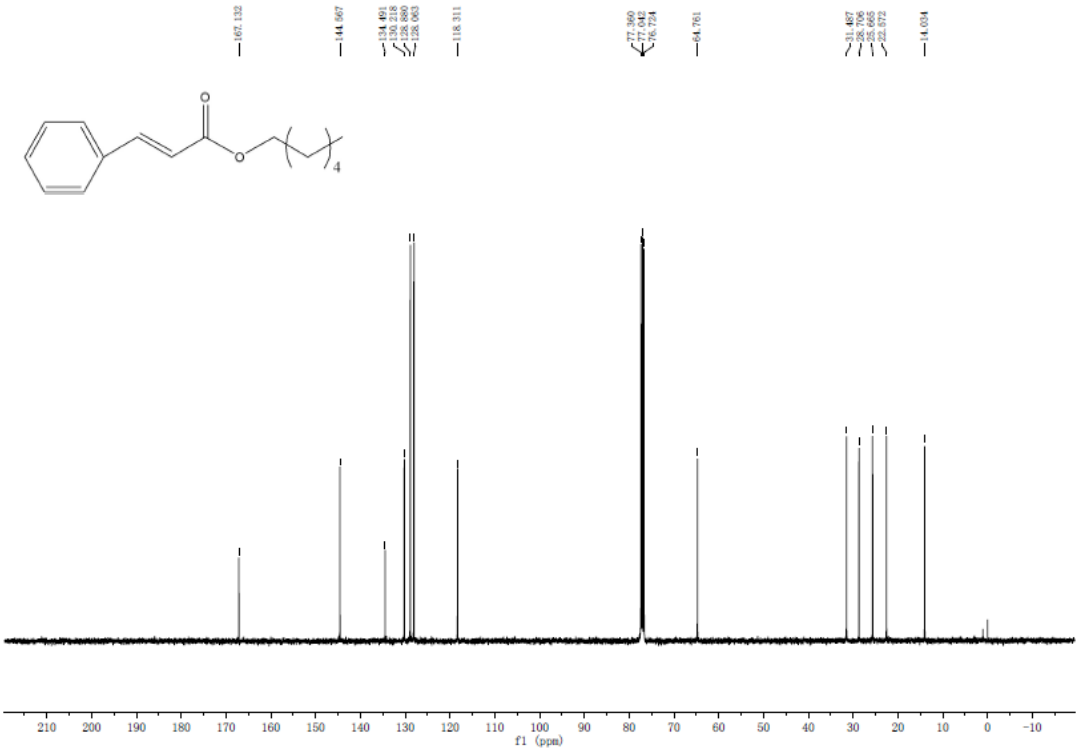


Fig. S33 The ^{13}C NMR spectrum of hexyl cinnamate (11).

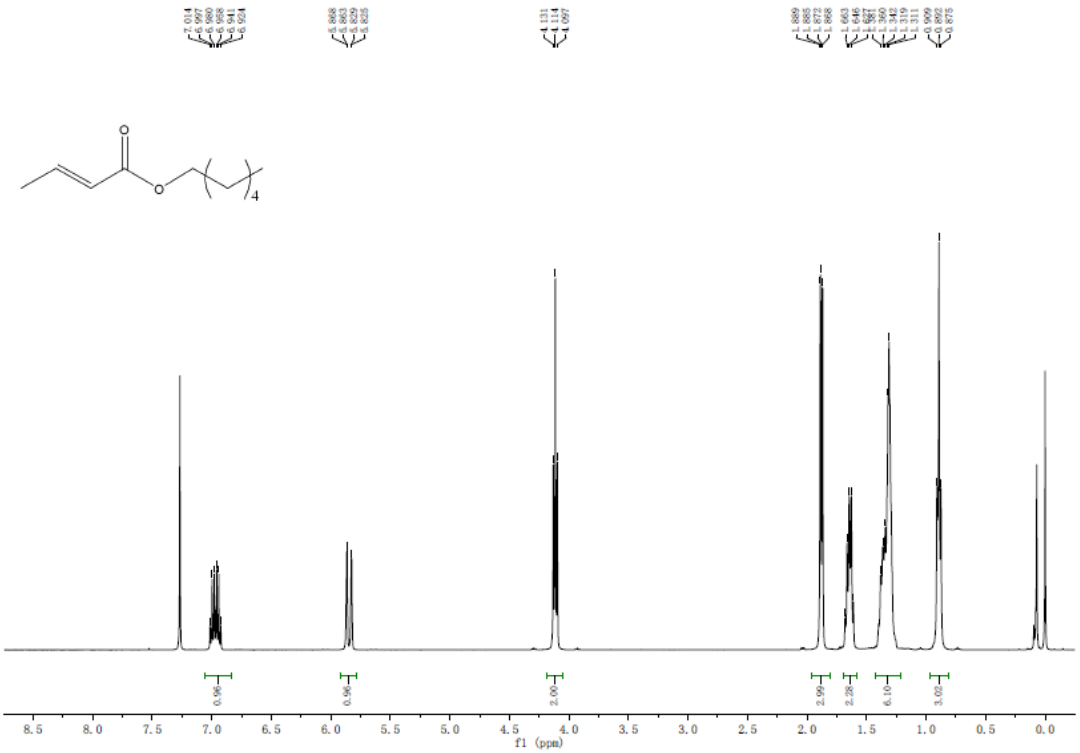


Fig. S34 The ^{1}H NMR spectrum of hexyl 2-butenoate (12).

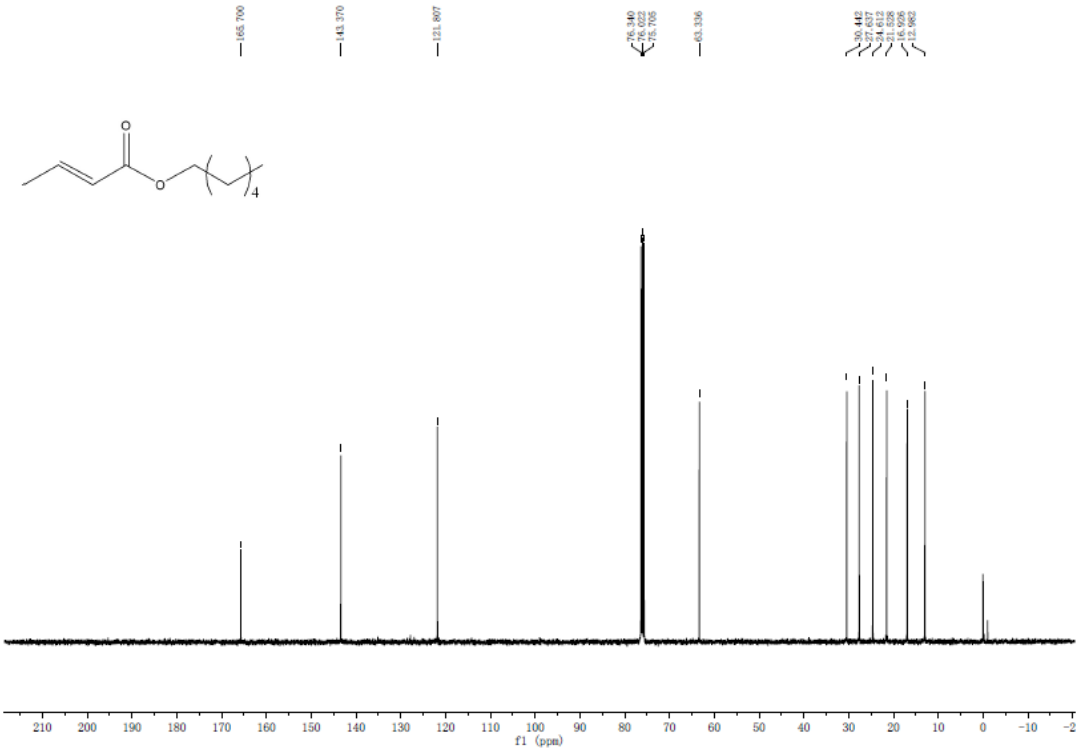


Fig. S35 The ^{13}C NMR spectrum of hexyl 2-butenoate (12).

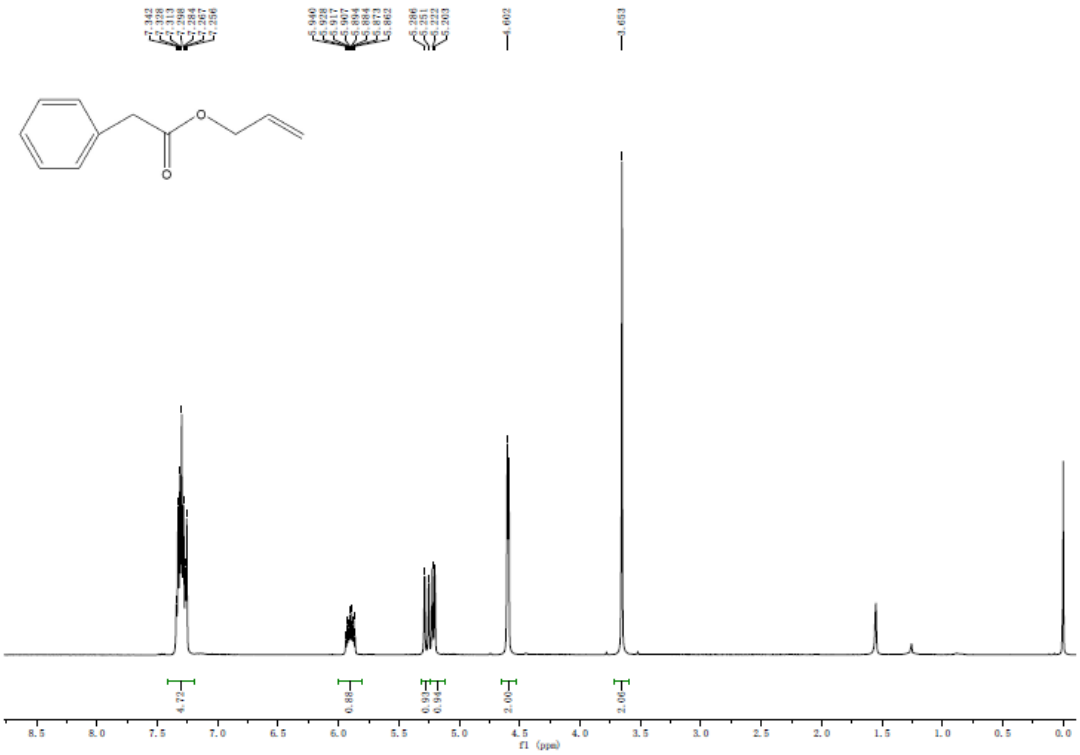


Fig. S36 The ^{1}H NMR spectrum of allyl 2-phenylacetate (13).

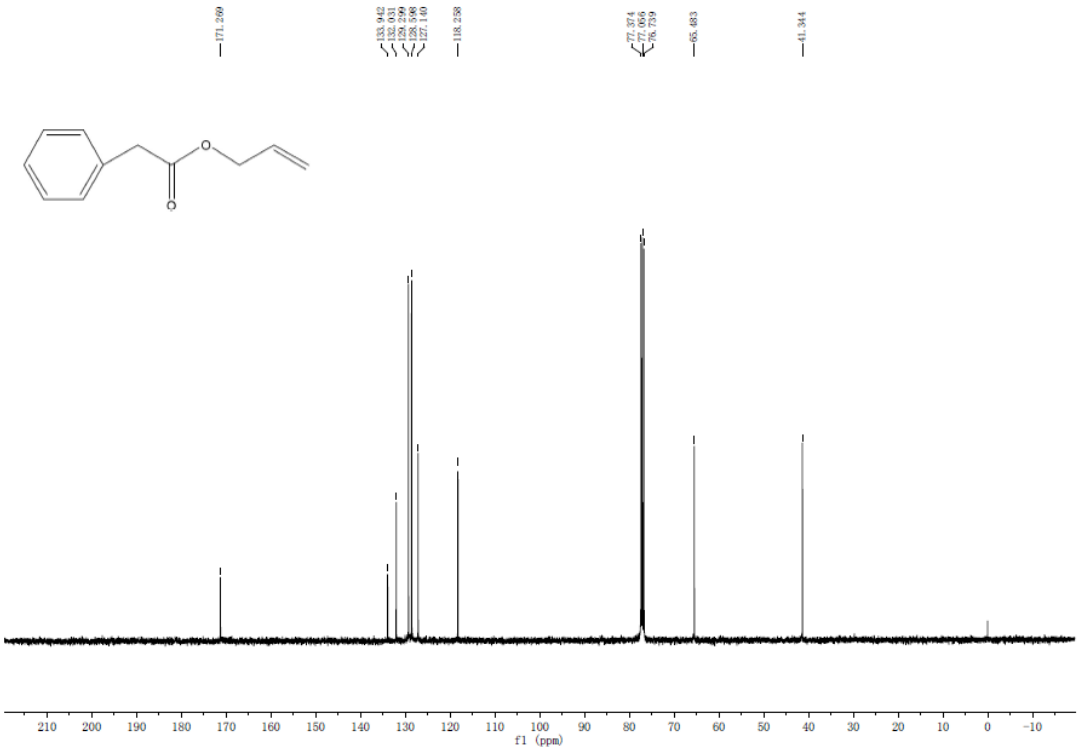


Fig. S37 The ^{13}C NMR spectrum of allyl 2-phenylacetate (13).

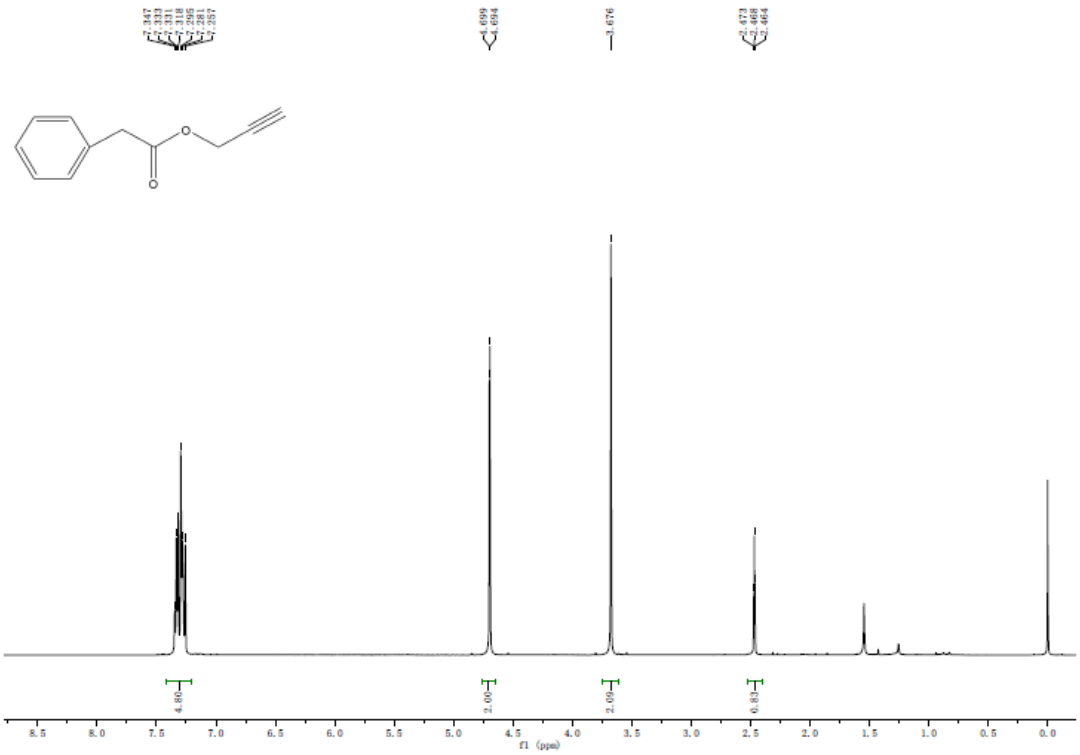


Fig. S38 The ^{1}H NMR spectrum of propargyl 2-phenylacetate (14).

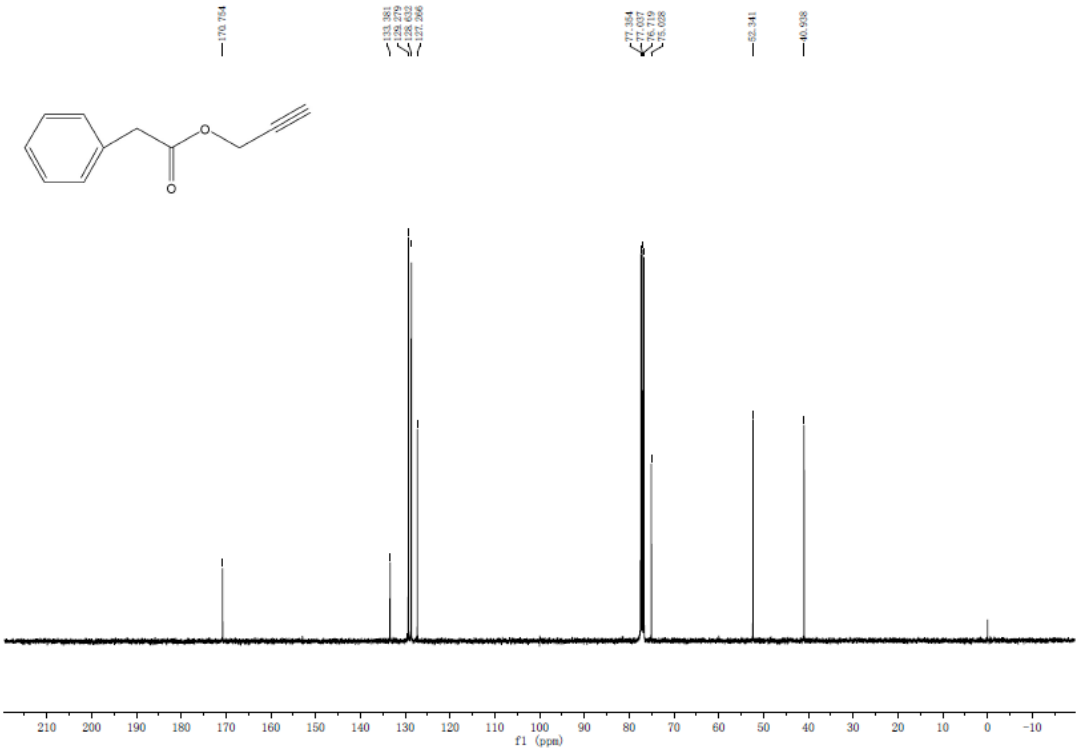


Fig. S39 The ^{13}C NMR spectrum of propargyl 2-phenylacetate (14).

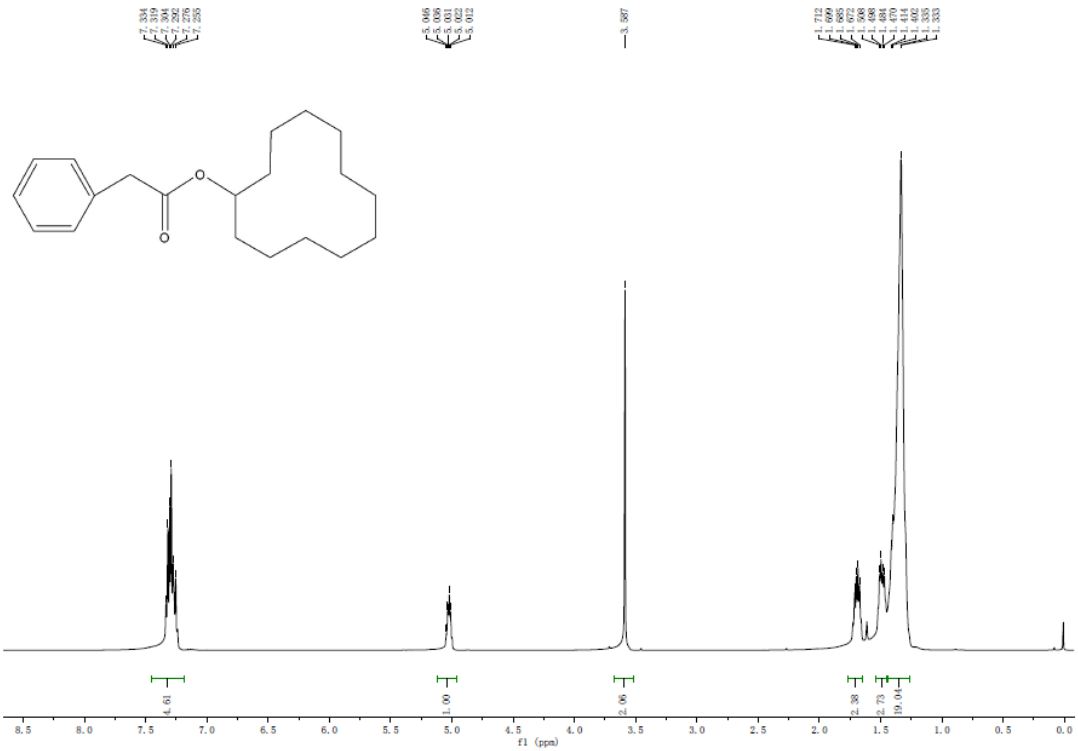


Fig. S40 The ^{1}H NMR spectrum of cyclododecyl phenylacetate (15).

Fig. S41 The ^{13}C NMR spectrum of cyclododecyl phenylacetate (15).

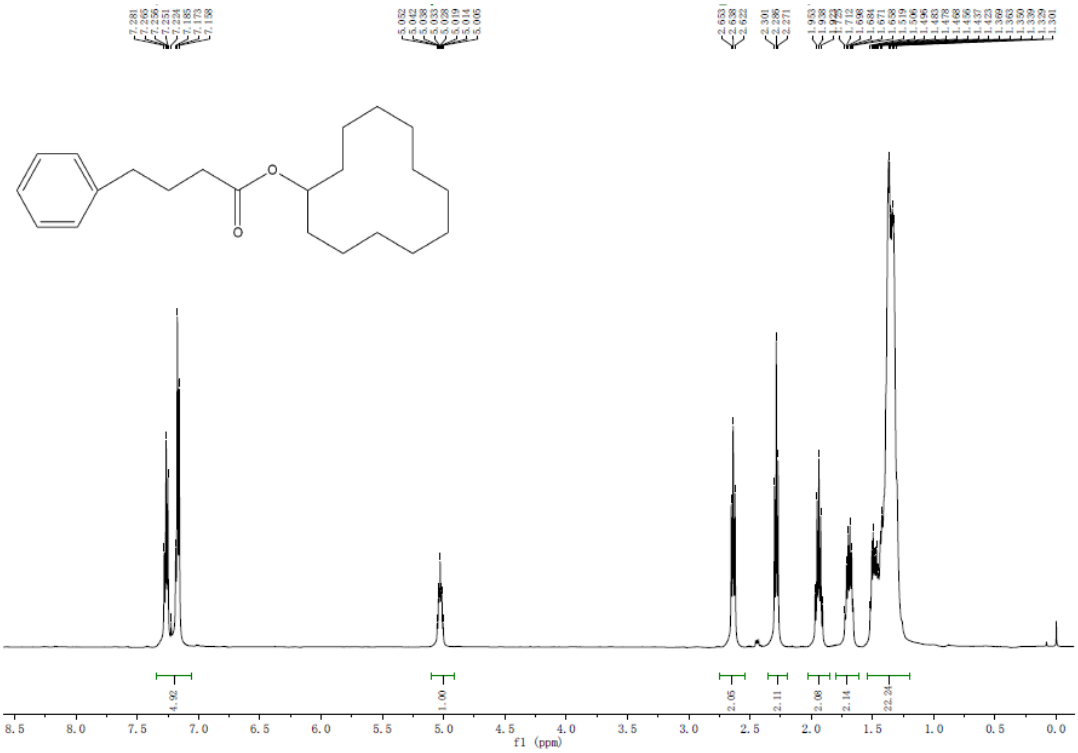


Fig. S42 The ^{1}H NMR spectrum of cyclododecyl 4-phenylbutyrate (16).

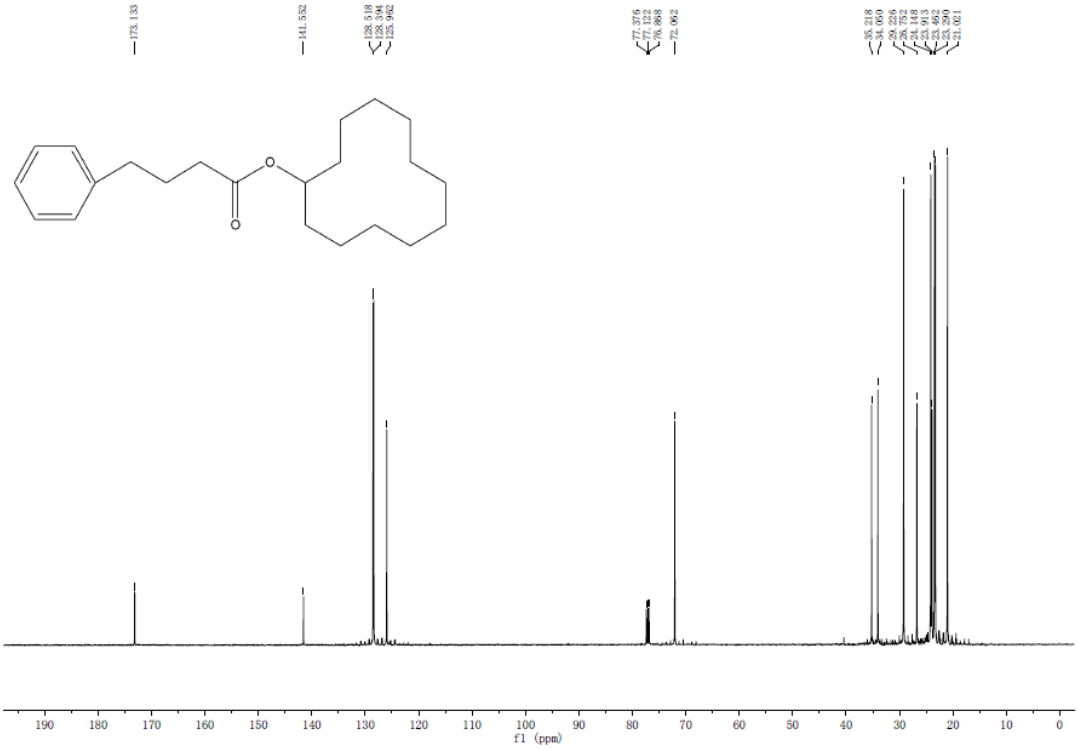


Fig. S43 The ^{13}C NMR spectrum of cyclododecyl 4-phenylbutyrate (16).

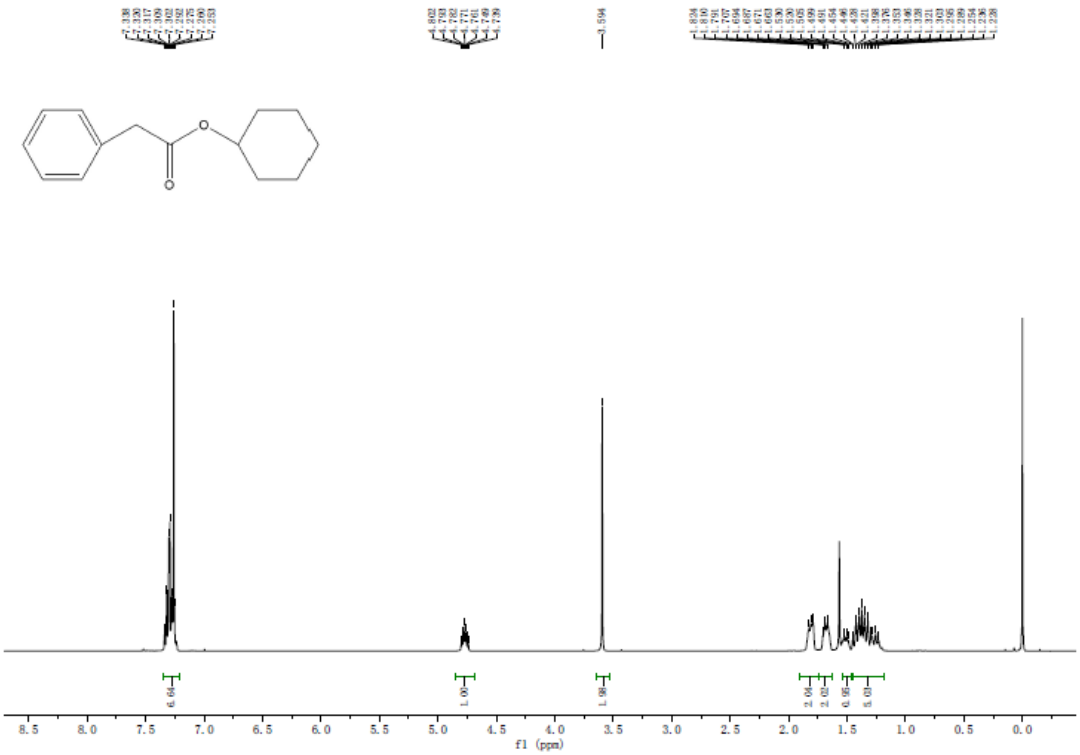


Fig. S44 The ^{1}H NMR spectrum of cyclohexyl phenylacetate (17).

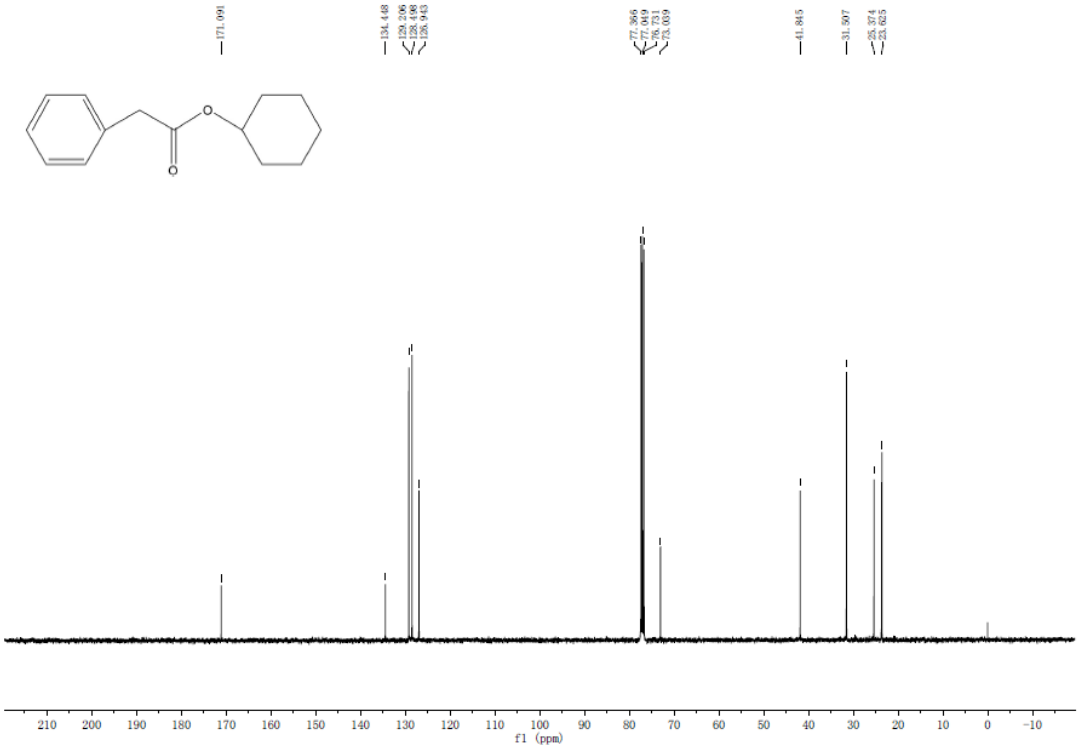


Fig. S45 The ^{13}C NMR spectrum of cyclohexyl phenylacetate (17).

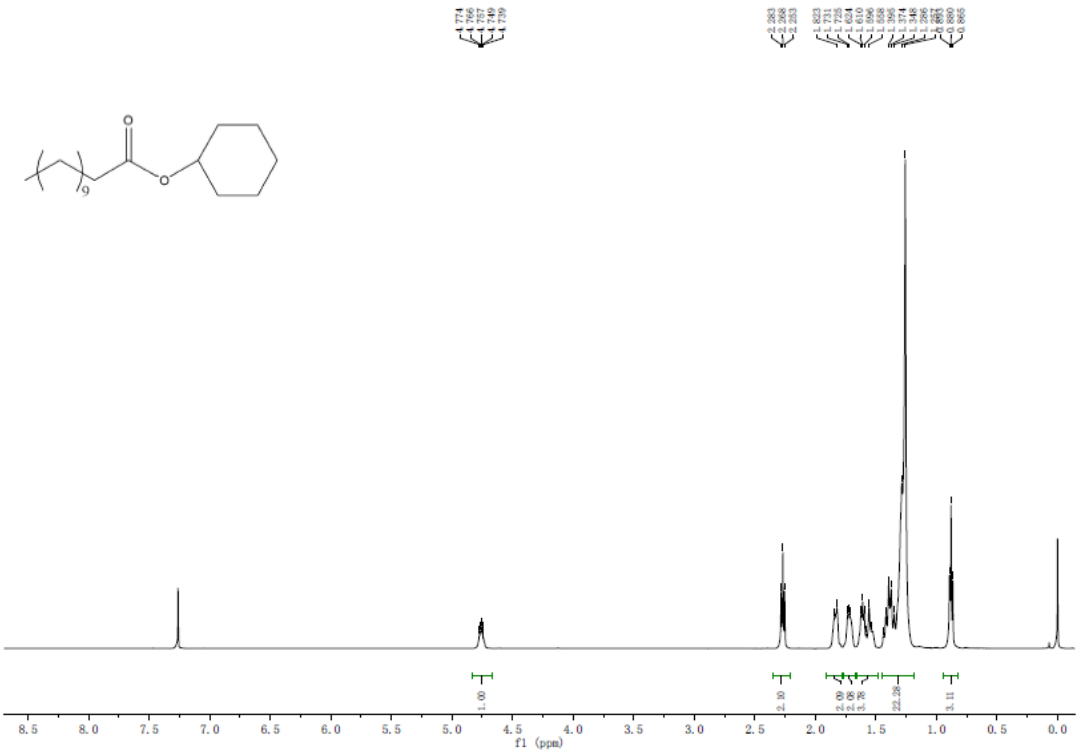


Fig. S46 The ^{1}H NMR spectrum of cyclohexyl dodecanoate (18).

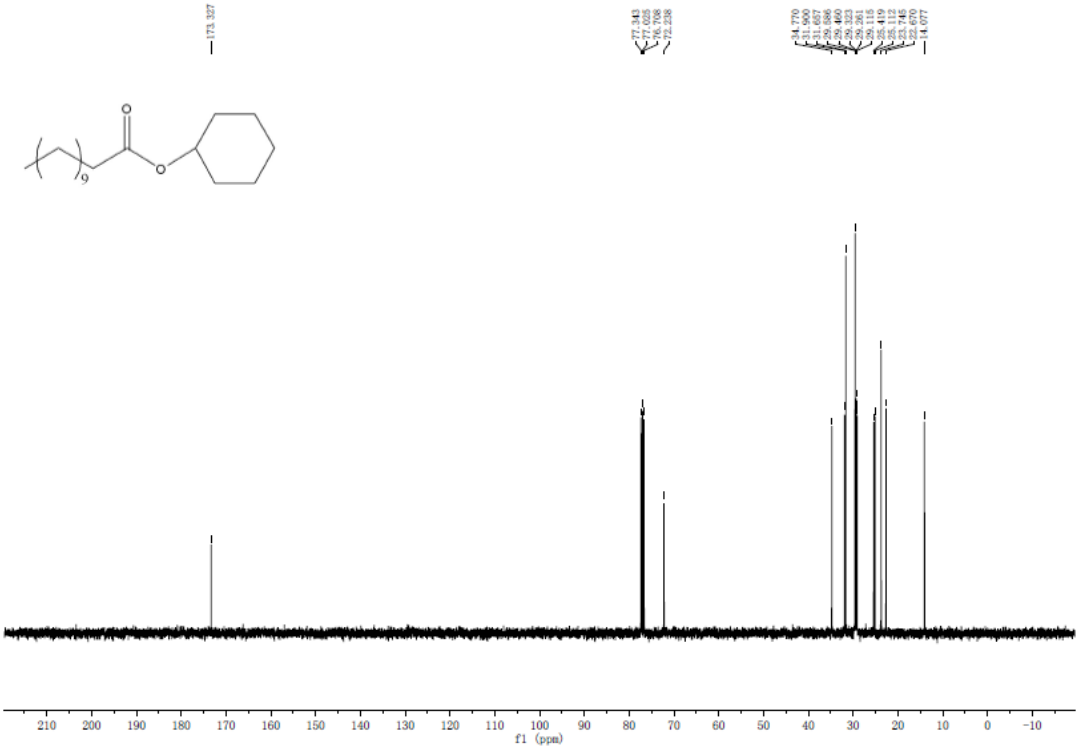


Fig. S47 The ^{13}C NMR spectrum of cyclohexyl dodecanoate (18).

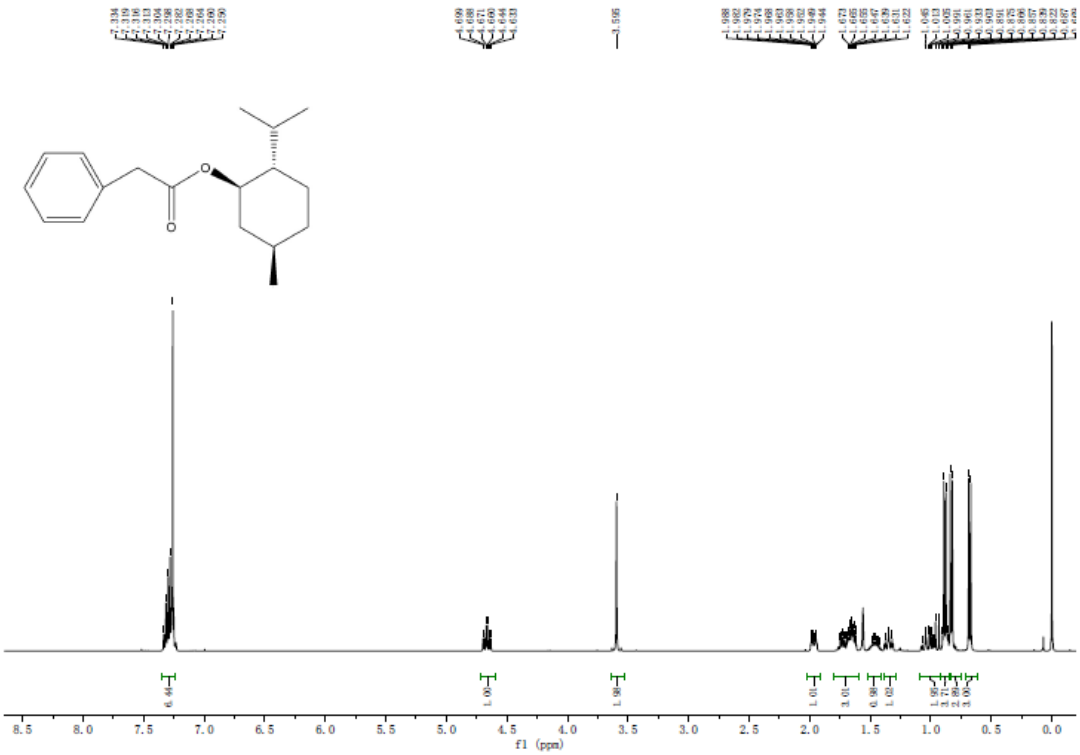


Fig. S48 The ^{1}H NMR spectrum of L-(−)-menthyl phenylacetate (19).

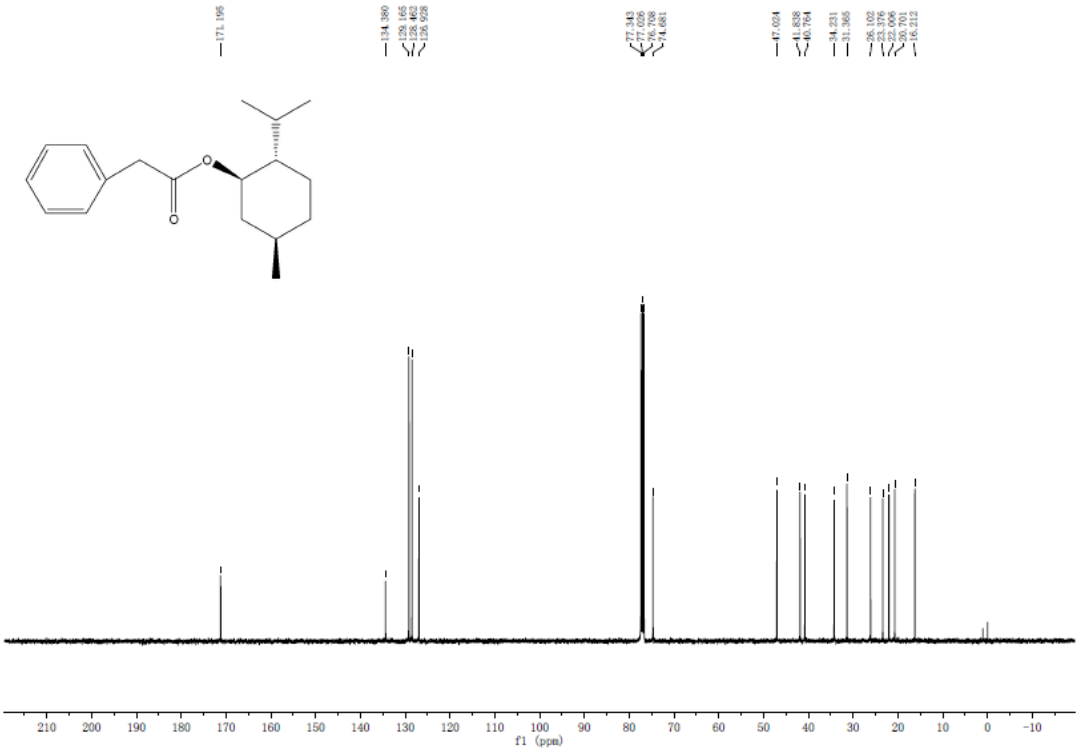


Fig. S49 The ^{13}C NMR spectrum of L-(−)-menthyl phenylacetate (19).

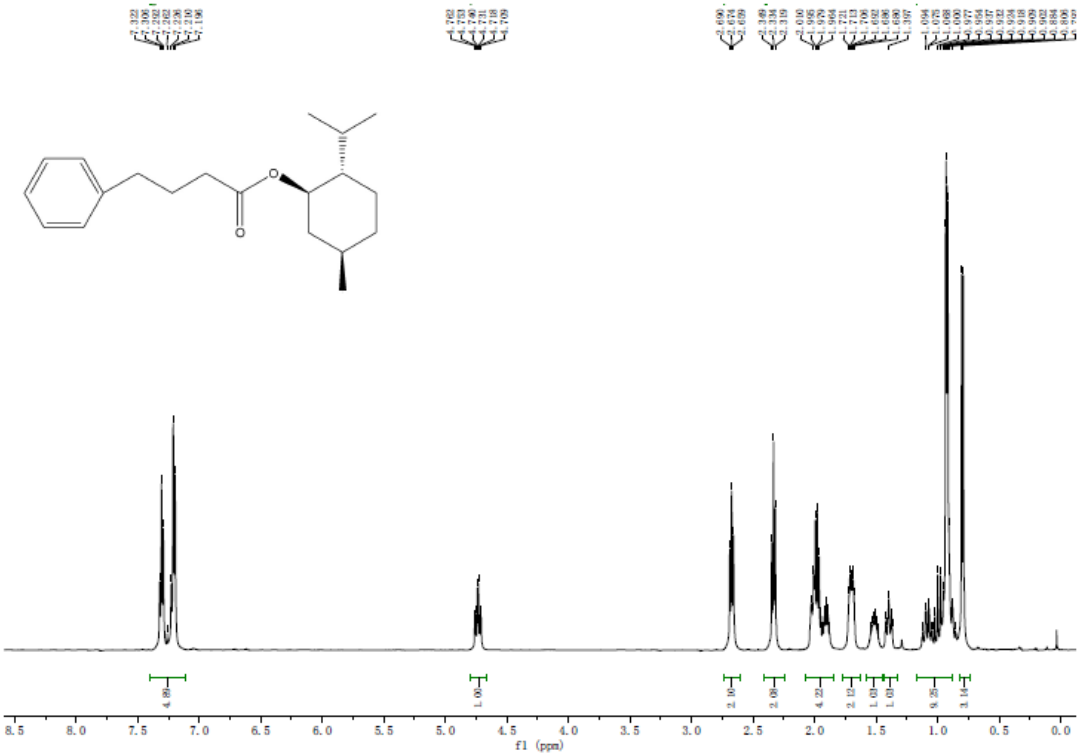


Fig. S50 The ^{1}H NMR spectrum of L-(−)-menthyl 4-phenylbutyrate (20).

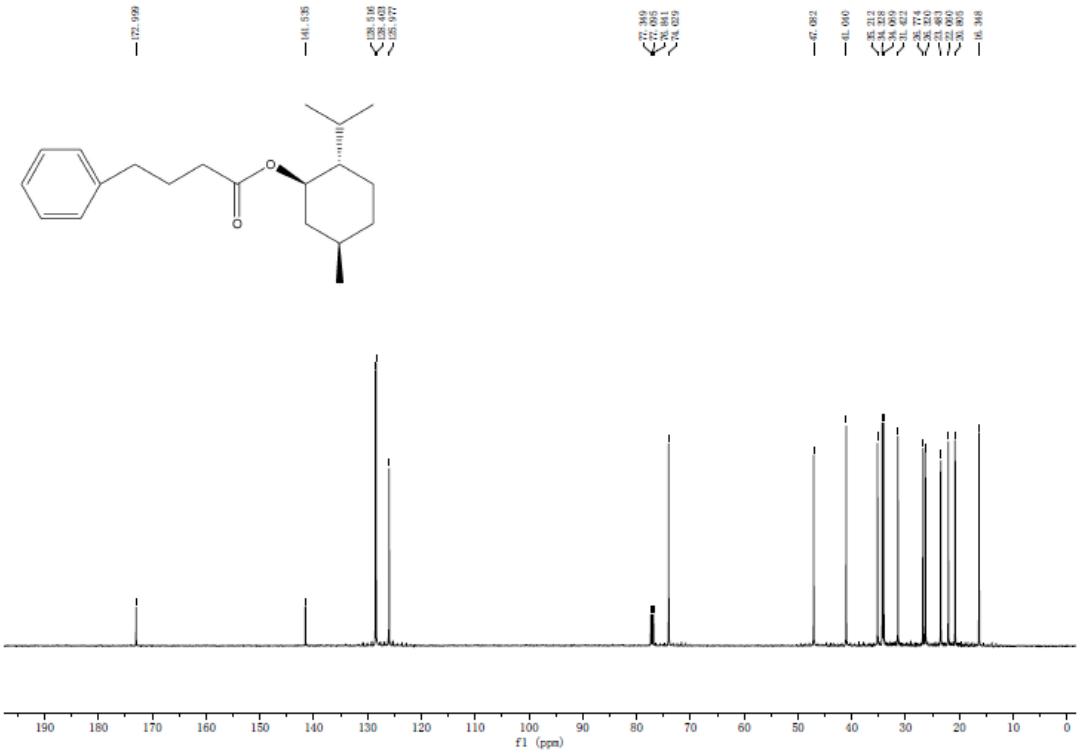


Fig. S51 The ^{13}C NMR spectrum of L-(−)-menthyl 4-phenylbutyrate (20).

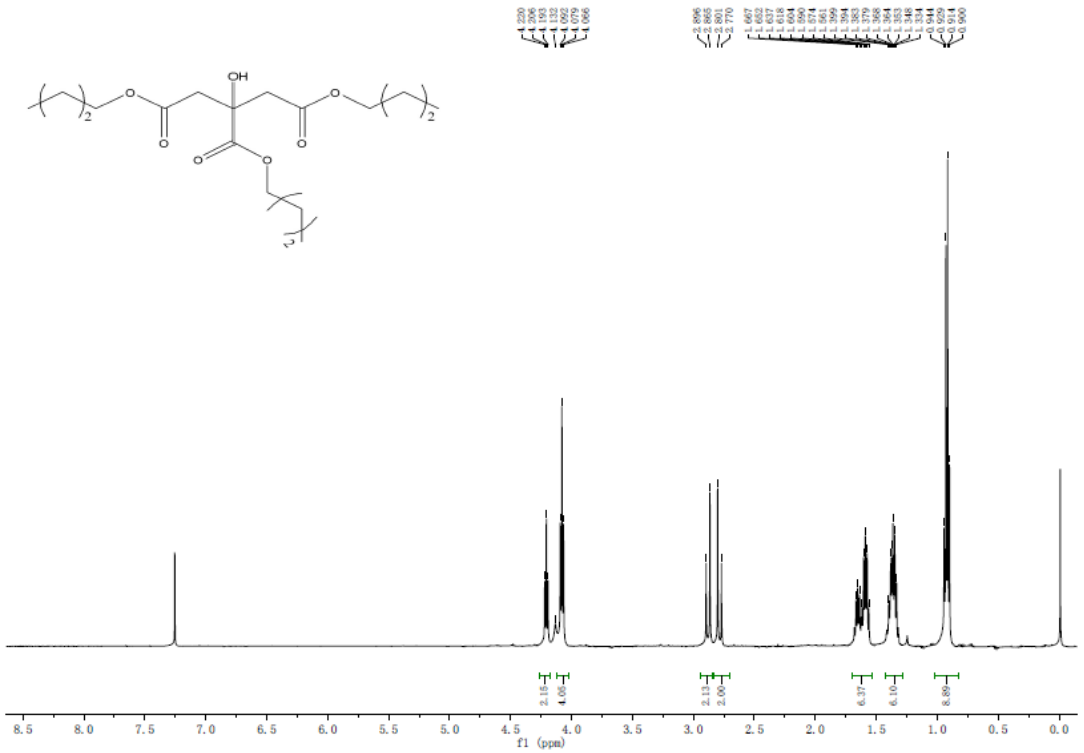


Fig. S52 The ^{1}H NMR spectrum of tributyl citrate (21).

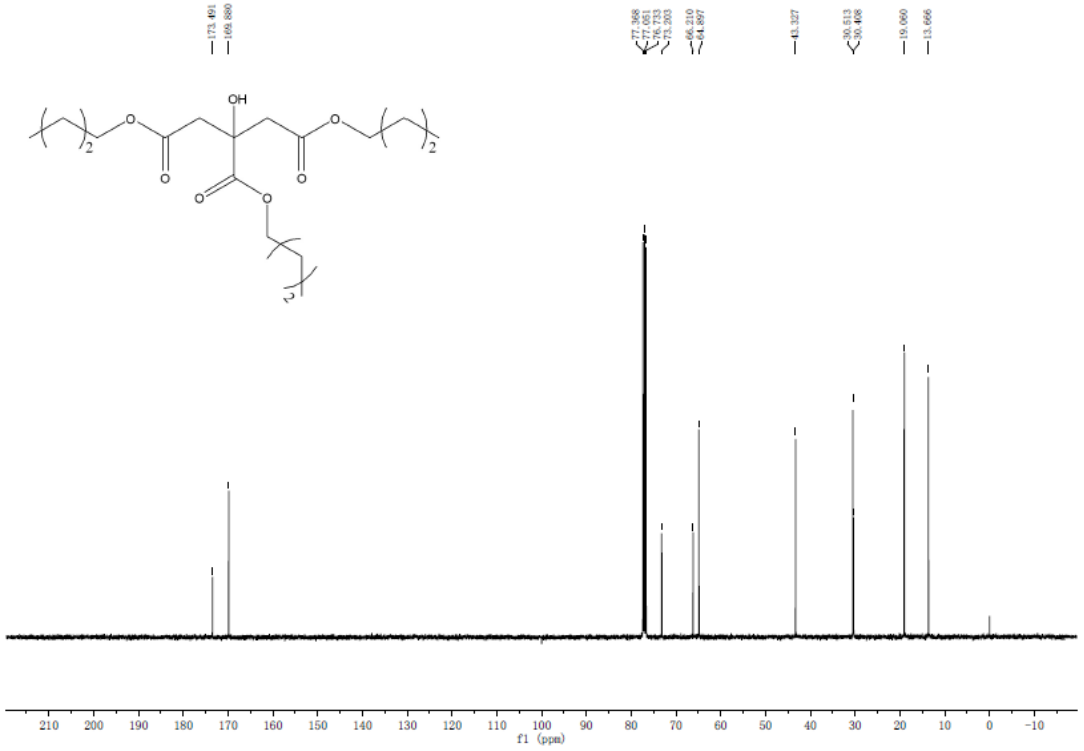


Fig. S53 The ^{13}C NMR spectrum of tributyl citrate (21).

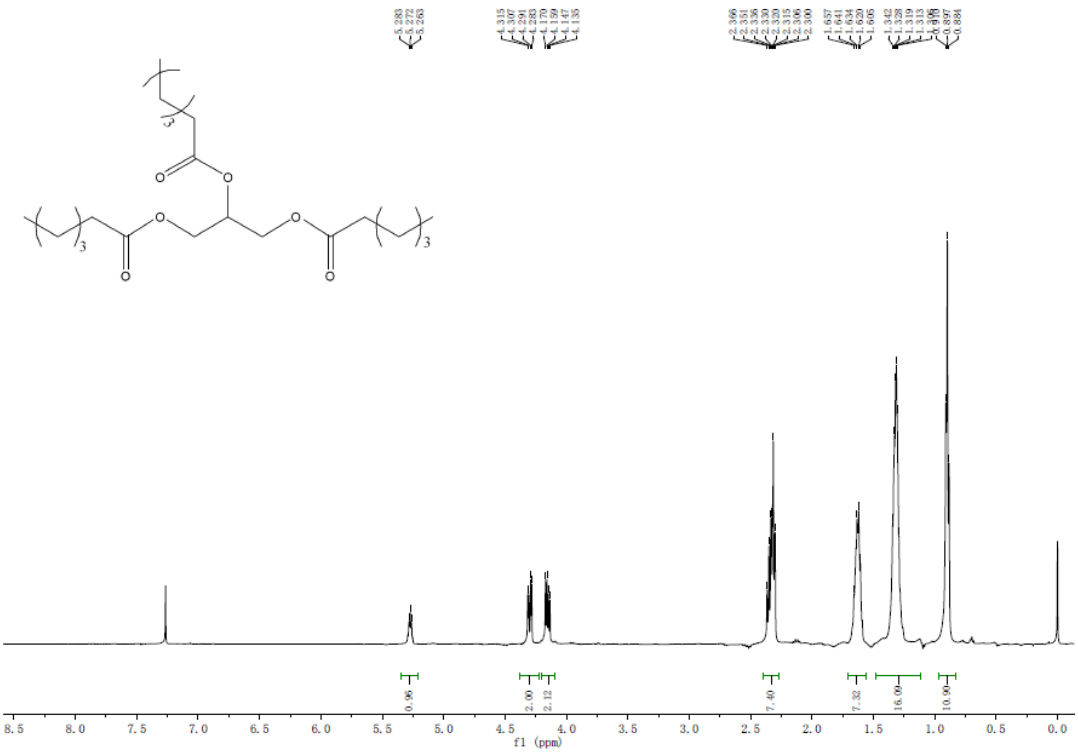


Fig. S54 The ^{1}H NMR spectrum of glycerol trihexanoate (22).

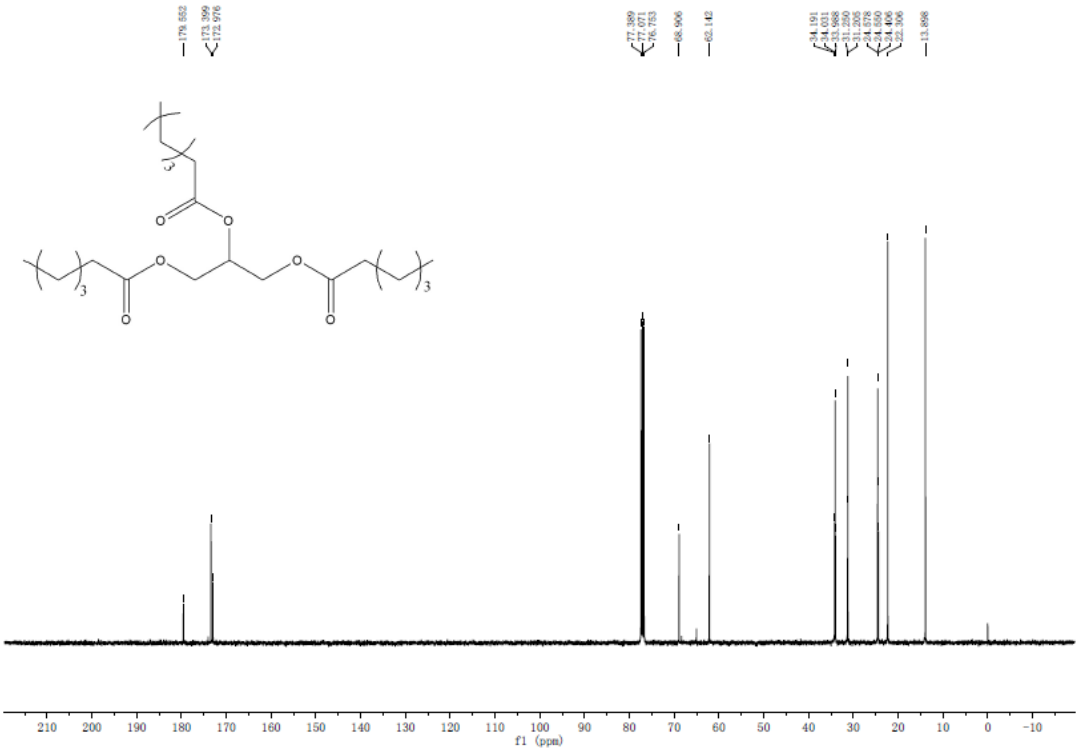


Fig. S55 The ^{13}C NMR spectrum of glycerol trihexanoate (22).

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