Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Periodic mesoporous organosilica functionalized sulfonic acid in the esterification and selective acylation reactions

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Table of Contents

1. Experimental Procedure

1-1. General

^{1}H NMR spectra were recorded on commercial instruments (250 MHz and 400 MHz). Chemical shifts were reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ= 7.26). Spectra are reported as follows: chemical shift (= ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constants (Hz), integration. ^{13}C NMR spectra were collected on commercial instruments (62.90 MHz and 100.60 MHz) with complete proton decoupling. Reagents obtained from commercial sources were used without further purification. Thermal treatments were conducted from room temperature to 800 °C in argon flow using a Pheometric Scientific analyzer.

1-2. Chemicals

BTEB (1,4-bis(triethoxysilyl)benzene), BTEE (1,2-bis(triethoxysilyl)ethane), MPMDS (3-mercaptopropylmethyldimethoxysilane), and triblock co-polymer P123 (Eo_{70} Po_{20} Eo_{70}) were obtained from Aldrich and used as received.

1-3. Preparation of Et-PMO-Me-PrSO_3H (1b)

Organosulfonic acid-functionalized mesoporous organosilicas (1a and 1b) were synthesized as our previous publication:[1]

In this synthesis procedure, P123 (1.95 g) was added under vigorous stirring to 70 ml of HCl solution (2N). After complete dissolution of surfactant at 35 °C, BTEE (2.77 g) was added and the agitation was continued for 3h before the drop wise incorporation of MPMDS (0.478 g). The stirring was followed for 24 h at 35 °c. Then the suspension was aged for 24 h at 87 °C. The solid material were separated by filtration, washed with deionized water and dried at room temperature. The surfactant was removed by solvent extraction with anhydrous ethanol in a soxhlet apparatus for 24 h. Typically, 0.2 g of extracted material was contacted with 8 g H_2O_2 (30 wt%) and the suspension was stirred at room temperature for 24 h. After filtration and washing with deionized water and warm ethanol separately, the oxidized samples were acidified in 100 ml 0.1M H_2SO_4 solution during 2 h. Next, the samples were washed thoroughly with deionized water until neutral pH, filtered and vacuum dried at 60 °C overnight.

1-4. Preparation of Ph-PMO-Me-PrSO_3H (1a)

In a typical one-step synthesis, 0.66 g pluronic P123 was dissolved in 23.6 g deionized water, 0.57 g H_2O_2 (30wt%), and 0.13 g of HCl (37 wt%). Then 0.47 g BTEB and 0.0902 g (30 mol% in total silica precursors) of MPMDS were added to the solution. The resulting mixture was agitated for 2 h at 40 °C and thereafter aged for 24 h at 100 °C. The resulting solid material was filtered and air-dried. To extract the residual block co-polymer, the solid material (0.5 g) was stirred in acetone (60 ml) for 10 h at 56 °C, followed by washing with deionized water. The final products were obtained after drying the samples in oven for 1 day at 100 °C.

1-5. Preparation of SBA-15-Pr-SH

The synthesis of SBA-15-PrSH has been achieved similar to our previous publication[1] using known procedure described by Stucky and his co-workers.[2] This procedure involved a synthetic strategy based on cocondensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as structure

directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6 g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h.

1-6. Preparation of SBA-15-Ph-PrSH [3]

To a suspension of SBA-15-Pr-SH (3 g) in dry toluene $PhSi(OEt)_3$ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24 h. The solid materials was filtered and successively washed with toluene, EtOH, and Et_2O and dried overnight at 120 °C to afford the corresponding SBA-15-Ph-PrSH.

1-7. Preparation of SBA-15-PrSO$_3$H

Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with deionized water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

1-8. Preparation of SBA-15-Ph-PrSO$_3$H [2]

Conversion of thiol groups of catalyst to sulfonic acid moiety was accomplished by hydrogen peroxide. Typically, 0.3 g of solid hodrophobic material was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

1-9. Characterization

The textural properties of the functionalized mesoporous organosilicas were measured from nitrogen adsorption-desorption isotherms at 77 k with a BELSORB system. The surface area and pore size distribution were calculated with the BET and BJH methods, respectively. Organic material present in the solids was determined by elemental analysis and the organic composition of the modified mesoporous materials was determined by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) with TGA Q50 V6.3 Build 189 instrument, with heating from room temperature to 800 $^{\circ}$C under Argon flow. The ion exchange capacities of the functionalized mesoporous organosilicas were determined by acid-base titration and *p*H metery. The TEM images also demonstrate that the mesostructures Et-PMO-Me-PrSO$_3$H exhibit ordered 2D-hexagonal (p6mm) patterns.

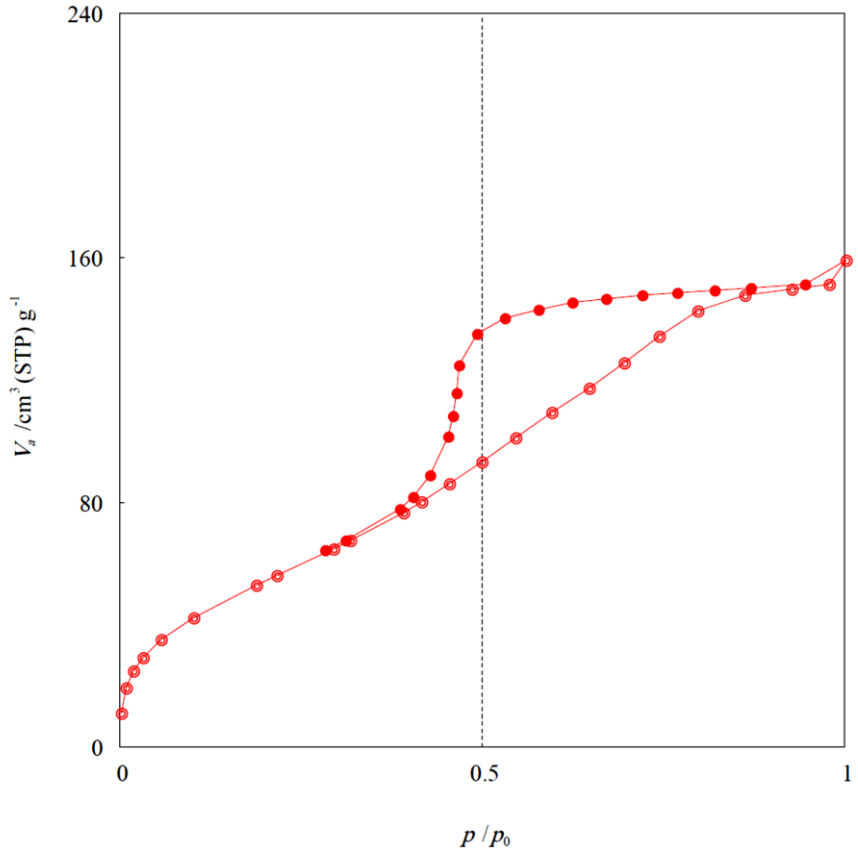


Fig. S1. N_2 adsorption-desorption of Et-PMO-Me-PrSH

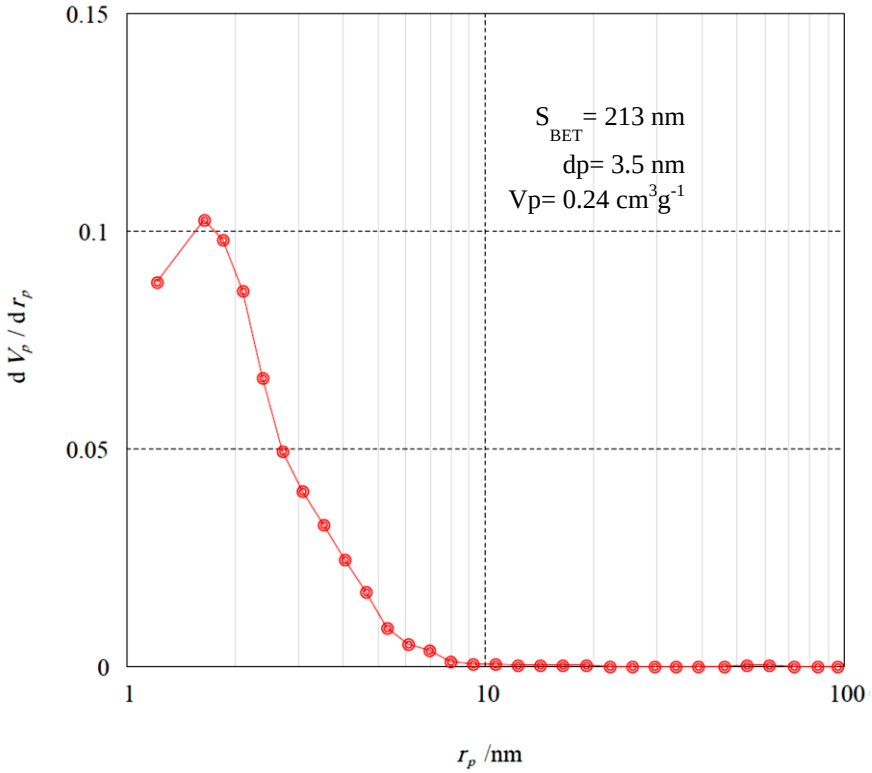


Fig. S2. BJH analysis of Et-PMO-Me-PrSH

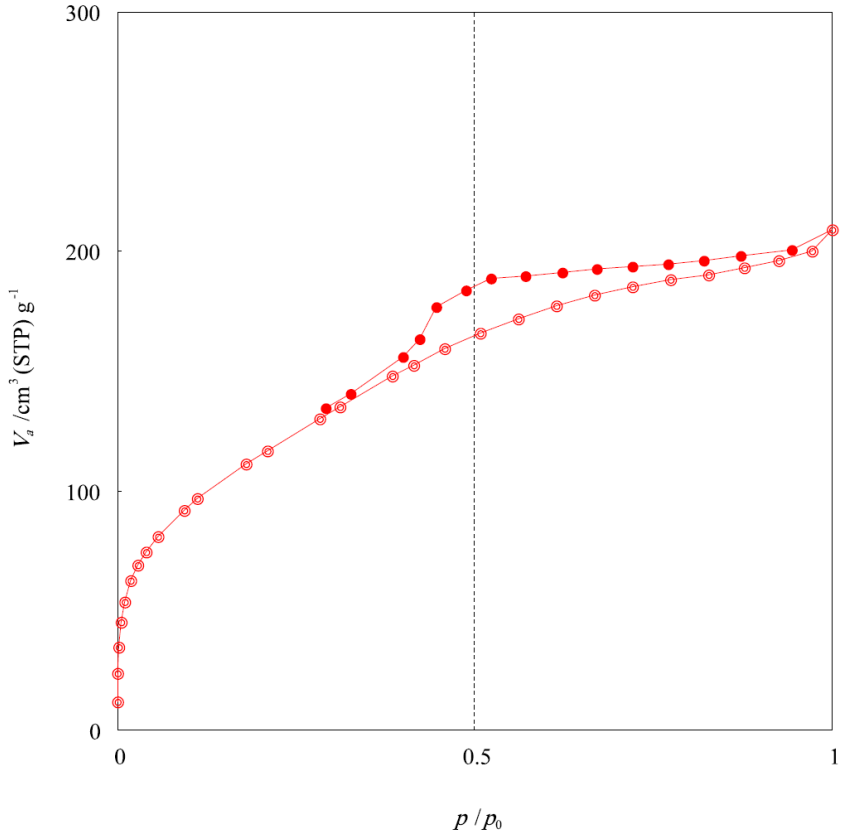


Fig. S3. N_2 adsorption-desorption of Et-PMO-Me-PrSO_3H catalyst

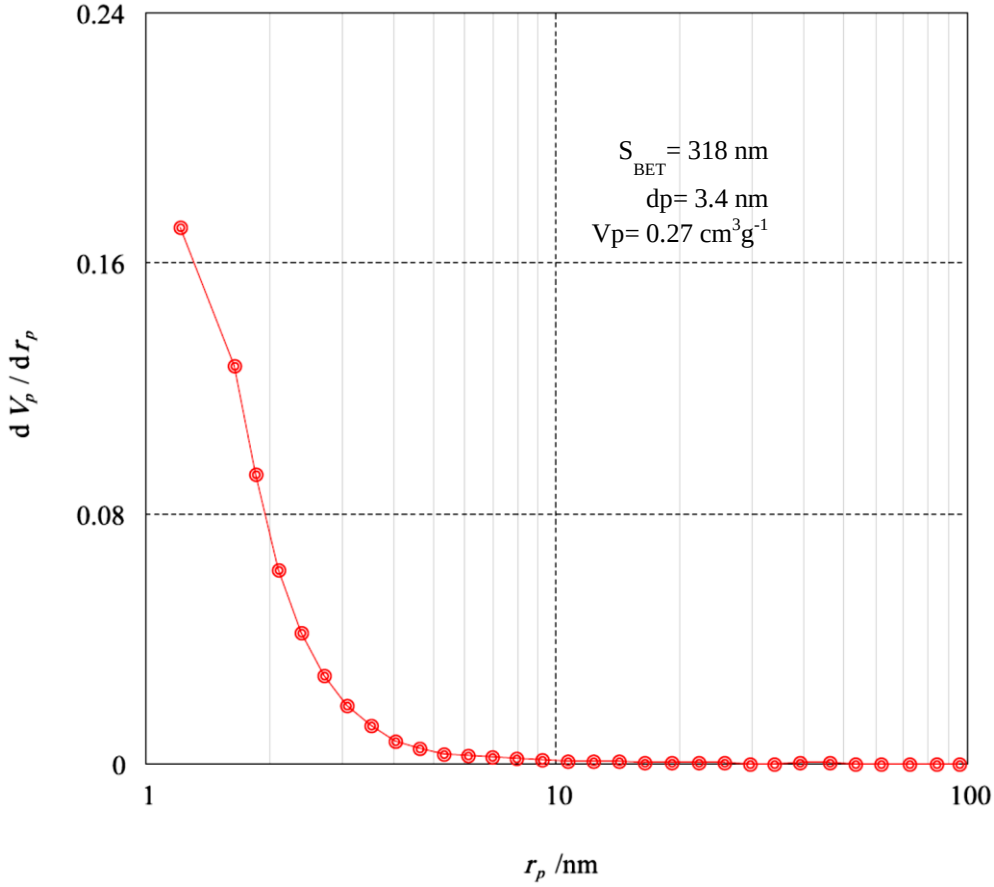


Fig. S4. BJH analysis of Et-PMO-Me-PrSO_3H catalyst

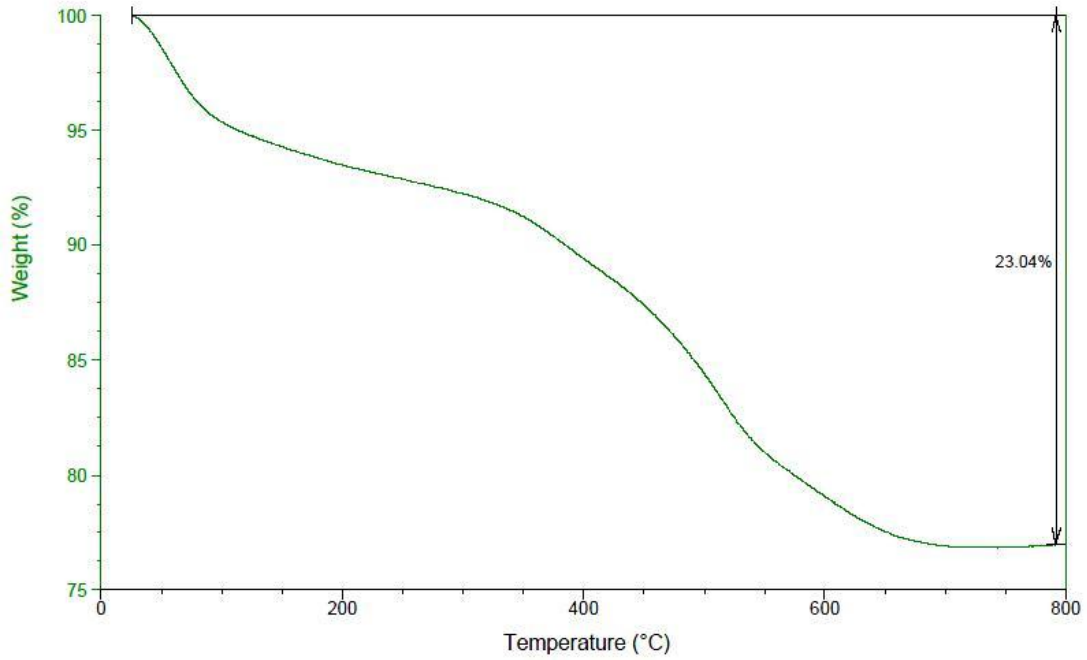


Fig. S5. TGA analysis of Et-PMO-Me-PrSO_3H catalyst

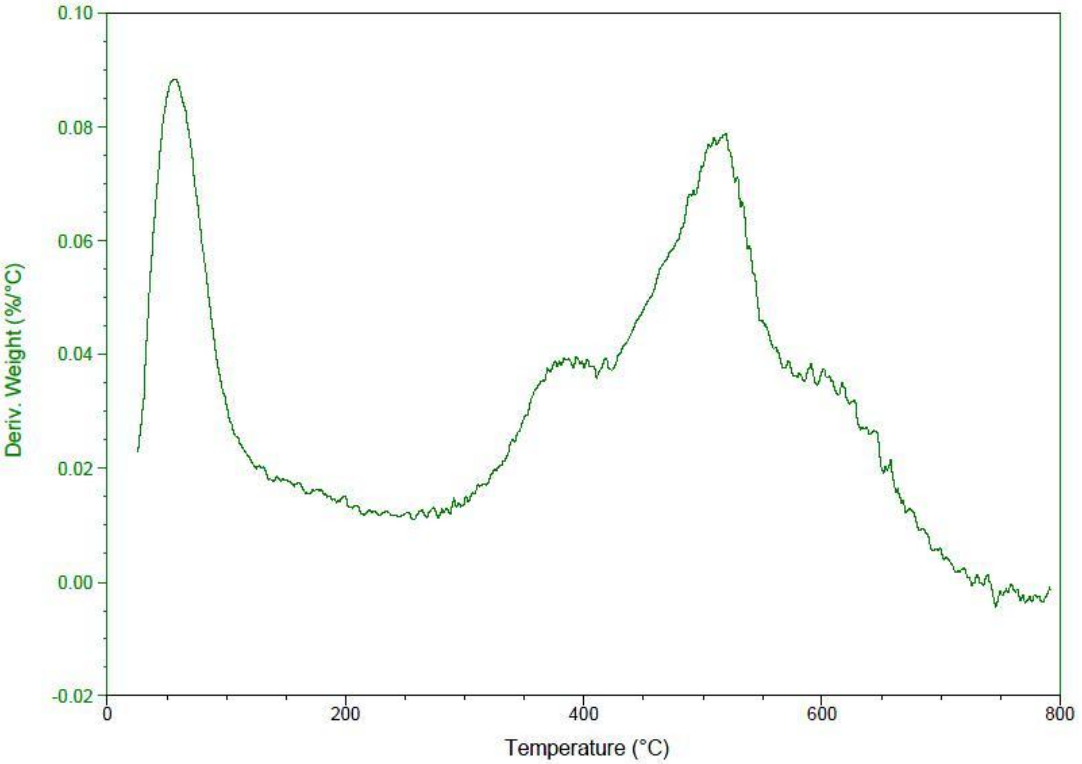


Fig. S6. DTA diagram for Et-PMO-Me-PrSO_3H catalyst

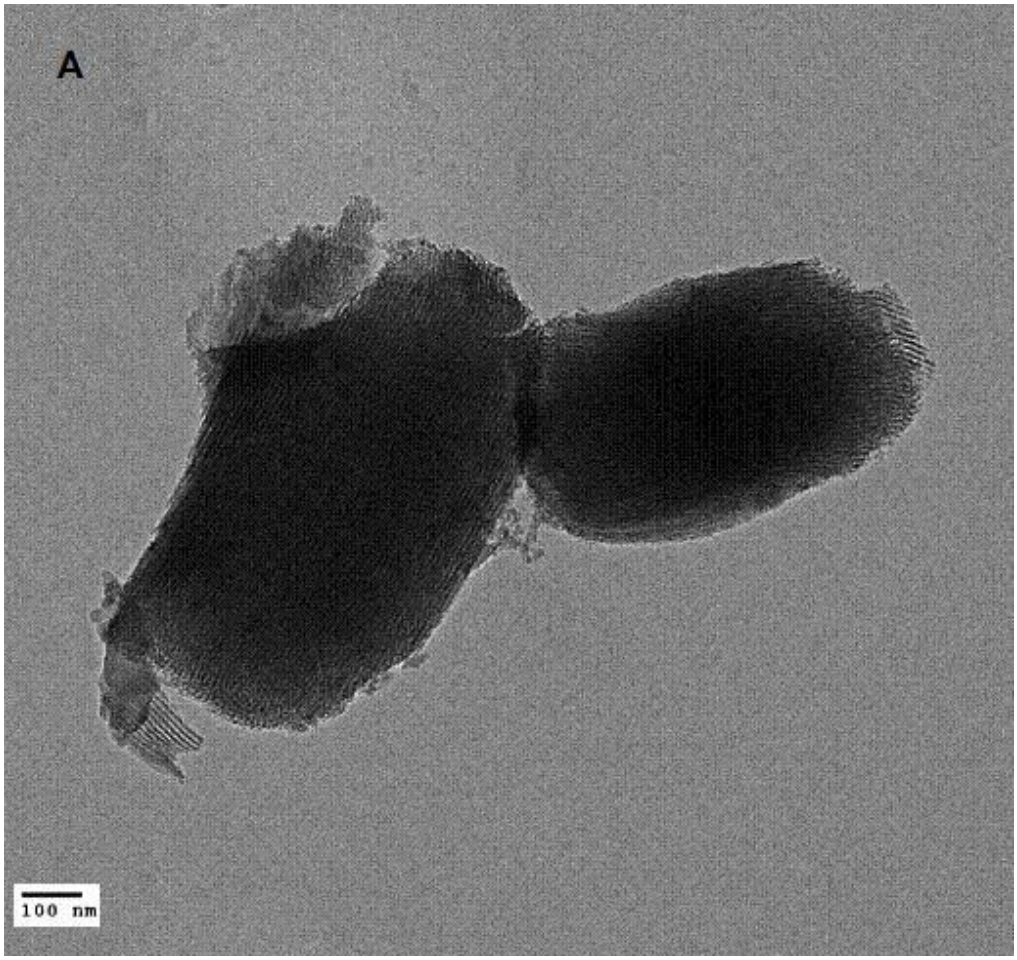


Fig. S7. TEM image of Et-PMO-Me-PrSO_3H catalyst

Hydrophilicity index

H-index developed by Thommes is measured according to the volume of liquid adsorbed using Gurvich rule (Eq. 1). The Gurvich rule allows conversion of the adsorbed amount (at a relative pressure of 0.92) into a pore volume by assuming that the pores are filled with the liquid adsorptive (at P/P^0=0.92 all micro- and mesoporous are filled with the liquid adsorptive).

(Eq. 1): $\mathbf{V_p = V_a/22414 \times M_g / \rho_a}$
Where M_g is molecular weight of the adsorptive gas and ρ_a is density of adsorptive.
Having ρ_a (nitrogen)= 0.808 g/cm^3 and ρ_a (water)=0.997 g/cm^3

Thus: V_p(nitrogen) = V_a(nitrogen) × 0.001547
V_p(water) = V_a(water) × 0.0008055

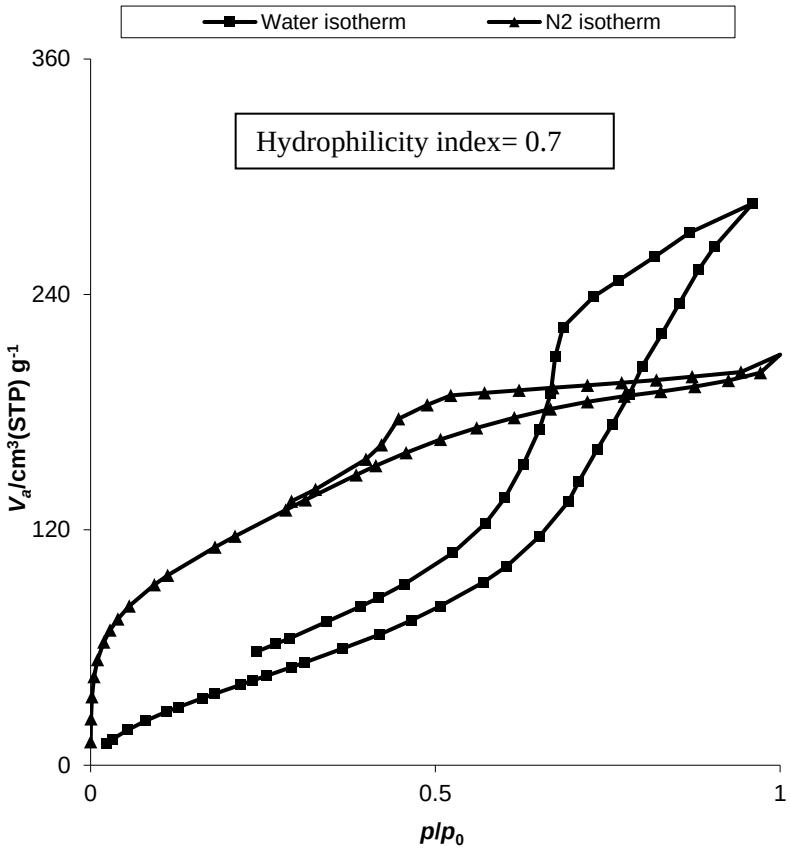


Fig. S8. Both nitrogen and water sorption analysis of **1b** catalyst

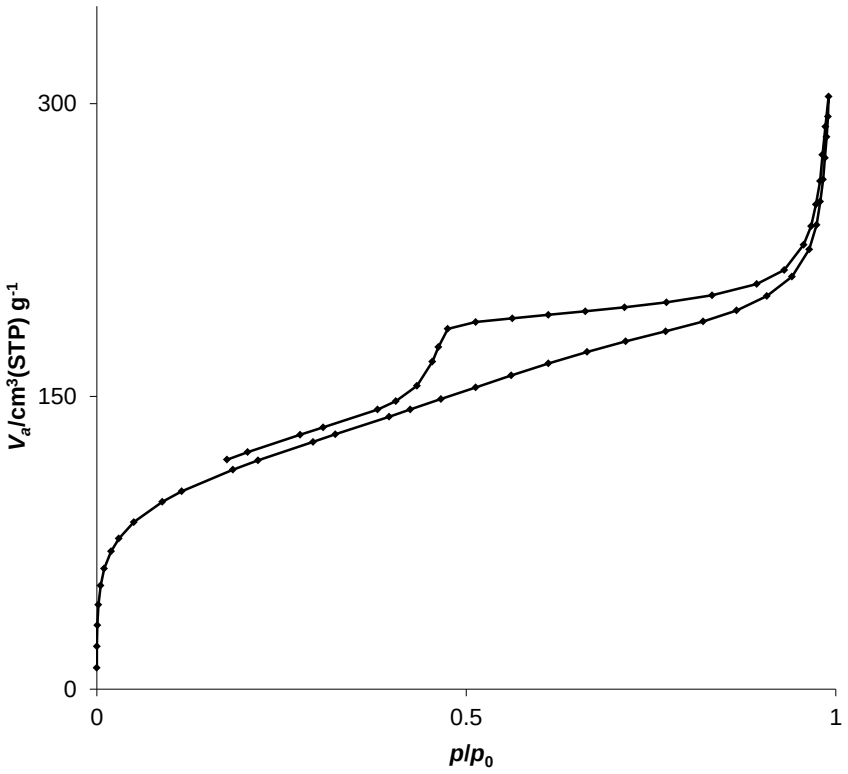


Fig. S9. N_2 adsorption-desorption of Ph-PMO-Me-PrSO_3H catalyst

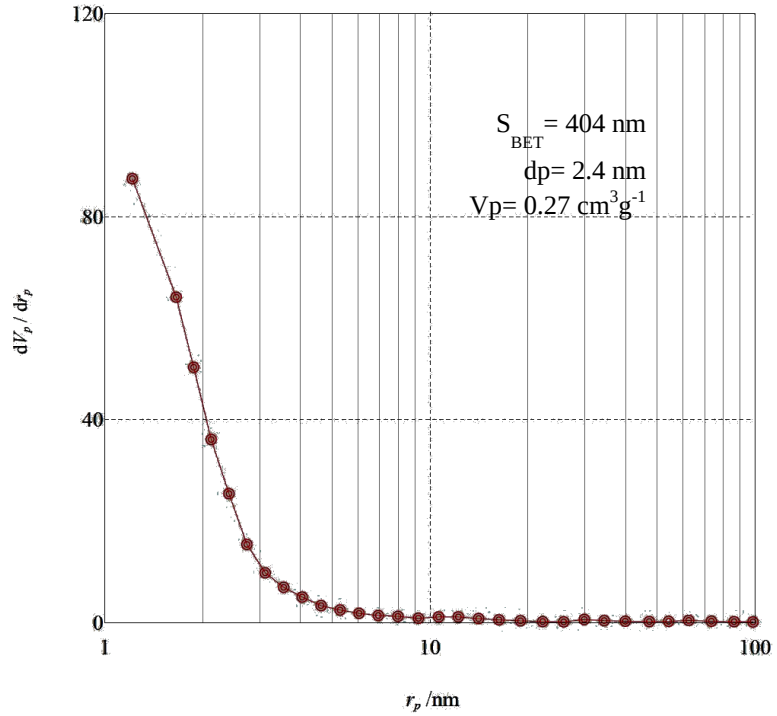


Fig. S10. BJH analysis of Ph-PMO-Me-PrSO_3H catalyst

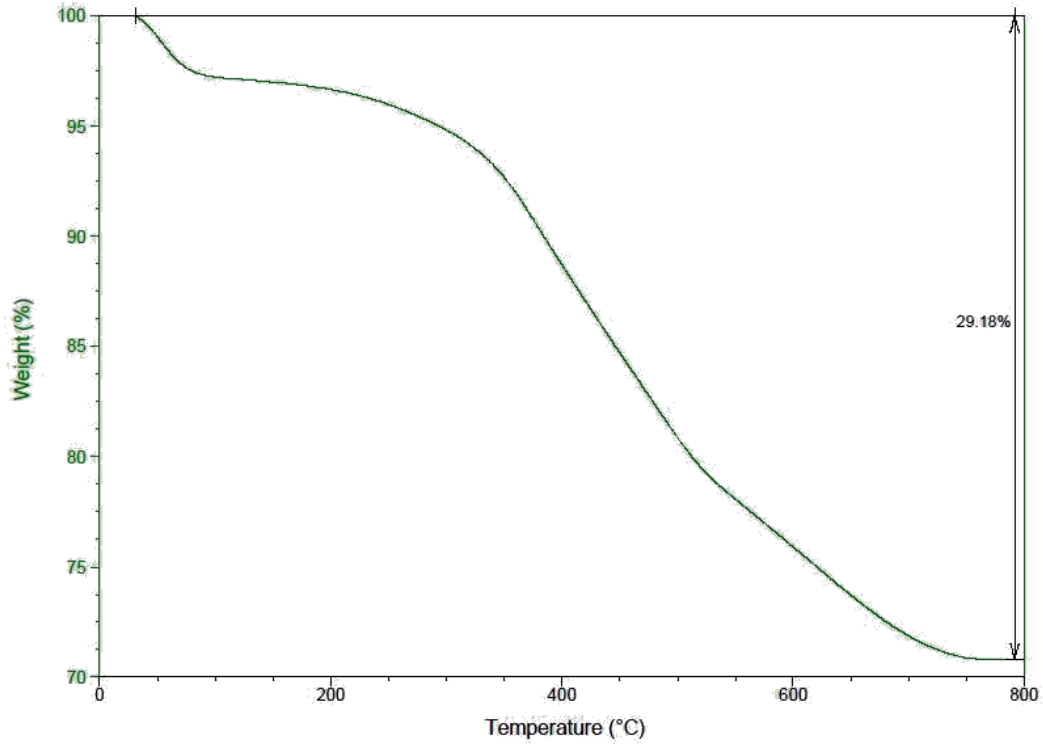


Fig. S11. TGA analysis of Ph-PMO-Me-PrSO$_3$H catalyst

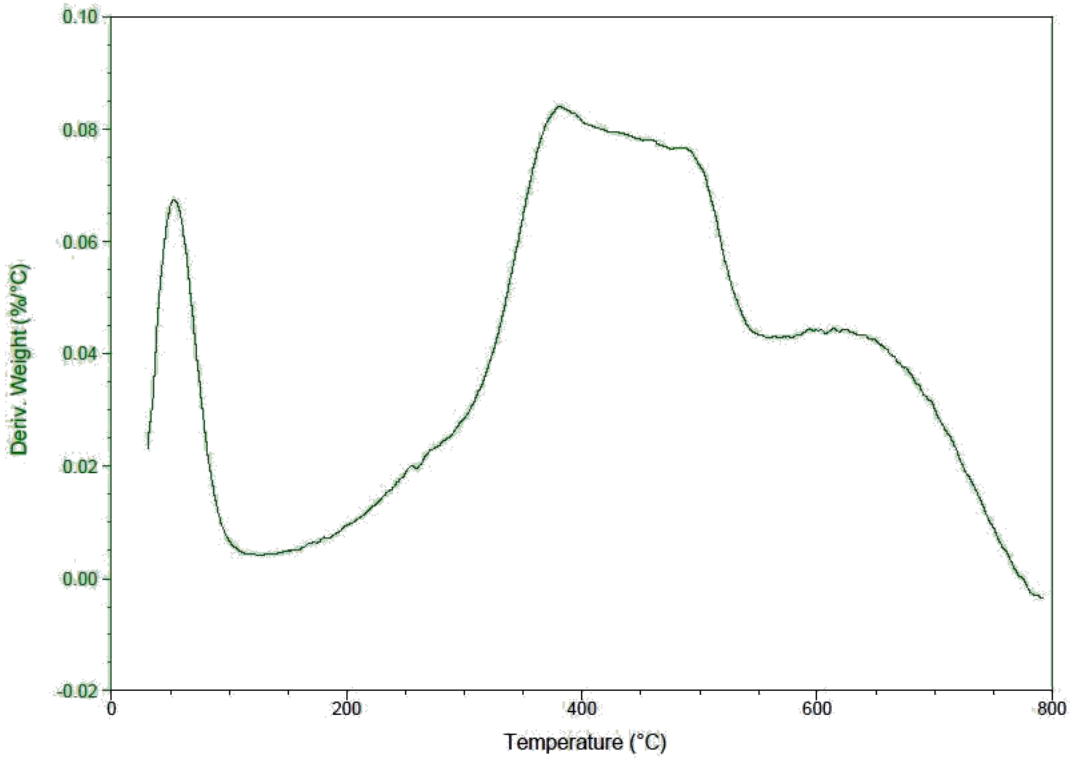


Fig. S12. DTA diagram for Ph-PMO-Me-PrSO$_3$H catalyst

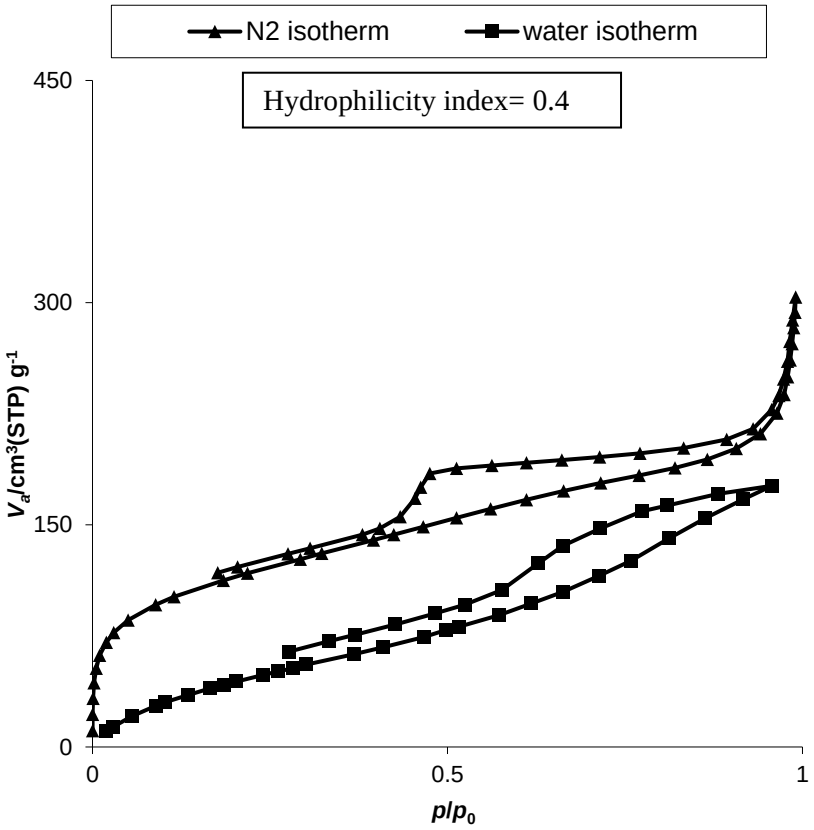


Fig. S13. Both nitrogen and water sorption analysis of **1a** catalyst

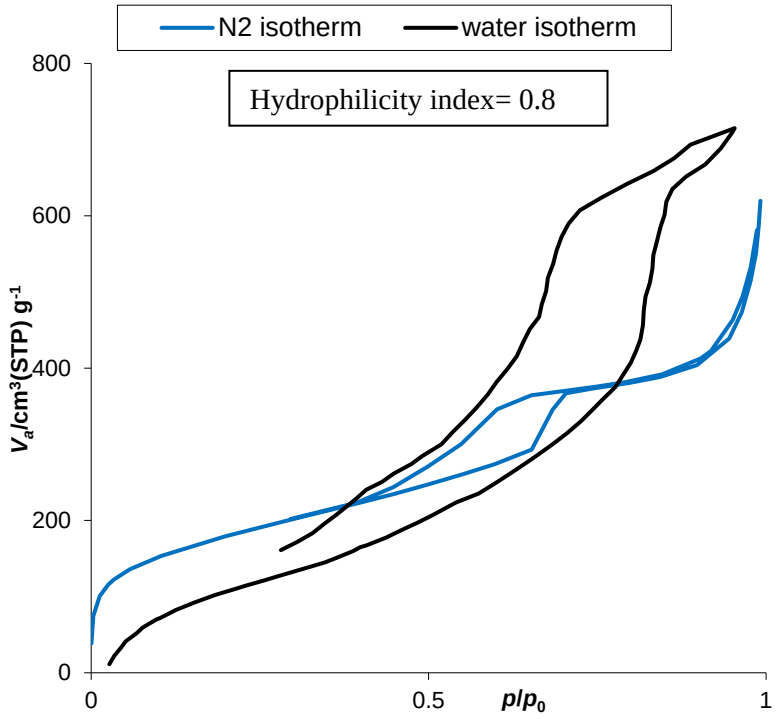


Fig. S14. Both nitrogen and water sorption analysis of **SBA-15-PrSO$_3$H** catalyst

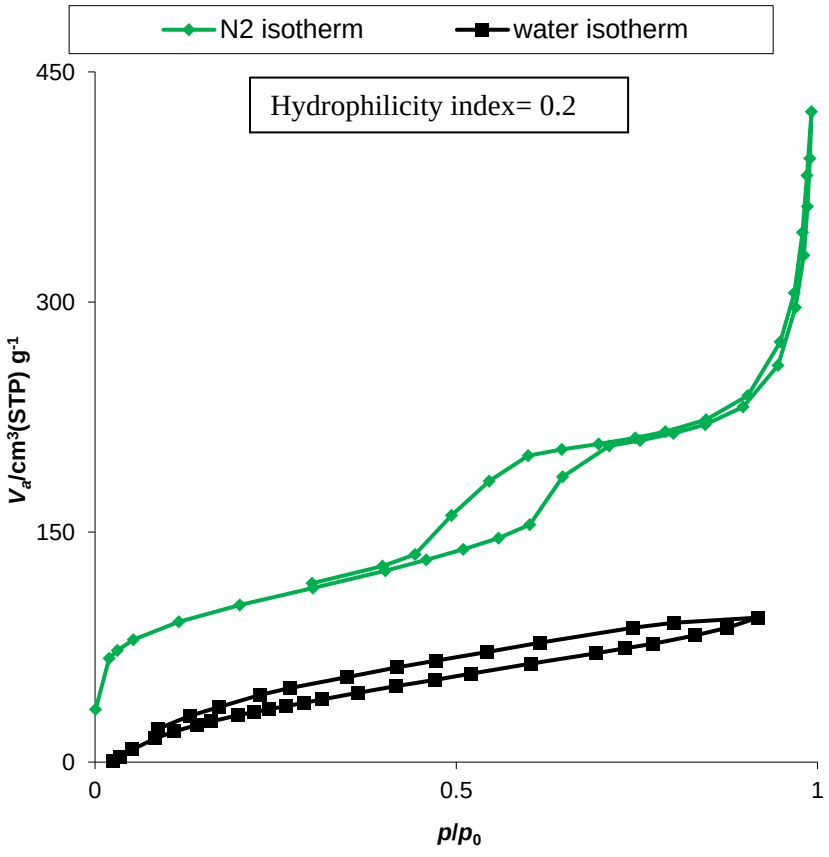
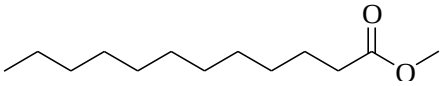


Fig. S15. Both nitrogen and water sorption analysis of **SBA-15-Ph-PrSO$_3$H** catalyst

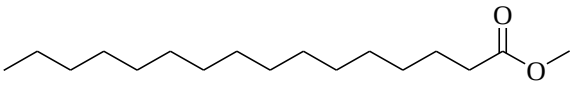
1-10. Characterization of the products

1. Methyl laurate



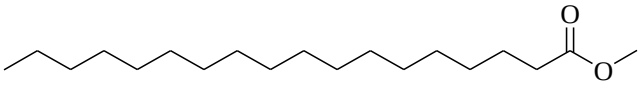
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 3.65 (s, 3H), 2.28 (t, *J*= 7.2 Hz, 2H), 1.50-1.70 (qui, *J*= 6.7 Hz, 2H), 1.24 (brs, 16H), 0.86 (t, *J*= 6.5 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 174.3, 51.4, 34.0, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 22.6, 14.0
IR (neat): 723, 872, 1017, 1113, 1172, 1362, 1451, 1743, 2925

2. Methyl palmitate



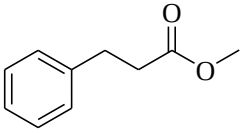
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 3.65 (s, 3H), 2.29 (t, *J*= 7.5 Hz, 2H), 1.55-1.67 (quin, *J*= 7 Hz, 2H), 1.24 (brs, 24H), 0.86 (t, *J*=6.0 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 174.3, 51.4, 34.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 22.6, 14.1
IR (neat): 591, 723, 873, 1016, 1114, 1169, 1245, 1364, 1454, 2037, 2678, 2923

3. Mthyl stearate



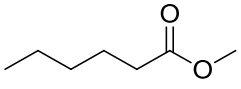
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 3.65 (s, 3H), 2.29 (t, *J*= 7.5 Hz, 2H), 1.55-1.65 (quin, *J*= 6.5 Hz, 2H), 1.24 (brs, 28H), 0.86 (t, *J*=6.0 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 174.3, 51.4, 34.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 22.6, 14.1
IR (neat): 585, 724, 805, 882, 1029, 1108, 1172, 1255, 1376, 1465, 1629, 1742, 2919

4. Methyl-3-phenylpropanate



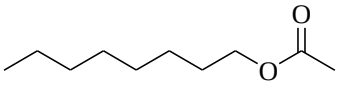
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 7.00-7.38 (m, 5H), 3.67 (s, 3H), 2.96 (t, *J*= 7.5 Hz, 2H), 2.63 (t, *J*= 7.5 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 173.3, 140.5, 128.5, 128.2, 126.2, 51.6, 35.7, 30.9
IR (neat): 500, 559, 701, 748, 832, 990, 1029, 1078, 1162, 1254, 1362, 1443, 1494, 1602, 1637, 1737, 2950, 3026

5. Methyl hexanoate



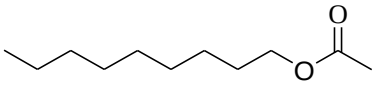
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 3.64 (s, 3H), 2.23-2.32 (m, 2H), 1.27-1.90 (m, 11H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 176.6, 51.4, 43.0, 28.9, 25.7, 25.4
IR (neat): 457, 606, 709, 754, 803, 890, 989, 1038, 1175, 1246, 1317, 1372, 1445, 1736, 2934

6. Octyl acetate



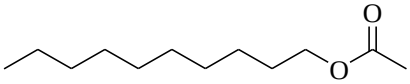
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.06 (t, *J*= 6.8 Hz, 2H), 2.05 (s, 3H), 1.59-1.67 (quin, *J*= 6.8 Hz, 2H), 1.29 (m, 10H), 0.89 (t, *J*= 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 171.2, 64.6, 31.7, 29.2, 29.1, 28.6, 25.9, 22.6, 20.9, 14.1
IR (neat): 605, 638, 725, 807, 881, 964, 1040, 1240, 1372, 1461, 1742, 2927

7. Nonyl acetate



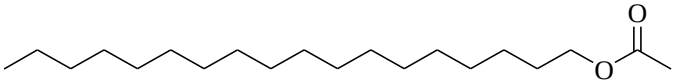
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.02 (t, *J*= 6.8 Hz, 2H), 2.01 (s, 3H), 1.54-1.68 (quin, *J*= 6.8 Hz, 2H), 1.24 (brs, 12H), 0.85 (t, *J*= 6.2 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 171.1, 64.6, 31.8, 29.4, 29.2, 29.2, 28.5, 25.8, 22.6, 20.9, 14.0
IR (neat): 485, 605, 638, 723, 806, 886, 1039, 1239, 1372, 1461, 1742, 2926

8. Decyl acetate



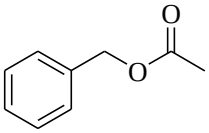
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.03 (t, *J*=6.8 Hz, 2H), 2.03 (s, 3H), 1.55-1.65 (quin, *J*= 6.8 Hz, 2H), 1.25 (brs, 14H), 0.86 (t, *J*= 6.2 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 171.2, 64.6, 31.8, 29.5, 29.2, 29.2, 28.5, 25.8, 22.6, 21.0, 14.0
IR (neat): 455, 607, 723, 805, 881, 1041, 1240, 1371, 1460, 1742, 2926

9. Octadecyl acetate



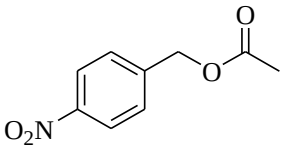
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.07 (t, *J*=6.8 Hz, 2H), 2.06 (s, 3H), 1.60-1.67 (quin, *J*= 6.8 Hz, 2H), 1.27 (brs, 30H), 0.90 (t, *J*= 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 171.2, 64.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 28.6, 25.9, 22.7, 21.0, 14.1
IR (neat): 605, 638, 722, 890, 971, 1040, 1238, 1370, 1460, 1743, 2924

10. Benzyl acetate



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 7.25-7.35 (m, 5H), 5.11 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 170.8, 135.9, 128.5, 128.2, 128.2, 66.3, 21.0
IR (neat): 498, 577, 611, 698, 744, 833, 914, 968, 1032, 1227, 1373, 1451, 1496, 1600, 1741, 1959, 2952, 3033

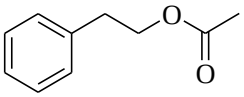
11. 4-Nitrobenzyl acetate



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 8.22 (d, *J*= 8.8 Hz, 2H), 7.51 (d, *J*=8.8 Hz, 2H), 5.18 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 170.5, 147.6, 143.2, 128.3, 123.7, 64.7, 20.8

IR (neat): 463, 529, 605, 666, 740, 841, 919, 1045, 1106, 1237, 1343, 1447, 1517, 1602, 17435, 1950, 2939, 3080

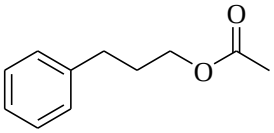
12. Phenethyl acetate



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 7.25-7.37 (m, 5H), 4.32 (t, *J*= 7.2 Hz, 2H), 2.98 (t, *J*= 7.2 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 171.0, 137.8, 128.9, 128.5, 126.6, 64.9, 35.1, 21.0

IR (neat): 494, 572, 604, 643, 699, 746, 814, 906, 981, 1037, 1240, 1373, 1451, 1492, 1601, 1738, 2956, 3028, 3063

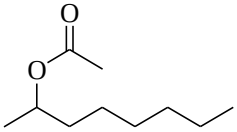
13. 3-Phenylpropyl acetate



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 7.17-7.31 (m, 5H), 4.08 (t, *J*= 6.5 Hz, 2H), 2.69 (t, *J*= 7.2 Hz, 2H), 2.05 (s, 3H), 1.93 (quin, *J*= 6.8 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 171.1, 141.2, 128.4, 128.3, 126.0, 63.8, 32.1, 30.1, 20.9

IR (neat): 476, 605, 701, 745, 887, 953, 1040, 1241, 1371, 1451, 1493, 1601, 1739, 1878, 1949, 2118, 2948, 3026

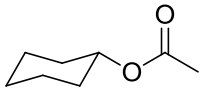
14. Octan-2-yl acetate



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.87-4.95 (m, 1H), 2.05 (s, 3H), 1.28-1.62 (m, 10H), 1.23 (d, *J*= 6.0 Hz, 3H), 0.90 (t, *J*= 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 170.8, 71.0, 35.9, 31.7, 29.1, 25.3, 22.5, 21.4, 19.9, 14.0

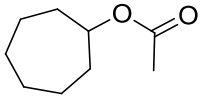
IR (neat): 614, 725, 806, 952, 1026, 1122, 1246, 1373, 1457, 1737, 2929

15. Cyclohexyl acetate



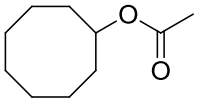
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.65-4.75 (m, 1H), 2.00 (s,3H), 1.2-1.9 (m, 10H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 170.5, 72.6, 31.6, 25.3, 23.7, 21.4

16. Cycloheptyl acetate



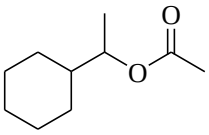
^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.85-4.95 (m, 1H), 2.01 (s, 3H), 1.44-1.93 (m, 12H)
IR (neat): 456, 609, 728, 826, 875, 970, 1022, 1246, 1370, 1456, 1736, 2683, 2926

17. Cyclooctyl acetate



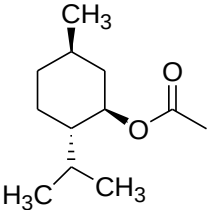
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.90-4.96 (m, 1H), 2.01 (s, 3H), 1.63-1.85 (m, 6H), 1.50-1.63 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 170.4, 75.0, 31.4, 27.0, 25.3, 22.9
IR (neat): 456, 608, 735, 806, 865, 955, 1035, 1097, 1248, 1370, 1456, 1732, 2696, 2925

18. 1-Cyclohexylethyl acetate



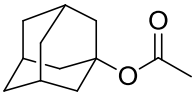
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.70-4.77 (quin, J= 6.4 Hz, 1H), 2.05 (s, 3H), 0.88-1.78 (m, 14H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 170.8, 74.6, 42.5, 28.5, 26.3, 26.0, 25.9, 21.3, 17.0, 14.1
IR (neat): 461, 547, 608, 805, 840, 886, 949, 1047, 1131, 1246, 1373, 1449, 1736, 2930

19. 2-Isopropyl-5-methylcyclohexyl acetate



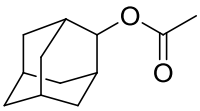
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.66-4.73 (td, J_1= 4.4 Hz, J_2= 10.8 Hz, 1H), 2.06 (s, 3H), 0.94-2.03 (m, 9H), 0.93 (d, J= 2.4 Hz, 3H), 0.91 (d, J= 2.4 Hz, 3H), 0.78 (d, J= 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 170.7, 74.1, 47.0, 40.9, 34.2, 31.3, 26.3, 23.4, 22.0, 21.3, 20.7, 16.3
IR (neat): 473, 607, 651, 806, 838, 907, 975, 1026, 1092, 1186, 1244, 1373, 1456, 1735, 2953

20. Adamantan-1-yl acetate



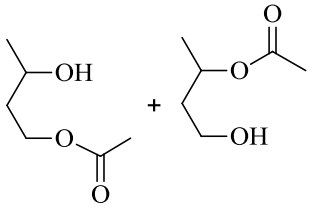
^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 2.16 (s, 3H), 2.11 (d, *J*= 7.6 Hz, 6H), 1.97 (s, 3H), 1.60-1.70 (brs, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 170.2, 80.2, 41.2, 36.2, 30.7, 22.7
IR (neat): 455, 542, 605, 675, 729, 809, 864, 950, 1016, 1058, 1102, 1240, 1363, 1448, 1732, 2669, 2913

21. 2-Adamantanyl acetate



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.88 (s, 1H), 1.50-2.04 (m, 17H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 170.5, 77.0, 37.3, 36.3, 31.8, 31.7, 27.2, 26.9, 21.4
IR (neat): 442, 531, 612, 672, 810, 901, 979, 1031, 1095, 1245, 1367, 1445, 1733, 2672, 2912

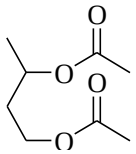
22. **3-Hydroxybutyl acetate compound with 4-hydroxybutan-2-yl acetate (2.5:1)**



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 5.09-5.17 (m, 0.4H), 4.32-4.38 (m, 1H), 4.11-4.17 (m, 1H), 3.87-3.95 (m, 1H), 3.58-3.70 (m, 0.8H), 2.08 (s, 4H), 2.02 (brs, 1OH), 1.68-1.87 (m, 2H), 1.30 (d, *J*= 6.40 Hz, 1H), 1.25 (d, *J*= 6.40 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 171.5, 68.2, 64.8, 61.7, 58.7, 39.0, 38.0, 23.4, 21.3, 21.0, 20.4

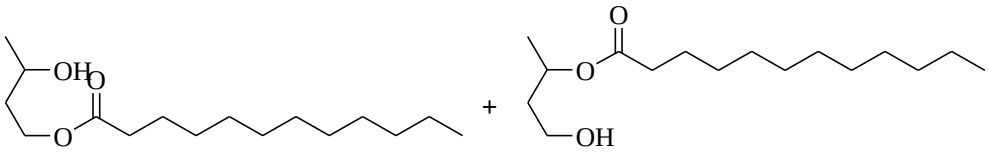
IR (neat): 424, 538, 609, 782, 838, 911, 976, 1048, 1097, 1133, 1261, 1375, 1736, 2970, 3500-3700 (broad)

23. **Butane-1,3-diyl diacetate**



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 5.00-5.05 (m, 1H), 4.14 (t, *J*= 6.4 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.85-1.95 (m, 2H), 1.28 (d, *J*=6.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 171.0, 170.6, 67.8, 60.8, 34.7, 21.2, 20.9, 20.0

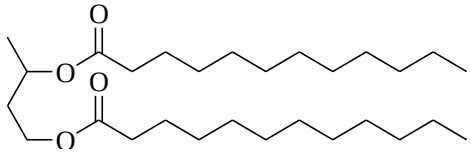
24. **3-Hydroxybutyl dodecanoate compound with 4-hydroxybutan-2-yl dodecanoate (2.5:1)**



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 5.08-5.16 (m, 0.4H), 4.32-4.40 (m, 1H), 4.06-4.15 (m, 1H), 3.82-3.90 (m, 1H), 3.50-3.64 (m, 0.8H), 2.30 (t, *J*= 7.5 Hz, 3H), 2.00 (brs, 1OH), 1.58-1.82 (m, 7H), 1.28 (brs, 22H), 0.87 (t, *J*= 6.2 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 174.4, 174.3, 67.9, 64.8, 61.5, 58.7, 39.1, 38.0, 34.6, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 25.0, 24.9, 23.4, 22.6, 20.4, 14.1

IR (neat): 456, 604, 733, 984, 1182, 1373, 1459, 1729, 2925, 3442

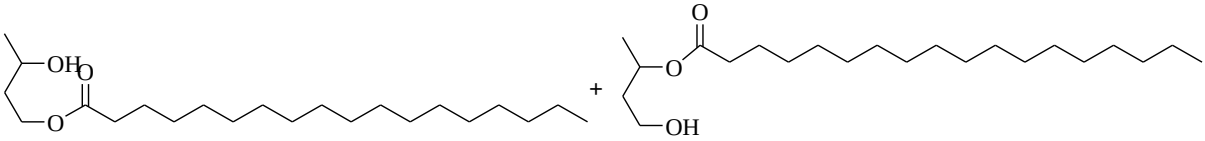
25. **Butane-1,3-diyl didodecanoate:**



^{1}H NMR (250 MHz; $CDCl_3$): δ_H= 4.95-5.05 (m, 1H), 4.08 (t, *J*= 6.50 Hz, 2H), 2.22-2.29 (m, 4H), 1.80-1.90 (m, 2H), 1.55-1.65 (m, 4H), 1.24 (brs, 35H), 0.86 (t, *J*= 6.2 Hz, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ_C= 173.8, 173.3, 67.5, 60.5, 34.8, 34.5, 34.2, 31.8, 29.5, 29.3, 29.2, 29.1, 24.9, 24.9, 22.6, 20.0, 14.0

IR (neat): 455, 604, 721, 1111, 1174, 1372, 1459, 1459, 1737, 2925

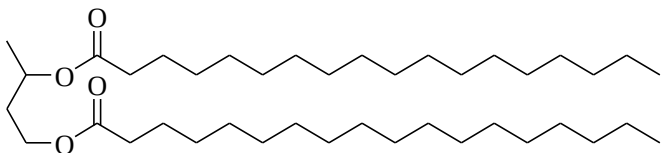
26. **3-Hydroxybutyl stearate compound with 4-hydroxybutan-2-yl stearate (2.5:1)**



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 5.11-5.19 (m, 0.4H), 4.35-4.41 (m, 1H), 4.11-4.17 (m, 1H), 3.86-3.94 (m, 1H), 3.65-3.70 (m, 0.4H), 3.56-3.62 (m, 0.4H), 2.60 (brs, 1 OH), 2.33 (t, *J*= 7.6 Hz, 3H), 1.60-1.86 (m, 6H), 1.29 (brs, 46H), 0.90 (t, *J*= 6.4 Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 174.4, 174.3, 67.8, 64.9, 61.5, 58.7, 39.1, 38.1, 34.6, 34.3, 31.7, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 29.1, 29.1, 25.0, 24.9, 24.7,14.0

IR (neat): 456, 606, 723, 1050, 1103, 1176, 1264, 1378, 1463, 1731, 2918, 3427

27. **Butane-1,3-diyl distearate**



^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 4.99-5.08 (m, 1H), 4.13 (brs, 2H), 2.30 (t, *J*= 7.2, 4H), 1.85-1.95 (m, 2H), 1.63 (brs, 4H), 1.28 (brs, 62H), 0.91 (t, *J*= 6.0 Hz, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 173.8, 173.4, 67.6, 60.6, 34.8, 34.6, 34.3, 33.6, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 29.0, 25.0, 24.9, 24.6, 14.0

IR (neat): 457, 607, 653, 719, 800, 872, 1097, 1167, 1259, 1462, 1735, 2357, 2918

1-11. ^{1}H, $^{13}CNMR$, and FT-IR spectra

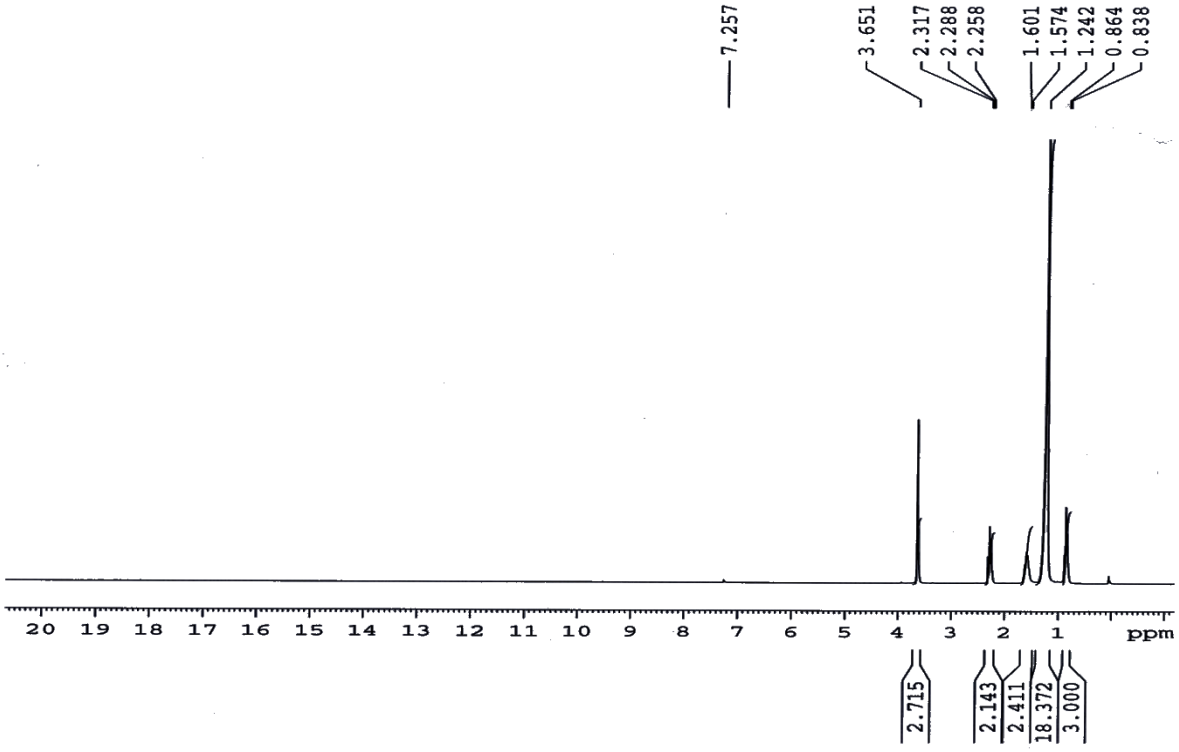


Fig. S16. $^{1}HNMR$ of Methyl Laurate in $CDCl_3$

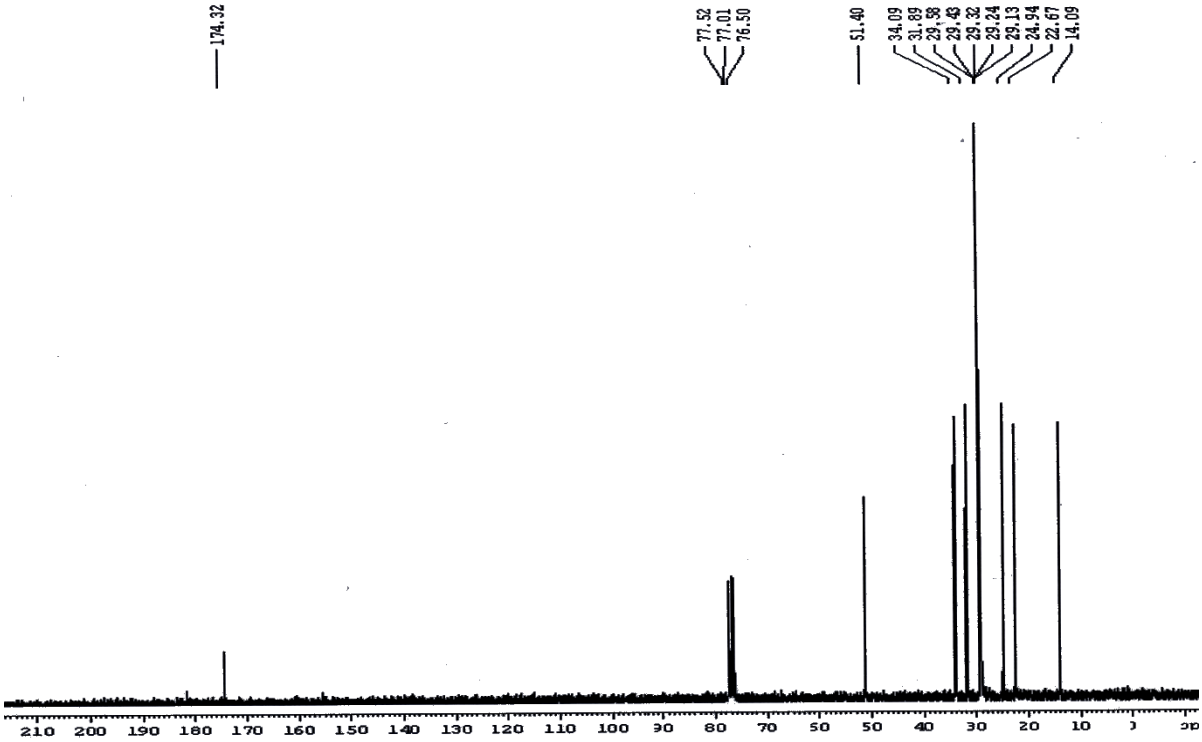


Fig. S17. $^{13}CNMR$ of Methyl Laurate in $CDCl_3$

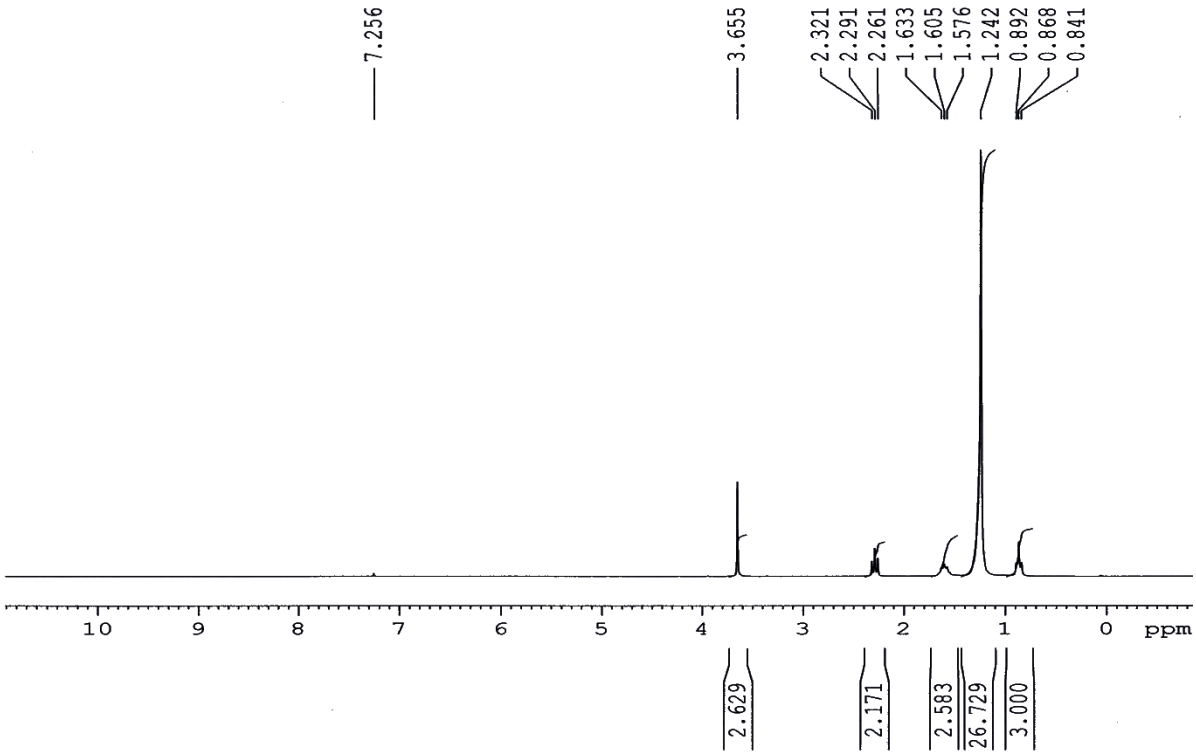


Fig. S18. ^{1}HNMR of Methyl Palmitate in $CDCl_3$

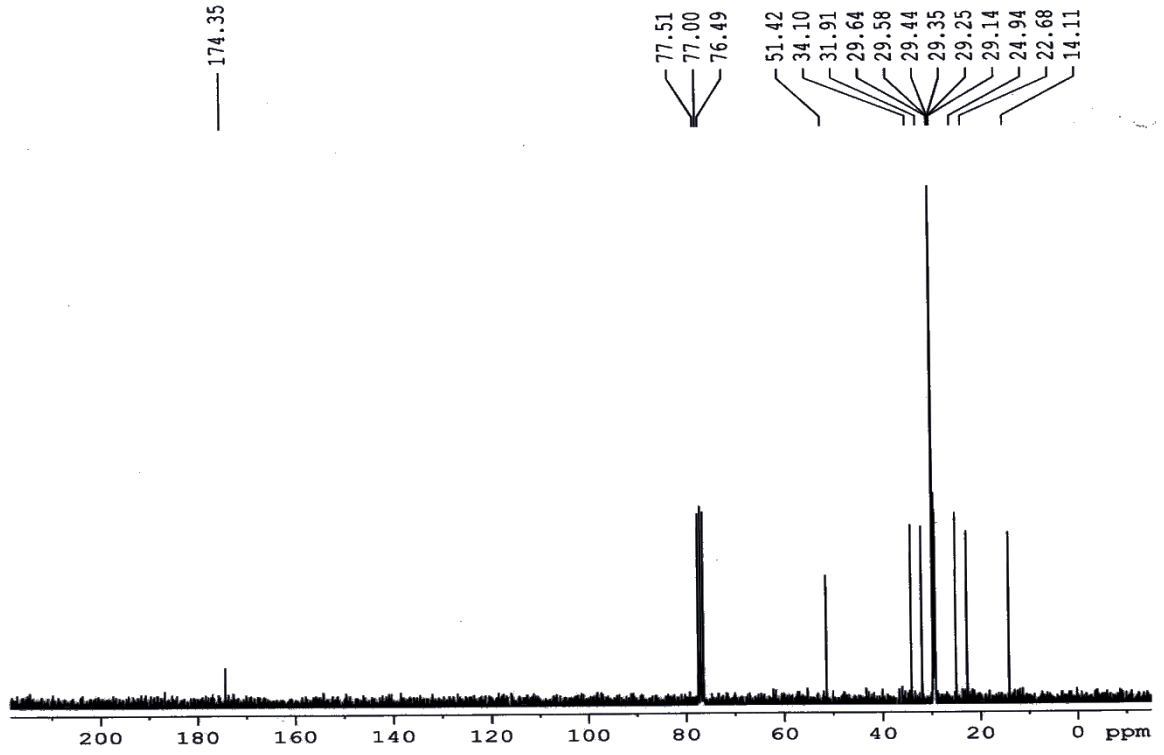


Fig. S19. ^{13}CNMR of Methyl Palmitate in $CDCl_3$

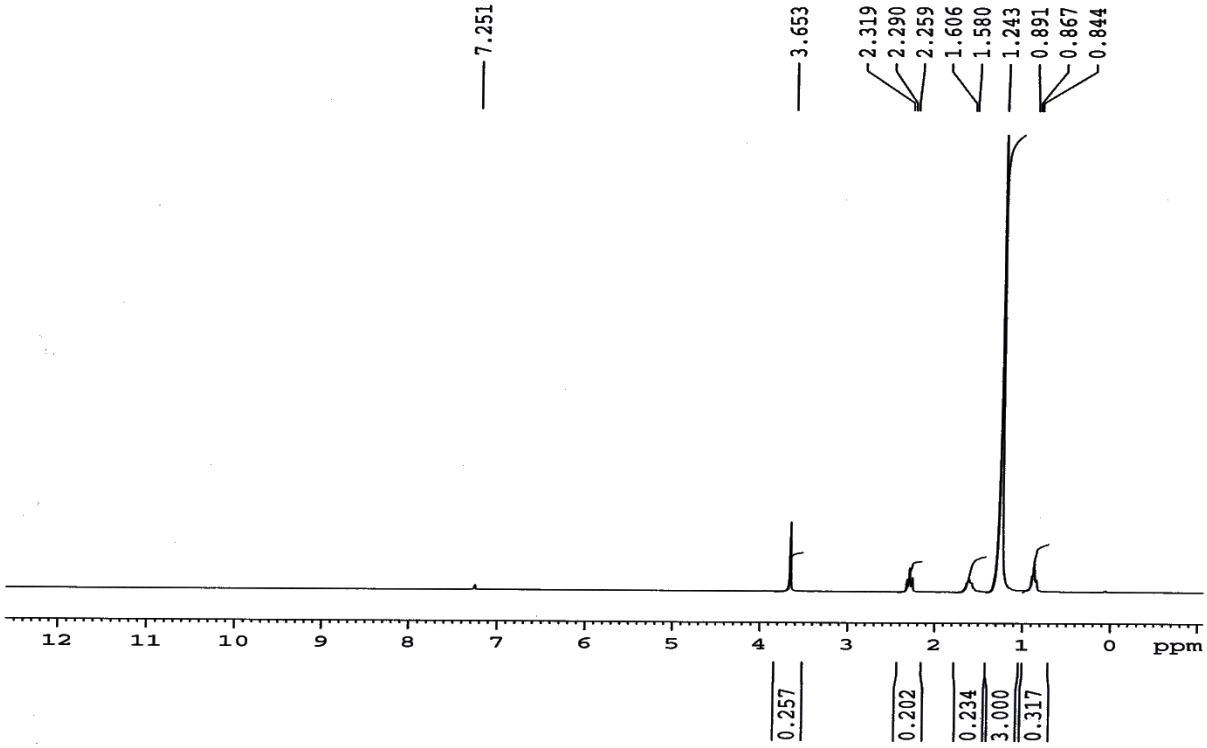


Fig. S20. ^{1}HNMR of Methyl Stearate in $CDCl_3$

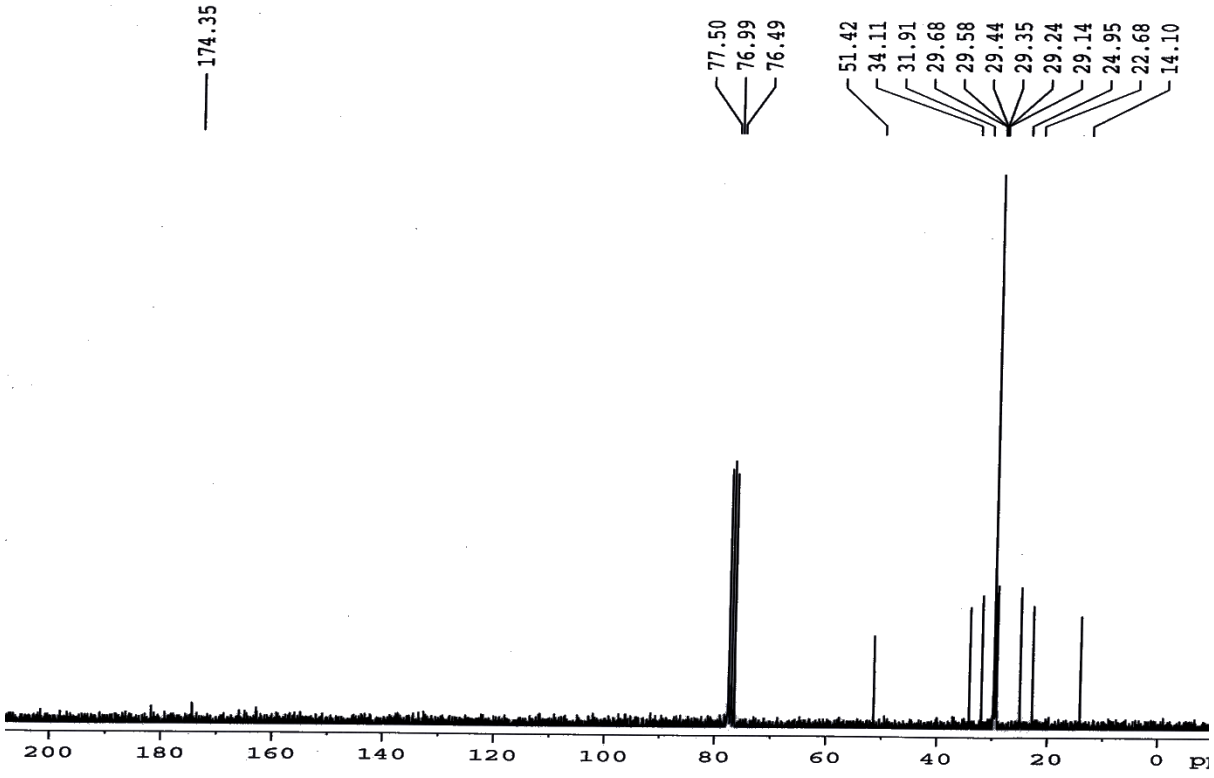


Fig. S21. ^{13}CNMR of Methyl Stearate in $CDCl_3$

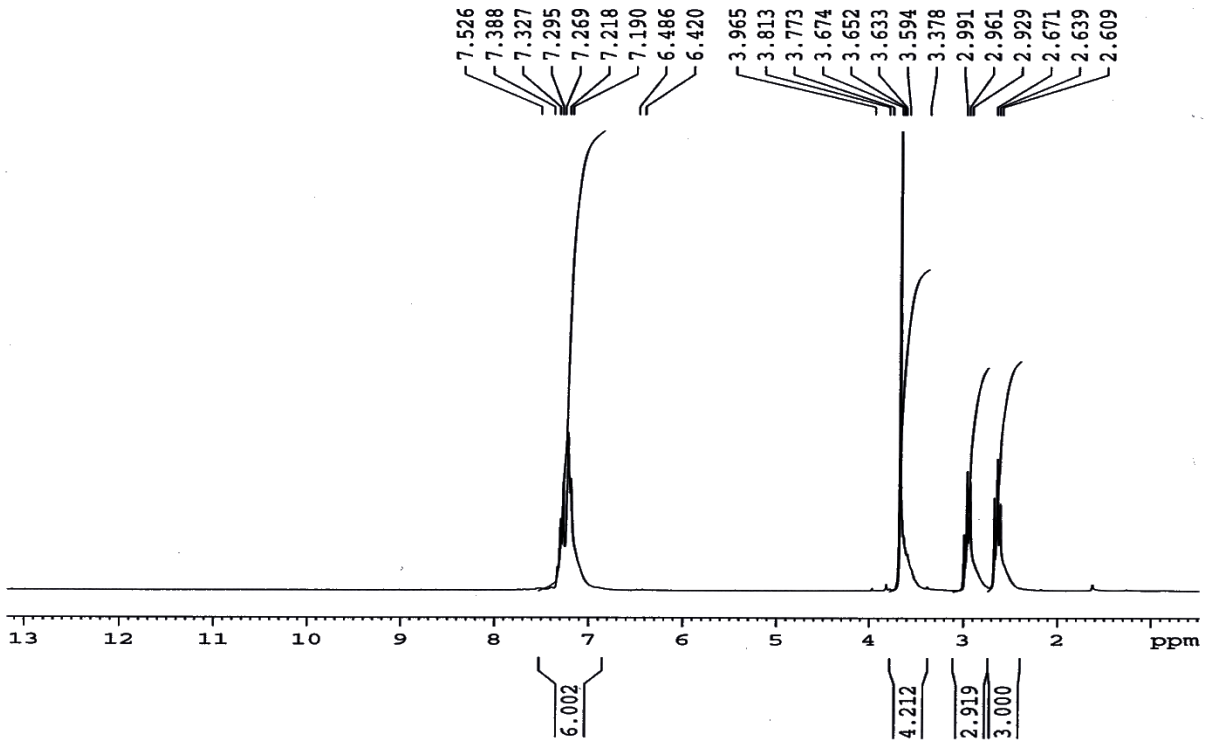


Fig. S22. ^{1}HNMR of 3-phenylpropanate in $CDCl_3$

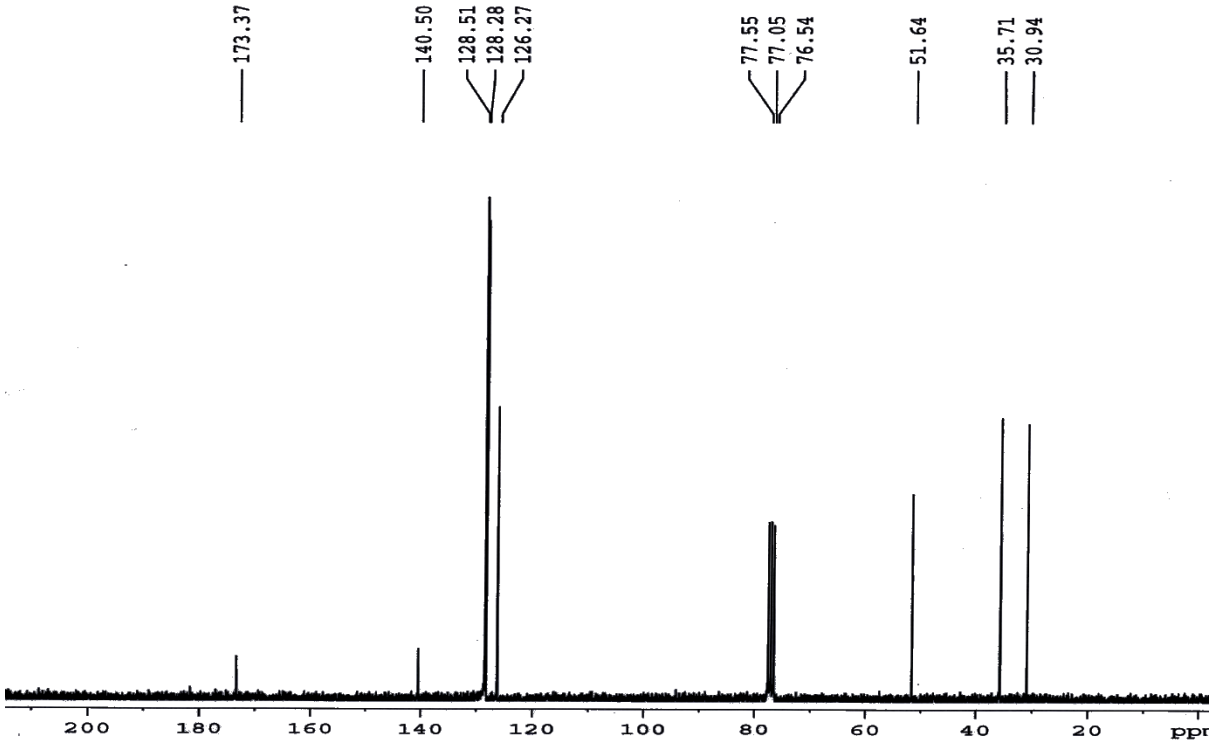


Fig. S23. ^{13}CNMR of 3-phenylpropanate in $CDCl_3$

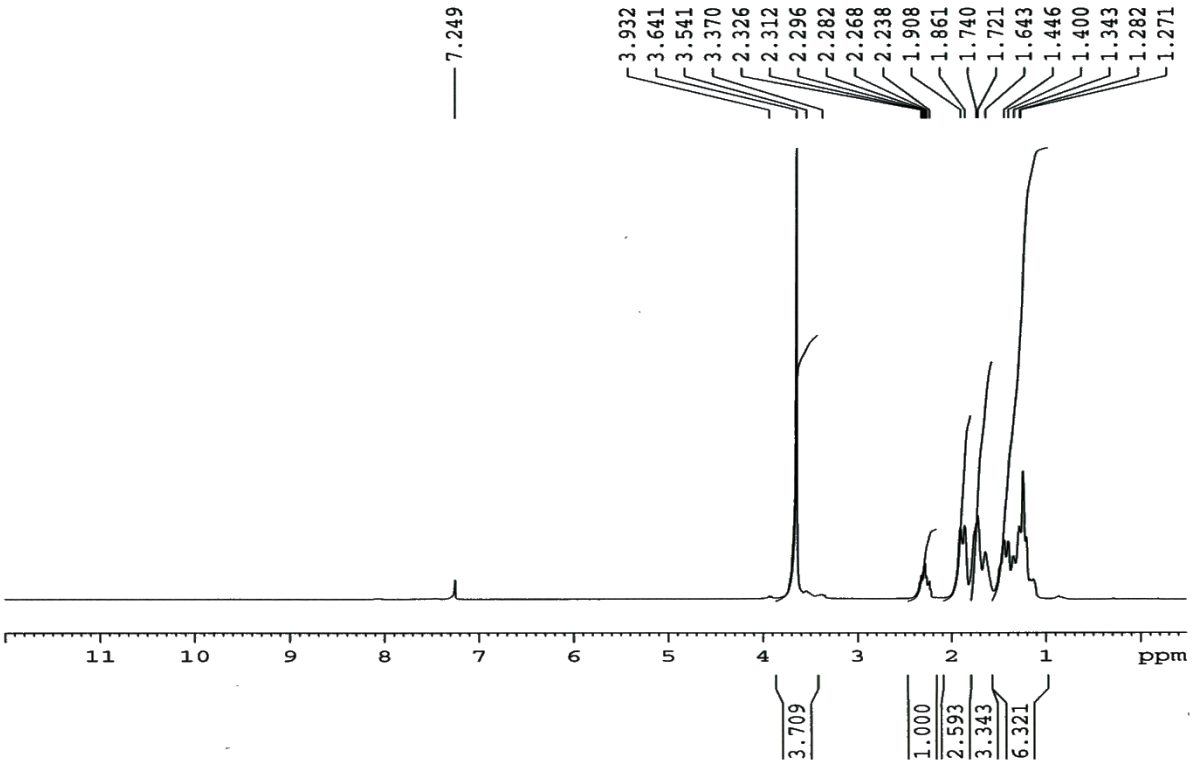


Fig. S24. ^{1}HNMR of methylhexanoate in $CDCl_3$

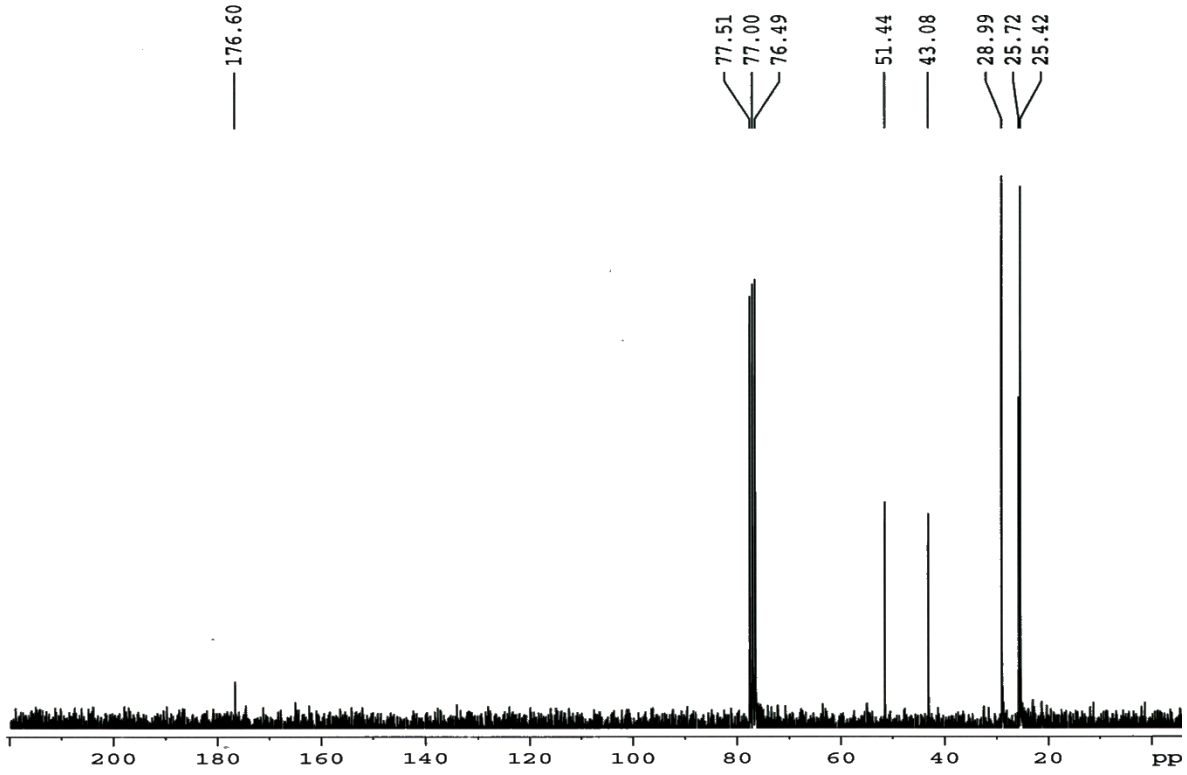


Fig. S25. ^{13}CNMR of methylhexanoate in $CDCl_3$

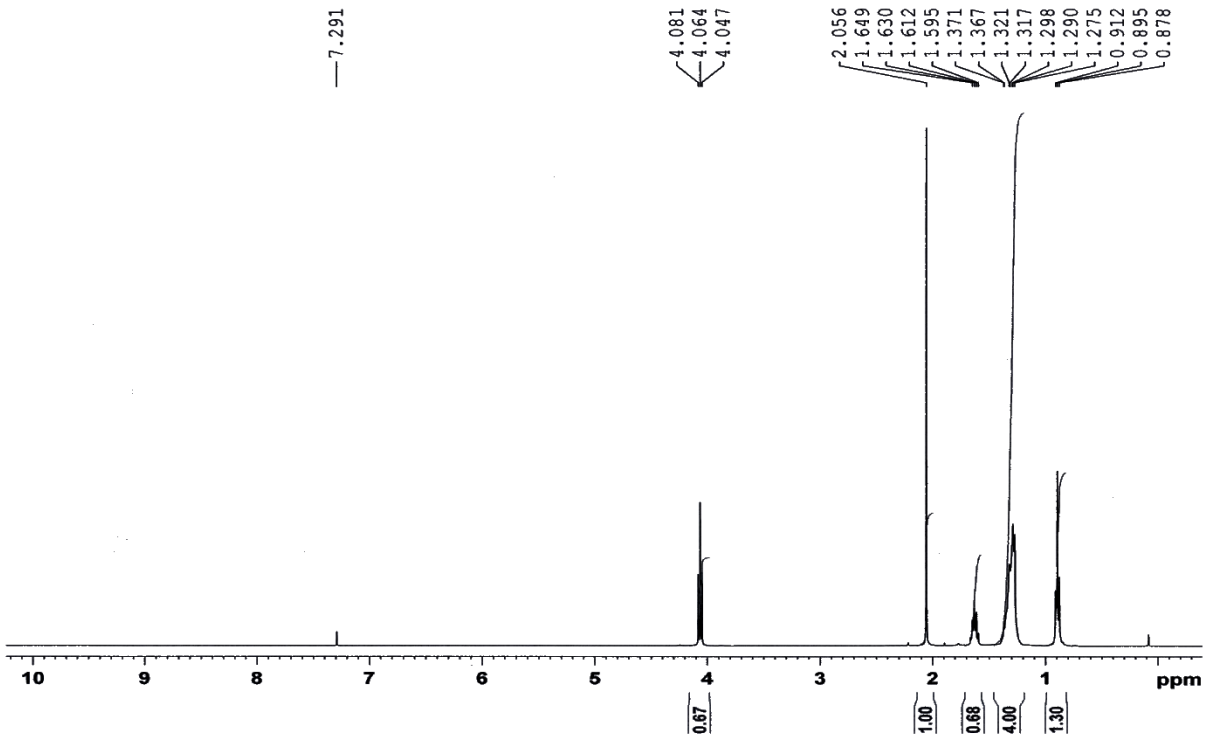


Fig. S26. ^{1}HNMR of octylacetate in $CDCl_3$

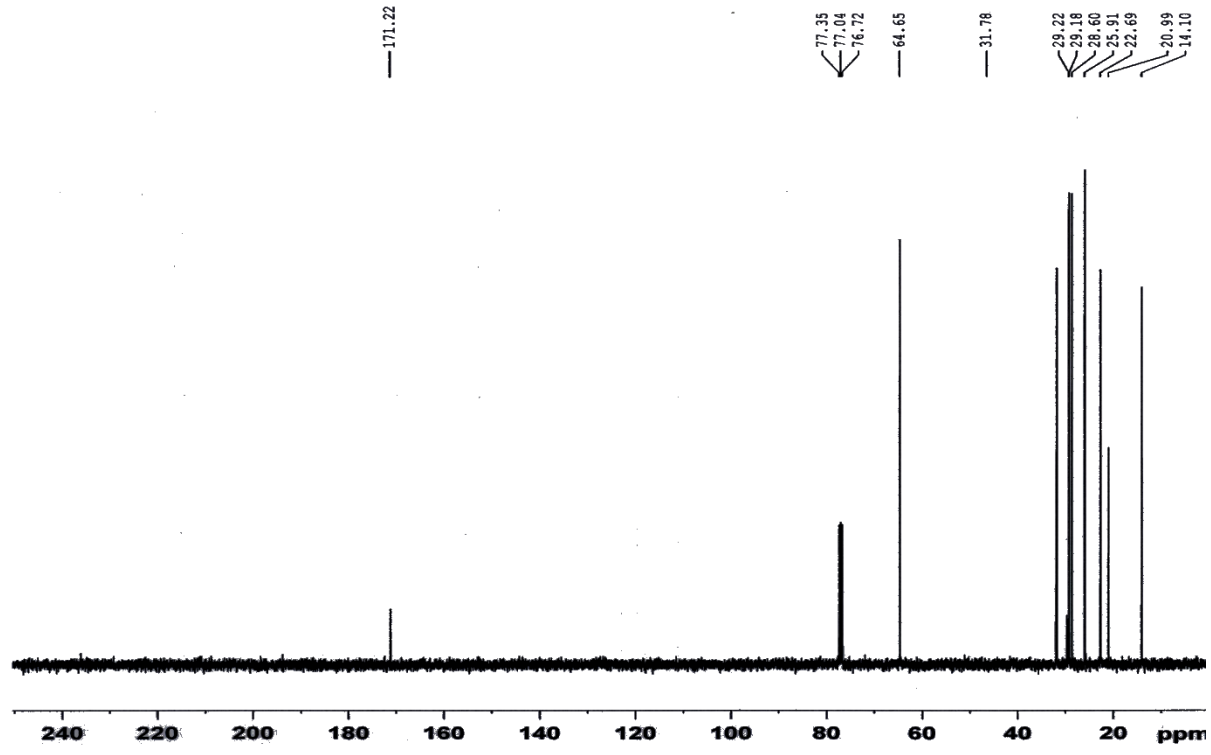


Fig. S27. ^{13}CNMR of octylacetate in $CDCl_3$

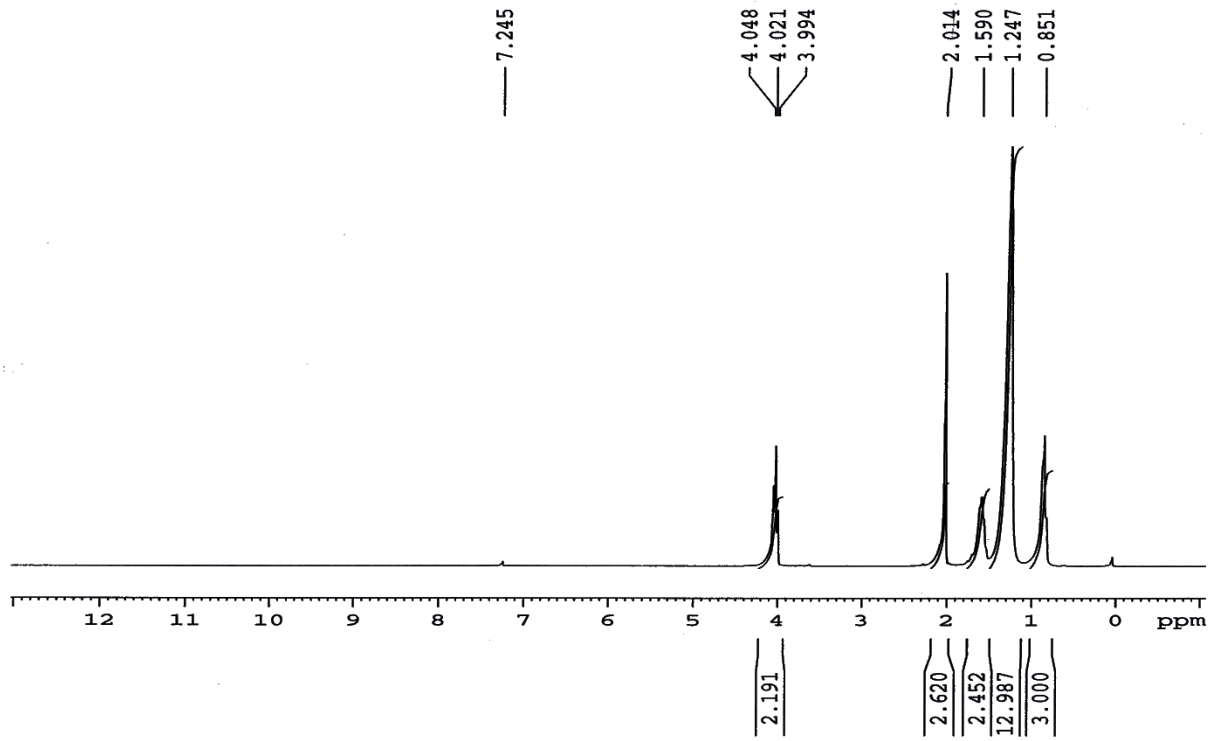


Fig. S28. ^{1}HNMR of nonylacetate in $CDCl_3$

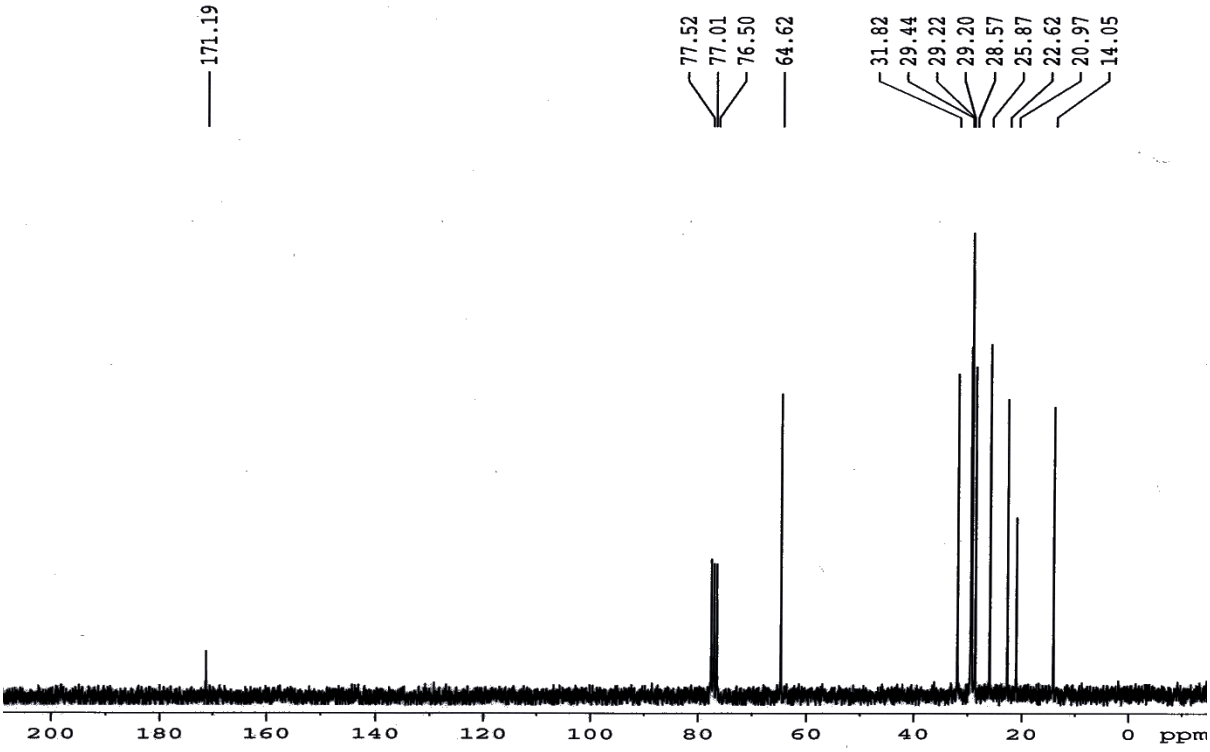


Fig. S29. ^{13}CNMR of nonylacetate in $CDCl_3$

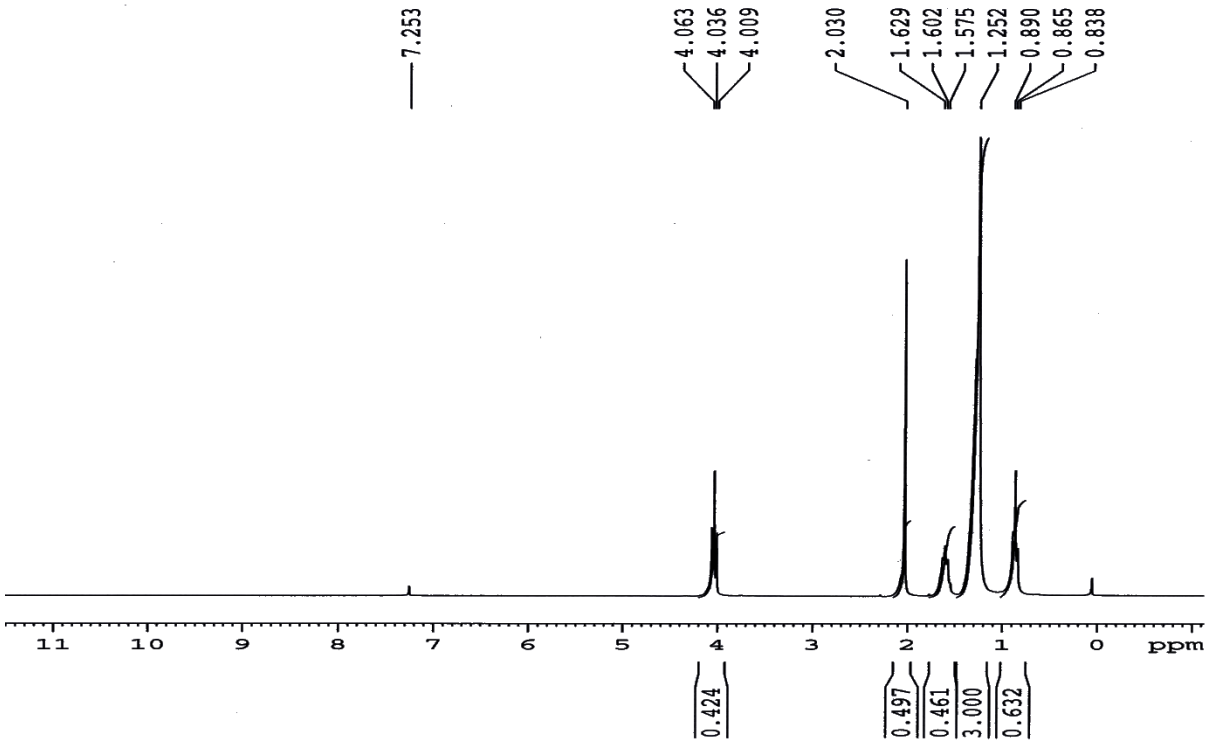


Fig. S30. ^{1}HNMR of decylacetate in $CDCl_3$

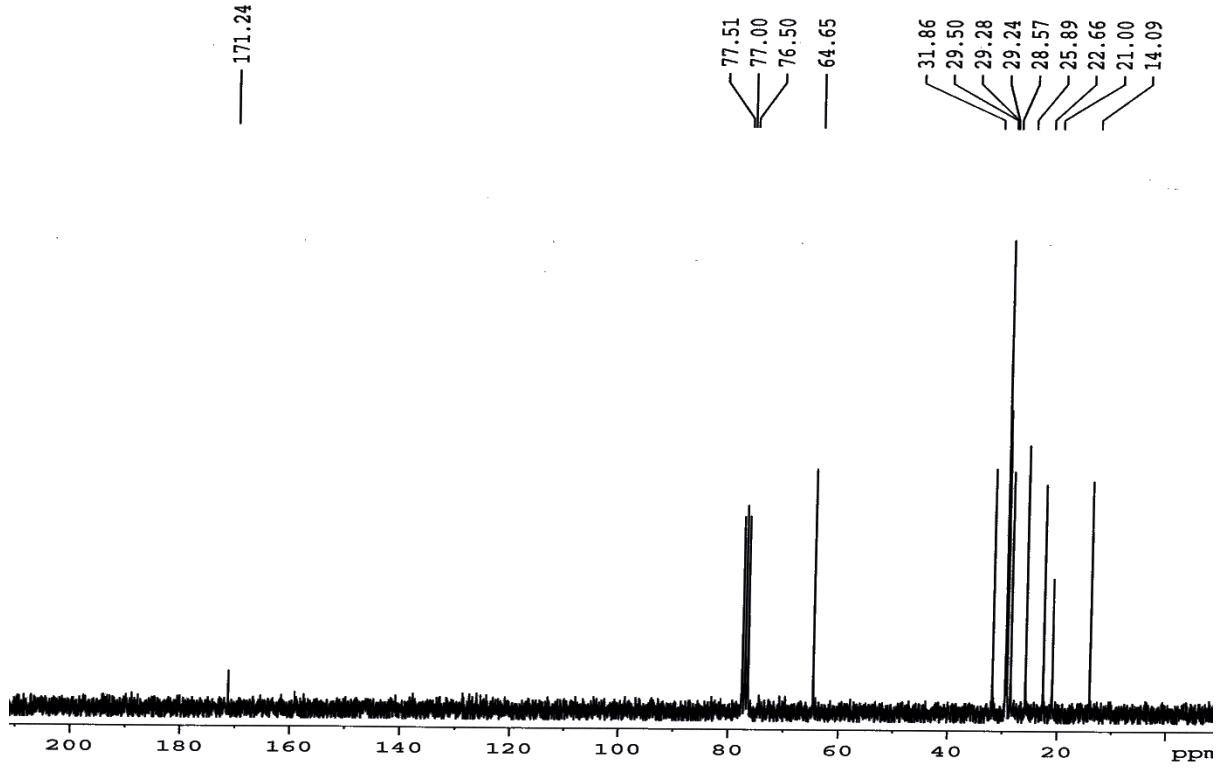


Fig. S31. ^{13}CNMR of decylacetate in $CDCl_3$

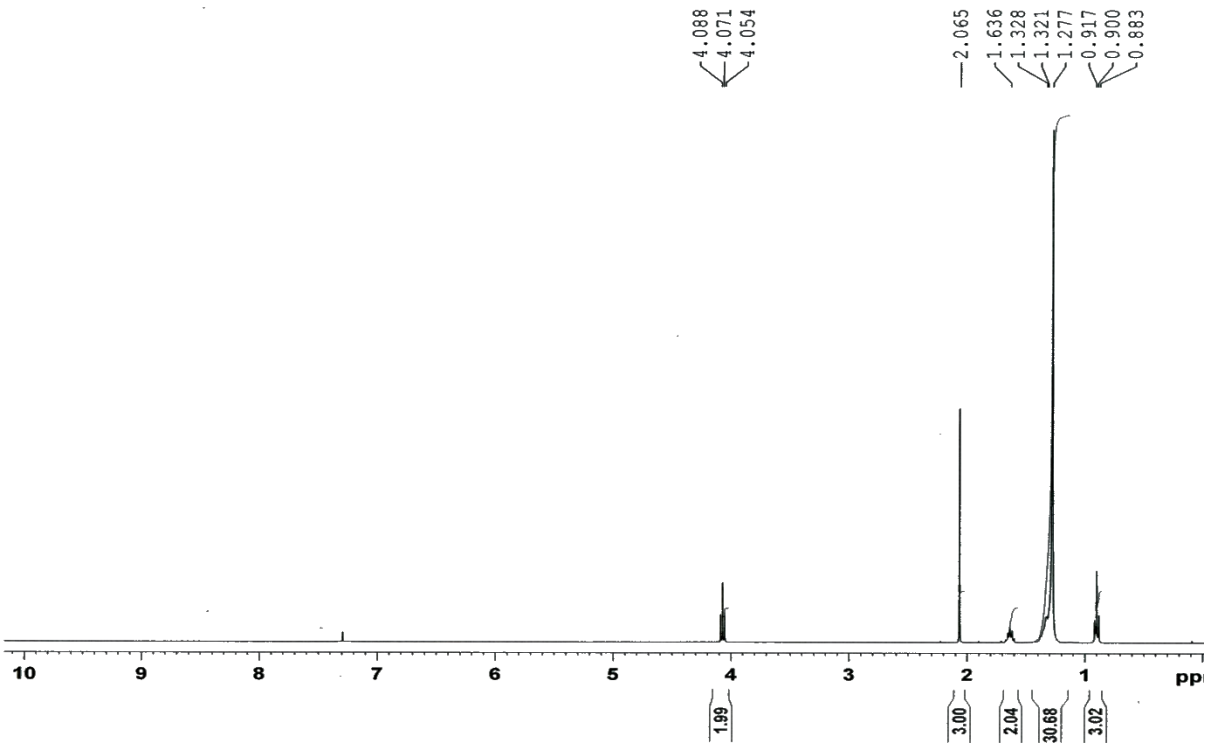


Fig. S32. ^{1}HNMR of octadecylacetate in $CDCl_3$

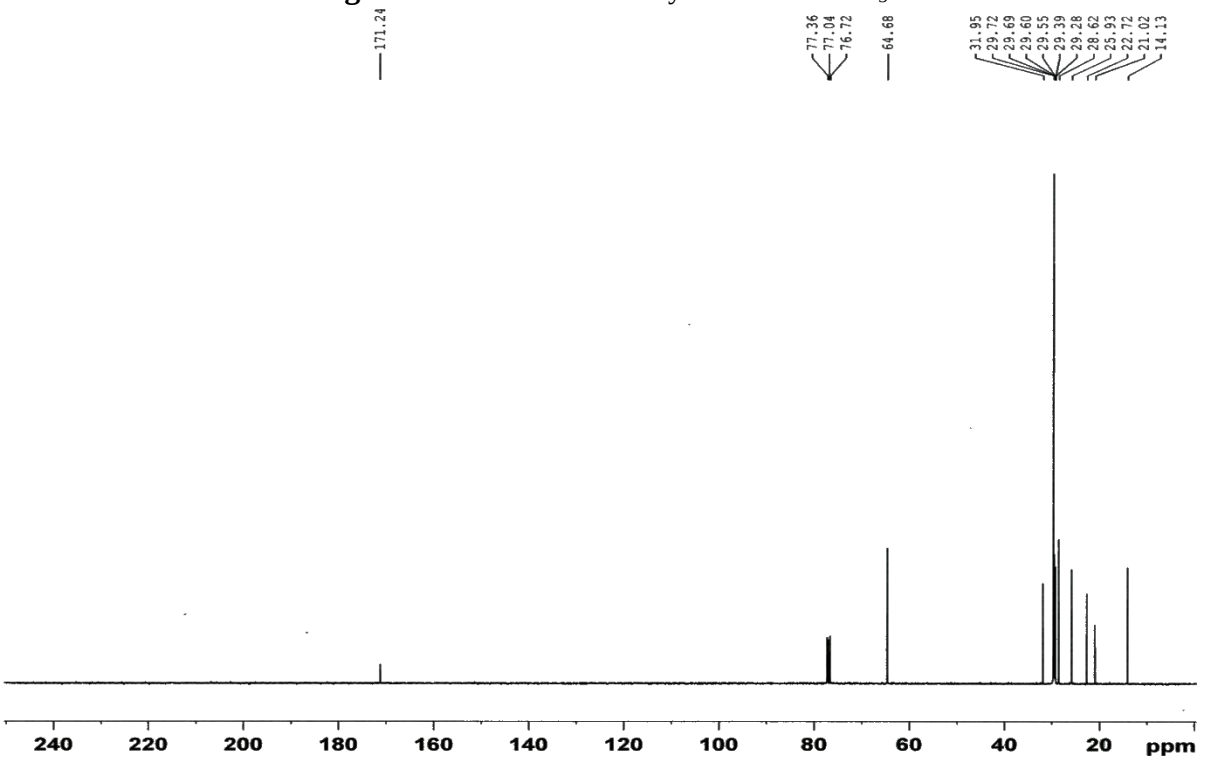


Fig. S33. ^{13}CNMR of octadecylacetate in $CDCl_3$

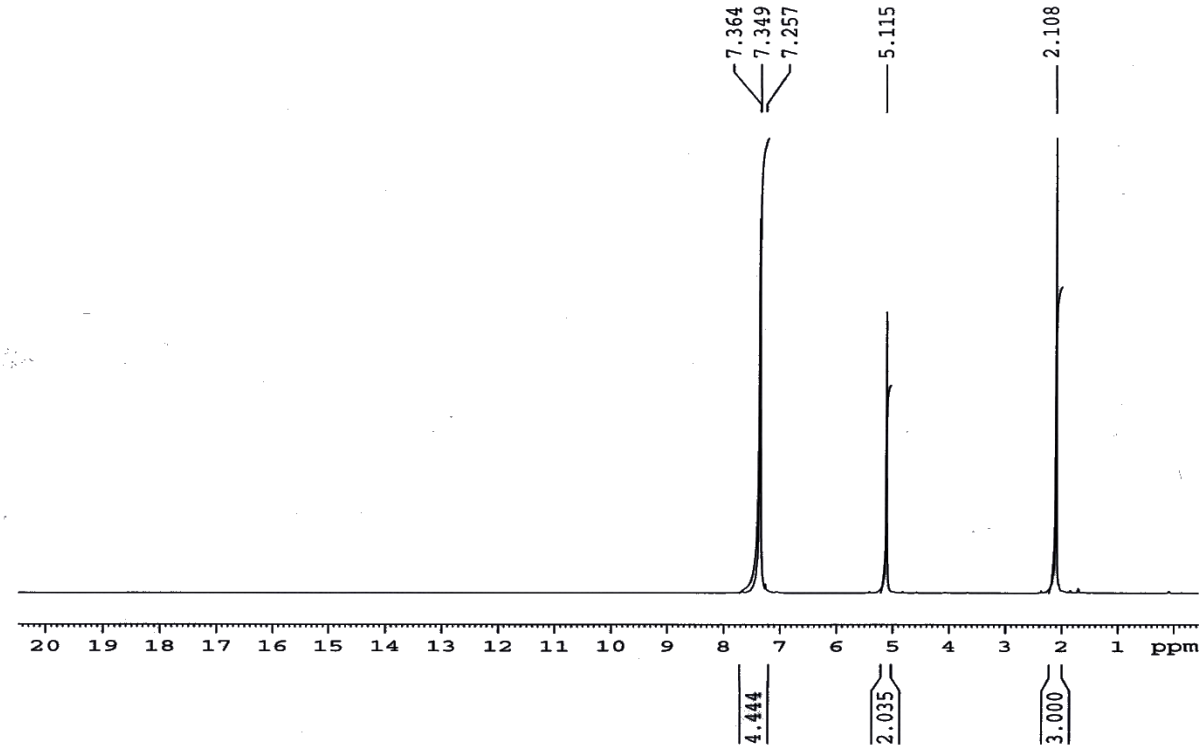


Fig. S34. ^{1}HNMR of benzylacetate in $CDCl_3$

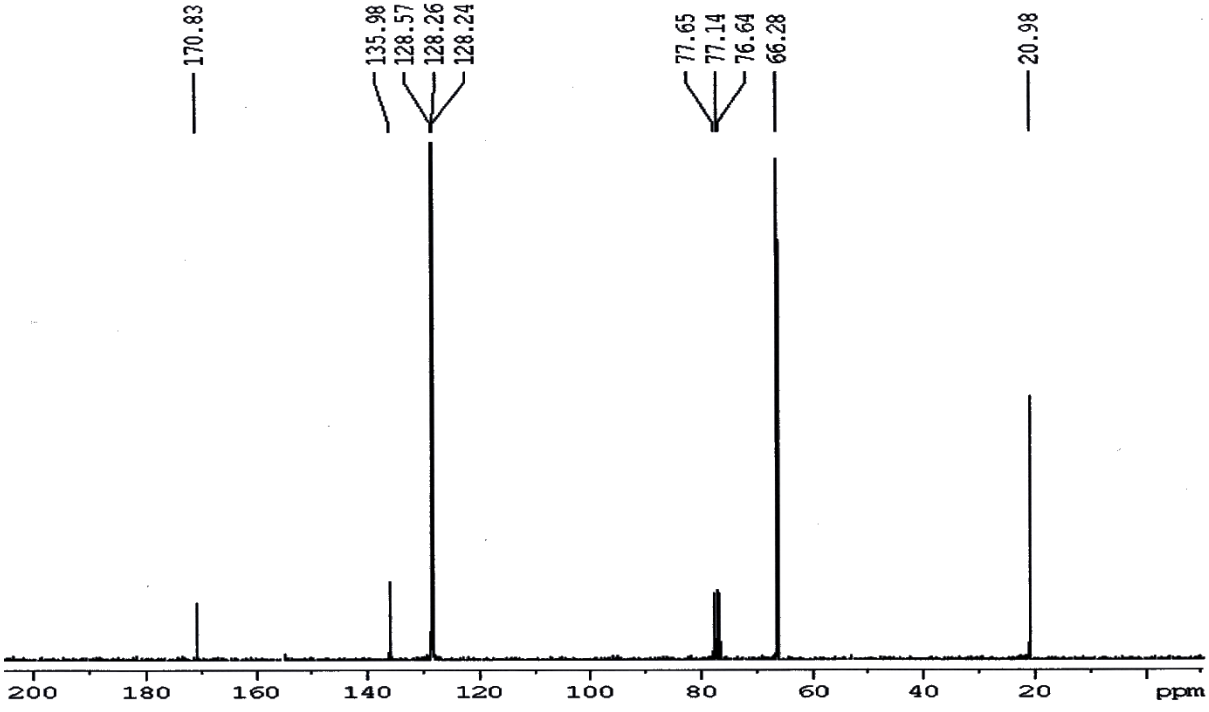


Fig. S35. ^{13}CNMR of benzylacetate in $CDCl_3$

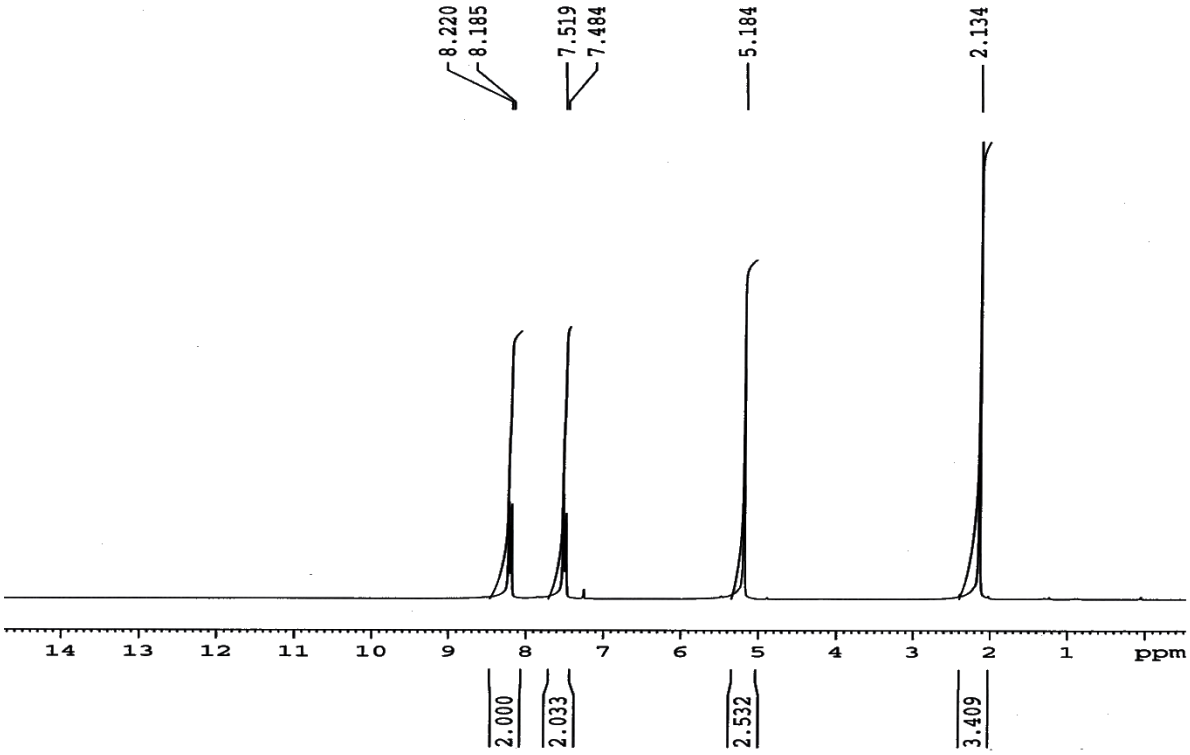


Fig. S36. ^{1}HNMR of 4-nitrobenzylacetate in $CDCl_3$

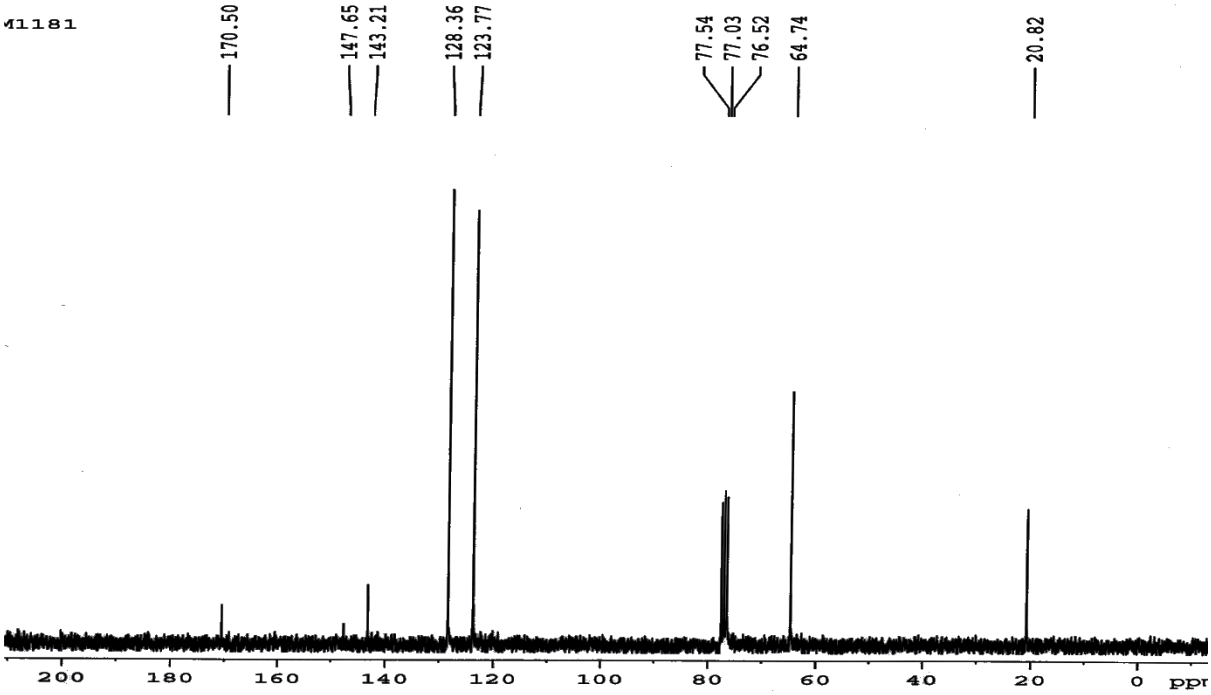


Fig. S37. ^{13}CNMR of 4-nitrobenzylacetate in $CDCl_3$

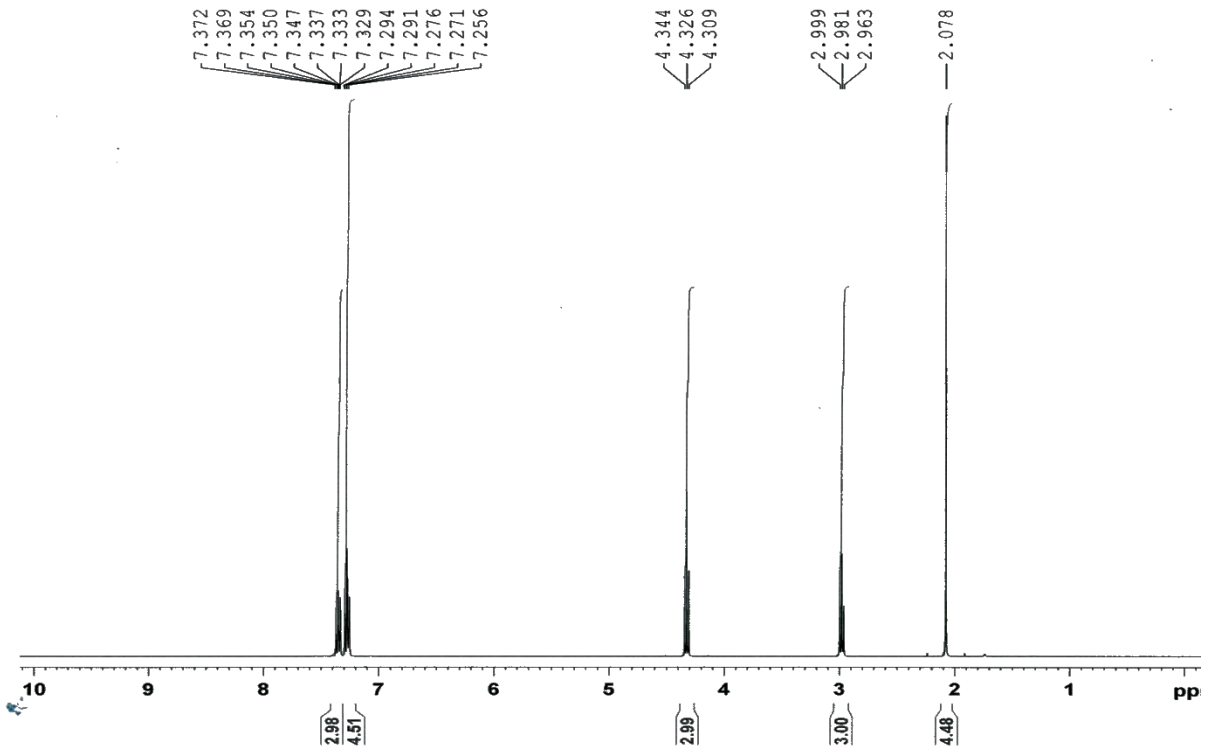


Fig. S38. ^{1}HNMR of phenetylacetate in $CDCl_3$

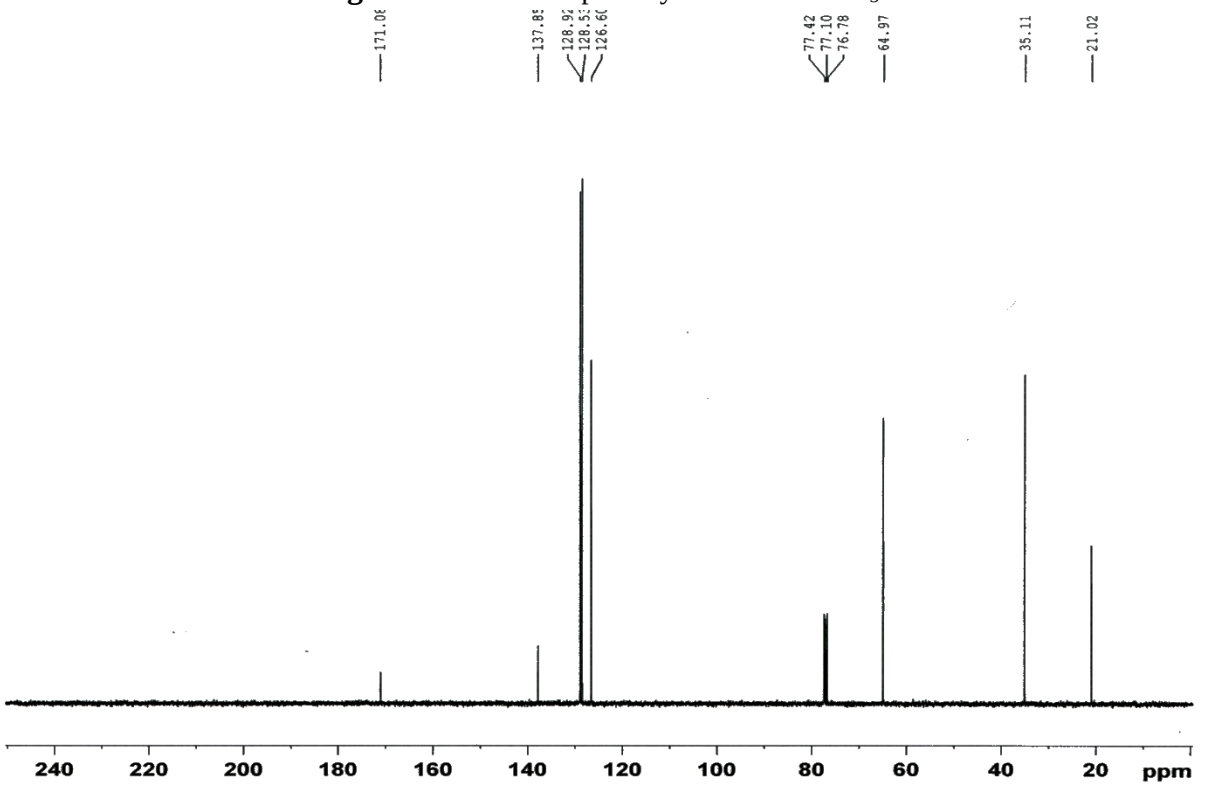


Fig. S39. ^{13}CNMR of phenetylacetate in $CDCl_3$

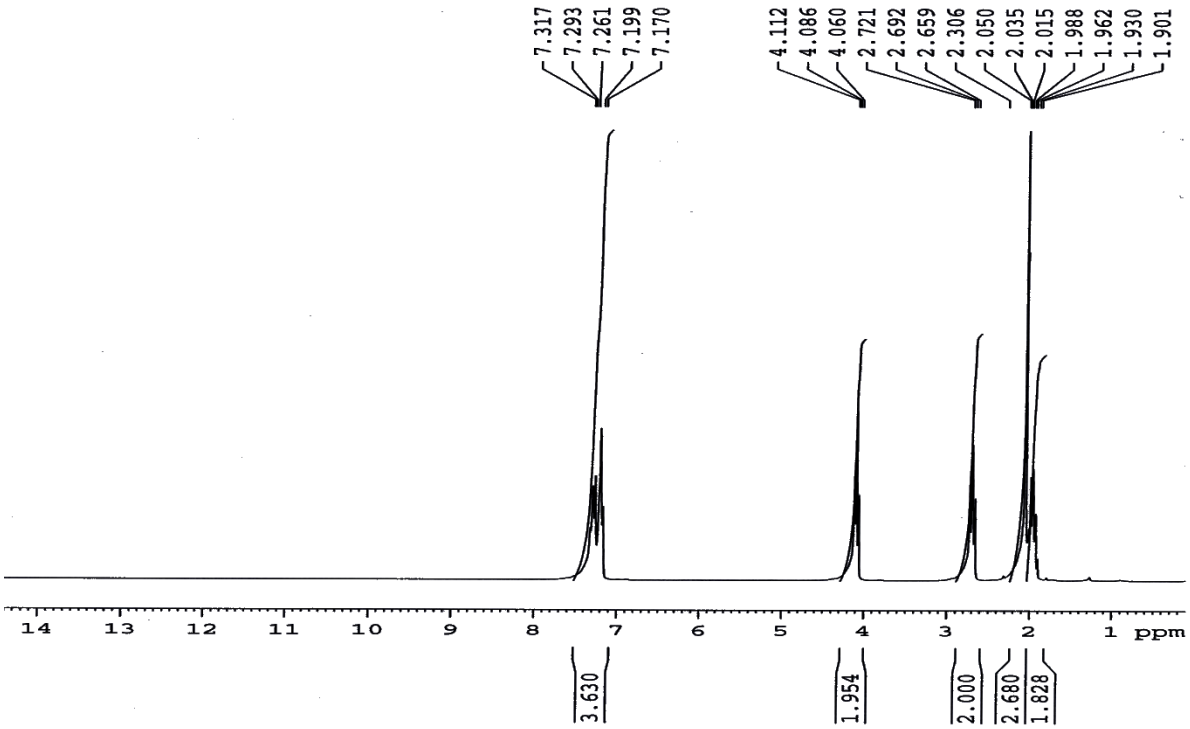


Fig. S40. ^{1}HNMR of 3-phenylpropylacetate in $CDCl_3$

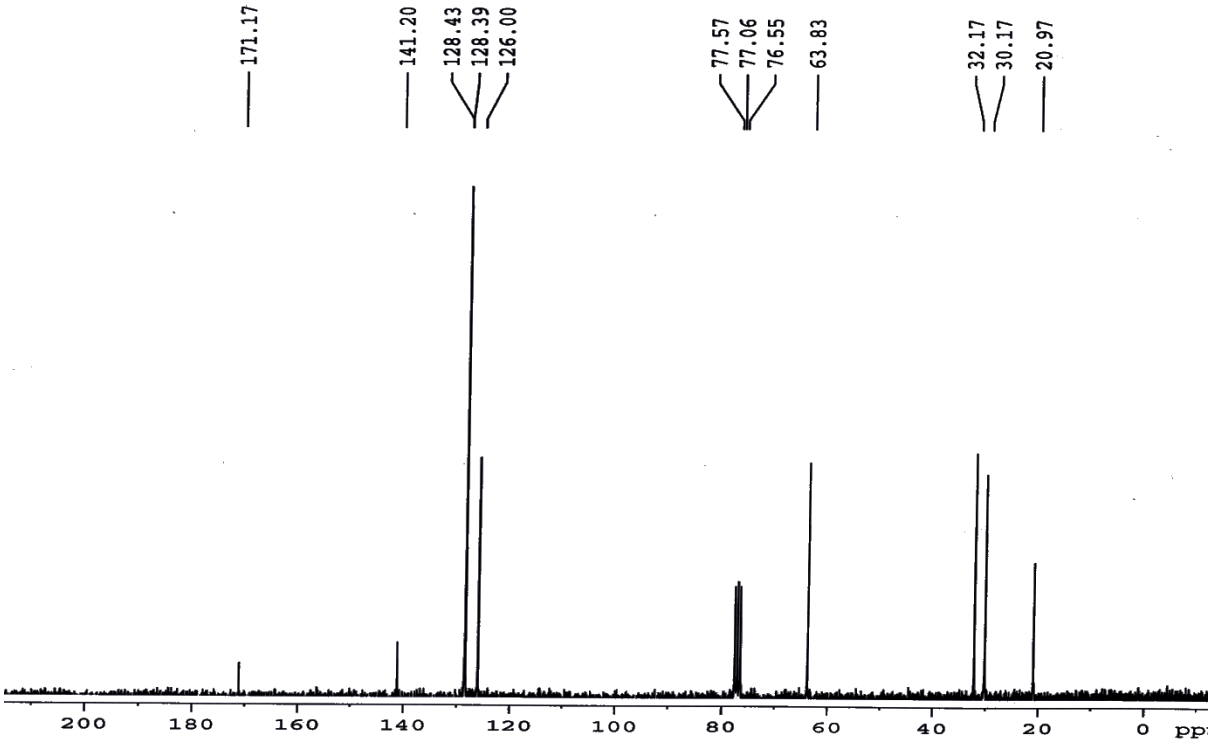


Fig. S41. ^{13}CNMR of 3-phenylpropylacetate in $CDCl_3$

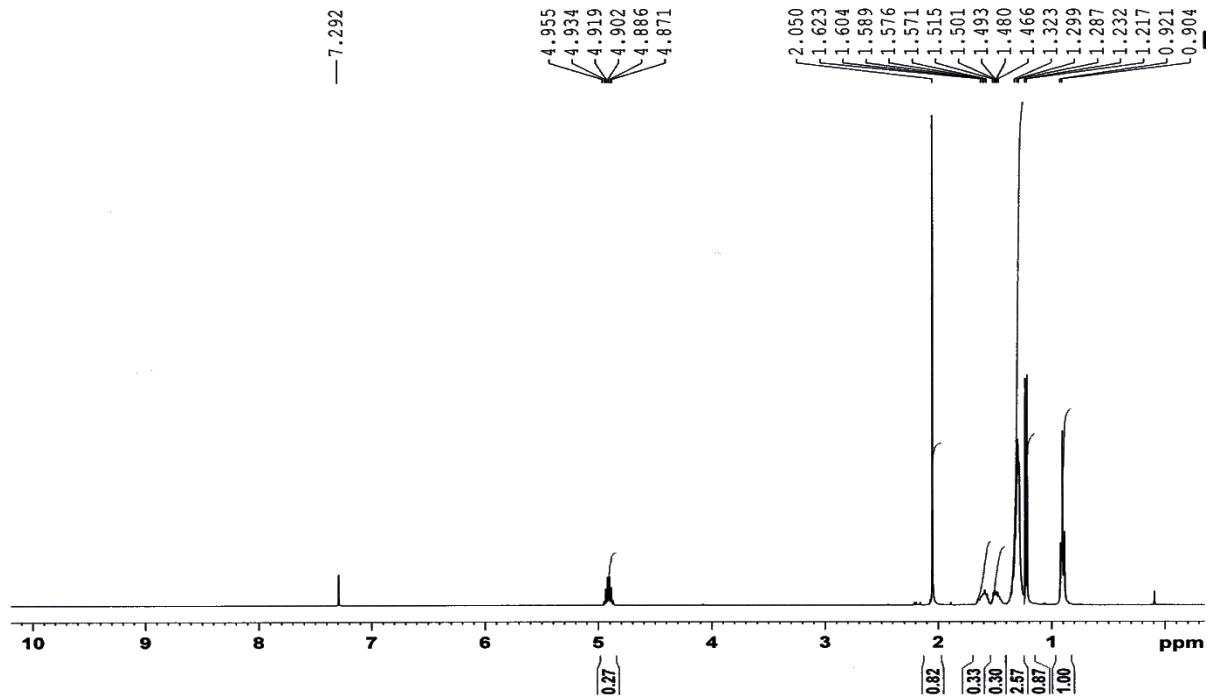


Fig. S42. ^{1}HNMR of occtan-2-yl-acetate in $CDCl_3$

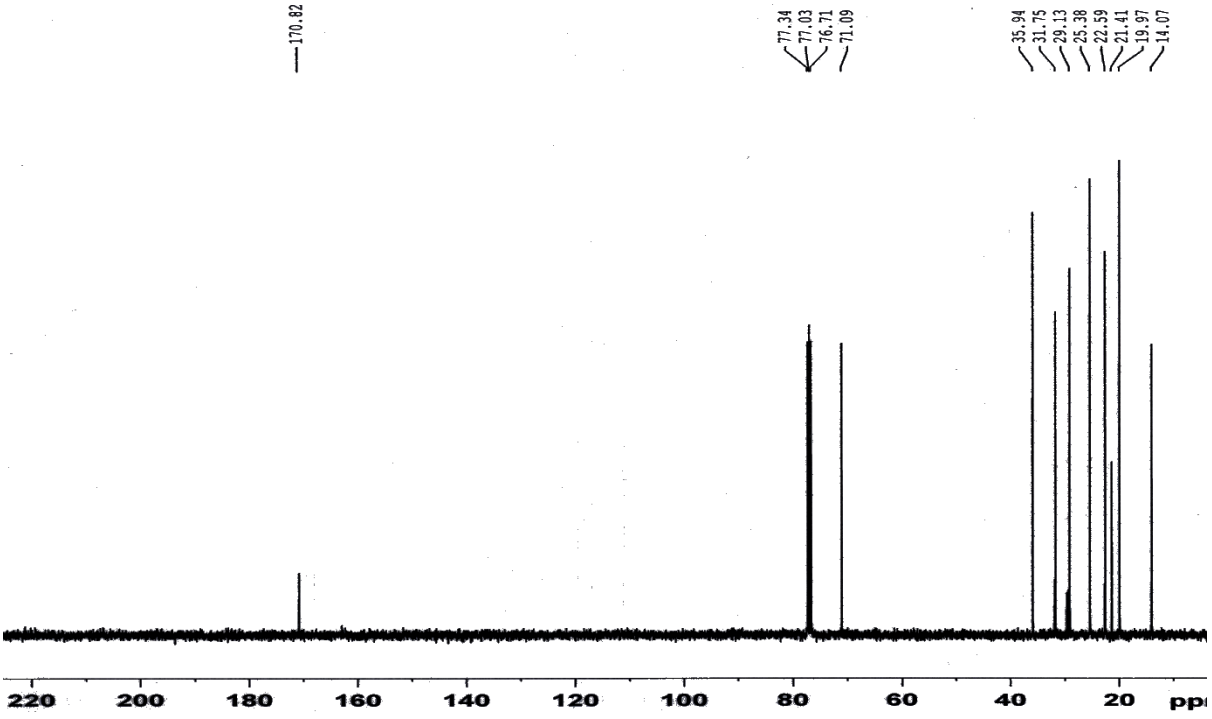


Fig. S43. ^{13}CNMR of occtan-2-yl-acetate in $CDCl_3$

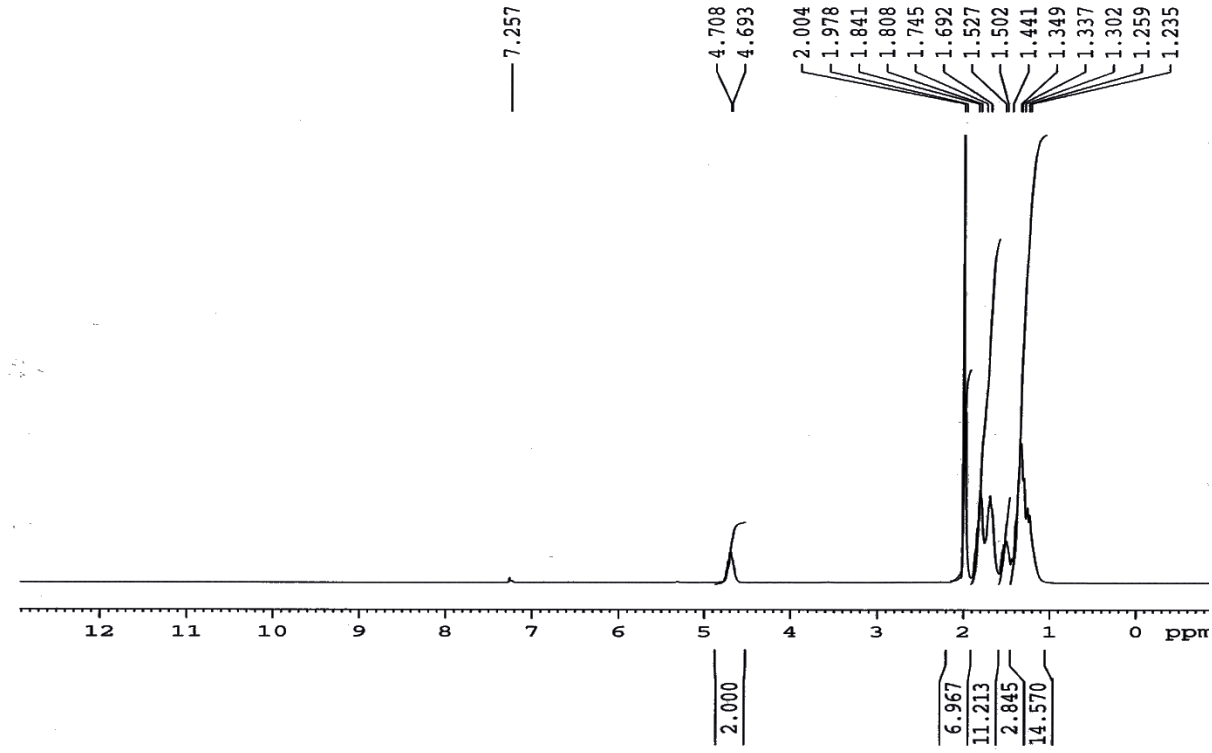


Fig. S44. ^{1}HNMR of cyclohexylacetate in $CDCl_3$

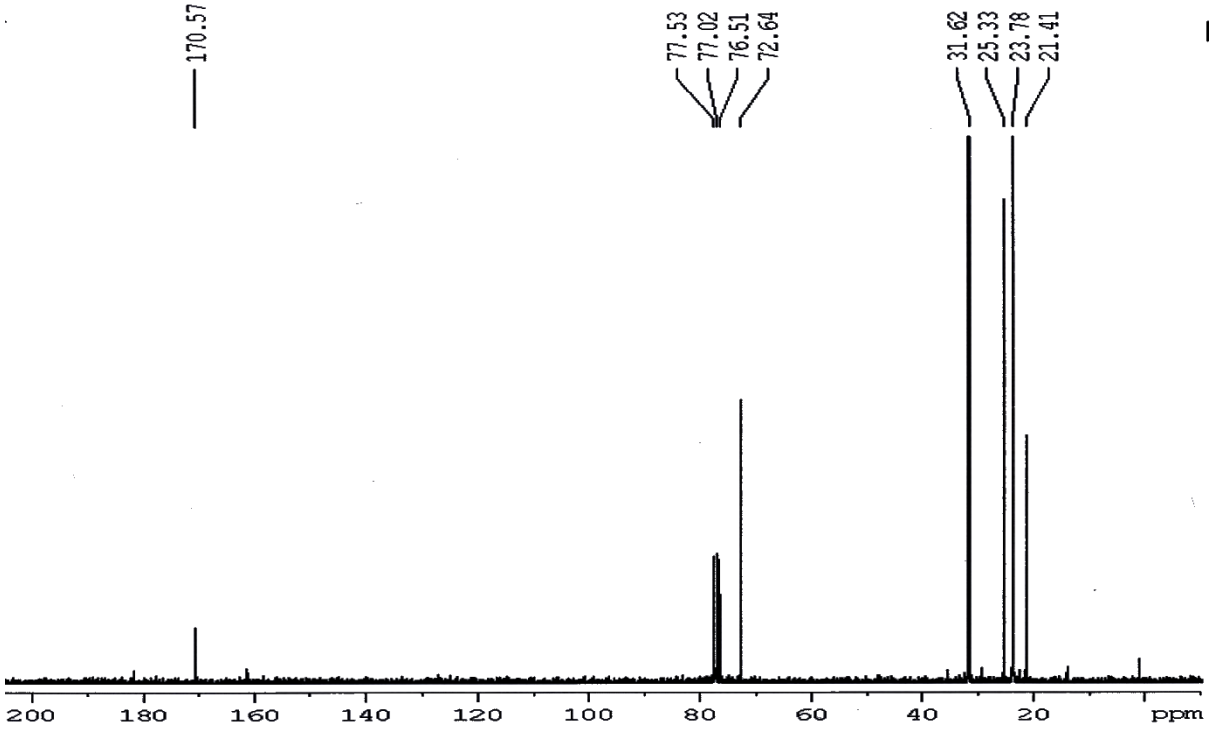


Fig. S45. ^{13}CNMR of cyclohexylacetate in $CDCl_3$

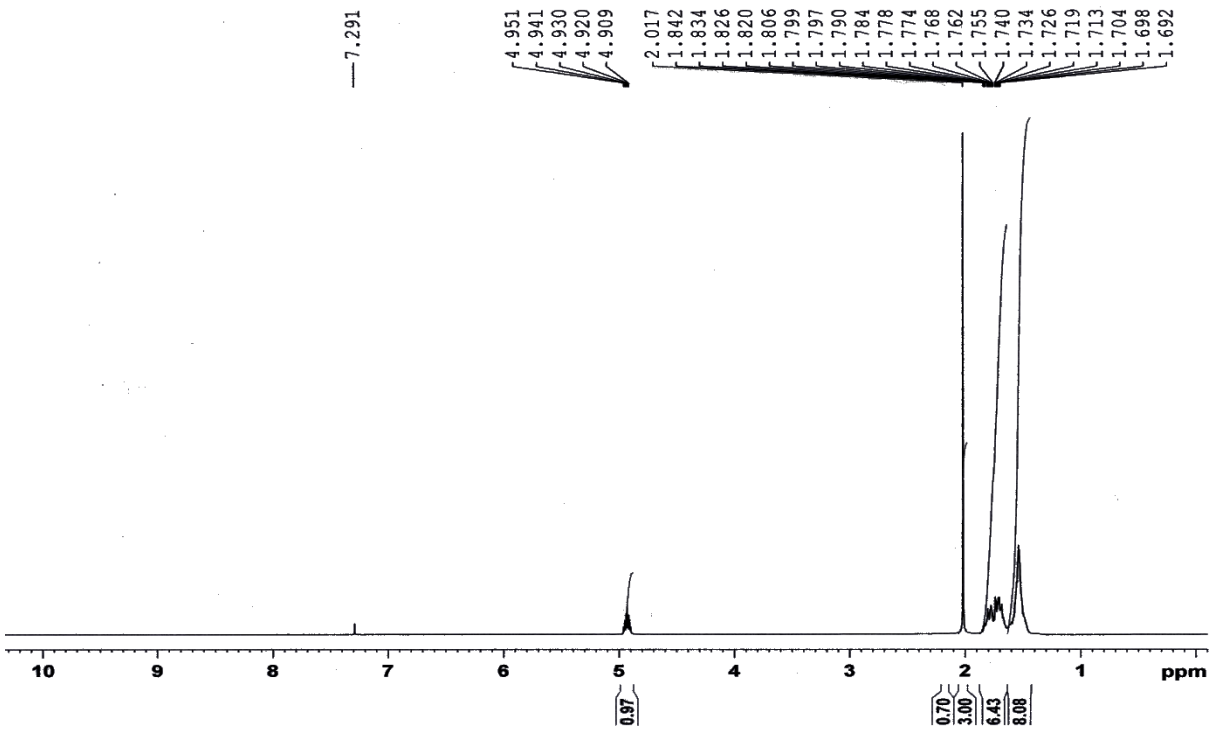


Fig. S46. ^{1}HNMR of cyclooctylacetate in $CDCl_3$

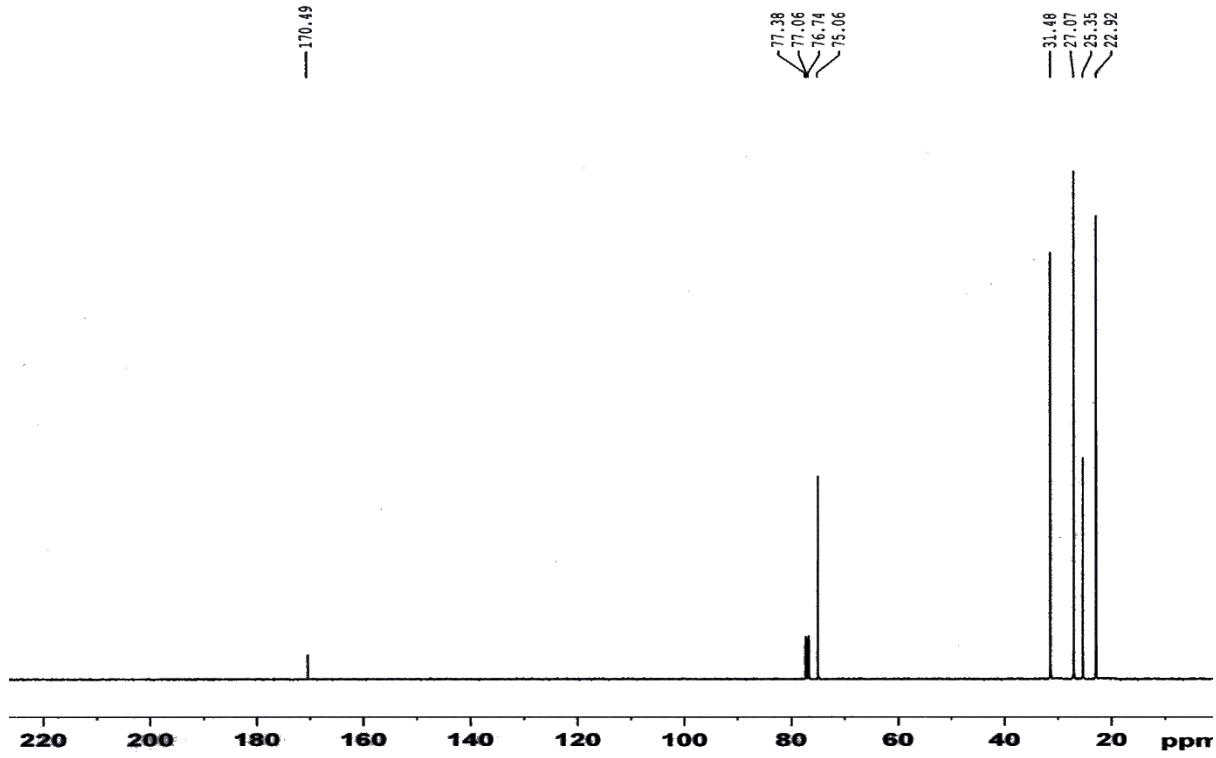


Fig. S47. ^{13}CNMR of cyclooctylacetate in $CDCl_3$

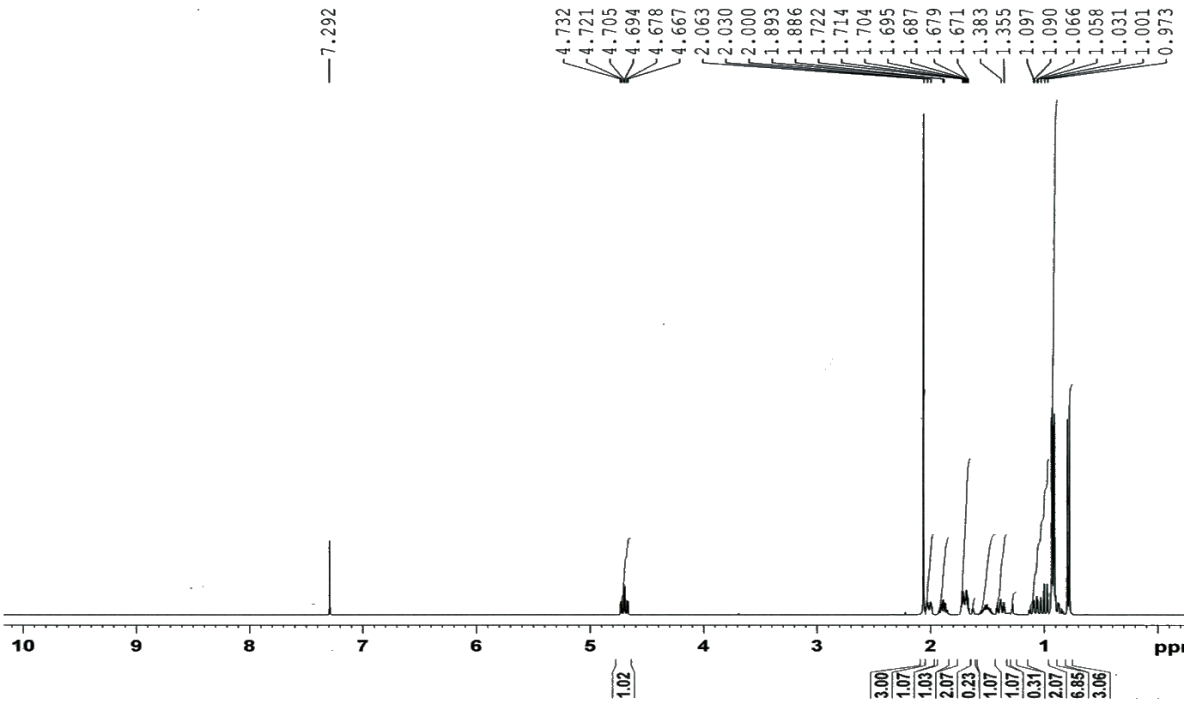


Fig. S48. ^{1}HNMR of 2-isopropyl-5-methylcyclohexylacetate in $CDCl_3$

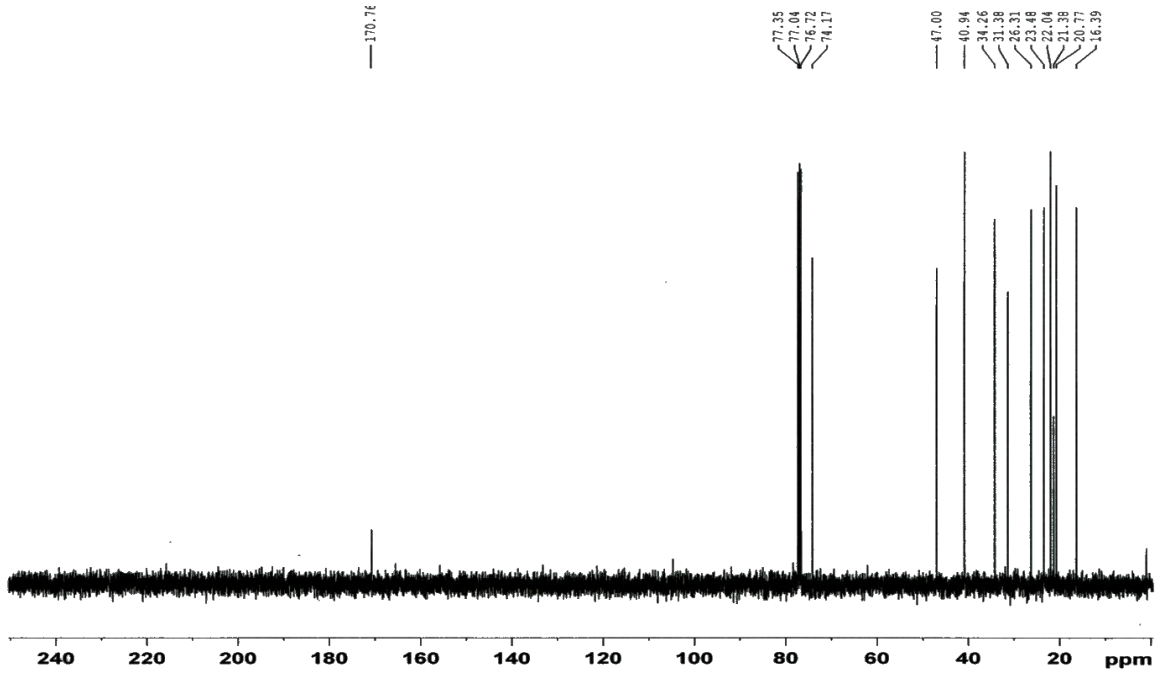


Fig. S49. ^{13}CNMR of 2-isopropyl-5-methylcyclohexylacetate in $CDCl_3$

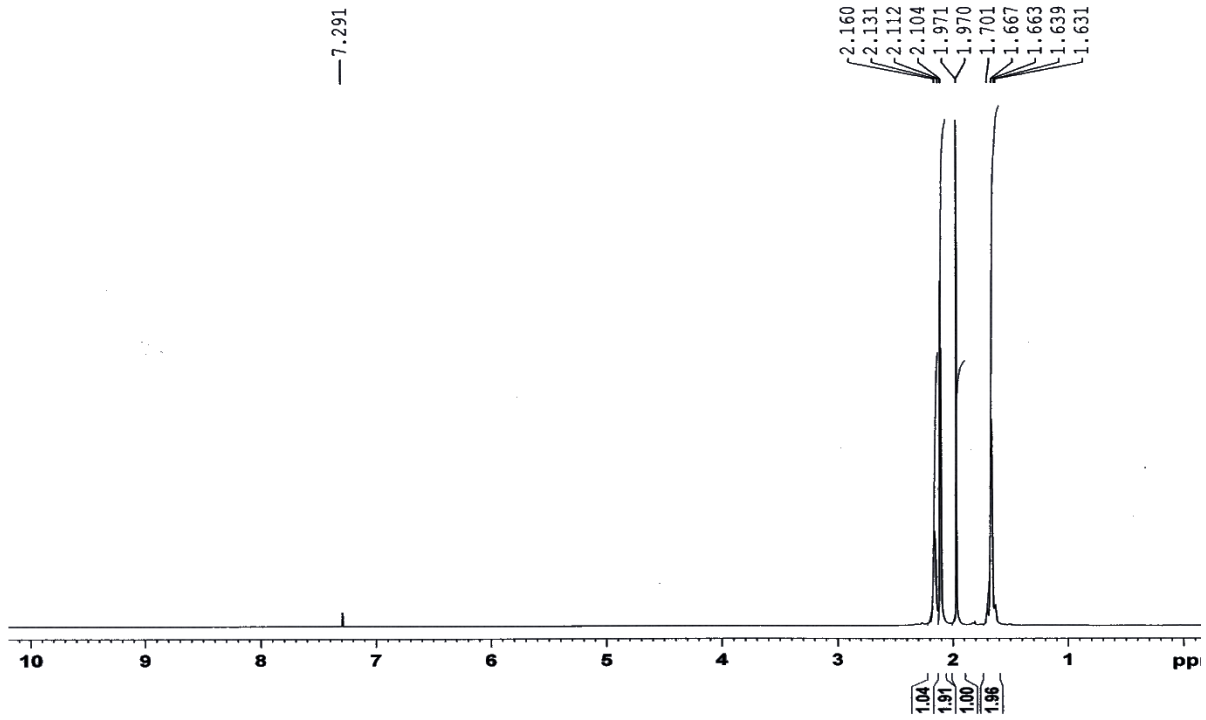


Fig. S50. ^{1}HNMR of adamantane-1-yl-acetate in $CDCl_3$

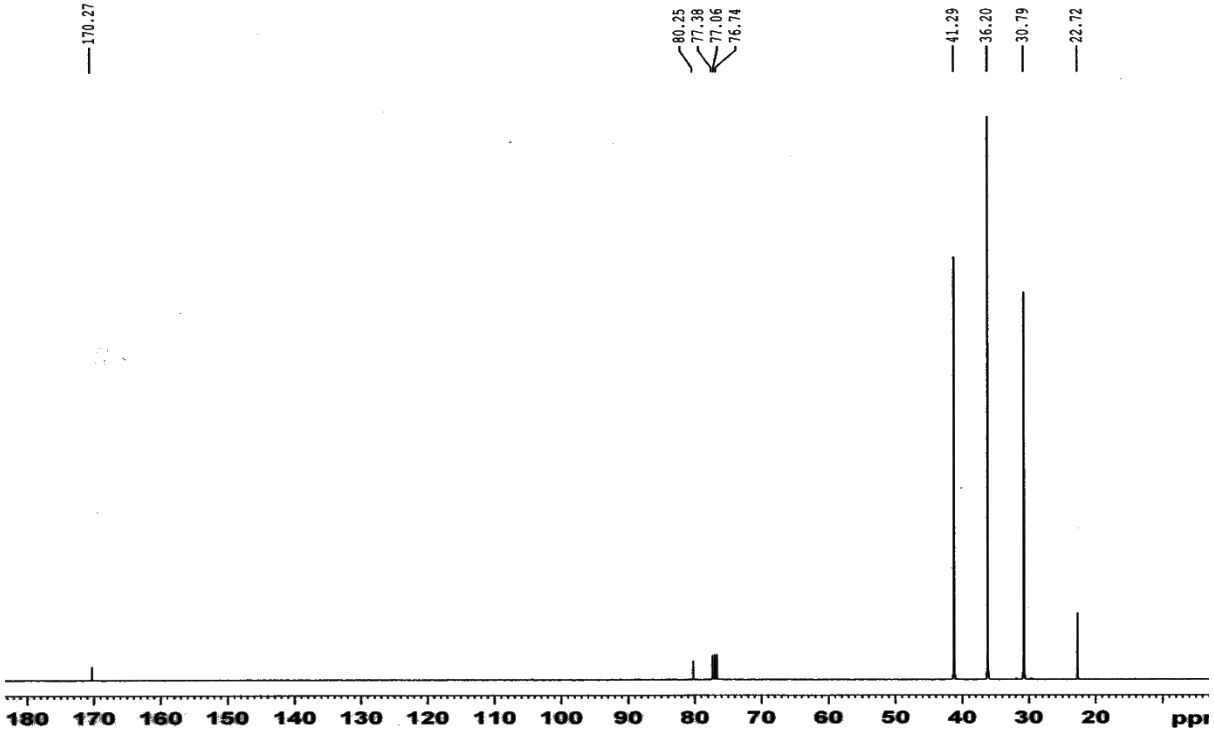


Fig. S51. ^{13}CNMR of adamantane-1-yl-acetate in $CDCl_3$

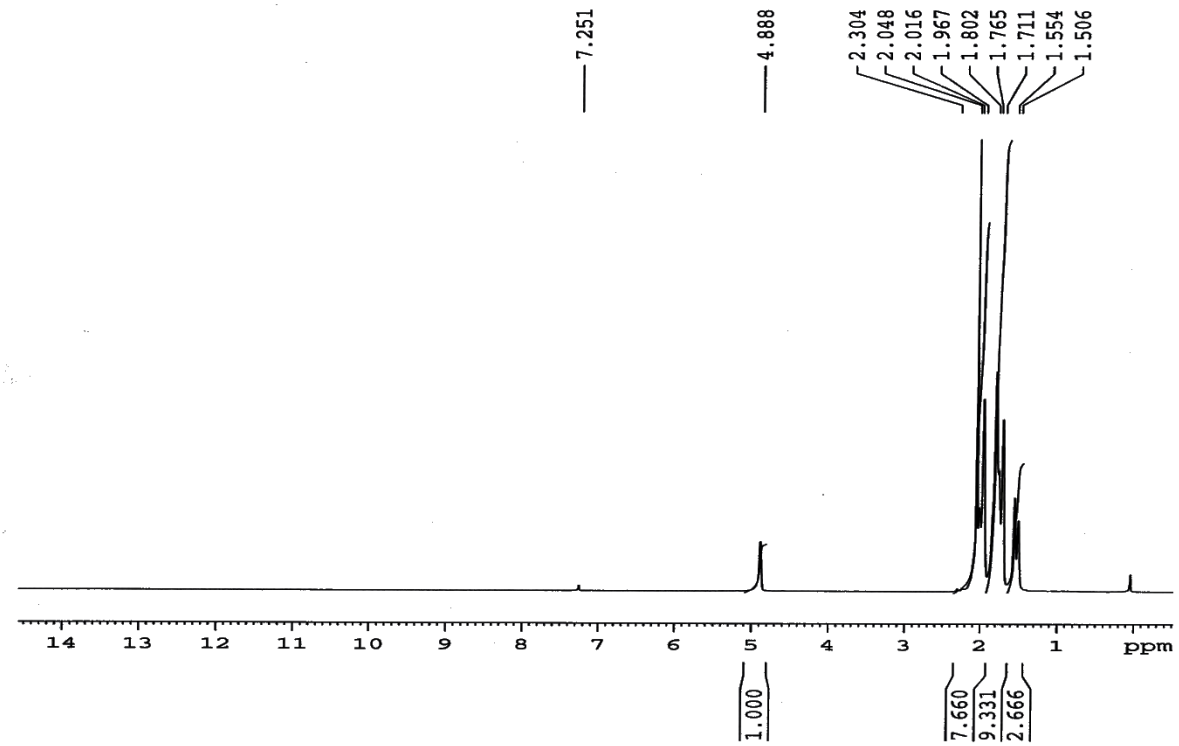


Fig. S52. ^{1}HNMR of adamantane-2-yl-acetate in $CDCl_3$

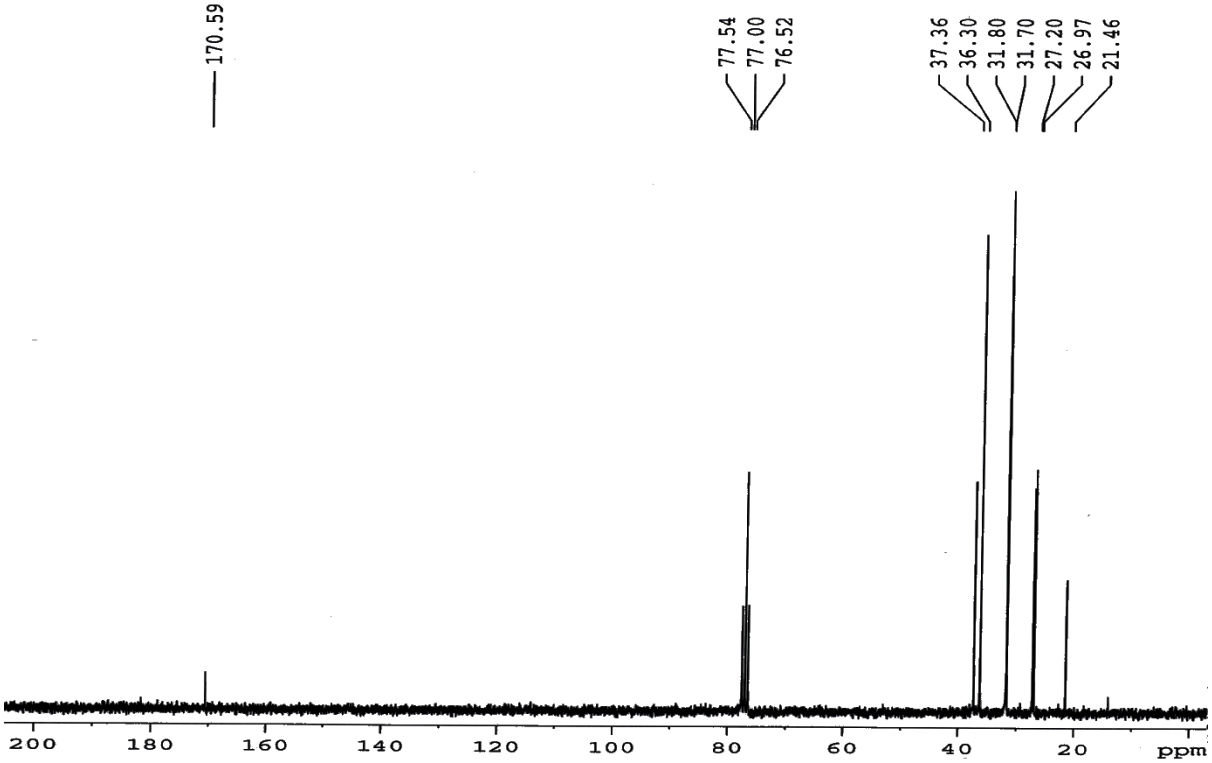


Fig. S53. ^{13}cNMR of adamantane-2-yl-acetate in $CDCl_3$

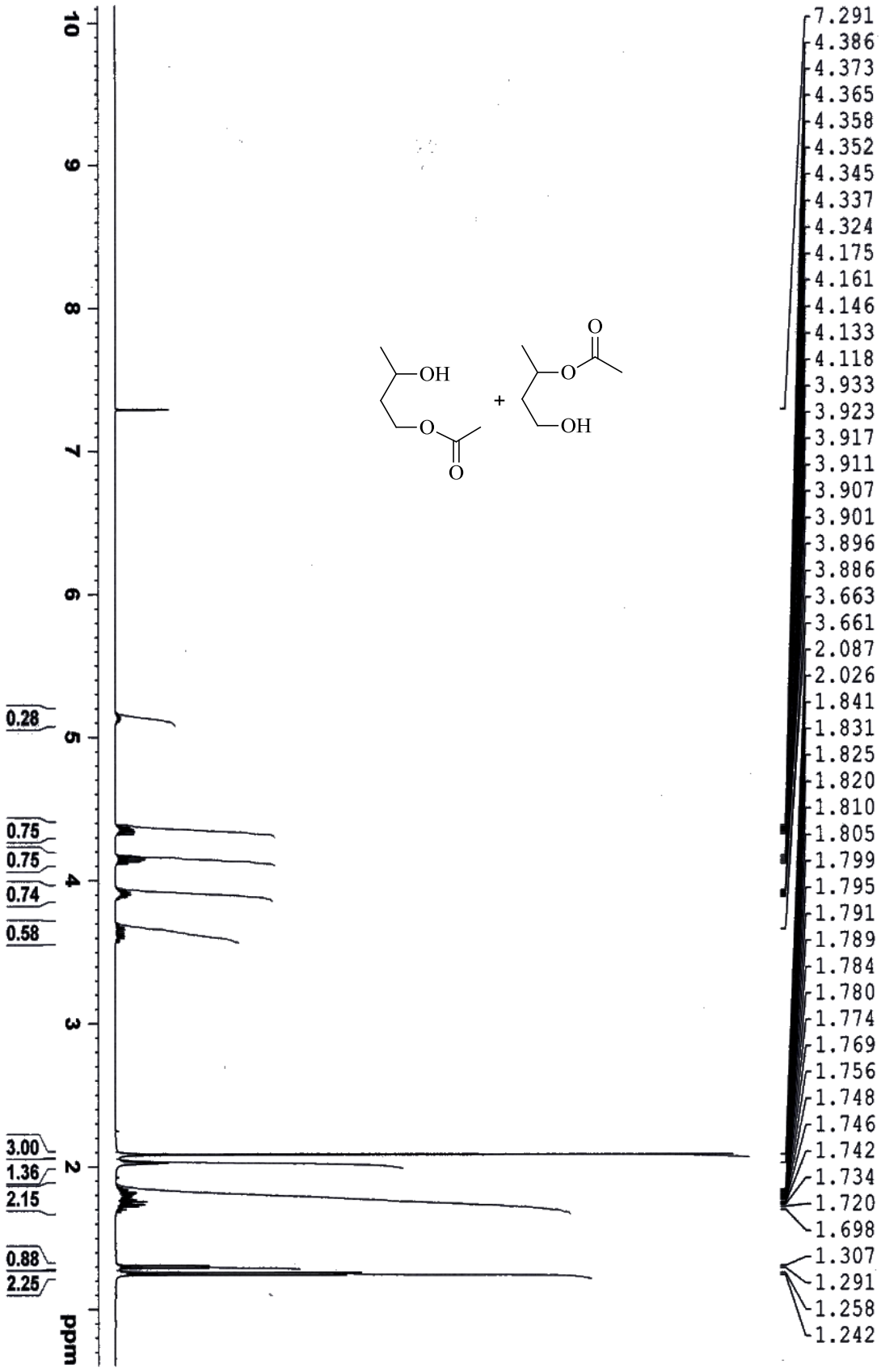


Fig. S54. [1]HNMR 3-Hydroxybutyl acetate compound with 4-hydroxybutan-2-yl acetate (2.5:1)

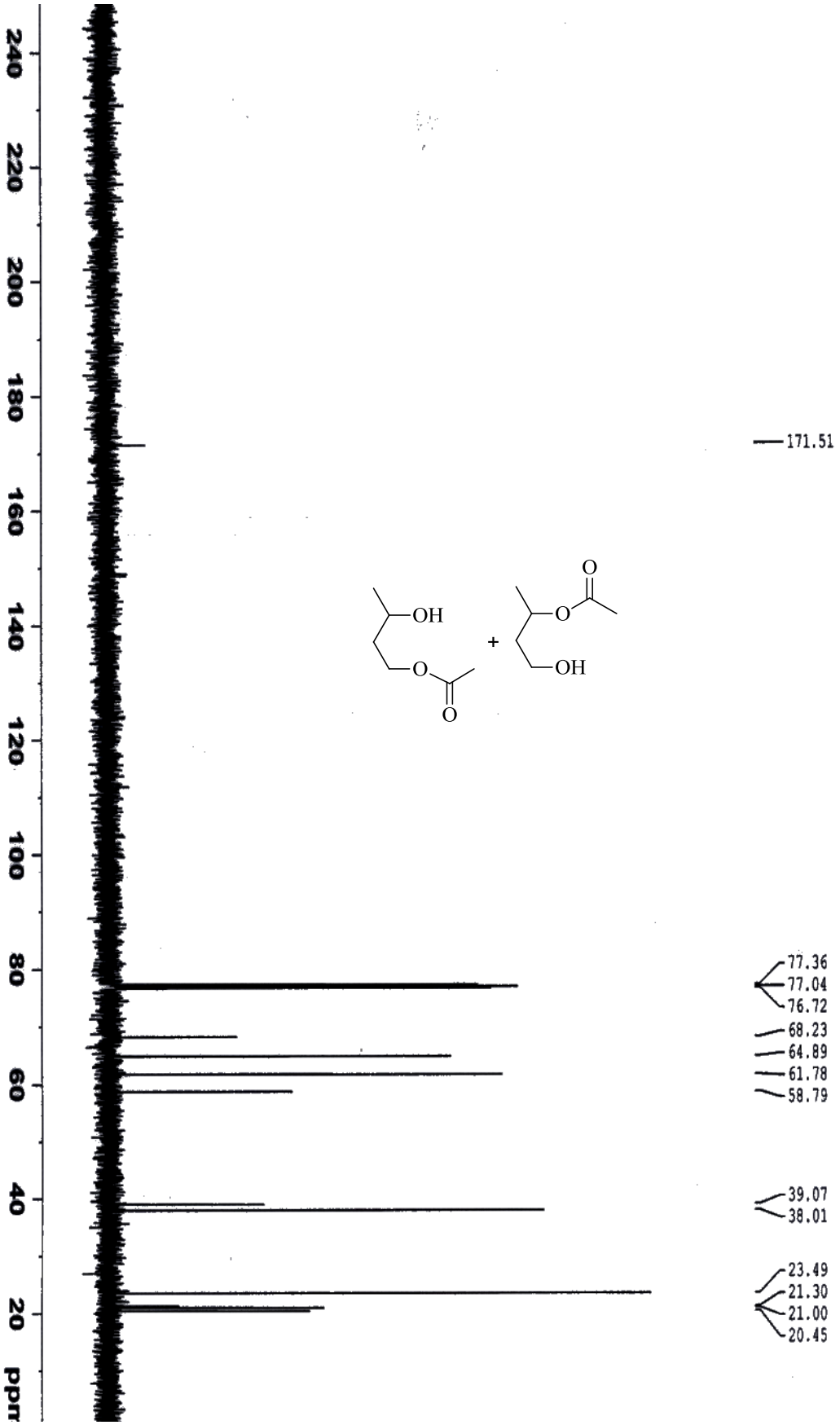


Fig. S55. ^{13}CNMR 3-Hydroxybutyl acetate compound with 4-hydroxybutan-2-yl acetate (2.5:1)

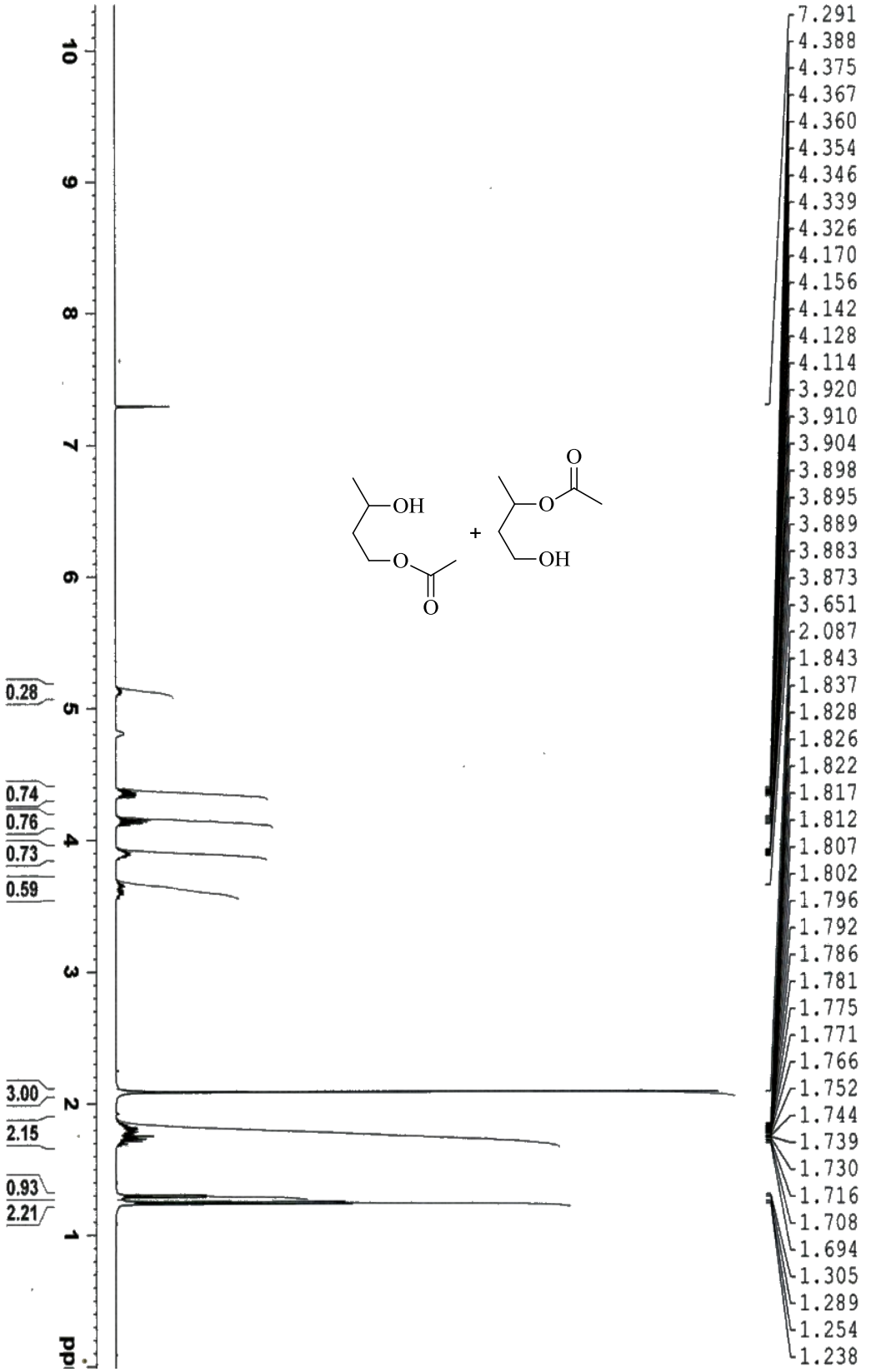


Fig. S56. ^{1}H NMR (D_2O) 3-Hydroxybutyl acetate compound with 4-hydroxybutan-2-yl acetate (2.5:1)

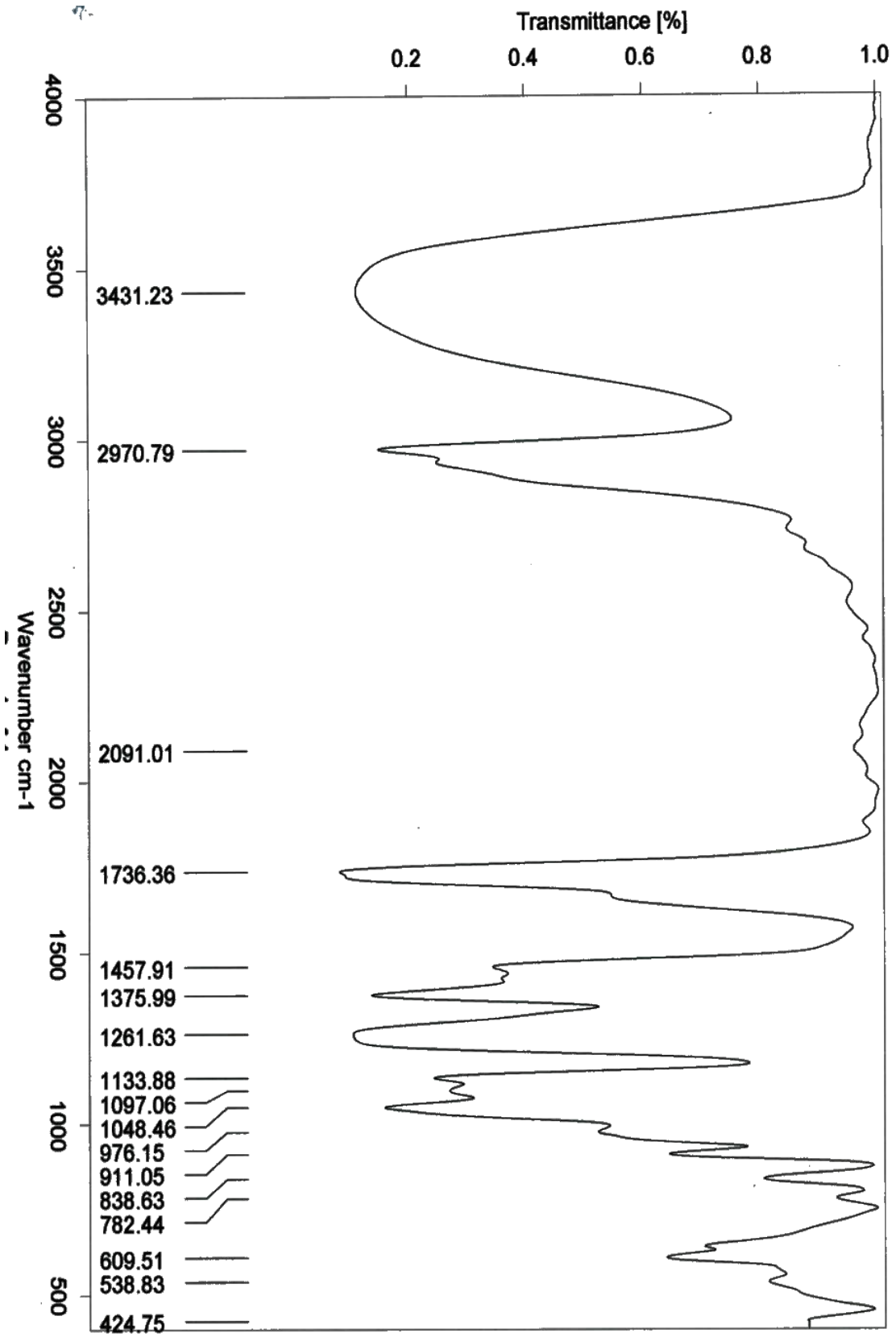


Fig. S57. IR (neat) 3-Hydroxybutyl acetate compound with 4-hydroxybutan-2-yl acetate (2.5:1)

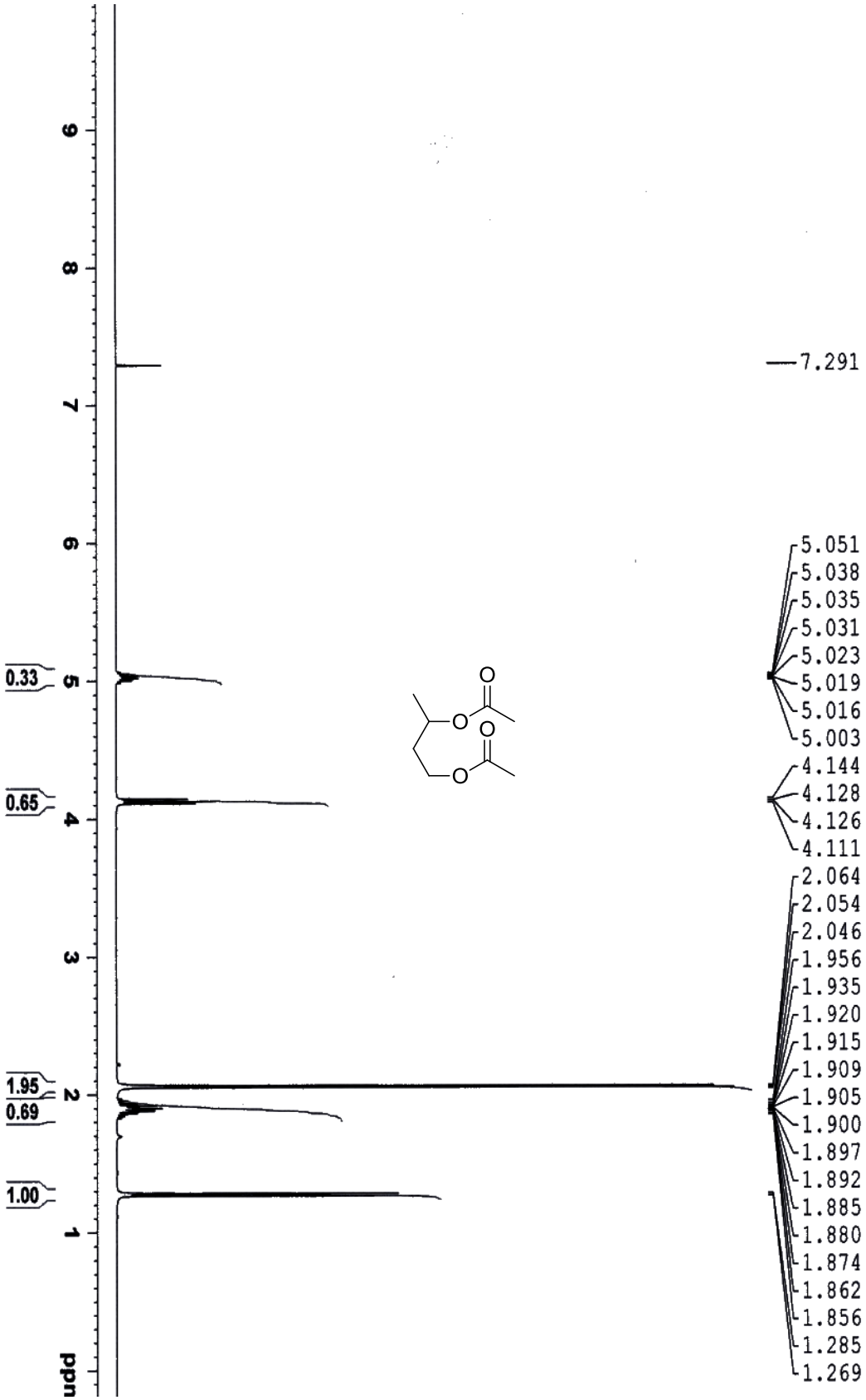


Fig. S58. ^{1}H NMR Butane-1,3-diyl diacetate

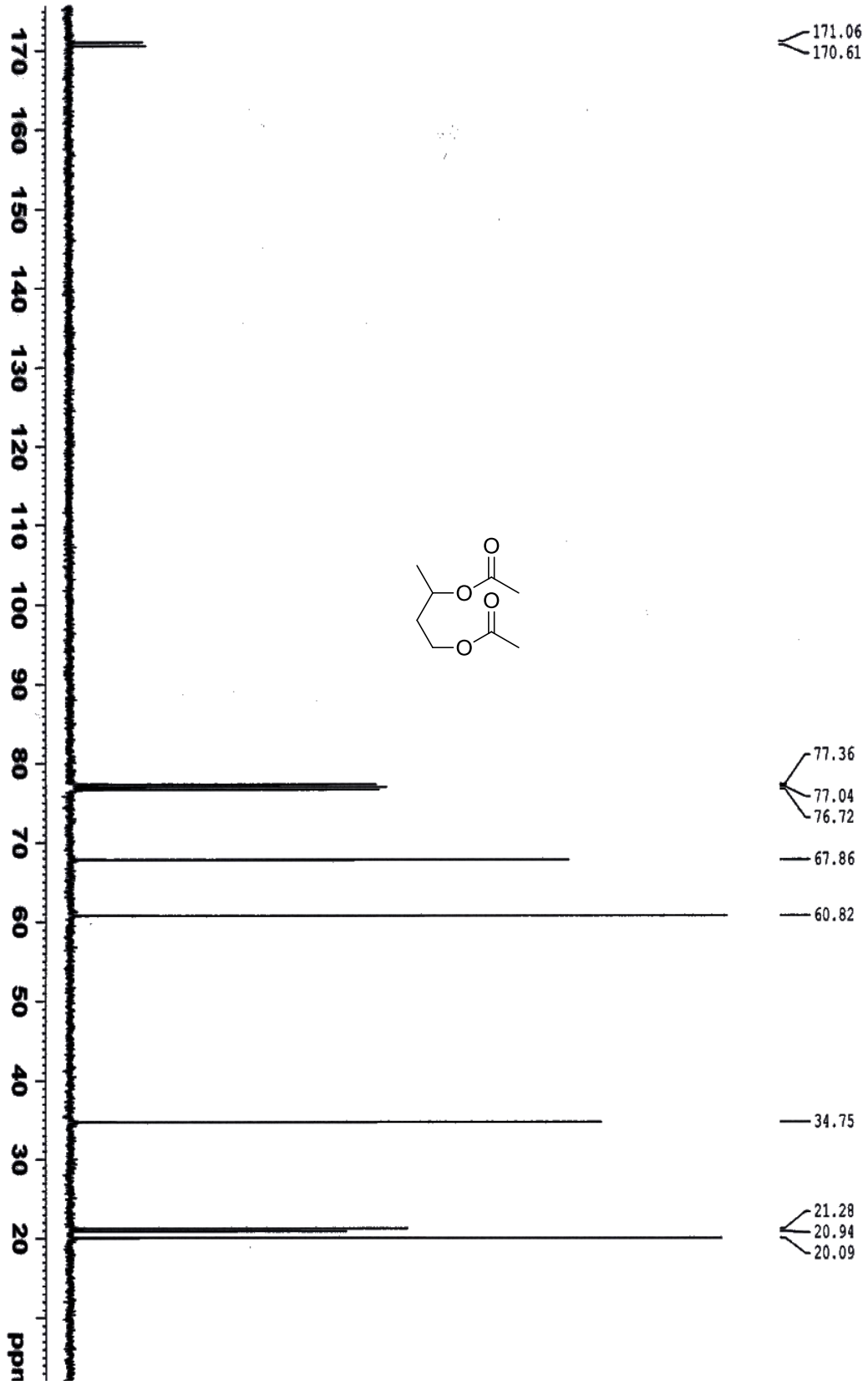


Fig. S59. ^{13}C NMR Butane-1,3-diyl diacetate

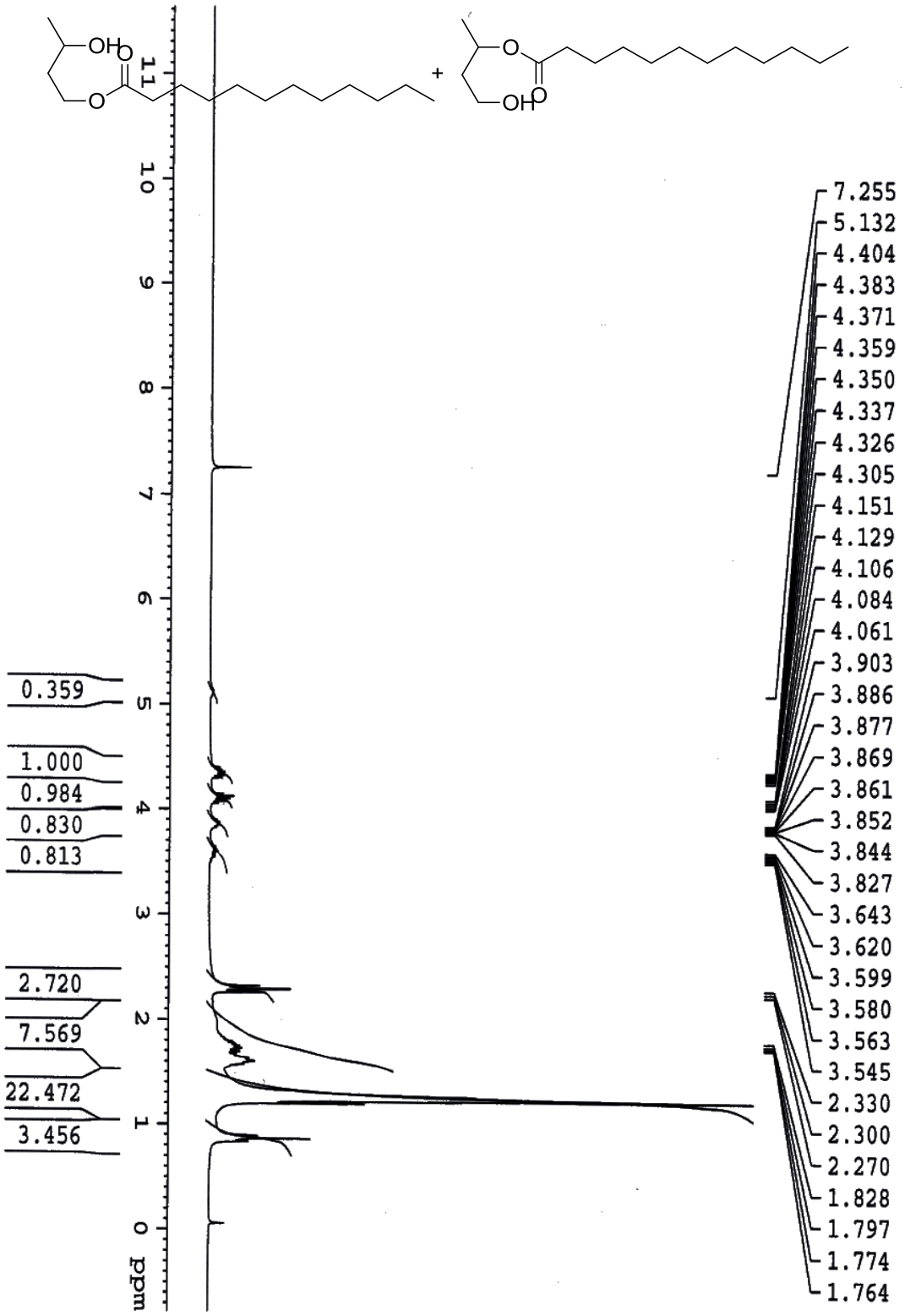


Fig. S60. ^{1}H NMR 3-Hydroxybutyl dodecanoate compound with 4-hydroxybutan-2-yl dodecanoate (2.5:1)

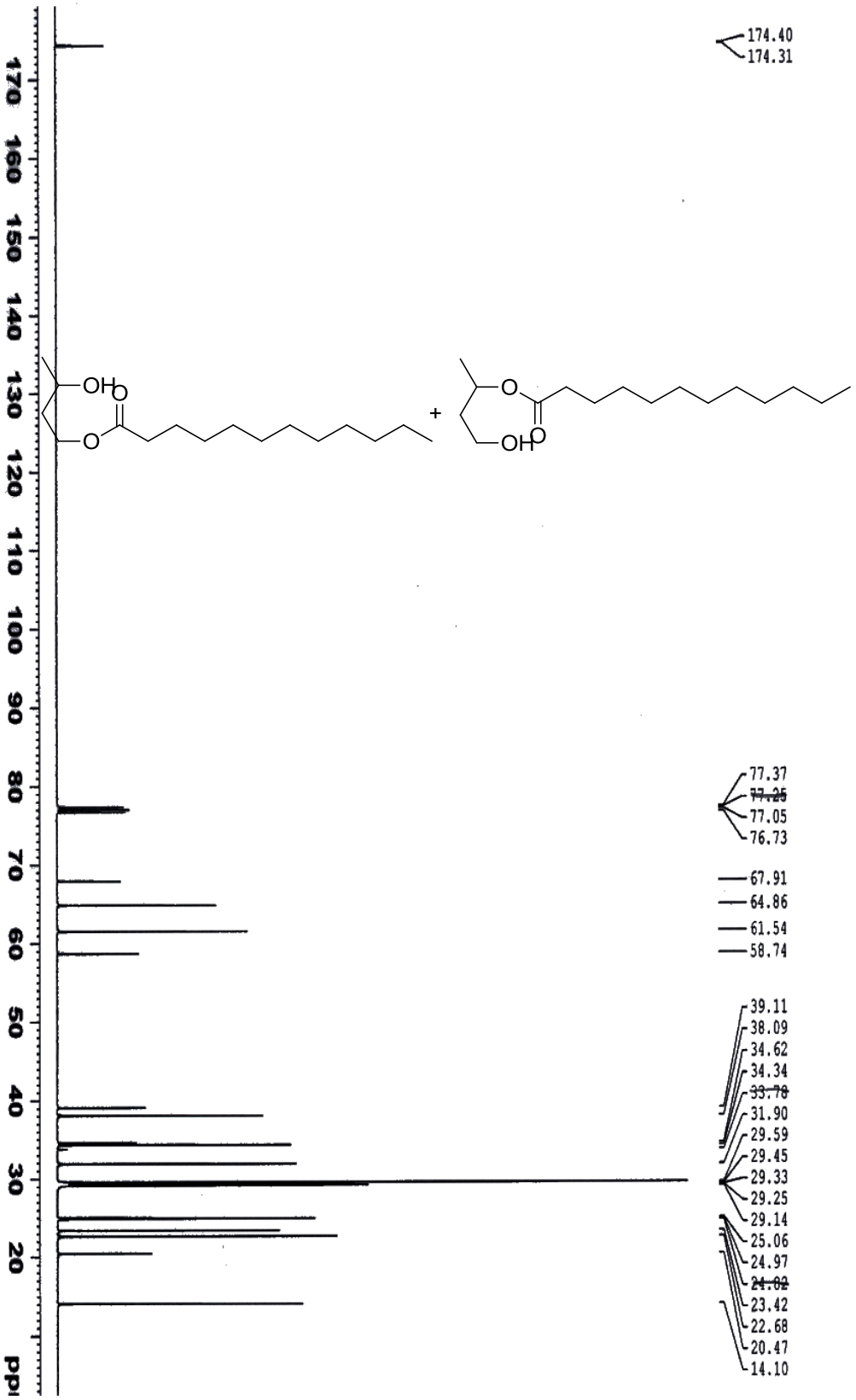


Fig. S61. ^{13}C NMR 3-Hydroxybutyl dodecanoate compound with 4-hydroxybutan-2-yl dodecanoate (2.5:1)

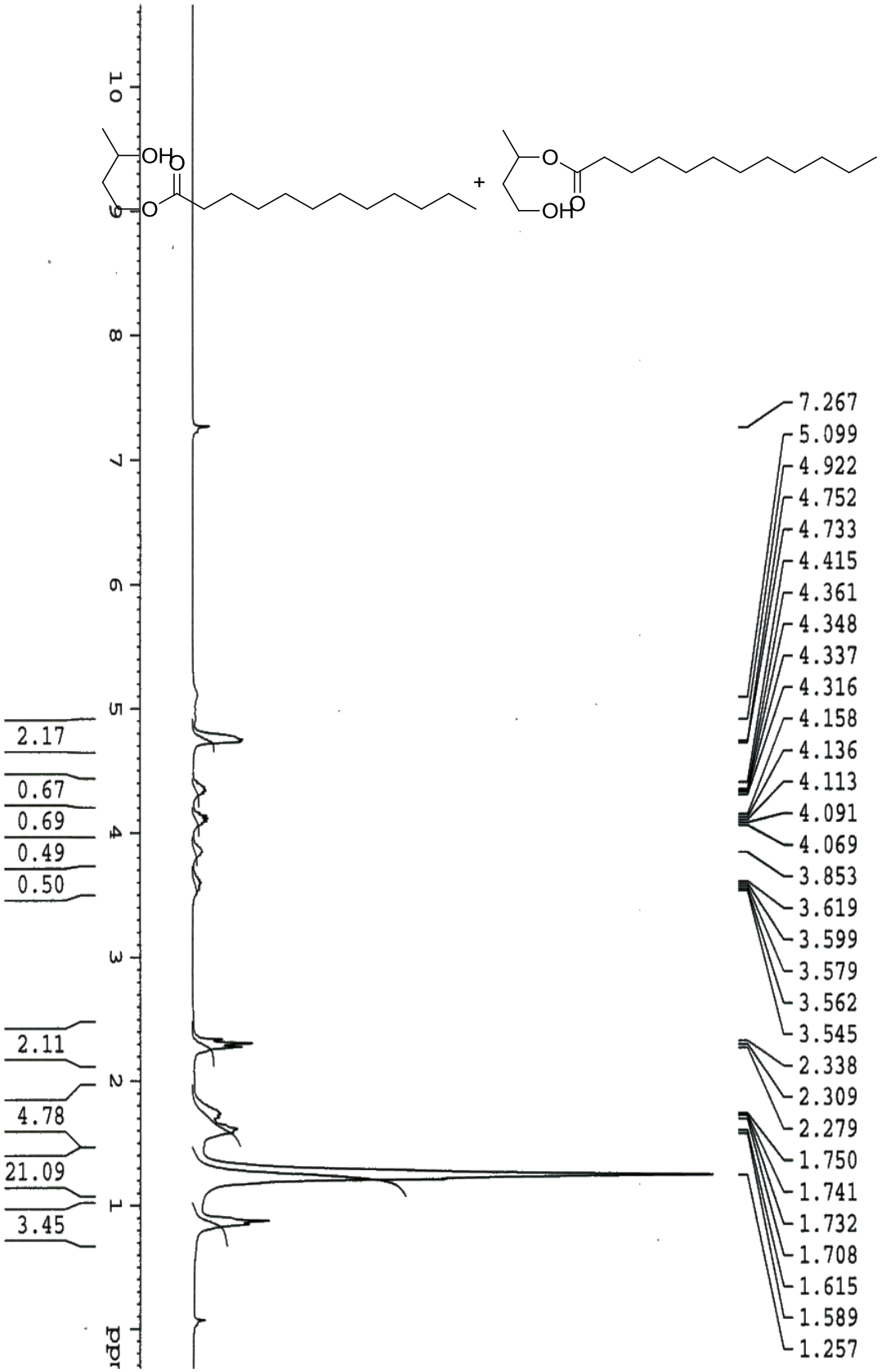


Fig. S62. ^{1}H NMR (D_2O) 3-Hydroxybutyl dodecanoate compound with 4-hydroxybutan-2-yl dodecanoate (2.5:1)

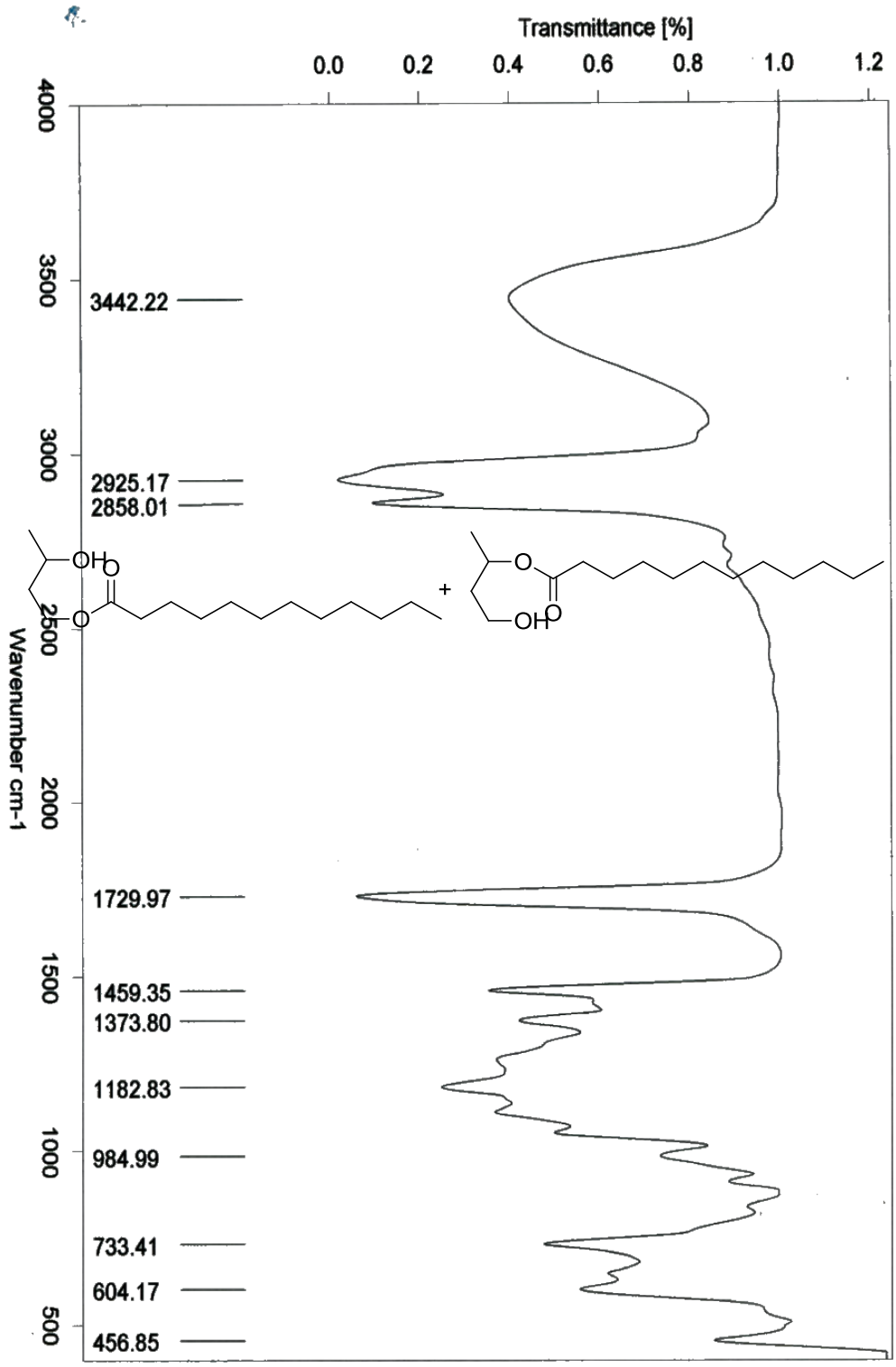


Fig. S63. IR (neat) 3-Hydroxybutyl dodecanoate compound with 4-hydroxybutan-2-yl dodecanoate (2.5:1)

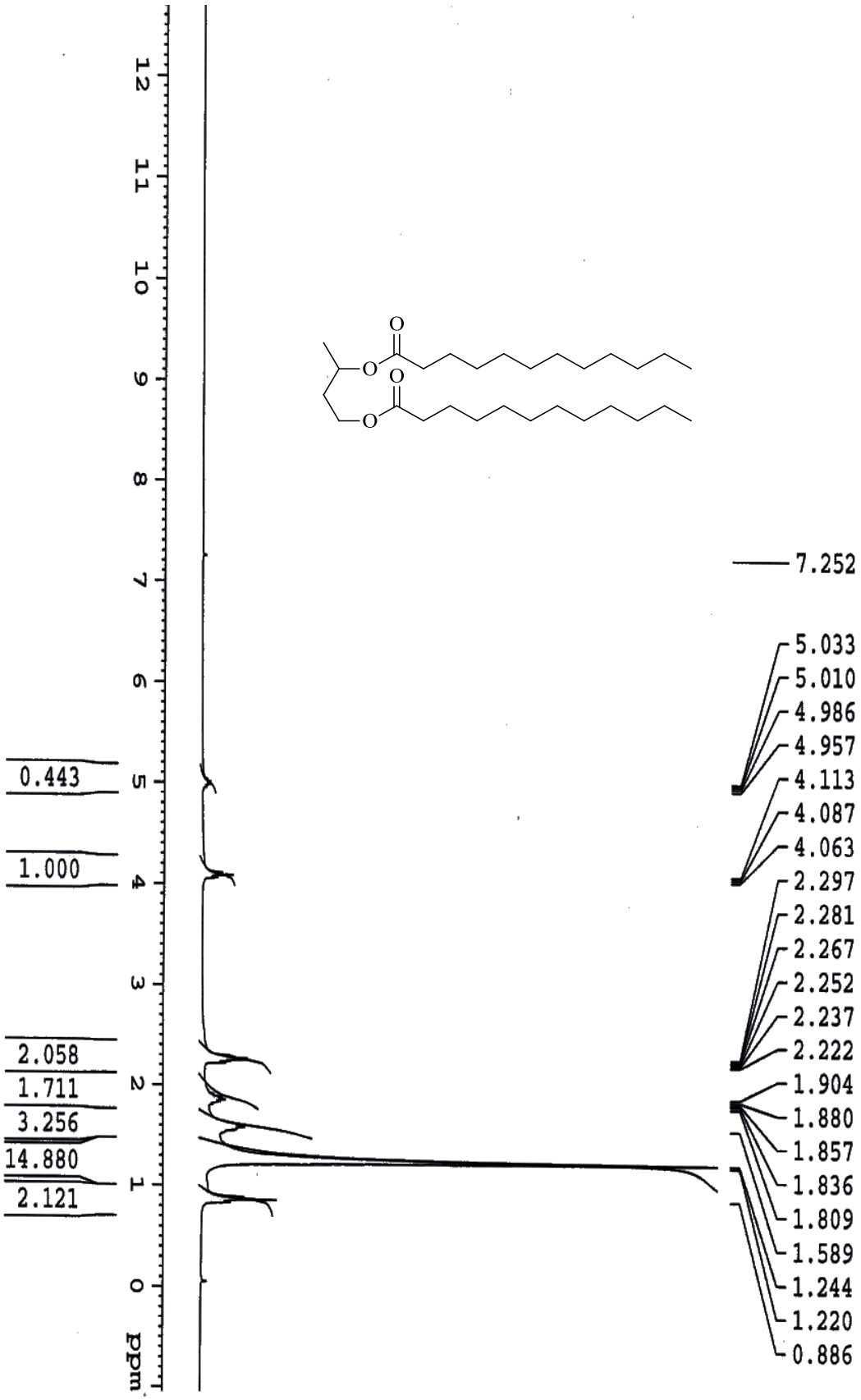


Fig. S64. ^{1}H NMR Butane-1,3-diyl didodecanoate

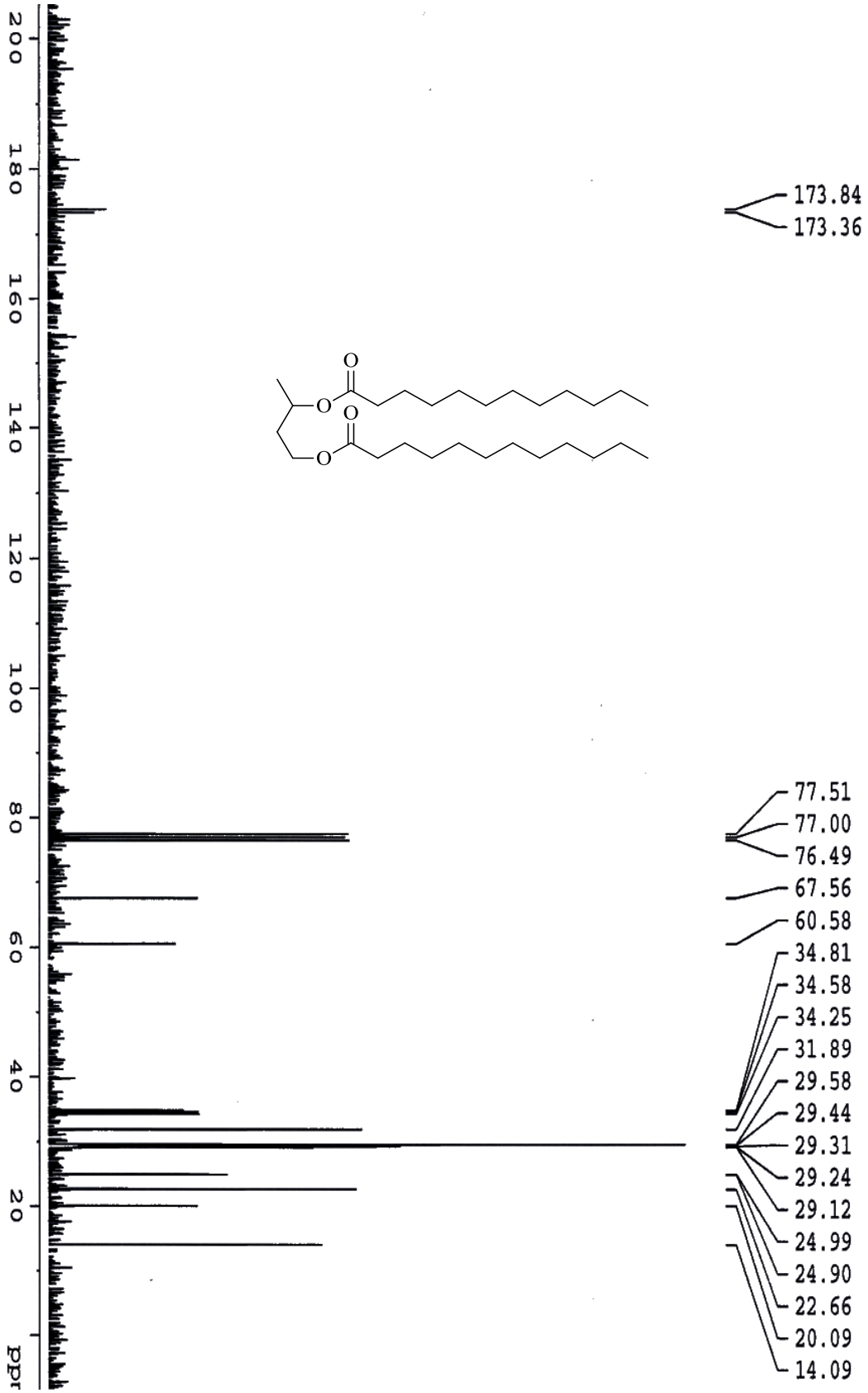


Fig. S65. ^{13}C NMR Butane-1,3-diyl didodecanoate

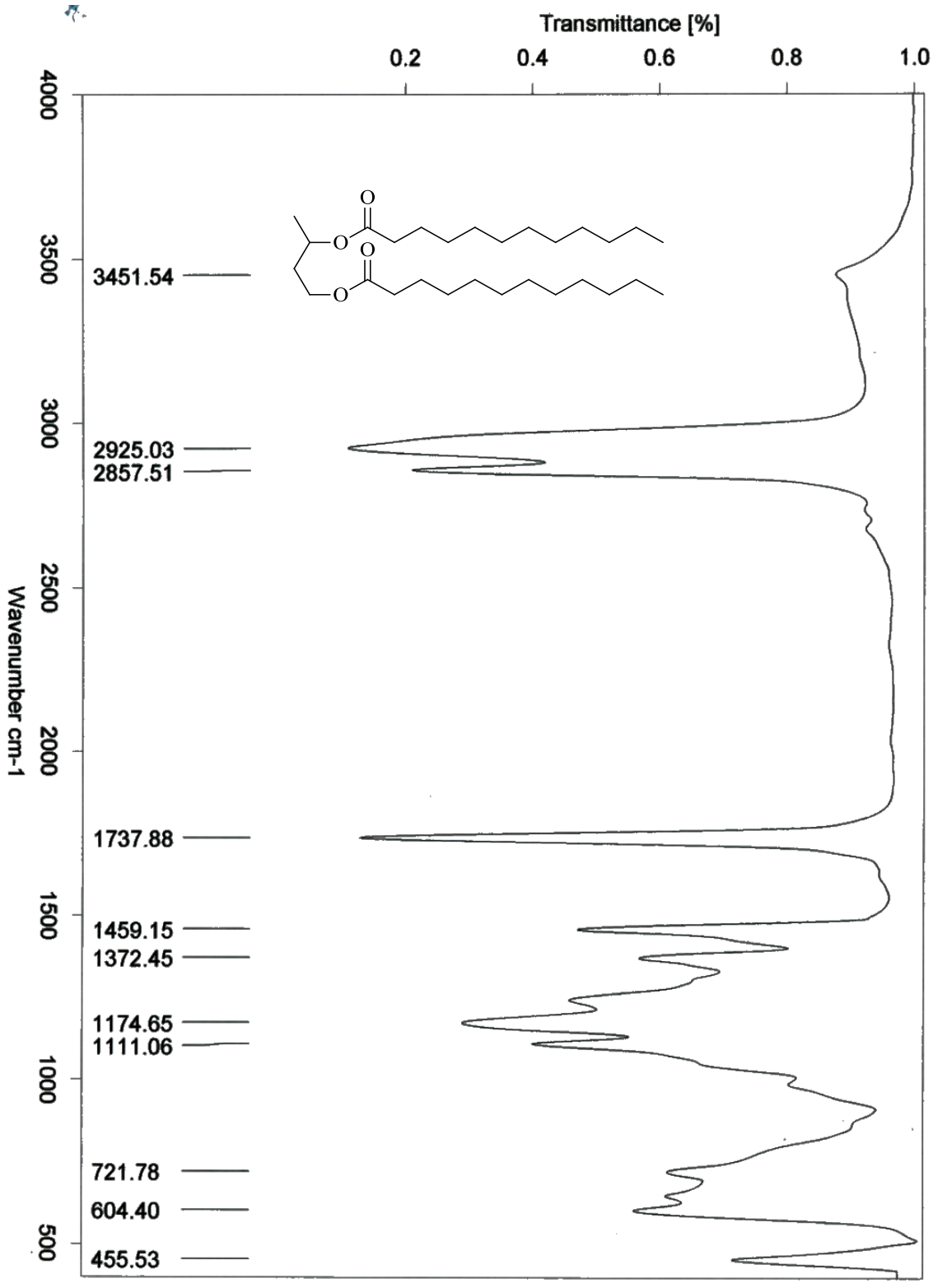


Fig. S66. IR (neat) Butane-1,3-diyl didodecanoate

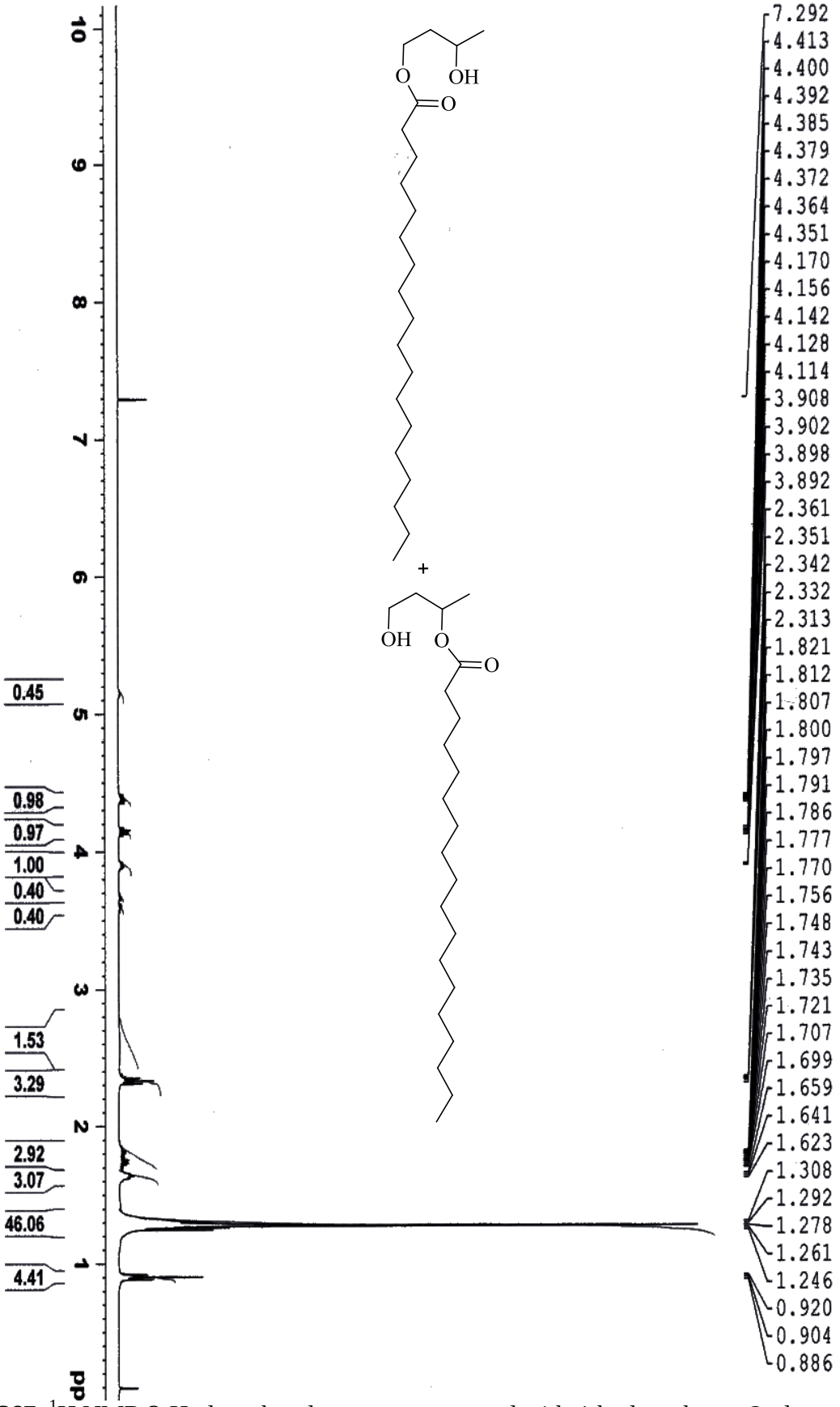


Fig. S67. ^{1}H NMR 3-Hydroxybutyl stearate compound with 4-hydroxybutan-2-yl stearate (2.5:1)

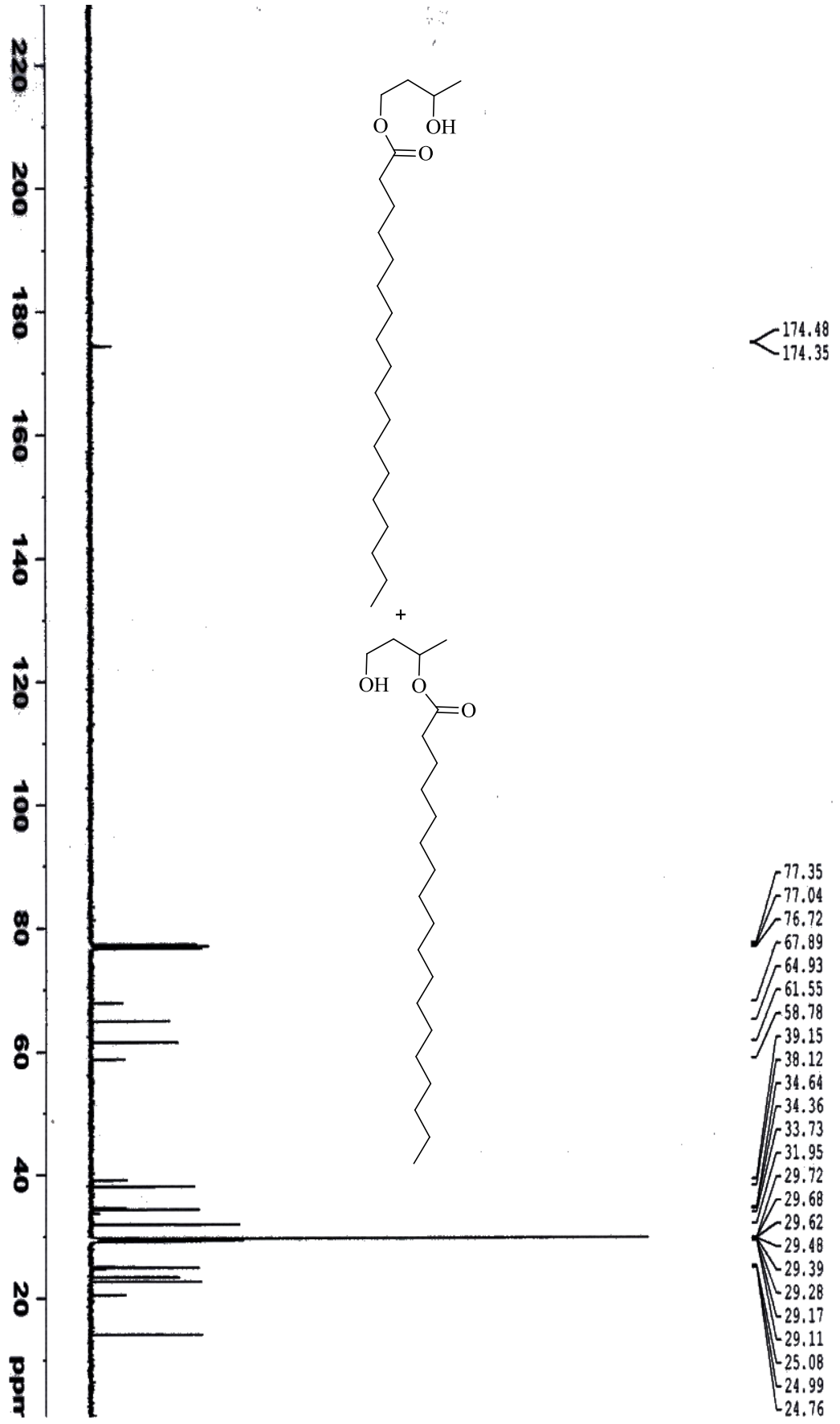


Fig. S68. ^{13}C NMR 3-Hydroxybutyl stearate compound with 4-hydroxybutan-2-yl stearate (2.5:1)

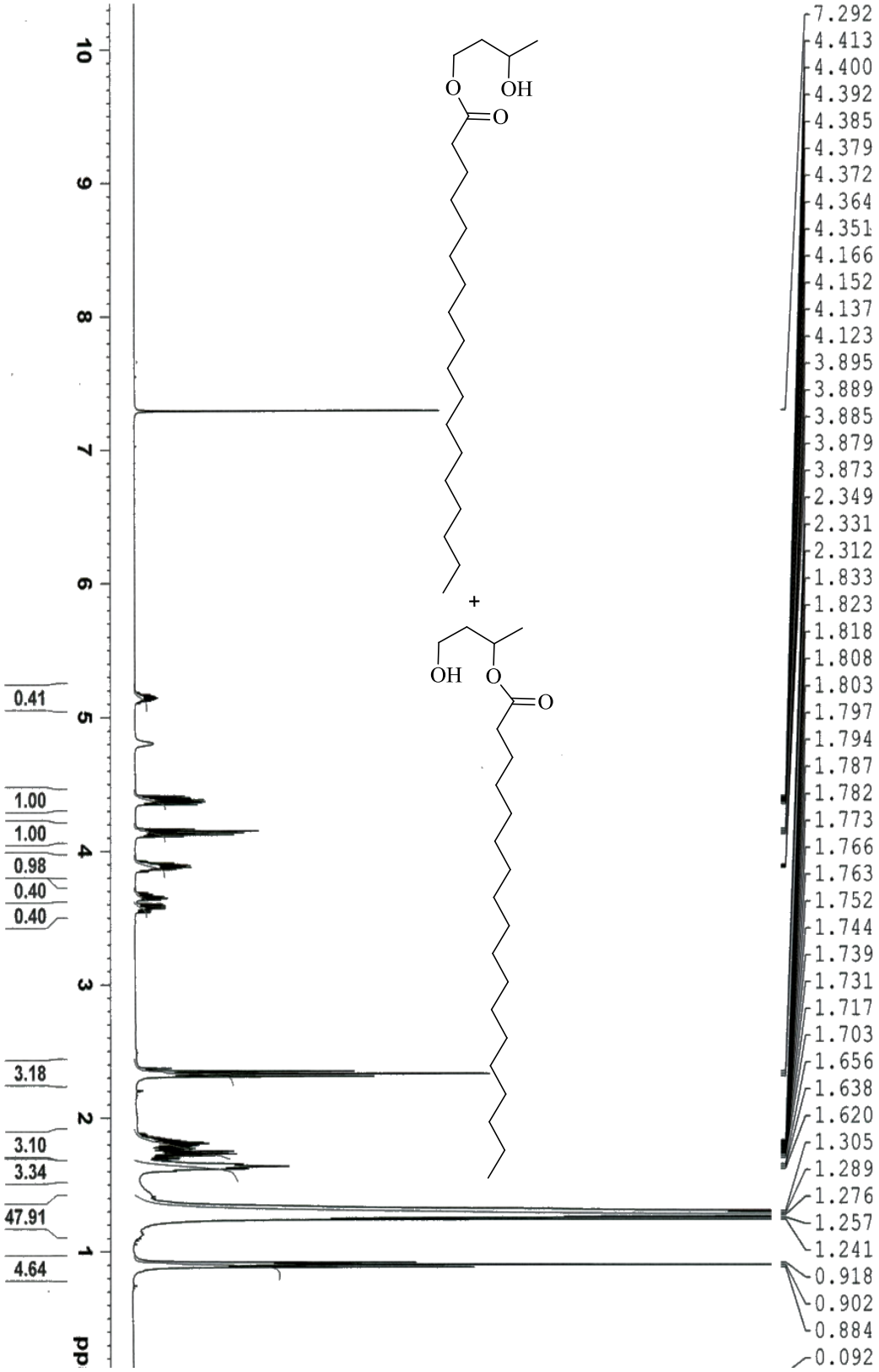


Fig. S69. ^{1}H NMR (D_2O) 3-Hydroxybutyl stearate compound with 4-hydroxybutan-2-yl stearate (2.5:1)

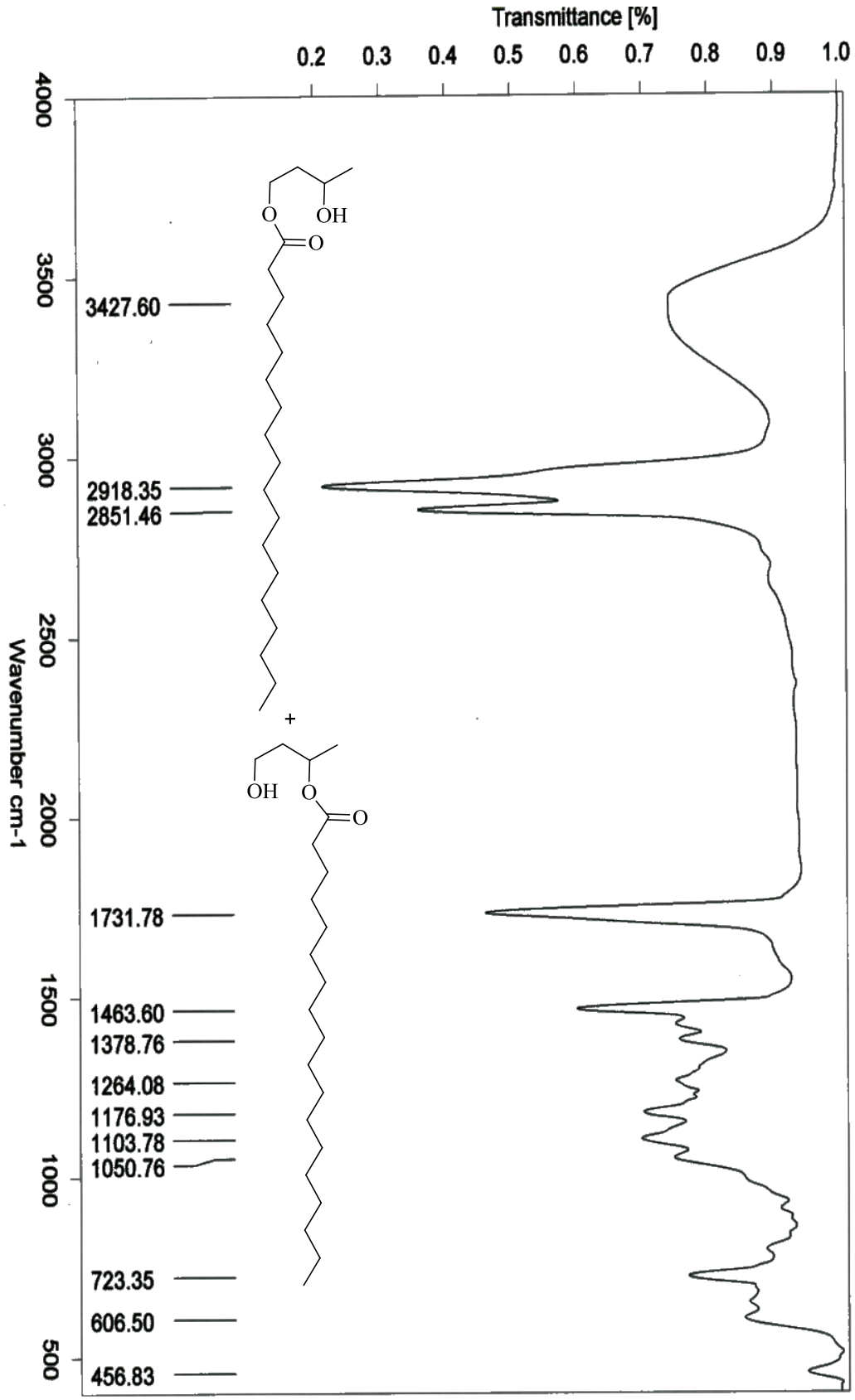


Fig. S70. IR (neat) 3-Hydroxybutyl stearate compound with 4-hydroxybutan-2-yl stearate (2.5:1)

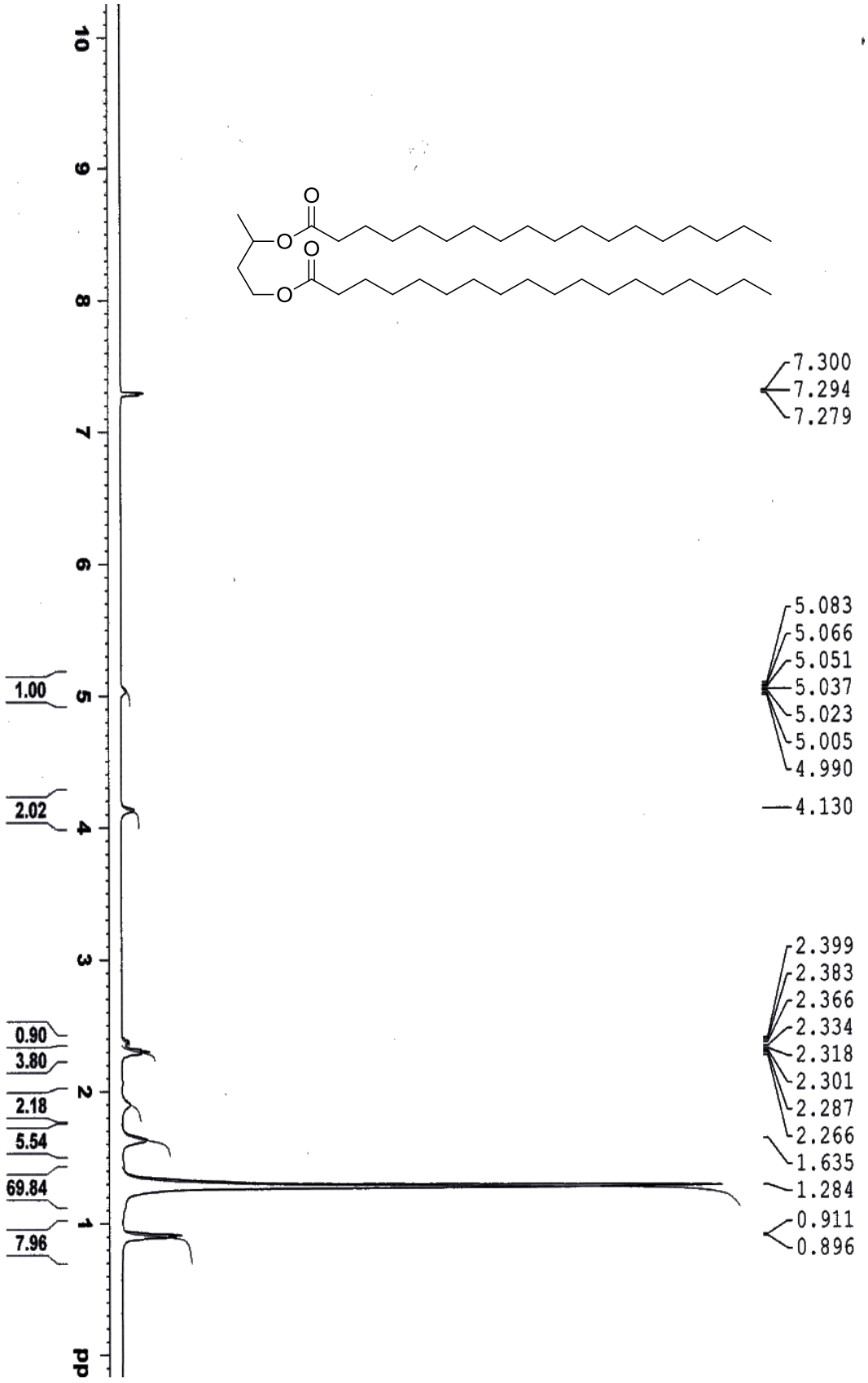


Fig. S71. ^{1}H NMR Butane-1,3-diyl distearate

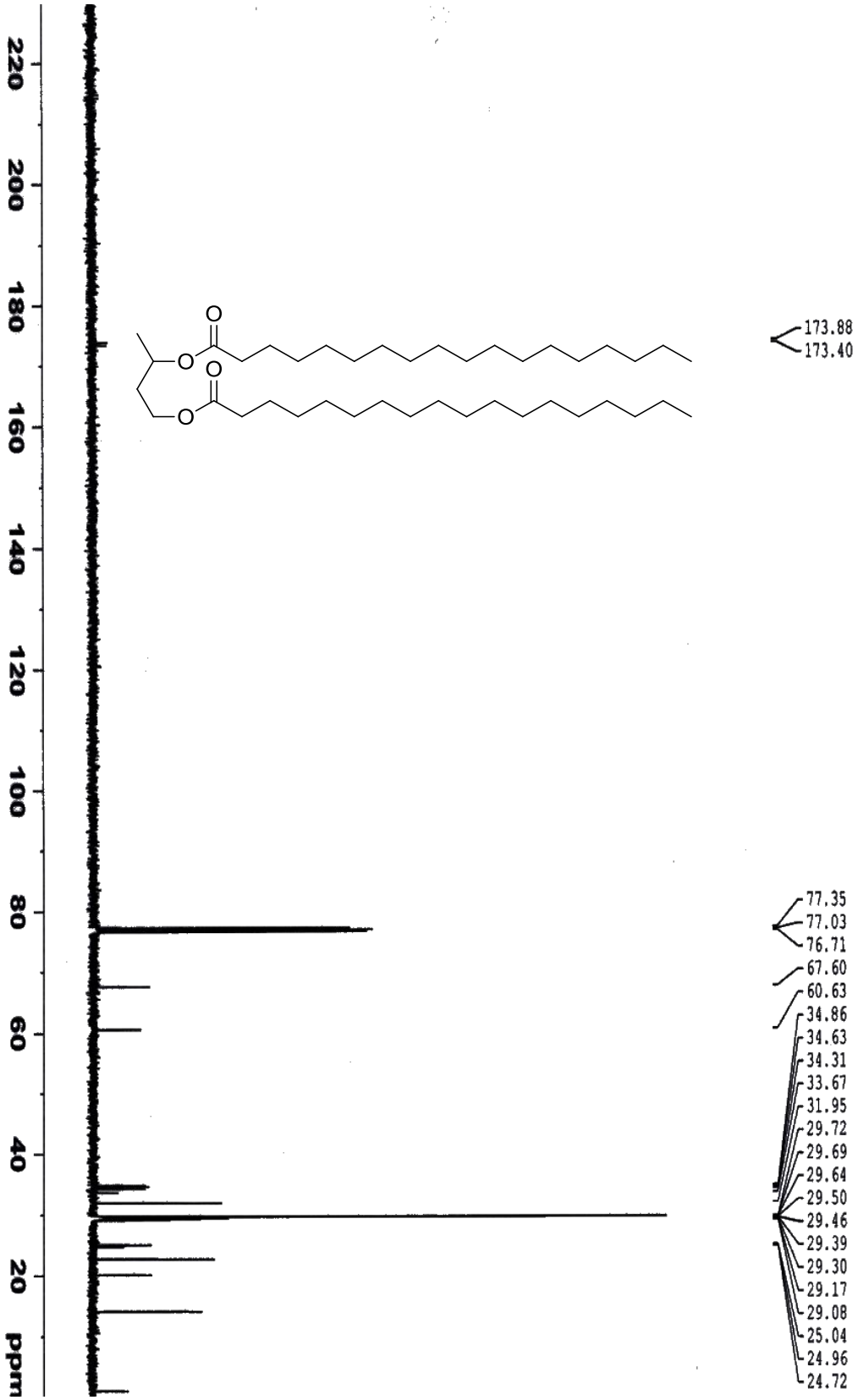


Fig. S72. ^{13}C NMR Butane-1,3-diyl distearate

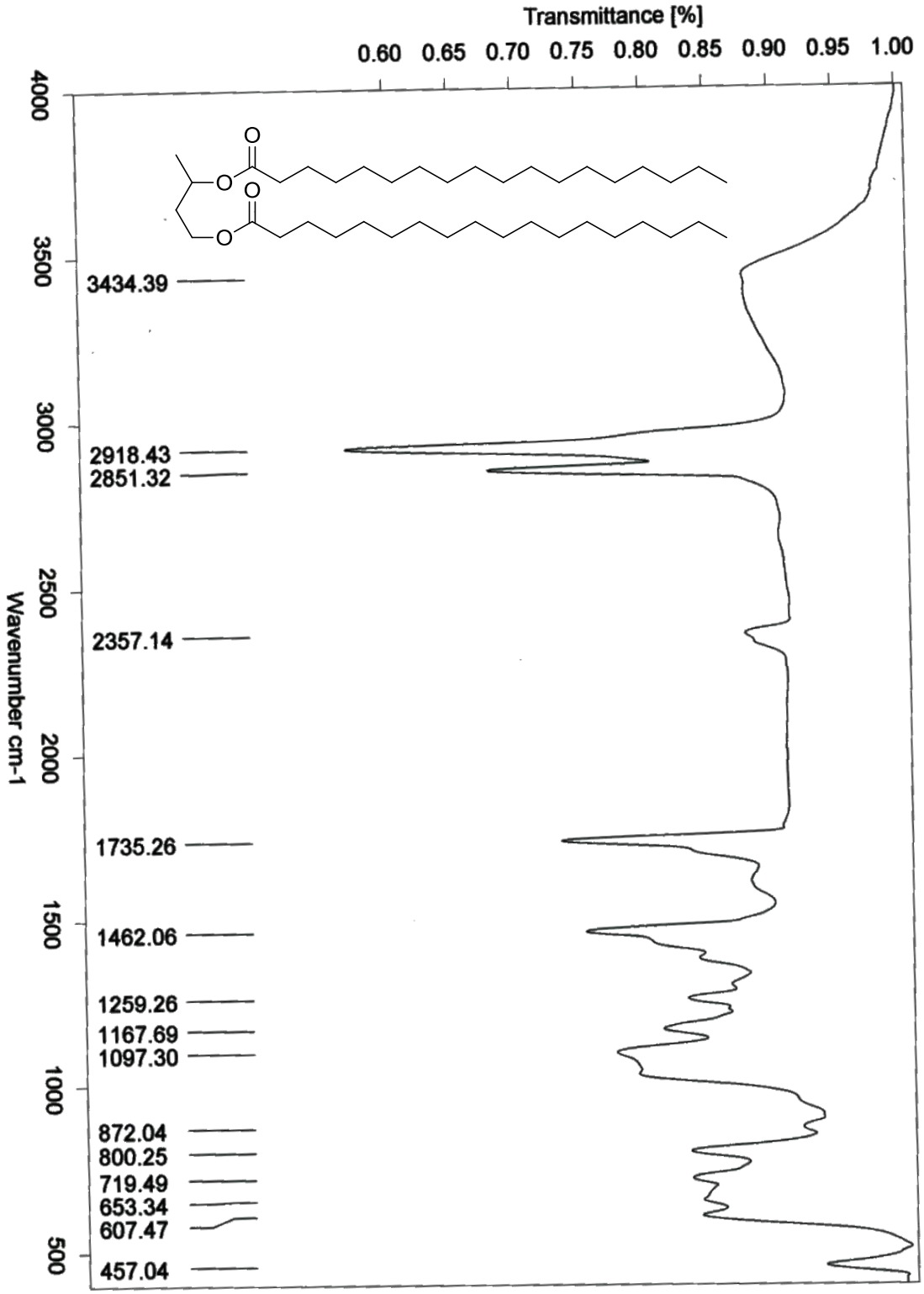


Fig. S73. IR (neat) butane-1,3-diyl distearate

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[2] D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater*., 2000, **12**, 2448.
[3] B. Karimi and D. Zareyee, *Org. Lett.*, 2008, **10**, 3989.