Electronic Supplementary Material (ESI) for Chemical Communications.

A new hypercrosslinked supermicroporous polymer, scope for sulfonation and its catalytic potential for the efficient synthesis of biodiesel at room temperature

Subhajit Bhunia, Biplab Banerjee and Asim Bhaumik*

*Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur 700 032, India, *Corresponding author. E-mail: msab@iacs.res.in*

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Section S1

Materials and Methods:

α,α′-di bromo p-xylene and carbazole were purchased from Sigma Aldrich, India. Anhydrous $FeCl_3$ and all other remaining organic solvents were taken from E-Merck, India and used without further purification.

X-Ray diffraction patterns of the powder samples were obtained by Bruker AXS D-8 Advanced SWAX diffractometer using Cu-Kα (0.15406 nm) radiation. N_2 adsorption/desorption isotherms of the samples were recorded using Autosorb 1C (Quantachrome,USA) at 77 K. Prior to the measurement, the samples were degassed at 403 K for 12 h under high vacuum conditions. Transmission electron microscopy (TEM) images of the microporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operated at 200 kV. The samples were prepared by dropping a sonicated solution over the carbon-coated copper grids. Scanning electron microscopic measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope (FESEM). FT–IR spectra of these samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. Solid-state MAS NMR studies have been performed by using Bruker Avance III HD 400 MHz NMR spectrometer. Thermogravimetric analysis (TGA) and DTA of the samples were carried out between the temperature range from 308 to 873 K in a TGA instrument thermal analyzer TA-SDT Q-600 under N_2 flow. Iron content was estimated by using a Shimadzu AA-6300 atomic absorption spectrometer (AAS) fitted with a double beam monochromator.

Temperature programmed desorption of ammonia (TPD-NH_3) was carried out in a Micromeritics Chemisorb 2720 instrument. GC-MS analysis was carried out by Perkin elmer SQ-8 GC-MS. ^{1}H and ^{13}C NMR experiments were carried out on Bruker DPX-300/500 NMR Spectrometer.

Section S2

Synthesis of hypercrosslinked microporous polymer (HMP-1):

Hypercrosslinked microporous polymer was synthesized by using the Friedel-Crafts alkylation reaction between α,α′-di bromo p-xylene and carbazole. In a typical synthesis 26.4 g (100 mmol) α,α′-di bromo p-xylene and 8.3 g (50 mmol) carbazole were mixed in anhydrous dichloroethane. Then 17 g anhydrous $FeCl_3$ was added to that solution and the mixture turned into blue. It was then stirred at room temperature for 6 h under N_2 atmosphere. Then the temperature was raised to 80^0C and refluxed for 18h. The precipitate was then filtered and washed by plenty of methanol using Soxhlet apparatus. The material was washed by acetone,THF, hexane successively and then dried in vacuum overnight. The yield of the reaction is 89% (16.6 g). Elemental analysis found by combustion: C, 79.34%; H, 5.40%; N, 4.03%. Calcd. Theoretical formula from an infinite HMP-1 framework $[C_{68}H_{53}N_3]_n$: C, 89.54%; H, 5.86%; N, 4.61%.

Detection of residual iron by atomic absorption spectroscopy (AAS):

Atomic absorption spectroscopic experiment was carried out by dissolution of solid HMP-1 with minimum amount of conc. Nitric acid followed by evaporation to dryness. Then the dry mass was dissolved in 250 ml distilled water and the reulting solution was used for AAS experiment using reference primary standard iron solution. It gave extremely trace amount of iron present (0.0035 mmol/g).

Sulfonation of HMP-1:

0.2 g sample was charged to 50 ml anhydrous dichloromethane and the mixture was stirred for 30 min. at 0^0C. 5 ml chlorosulfonic acid was added dropwise to this mixture slowly and then the

mixture stirred continuously for 3 days under N_2 atm. Then the blackish powder was filtered and washed by plenty of distilled water repeatedly. Then it was dried in vacuum at 80^0C.

Catalysis Protocol:

In a typical catalytic process, 0.5 mmol of fatty acid was dissolved in 2 ml methanol (which could act both as a solvent and reactant) and then 10 mg HMP-1-SO_3H was added to the reaction mixture immediately under stirring. The reaction was carried out in a capped 10 ml glass vial at room temperature. The progress of the reaction was monitored by analysis of the reaction mixture by TLC (thin layer chromatography) at different time interval. After completion of the reaction the mixture was filtered (Whatman 42) to separate the catalyst and washed with methanol. Then the filtrate was evaporated to get the final product. TLC suggested that there was no unreacted acid in the final product which indicates fatty acid conversion was full. Then the final product was characterized by ^{1}H and ^{13}C NMR spectra. The yield was calculated by the purified products.

We had performed the esterification reactions using only HMP-1 maintaining the same procedure to compare the activity of HMP-1 and HMP-1-SO_3H .No esterification was observed for only HMP-1.

Catalytic recycling efficiency

The catalyst was used for 4 consecutive cycles for esterification of lauric acid at room temperature. The catalyst was filtered , washed with ethanol-water mixture and dried at oven overnight.

Calculation of Acid strength of HMP-1-SO_3H

100 mg sulfonated material (HMP-1-SO_3H) was stirred in 50 ml water for 8 h at 313 K. After cooling to room temperature, 10 ml sodium hydroxide solution of strength 0.03125 (N) was added to 10 ml aqueous mixture of HMP-1-SO_3H and stirred overnight. Then after filtration, the excess NaOH solution was back titrated with 0.112 (N) oxalic acid solutions. 2.1 ml oxalic acid was required to reach the first equivalence point of oxalic acid.

$V_{NaOH} X S_{NaOH} \equiv V_{OX} X S_{OX}$

$V_{NaOH} X 0.03125 \equiv 2.1 X 0.112$

$V_{NaOH} = 7.5264$ ml

So the NaOH required to neutralized the acidic site of the HMP-1-SO_3H = (10-7.5264) ml = 2.4736 ml.

$V_{NaOH} X S_{NaOH} \equiv V_{HMP\text{-}1\text{-}SO3H} X S_{HMP\text{-}1\text{-}SO3H}$

$2.4736 X 0.03125 \equiv 10 X S_{HMP\text{-}1\text{-}SO3H}$

$S_{HMP\text{-}1\text{-}SO3H} = 0.00773$ (N)

The equivalent weight of sulfonic acid group (-SO_3H) is 81.

So, 50 ml 0.00773 (N) HMP-1-SO_3H mixture solution contains 0.0313065 g free sulfonic acid side.

Calculation: 1000 ml 1 (N) HMP-1-$SO_3H \equiv$ 81 g free sulfonic acid in the solid matrix (HMP-1-SO_3H)

50 ml 0.00661 (N) HMP-1-$SO_3H \equiv$ 0.0313065 g free sulfonic acid.

=0.3865 mmol free sulfonic acid.

100 mg sample (HMP-1-SO_3H) contains 0.3865 mmol free sulfonic acid. 1000 mg sample (HMP-1-SO_3H) contains 3.865 mmol free sulfonic acid.

Calculation of the Turn over number of catalyst

To determine the turn over number of the catalyst we had tested the fatty acid esterification reaction taking 1 mmol of fatty acid with varying amount of catalyst to determine the minimum amount of catalyst required to perform the reaction . We have done thee esterification reaction taking 1 mmol of sebacic acid with methanol using 6 mg catalyst during 20 hrs at room temperature.The conversion is 96%

So the turn over number is =

$(mmol\ of\ substrate\ conversion)/(mmol\ of\ acid\ site\ present\ in\ catalyst)$ 1 g catalyst holds 3.865 mmol of acid site.

So 6 mg catalyst contains 0.02319 mmol acid site.

So the turn over number is $=\frac{0.96}{0.02319}$ = 41.4. (as the conversion is 96% , mmol of substrate conversion is 0.96).

Figure S1

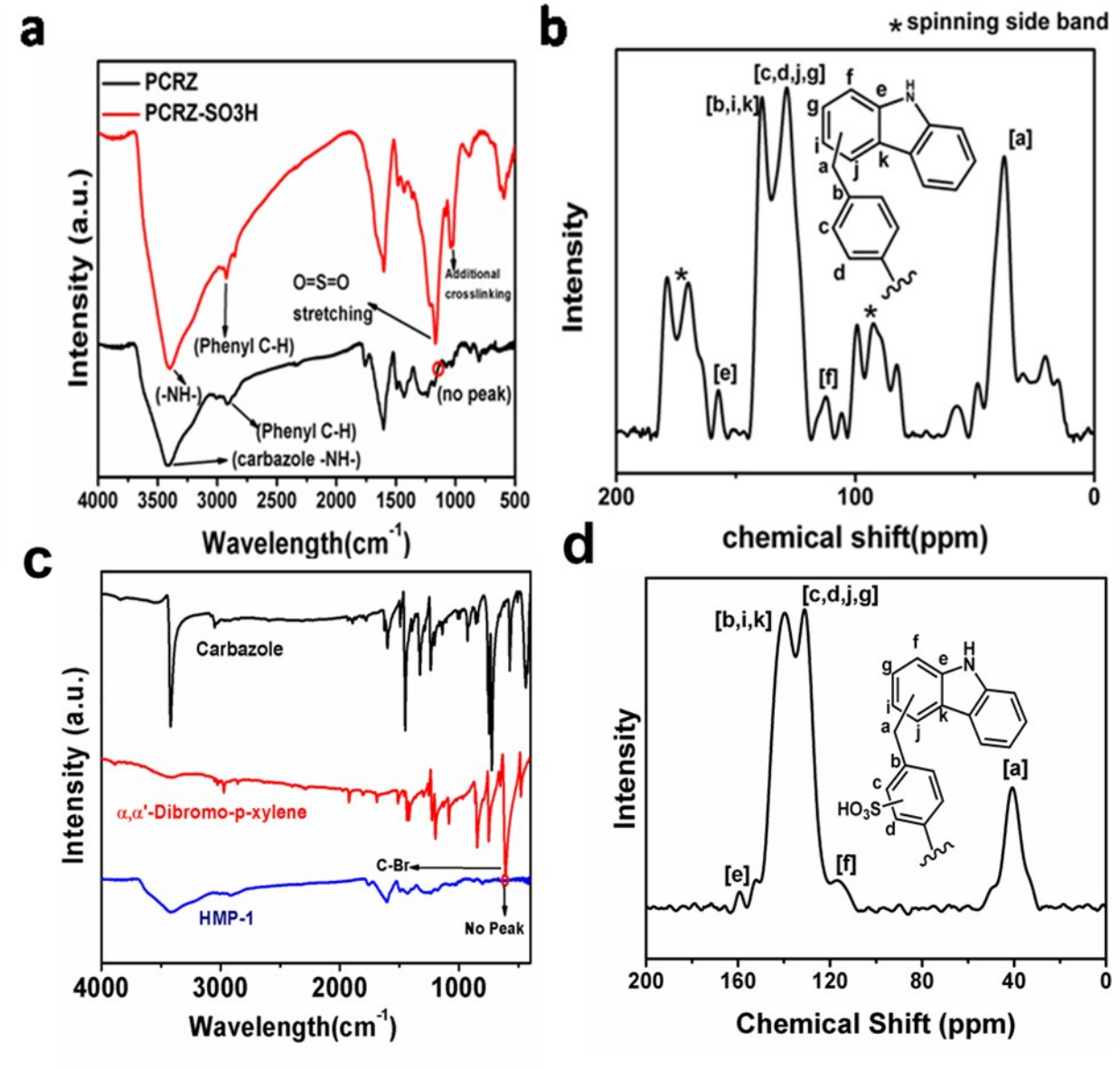


Figure S1 a) FTIR spectra of HMP-1 and HMP-1-SO_3H, b) ^{13}C solid state MAS NMR of HMP-1, c)comparative FTIR spectra of HMP-1, α,α′-Di bromo-p-xylene and carbazole, d) ^{13}C solid state MAS of HMP-1-SO_3H.

Figure S2

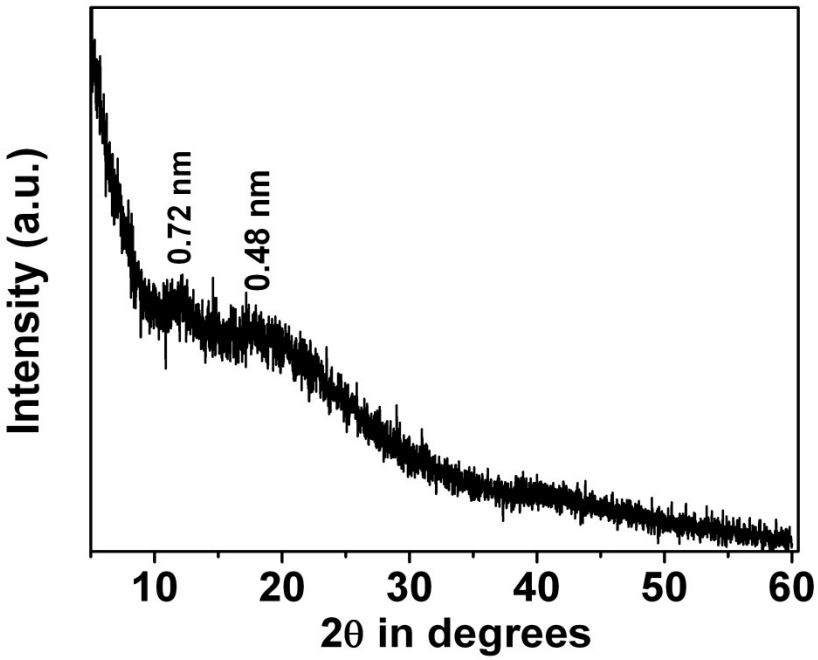


Figure S2 Wide angle PXRD of HMP-1

Figure S3

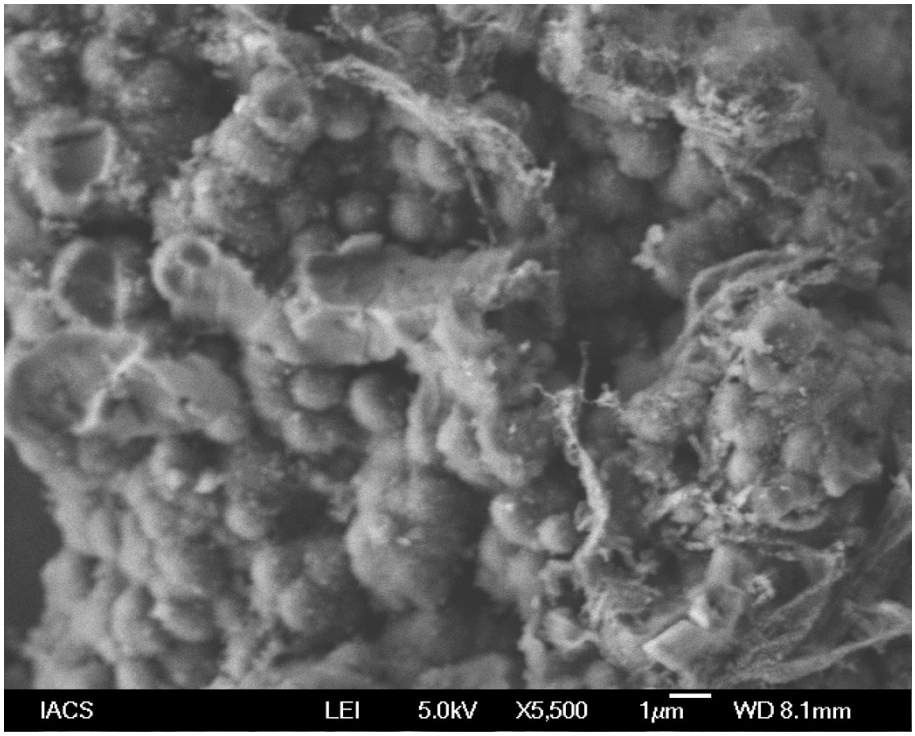


Figure S3 SEM image of HMP-1-SO_3H

Figure S4

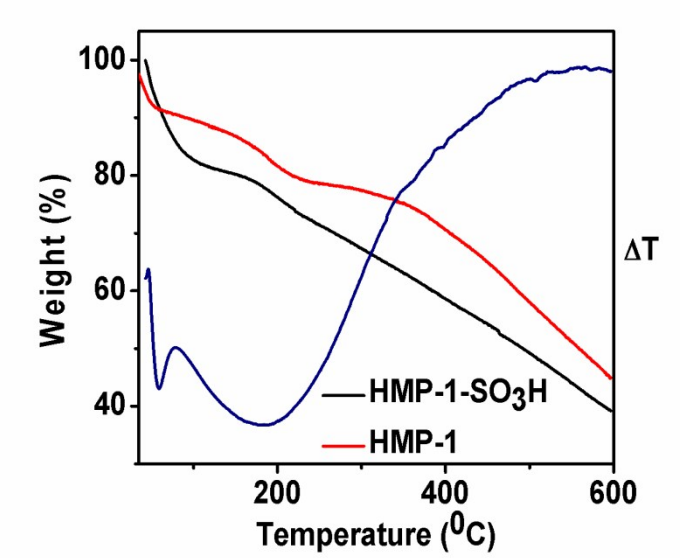


Figure S4 TGA-DTA data upto 600 ^{0}C of HMP-1 (red) and HMP-1-SO_3H (black).

Figure S5

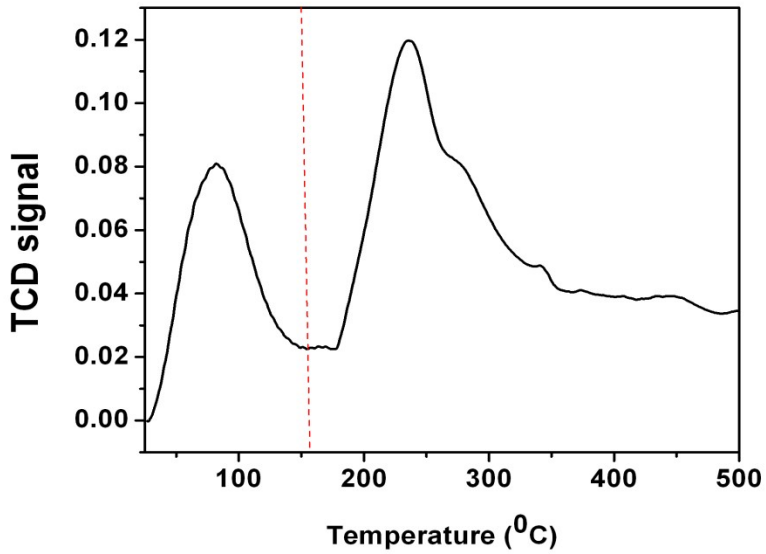


Figure S5 NH_3-TPD profile of HMP-1-SO_3H up to 500 ^{0}C temperature.

In a typical NH_3-TPD measurement 140 mg of HMP-1-SO_3H sample was degassed by the constant flow of He at 393 K for 3h followed by the cooling to room temperature. Then a constant flow of 10 wt% NH_3 in He was passed through the activated sample for 1 h to saturate the sample with NH_3 gas. Then He flow was passed through the sample to desorb the physically adsorbed NH_3.

Figure S6

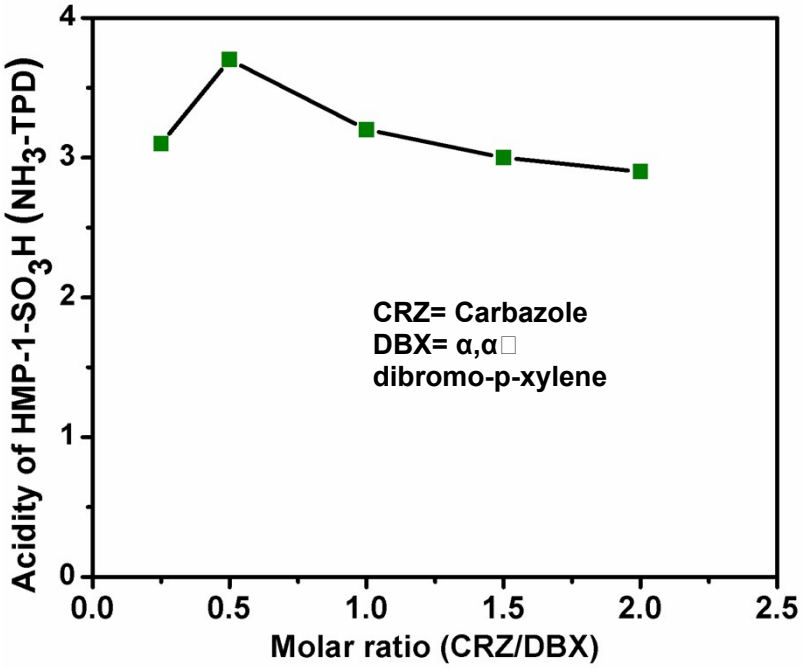


Figure S6 A comparative study of Solid state acidity of HMP-1-SO_3H prepared from different molar ratio of monomers.

Figure S7

Methyl ester of	**NMR DATA**
CH_3-$(CH_2)_{10}$-COOH (Lauric Acid)	^{1}H NMR (400 MHz, $CDCl_3$) δ =3.628 (3H, s); 2.303-2.265 (2H, t); 1.619-1.583 (2H, m); 1.267-1.242 (16H, m); 0.879-0.845 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.49; 51.53; 34.24; 32.03; 29.71; 29.57; 29.45; 29.38; 29.28; 25.09; 27.80; 14.20.
$CH_3(CH_2)_{12}COOH$ (Myristic Acid)	^{1}H NMR (400 MHz, $CDCl_3$) δ =3.639 (3H, s); 2.291-2.261 (2H, t); 1.609-1.566 (2H, m); 1.265-1.185 (20H, m); 0.871-0.843 (3H, t); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.37; 51.46; 34.22; 32.04; 29.77; 29.72; 29.57; 29.47; 29.38; 29.28; 29.09; 22.80; 14.18.
$CH_3(CH_2)_{14}COOH$ (Palmitic Acid)	^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.651 (3H, s); 2.302-2.272 (2H, t); 1.619-1.591 (2H, m); 1.274-1.244 (24H, m); 0.881-0.854 (3H, t); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.44; 51.51; 34.25; 32.07; 29.82; 29.74; 29.59; 29.50; 29.40; 29.30; 25.11; 22.82; 14.22.
$CH_3(CH_2)_{16}COOH$ (Stearic Acid)	^{1}H NMR (500 MHz $CDCl_3$) δ = 3.634 (3H, s); 2.286-2.256 (2H, t); 1.607-1.579 (2H, m); 1.263-1.232 (28H, m); 0.868-0.841 (3H, t); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 174.32; 51.42; 34.19; 32.04; 29.80; 29.71; 29.56; 29.47; 29.37; 29.27; 25.07; 22.79; 14.16.
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (Oleic Acid)	^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.277-5.219 (2H, m); 3.554 (3H, s); 2.214-2.184(2H, t); 1.982-1.904 (4H, m); 1.543-1.515 (2H, m); 1.220-1.177 (20H, m); 0.816-0.779 (3H, m); ^{13}C NMR (75 MHz) δ= 174.30; 130.25; 130.06; 51.43; 34.17; 32.00; 29.87; 29.78; 29.69; 29.62; 29.55; 29.41; 29.35; 29.25; 29.23; 29.18; 27.31; 27.25; 25.72; 25.04; 22.77; 14.16.
$(COOH)(CH_2)_8(COOH)$	^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.600 (6H, s); 2.254-2.217

(Sebacic Acid)	(4H, t); 1.568-1.533 (4H, m); 1.240 (8H, s), ^{13}C NMR (125 MHz, $CDCl_3$) δ= 174.24; 51.41; 34.07; 32.04; 29.06; 24.92.
$(COOH)(CH_2)_4(COOH)$ (Adipic Acid)	^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.599 (6H, s); 2.266 (4H, m); 1.594 (4H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ=173.75; 51.50; 33.66; 24.38.

Figure S8

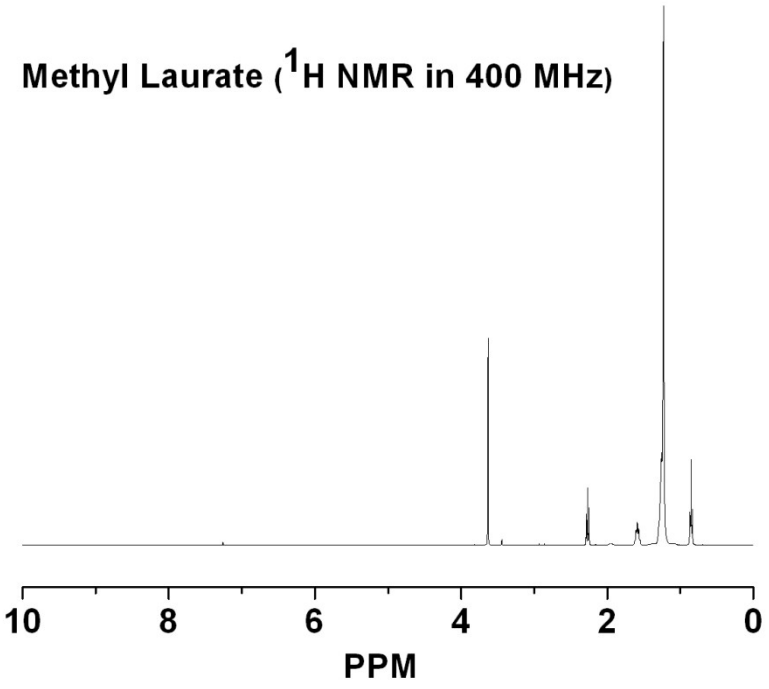
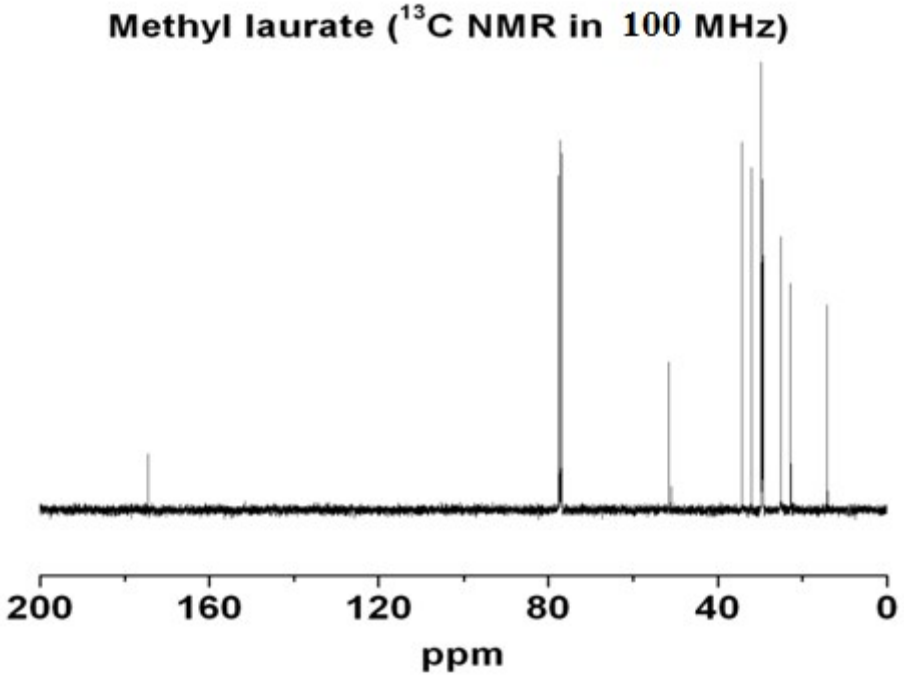


Figure S9



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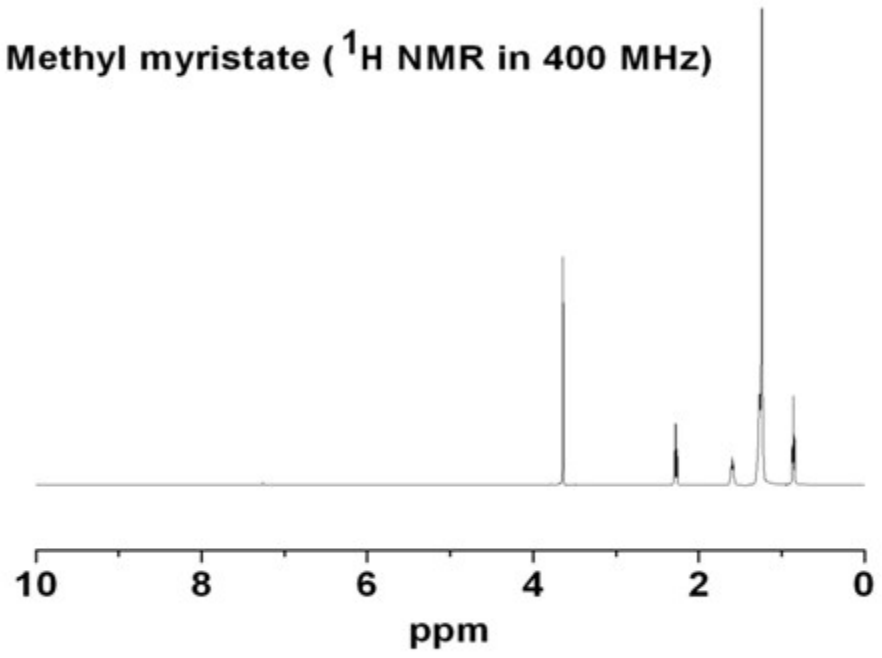

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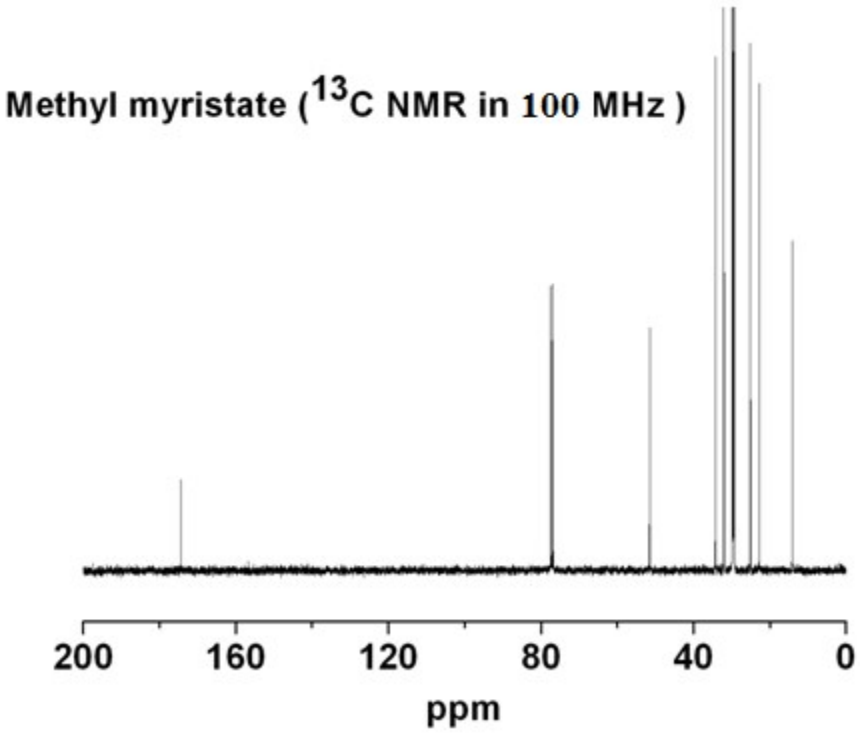

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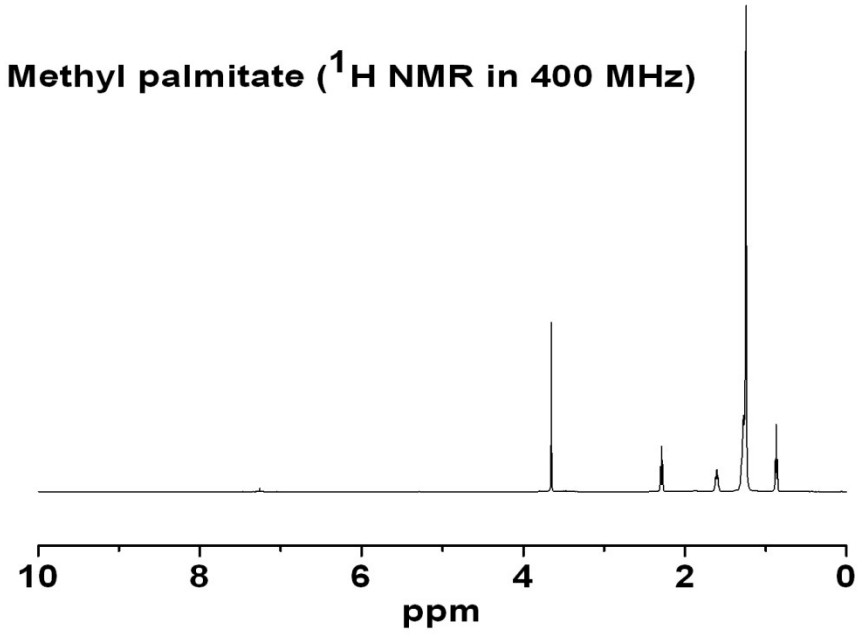

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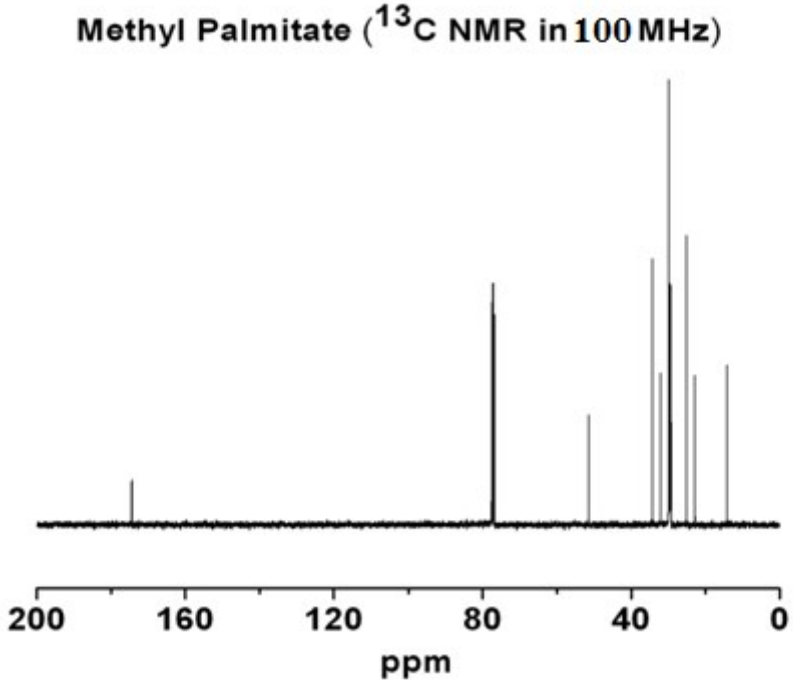

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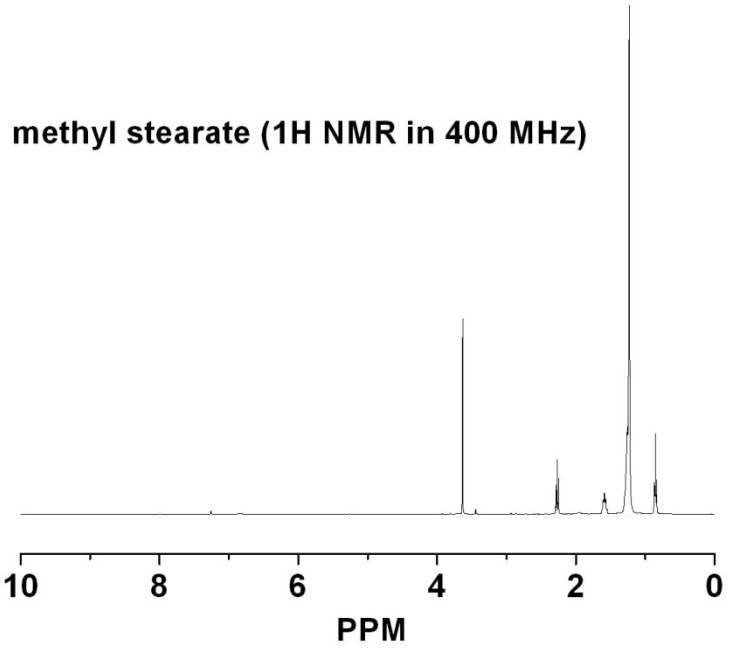
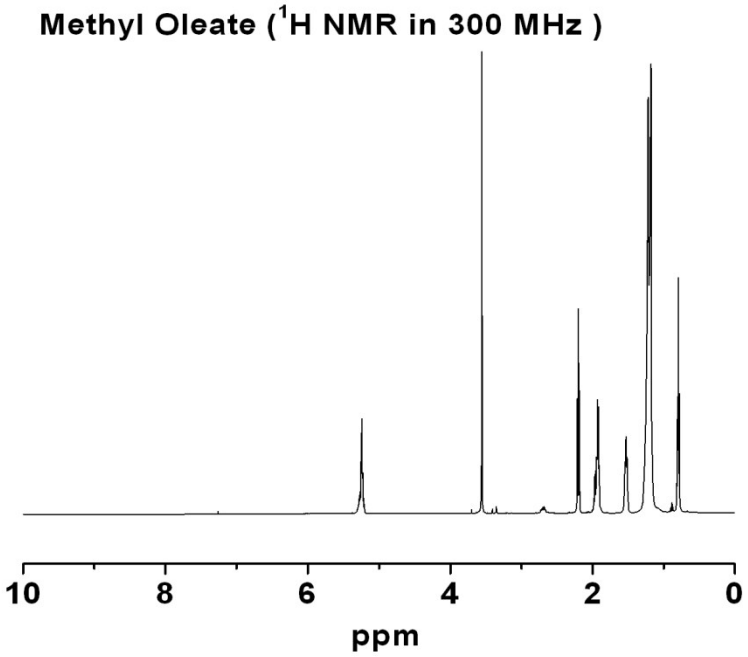


Figure S15

Figure S16



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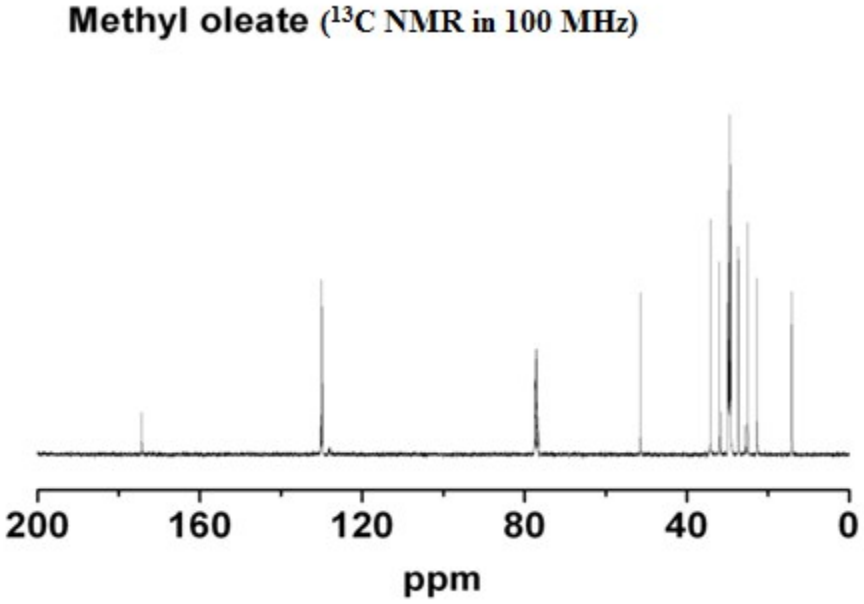

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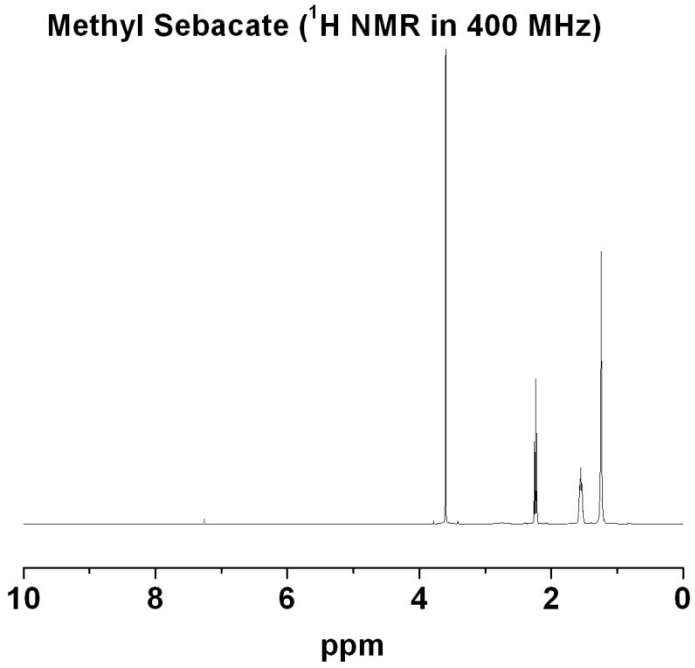

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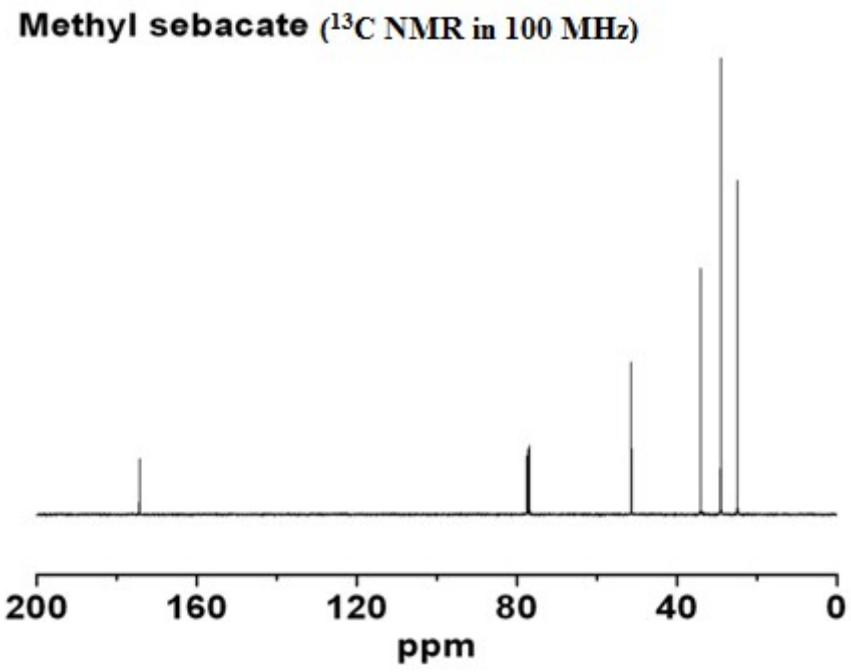

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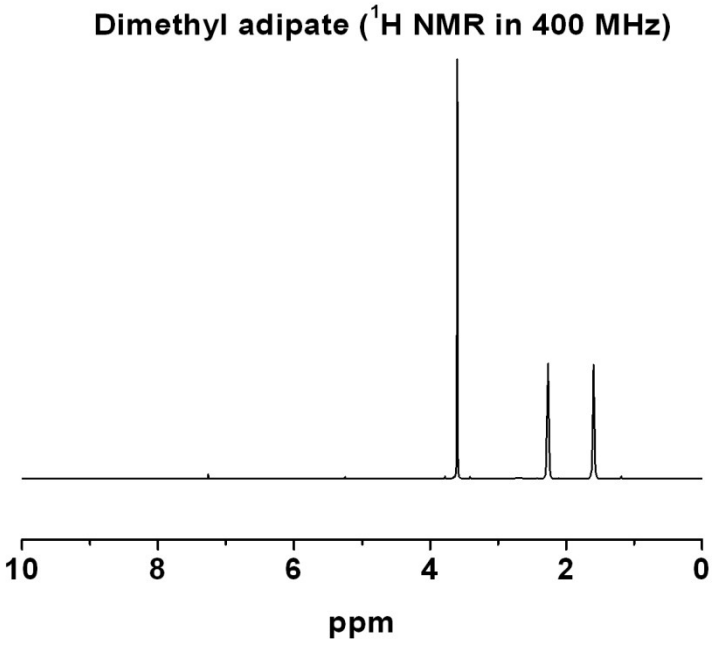

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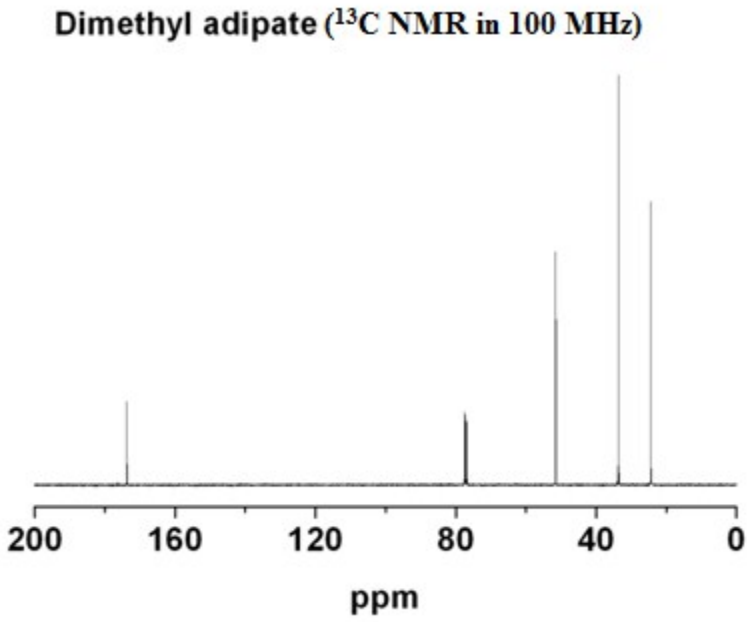
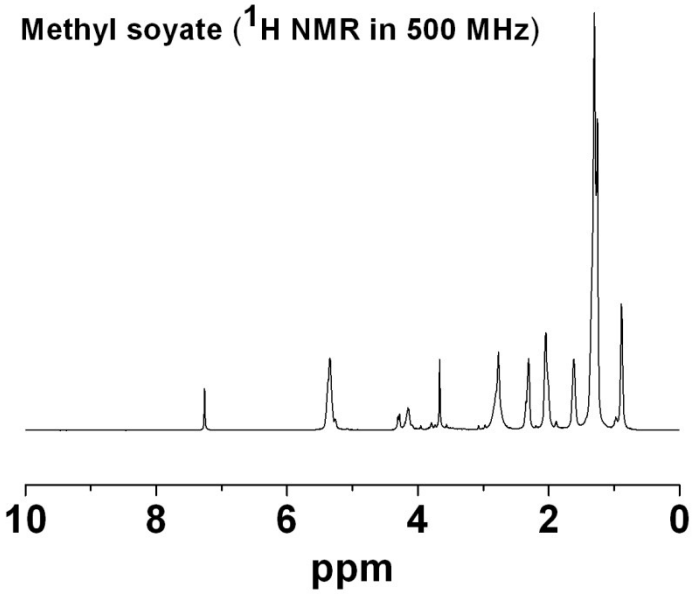


Figure S22



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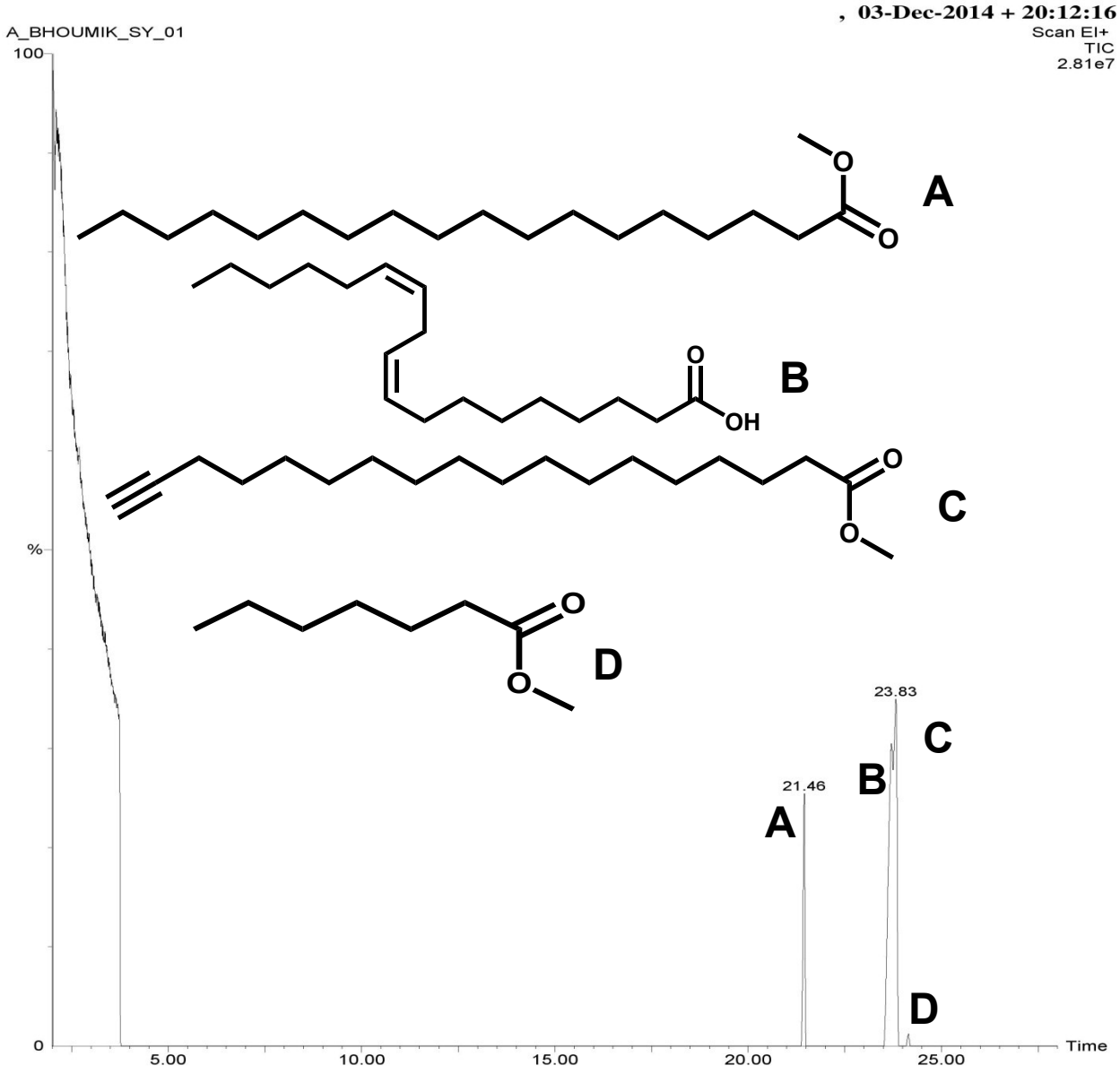
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