

Solvent-Free Chemical Upcycling of Poly (Bisphenol A carbonate) and Poly (Lactic Acid) Plastic waste Using SBA-15 Functionalized Basic Ionic Liquid

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This Supporting information has twenty-six pages (S1-S26),

One Supporting Scheme (Scheme S1)

Twenty Supporting Figures (Figures S1-S20)

Two Supporting Tables (Table S1& S2)

Contents

S1. Experimental section

S2. Catalysts characterization

S3. Procedure for the catalytic reaction

S4. Purification of Waste PC

S5. Sample preparation for ³¹P NMR

S6. Procedure for purification of PC

S7. Catalyst characterization and activity data

S8. Mechanistic investigation

S9. Catalyst recyclability

S10. References

Supporting Information Contents

Item	Title	Page no.
Fig. S1	Low angle PXRD pattern of SBA-15 and SBA-15-Pr-MIM-OH.	S9
Fig. S2	Wide angle PXRD pattern of SBA-15 and ionic liquid functionalized SAB-15.	S9
Fig. S3	N ₂ -adsorption-desorption isotherms and pore size distribution curves of catalysts.	S10
Fig. S4	Comparative FT-IR spectra of various functionalized SBA-15 catalysts.	S10
Fig. S5	SEM, TEM images of SBA-15 and ionic liquid functionalized SAB-15.	S11
Fig. S6	Thermograms of various functionalized SBA-15 catalysts investigated in this study.	S12
Fig. S7	The catalytic conversion and selectivity of PC and PLA.	S13
Fig. S8	Comparative ¹ H NMR spectra of bisphenol A (BPA); (a) Commercial BPA & (b) BPA produced form waste PC.	S14
Fig. S9	Comparative ¹ H NMR spectra of methyl lactate (ML); (a) Commercial ML & (b) ML produced form waste PLA.	S15
Fig. S10	Comparative DSC profile of bisphenol A (BPA).	S14
Fig. S11	GCMS spectrum of bisphenol A .	S16
Fig. S12	GCMS spectrum of methyl lactate .	S17
Fig. S13	FT-IR spectra of methanol to show the interaction between CH ₃ OH and SBA-15-Pr-MIM-OH with various concentration.	S18
Fig. S14	¹ H NMR spectra of methanol with and without catalyst to show the interaction between CH ₃ OH and SBA-15-Pr-MIM-OH.	S18
Fig. S15	³¹ P NMR spectrum of the methyl lactate.	
Fig. S16	Catalyst recyclability test for PC and PLA waste.	S19
Fig. S17	Hot filtration test for PC and PLA waste.	S19
Fig. S18	Comparative FT-IR spectra of fresh and recycled SBA-15-Pr-MIM-OH catalyst.	S20
Fig. S19	Comparative TGA profile of fresh and recycled SBA-15-Pr-MIM-OH catalyst.	S20
Fig. S20	SEM, and EDAX images of recycled SBA-15-Pr-MIM-OH catalyst.	S21
Table S1	Comparison of reported heterogeneous catalysts for the methanolysis of PC.	S22

Table S2	Comparison of reported heterogeneous catalysts for the methanolysis of PLA.	S23
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S 1. Experimental Section

S1.1. Materials and methods

S1.1.1. Chemicals used in catalyst preparation and depolymerization reactions

Tetraethyl orthosilicate (TEOS, 99 %) (Sigma Aldrich, 99 %), Pluronic P123 triblock copolymer (Sigma, 98 %), hydrochloric acid (HCl) (Mark, 35 % extra pure), N-methylimidazole (SDFL, 98 %), (3-Chloropropyl) triethoxysilane (Sigma, 99%), toluene (Merk, 99%), diethyl ether (SDFL, 98%), 1, 4 diazabicyclo[2.2.2]octane (DABCO) (Sigma, 99 %), DMF (Merk, 99 %), N,N-dimethylamino pyridine (Sigma, 99%), acetone (Merk, 99.8 %), TMAOH (25% in methanol-Sigma), potassium bicarbonate (Merk 99.9 %), Methanol (Merk, 99%), DMSO-d₆ (euroisotop, 99.8 % D), CDCl₃ (euroisotop, 99.8 % D), bisphenol A (Sigma, 97 %), methyl lactate (SDFL 98 %), poly(bisphenol A carbonate) (Sigma, Pcode 1003475592), poly(lactic acid) (Compostable Biobased Garde LX 175, Banka Bio Lim, India, Mw ~163,000, Composition (L-Lactide 95.7%, D-Lactide = 4.1%, Meso form = 0.2%)), hydrogen (H₂, 99.9 %), nitrogen (N₂, 99.9 %), air (99.9 %), helium (99 %), from Sigma Gases and Service New Delhi, India.

S1.1.2. Glassware and equipment used in catalyst preparation and depolymerization reactions

Round bottom flask (50 mL, and 100 mL), water condenser, magnetic stirrer with the heat control system, vacuum filtration set-up, measuring cylinder (5, 25, and 100 mL), burette (50 mL), volumetric flask, conical flask (50 mL), stainless steel high-pressure hydrothermal autoclave equipped with Teflon liner, stainless steel high-pressure parr reactor equipped with stirrer and temperature controller, rota-evaporator (Heidolph).

S 1.2 Catalysts synthesis

S 1.2.1 Synthesis of SBA-15

SBA-15 was synthesized using a method by the previously reported method.^{S1} Typically, 2 g of pluronic P123 triblock copolymer was dissolved in 75 mL of a 1.9 M HCl aqueous solution under stirring at room temperature in a PPE bottle. 30 mL of deionized water and 4.25 g of

tetraethyl orthosilicate were added consecutively. Then, the solution was placed in a water bath for 20 h, stirring at 50 °C. When the colour of the solution changed from transparent to milky white, the solution was heated at 100 °C for 24 h. The resulting materials were washed with water and ethanol, followed by drying at 80 °C for 8 h. The template was removed by heating at 550 °C for 6 h.

S 1.2.2. Preparation of silylated Ionic-Liquid

Synthesis of MIM based ILs

The schematic presentation of the synthetic route followed in the preparation of functionalized ionic liquids (ILs) is presented in **Scheme 1**.^{S2} For the synthesis of MIM-based IL, N-methylimidazole (10 mmol) and 30 mL of dry toluene were taken in a 100 mL two-necked RB flask. (3-Chloropropyl) triethoxysilane (10 mmol) was slowly added in 10 min. The following mixture was refluxed for 1 day in an N₂ environment under stirring conditions. After the reaction, the toluene was evaporated. The resulting material was treated with diethyl ether several times to remove unreacted reactants. Finally, the material was dried in a vacuum at 353 K to get silylated chloropropyl-methyl imidazolium chloride (Pr-MIM-Cl).

¹H NMR data for (silylated chloropropyl methyl imidazolium chloride): ¹H NMR (400 MHz, CDCl₃) δ 10.6 (s, 1H), 7.3 (s, 1H), 7.22 (s, 1H), 4.29 (t, 2H), 4.12 (s, 3H), 3.81–3.78 (q, 6H), 2.0–1.94 (m, 2H), 1.20–1.15 (t, 9H), 0.61–0.54(t, 2H).

Synthesis of DABCO based ILs

For the preparation of 1,4-diazabicyclo[2.2.2]octane (DABCO)-based ILs, first 1-(triethoxysilyl)propyl DABCO chloride was prepared. 10 mmol s of DABCO and 11 mmol of (3-chloropropyl)triethoxysilane were mixed with 25 mL of DMF and stirred at 100 °C for 2 days. The solvent was evaporated under reduced pressure; a viscous jelly-like product was obtained.

¹H NMR data for (1-(triethoxysilyl)propyl DABCO chloride): ¹H NMR (400 MHz, D₂O) δ 3.83–3.79 (m, 3H), 3.61–3.52 (m, 3H), 3.38–3.33 (m, 6H), 3.20–3.12(t, 2H), 3.15–3.07(q, 6H), 1.9–1.79 (m, 2H), 1.2–1.14 (t, 9H), 0.60–0.53 (t, 2H).

Synthesis of DMAP based ILs

For the preparation of DMAP-based ILs, first 1-(triethoxysilyl)propyl-4-dimethylpyridinium chloride was prepared. 10 mmol of N,N-Dimethylamino pyridine and 20 mL of acetone were

taken in a 100 mL double necked flask. Then, the 11 mmol of 3-Chloropropyl triethoxysilane was added slowly over 10 min. The flask was heated at reflux for 1 day in an N₂ environment under constant stirring. Acetone was evaporated, and the white residue was treated with acetone three to five times. The resultant material was dried in a vacuum at 60 °C to get 1-(triethoxysilyl)propyl-4-dimethylpyridinium chloride.

¹H NMR data for (1-(triethoxysilyl)propyl-4-dimethylpyridinium chloride): ¹H NMR (400 MHz, D₂O) δ 8.0–7.90 (m, 2H), 6.83–6.76 (m, 2H), 4.780–4.75 (t, 2H), 3.10–3.15 (q, 6H), 3.0 (s, 6H), 1.82–1.78 (m, 2H), 1.2–1.15 (t, 9H), 0.6–0.53 (t, 2H).

S 1.1.3. Preparation of SBA-15 functionalized ionic liquids

A 3.0 mmol of silylated ionic liquids was added into 30 mL dry toluene containing 1 g of SBA-15. The mixture was refluxed in the N₂ atmosphere for 1 day under constant stirring. After completion of the reaction, the flask was cooled to room temperature. The solid was filtered off and washed with dry toluene and methanol several times. Finally, it was dried in a vacuum at 80 °C for 8 h to get SBA-15 functionalized chloride-based ionic liquids such as SBA-15-Pr-MIM-Cl, SBA-15-Pr-DMAP-Cl, and SBA-15-Pr-DABCO-Cl.

A 1 g sample of SBA-15-Pr-MIM-Cl/ SBA-15-Pr-DMAP-Cl/ SBA-15-Pr-DABCO-Cl was treated with a 0.2 M methanol solution of TMAOH (25% in methanol, using a liquid/solid mass ratio of 50) at room temperature for 4 h. The solid was filtered off and washed several times with methanol. Finally, it was dried in a vacuum at 80 °C for 6 h. The resulted materials were named SBA-15-Pr-MIM-OH/ SBA-15-Pr-DMAP-OH/ SBA-15-Pr-DABCO-OH.

A 1 g sample of SBA-15-Pr-MIM-Cl/ SBA-15-Pr-DMAP-Cl/ SBA-15-Pr-DABCO-Cl was treated with 50 mL of 0.4 M aqueous solution of KHCO₃ at room temperature for 1 day. The solid was filtered off and washed several times with water. Finally, it was dried in a vacuum at 80 °C for 1 day. The resulted materials were named as SBA-15-Pr-MIM-HCO₃/ SBA-15-Pr-DMAP-HCO₃/ SBA-15-Pr-DABCO-HCO₃.

S 3. Catalyst characterizations

In this study, we conducted various characterization techniques to analyze and understand the properties of a catalyst material.

3.1. X-ray diffraction

The X-ray diffraction (XRD) patterns were examined by RIGAKU (Japan) Mini-flex diffractometer with Cu $k\alpha$ ($\lambda = 0.154$ nm) radiation source operating at 40 kV and 40 mA and patterns were recorded in the 2θ range of 5-80°.

3.2. N₂-adsorption-desorption

The specific surface area and porosity of the catalyst were determined by an N₂-adsorption-desorption isotherm measurement using the Belsorp-mini instrument. The catalysts were degassed at 180 °C for 3 h before the acquiring of adsorption isotherm. The specific surface area of catalysts was determined using the Brunauer – Emmett –Teller (BET). The average pore size and distribution in the material were determined by using a method known as the Barrett–Joyner–Halenda (BJH) method.

3.3. Electron microscopy

Moving on to the physical features of the catalyst, we used Scanning Electron Microscopy (SEM) with a JEOL JSM-6610-LV instrument and High-Resolution Transmission Electron Microscopy (HR-TEM) to examine its structural and morphological characteristics in detail.

3.4. FT-IR analysis

The FT-IR spectra were recorded on the ThermoScientific Nicolet iS50 FT-IR instrument to identify the different functional groups in catalysts. Additionally, we also used the same FT-IR instrument to understand the depolymerization pathway of plastic waste. To determine the interaction between the methanol and catalyst, the methanol-adsorbed FT-IR was carried out using the same instrument.

3.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a TGA/DSC 1 STARe SYSTEM from the Mettler Toledo instrument with temperature increments of 10 °/min in the air stream from ambient temperature 50 °C to 800 °C.

3.6. NMR spectroscopy

In which, after completion of the reaction, methanol was evaporated and mixture containing polymer, oligomer, and monomer were dissolve in suitable NMR solvent such as CDCl₃ and DMSO-d₆. ¹H NMR was carried out using a 400 Hz JEOL NMR spectrometer.

3.7. Acidity measurement

Lastly, we calculated the concentration of the basic site in the catalyst by performing acid–base titration. This measurement provided insights into the basicity of the material. In which, 50 mg of catalysts were mixed with 20 mL of aq. 0.005 M benzoic acid solution and stirred at room temperature for 12 h. To calculate the reacted and unreacted benzoic acid, the solution was neutralized with aq. 0.005 M NaOH solution using phenolphthalein as an indicator.

S 4. Procedure for the catalytic reaction

S 4.1. Methanolysis of polycarbonate (Bisphenol A)

Typically, the depolymerization of the polycarbonate was carried out in a 50 mL stainless steel high-pressure reactor. For each catalyst test, 1 g of a PC, and the desired amount of catalyst were mixed in the required amount of methanol. The reactor was heated at the desired temperature under a stirring rate of 700 rpm. The reaction time was noted when the desired temperature was achieved. After, completing the reaction, the reaction mixture was quenched with cool water to ambient temperature. The catalyst was separated by filtration, the filtrate was concentrated by rotary evaporation and analyzed FT–IR, ¹H NMR, and TGA analysis. The product purification was identified and confirmed by gas chromatography (GC) (Yonglin; 6100; GC column: BP-5; 30 m×0.25 mm×0.25μm) fitted with an FID detector. The products formed during the reaction were confirmed by GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

S 4.2. Methanolysis of polylactic acid

Typically, the depolymerization of the polylactic acid was carried out in a 50 mL stainless steel high-pressure reactor. For each catalyst test, 1 g of a PLA, and the desired amount of catalyst mixed in the required amount of methanol. The reactor was heated at the desired temperature under a stirring rate of 700 rpm. The reaction time was noted when the desired temperature was achieved. After, completing the reaction the reaction mixture was quenched with cool water to ambient temperature. The catalyst was separated by filtration, the filtrate was concentrated by rotary evaporation and analyzed FT–IR, ¹H NMR, and TGA analysis. The product purification was identified and confirmed by gas chromatography (GC) (Yonglin; 6100; GC column: BP-5; 30 m×0.25 mm×0.25μm) fitted with an FID detector. The products formed during the reaction were confirmed by GC-MS (Shimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 μm).

The conversion of PC/PLA yield and the selectivity of products were determined by the following equations,

$$C_{PC/PLA} = \frac{(W_1 - W_2)}{W_1} \times 100 \quad \text{Eq (S1)}$$

$$Y_{BPA} = \frac{W_3}{W_1} \times \frac{M(PC)}{M(BPA)} \times 100 \quad \text{Eq (S2)}$$

$$Y_{ML} = \frac{W_3}{W_1} \times \frac{M(PLA)}{M(ML)} \times 100 \quad \text{Eq (S3)}$$

$$S_{BPA/ML} = \frac{W_3}{(W_1 - W_2)} \times 100 \quad \text{Eq (S4)}$$

Where W_1 is the initial weight of the PC/PLA and W_2 is the weight of the unreacted PC/PLA. W_3 denotes the weight of the obtained product BPA/ML.

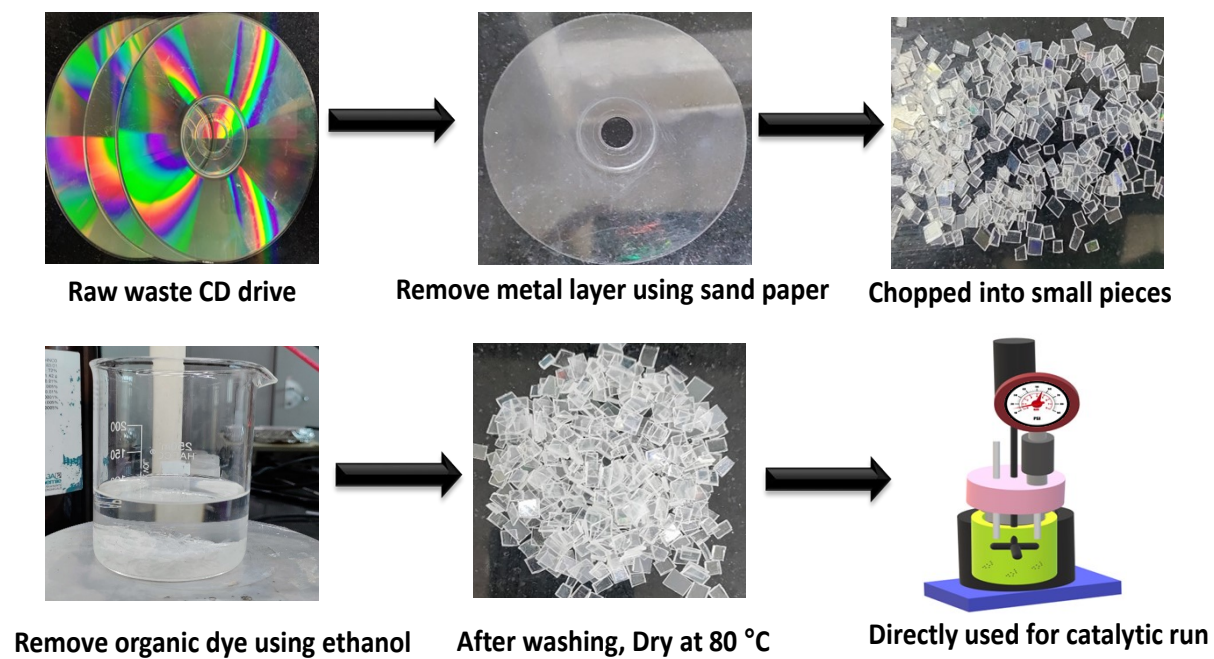
$M(PC)$ and $M(PLA)$ stands for the molecular mass of PC (254 g/mol) and PLA (72 g/mol). Similarly, $M(BPA)$ and $M(ML)$ are a molecular mass of BPA (228 g/mol) and ML (90 g/mol).

S5. Sample preparation for ^{31}P NMR

The equimolar amount of methyl lactate (0.5 mmol) and pyridine (0.5 mmol) was mixed with 1 mL of CDCl_3 and stirred for a few minutes. To the stirred solution, the mixture of PCl_3 (0.25 mmol) and CDCl_3 (1 mL) was added slowly and stirred at room temperature for 15 min. Subsequently, the mixture was transferred, without the necessity of any workup for purification, into a 10 mm NMR tube, and the ^{31}P NMR spectrum was recorded.^{S4}

The spectrum depicted in **Fig S15** revealed the presence of stereoisomeric phosphonates, specifically the RR (L-pair) and the meso-pairs (RS and SR).^{S3, S4} In the ^{31}P NMR spectrum, the RR resonance peak at 7.0 ppm corresponds to the L-form of the phosphonate, while the two minor signals at 8.16 ppm and 5.67 ppm correspond to the meso forms. A quantitative assessment of the ^{31}P NMR spectrum was carried out through integration, which facilitated determining the L-methyl lactate content in these samples. This analysis revealed that the L-methyl lactate content was ~88% in the methyl lactate sample.

S6. Purification of CD disk-derived polycarbonate



Scheme S1. Purification process of polycarbonate source

S7. Catalyst characterization

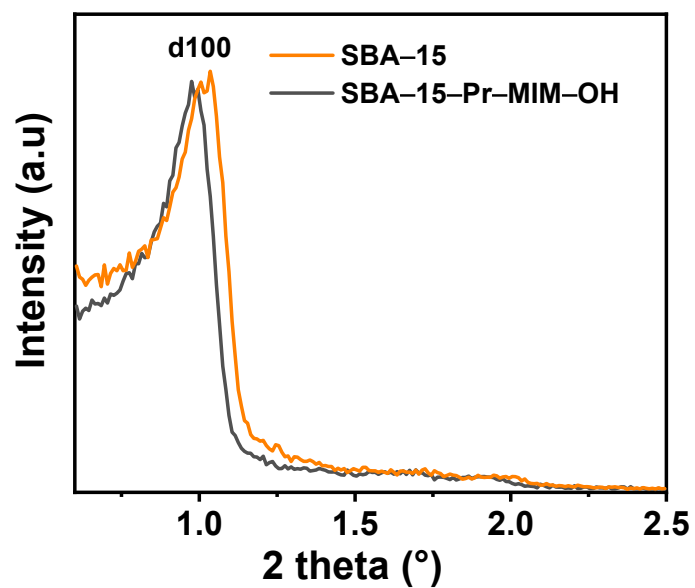


Fig. S1 Low-angle XRD patterns of SBA-15 and SBA-15-Pr-MIM-OH.

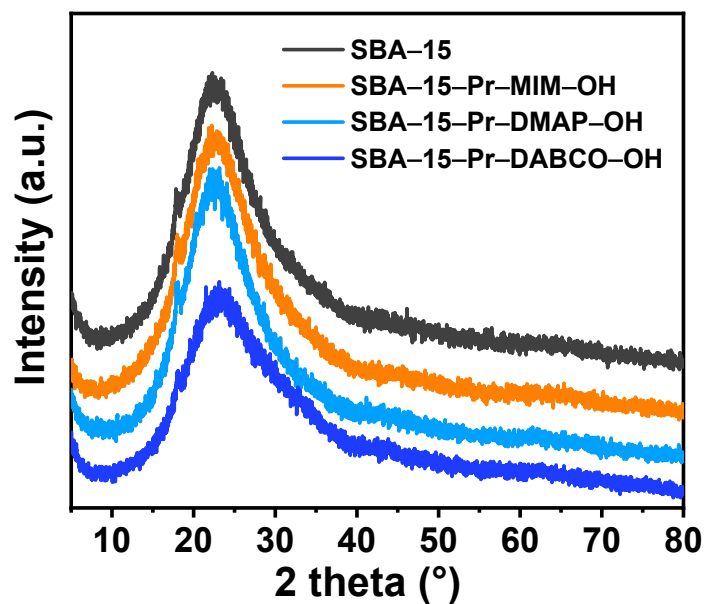


Fig. S2 XRD patterns of SBA-15 and ionic liquid functionalized SBA-15 catalysts.

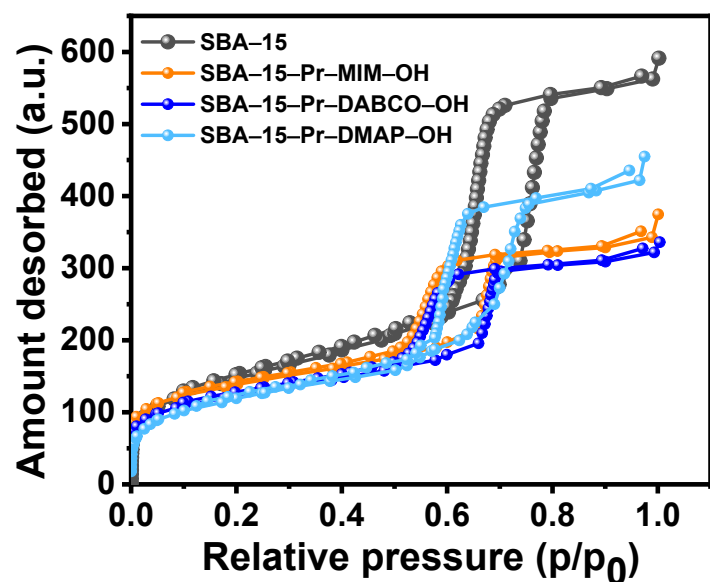


Fig. S3 N_2 -adsorption-desorption isotherms of synthesized catalysts.

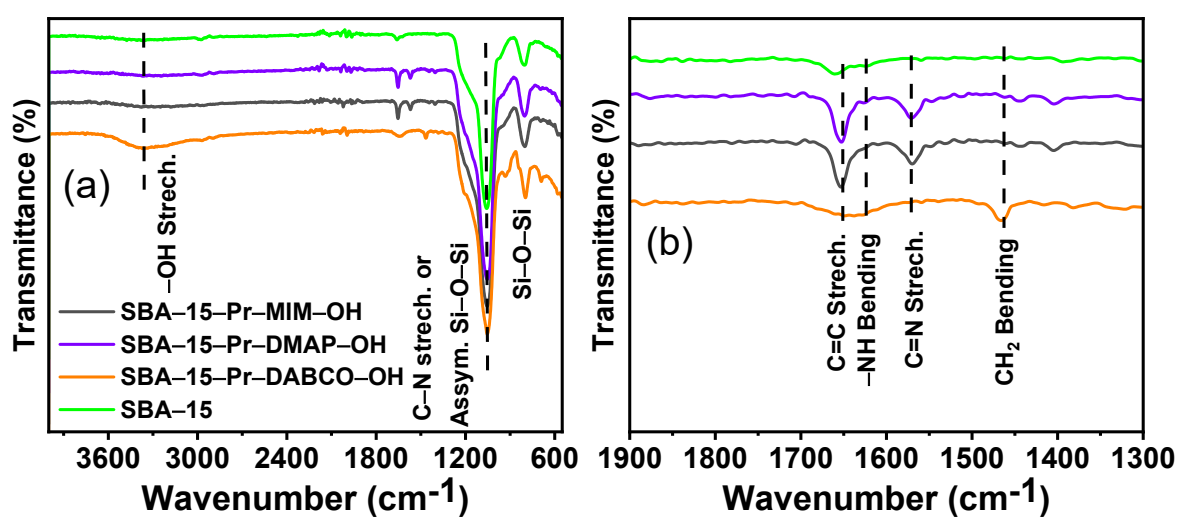


Fig. S4 Comparative FT-IR spectra of various functionalized SBA-15 catalysts.

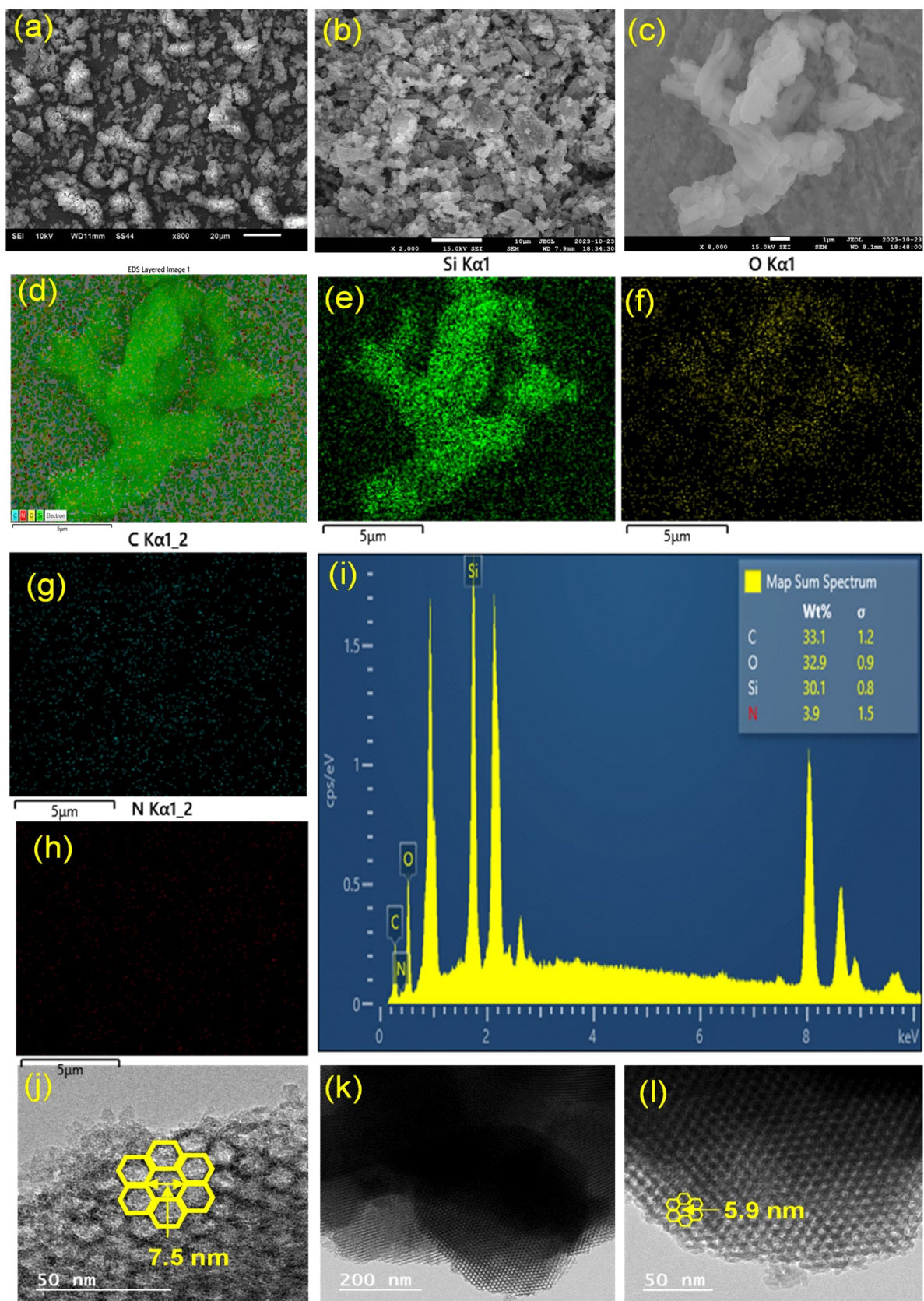


Fig. S5 SEM images of SBA-15 (a) and SBA-15-Pr-MIM-OH (b & c); SEM elemental distribution mapping of SBA-15-Pr-MIM-OH (d-l), overall elemental mapping(d), Si (e), O

(f), C (g), N (h), EDAX spectrum of SBA-15-Pr-MIM-OH (i). TEM images of SBA-15 (j) and SBA-15-Pr-MIM-OH (k & l).

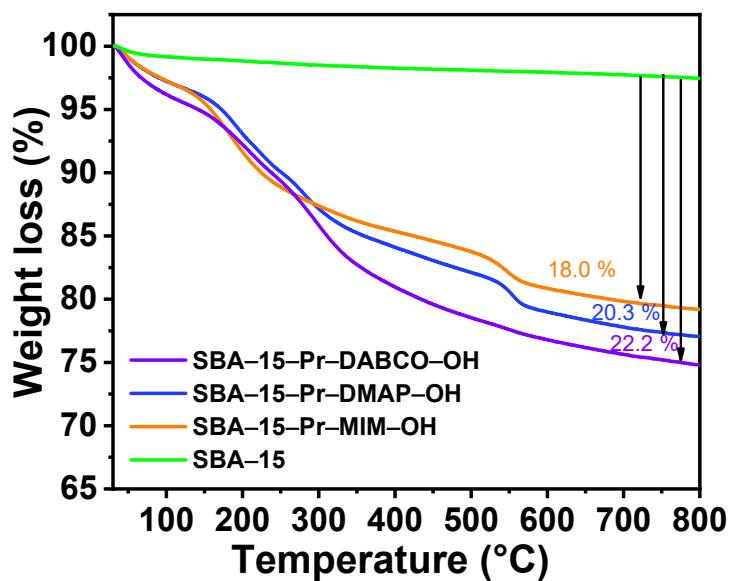


Fig. S6 Thermograms of various functionalized SBA-15 catalysts investigated in this study.

S8. Catalytic activity

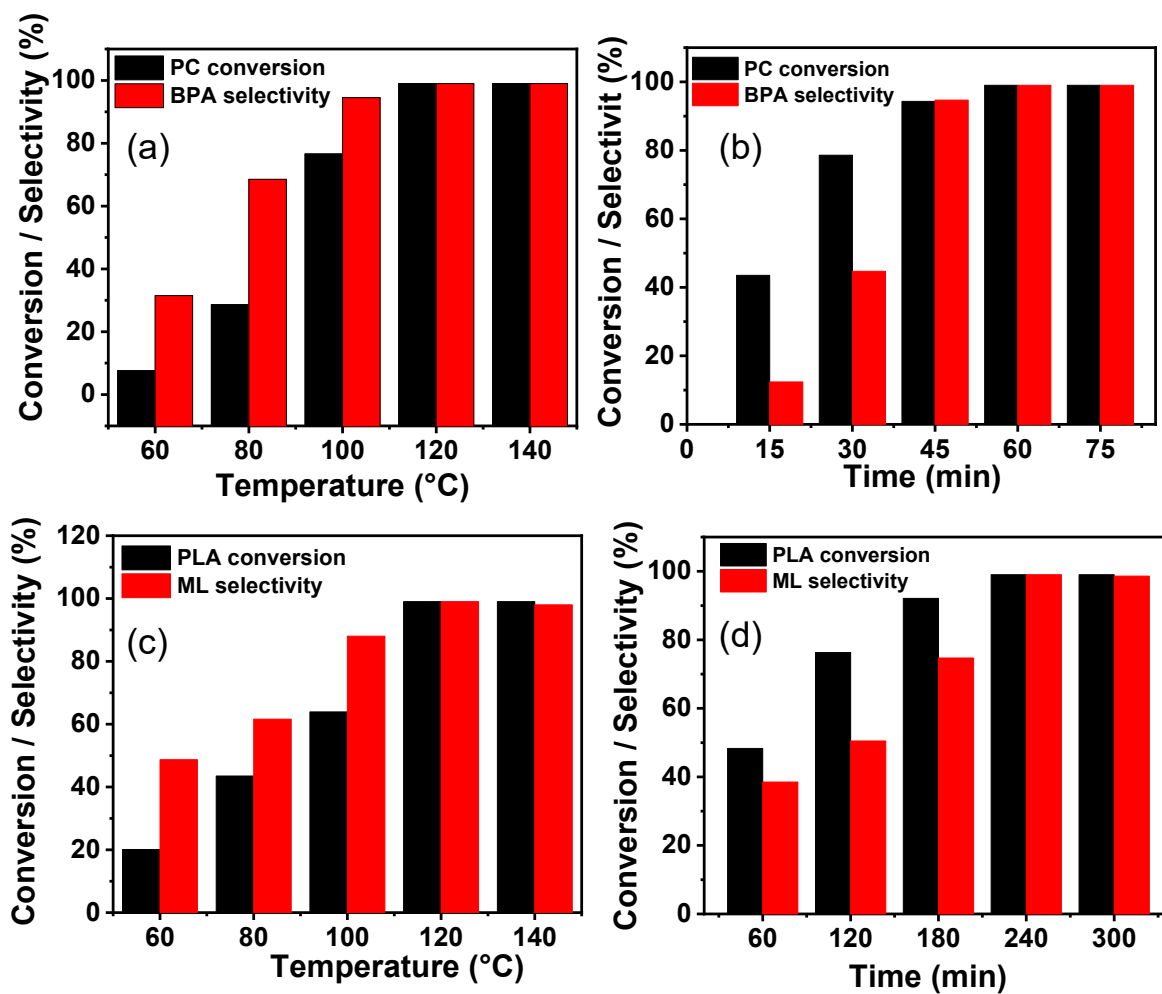


Fig. S7 The catalytic conversion and selectivity of PC and PLA (a-d). (a) Reaction temperature, Reaction condition: PC (3.93 mmol = 1 g), methanol (46 mmol = 1.5 g), catalyst (0.03 g), and 1 h. (b) Reaction time, Reaction condition: PC (3.93 mmol = 1 g), methanol (46 mmol = 1.5 g), catalyst (0.03 g), and temperature 120 °C.

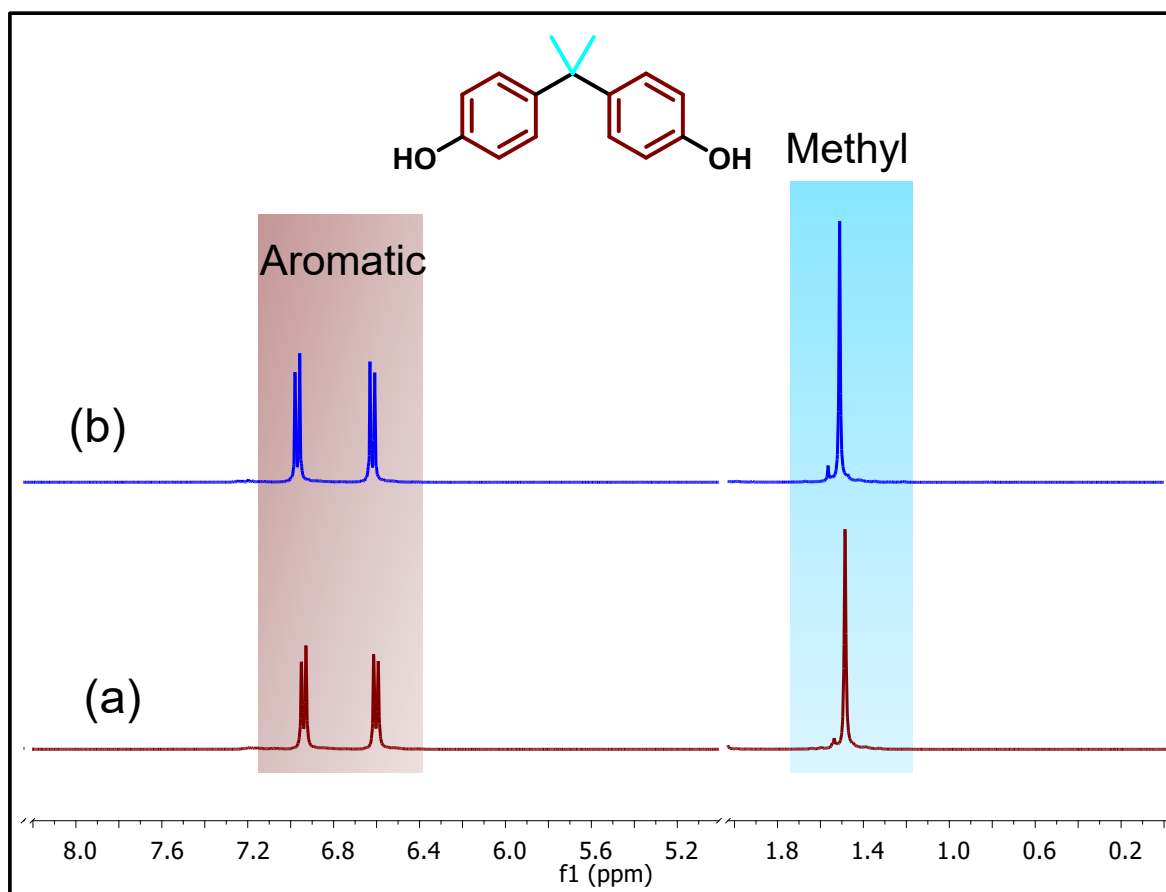


Fig. S8 Comparative ^1H NMR spectra of bisphenol A (BPA); (a) Commercial BPA & (b) BPA produced from waste PC.

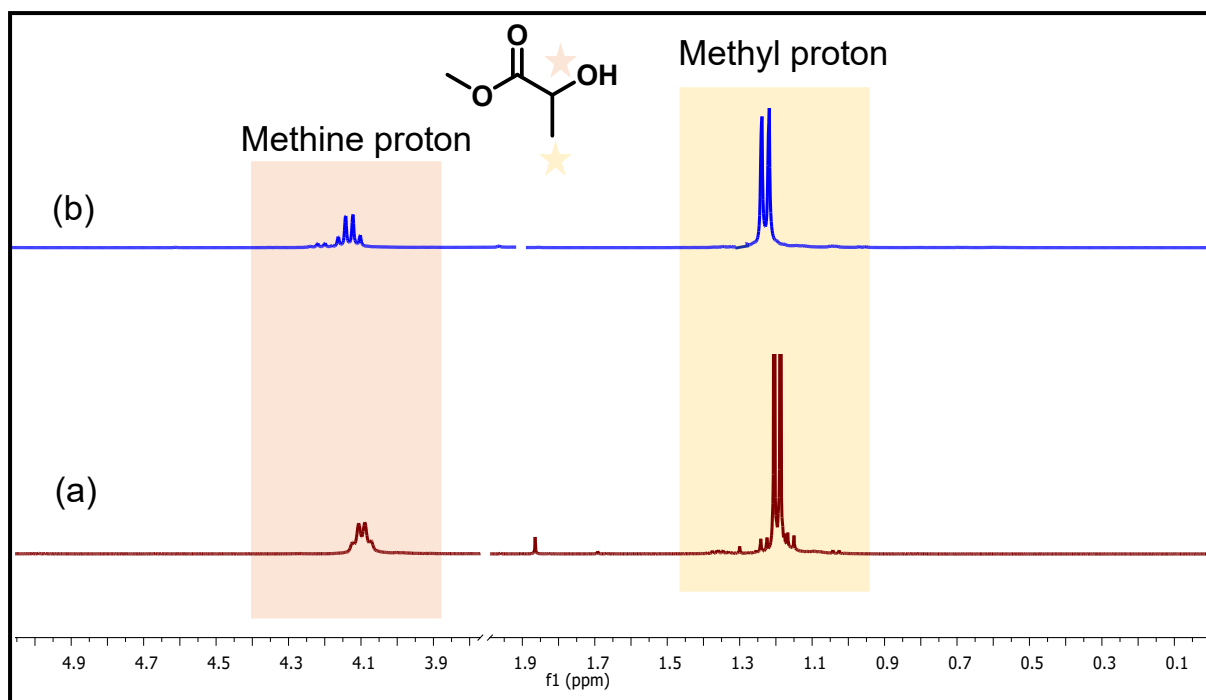


Fig. S9 Comparative ^1H NMR spectra of methyl lactate (ML); (a) Commercial ML & (b) ML produced from waste PLA.

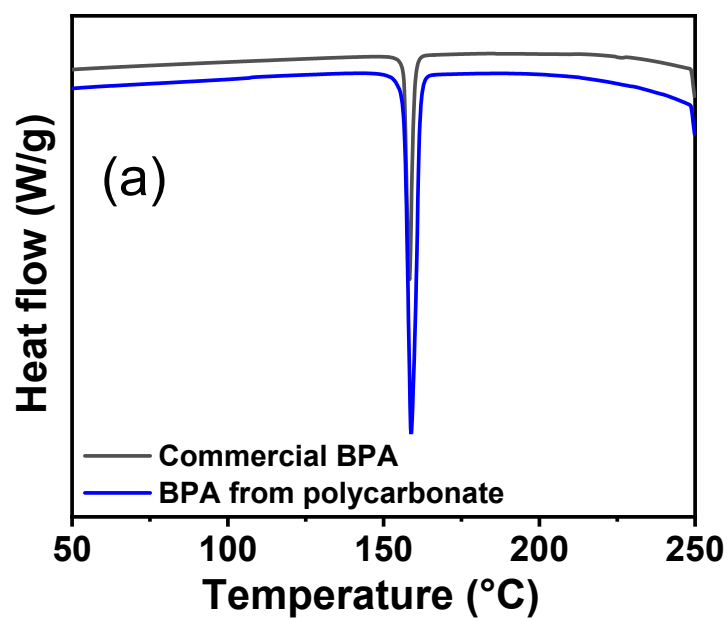
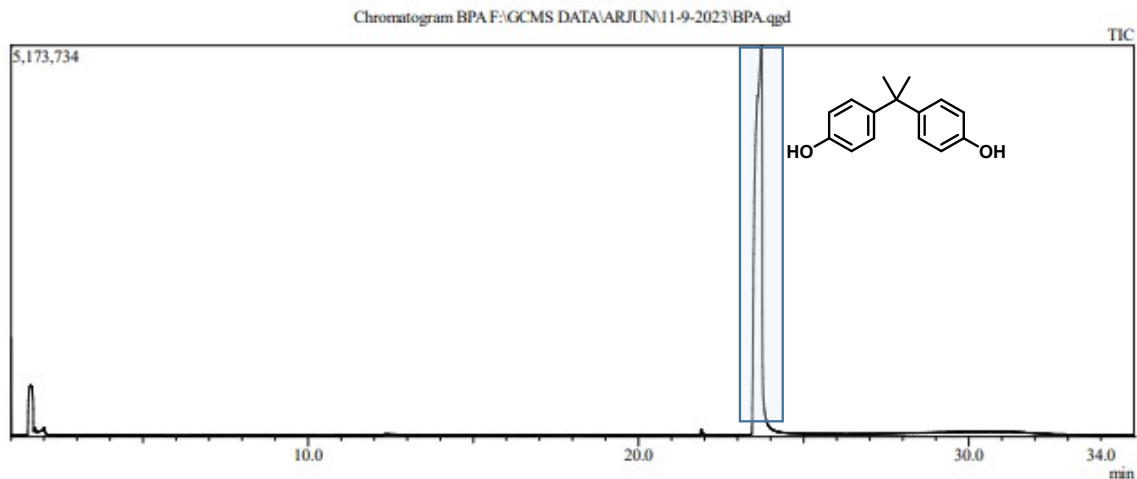


Fig. S10 Comparative DSC profiles of bisphenol A (BPA)



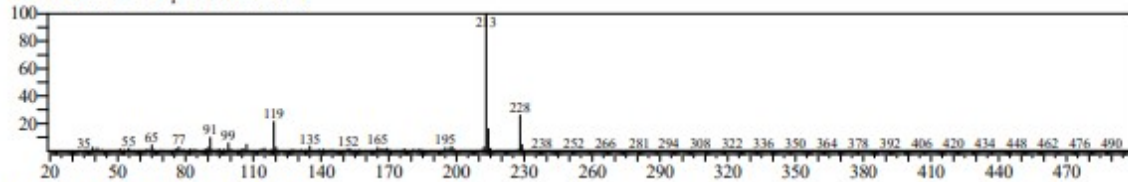
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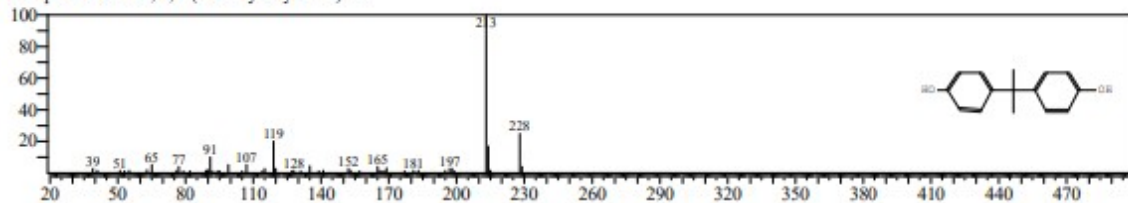
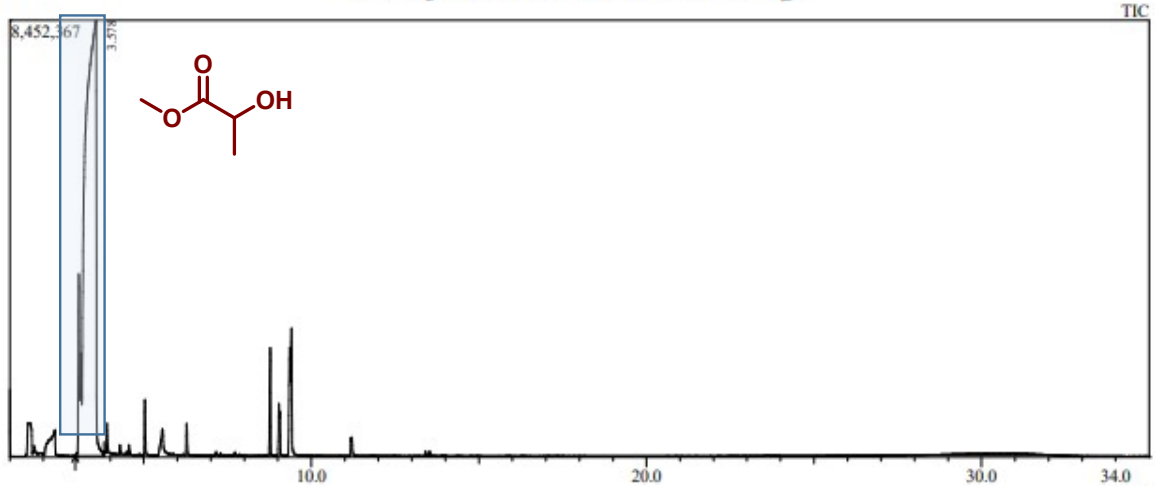


Fig. S11 GC-MS spectrum of bisphenol A.



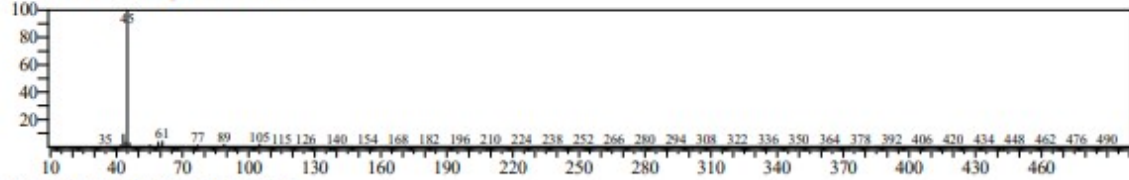
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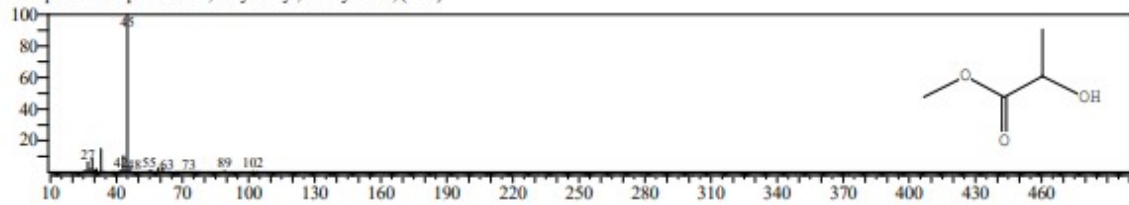
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**Fig. S12** GC-MS spectrum of methyl lactate.

S9. Mechanistic investigation

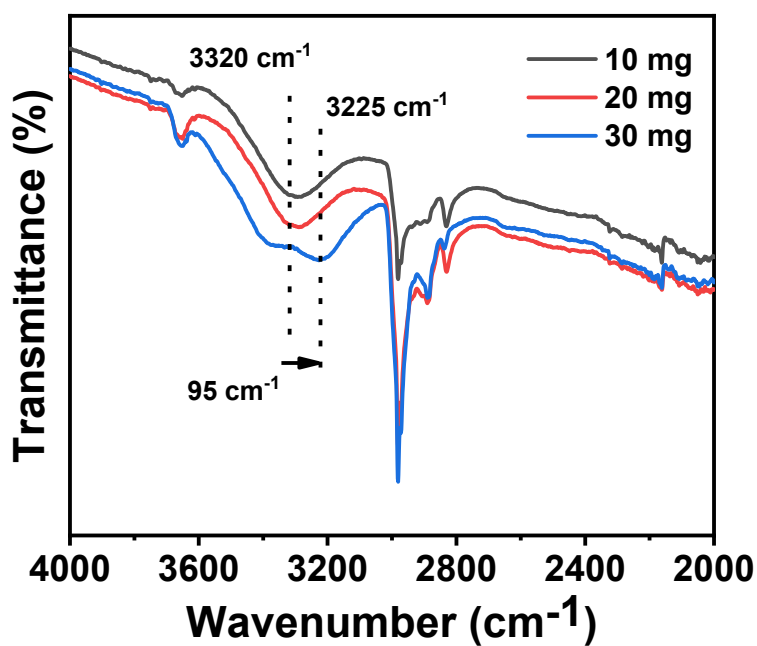


Fig. S13 FT-IR spectra of methanol to show the interaction between CH_3OH and SBA-15-Pr-MIM-OH with various concentration.

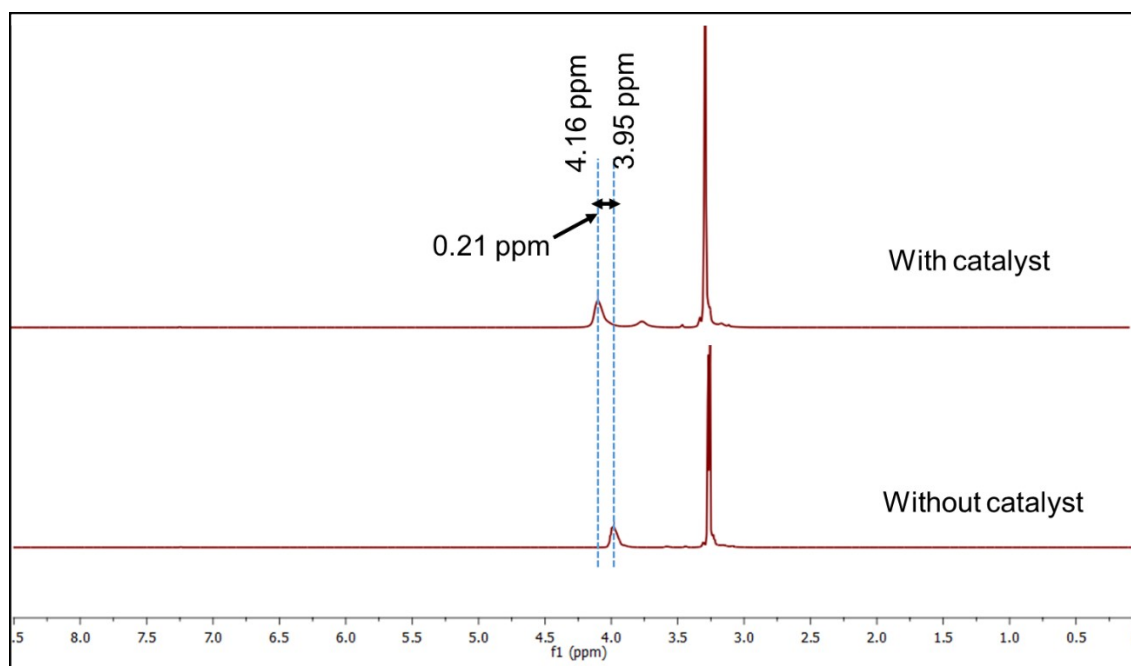


Fig. S14 ^1H NMR spectra of methanol with and without catalyst to show the interaction between CH_3OH and SBA-15-Pr-MIM-OH.

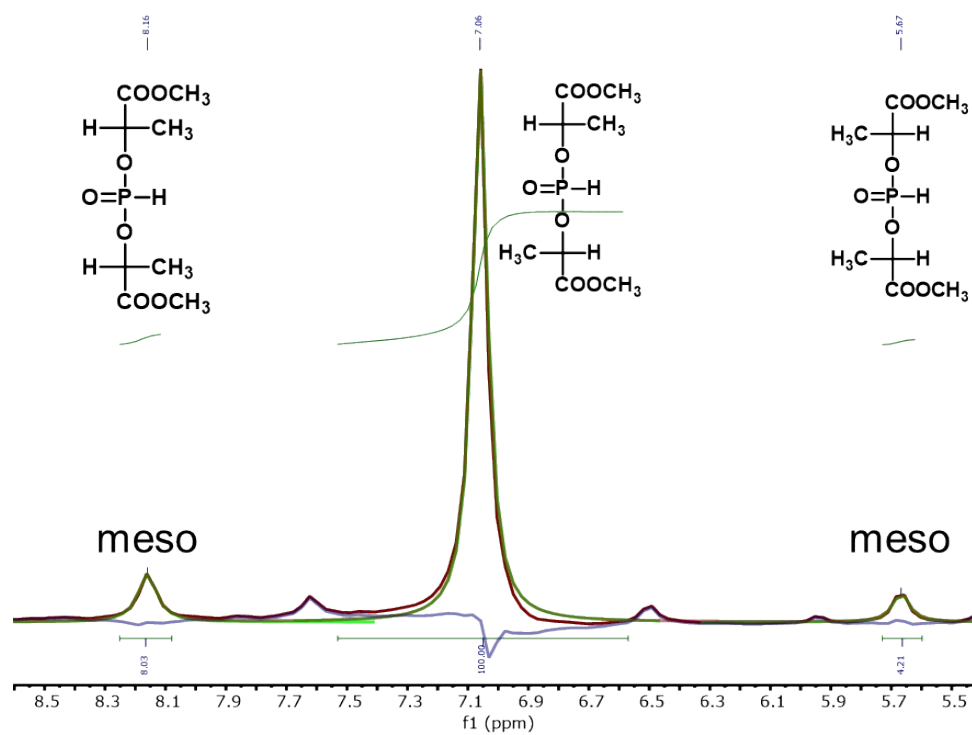


Fig. S15 ^{31}P NMR spectrum of the methyl lactate (signal assignments according to Majaonkar et al. and Feringa et al.)^{S3, S4}

Catalyst recyclability

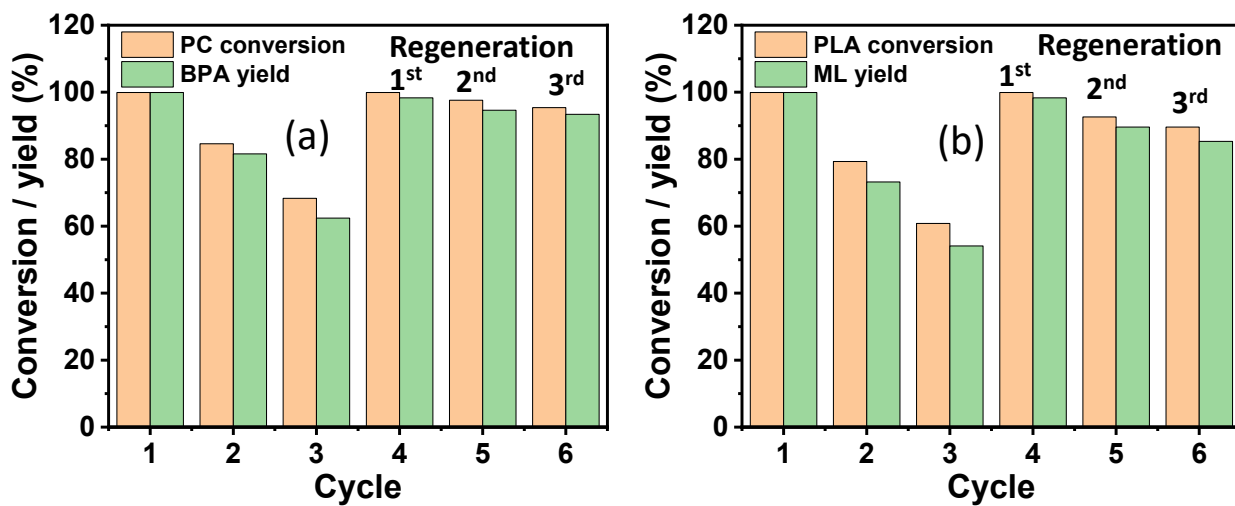


Fig. S16 Catalyst recyclability test for PC and PLA waste.

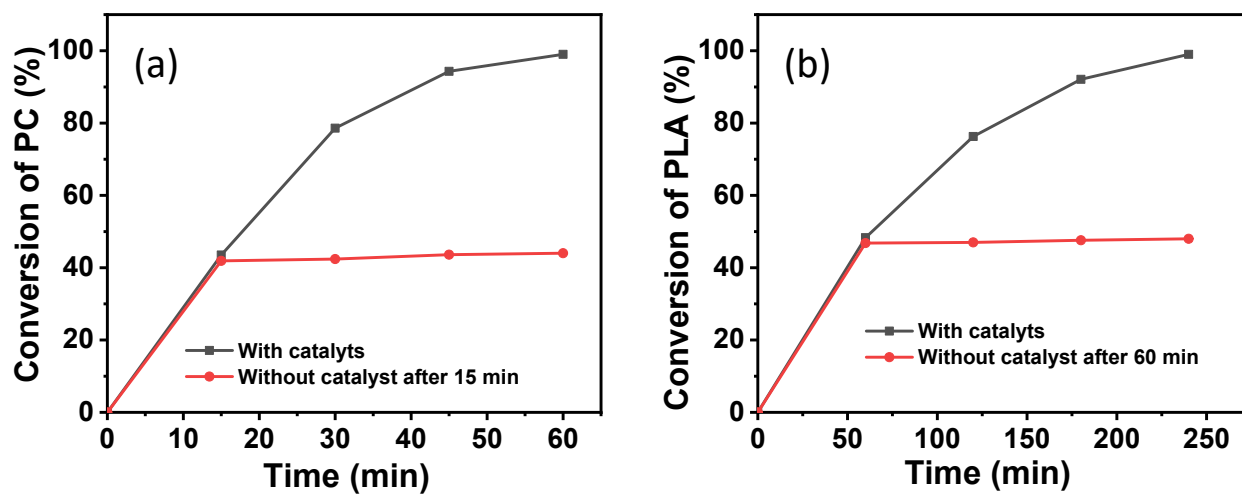


Fig. S17 Hot filtration test of PC (a), and PLA (b).

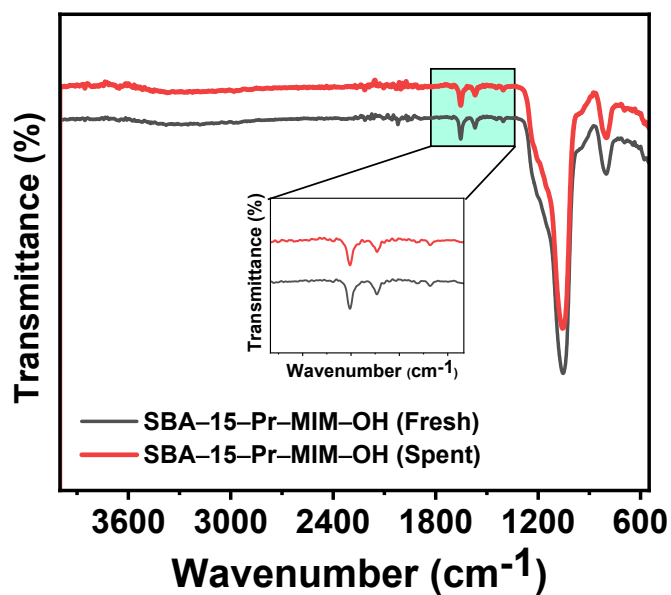


Fig. S18 Comparative FT-IR spectra of fresh and spent SBA-15-Pr-MIM-OH catalyst.

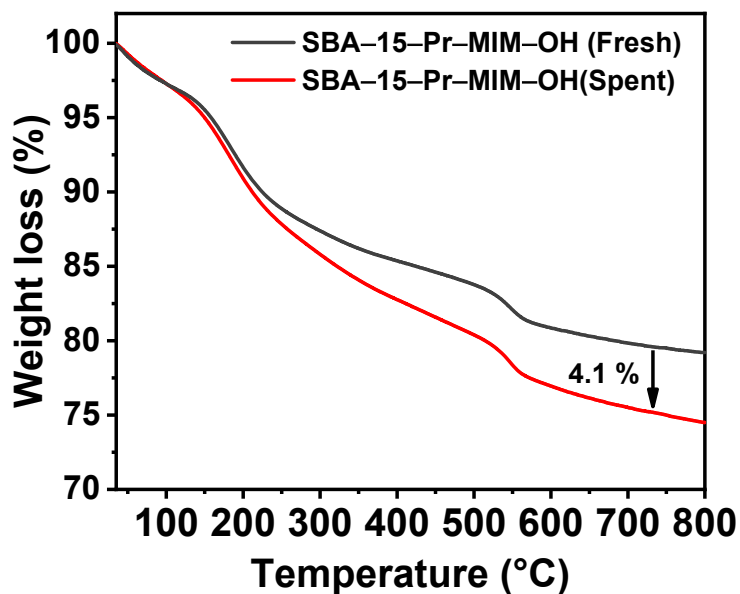


Fig. S19 TGA profiles of fresh and spent SBA-15-Pr-MIM-OH catalyst.

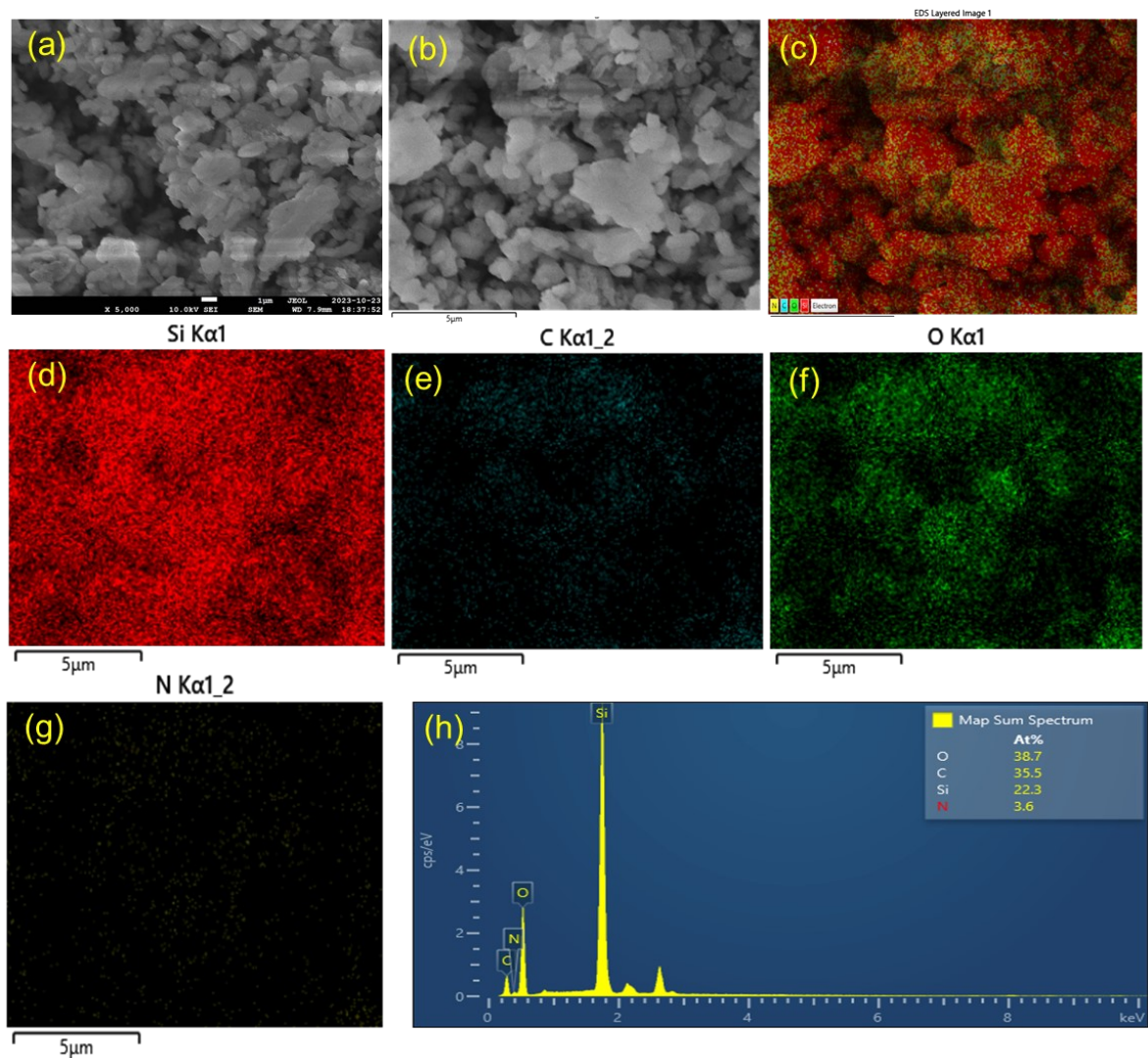


Fig. S20 SEM images of spent SBA-15-Pr-MIM-OH (a & b); SEM elemental distribution mapping of SBA-15-Pr-MIM-OH (c-h), overall elemental mapping(c), Si (d), C (e), O (f), N (g), EDAX spectrum of SBA-15-Pr-MIM-OH (h).

Table S1. Comparative assessment of the developed catalyst with the reported catalysts in the methanolysis of PC

Catalyst	Mass of solvent /PC	Mass of Catal. /PC	Temperature (°C)	Time (h)	Yield of BPA (%)	(ϵ) _{factor}	E _{factor}	ξ factor	Ref.
SBA-15-Pr-MIM-OH	1.5	0.03	120	1	99	0.000136806	0.18393	1344.46	This work
CaO/SBA-15	2.98	0.3	130	3	96.8	4.13675E-05	0.64325	15549.85	S5
Mg ₃ Al-LDO	2.5	0.03	110	2	98	7.42424E-05	0.28410	3826.69	S6
15% CaO/ Ce-SBA-15	1.42	0.3	130	2.5	91.7	4.70256E-05	0.50646	10769.88	S7
Ca-Al ₂ O ₃	1.08	0.03	110	3	99.9	5.04545E-05	0.14145	2803.60	S8
ChCl-2Urea (DES)	0.62	0.01	130	2.5	99.9	5.12308E-05	0.07315	1427.88	S9
[EmimOH]Cl-2Urea	0.62	0.1	120	2	99.9	0.000069375	0.17351	2501.11	S10
[HDBU][LAc]	0.62	0.0075	120	1	99	0.0001375	0.0704	512.28	S11
[Bmim][Cl].2FeCl ₃	0.75	0.4	120	3	97.2	0.000045	0.53345	11854.45	S12

Table S2. Comparative assessment of the developed catalyst with the reported catalysts for the methanolysis of PLA

Catalyst	Mass of solvent /PLA	Mass of Catal. /PLA	Temperature (°C)	Time (h)	Yield of ML (%)	(ϵ) _{factor}	E _{factor}	ξ factor	Ref.
SBA-15-Pr-MIM-OH	1.5	0.03	120	4	99	0.000136111	0.171193093	1257.74517	This work
SO ₂ ⁻⁴ /ZrO ₂ /SiO ₂	20	0.01	140	5	92.7	2.20714E-05	2.00746826	90953.25449	S13
[Bmim][Ac]	2.15	0.02	110	3	87.1	4.39899E-05	0.230896847	5248.860589	S14
2[Bmim] [OAc]- [Zn(OAc) ₂]	2.2	0.01	110	2	92	6.9697E-05	0.227525084	3264.49033	S15
[HDBU][AA]	2.2	0.14	100	5	91	3.03333E-05	0.326508876	10764.02887	S16
[HTBD][OdmGly]	4.4	0.071	70	3	71	5.63492E-05	0.509230769	9037.053088	S17
TMAF	250	0.23	90	1	99	0.000183333	25.16083916	137240.9409	S18

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