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Supplementary information for

Coupling of CO_2 with Epoxides Catalyzed by a Periodic Mesoporous Organosilica with Ionic Liquid Frameworks

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Table of Contents

Title Page

1. Materials and Methods

1.1. Characterization methods

The pore structures of the prepared materials were observed by transmission electron microscopy (Philips CM-200) and were verified further by the nitrogen sorption analysis. N_2 adsorption isotherms were measured at 77 K on Belsorp (BELMAX, Japan) analyzer using standard continuous procedures, and samples were first degassed at 353 K for 5 h. The specific surface area was determined from the linear part of the BET plot ($P/P0 \approx 0.05$-0.15), the pore size distribution was calculated from the adsorption branch using Barrett-Joyner-Halenda (BJH) method, total pore volume was estimated based on the N_2 adsorbed at $P/P0 \approx 0.995$. The pore structure of the BFPMOs was determined by a transmission electron microscope (TEM, Philips CM-200). Thermogravimetric analysis was performed by using a NETZSCH STA 409 PC/PG instrument at scan rates of 20 K min^{-1}, with typically 5 mg sample under flowing N_2. Solid-state NMR spectroscopy was performed on a Varian INFINITY PLUS 400 equipment. ^{29}Si MAS-NMR spectra were recorded with a frequency of 79.4 MHz and magic-angle spinning of 6 kHz. XRD measurements were collected in a Philips X'PERT MPD diffractometer using Cu K_α radiation. DRIFT spectra were recorded on a Brüker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector. Gas chromatography analyses were performed on Varian CP-3800 using a flame ionization detector (FID) using suitable internal standards. NMR spectra were recorded using a Brüker (^1H frequency: 400 MHz, ^{13}C frequency: 100 MHz).

1.2. Materials

Sodium Hydride 95%, Pluronic P123 ($M_W \approx 5800$, $EO_{20}PO_{70}EO_{20}$), 1,4-bis(trimethoxysilyl)ethane (BTME), 1-methyl imidazole and tetramethoxyorthosilicate (TMOS) were obtained from Sigma-Aldrich Company. N-trimethoxysilylpropyl-N,N,N-trimethylammonium Chloride was purchased from abcr GmbH, Germany. Imidazole, 3-chloropropyl-trimethoxysilan (CPTMS), potassium chloride, potassium iodide and *c*-HCl (37%) were purchased from Merck Company. Imidazole was first re-crystallized in distilled CH_2Cl_2 and dried in a desiccator under vacuum over P_2O_5 for the several days at room temperature.

1.3. Synthesis

1.3.1. Synthesis of ionic liquid precursor (BTMSPICl)

The ionic liquid BTMSPICl precursor was prepared by a few modifications of our last synthetic report.[1] In a typical experiment, a suspension of sodium imidazolide in dry THF was prepared from the direct reaction of freshly dried imidazole (2 g) and NaH 95% (0.77 g) at a flame-dried two necks flask containing dry THF (60 ml) under argon atmosphere. 3-chloropropyltrimethoxysilan (5.4 ml) was added to the mentioned stirred suspension and the resulting mixture was refluxed for 30h. Then, the reaction mixture was allowed to cool to room temperature followed by the solvent removed under reduced pressure until an oily mixture containing NaCl obtained. Then, 3-

chloropropyltrimethoxysilan (5.4 ml) and dry toluene (60 ml) were added and the resulting mixture was refluxed for 48h until a two-phase mixture comprising toluene and ionic liquid (BTMSPICl) obtained. Then, the toluene phase was removed and dry CH_2Cl_2 (60 ml) was added to remove the precipitated NaCl. In the next stage, the CH_2Cl_2 phase was transferred to the well-dried/two-necks flask and the volatiles removed by reduced pressure until the ionic liquid (BTMSPICl) and unreacted starting materials obtained. Finally, the ionic liquid was washed by dry toluene (5×50ml) for the removal of unreacted starting materials to give almost pure BTMSPICl.

1.3.2. Synthesis of Cl@BFPMO-IL

Cl@BFPMO-IL was also synthesized according to our method.[1] In a typical method, Pluronic P123 (0.432 mmol, 2.505 g) was dissolved in a mixture of H_2O (0.875 mol, 15.750 g), HCl, (2M, 69.230 g) and KCl (13.200 g) and the system stirred until a homogenous solution obtained. A pre-mixture of BTMSPICl (3.000 mmol, 1.290 g), and 1,2-bis(trimethoxysilyl)ethane (4.500 mmol, 1.267 g) in dry methanol was added to the mentioned solution and stirred at 40 °C for 15 minutes. Then, TMOS (22.500 mmol, 3.425 g) was added and the resulting mixture stirred at 40 °C for 24h. Finally, the resulting mixture was aged without stirring at 100 °C for 72h. The obtained Cl@BFPMO-IL with surfactant was filtered and washed with deionized water, and dried at room temperature. The surfactant was finally extracted from the Cl@BFPMO-IL by a Soxhlet apparatus by using ethanol (100 ml) and c-HCl (3 ml). In a typical extraction, as synthesized PMO (1g) washed four times with acidic ethanol over 12 h.

1.3.3. Synthesis of SBA-15

The SBA-15 was synthesized according to Stucky's report with slight modifications.[3] For a typical method, 2.4 g P123 was added to a solution containing 10.1 ml HCl (*c*) and 50.5 ml distilled water. Then 5.4 ml TEOS was added and resulted mixture vigorously stirred at 35 °C for 18-20h. Then, the resulting mixture was aged without stirring at 80 °C for 24h. The obtained mesoporous silica was filtered and washed with deionized water, and dried at room temperature. The surfactant was extracted from the SBA-15 channels by a Soxhlet apparatus by using ethanol.

1.3.4. Preparation of I@BFOMO-IL

The catalysts were synthesized by a simple ion-exchange technique according to our previous procedure with slight modifications.[2] For a typical method, Cl@BFPMO-IL (1.0 g, 1 mmol IL/g) was added to 20 ml of deionized water and sonicated for at least 10 minutes. Then, KI (1.992 g, 12 mmol) in 3 mL of deionized water was gradually added to the aforementioned suspension and stirred at room temperature for 4 h under Ar atmosphere. The resulting system was filtered and washed with deionized water (3×20 mL) and acetone (2×10 mL), respectively. The resulting solid was dried at room temperature in vacuum.

1.3.5. Preparation of Br@BFOMO-IL

This catalyst was synthesized by the method introduced in section 1.3.3 while KBr (1.43 g, 12 mmol) was just used simple ion-exchange technique according to our previous procedure

1.3.6. Synthesis of I@PMO-IL

In the first step, PMO-IL was synthesized according to our previously reported methods.[4] In a typical procedure, Pluronic P123 (1.67g) was dissolved in a mixture of H_2O (10.5g), HCl, (2M, 46.14g), and KCl (8.8 g), and the mixture was stirred at 40 °C until a homogenous solution obtained. Then, a pre-mixed of BTMSPICl (2 mmol, 0.86g) and TMOS (18 mmol, 2.74 g) in dried methanol were immediately added to the above-mentioned solution and stirred at 40 °C for 24 h. The resulting mixture was posed in hydrothermal treatment without stirring at 100 °C for 72 h. The obtained solid material containing the surfactant was filtered and carefully washed with deionized water. The surfactant residue was then extracted from the materials through a Soxhlet apparatus by using ethanol (100 ml) and concentrated HCl (37%, 3 mL). In a typical extraction, as-synthesized PMO (1g) washed four times with acidic ethanol over 12 h, dried under vacuum for 24 h, to afford PMO-IL as a bright yellow powder. As the final step, resulting PMO-IL (1.0 g, 1 mmol IL/g) was added to 20 ml of deionized water and sonicated for at least 10 minutes. Then, KI (1.992 g, 12 mmol) in 3 mL of deionized water was gradually added to the aforementioned suspension and stirred at room temperature for 4 h under Ar atmosphere. The resulting system was filtered and washed with deionized water (3×20 mL) and acetone (2×10 mL), respectively. The resulting solid denoted as I@PMO-IL was dried at room temperature in vacuum.

1.3.7. Synthesis of I-N^+Me_3@SBA-15

In the first step, Cl-N^+Me_3@SBA-15 was synthesized by the post-grafting method.[4] For a typical procedure, SBA-15 (1.00 gr) was first dispersed in 20 ml dry toluene and sonicated for 5 minutes at room temperature. Then, N-trimethoxysilylpropyl-N,N,N-trimethylammonium Chloride, 50% in methanol (1.2 mmol, 0.7 ml) was added and the mixture was refluxed for 24 h under Ar atmosphere. Then, the resulted material was filtered and unreacted organosilica precursors were removed by washing with ethanol overnight using a Soxhlet apparatus. The resulting material was dried at 80 °C for at least 12h and directly used in the next step. For the preparation of I-N^+Me_3@SBA-15, resulting SBA-15 modified by ammonium chloride (1.0 g, 0.89 mmol IL/g) was added to 20 ml of deionized water and sonicated for at least 10 minutes. Then, KI (1.992 g, 12 mmol) in 3 mL of deionized water was gradually added to the aforementioned suspension and stirred at room temperature for 4 h under Ar atmosphere. The resulting system was filtered and washed with deionized water (3×20 mL) and acetone (2×10 mL), respectively. The resulting solid denoted as I-N^+Me_3@SBA-15 was dried at room temperature in vacuum.

1.3.8. Synthesis of I-MPIM@SBA-15

As the first step, imidazolium-based organosilica was prepared according to our report.[5] In this regard, in a flame dried round bottom three-necked flask, N-Methyl imidazole (10 mmol, 0.82 g), 20 ml dry toluene and then 3-chloropropyltrimethoxysilan (12 mmol, 2.16 ml) were added under Ar atmosphere. After refluxing mixture for 24 h a biphasic solution containing insoluble 1-methyl-3-[(3-trimethoxysilyl)propyl] imidazolium chloride as IL in toluene was obtained. IL was washed with 3×

20 ml dry toluene to removed unreacted substrates. Then, IL (1.2 mmol. 0.33 g) was added to a solution containing SBA-15 (1 g) and 50 ml dry toluene. The mixture was refluxed for 24 h. The resulting material was filtered and washed with toluene and acetone and then dried at 80 °C overnight. For the preparation of I-MPIM@SBA-15, the SBA-15 functionalized by imidazolium (1.0 g, 1 mmol IL/g) was first added to 20 ml of deionized water and sonicated for at least 10 minutes. Then, KI (1.992 g, 12 mmol) in 3 mL of deionized water was gradually added to the aforementioned suspension and stirred at room temperature for 4 h under Ar atmosphere. The resulting system was filtered and washed with deionized water (3×20 mL) and acetone (2×10 mL), respectively. The resulting solid denoted as I-MPIm@SBA-15 was dried at room temperature in vacuum.

1.3.9. General procedure for the coupling CO_2 with epoxides

Epoxide (10 mmol) and I@BFPMO-IL (1 mol% with regard to the substrate) were added to a stainless steel high-pressure reactor. The reactor was sealed and flushed 3 times with CO_2 at room temperature. The reactor was then pressurized to 10 bar and the reaction mixture was stirred at 70 °C for the desired time. After the completion of the reaction, the reaction mixture was allowed to cool down to room temperature and a slow depressurization of the reactor was carried out. Followed by, 10 ml ethyl acetate was added and the separation of the catalyst from the reaction mixture was easily performed by centrifugation (10 min at 6000 rpm). The supernatant solution was sampled and analyzed by gas chromatography using a suitable internal standard. Then, the collected ethyl acetate was removed by reduced pressure to give the corresponding 5-ring cyclic carbonate. Further purification was also performed through column chromatography by ethyl acetate:*n*-hexane (1:5) if it was needed. All products were also confirmed by ^{1}H- and ^{13}C-NMR.

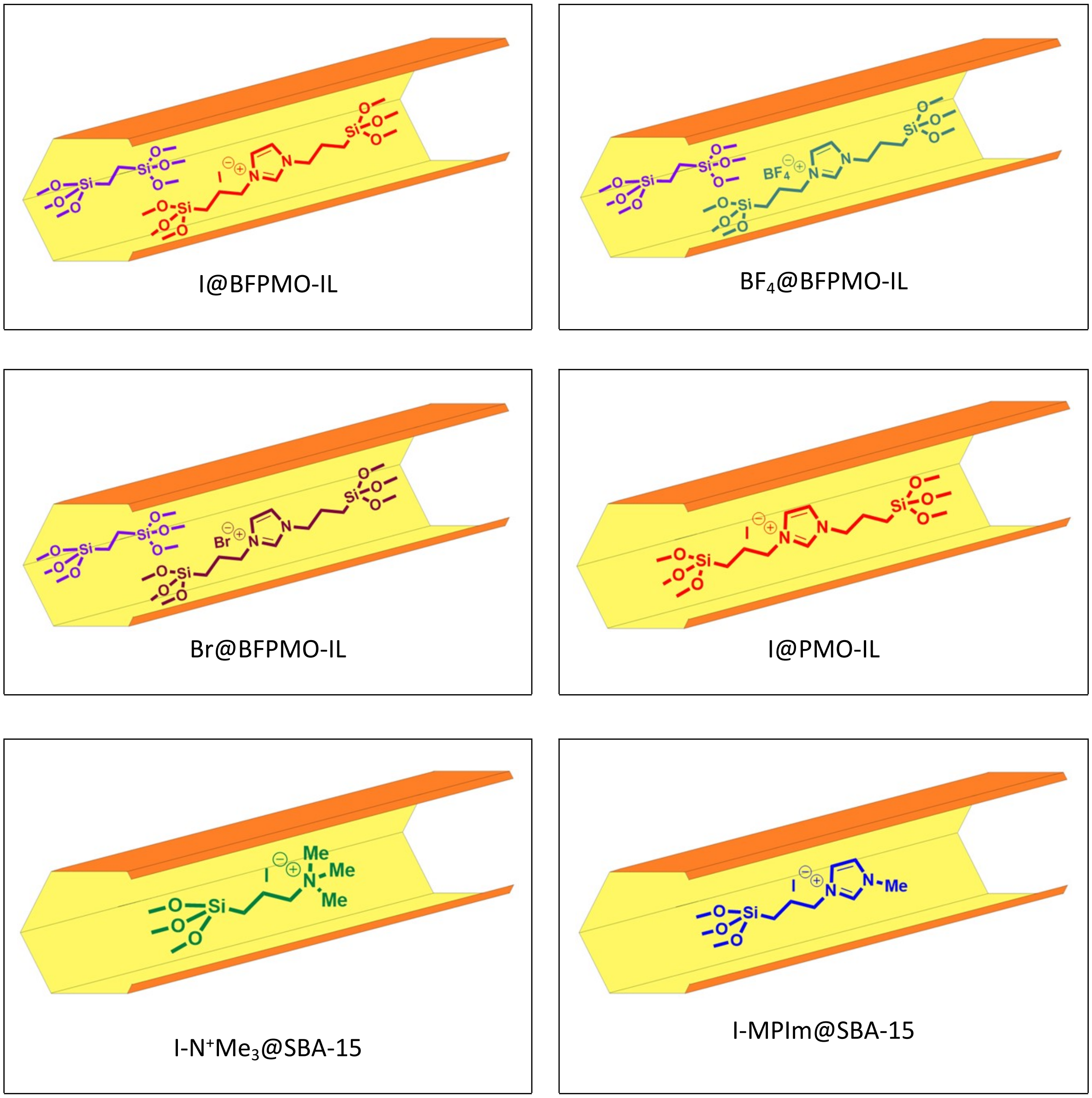
1.3.10. General procedure for recycling I@BFPMO-IL

For the recycling of catalyst, after the first run, the catalyst was isolated via simple filtering and subsequently washed with ethyl acetate (3 ×10 ml) and dried under vacuum for 12h. The recovered catalyst could be used in four other runs under the same manner reported in the first run (Table S2).

1.3.11. References

[1] B. Karimi, M. Khorasani, H. Vali, R. Luque, *J. Mater. Chem.* A, 2015, **3**, 6575-6585.
[2] B. Karimi, M. Khorasani, H. Vali, C. Vargas, R. Luque, *ACS Catal.*, 2015, **5**, 4189-4200.
[3] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024-6036.
[4] B. Karimi, M. Khorasani, *ACS. Catal.*, 2013, **3**, 1657-1664.
[5] B. Karimi, D. Enders, *Org. Lett.*, 2005, **6**, 1237-1240.

2. Schemes


I@BFPMO-IL

BF$_4$@BFPMO-IL

Br@BFPMO-IL

I@PMO-IL

I-N$^+$Me$_3$@SBA-15

I-MPIm@SBA-15

Scheme S1. Schematically presentation of all catalysts

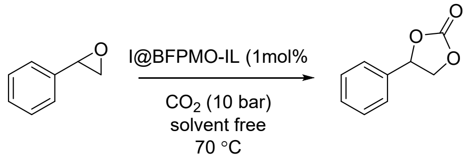
3. Tables

Table S1. Textural properties of the synthesized materials.

Material	S_{BET}[a] (m^{2}g^{-1})	V_t[b] (cm^{3}g^{-1})	D_{BJH} [c] (nm)	C [d] (%)	N[e] (%)	IL loading [f] (mmol g^{-1})	Halide loading [g] (mmol g^{-1})
Cl@BFPMO-IL	511	0.90	10.6	13.5	2.7	0.98	0.98 (Cl)
I@BFPMO-IL	481	0.88	10.3	13.6	2.7	0.97	0.97 (I)
Reused I@BFPMO-IL	450	0.88	10.3	13.5	2.7	0.97	0.96 (I)
Br@BFPMO-IL	487	0.89	10.3	12.5	2.7	0.97	0.97 (Br)
BF_4@BFPMO-IL	453	0.84	10.3	12.9	2.8	1.00	-
PMO-IL	601	1.30	10.6	10.5	2.6	0.92	0.92 (Cl)
I@PMO-IL	485	1.02	10.6	10.4	2.6	0.92	0.92 (I)
SBA-15	940	1.21	7.06	-	-	-	-
I-N^+Me_3@SBA-15	669	1.01	8.06	8.5	1.1	0.78[h]	0.77 (I)
I-MPIm@SBA-15	619	0.93	7.06	7.2	2.0	0.71	0.71 (I)

[a] S_{BET}: specific surface area determined from linear part of BET plot (P/P0 ≈ 0.05-0.15), [b] V_t: total pore volume estimated based on the N_2 adsorbed at $P/P_0 \approx 0.995$., [c] D_{BJH}: average pore size diameter calculated from the adsorption branch using BJH method. [d] Carbon content determined by CHNX analysis. [e] Nitrogen content determined by CHNX analysis. [f] Loading of Ionic liquids were determined by $\frac{N(\%) \times 10}{2 \times 14}$. [g] Loading of chloride and bromide ions were directly estimated from results of CHNX by using $\frac{Cl(\%) \times 10}{1 \times 35.5}$ and $\frac{Br(\%) \times 10}{1 \times 79.9}$, respectivelly. The iodide content was determined by Andrew's titration. [h] Loading of quaternary ammonium was determined by $\frac{N(\%) \times 10}{14}$

Table S2: Reusability results for I@BFPMO-IL catalyst in the coupling CO_2 with styrene oxide.[a]



Run	Time (h)	Yield (%)[b]
1	3	97
2	3	98
3	3	95
4	4	95
5	4	94

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[a]Reaction conditions: Styrene oxide (10 mmol), catalyst (1 mol%) and CO_2 (10 Bar) at 70 °C.

[b] GC yield by using suitable internal standard.

4. Figures

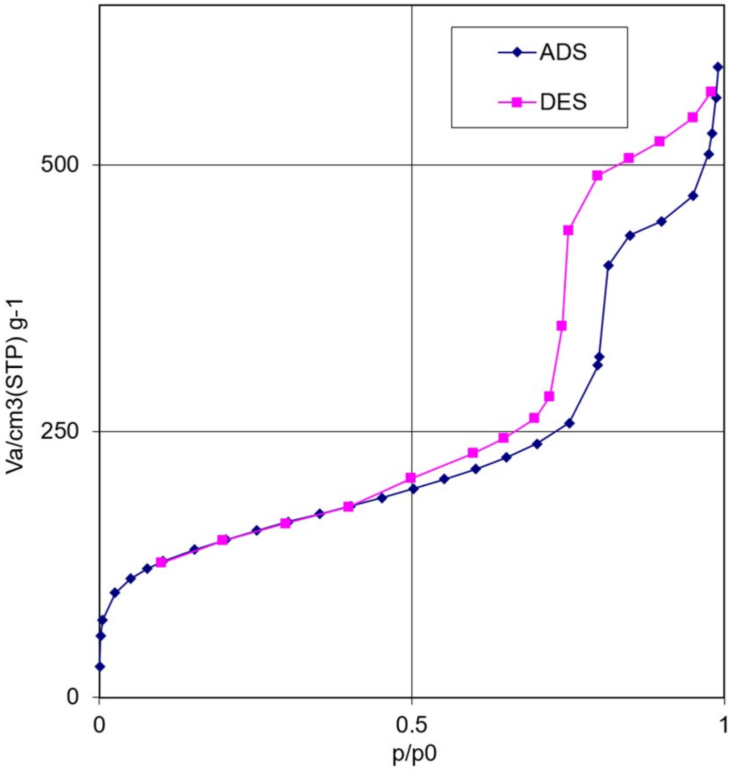

Figure S1: Nitrogen adsorption-desorption isotherm for Cl@BFPMO-IL

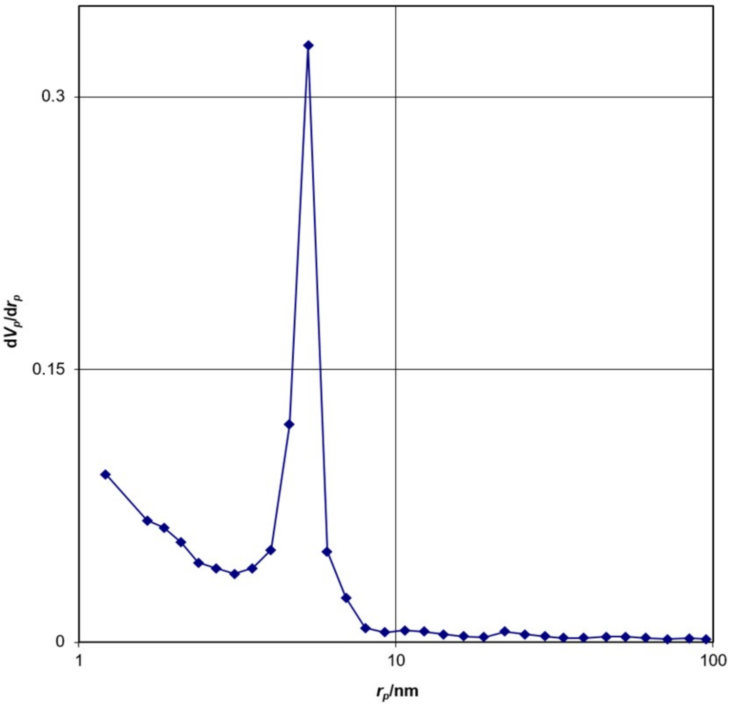

Figure S2. BJH Pore size distribution for Cl@BFPMO-IL.

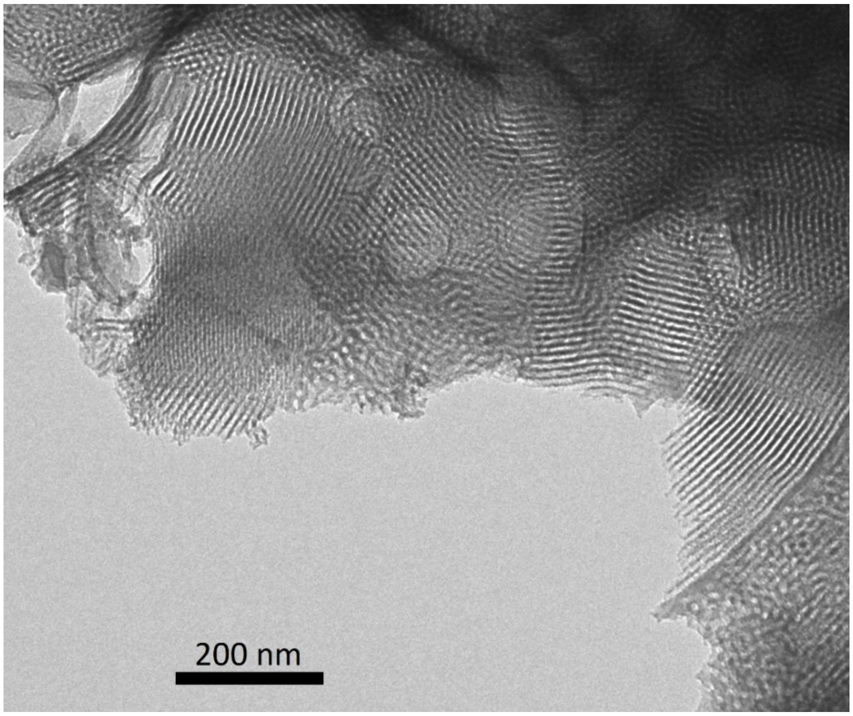

Figure S3: TEM image for Cl@BFPMO-IL

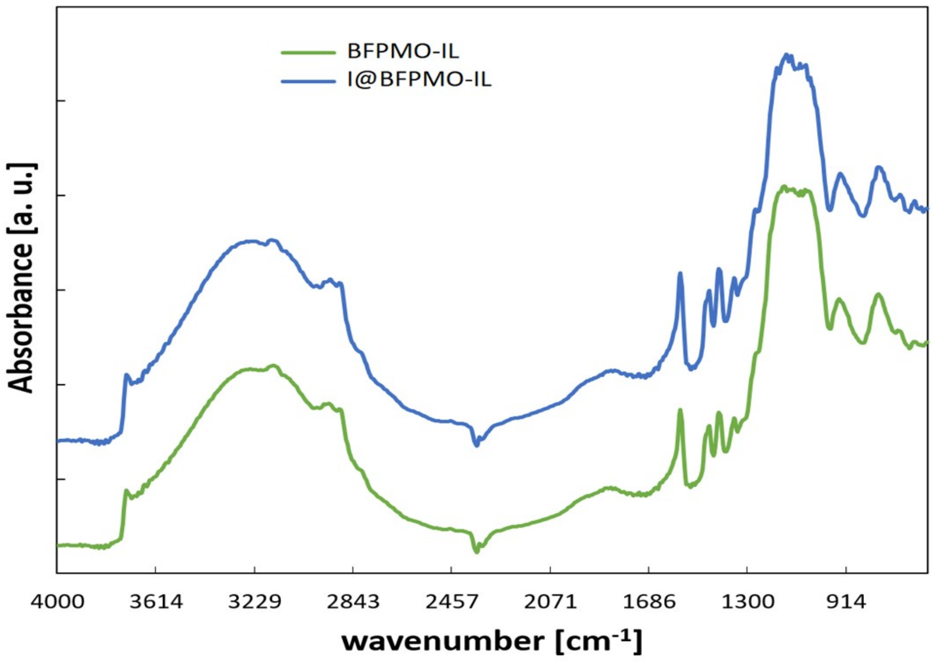

Figure S4. DRIFT spectrum for Cl@BFPMO-IL (green) and I@BFPMO-IL (blue)

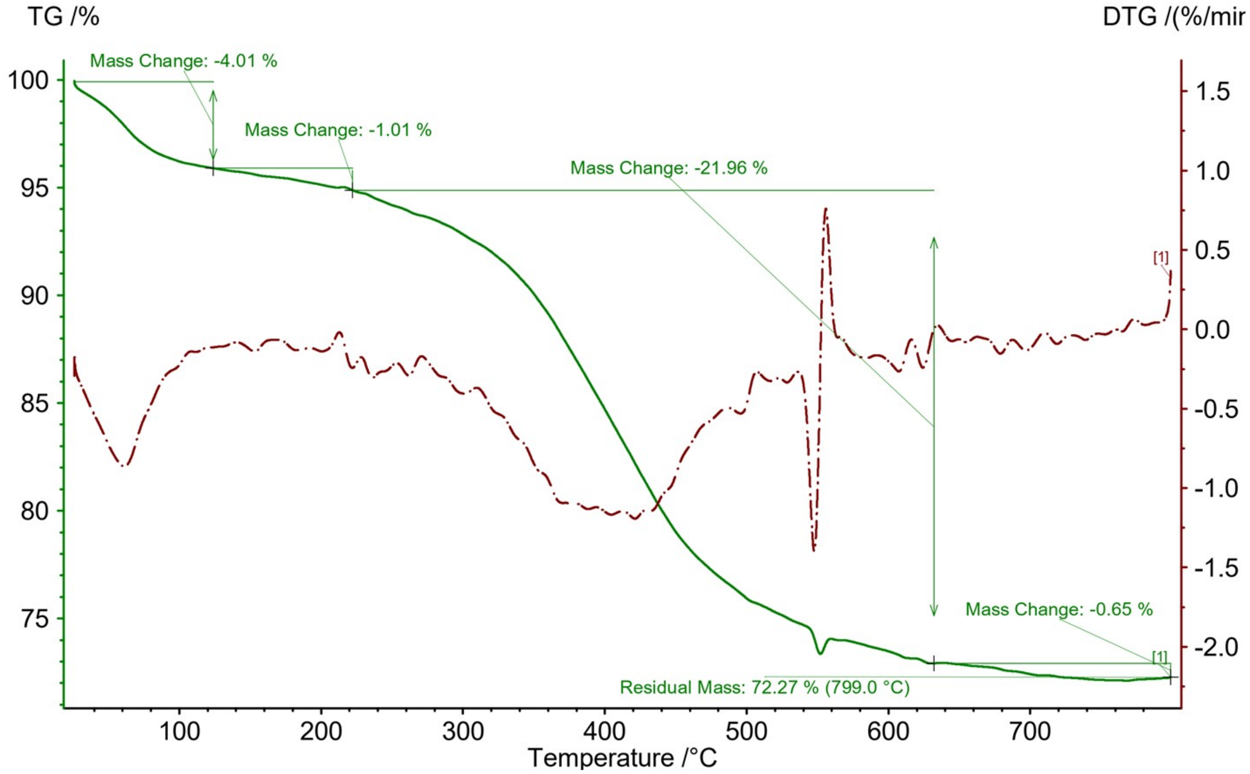

Figure S5. TG and DTG patterns for Cl@BFPMO-IL

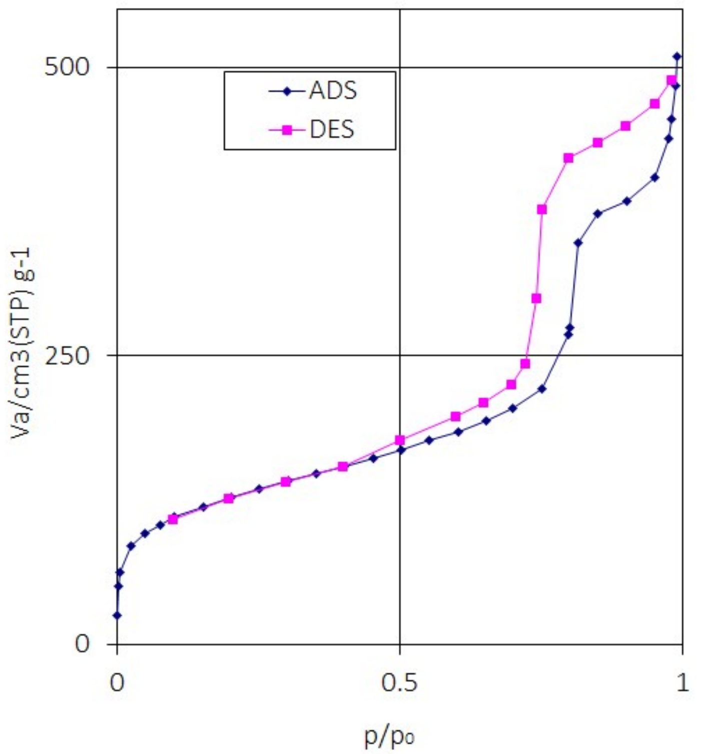

Figure S6. Nitrogen adsorption-desorption isotherm for Br@BFPMO-IL

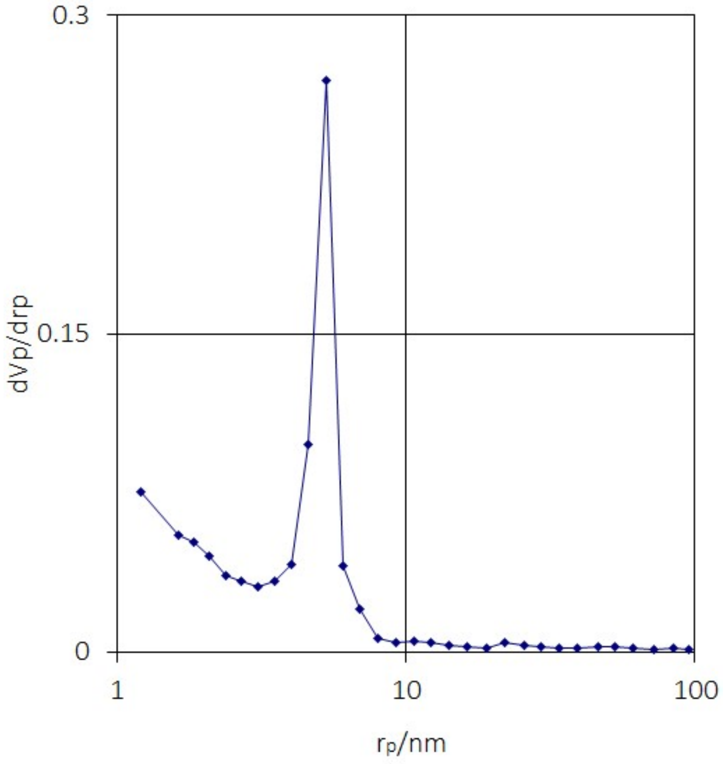

Figure S7. BJH Pore size distribution for Br@BFPMO-IL

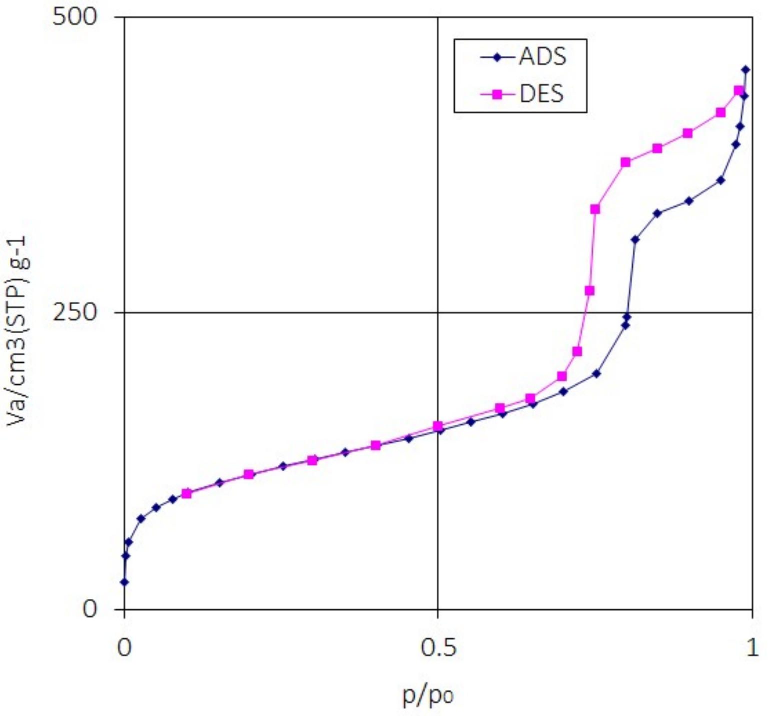

Figure S8. Nitrogen adsorption-desorption isotherm for BF_4@BFPMO-IL

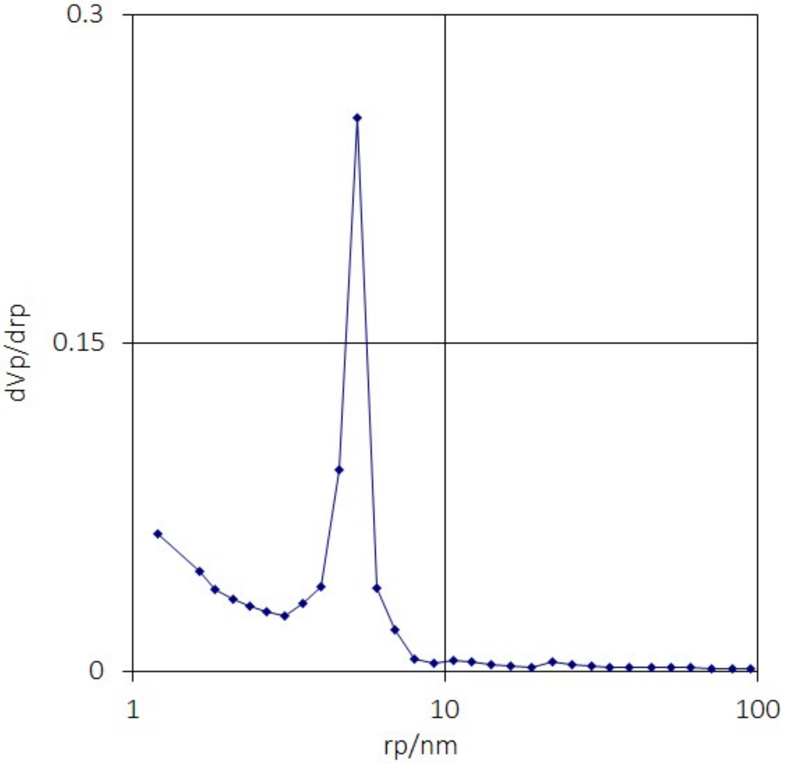

Figure S9. BJH Pore size distribution for BF_4@BFPMO-IL

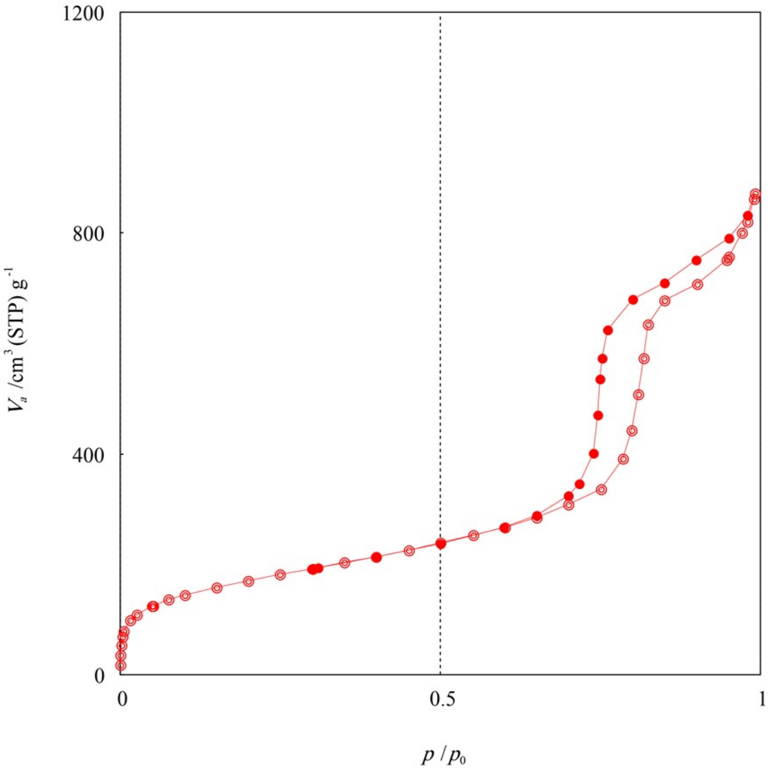

Figure S10. Nitrogen adsorption-desorption isotherm for PMO-IL

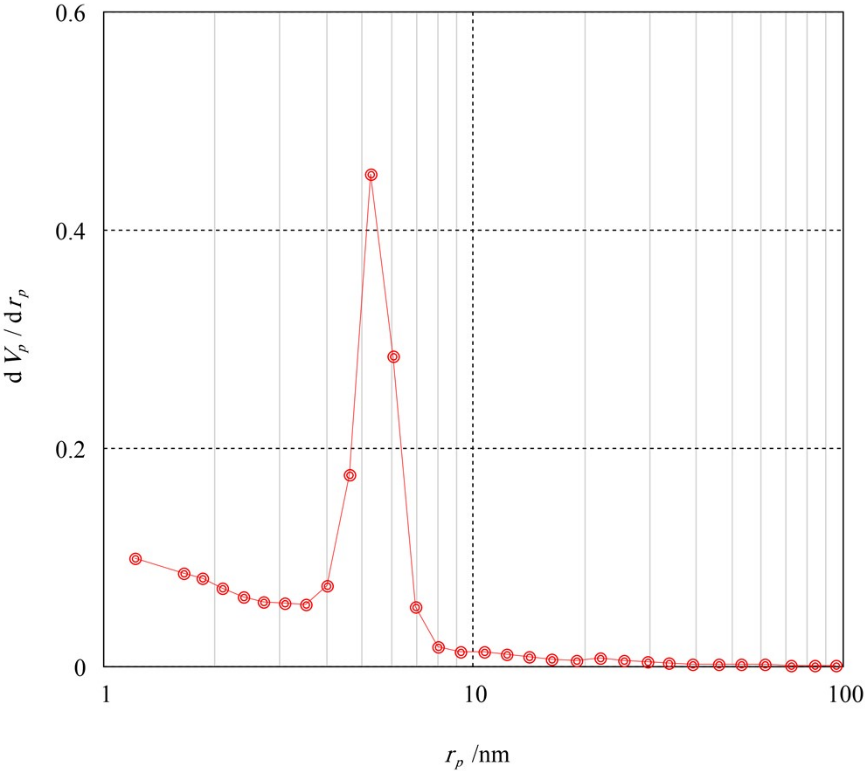

Figure S11. BJH Pore size distribution for PMO-IL

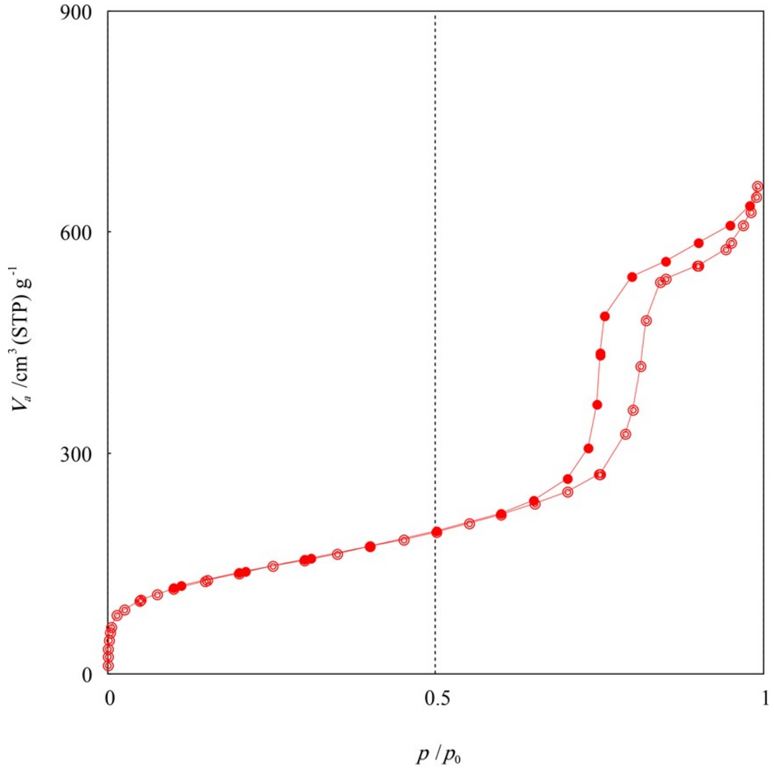

Figure S12. Nitrogen adsorption-desorption isotherm for I@PMO-IL

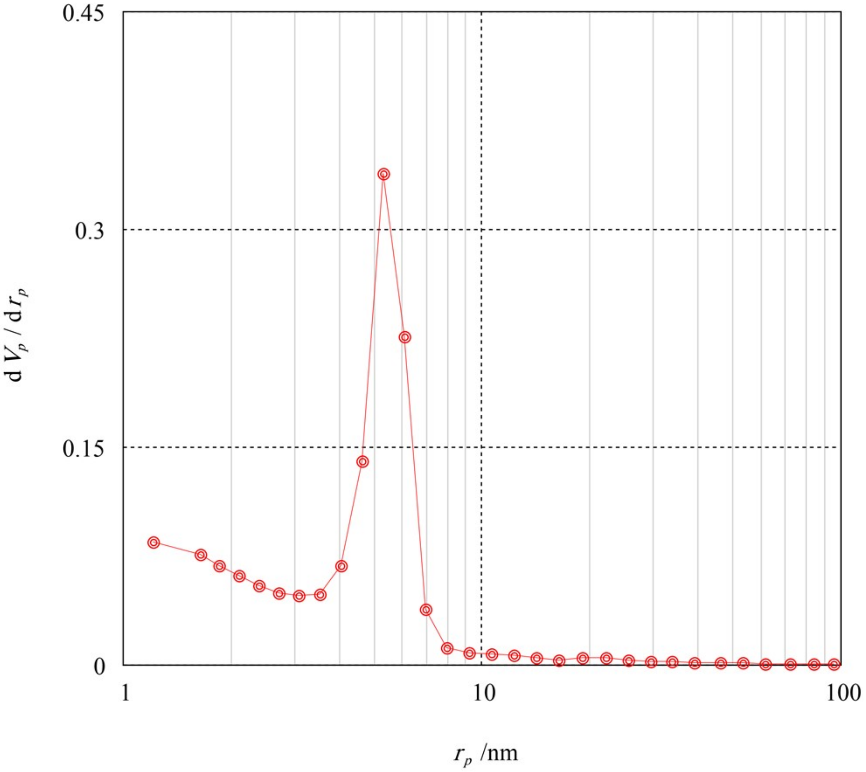

Figure S13. BJH Pore size distribution for I@PMO-IL

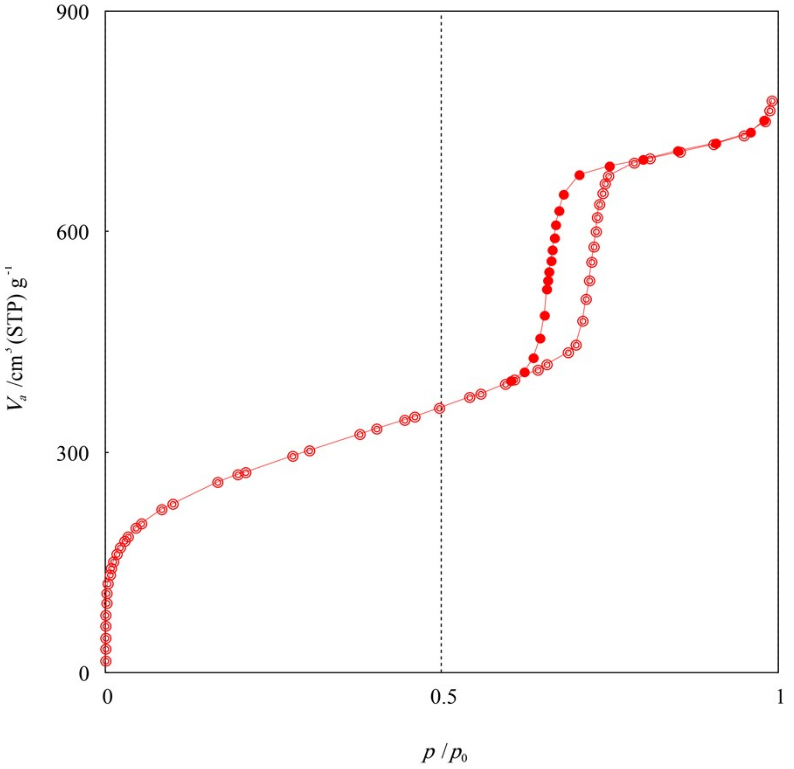

Figure S14. Nitrogen adsorption-desorption isotherm for SBA-15

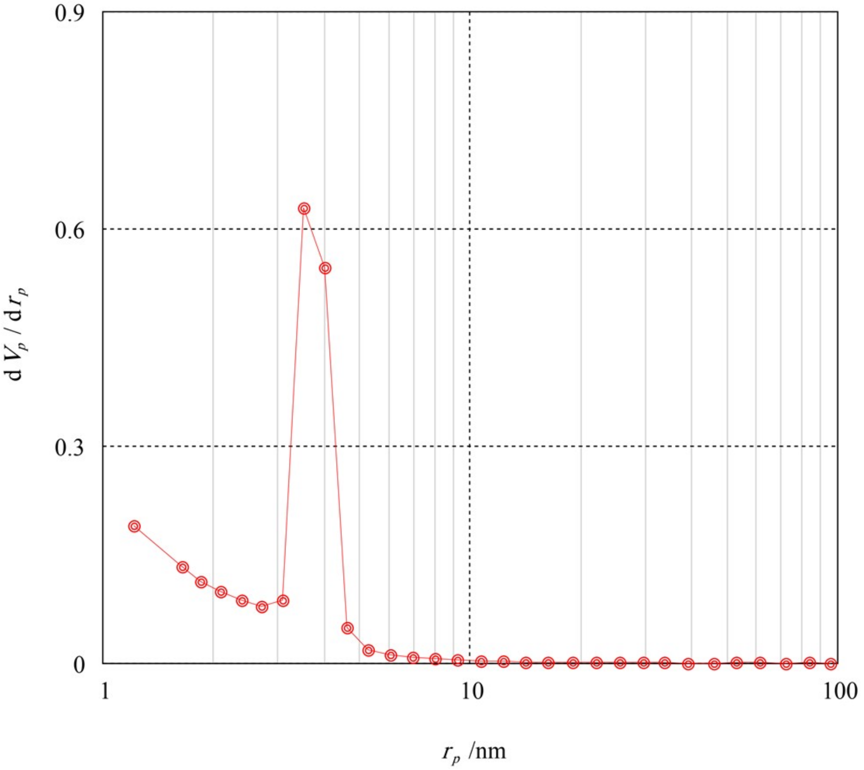

Figure S15. BJH Pore size distribution for SBA-15

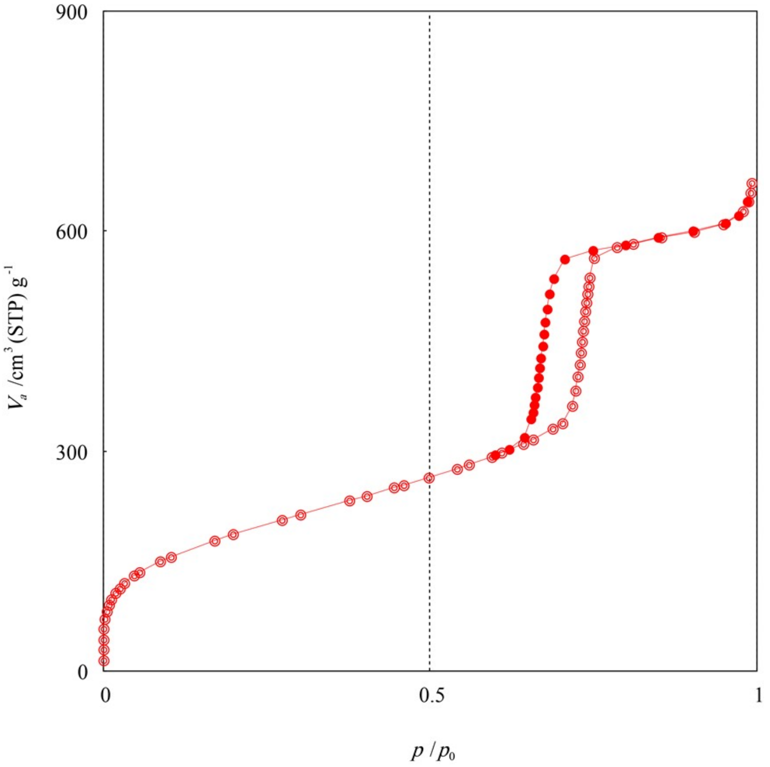

Figure S16. Nitrogen adsorption-desorption isotherm for I-N$^+$Me$_3$@SBA-15

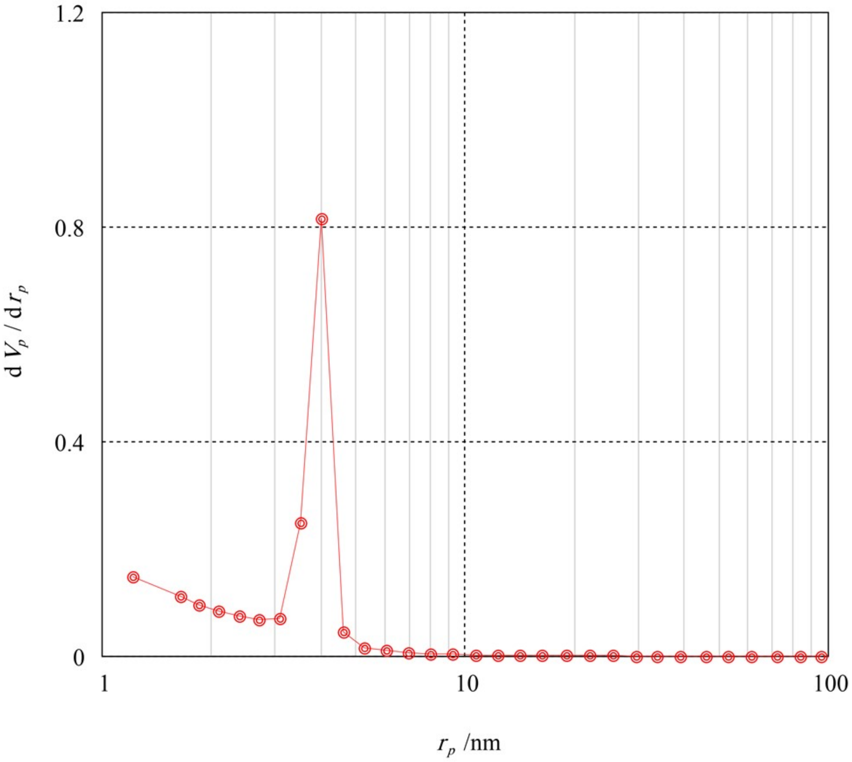

Figure S17. BJH Pore size distribution for I-N$^+$Me$_3$@SBA-15

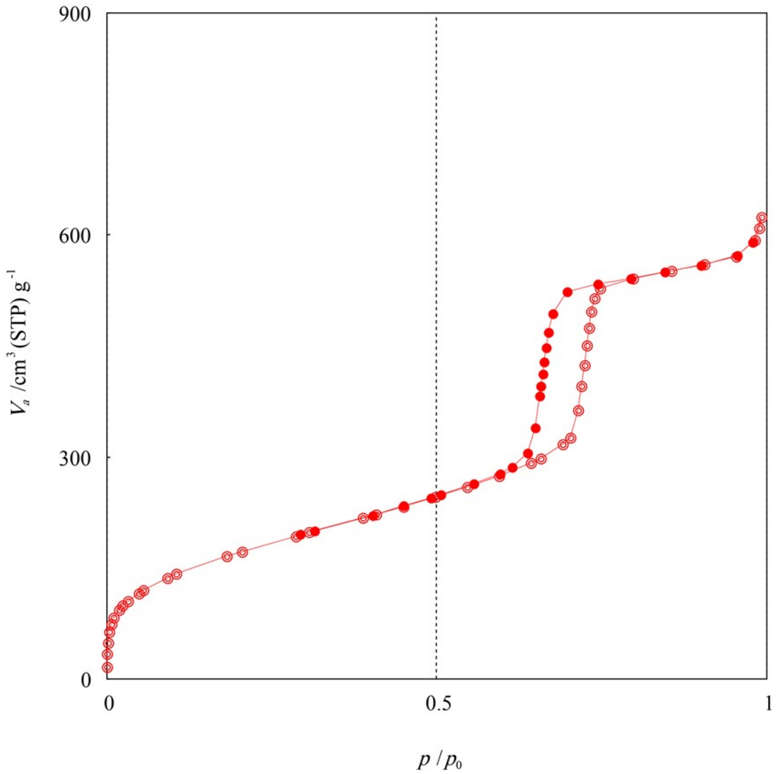

Figure S18. Nitrogen adsorption-desorption isotherm for I-MPIm@SBA-15

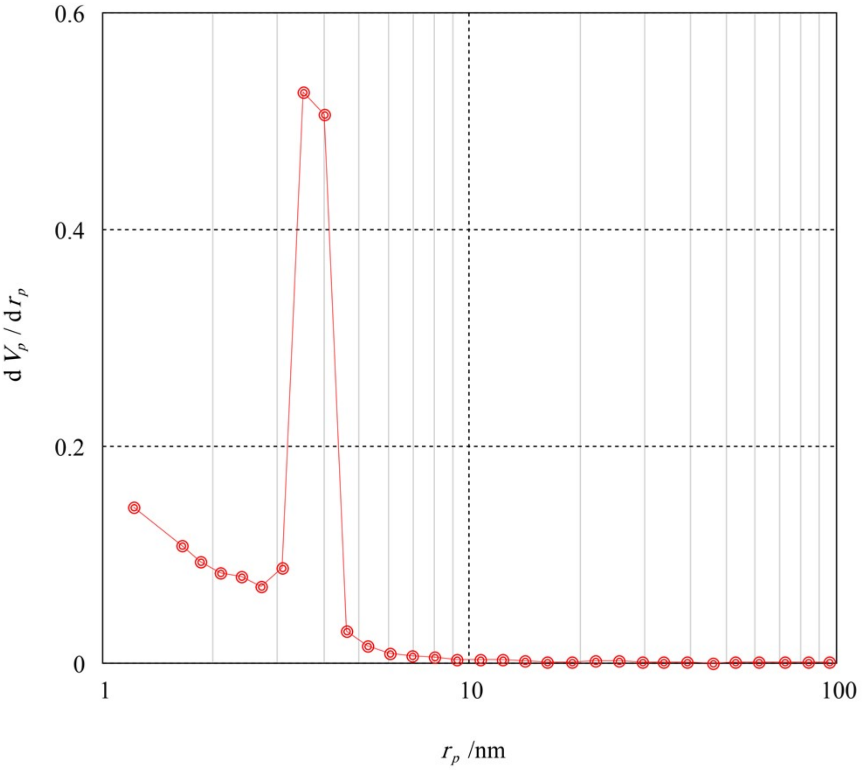

Figure S19. BJH Pore size distribution for I-MPIm@SBA-15

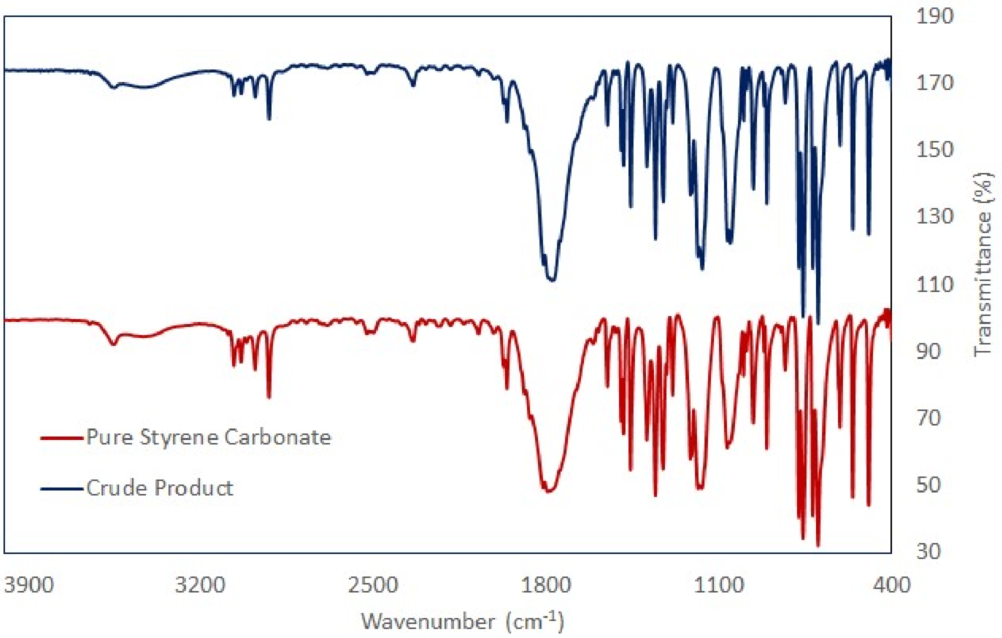

Figure S20. FT-IR spectra for crude product and pure styrene carbonate

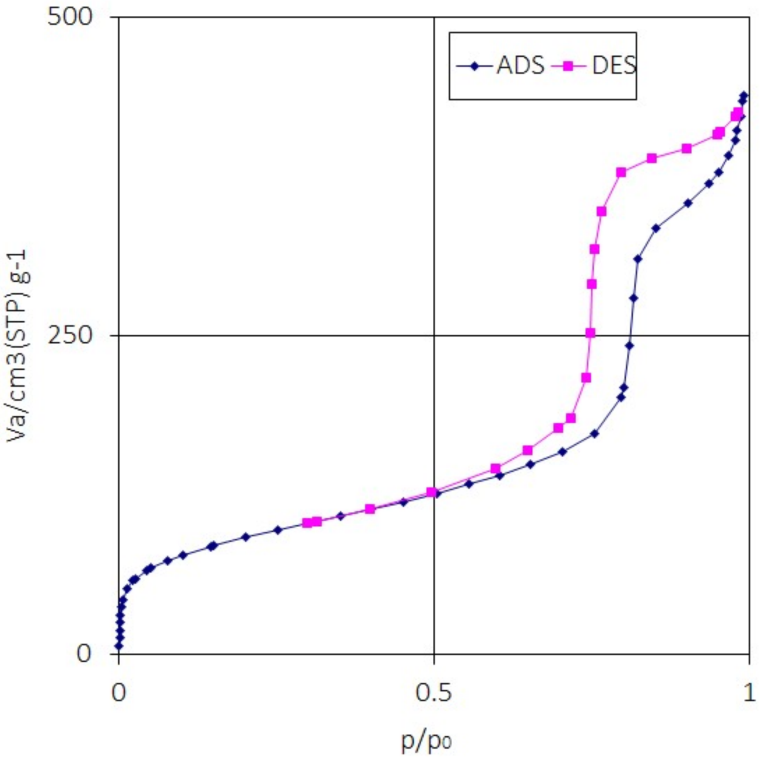

Figure S21. Nitrogen adsorption-desorption isotherm for recovered I@BFPMO-IL

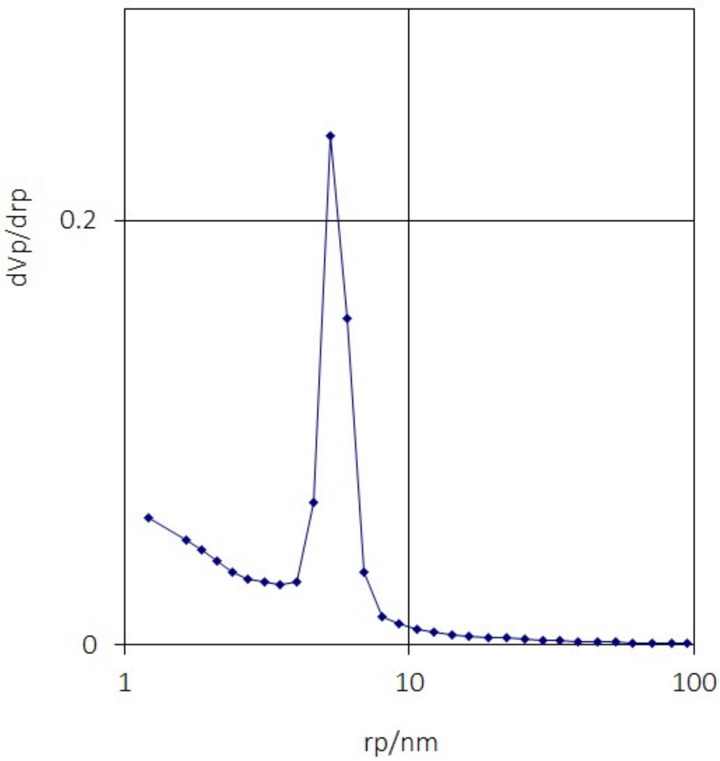

Figure S22. BJH Pore size distribution for recovered I@BFPMO-IL

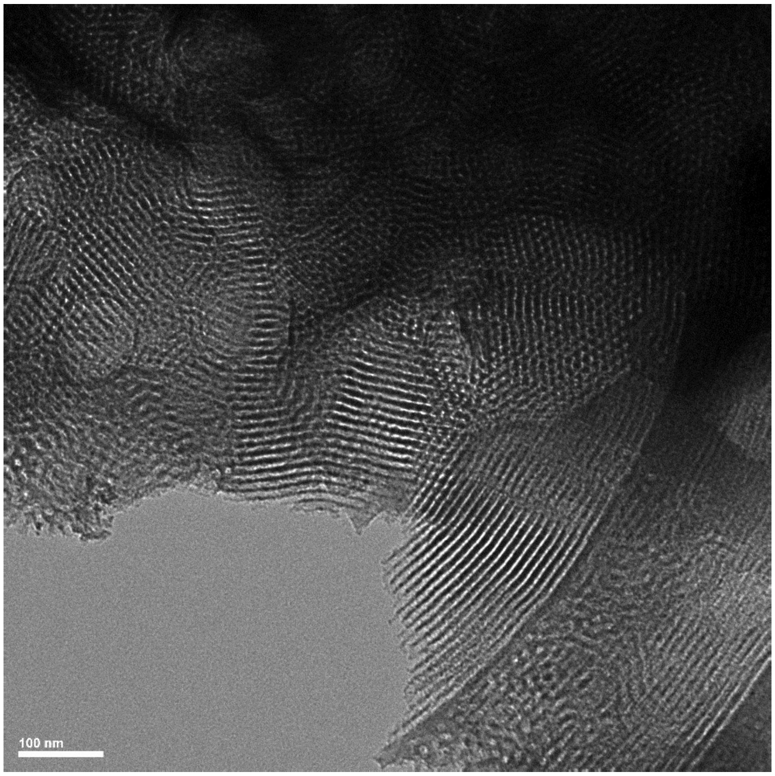

Figure S23. TEM Image for recovered I@BFPMO-IL

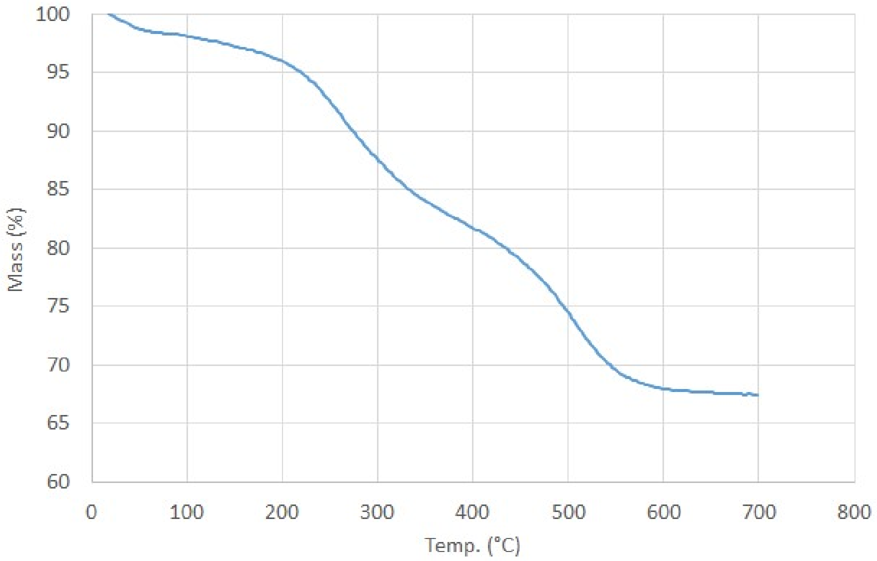

Figure S24. TG pattern for recovered I@BFPMO-IL

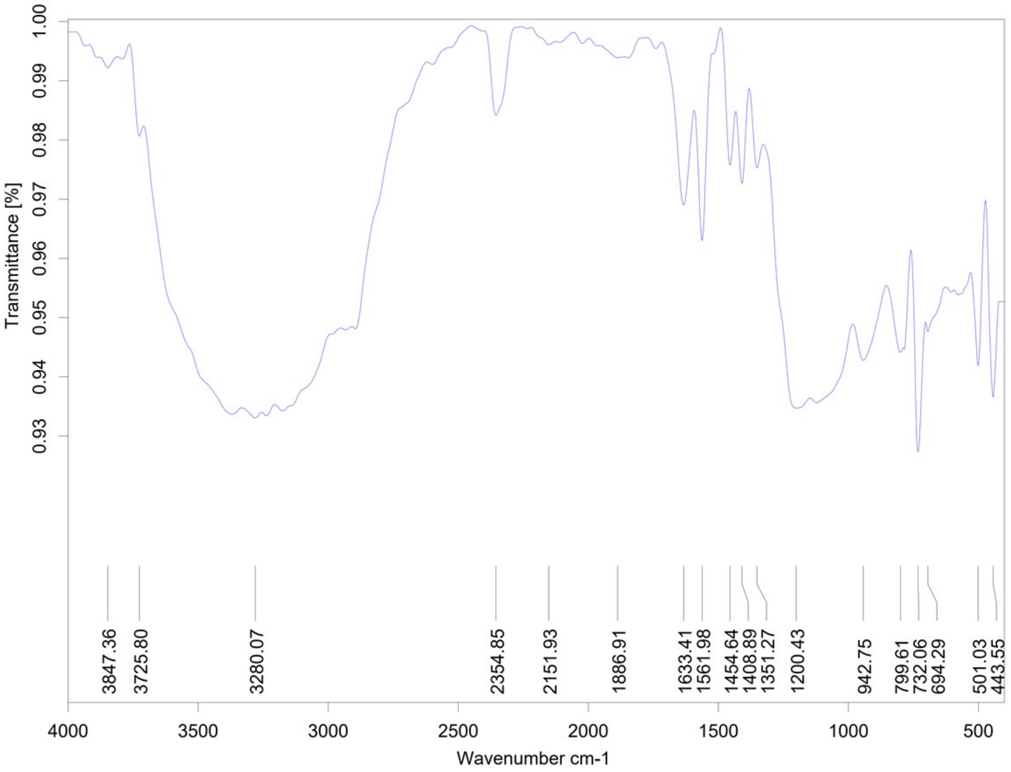

Figure S25. DRIFT spectrum for recovered I@BFPMO-IL

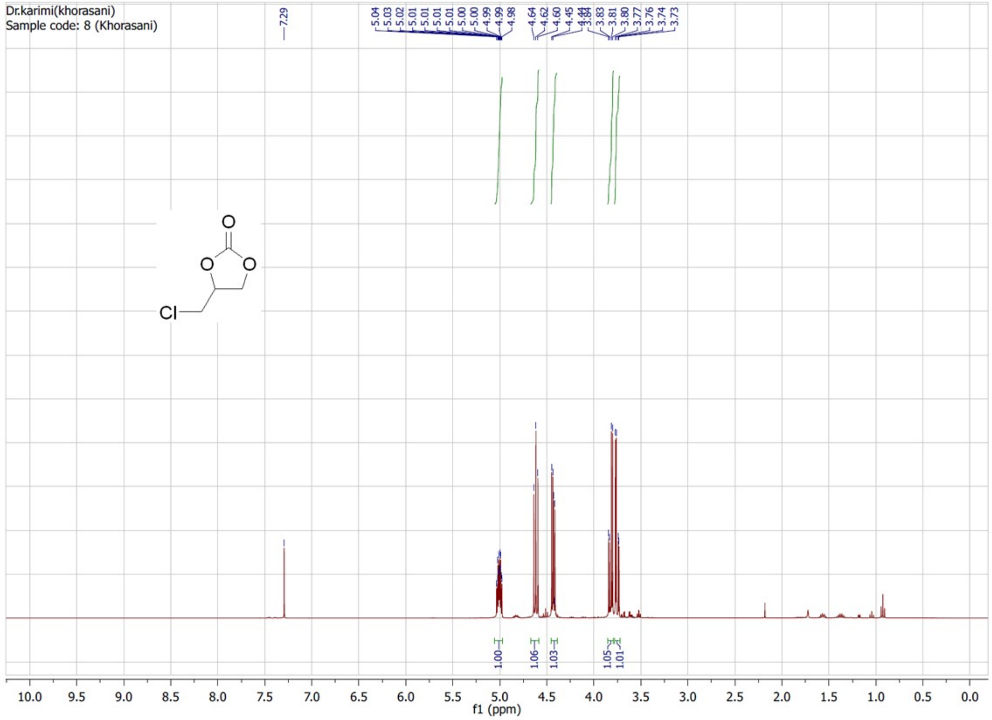

Figure S26. ^{1}H-NMR spectrum for (Chloromethyl)ethylene carbonate in $CDCl_3$ as solvent.

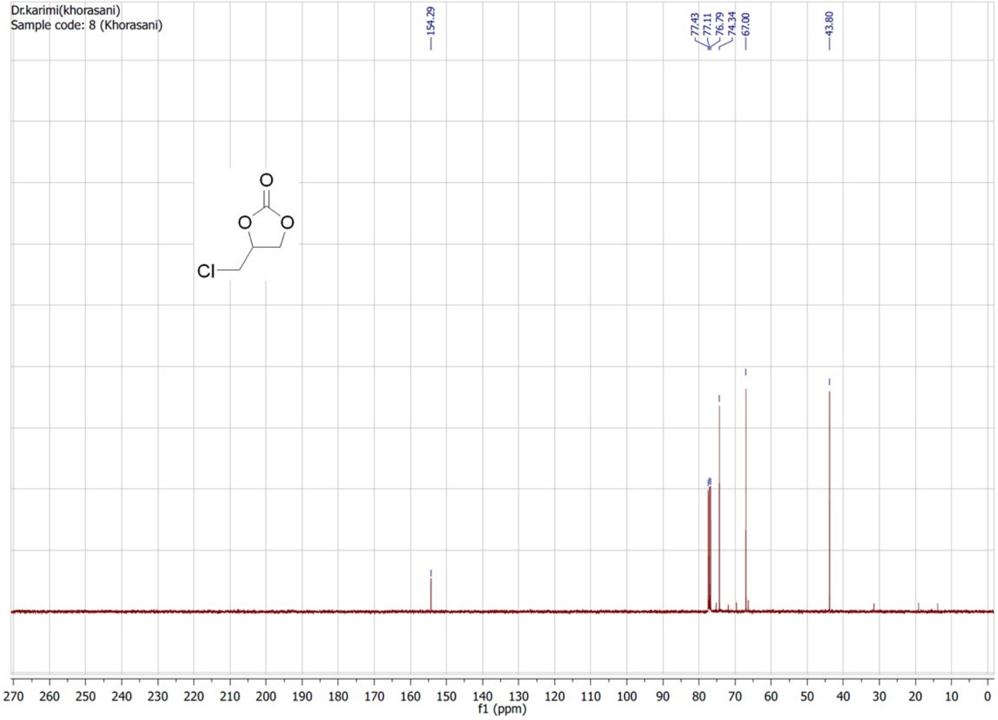

Figure S27. ^{13}C-NMR spectrum for (Chloromethyl)ethylene carbonate in $CDCl_3$ as solvent

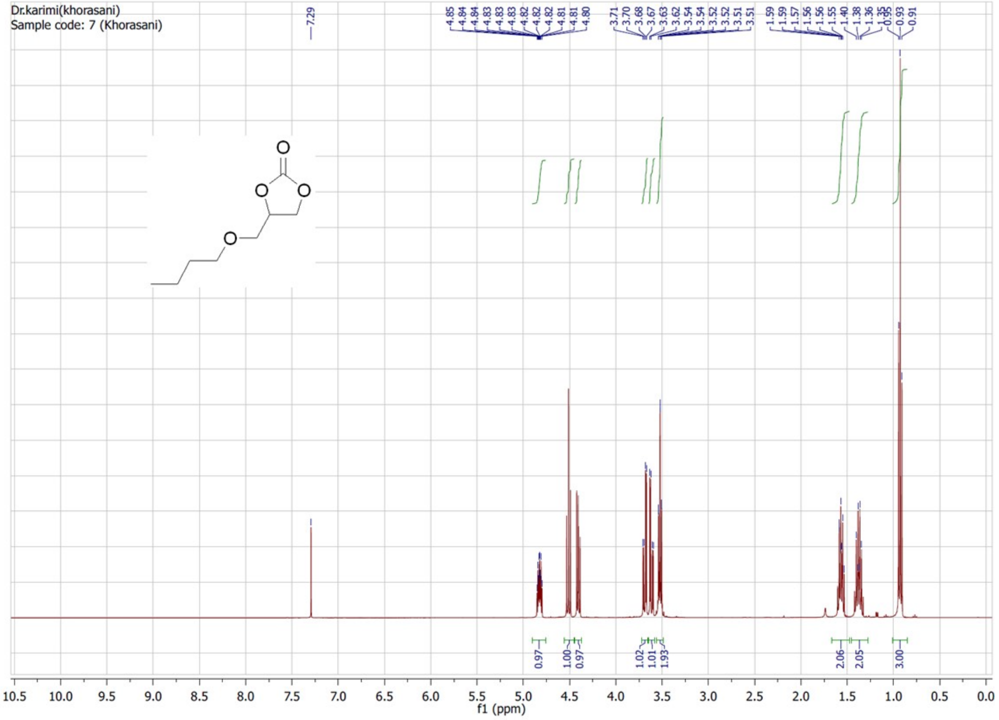

Figure S28. ^{1}H-NMR spectrum for (butoxymethyl)ethylene carbonate in $CDCl_3$ as solvent.

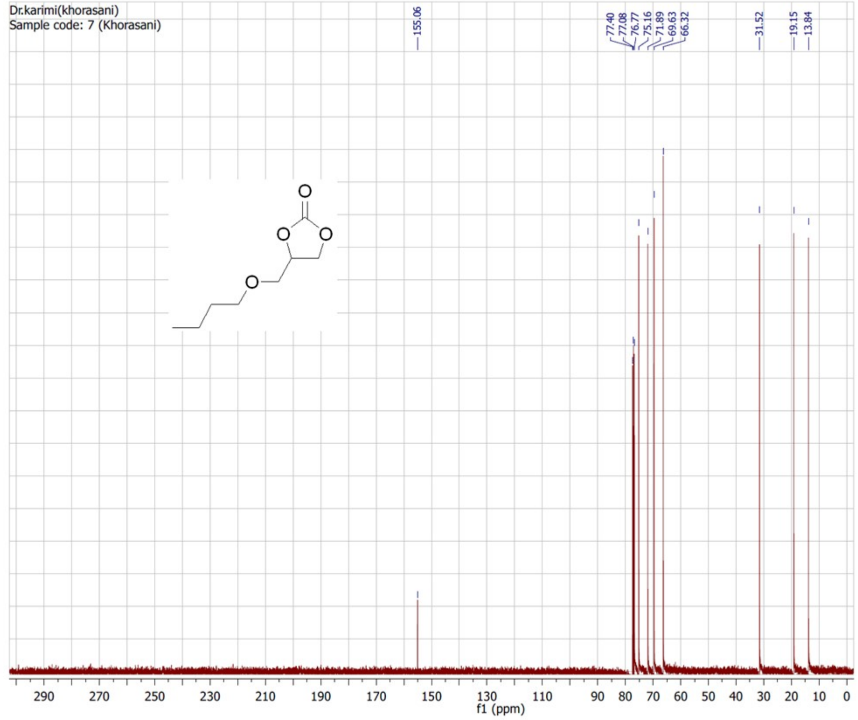

Figure S29. ^{13}C-NMR spectrum for (butoxymethyl)ethylene carbonate in $CDCl_3$ as solvent

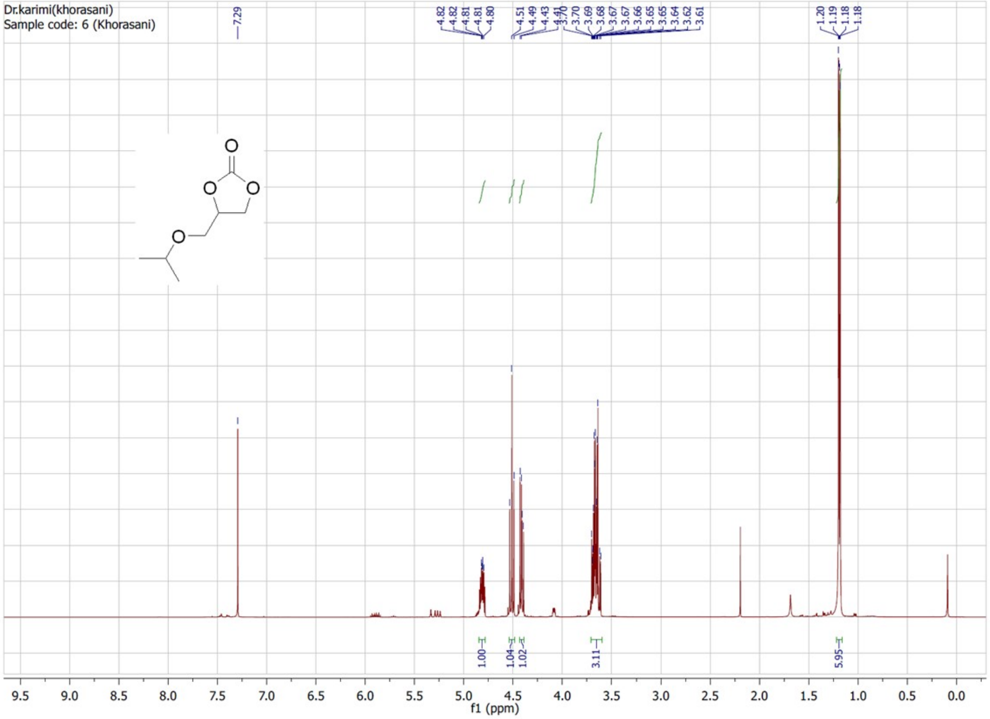

Figure S30. ^{1}H-NMR spectrum for (isopropoxymethyl)ethylene carbonate in $CDCl_3$ as solvent.

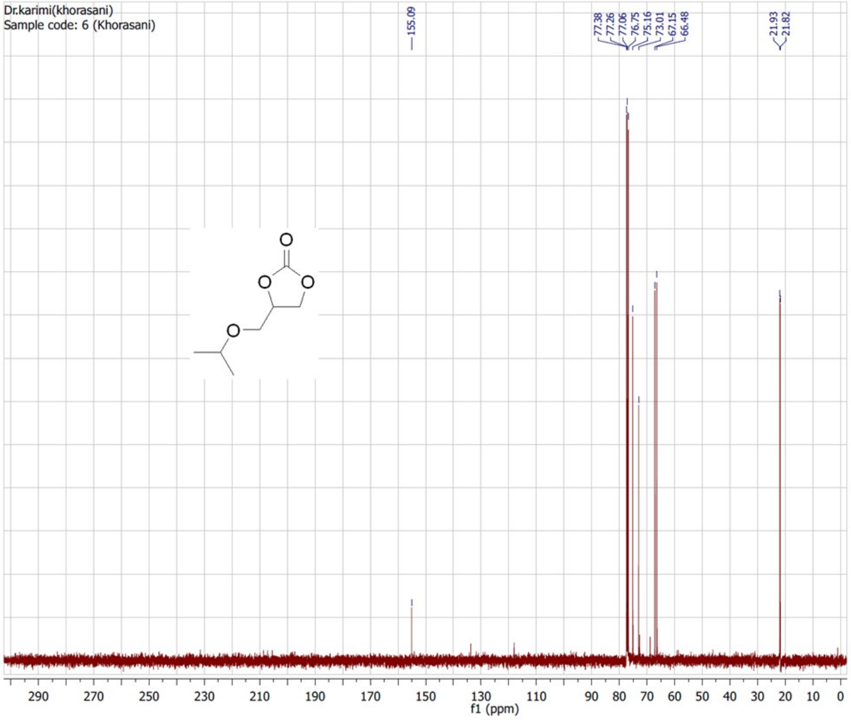

Figure S31. ^{13}C-NMR spectrum for (isopropoxymethyl)ethylene carbonate in $CDCl_3$ as solvent

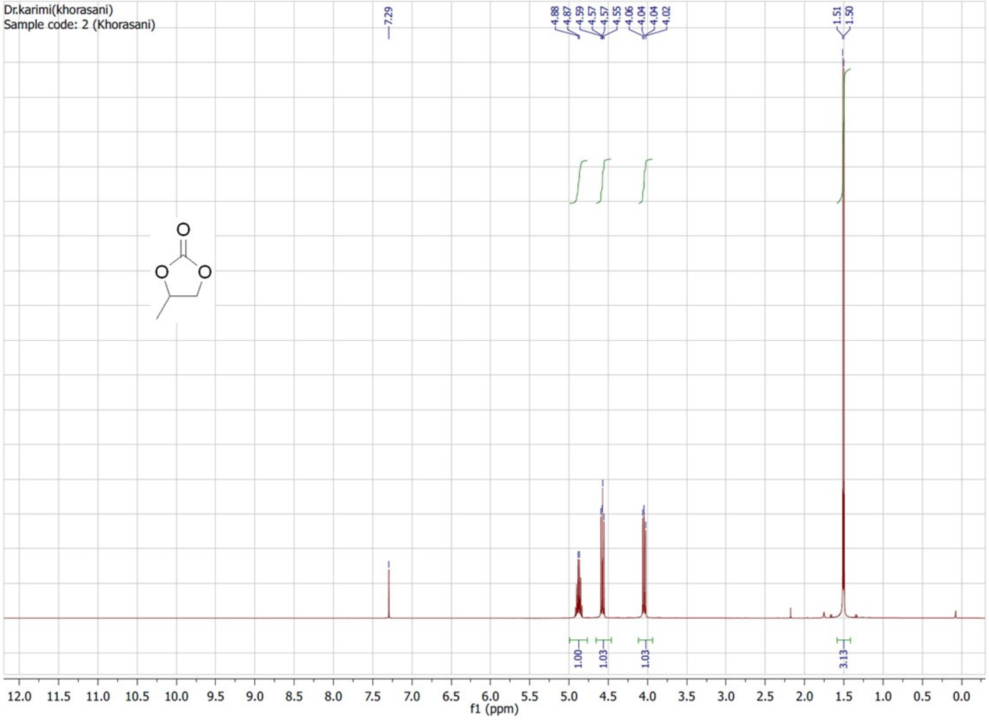

Figure S32. ^{1}H-NMR spectrum for propylene carbonate in $CDCl_3$ as solvent.

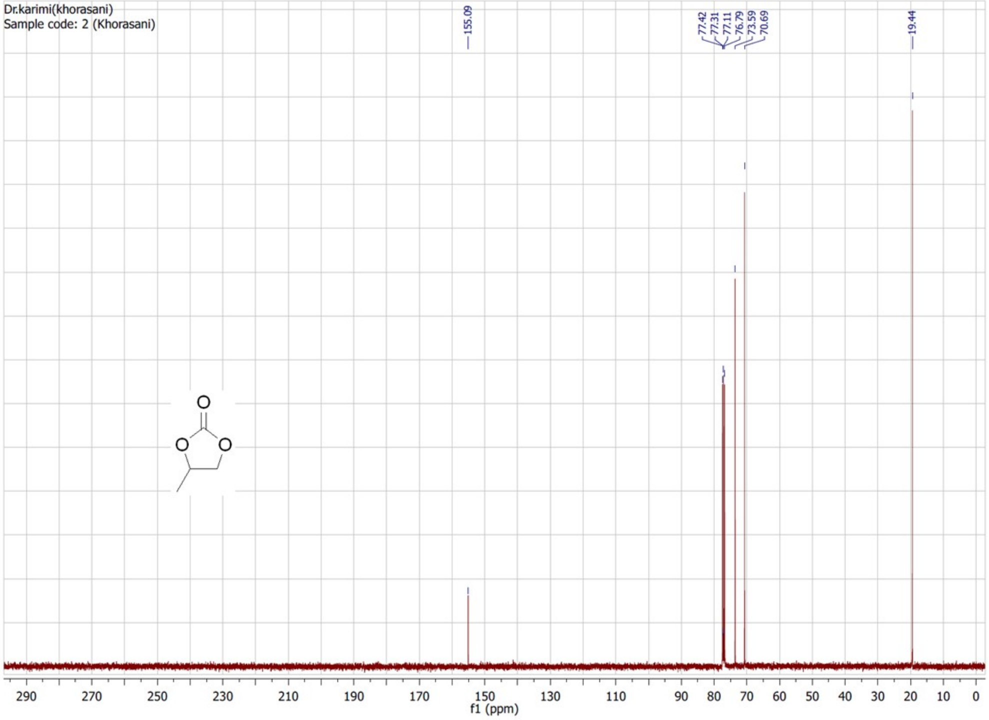

Figure S33. ^{13}C-NMR spectrum for propylene carbonate in $CDCl_3$ as solvent

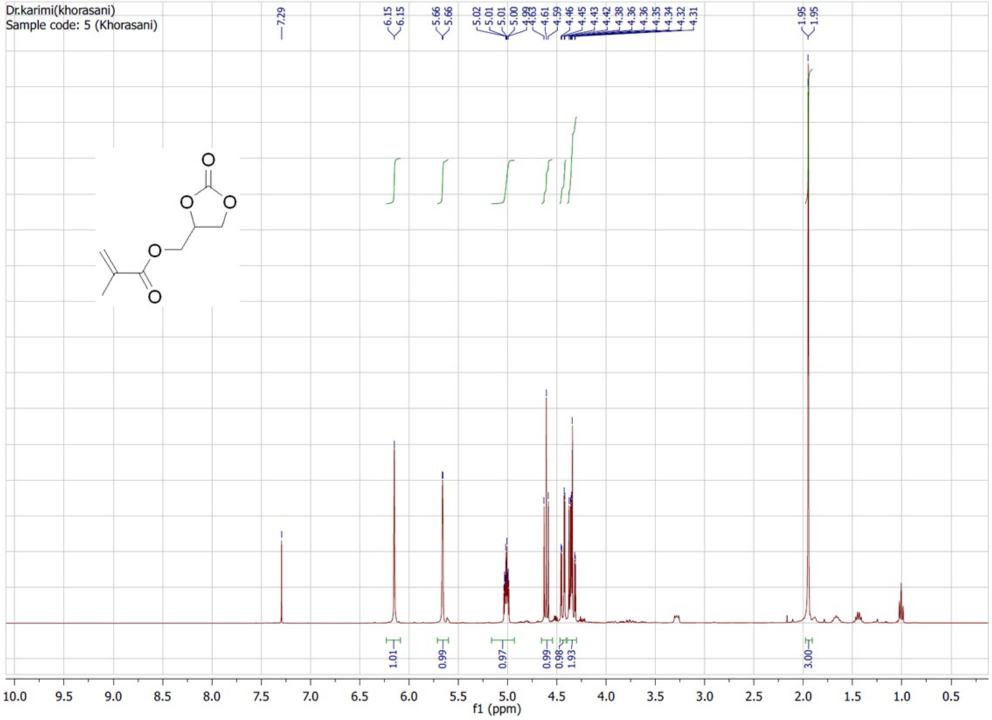

Figure S34. ^{1}H-NMR spectrum for (2-oxo-1,3-dioxolan-4-yl)-methyl methacrylate in $CDCl_3$ as solvent

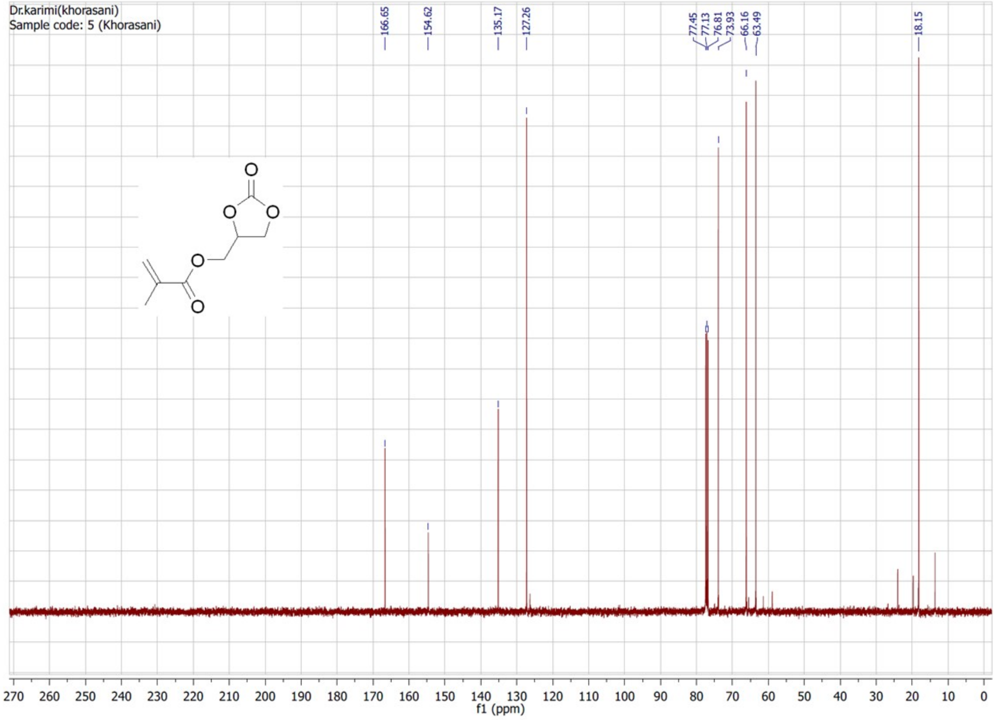

Figure S35. ^{13}C-NMR spectrum for (2-oxo-1,3-dioxolan-4-yl)-methyl methacrylate in $CDCl_3$ as solvent

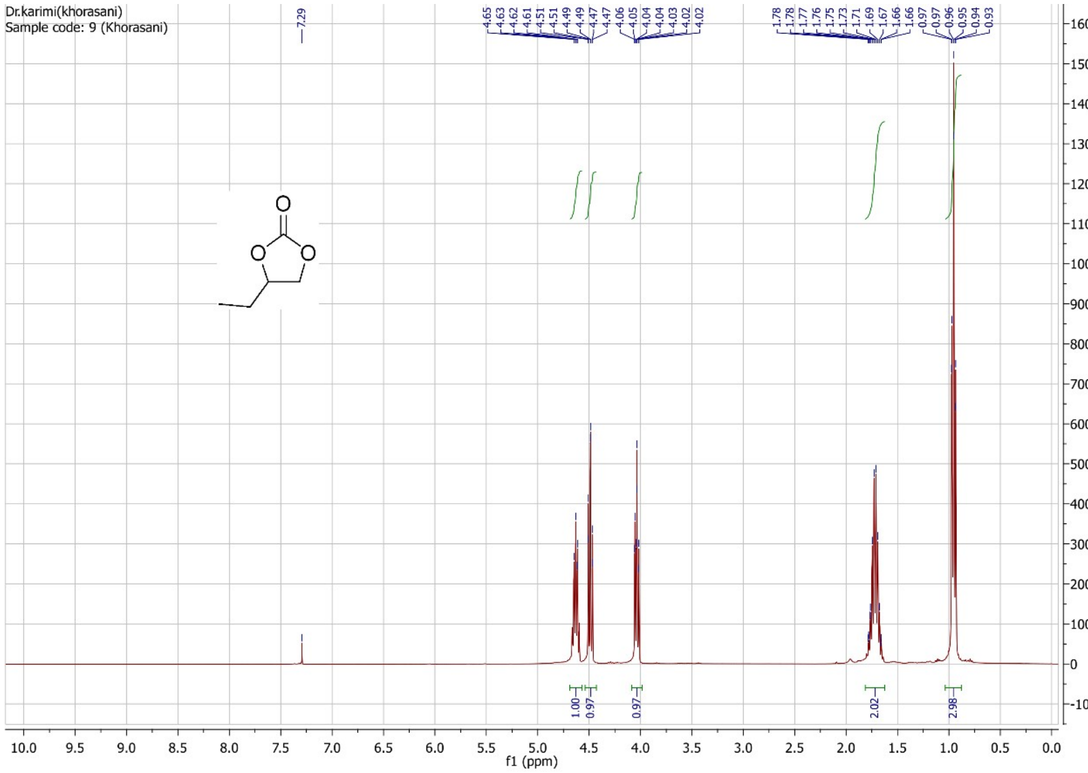

Figure S36. ^{1}H-NMR spectrum for 1,2-butylene carbonate in $CDCl_3$ as solvent

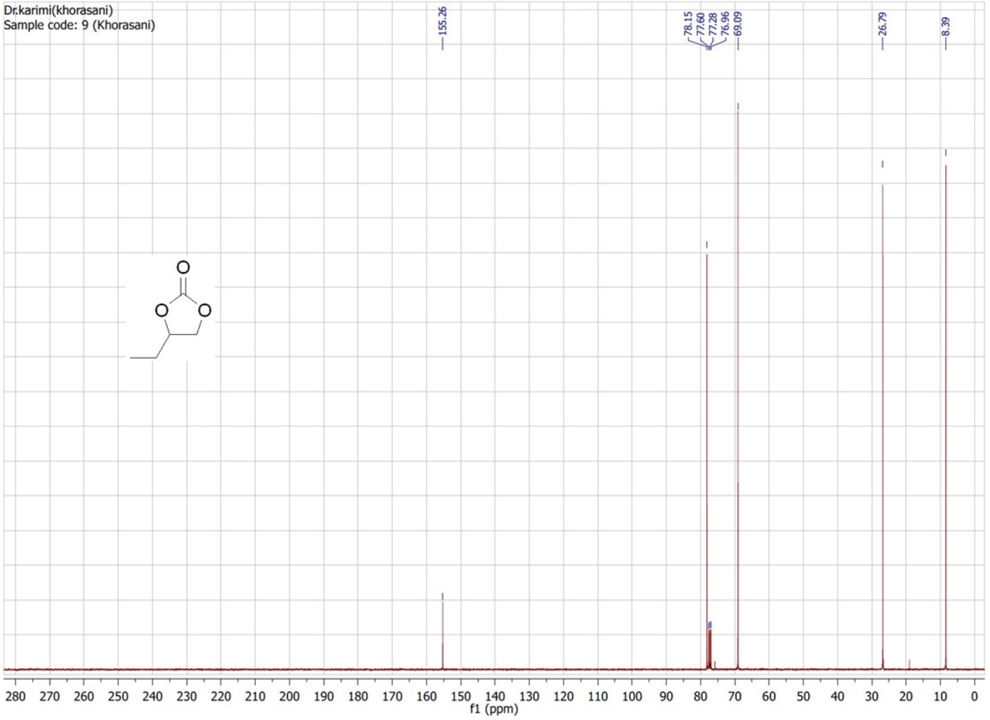

Figure S37. ^{13}C-NMR spectrum for 1,2-butylene carbonate in $CDCl_3$ as solvent

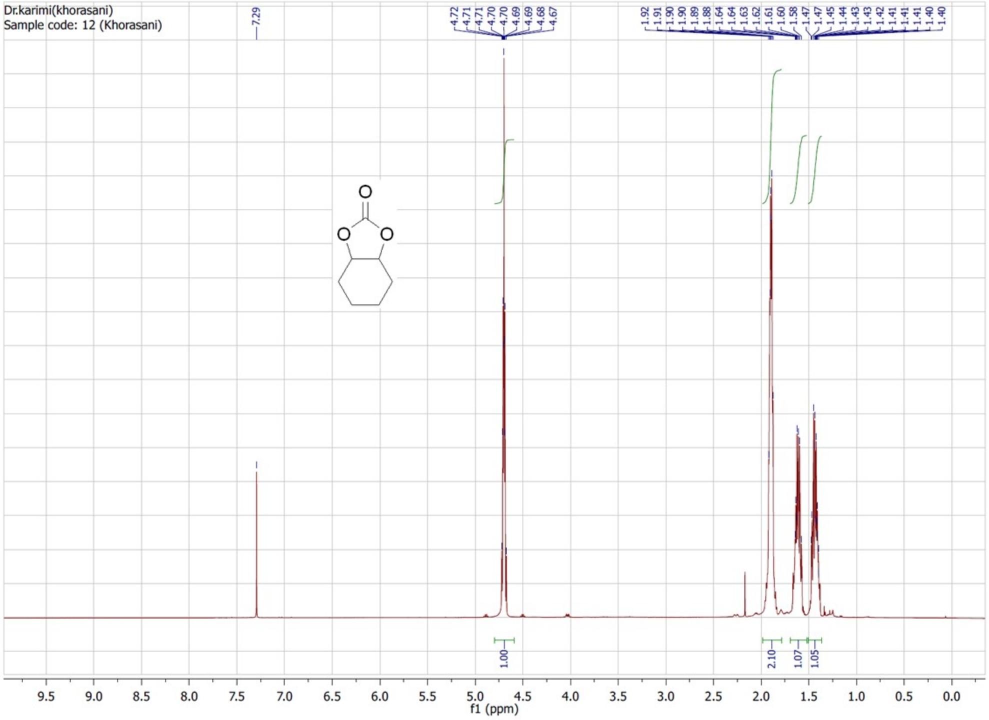

Figure S38. ^{1}H-NMR spectrum for cyclohexene carbonate in $CDCl_3$ as solvent

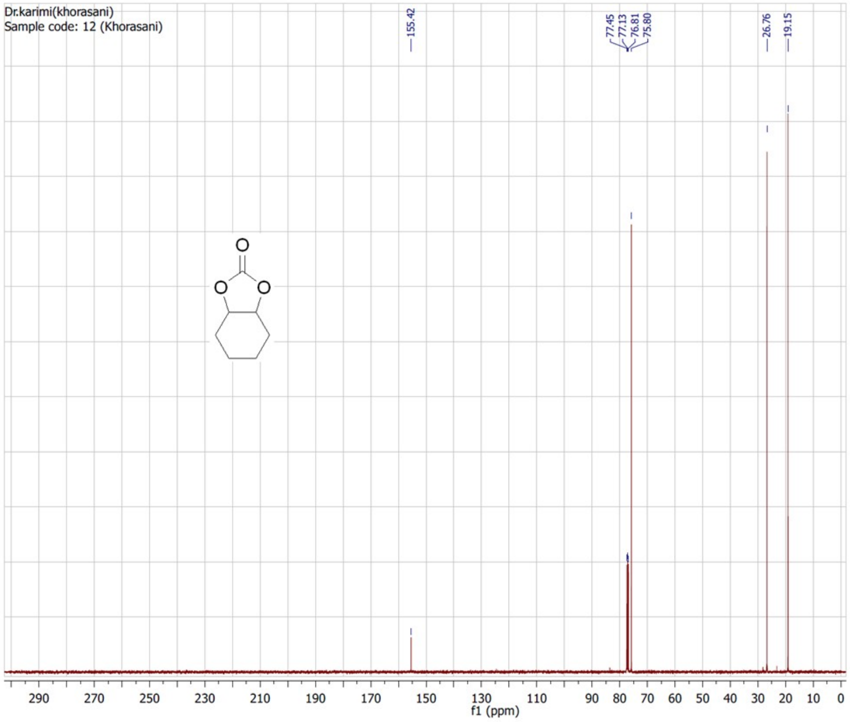

Figure S39. ^{13}C-NMR spectrum for cyclohexene carbonate in $CDCl_3$ as solvent