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# Supporting information

# Cycloaddition of carbon dioxide to epoxides catalysed by supported ionic liquids

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# 1 Experimental

All reagents were purchased from Sigma-Aldrich and used without further purification. $CO_2$ 98% was purchased by Linde and the pattern mixture of $CO_2$ (composition %: 15.83 $CO_2$, 0.40 $CH_4$, 0.41 CO, 84.36 $N_2$) was provided by Praxair.

## 1.1. Synthesis and characterization of Ionic Liquids and SILP materials

The synthesis of the BMIm.X ionic liquids (where X = Cl, Br, I) were synthetized as follow: a solution of fresh distilled 1-methyimidazol (37.47 g, 0.4563 mol.) and butyl halide (0.9127 mol.) was kept in refluxing for 48 h. After this, the solution was cooled until room temperature and then all the volatiles removed under vacuum. The resulting yellow oil solution was dissolved in a hot mixture acetone/methanol and left in fridge overnight until crystallization, filtered and dried under vacuum. In all the cases the desired products were obtained in high yields and purity. Once prepared, they were used as catalysts in the reaction of cycloaddition of carbon dioxide to epoxides and as substrates in the preparation of adsorbed SBMIm.X.

*1-Butyl-3-methylimidazolium chloride (BMIm.Cl).*[1] White solid (82%). $^1H$ NMR (300 MHz, $D_2O$) δ ppm 0.89 (t, J = 7.4 Hz, 3H); 1.22–1.35 (m, 2H); 1.82 (qp, J = 7.4 Hz, 2H); 3.86 (s, 3H); 4.17 (t, J = 7.2 Hz, 2H); 7.40 (d, J = 2.0 Hz, $^1H$); 7.45 (d, J = 2.0, 1H).

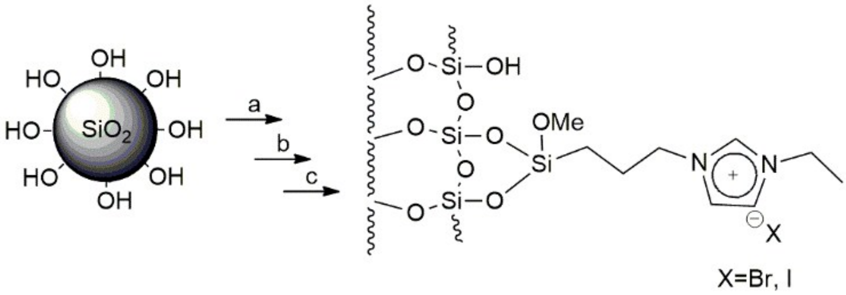
*1-Butyl-3-methylimidazolium bromide (BMIm.Br).*[2] Pale yellow solid (93%). $^1H$ NMR (400 MHz, $CDCl_3$) δ ppm 0.93–1.00 (m, 3H); 1.35–1.46 (m, 2H); 1.91–1.98 (m, 2H); 4.16 (s, 3H); 4.41 (t, J = 7.3 Hz, 2H); 7.79 (t, J = 1.7 Hz, 1H); 7.86 (t, J = 1.7 Hz, 1H); 10.19 (s, 1H).

*1-Butyl-3-methylimidazolium iodide (BMIm.I).*[2] Yellow oil (90%). $^1H$ NMR (400 MHz, $CDCl_3$) δ ppm 4.16 (s, 3H); 4.40 (t, J = 7.2 Hz, 2H); 7.73 (d, J = 1.5 Hz, 1H); 7.77 (d, J = 1.5 Hz, 1H); 9.81 (s, 1H).

SBMIm.Xn% SILPs (**1-5**) were prepared as follow, the corresponding ionic liquid (x g.) were dissolved in 10 mL of methanol and comercial $SiO_2$ (5-x g.) was added in constant stirring during 16 h. Finally, methanol was evaporated, and the resulting white solid dried off by vacuum at 80 °C for 6 h.

SEPIm.X SILPs (**8** and **9**) were prepared as reported in literature.[3] As observed in Scheme S2, first step is the activation of $SiO_2$ in acidic media, secondly, activated $SiO_2$ (5 g) was suspended in fresh distilled toluene (30 mL) and 3-chloropropyl(trimethoxy)silane was added drop by drop (4.95 g; 0.025 mol). This solution was refluxed for 72 h, then all the volatiles were removed under vacuum. The product chloropropyl silica gel was washed with ethanol-water-ethanol and finally dried under vacuum.

In the next reaction step, this product was dissolved with stoichiometric amounts of imidazole and refluxed during 24 h; then triethylamine was added (4 mL) and left to stirring during 4h. The resulting precipitated was filtered, washed with ethyl acetate-water-ethyl acetate and the resulting solution dried off by vacuum during 4 h. Finally, the resulting product was refluxed in acetone for 48 h with stoichiometric amounts of the corresponding ethyl halide (Br and I), filtered and washed tree times with ethyl acetate-water-ethyl acetate, finally dried under vacuum at 60 °C during 16 h to obtain 1-ethyl-3-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium halide (SEPIm.X).



**Scheme S1.** Synthetic route for synthesis of SILP materials and conditions. (a) 3-chloropropyltrimethoxysilane, toluene, 72 h, reflux, N2. (b) Imidazole, Toluene, 24h, reflux, $N_2$, triethylamine. (c) Ethane halide, acetone, room temperature, 24h.

### 1.2. Infra Red (IR)

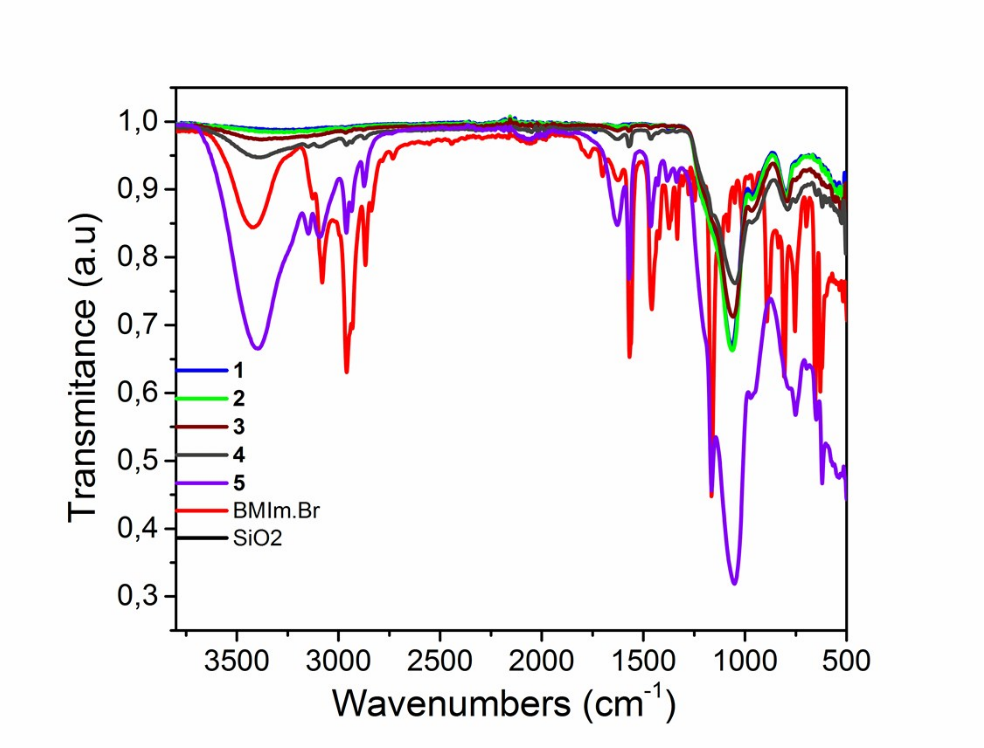


**Figure S1.** FTIR spectra corresponding to $SiO_2$, BMIm.Br and **1**-**5**.

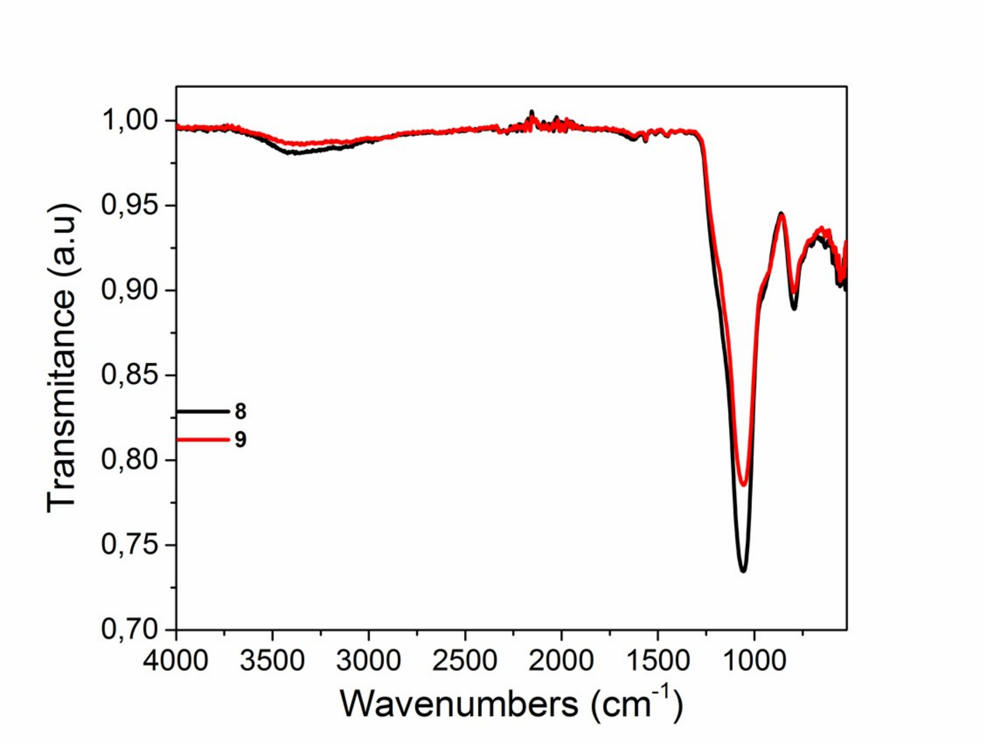


**Figure S2.** FTIR spectra corresponding to **8** and **9**.

### 1.3. Nuclear Magnetic Resonance (NMR)

SBMIm.$Br_{20}$ (**3**)*:* $^{29}Si$ CP-MAS NMR (99 MHz) δ ppm -98.36 (s) 105.73 (s) 107.96 (s); $^{13}C$ CP-MAS NMR (126 MHz) δ ppm 16.86 (s) 22.69 (s) 35.33 (s) 40.67 (s) 52.83 (s) 126.22 (s) 127.68 (s) 140.31 (s); FTIR: 2963.02 $cm^{-1}$(υC-H), 1629 $cm^{-1}$ (υC=N), 1569 $cm^{-1}$, 1163 $cm^{-1}$, 1058 $cm^{-1}$. BET area: 178.17 $m^2/g$; Ads $CO_2$: 0.001139641 mol/g.

SBMIm.$Br_{40}$ (**4**)*:* $^{29}Si$ CP-MAS NMR (99 MHz) δ ppm -114.03 (s) -110.95 (s) -104.80 (s) -101.10 (s) -98.03 (s) -94.95 (s); $^{13}C$ CP-MAS NMR (126 MHz) δ ppm 16.86 (s) 22.69 (s) 35.33 (s) 40.67 (s) 52.83 (s) 126.22 (s) 127.68 (s) 140.31 (s). FTIR: 2961 $cm^{-1}$(υC-H), 1629 $cm^{-1}$ (υC=N), 1569 $cm^{-1}$, 1167 $cm^{-1}$, 1048 $cm^{-1}$. BET area: 24.50. Ads $CO_2$: 0.001192093 mol/g.

SBMIm.$Cl_{40}$ (**6**)*:* $^{29}Si$ CP-MAS NMR (99 MHz) δ ppm -118.27 (s) -109.06 (s) -102.73 (s); $^{13}C$ CP-MAS NMR (126 MHz) δ ppm 11.65 (s) 17.43 (s) 30.24 (s) 34.79 (s) 47.53 (s) 121.48 (bs) 135.09 (s). BET area: 7.05.

SBMIm.$I_{40}$ (**7**)*:* $^{29}Si$ CP-MAS NMR (99 MHz) δ ppm -111.63 (s) -103.81 (s) -93.63 (s); $^{13}C$ CP-MAS NMR (126 MHz) δ ppm 12.21 (s) 17.79 (s) 30.34 (s) 36.14 (s) 48.11 (s) 121.90 (bs) 135.15 (s). BET area: 60.24 $m^2/g$.

SEPIm.Br (**8**): $^{29}Si$ CP-MAS NMR (99 MHz) δ ppm -112.4 (s) -103.37 (s) -69.59 (s) -60.12; $^{13}C$ CP-MAS NMR (126 MHz) δ ppm 7.56 (s) 11.45 (s) 13.49 (s) 22.13 (s) 43.39 (s) 49.94 (s) 120.69 (s) 133.96 (s). FTIR: 1629 $cm^{-1}$ (υC=N), 1567 $cm^{-1}$, 1057 $cm^{-1}$. BET area: 186.72 $m^2/g$.

### $^{29}$Si CP-MAS NMR

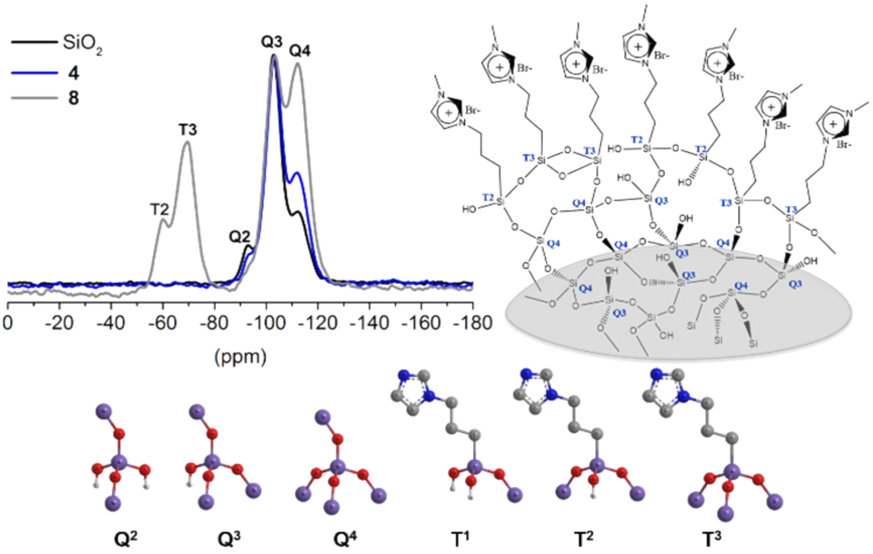


**Figure S3.** $^{29}$Si CP-MAS spectrum obtained for SILPs **4** and **8** with regard to $SiO_2$ and graphical interpretation.

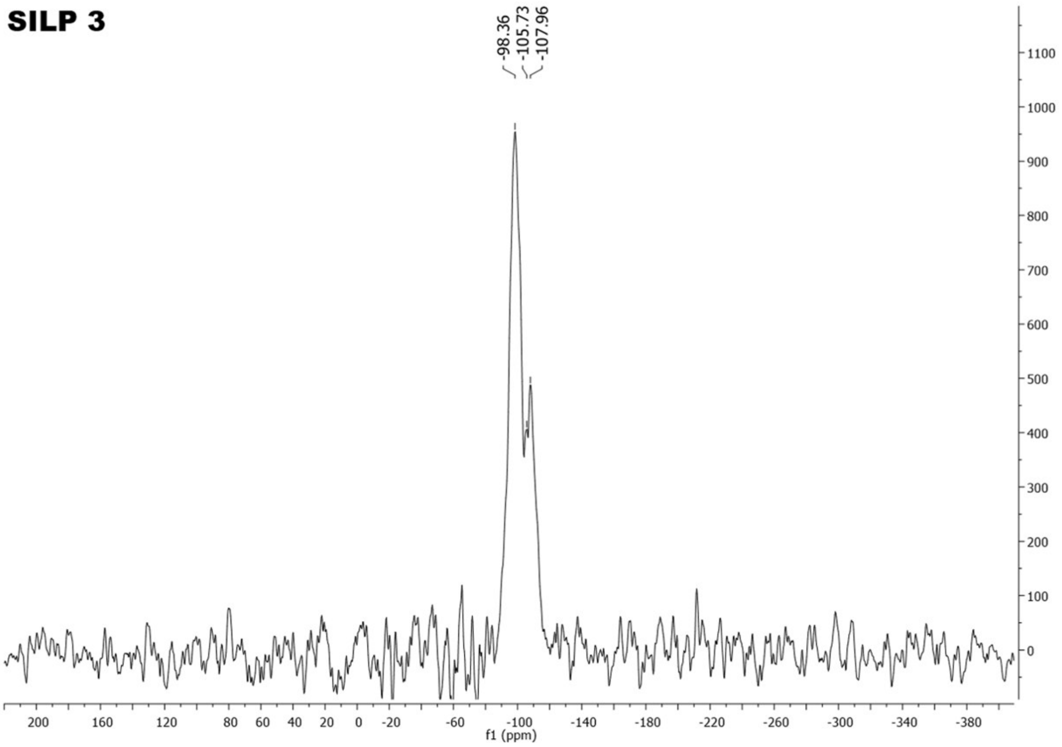


**Figure S4.** Solid-state $^{29}$Si CP-MAS NMR spectra of **3**

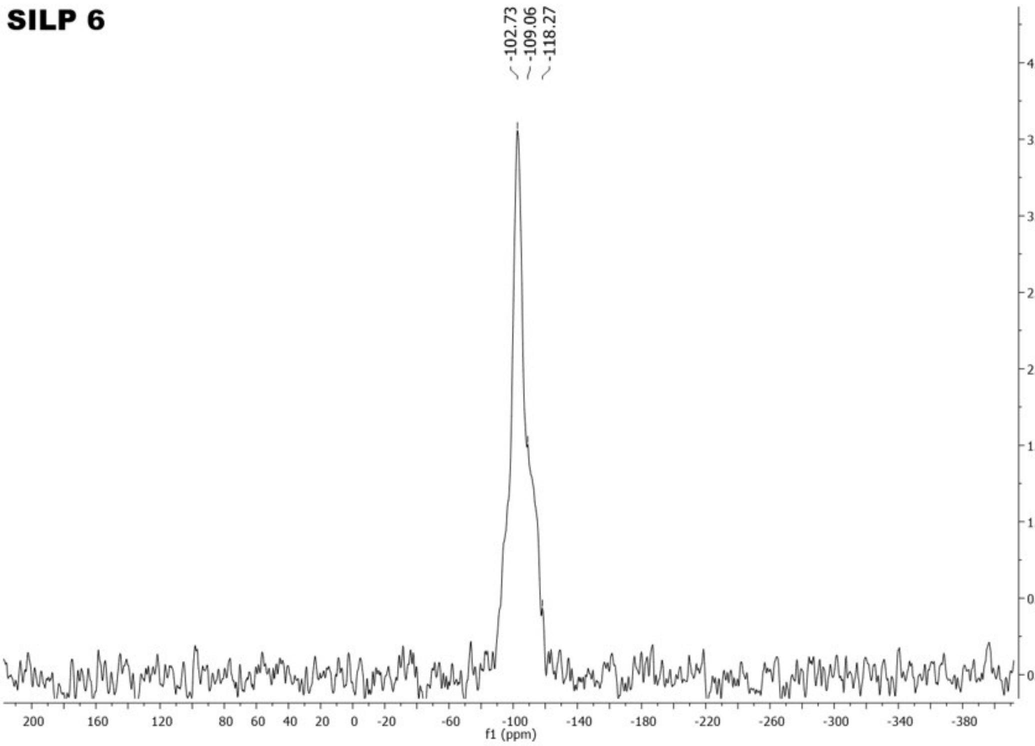


**Figure S5.** Solid-state $^{29}$Si CP-MAS NMR spectra of **6**

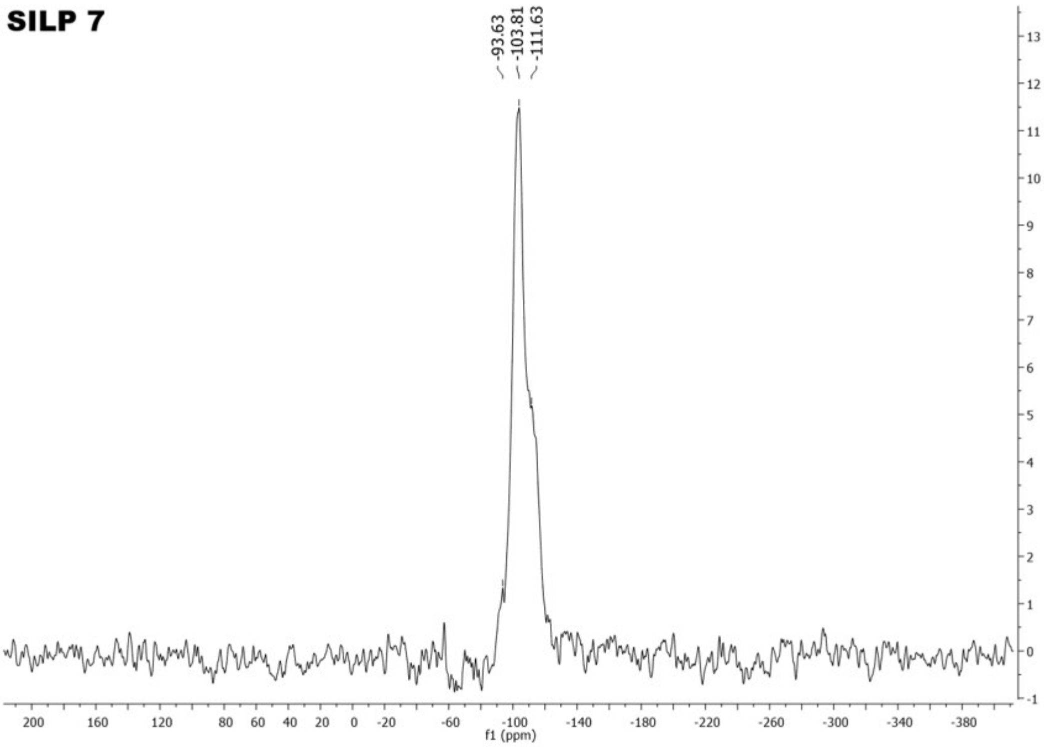


**Figure S6.** Solid-state $^{29}$Si CP-MAS NMR spectra of **7**

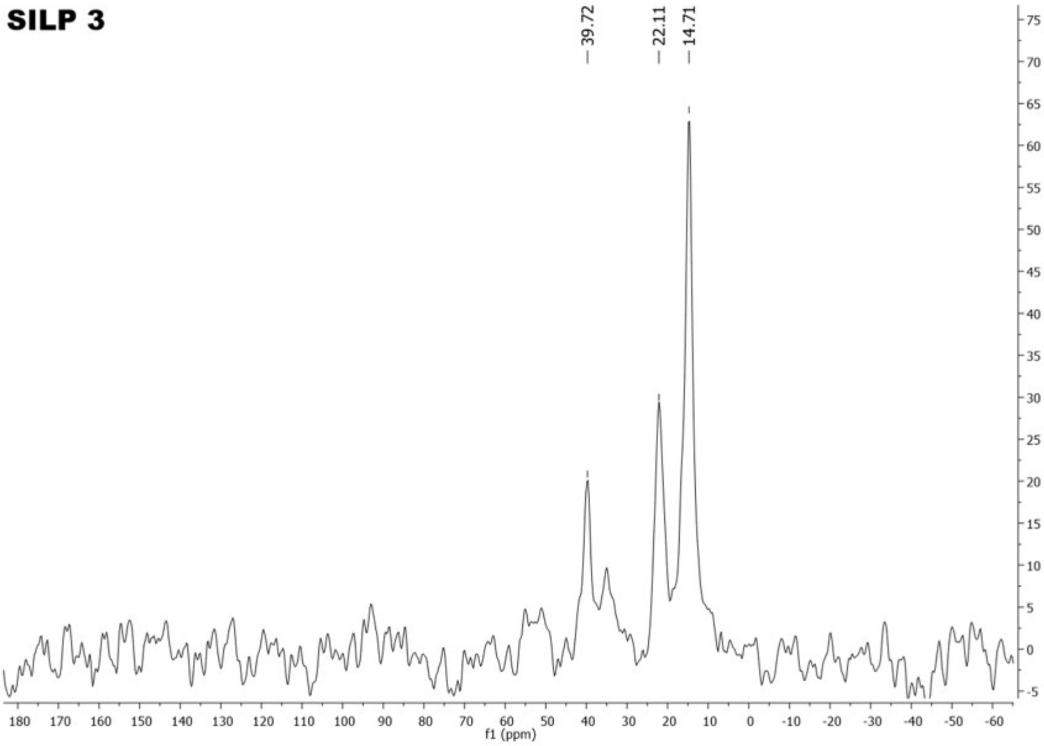


**Figure S7.** Solid-state $^{13}$C CP-MAS NMR spectra of **3**

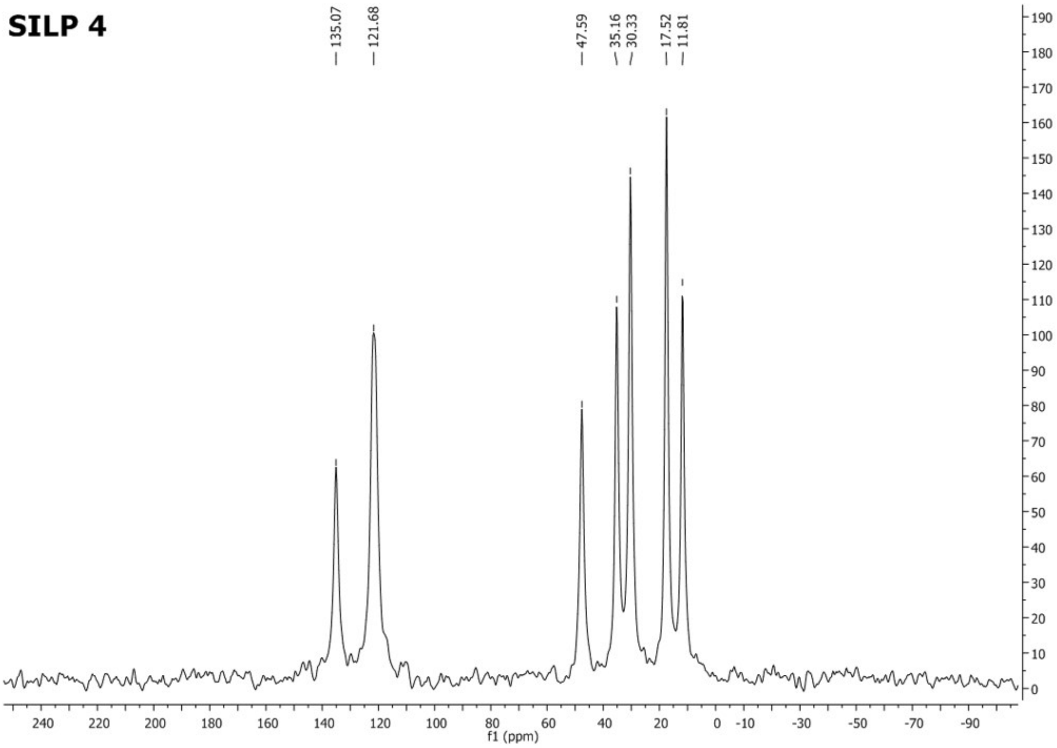


**Figure S8.** Solid-state $^{13}$C CP-MAS NMR spectra of **4**

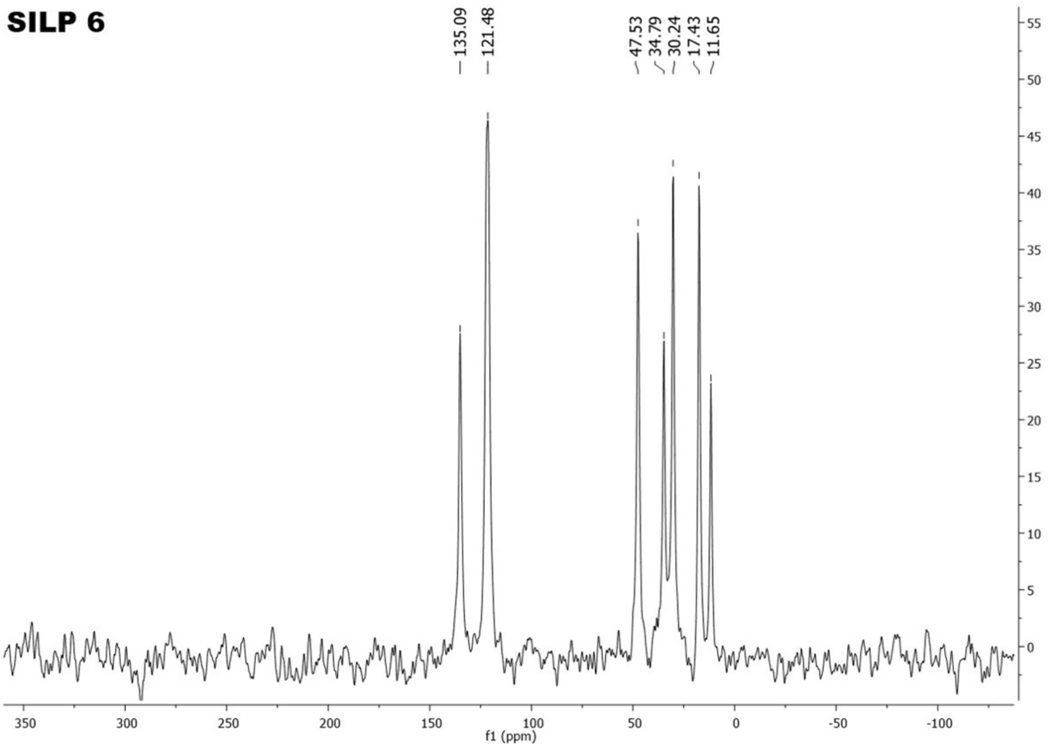


**Figure S9.** Solid-state $^{13}$C CP-MAS NMR spectra of **6**

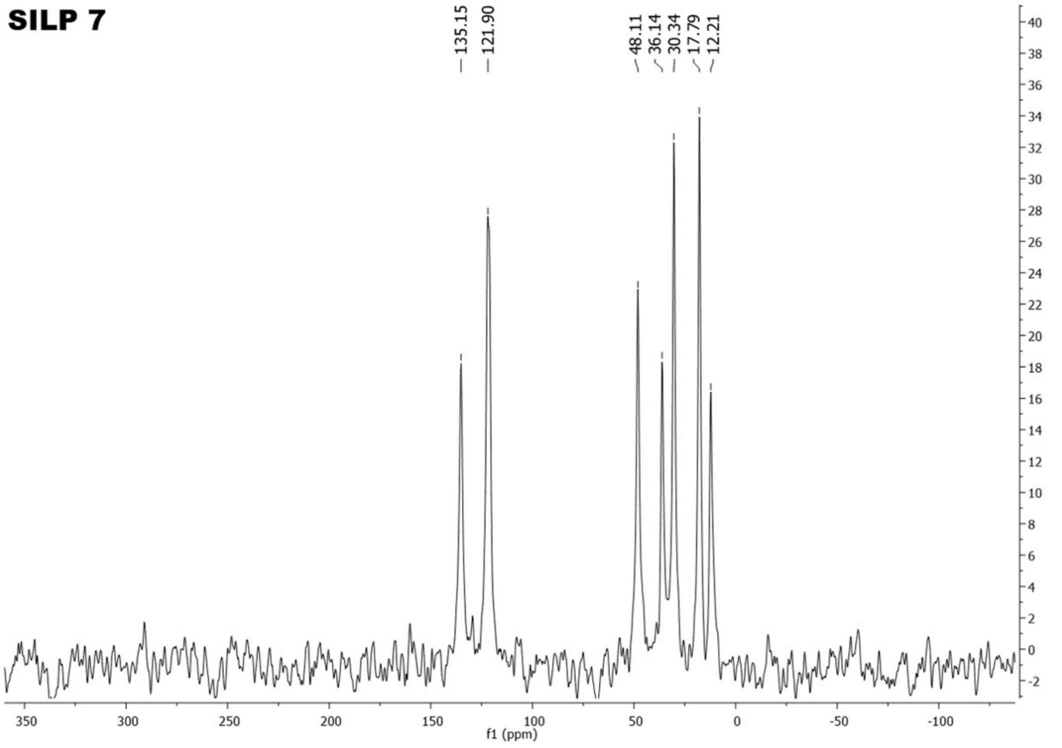


**Figure S10.** Solid-state $^{13}$C CP-MAS NMR spectra of **7**

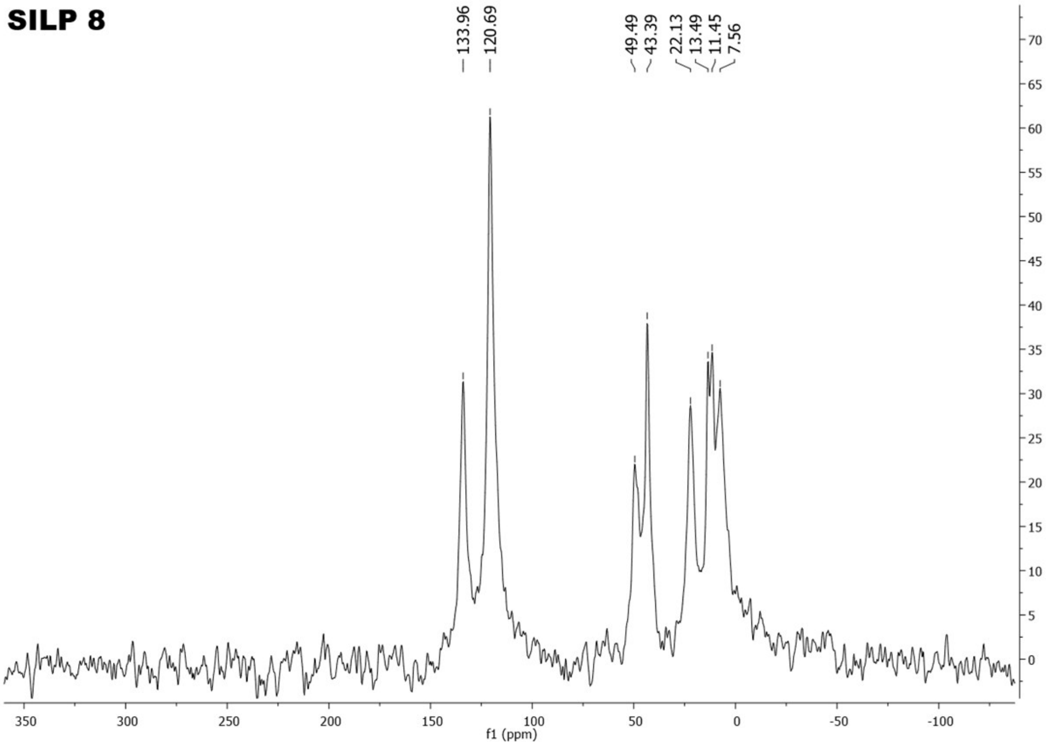


**Figure S11.** Solid-state $^{13}C$ CP-MAS NMR spectra of **8**

### 1.4. Thermogravimetric analysis (TGA)

**Table S1.** TGA results for diferent prepared ionic liquids and SILP materials

| IL/SILP | IL content (%) | Lost water (%) | IL lost weight (%) |
|---|---|---|---|
| **1** | 5 | 4.10 | 6.53 |
| **2** | 10 | 5.50 | 12.34 |
| **3** | 20 | 4.20 | 22.85 |
| **4** | 40 | 5.35 | 40.22 |
| **5** | 60 | 3.39 | 61.11 |
| BMIm.Br | 100 | 4.94 | 95.06 |
| **6** | 40 | 7.07 | 39.18 |
| BMIm.Cl | 100 | 5.40 | 94.60 |
| **7** | 40 | 2.52 | 39.89 |
| BMIm.I | 100 | 5.60 | 94.40 |
| **8** | -- | 4.75 | 19.20 |
| **9** | -- | 5.28 | 19.80 |

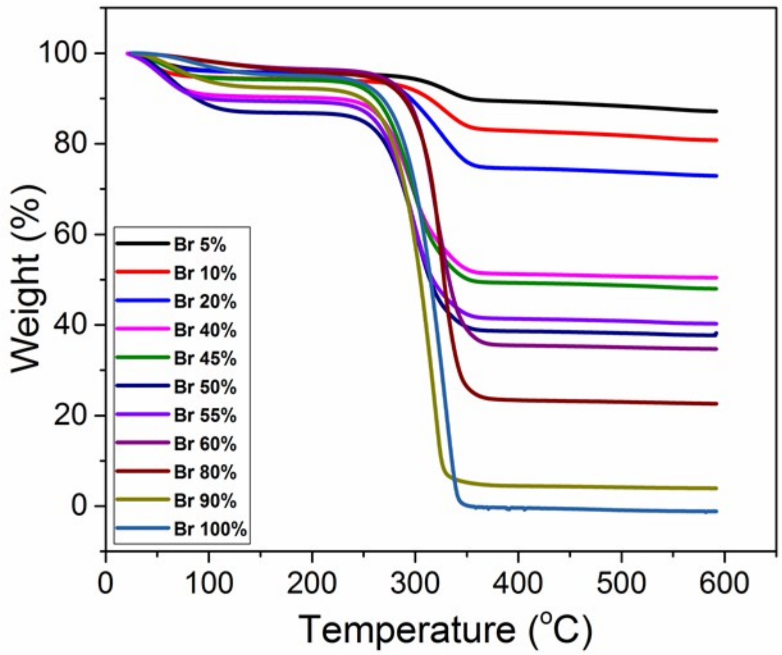


**Figure S12.** TGA analysis of prepared SILP materials at different IL concentrations (% weight).

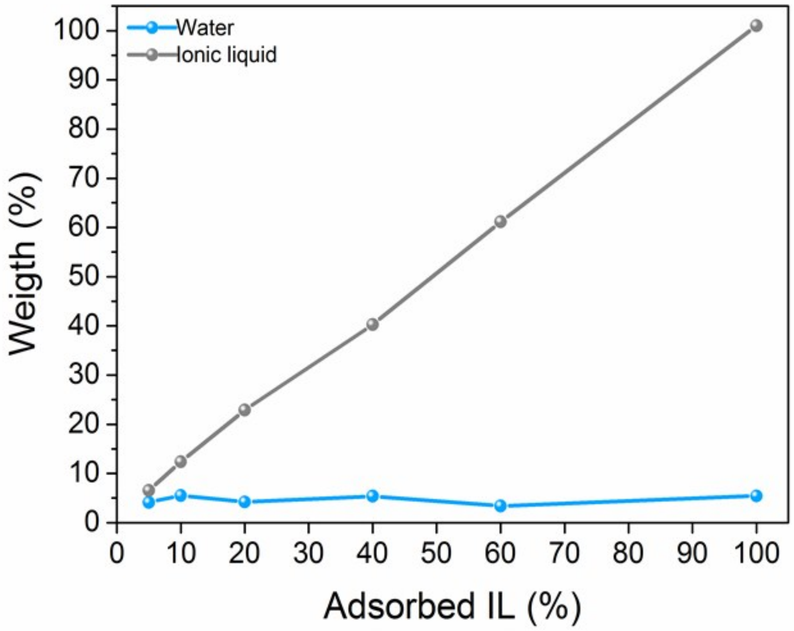


**Figure S13.** TGA distribution analysis of **1**-**5** at different IL concentrations.

## 1.5. Specific surface area (SBET)

The specific surface area was obtained from the nitrogen physisorption isotherms using a Micromeritics ASAP 2020 automatic system and the Brunauer-Emmett-Teller (BET) equation. 0.1-0.2g of sample were heated under vacuum at 115ºC for 4h, and further adsorption of $N_2$ at -196 °C.[4] The BET analysis was performed under at -196 °C and 0.01-0.3 relative vapour pressure. O pore diameter was estimated using the proper equation (Eq. 1) and the experimental BET surface area. Average pore size was determined from thermal desorption of $N_2$ according to Barrett-Joyner-Halendar (BJH) analysis.[5]

$$d = \frac{4}{\rho c \; x \; BET} \qquad \text{(Eq. 1)}$$

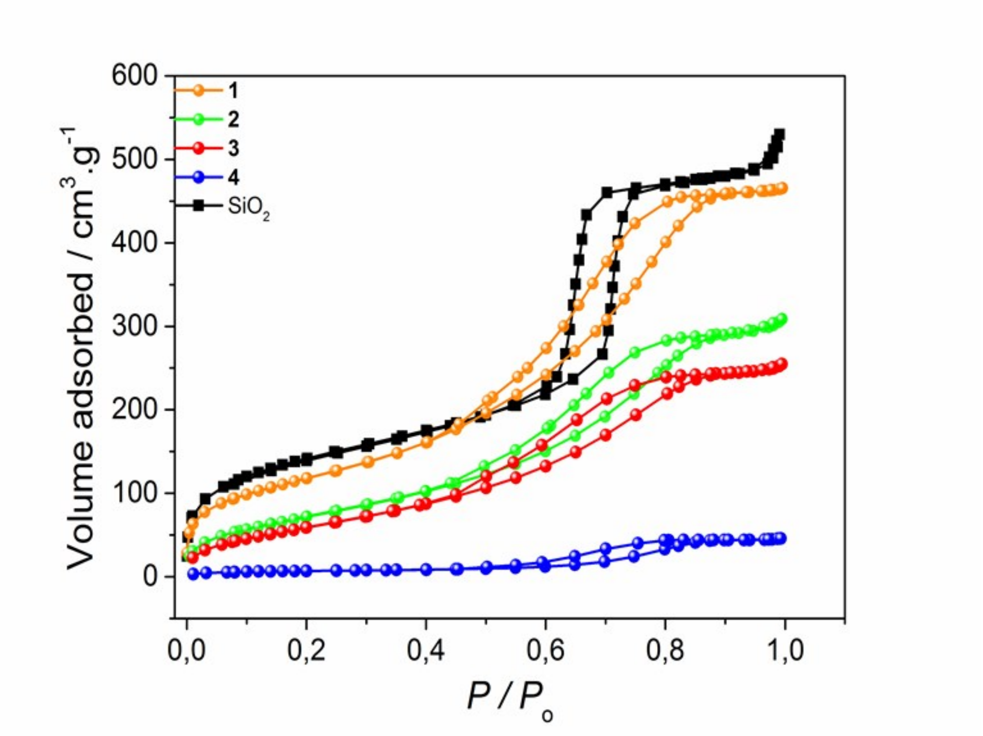


**Figure S14.** Nitrogen adsorption–desorption isotherms of **1-4** SILP materials and SiO2

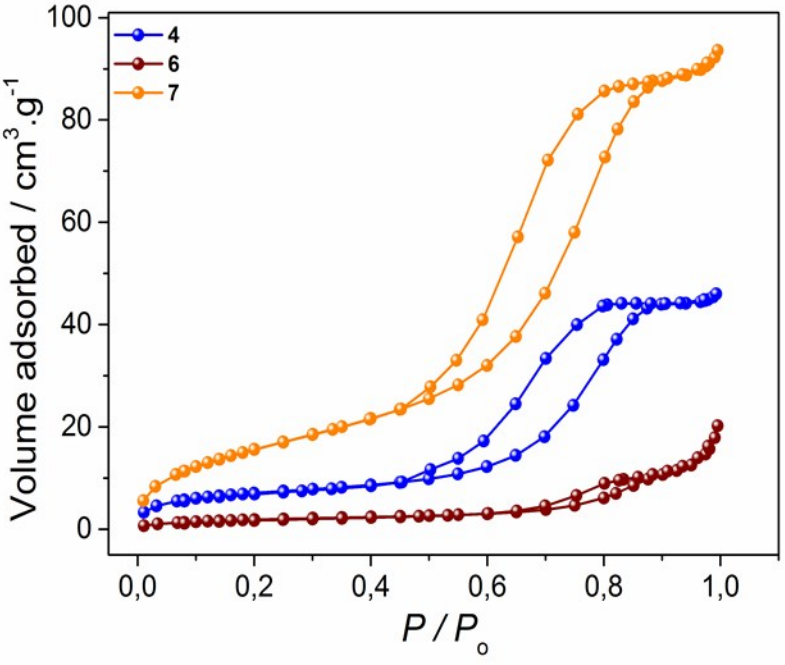


**Figure S15.** Nitrogen adsorption–desorption isotherms of **4**, **6** and **7** SILP materials

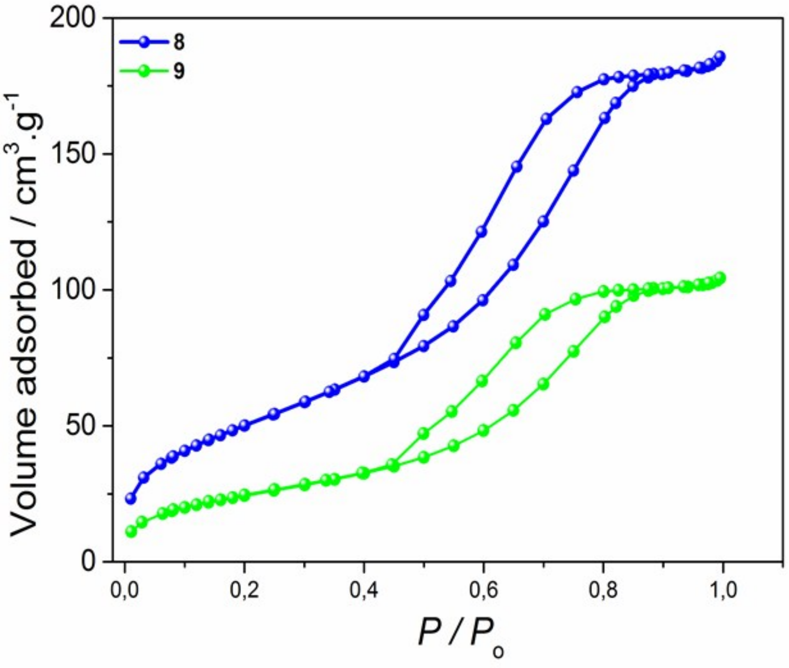


**Figure S16.** Nitrogen adsorption–desorption isotherms of **8** and **9** SILP materials.

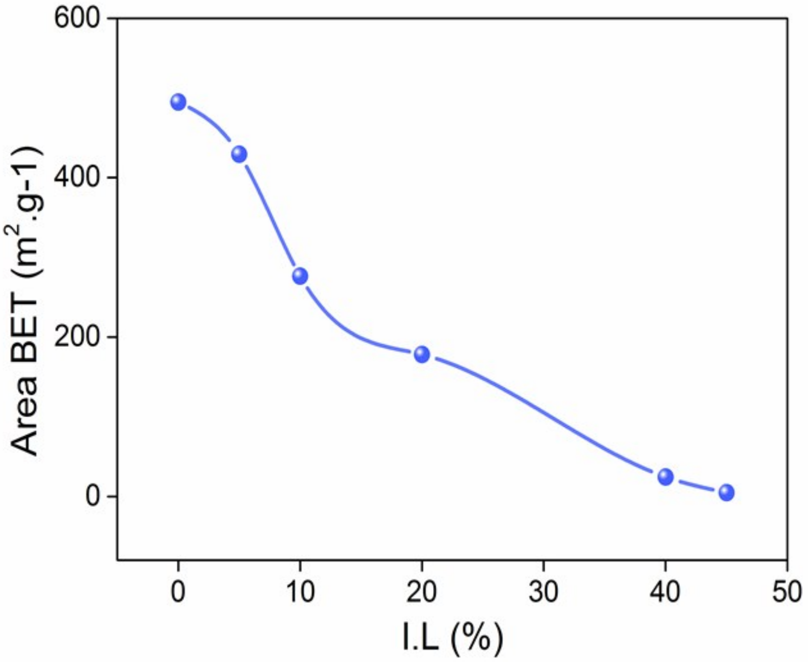


**Figure S17.** Graphic representation of Area BET vs % of IL content of **1-5** .

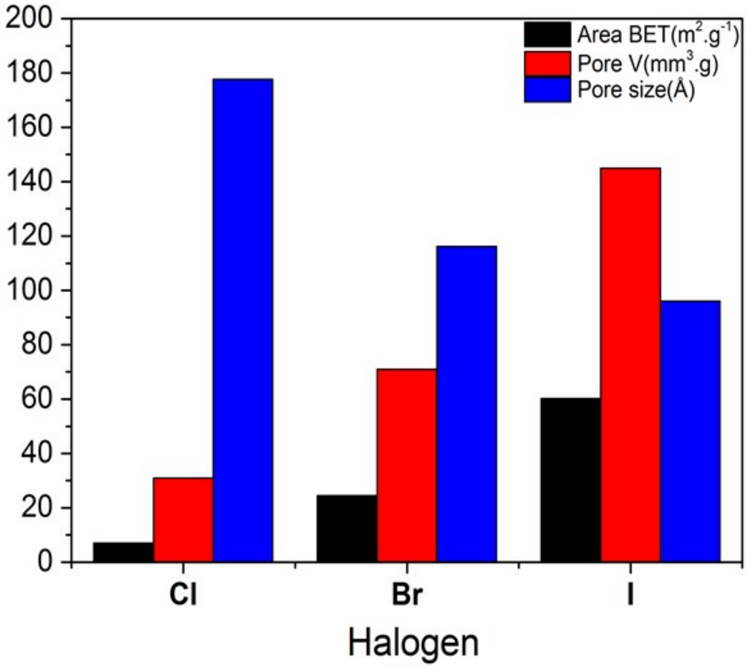


**Figure S18.** Area BET, Pore volume and pore size distribution of **4, 6** and **7**.

## 1.6. X-ray Diffraction (XRD)

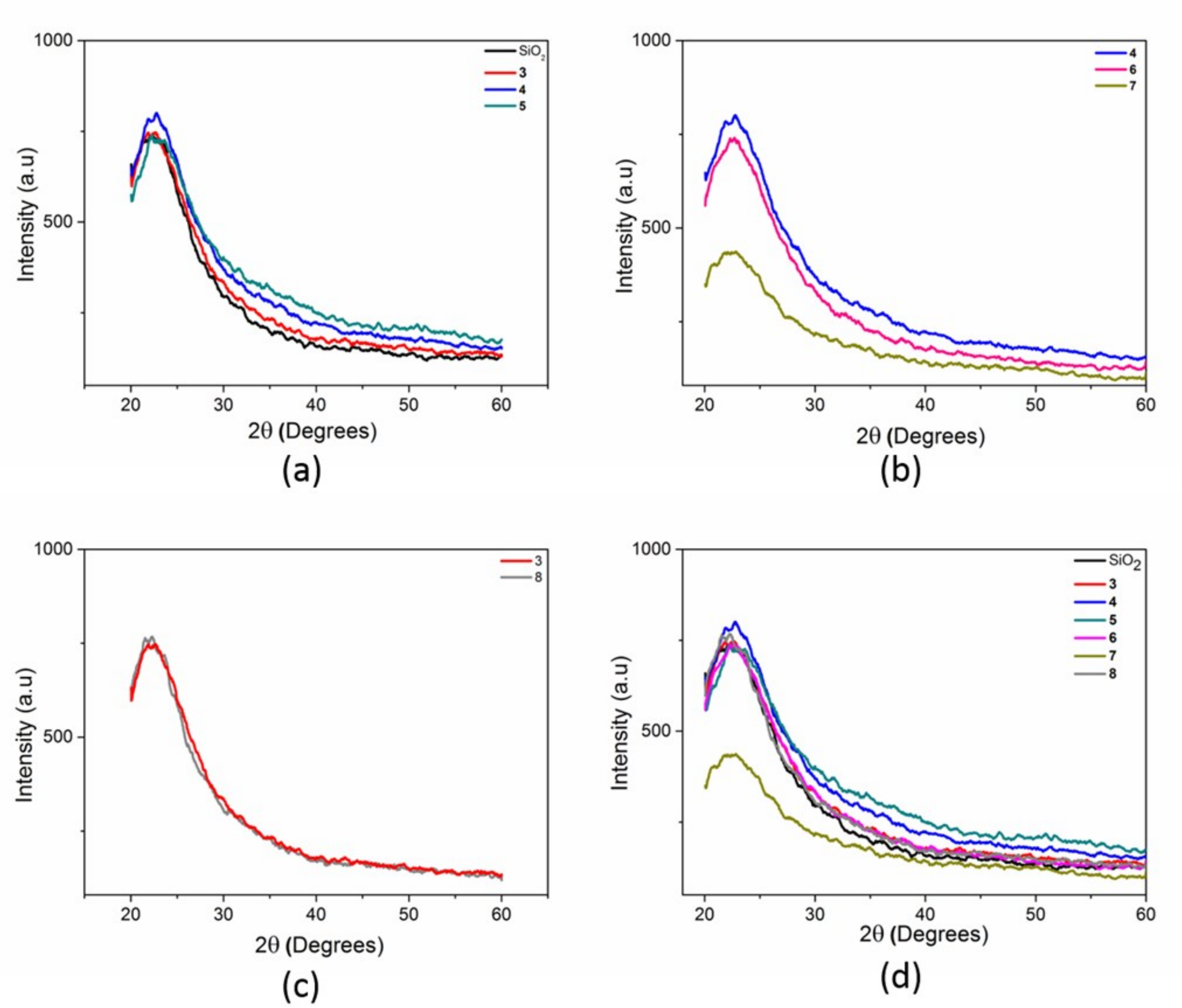


**Figure S19.** XRD analysis of the SILP materials prepared by absorption (a, b and d) and covalent anchoring (c) of IL in SiO$_2$ at different concentrations (% weight).

### 1.7. Energy Dispersive Spectroscopy (EDS)

**Table S2**. Percentages of N, O, Cl, Br and I from EDX of SILP*

| SILP | N | O | Cl | Br | I |
|---|---|---|---|---|---|
| **3** | 4.72 | 65.54 | | 2.06 | |
| **4** | 9.46 | 65.28 | | 4.87 | |
| **6** | 10.72 | 59.17 | 5.47 | | |
| **7** | 7.15 | 63.23 | | | 4.50 |
| **8** | 6.31 | 65.40 | | 1.52 | |
| **9** | 5.56 | 64.87 | | | 1.73 |

* All results in atomic %

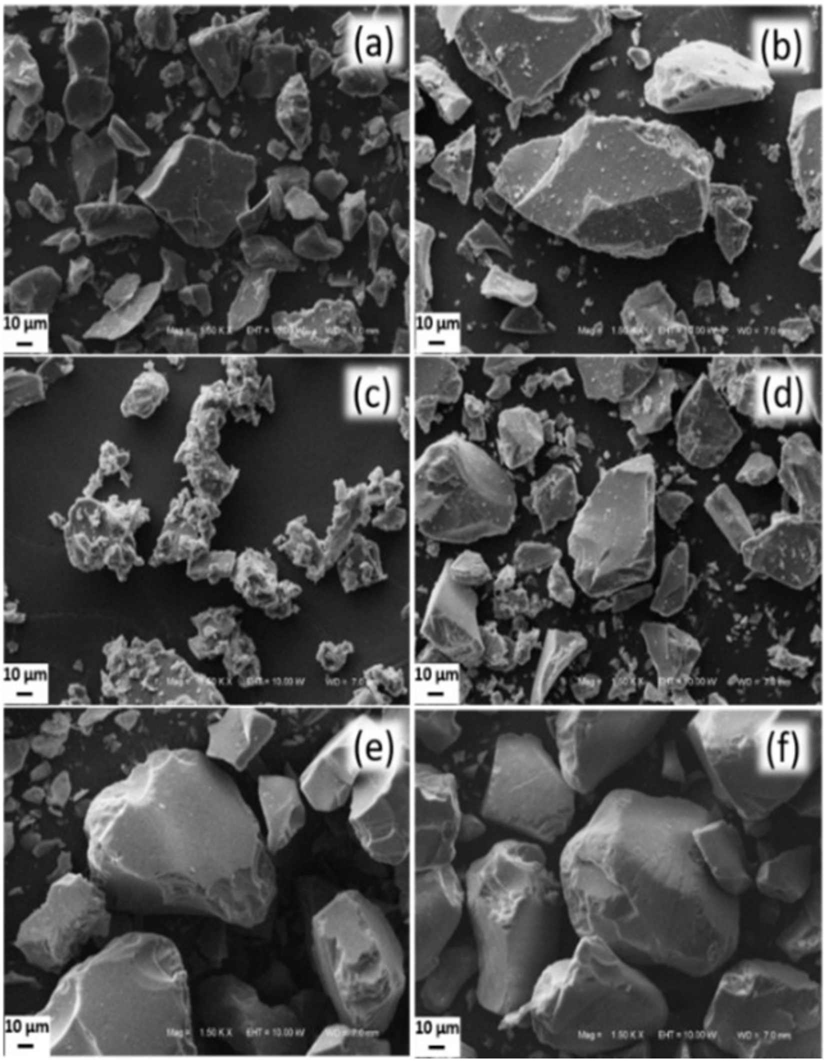


**Figure S20.** SEM images (×1500) of SILP materials: 3(a), 4(b), 8(c), 6(d), 7(e) and 9 (f).

## 1.8. Low-Energy Ion Scattering (LEIS)

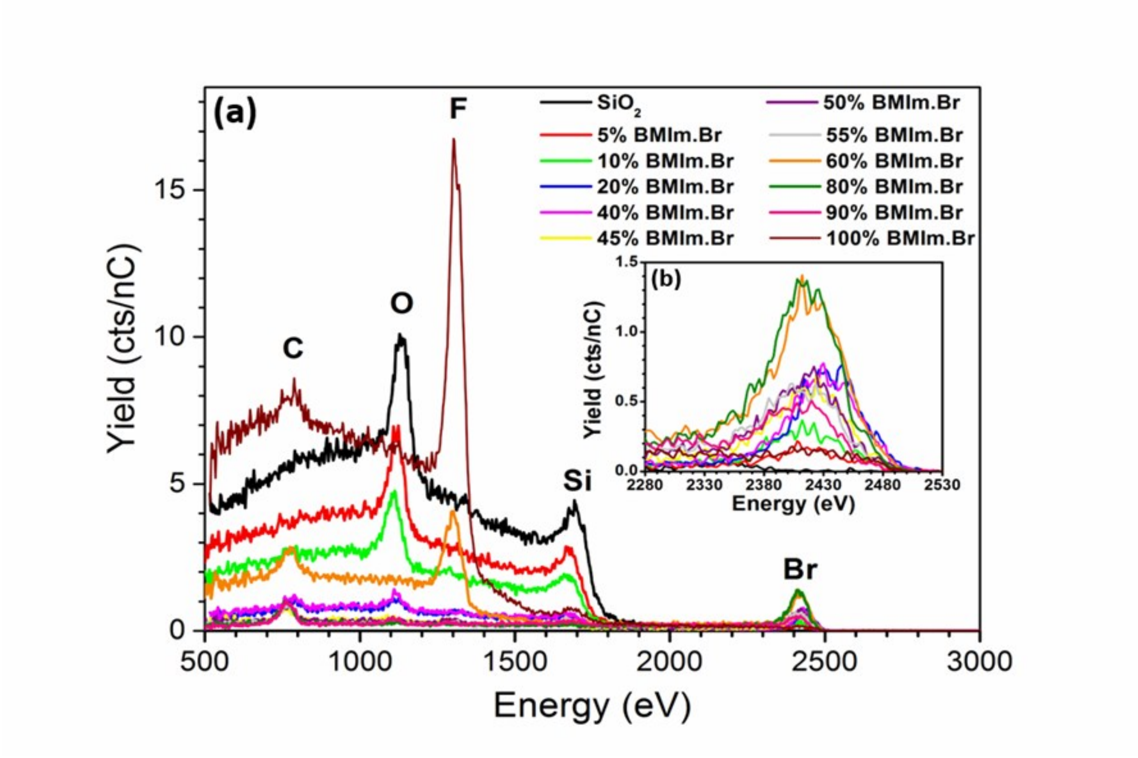


**Fig S21. (a).** HS-LEIS spectra of the SILP BMImBr samples with different amounts of IL where the Br peak is highlighted in the inset and **(b)** Br surface peak intensity as a function of the amount of IL used in the sample.

## 1.9. X-ray Photoelectron Spectroscopy (XPS)

**Table S3** Binding energy position of the Br 3d$_{5/2}$ component as a function of the sample

| Sample | Br 3d$_{5/2}$ position (eV) |
|---|---|
| 10% BMI.Br | 68.1 |
| 20% BMI.Br | 67.8 |
| 40% BMI.Br | 67.8 |
| 50% BMI.Br | 67.6 |
| 60% BMI.Br | 67.6 |
| 80% BMI.Br | 67.6 |
| 90% BMI.Br | 67.6 |

# 2 Catalytic activity of Ionic Liquids and SILP materials

## 2.1. General procedure for cycloaddition of $CO_2$ to epoxides catalyzed by IL and SILP materials.

The cycloaddition of $CO_2$ to epoxides reaction was carried out in a 50 ml fischer porter reactor equipped with a magnetic stirrer. Catalist were charged and propylene oxide (406 mg, 3.34 mmol) was added, sealed and flushed 3 times at room temperature with Argon, vacuum and then $CO_2$ to remove the air from the vessel. The pressure was adjusted to 5 bar. The reaction was stirred at 80–150 °C for 30 minutes. Then, Fischer-Porter was cooled to room temperature and the pressure was released. The contents were analysed by $^1$H NMR spectroscopy to determine the conversion, yield and selectivity to carbonate.

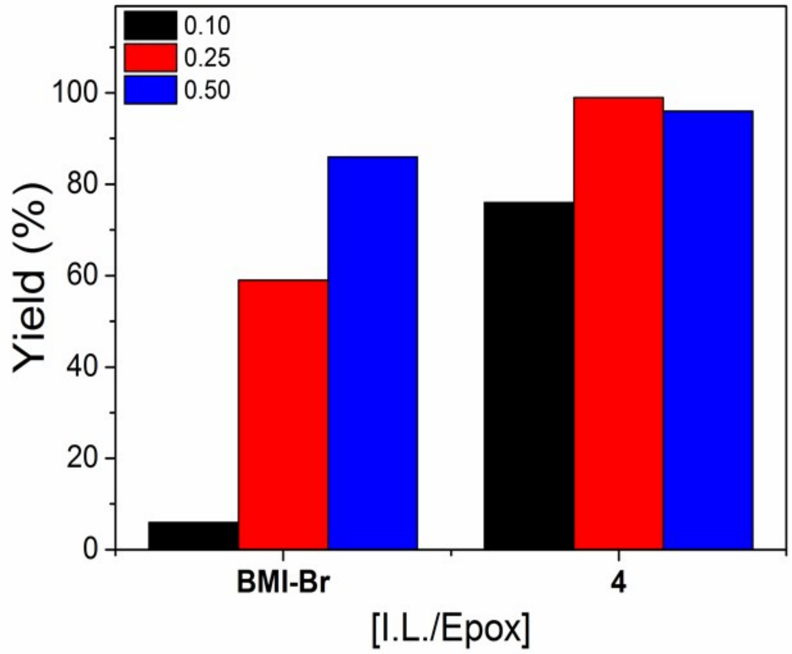


**Fig S22.** Comparative study on catalytic activity of cycloaddition of carbon dioxide to butene oxide promoted by BMIm.Br and **4.**

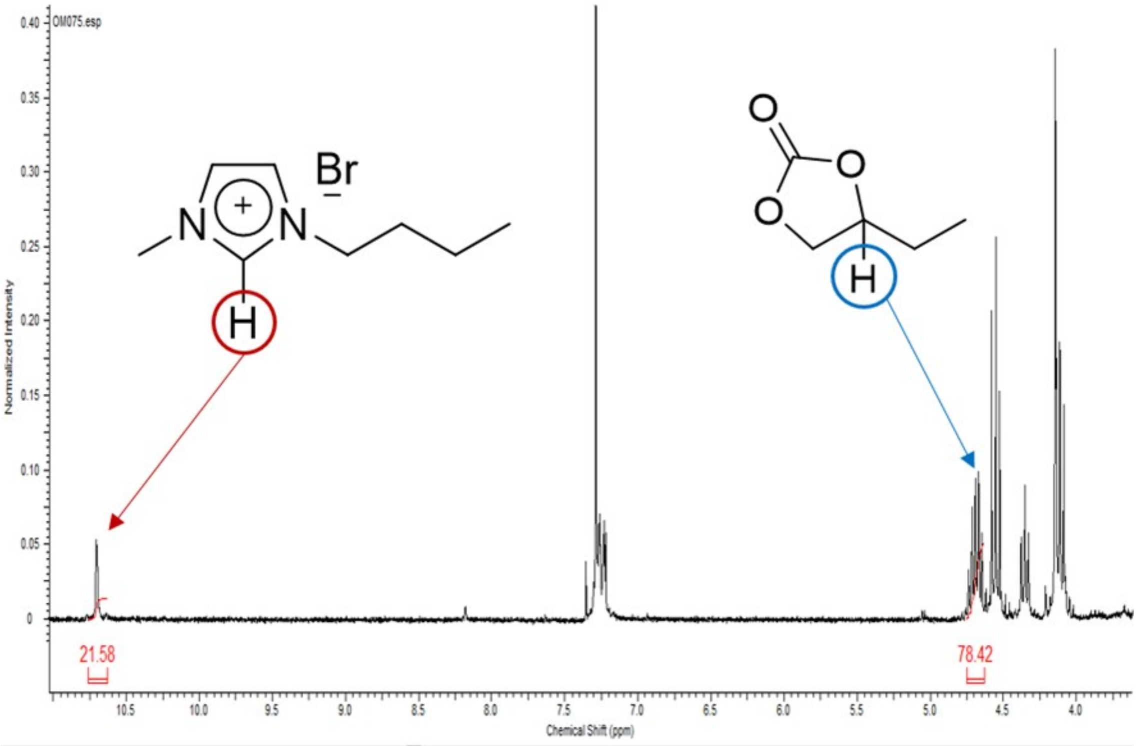


**Fig S23.** $^1$H NMR obtained for cycloaddition of carbon dioxide to butene oxide catalized by **4**.

## 2.2. Recycling of SILP catalyst

After depressurization of the Fischer-Porter, SILP material was washed five times with diethyl ether and filtered by cannulation. Remaining solvent was dried off under vacuum during 3h at 50 °C for reutilization.

**Table S4**. Comparative study on catalytic activity of cycloaddition of carbon dioxide to butene oxide promoted by BMIm.Br and **4**.

| [Cat/Epox] | BMIm.Br | | **4** | |
|---|---|---|---|---|
| | Yield (%)$^a$ | Sel. (%)$^a$ | Conv.(%)$^a$ | Sel.(%)$^a$ |
| 0.1 | 6 | 100 | 76 | 91 |
| 0.25 | 59 | 100 | 99 | 90 |
| 0.5 | 86 | 100 | 96 | 94 |

Reaction conditions: $P\text{CO}_2$ = 5 bar, T = 1h, t = 150 ºC, [S] = 3.34 mmol. [a] calculated by $^1$H-NMR.

**Table S5.** Comparative study on catalytic activity of cycloaddition of carbon dioxide to butene oxide promoted by SILP BMIm.Br.

| Entry | Catalyst | T (ºC) | Conv.(%)[a] | Sel.(%)[a] |
|---|---|---|---|---|
| 1 | **3** | 80 | 85 | 82 |
| 2 | **4** | 80 | 95 | 96 |
| 3 | **5** | 80 | 23 | 55 |
| 4 | **6** | 80 | 55 | 43 |
| 5 | **4** | 115 | 99 | 92 |
| 5 | **6** | 115 | 89 | 64 |
| 6 | **4** | 150 | 99 | 90 |
| 7 | **6** | 150 | 90 | 69 |

[S]=3.34 mmol, [cat]/[S] = 0.25, 30 min., 5 bar de $CO_2$. [a] Calculated by $^1H$ NMR.

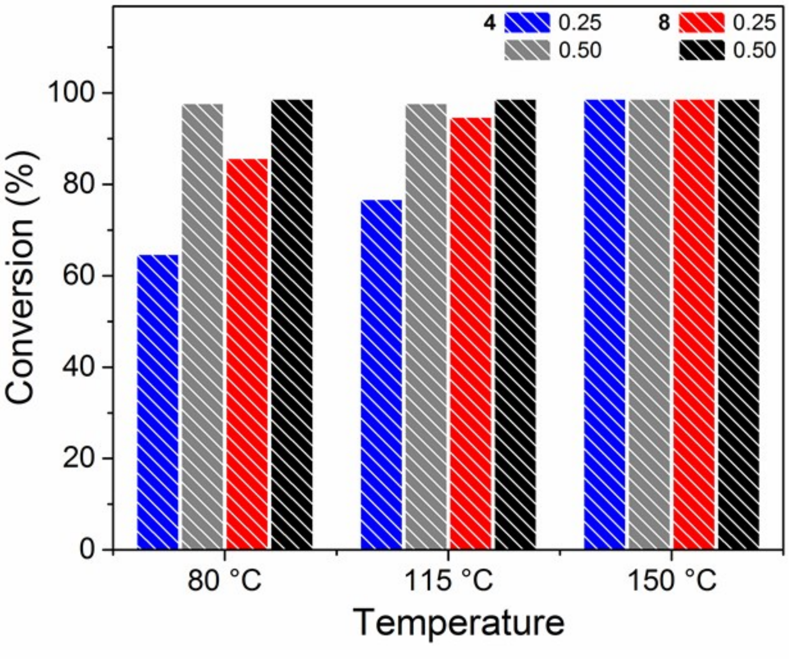
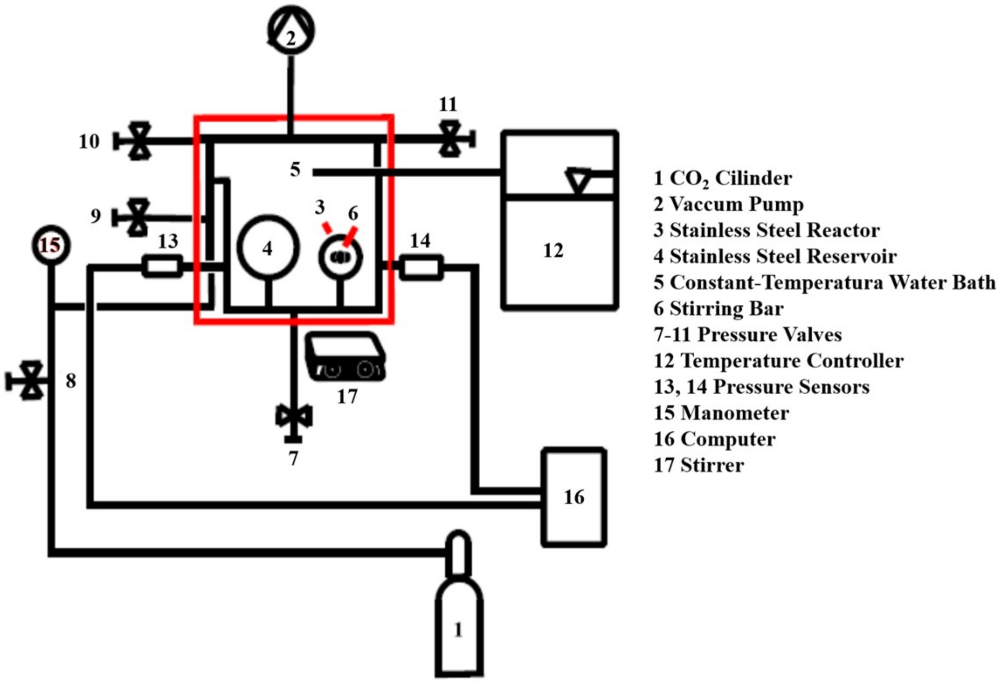


**Fig S24.** Comparative study on catalytic activity of cycloaddition of carbon dioxide to propene oxide promoted by SILPs 4 and 8.

### 2.3. $CO_2$ adsorption studies



**Scheme S2.** $CO_2$ physisorption in IL and SILP Diagram. Thermobaric cell apparatus.

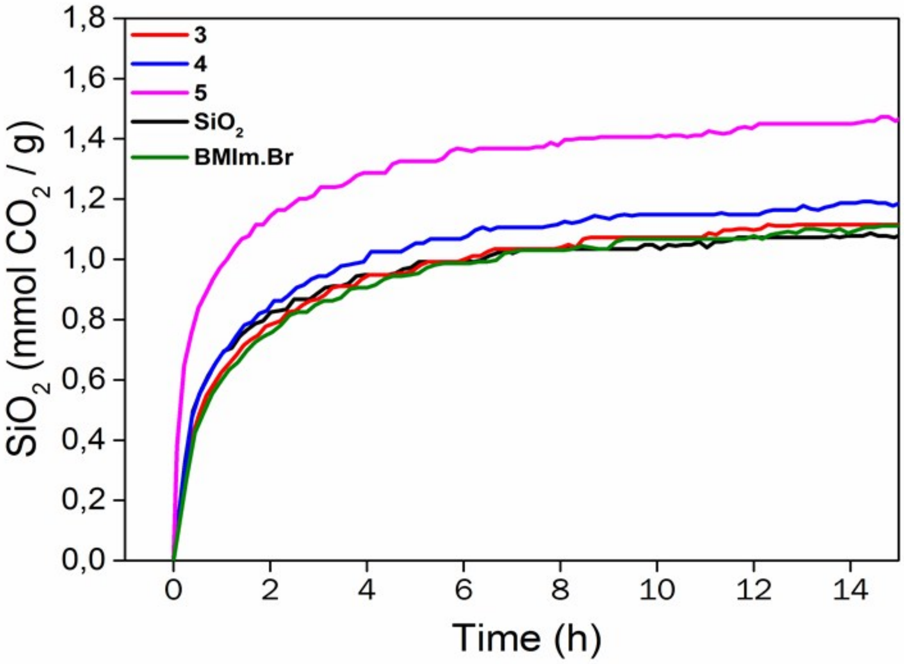


**Figure S25.** $CO_2$ absorption profile observed for SILP materials.

## 2.4. Continuous flow system

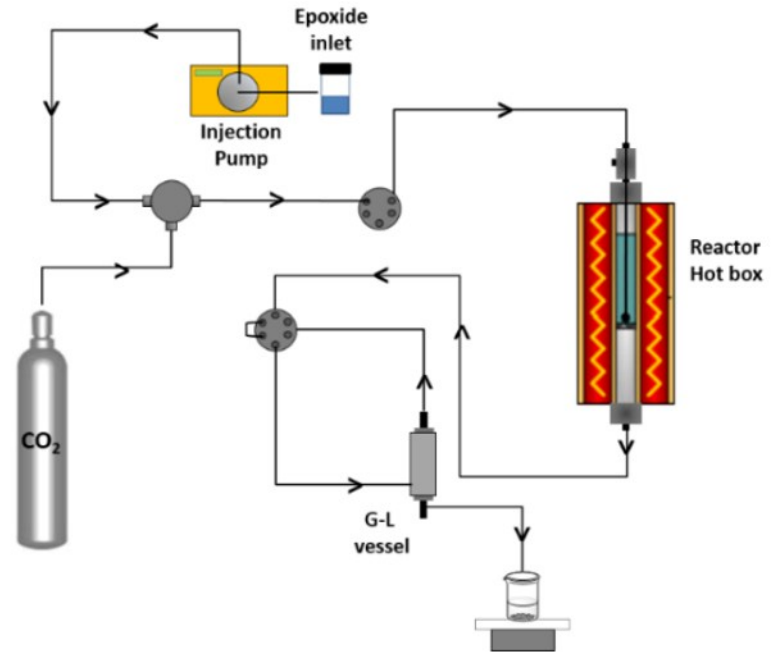


**Figure S26.** Schematic diagram of a PID continuous flow reactor used.

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