

# CO<sub>2</sub>-Induced Anion Exchange and Diffusion Behavior in Imidazolium-Based Ionic Liquids Studied by Multinuclear DOSY NMR

Rafael D. Zink,<sup>a</sup> Jean C. B. Vieira,<sup>a</sup> Lucas L. Baldassari,<sup>a</sup> and Francisco P. dos Santos<sup>a\*</sup>

<sup>a</sup> Instituto de Química, Universidade Federal do Rio Grande do Sul, UFRGS, Av. Bento Gonçalves 9500, 91501-970, Porto Alegre, RS, Brazil.

\*[fpsantos@ufrgs.br](mailto:fpsantos@ufrgs.br)

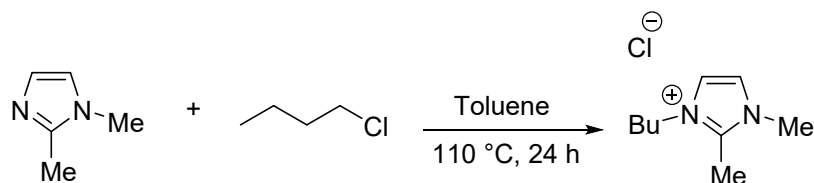
## SUPPORTING INFORMATION FILE

### TABLE OF CONTENTS

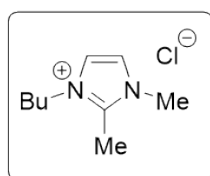
<b>1. General Procedure for the Synthesis of the Ionic Liquids</b> .....	2
<b>2. NMR Spectra of Ionic Liquids</b> .....	4
<b>3. NMR Experiments</b> .....	7
<b>3.1 Sample preparation</b> .....	7
<b>3.2 <sup>1</sup>H NMR</b> .....	7
<b>3.3 <sup>13</sup>C NMR</b> .....	11
<b>3.4 DOSY experiments</b> .....	20

## 1. General Procedure for the Synthesis of the Ionic Liquids

### 1.1 Synthesis of 3-n-butyl-1,2-dimethyl-1*H*-imidazol-3-ium chloride ([BMMIm][Cl])

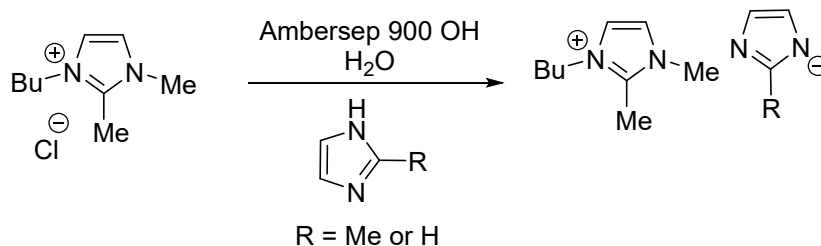


The ionic liquid was prepared according to the literature [1]. Into a three neck round bottom flask of 50 mL, equipped with a reflux condenser, were added toluene (50 mL), 1,2-dimethylimidazole (10 mL, 0.125 mol, 1 equiv.) and 1-chlorobutane (14.3 mL, 0.137 mol, 1.1 equiv.). The mixture was heated under an inert atmosphere of N<sub>2</sub> at gentle reflux for 24 h (110 °C). The mixture separated into two layers when cooled to room temperature, the top layer being toluene and the bottom layer an oil ([BMMIm][Cl]). The flask was then placed in a freezer at -18 °C overnight, whence a white solid formed. The toluene was decanted under a stream of N<sub>2</sub>. The obtained salt was purified through recrystallization with a MeCN/MeOH solvent mixture.

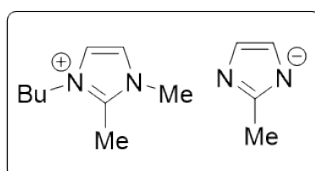


White solid. **Yield:** 23.3 g, 90%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 7.79 – 7.74 (m, 2H); 4.14 (t, *J* = 7.3 Hz, 2H); 3.78 (s, 3H); 2.61 (s, 3H); 1.68 (quint, *J* = 7.4 Hz, 2H), 1.27 (sext, *J* = 7.7 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101.6 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 144.2; 122.3; 120.9; 47.2; 34.7; 31.2; 18.8; 13.4; 9.3.

### 1.2 Synthesis of 1-butyl-2,3-dimethylimidazolium imidazolate and 1-butyl-2,3-dimethylimidazolium 2methyl-imidazolate

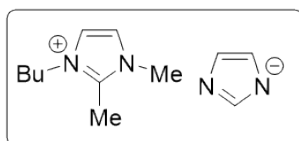


The ion exchange was carried out according to the literature [2]. The [BMMIm][Cl] salt (20 mmol, 3.77 g) was dissolved in a minimum amount of water and eluted through an ion exchange resin column (Ambersep900 OH). An aliquot of the solution was used to monitor the chloride exchange using AgNO<sub>3</sub> 1.0 M and no AgCl precipitation was observed. Imidazole (1.36 g, 20 mmol), or 2-methyl imidazole (1.64 g, 20 mmol), was added to the resulting aqueous imidazolium hydroxide solution and water was evaporated under reduced pressure and mild heating (45 °C) to afford the corresponding ionic liquid.



Purple solid. **Yield:** 4.45 g, 95%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) 7.67 (d, *J* = 2.0 Hz, 1H); 7.64 (d, *J* = 2.0 Hz, 1H); 6.59 (s, 2H); 4.10 (t, *J* = 7.2 Hz, 2H); 3.73 (s, 3H); 2.57 (s, 3H); 2.16 (s, 3H);

1.67 (sext,  $J = 7.2$  Hz, 2H); 1.27 (sext,  $J = 7.2$  Hz, 2H); 0.90 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 146.8; 144.2; 122.8; 122.3; 120.9; 47.2; 34.6; 31.2; 18.9; 16.0; 13.4; 9.1.



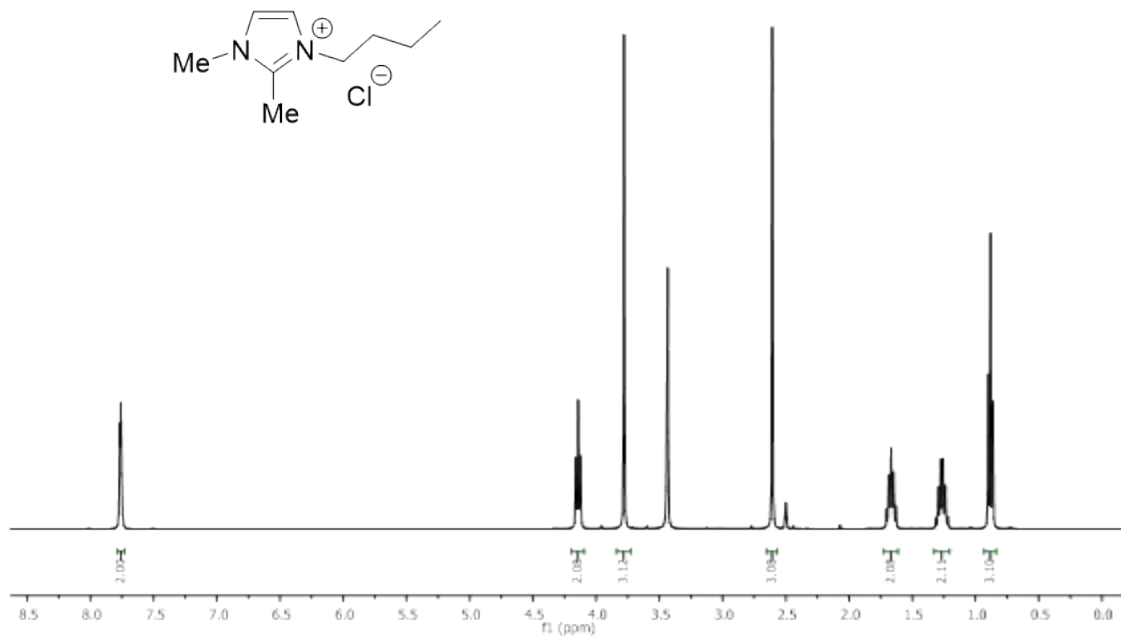
Yellow solid. **Yield:** 4.05 g, 92%.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 7.64 (d,  $J = 2.0$  Hz, 1H) 7.60 (d,  $J = 2.0$  Hz, 1H); 7.11 (s, 1H); 6.67 (s, 2H); 4.08 (t,  $J = 7.2$  Hz, 2H); 3.71 (s, 3H); 2.54 (s, 3H); 1.67 (quint,  $J = 7.6$  Hz, 2H); 1.27 (sext,  $J = 7.6$  Hz, 2H); 0.90 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101.6 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 144.2; 141.5; 124.2; 122.3; 120.9; 47.3; 34.6; 31.2; 18.9; 13.4; 9.1.

---

[1] V. Farmer, T. Welton, The oxidation of alcohols in substituted imidazolium ionic liquids using ruthenium catalysts, *Green Chem.* 4, (2002) 97–102, <https://doi.org/10.1039/B109851A>.

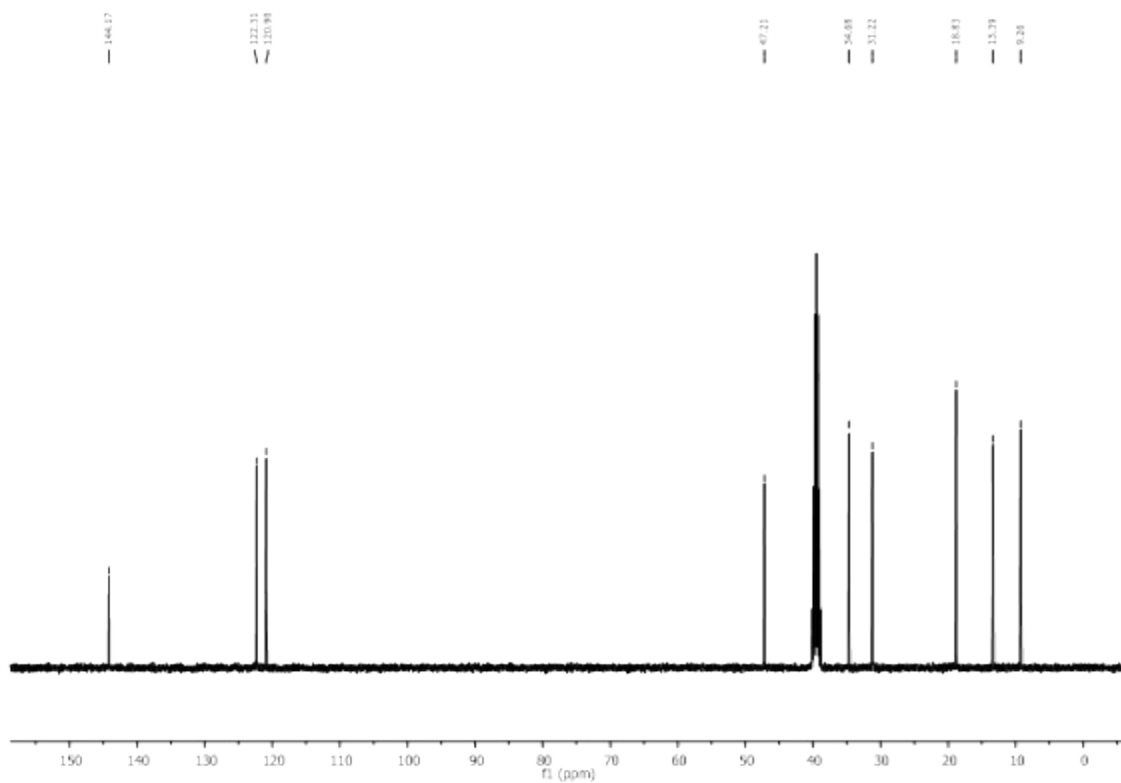
[2] M. Zanatta, A. Girard, G. Marin, G. Ebeling, F. P. dos Santos, C. Valsecchi, H. Stassen, P. R. Livotto, W. Lewis, J. Dupont, Confined water in imidazolium based ionic liquids: a supramolecular guest@host complex case, *Phys. Chem. Chem. Phys.* 18 (2016), 18297–18304, <https://doi.org/10.1039/C6CP03112A>.

## 2. NMR Spectra of Ionic Liquids



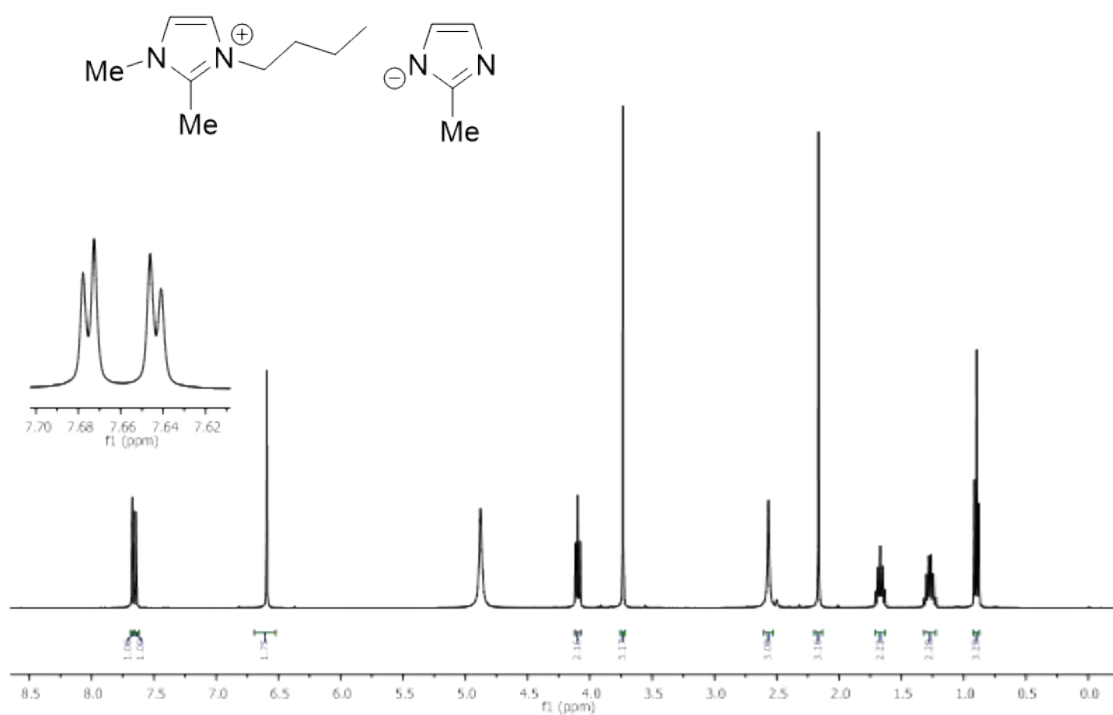
Figure

re S1. <sup>1</sup>H NMR spectrum for compound [BMMIm][Cl] in DMSO-*d*<sub>6</sub>, 400 MHz.

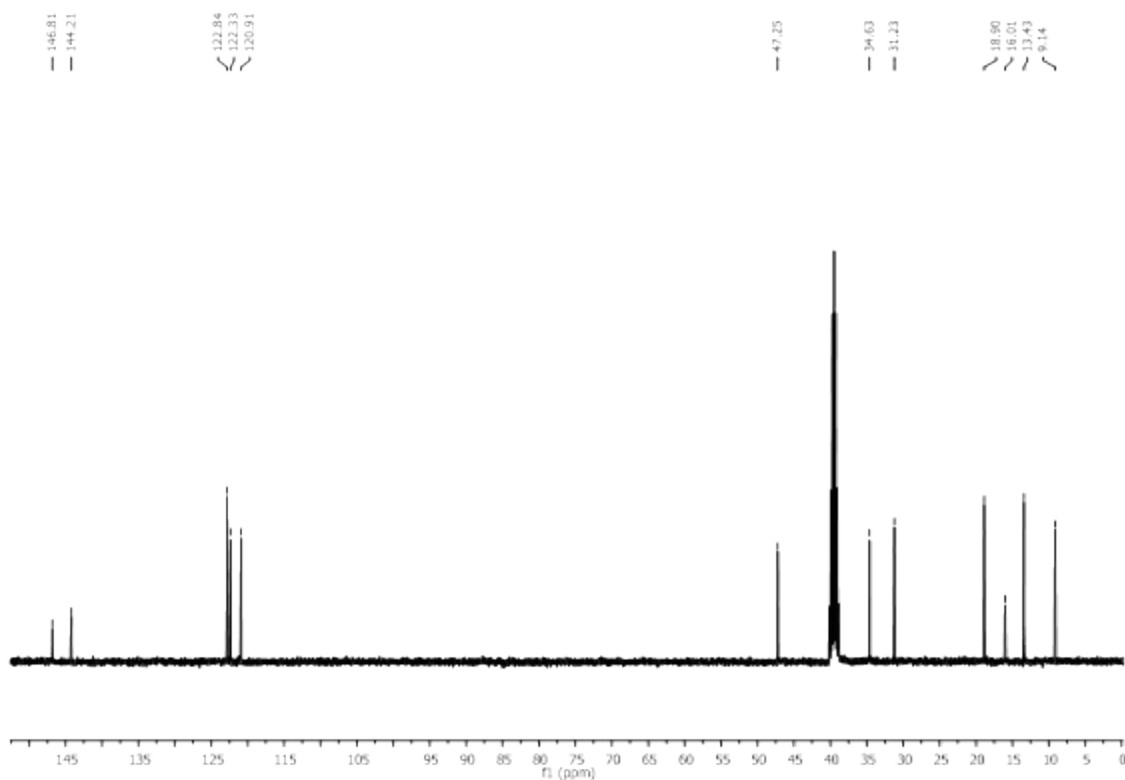


Figure

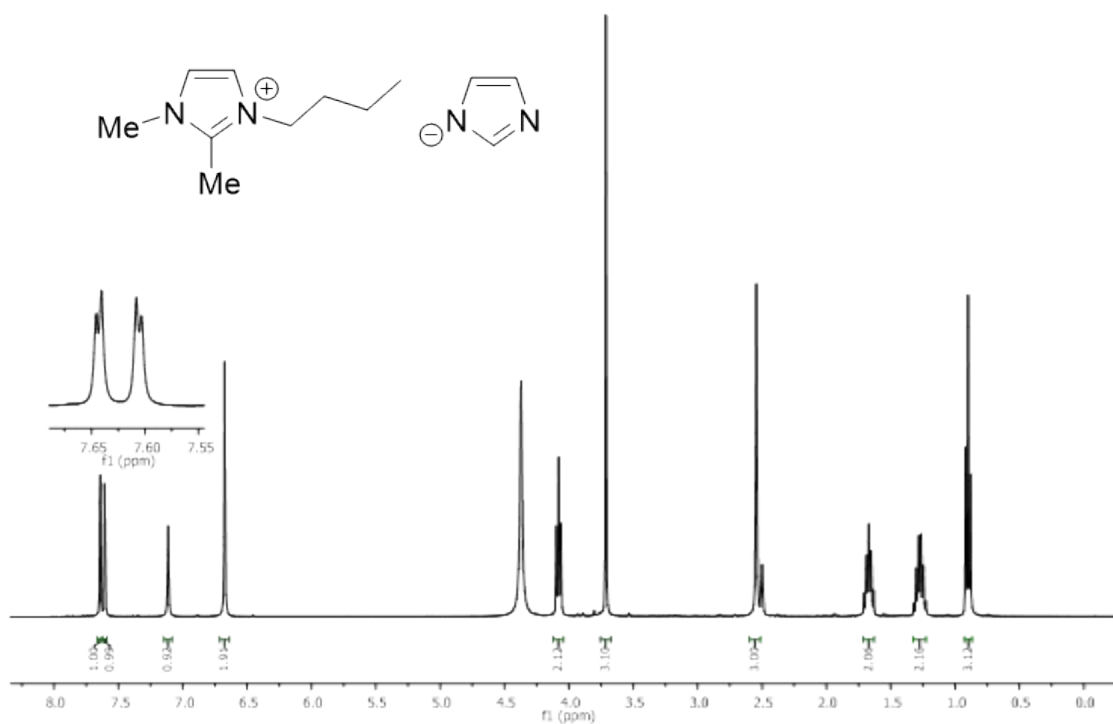
re S2. <sup>13</sup>C NMR spectrum for compound [BMMIm][Cl] in DMSO-*d*<sub>6</sub>, 101.6 MHz.



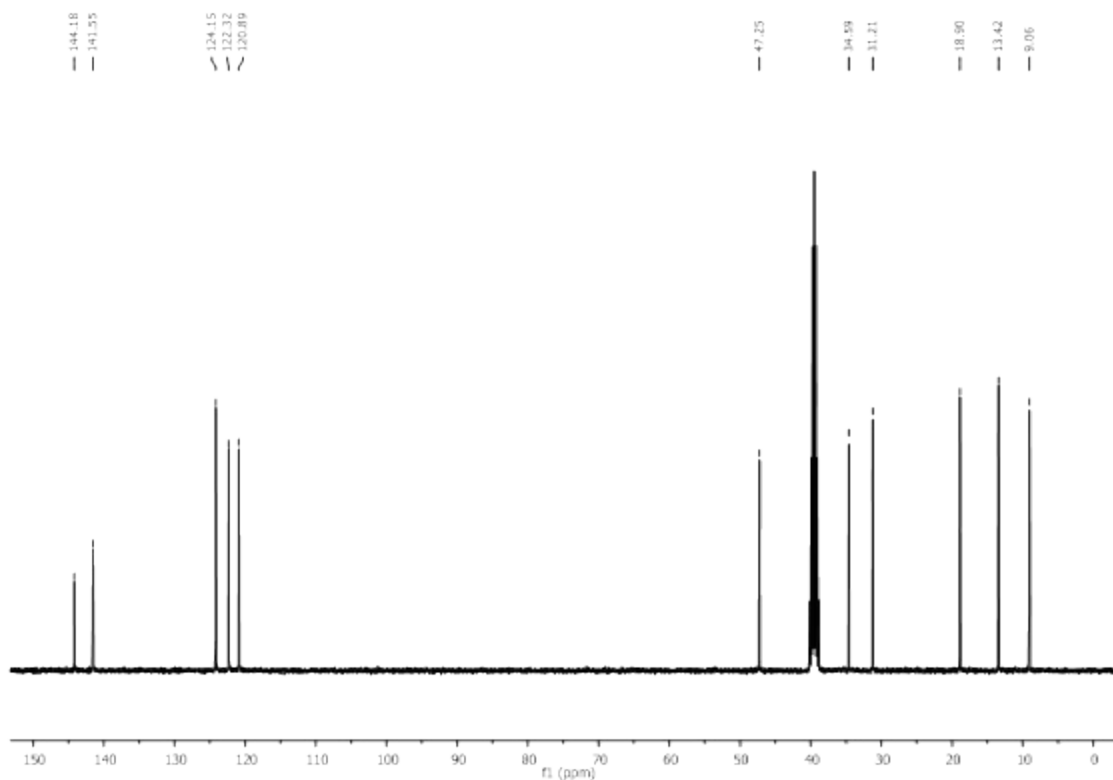
**Figure S3.**  $^1\text{H}$  NMR spectrum for compound [BMMIm][2-MeIm] in  $\text{DMSO-}d_6$ , 400 MHz.



**Figure S4.**  $^{13}\text{C}$  NMR spectrum for compound [BMMIm][2-MeIm] in  $\text{DMSO-}d_6$ , 101.6 MHz.



**Figure S5.**  $^1\text{H}$  NMR spectrum for compound [BMMIm][Im] in  $\text{DMSO-}d_6$ , 400 MHz.



**Figure S6.**  $^{13}\text{C}$  NMR spectrum for compound [BMMIm][Im] in  $\text{DMSO-}d_6$ , 101.6 MHz.

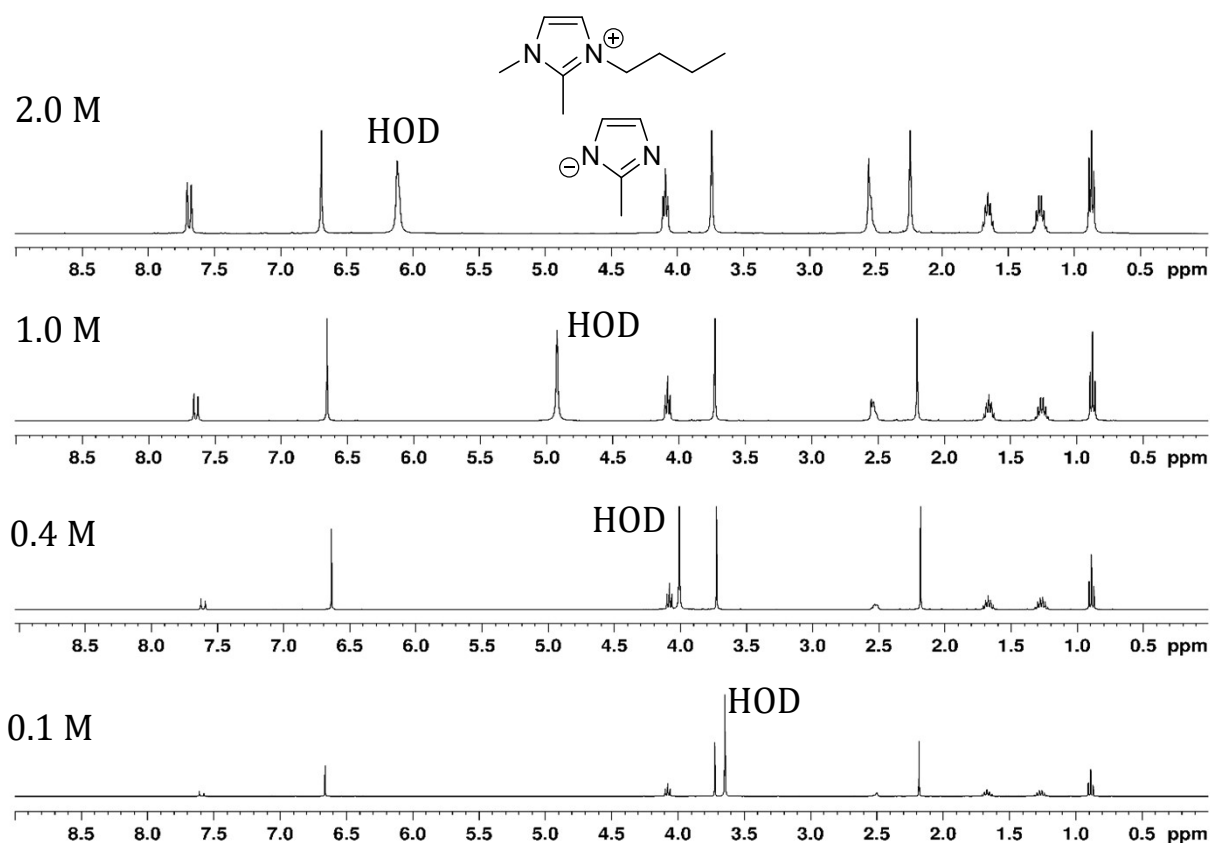
### 3. NMR Experiments

#### 3.1 Sample preparation

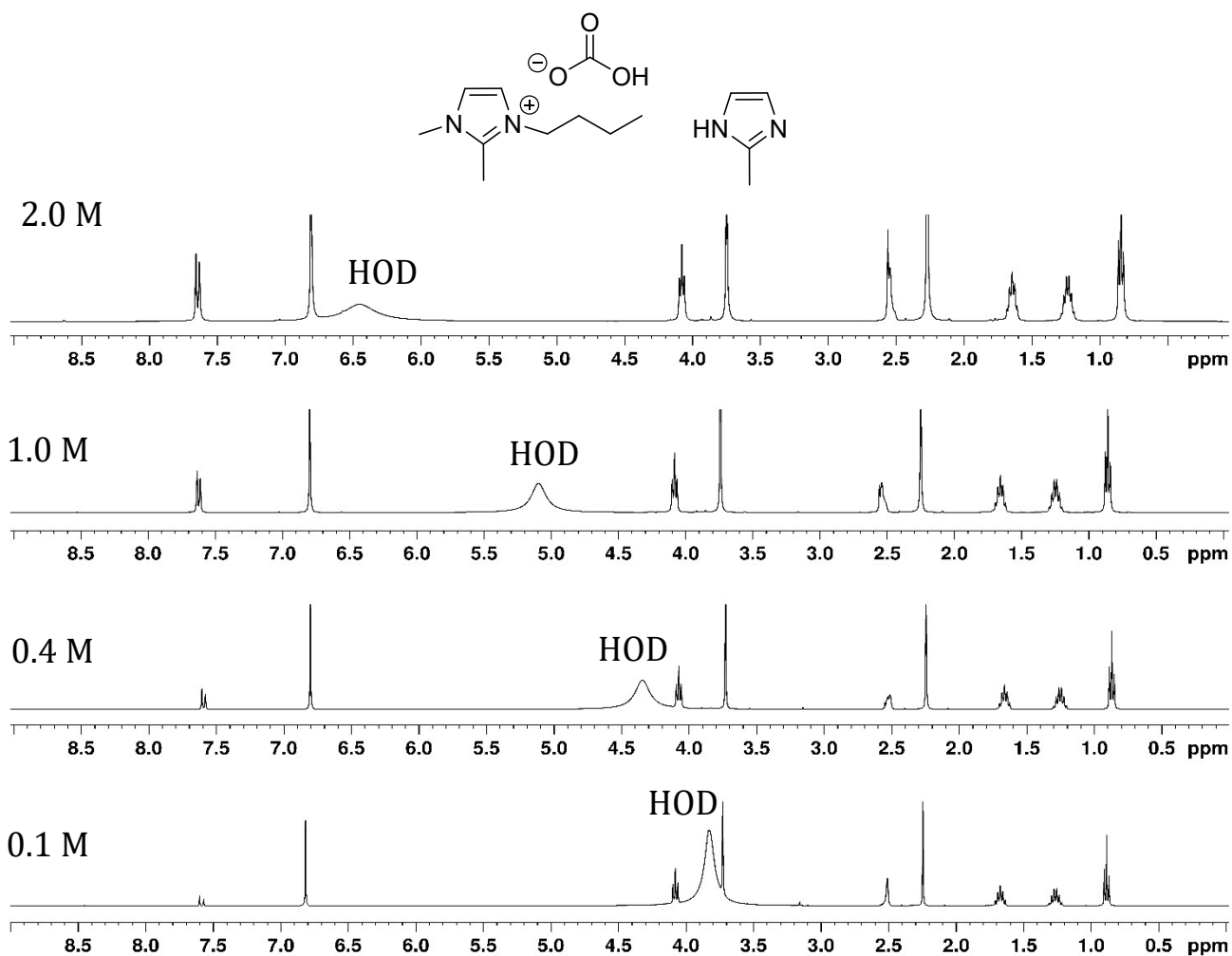
IL solutions used for the diffusion experiments were prepared from pure and dry compounds. Prior to solution preparation, the compounds were dried under vacuum at moderate temperature (50 °C) for 24 h. The solutions were prepared using a DMSO- $d_6$ /D $_2$ O solvent mixture (95:5, v/v). Each solution was prepared individually by weighing the appropriate amount of compound to reach the desired concentration and completing the volume with the DMSO- $d_6$ /D $_2$ O mixture. CO $_2$  capture experiments were performed by bubbling CO $_2$  (99.998% purity, AirLiquide Brasil, Brazil) through 1 mL of the ILs solution for 15 min with a flow rate of approximately 70 mL min $^{-1}$ , followed by transfer of the solution to an NMR tube for analysis.

#### 3.2 $^1\text{H}$ NMR

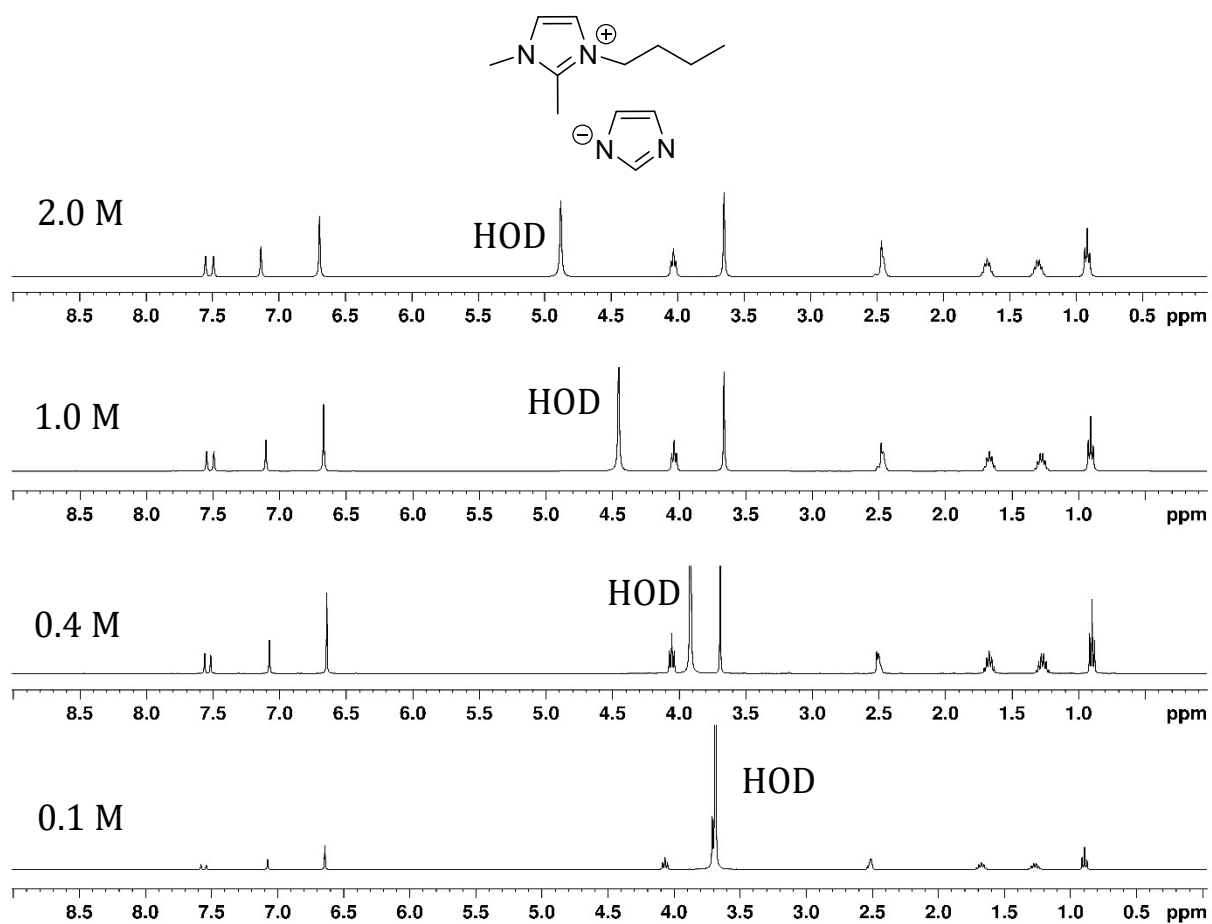
The figures S7-S10 below show the  $^1\text{H}$  NMR spectra of the solutions of ionic liquids [BMMIm][Im] and [BMMIm][2-MeIm] at the different concentrations evaluated, before and after CO $_2$  bubbling.



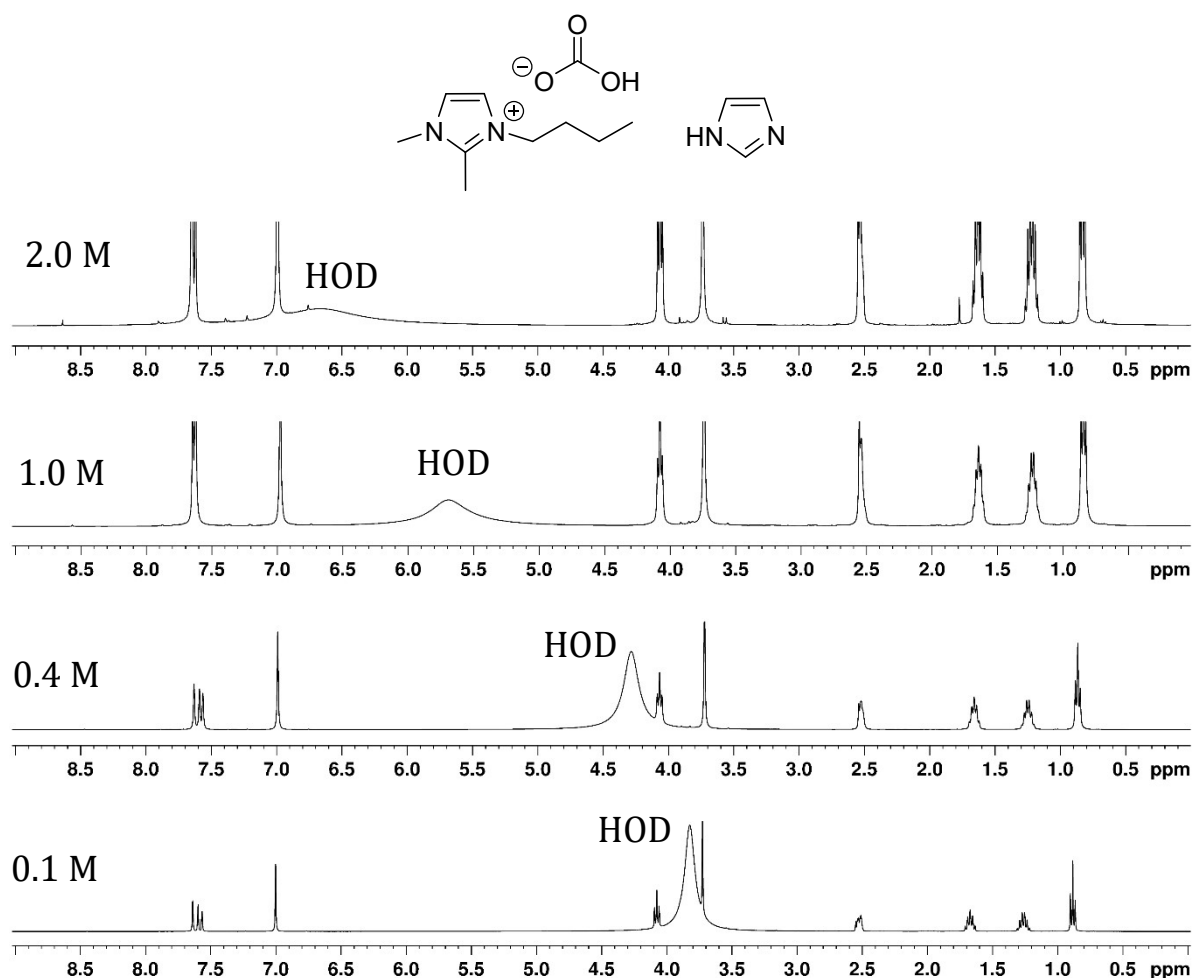
**Figure S7.**  $^1\text{H}$  NMR spectra of [BMMIm][2-MeIm] at different concentrations in DMSO- $d_6$ /D $_2$ O solvent mixture (95:5, v/v), 400 MHz.



**Figure S8.** <sup>1</sup>H NMR spectra of [BMMIm][2-MeIm] at different concentrations in DMSO-d<sub>6</sub>/D<sub>2</sub>O solvent mixture (95:5, v/v), 400 MHz, after CO<sub>2</sub> bubbling for 15 minutes.



**Figure S9.** <sup>1</sup>H NMR spectra of [BMMIm][Im] at different concentrations in DMSO-d<sub>6</sub>/D<sub>2</sub>O solvent mixture (95:5, v/v), 400 MHz.



**Figure S10.**  $^1\text{H}$  NMR spectra of [BMMIm][Im] at different concentrations in  $\text{DMSO-}d_6/\text{D}_2\text{O}$  solvent mixture (95:5, v/v), 400 MHz, after  $\text{CO}_2$  bubbling for 15 minutes.

### 3.3 $^{13}\text{C}$ NMR

Figures S11-14 show a quantitative analysis of  $^{13}\text{C}$  NMR after  $\text{CO}_2$  bubbling for 15 min in the solution of [BMMIm][2-MeIm] and [BMMIm][Im] (1.0 M and 2.0 M of each solution), showing the bicarbonate anion at around 160 ppm. For these analysis, the longitudinal relaxation times ( $T_1$ ) were determined by NMR spectroscopy using inversion recovery with power gated decoupling pulse sequence (t1irpg). The experiments were carried out on a Bruker Avance III HD 400 spectrometer, operating at 101.6 MHz for  $^{13}\text{C}$  at 298 K. The relaxation delays ( $\tau$ ) were varied between 0.5 s and 50 s using 8 increments. For each experiment, 42 scans were accumulated with a recycle delay of 80 s. All fitted curves presented standard deviations lower than 0.05 s.

The  $T_1$  values were obtained by fitting the signal areas according to the equation:

$$I[t] = I[0] + P * \exp(-\tau/T1) \quad (1)$$

The values of  $T_1$  and their respective frequencies, for both ILs at 1.0 M and 2.0 M, are shown in Table S1-S4 below:

**Table S1.** T1 values for [BMMIm][2-MeIm] 1.0 M after CO<sub>2</sub> capture.

<b>Peak #</b>	<b>Frequency (ppm)</b>	<b>T1 (s)</b>
1	159.6	14.4
2	144.3	9.8
3	122.6	1.1
4	122.4	1.2
5	121.3	1.0
6	121.1	0.9
7	121.0	1.1
8	47.6	0.5
9	34.8	2.4
10	31.4	0.8
11	19.1	1.2
12	13.7	4.0
13	13.6	2.2
14	9.2	3.9

**Table S2.** T1 values for [BMMIm][2-MeIm] 2.0 M after CO<sub>2</sub> capture.

<b>Peak #</b>	<b>Frequency (ppm)</b>	<b>T1 (s)</b>
1	160.1	4.9
2	144.1	4.4
3	122.6	0.5
4	122.4	0.6
5	121.3	0.5
6	121.1	0.5
7	121.0	0.7
8	47.5	0.3
9	34.7	1.7
10	31.4	0.5
11	19.1	0.8
12	13.6	2.2
13	13.5	1.7
14	9.2	2.2

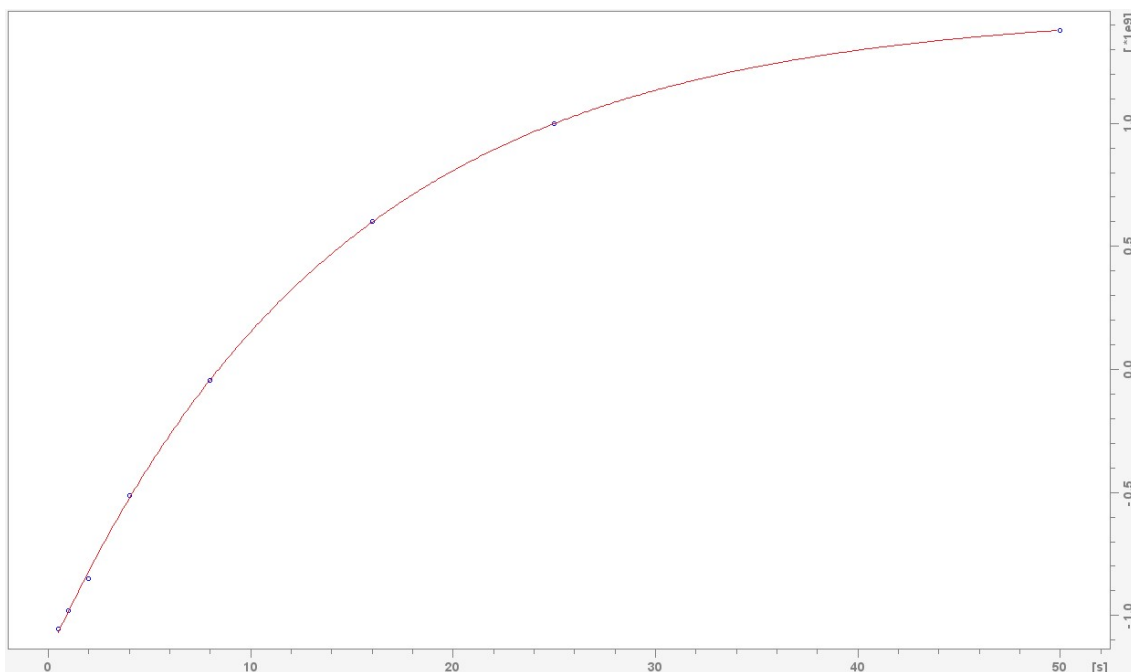
**Table S3.** T1 values for [BMMIm][Im] 1.0 M after CO<sub>2</sub> capture.

<b>Peak #</b>	<b>Frequency (ppm)</b>	<b>T1 (s)</b>
<b>1</b>	159.7	14.2
<b>2</b>	144.2	8.8
<b>3</b>	135.8	1.8
<b>4</b>	122.7	0.7
<b>5</b>	122.1	1.4
<b>6</b>	121.3	0.7
<b>7</b>	47.7	0.5
<b>8</b>	35	2.3
<b>9</b>	31.6	0.8
<b>10</b>	19.3	1.2
<b>11</b>	13.8	2.1
<b>12</b>	9.4	3.7

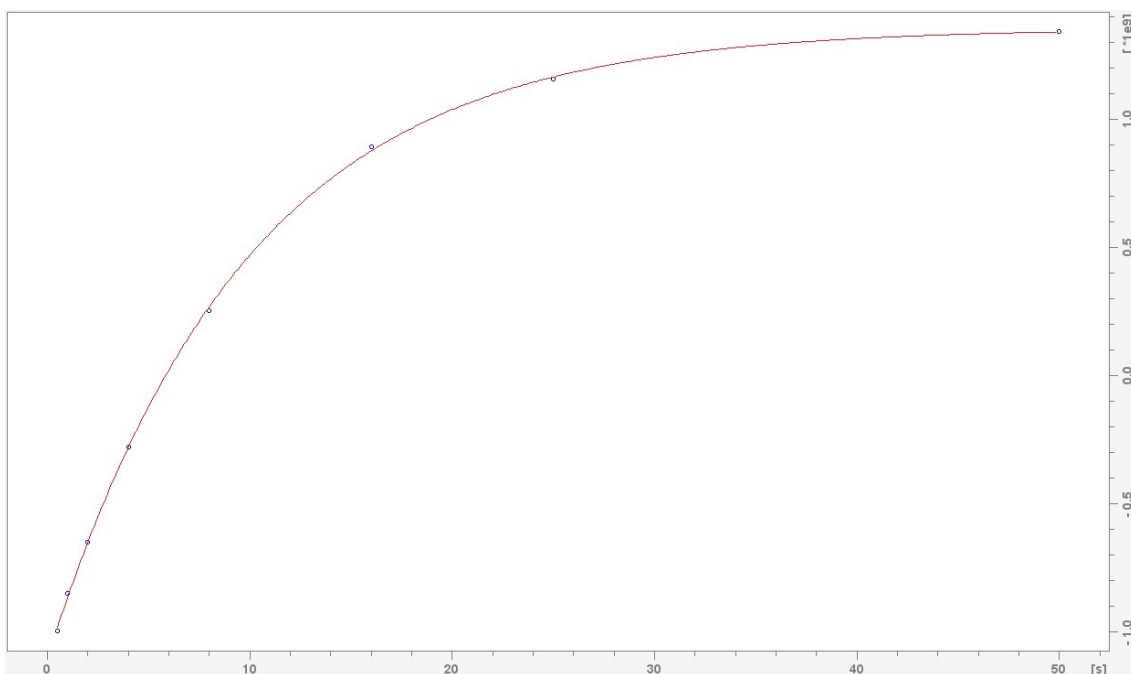
**Table S4.** T1 values for [BMMIm][Im] 2.0 M after CO<sub>2</sub> capture.

<b>Peak #</b>	<b>Frequency (ppm)</b>	<b>T1 (s)</b>
<b>1</b>	160.1	2.6
<b>2</b>	144.2	5.5
<b>3</b>	135.6	1.2
<b>4</b>	122.5	0.9
<b>5</b>	121.9	1.1
<b>6</b>	121.1	0.3
<b>7</b>	47.6	0.6
<b>8</b>	34.8	2.0
<b>9</b>	31.4	0.7
<b>10</b>	19.1	1.1
<b>11</b>	13.5	2.0
<b>12</b>	9.2	2.7

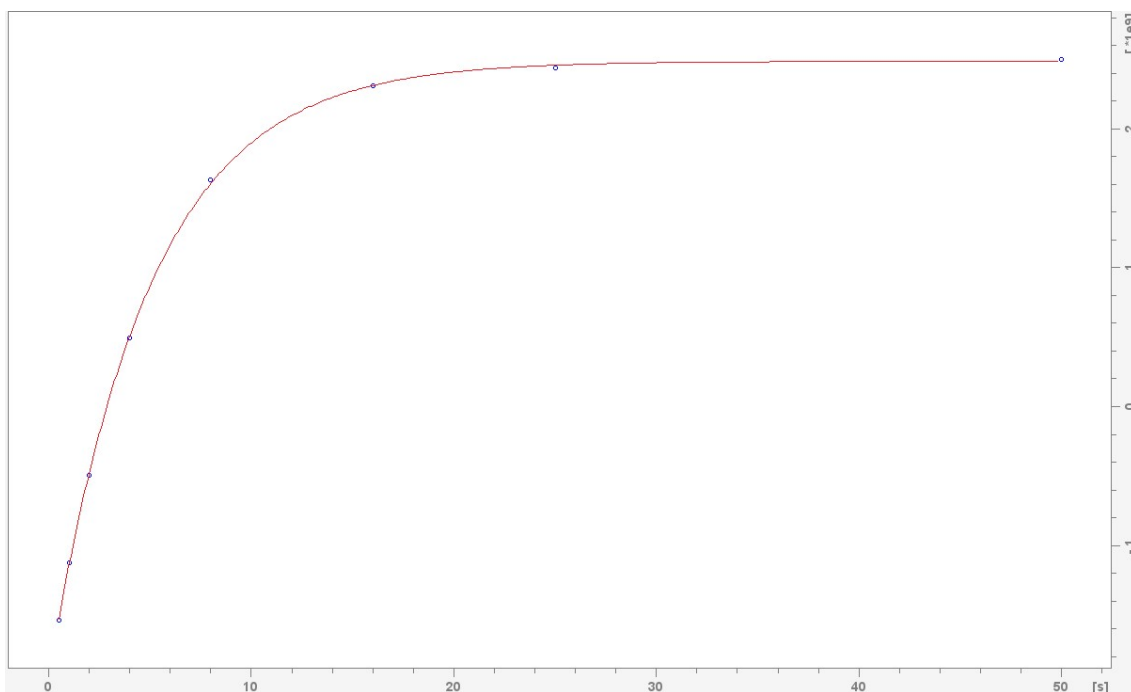
The fitting curves for the signals with the higher values are shown in Figures S11-S18 below:



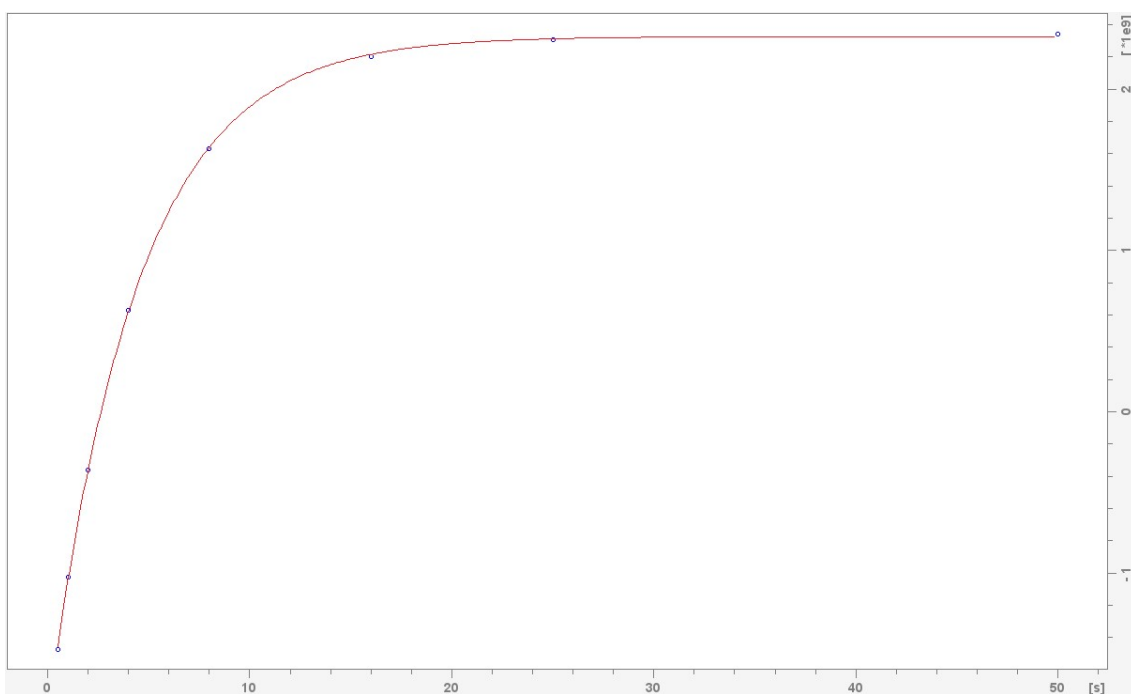
**Figure S11.** Exponential fitting curve used for T1 determination of signal #1 (159.6 ppm) for [BMMIm][MeIm] 1.0 M after CO<sub>2</sub> capture.



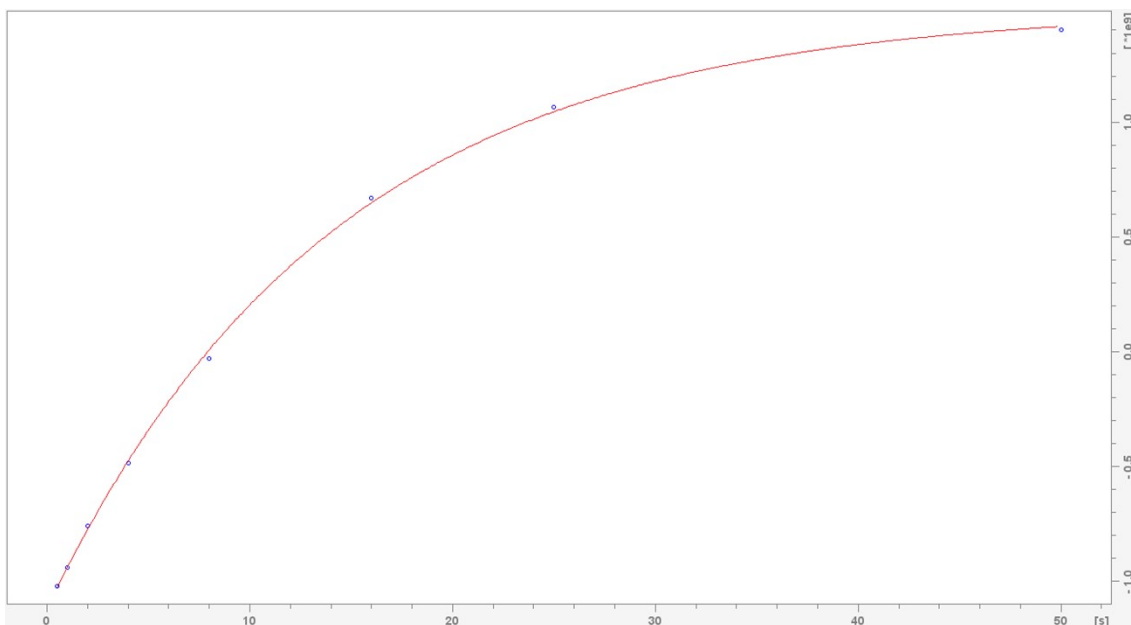
**Figure S12.** Exponential fitting curve used for T1 determination of signal #2 (144.3 ppm) for [BMMIm][MeIm] 1.0 M after CO<sub>2</sub> capture.



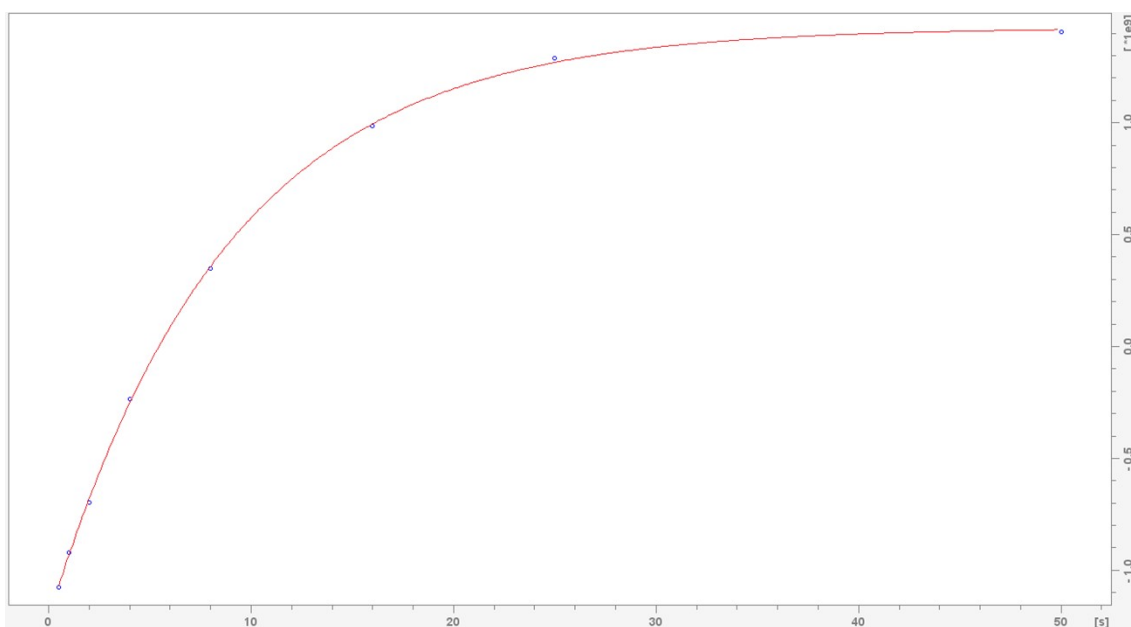
**Figure S13.** Exponential fitting curve used for T1 determination of signal #1 (160.1 ppm) for [BMMIm][MeIm] 2.0 M after CO<sub>2</sub> capture.



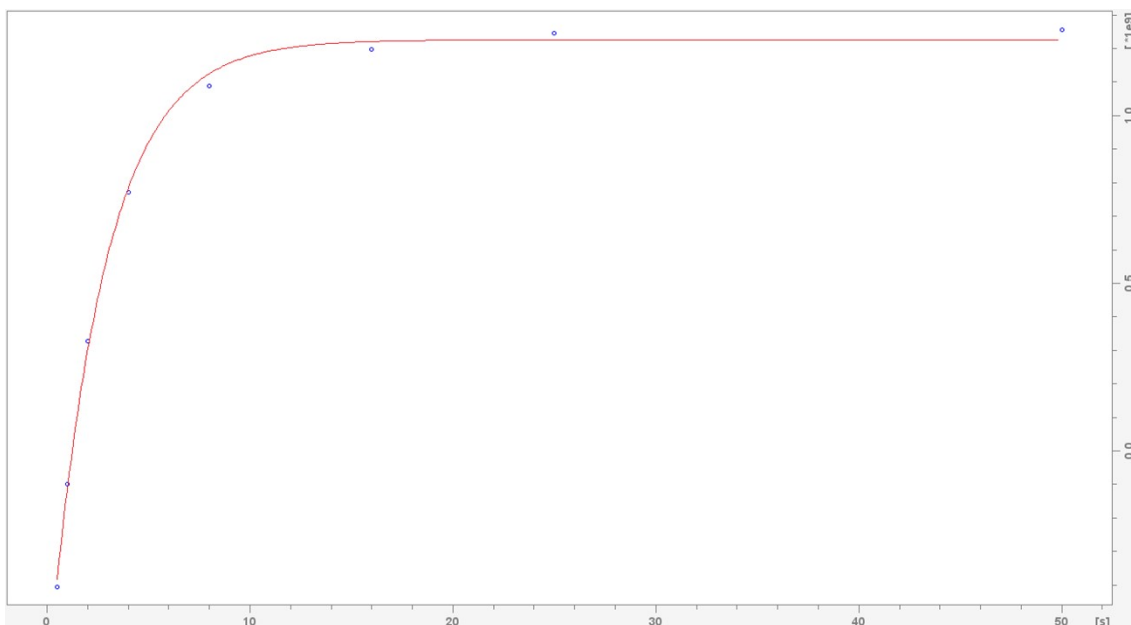
**Figure S14.** Exponential fitting curve used for T1 determination of signal #2 (144.1 ppm) for [BMMIm][MeIm] 2.0 M after CO<sub>2</sub> capture.



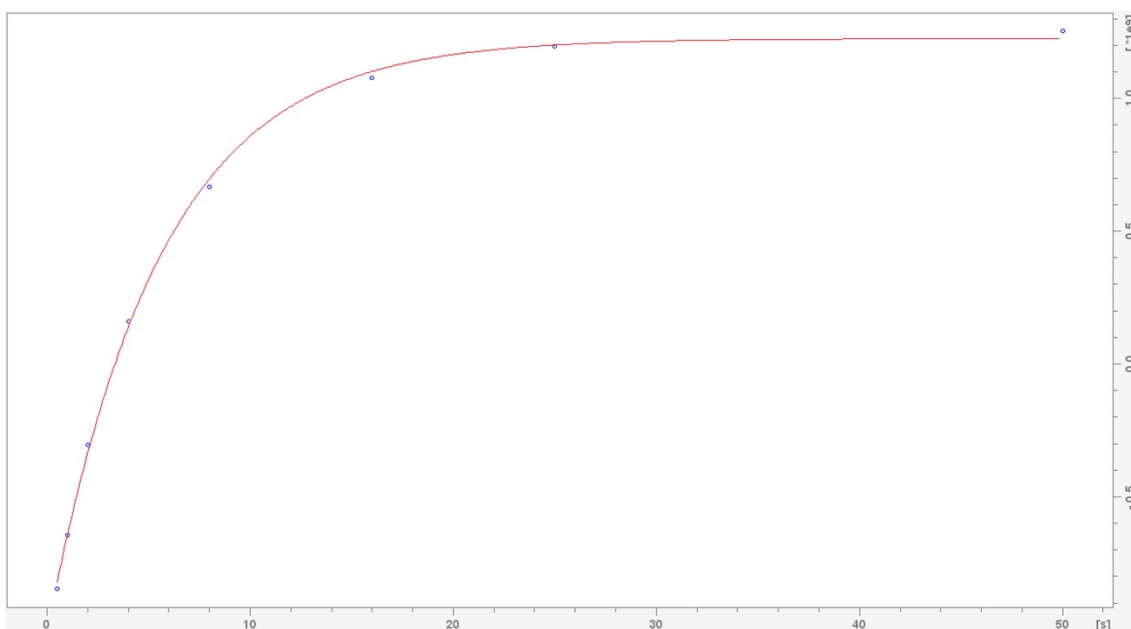
**Figure S15.** Exponential fitting curve used for T1 determination of signal #1 (159.7 ppm) for [BMMIm][Im] 1.0 M after CO<sub>2</sub> capture.



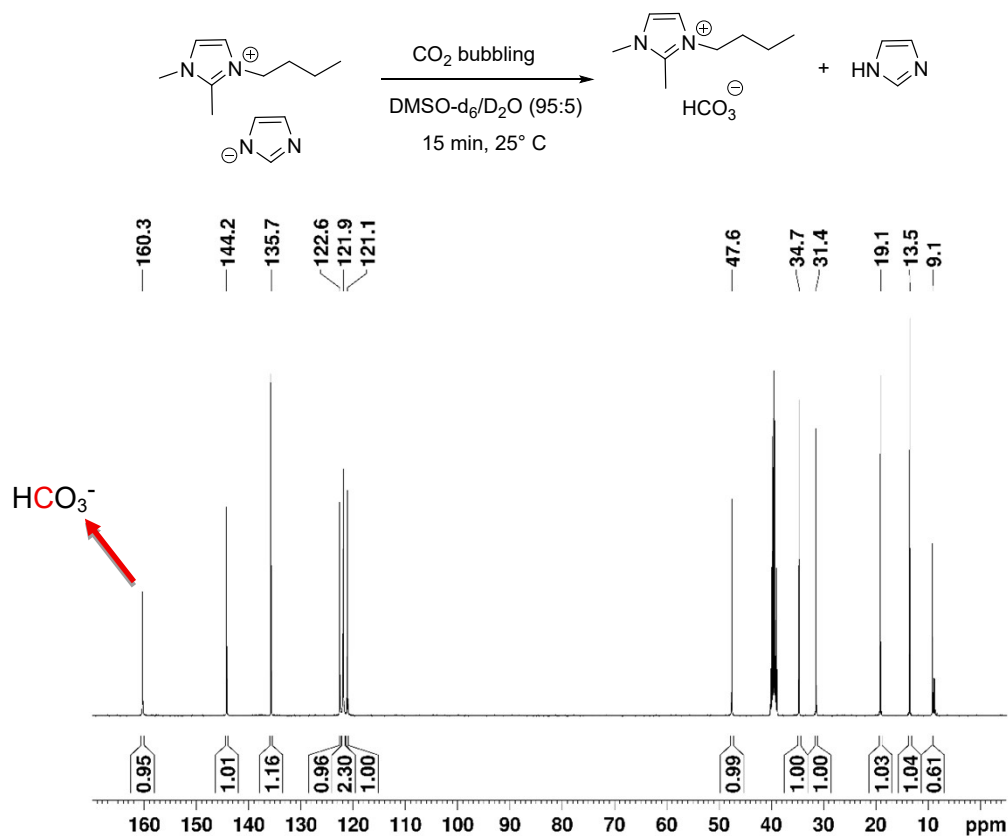
**Figure S16.** Exponential fitting curve used for T1 determination of signal #2 (144.2 ppm) for [BMMIm][Im] 1.0 M after CO<sub>2</sub> capture.



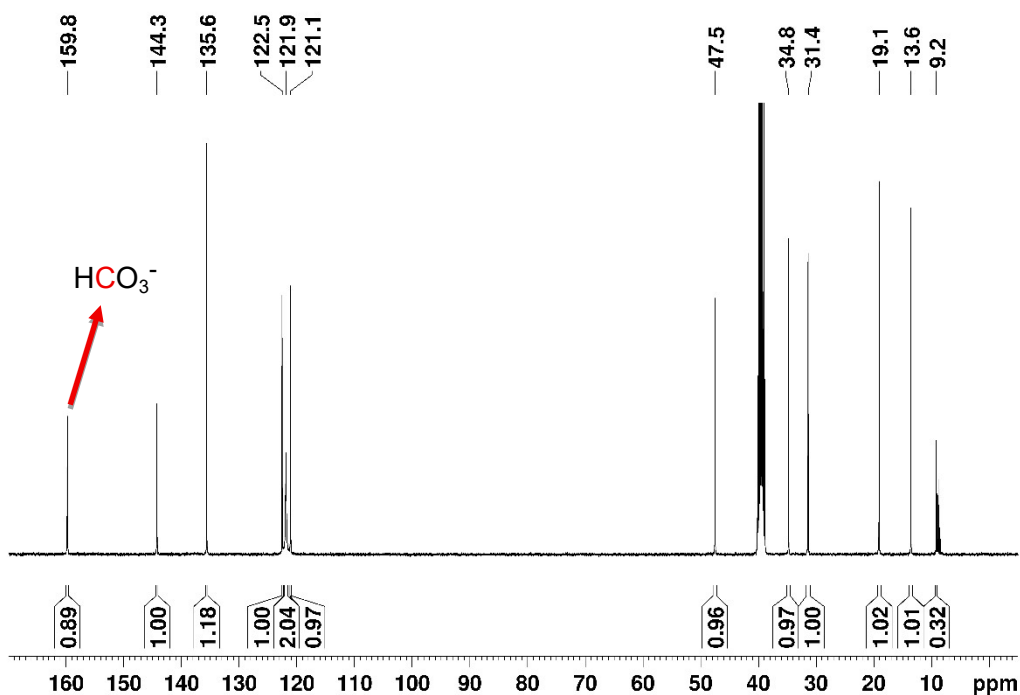
**Figure S17.** Exponential fitting curve used for T1 determination of signal #1 (160.1 ppm) for [BMMIm][Im] 2.0 M after CO<sub>2</sub> capture.



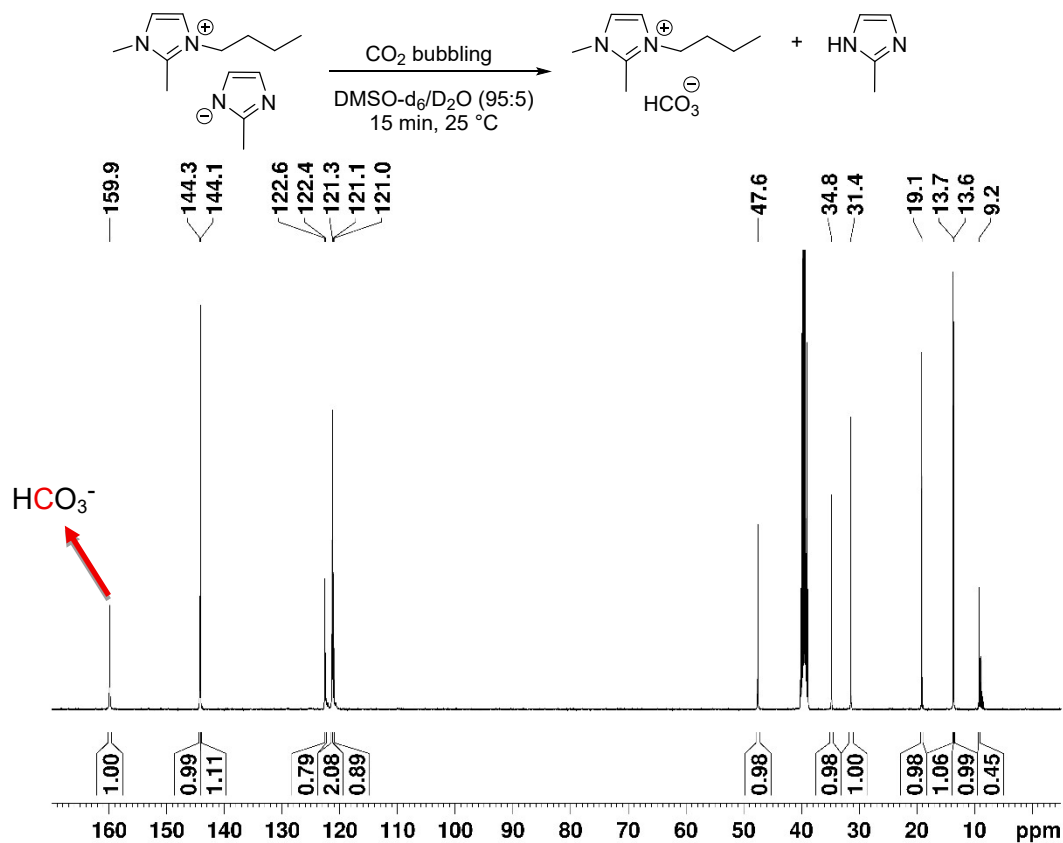
**Figure S18.** Exponential fitting curve used for T1 determination of signal #2 (144.2 ppm) for [BMMIm][Im] 2.0 M after CO<sub>2</sub> capture.



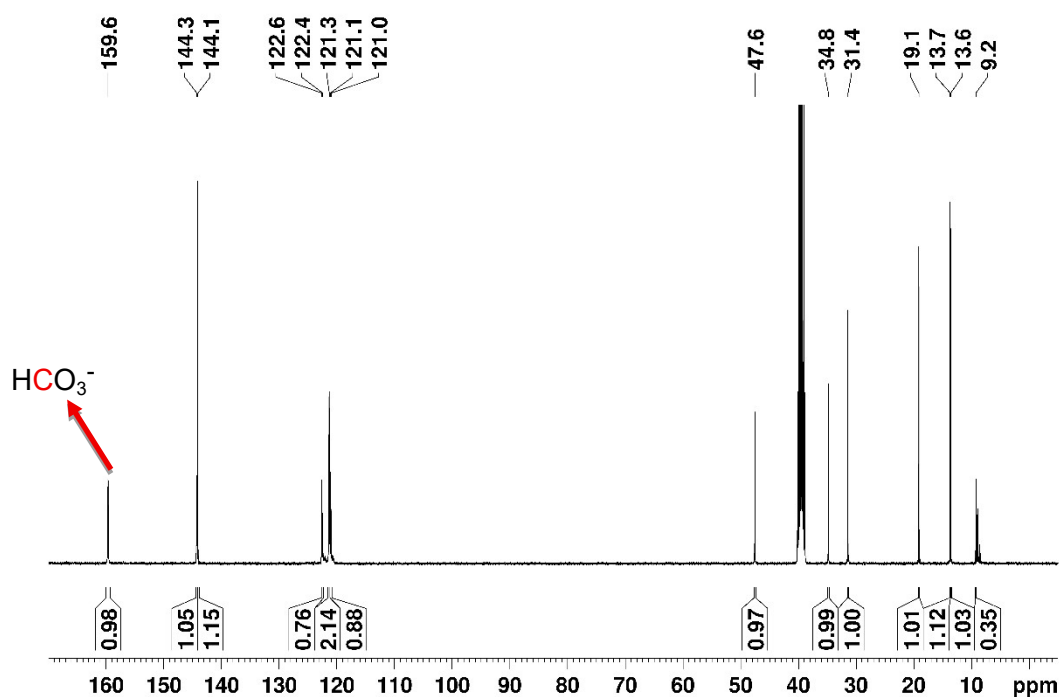
**Figure S19.** Quantitative <sup>13</sup>C NMR analysis for [BMMIm][Im] 2.0 M solution in DMSO-d<sub>6</sub>/D<sub>2</sub>O solvent mixture (95:5, v/v), 101.6 MHz, d1: 40 s.



**Figure S20.** Quantitative <sup>13</sup>C NMR analysis for [BMMIm][Im] 1.0 M solution in DMSO-d<sub>6</sub>/D<sub>2</sub>O solvent mixture (95:5, v/v), 101.6 MHz, d1: 80 s.



**Figure S21.** Quantitative  $^{13}\text{C}$  NMR analysis for [BMMIm][2-MeIm] 2.0 M solution in DMSO- $\text{d}_6/\text{D}_2\text{O}$  solvent mixture (95:5, v/v), 101.6 MHz, d1: 40 s.



**Figure S22.** Quantitative  $^{13}\text{C}$  NMR analysis for [BMMIm][2-MeIm] 1.0 M solution in DMSO- $\text{d}_6/\text{D}_2\text{O}$  solvent mixture (95:5, v/v), 101.6 MHz, d1: 80 s.

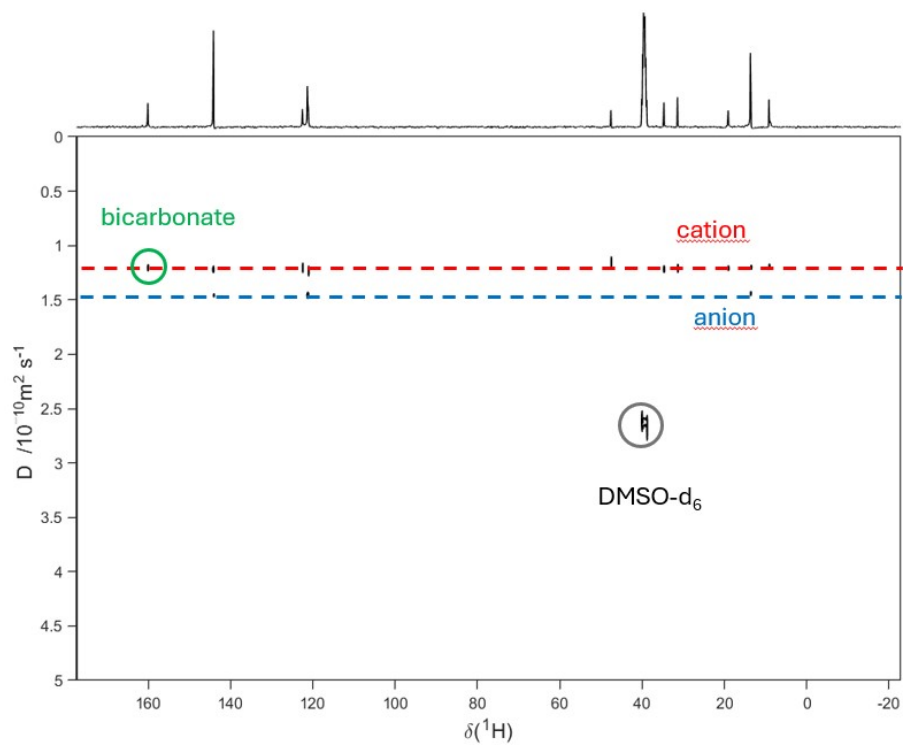
**Table S5.** Quantitative analysis of bicarbonate ( $\text{HCO}_3^-$ ) formation from  $^{13}\text{C}$  NMR for [BMMIm][Im] and [BMMIm][2-MeIm] at 1.0 M and 2.0 M.

Ionic Liquid	Ratio of $\text{HCO}_3^-$	Ratio of $\text{HCO}_3^-$
	1.0 M	2.0 M
[BMMIm][Im]	0.89	<b>0.95</b>
[BMMIm][2-MeIm]	<b>0.98</b>	<b>1.0</b>

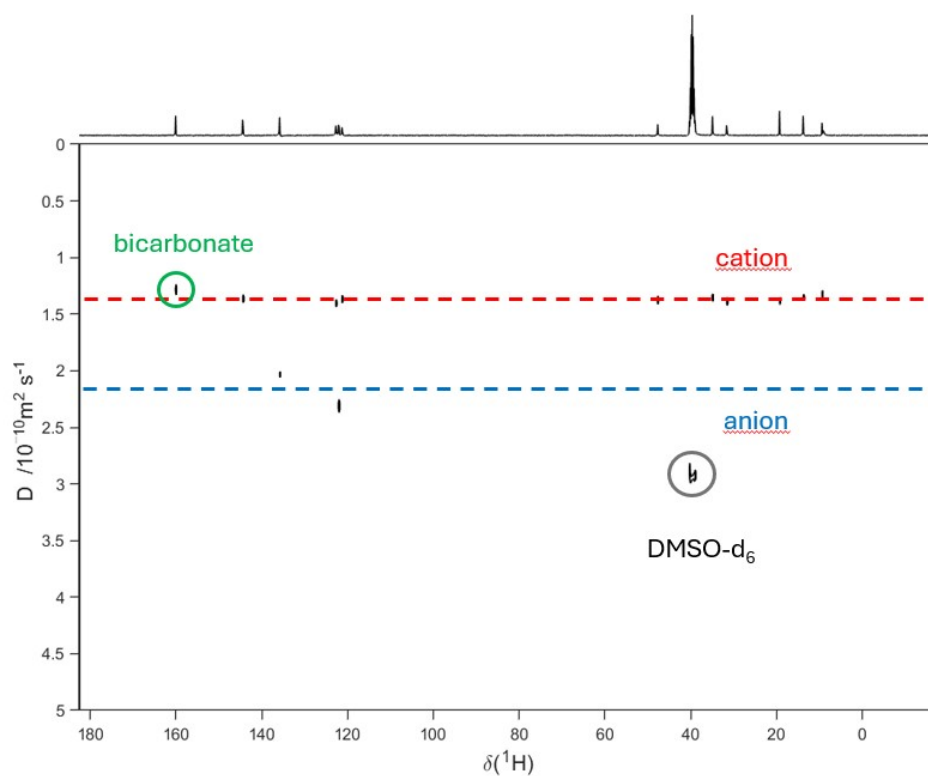
### 3.4 DOSY experiments

All NMR analyses were performed on a Bruker Avance III HD 400 spectrometer, operating at 400 MHz for  $^1\text{H}$  and 101.6 MHz for  $^{13}\text{C}$ .  $^1\text{H}$ -DOSY experiments were performed using the Doneshot45  $^1\text{H}$  pulse sequence with sine-shaped gradients, with the gradient strength varied between 10% and 80%. The parameters p30 (2000 – 2300  $\mu\text{s}$ ), d16 (2 ms), and d20 (90 – 170 ms) were optimized to achieve signal attenuation between 75% and 90%. The Doneshot  $^{13}\text{C}$  pulse sequence with sine-shaped gradients was employed, using d1 = 40 s, p30 = 5000  $\mu\text{s}$ , and d20 values in the range of 300 – 450 ms. The parameters were optimized to obtain signal attenuation between 75% and 90%. DOSY data processing was performed using the General NMR Analysis Toolbox (GNAT), version 2.0.

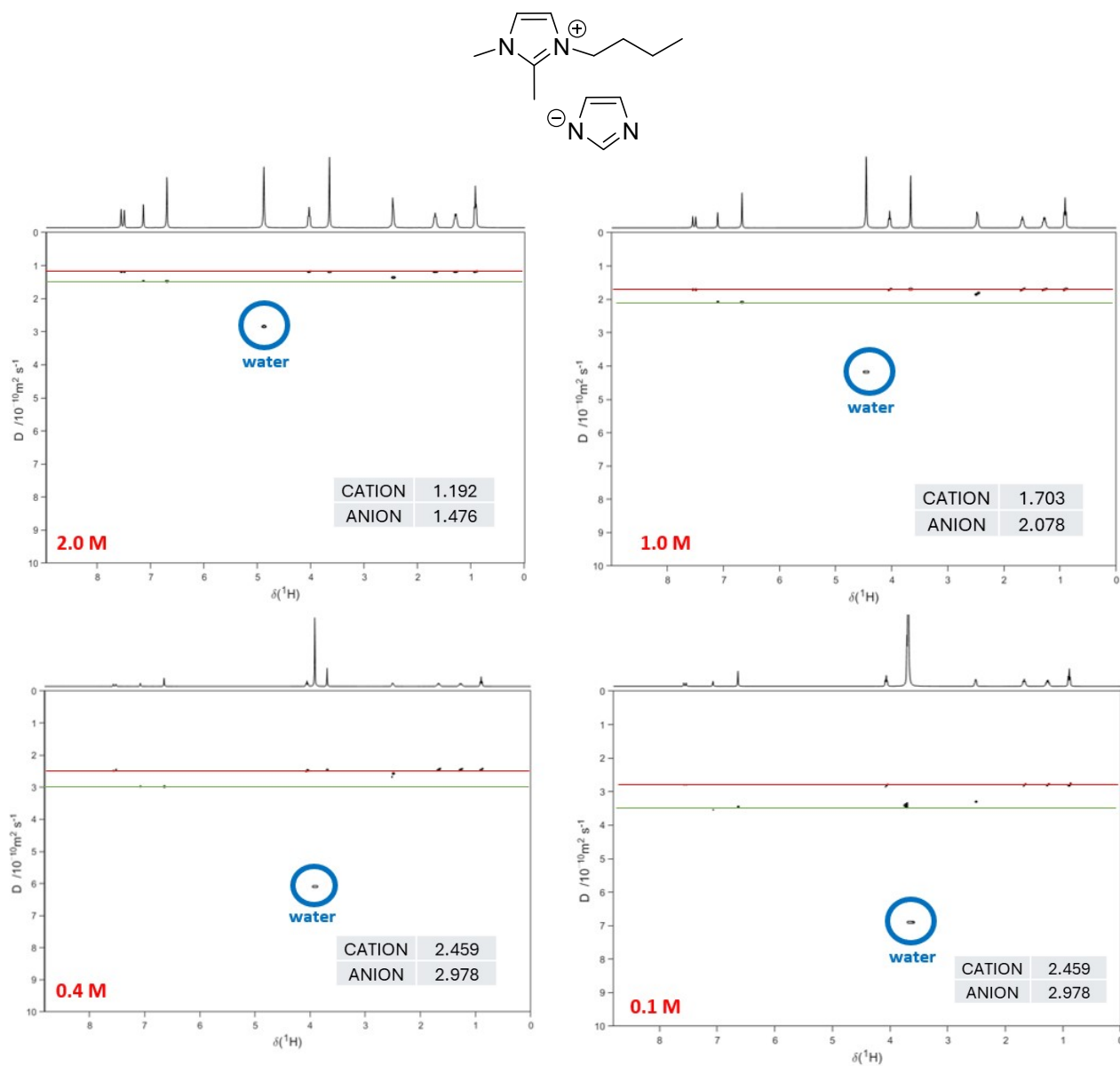
Figures S23 and S24 show some examples of  $^{13}\text{C}$ -DOSY experiments for 2.0 M solution of [BMMIm][2-MeIm] and 1.0 M solution of [BMMIm][Im], after bubbling  $\text{CO}_2$ .



**Figure S23.** [BMMIm][2-MeIm] 2.0 M with CO<sub>2</sub> obtained from the <sup>13</sup>C-DOSY experiments. Cation, anion and bicarbonate are represented in red, blue and green, respectively.

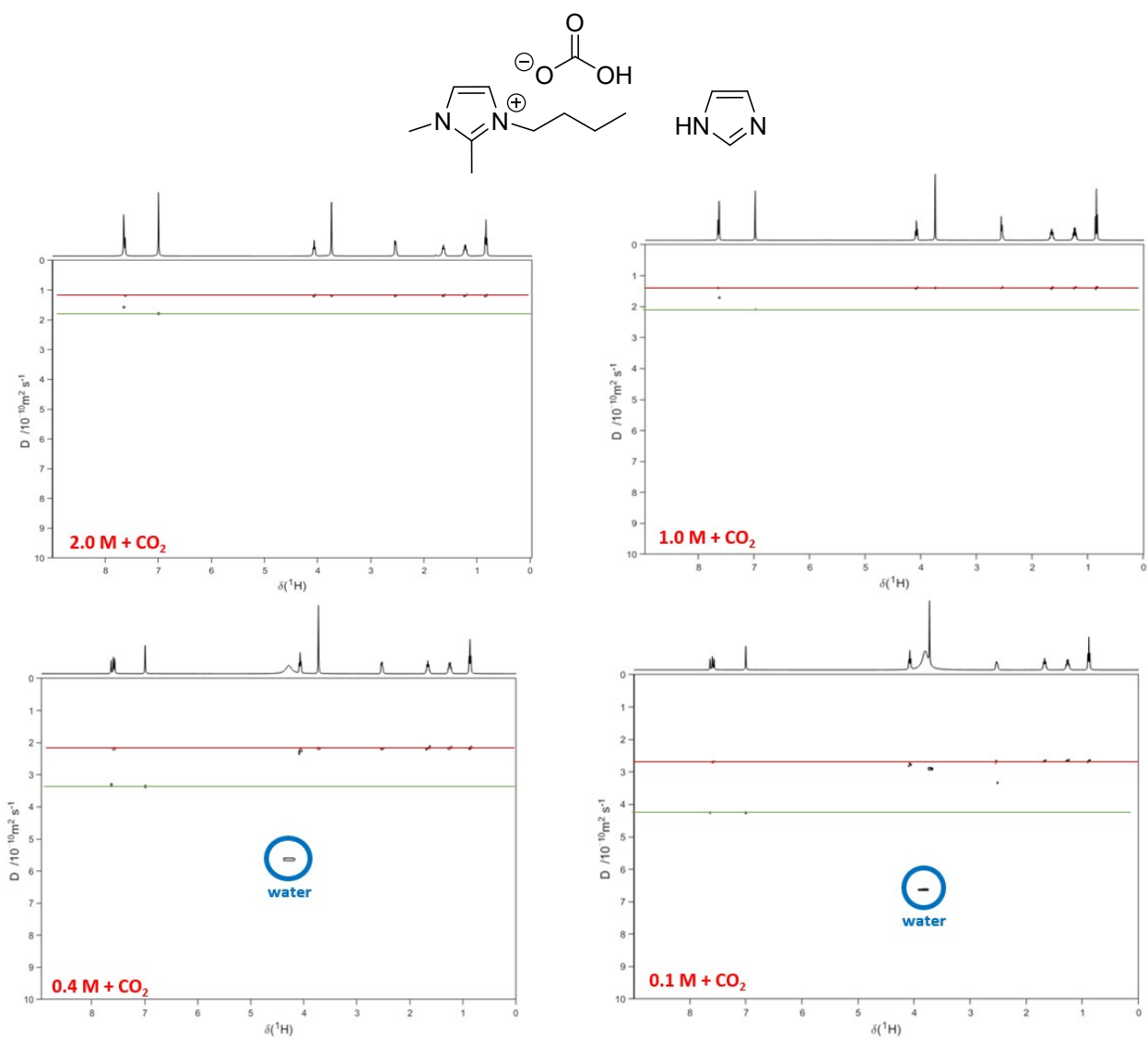


**Figure S24.** [BMMIm][Im] 1.0 M with CO<sub>2</sub> obtained from the <sup>13</sup>C-DOSY experiments. Cation, anion and bicarbonate are represented in red, blue and green, respectively.

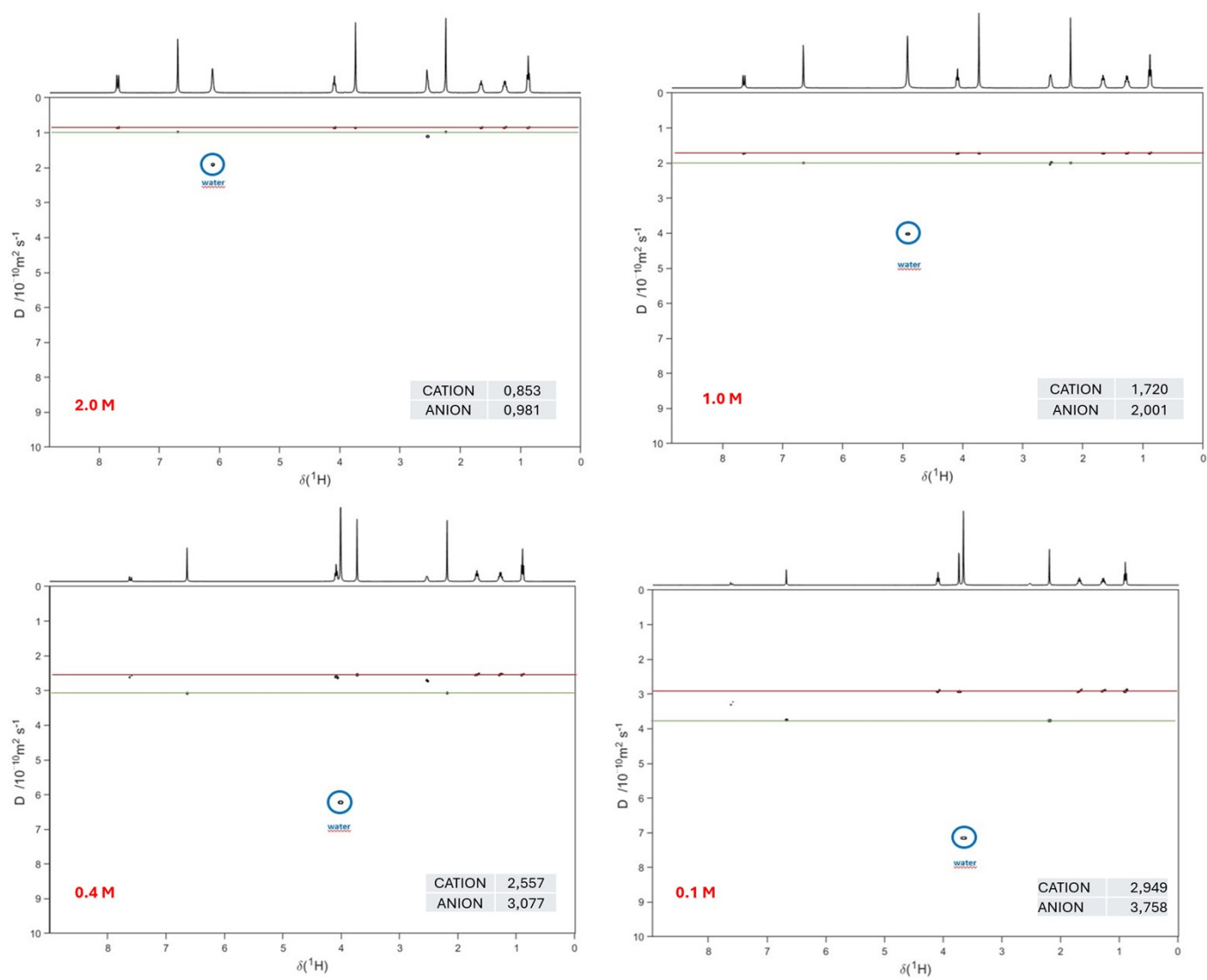
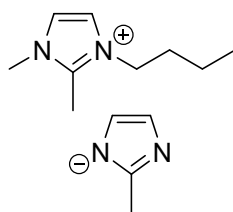


**Figure S25.** [BMMIm][Im] solutions obtained from the  $^1\text{H}$ -DOSY experiments. Cation and anion are represented in red and green, respectively.

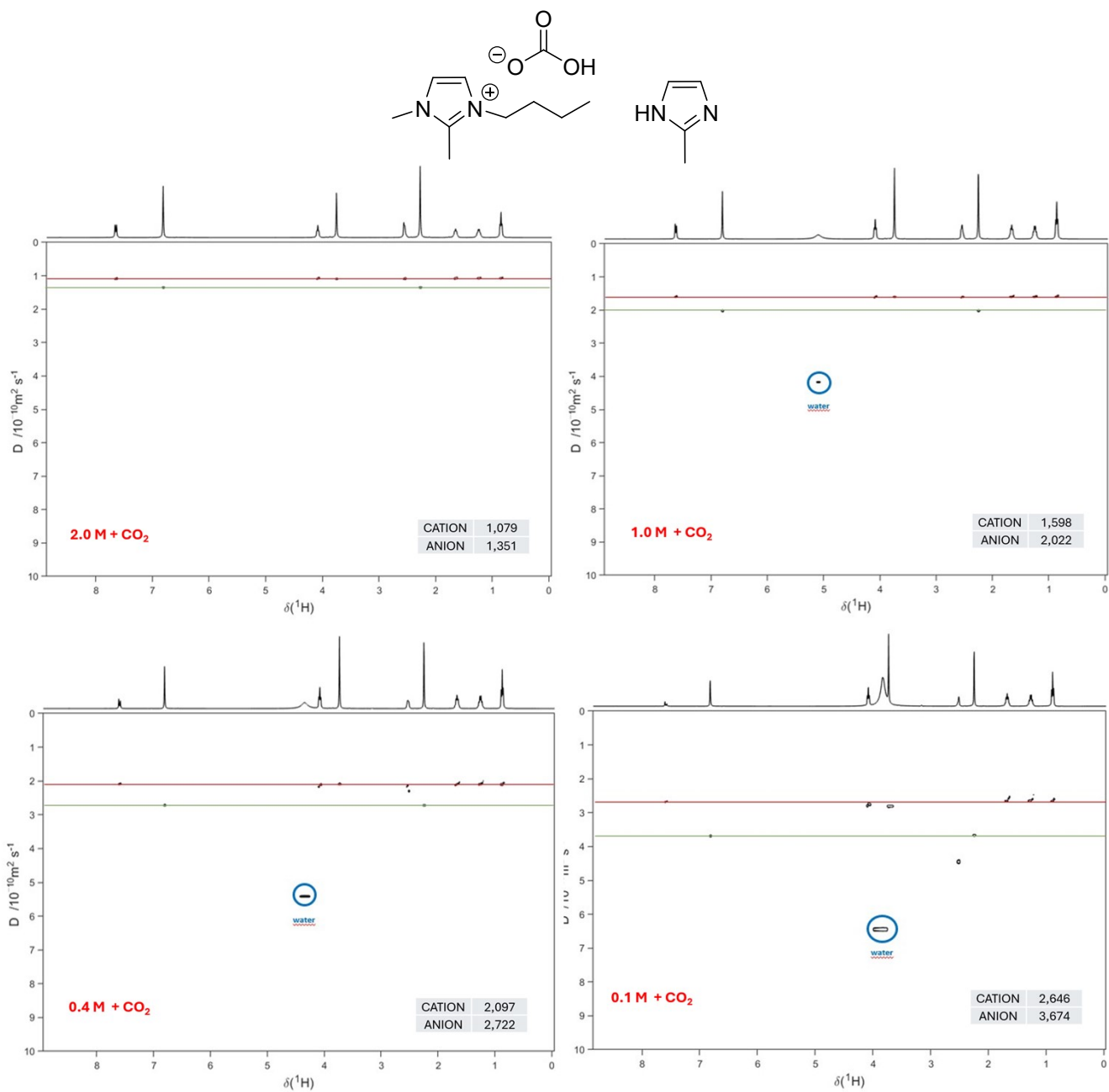
Figure S26 shows NMR  $^1\text{H}$ -DOSY experiments for solutions of [BMMIm][Im] after bubbling  $\text{CO}_2$  for 15 min at different concentrations.



**Figure S26.** [BMMIm][Im] solutions after  $\text{CO}_2$  bubbling obtained from the  $^1\text{H}$ -DOSY experiments. Cation and anion are represented in red and green, respectively.



**Figure S27.** [BMMIm][2-MeIm] solutions obtained from the  $^1\text{H}$ -DOSY experiments. Cation and anion are represented in red and green, respectively.



**Figure S28.** [BMMIm][2-MeIm] solutions after CO<sub>2</sub> bubbling obtained from the <sup>1</sup>H-DOSY experiments. Cation and anion are represented in red and green, respectively.

**Table S6.** Diffusion coefficients (D) measured for each signal (frequency) of the <sup>1</sup>H-DOSY spectra of IL [BMMIm][Im] at different concentrations before and after CO<sub>2</sub> bubbling. The colors indicate the signals from: cation in orange, anion in purple, residual solvent in green, water in blue and peaks unrelated to sample in gray.

[BMMIm][Im] 0.1 M			[BMMIm][Im] 0.4 M			[BMMIm][Im] 1.0 M			[BMMIm][Im] 2.0 M		
Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error
0.874	2.756	0.007	0.880	2.431	0.003	0.891	1.681	0.002	0.896	1.180	0.002
0.893	2.816	0.009	0.898	2.455	0.006	0.909	1.696	0.003	0.914	1.187	0.001
0.911	2.825	0.009	0.916	2.467	0.004	0.926	1.714	0.002	0.932	1.197	0.001
1.240	2.760	0.004	1.243	2.423	0.002	1.251	1.678	0.002	1.257	1.182	0.002
1.259	2.788	0.002	1.261	2.440	0.002	1.270	1.696	0.002	1.274	1.189	0.001
1.277	2.816	0.002	1.280	2.453	0.001	1.288	1.705	0.002	1.293	1.196	0.001
1.296	2.835	0.004	1.299	2.476	0.005	1.306	1.721	0.002	1.311	1.201	0.001
1.637	2.711	0.008	1.634	2.397	0.006	1.651	1.686	0.002	1.650	1.190	0.001
1.655	2.770	0.004	1.653	2.434	0.003	1.670	1.703	0.001	1.668	1.195	0.000
1.674	2.798	0.001	1.671	2.447	0.001	1.688	1.716	0.001	1.686	1.202	0.001
1.692	2.831	0.002	1.690	2.462	0.002	2.468	1.808	0.004	2.463	1.358	0.008
1.711	2.876	0.006	1.708	2.483	0.004	2.481	1.854	0.005	3.649	1.188	0.002
2.515	3.298	0.016	2.500	2.568	0.006	3.663	1.698	0.004	4.012	1.182	0.002
2.536	2.951	0.012	2.515	2.674	0.007	4.019	1.689	0.004	4.030	1.192	0.001
3.686	6.901	0.006	3.691	2.459	0.004	4.037	1.706	0.002	4.047	1.201	0.002
3.710	3.438	0.045	3.914	6.094	0.006	4.055	1.728	0.002	4.878	2.845	0.012
4.050	2.796	0.005	4.037	2.490	0.006	4.454	4.180	0.006	6.695	1.477	0.002
4.068	2.816	0.002	4.055	2.476	0.003	6.669	2.082	0.004	7.136	1.476	0.001
4.086	2.870	0.006	4.073	2.511	0.005	7.103	2.074	0.004	7.494	1.195	0.001
6.642	3.449	0.006	6.646	2.978	0.005	7.494	1.713	0.002	7.553	1.194	0.001
7.075	3.548	0.003	7.077	2.978	0.005	7.548	1.712	0.003			
7.540	2.813	0.007	7.518	2.465	0.004						
7.580	2.816	0.009	7.563	2.488	0.003						

[BMMIm][Im] 0.1 M + CO <sub>2</sub>			[BMMIm][Im] 0.4 M + CO <sub>2</sub>			[BMMI][Im] 1.0 M + CO <sub>2</sub>			[BMMIm][Im] 2.0 M + CO <sub>2</sub>		
Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error
0.866	2.634	0.002	0.848	2.151	0.002	0.826	1.360	0.002	0.813	1.166	0.002
0.884	2.663	0.001	0.866	2.172	0.003	0.844	1.390	0.003	0.831	1.190	0.002
0.902	2.689	0.002	0.884	2.195	0.002	0.863	1.407	0.003	0.850	1.203	0.002
1.235	2.618	0.003	1.220	2.145	0.003	1.188	1.279	0.005	1.193	1.158	0.003
1.253	2.645	0.001	1.238	2.160	0.001	1.206	1.353	0.002	1.212	1.173	0.001
1.272	2.660	0.002	1.257	2.180	0.002	1.224	1.379	0.001	1.230	1.186	0.001
1.291	2.663	0.002	1.276	2.186	0.003	1.243	1.392	0.001	1.249	1.201	0.002
1.653	2.644	0.002	1.622	2.122	0.005	1.262	1.402	0.002	1.613	1.165	0.002
1.672	2.660	0.002	1.641	2.155	0.003	1.280	1.399	0.006	1.632	1.183	0.001
1.691	2.677	0.002	1.660	2.177	0.001	1.609	1.322	0.004	1.650	1.198	0.001
2.514	3.334	0.022	1.678	2.193	0.002	1.627	1.371	0.001	2.532	1.177	0.002
2.530	2.671	0.013	1.697	2.209	0.006	1.646	1.395	0.001	2.548	1.207	0.001
2.549	2.734	0.011	2.527	2.190	0.002	1.664	1.413	0.001	3.739	1.197	0.002
3.726	2.903	0.013	2.542	2.203	0.002	1.682	1.428	0.004	4.047	1.165	0.002
3.802	6.628	0.004	3.724	2.187	0.002	2.541	1.380	0.003	4.065	1.188	0.001
4.059	2.780	0.012	4.050	2.246	0.005	2.556	1.415	0.002	4.083	1.207	0.002
4.076	2.739	0.006	4.068	2.235	0.004	3.742	1.403	0.002	6.996	1.792	0.003
4.095	2.814	0.010	4.086	2.314	0.011	4.060	1.372	0.004	7.624	1.195	0.002

7.003	4.258	0.003	4.283	5.644	0.006	4.078	1.398	0.002	7.651	1.578	0.004
7.568	2.682	0.004	6.992	3.361	0.006	4.096	1.417	0.002			
7.598	2.697	0.007	7.565	2.189	0.003	6.979	2.078	0.002			
7.639	4.256	0.005	7.590	2.195	0.004	7.626	1.698	0.004			
			7.632	3.324	0.009	7.645	1.444	0.003			
Cation mean value $\pm$ SD	2.686 $\pm$ 0.072		2.190 $\pm$ 0.041			1.386 $\pm$ 0.038			1.186 $\pm$ 0.016		
Anion mean value $\pm$ SD	4.257 $\pm$ 0.002		3.343 $\pm$ 0.026			2.078			1.792		

**Table S7.** Diffusion coefficients (D) measured for each signal (frequency) of the  $^1\text{H}$ -DOSY spectra of IL [BMMIm][2-MeIm] at different concentrations before and after  $\text{CO}_2$  bubbling. The colors indicate the signals from: cation in orange, anion in purple, residual solvent in green, water in blue and peaks unrelated to sample in gray.

[BMMIm][2-MeIm] 0.1 M			[BMMIm][2-MeIm] 0.4 M			[BMMIm][2-MeIm] 1.0 M			[BMMIm][2-MeIm] 2.0 M		
Frequency (ppm)	D ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	Error	Frequency (ppm)	D ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	Error	Frequency (ppm)	D ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	Error	Frequency (ppm)	D ( $10^{-10} \text{ m}^2 \text{ s}^{-1}$ )	Error
0.869	2.873	0.007	0.865	2.522	0.002	0.850	1.704	0.002	0.843	0.843	0.002
0.888	2.925	0.009	0.883	2.529	0.002	0.869	1.718	0.003	0.861	0.853	0.001
0.907	2.927	0.011	0.901	2.561	0.008	0.886	1.720	0.006	0.879	0.857	0.002
1.219	2.807	0.011	1.233	2.526	0.003	1.223	1.704	0.003	1.222	0.845	0.002
1.237	2.884	0.004	1.252	2.533	0.002	1.241	1.713	0.002	1.239	0.849	0.001
1.255	2.897	0.002	1.270	2.538	0.002	1.260	1.725	0.002	1.259	0.854	0.001
1.275	2.918	0.002	1.290	2.560	0.005	1.279	1.730	0.002	1.277	0.857	0.002
1.293	2.922	0.004	1.645	2.532	0.004	1.631	1.716	0.001	1.626	0.849	0.002
1.312	2.944	0.013	1.664	2.538	0.001	1.650	1.719	0.001	1.644	0.854	0.001
1.633	2.850	0.005	1.683	2.548	0.002	1.668	1.724	0.003	1.662	0.857	0.001



0.902	2.957	0.009	0.900	2.473	0.002	0.874	1.585	0.004	0.842	0.750	0.002
1.234	2.892	0.003	1.219	2.383	0.006	1.203	1.528	0.006	1.200	0.747	0.001
1.253	2.907	0.002	1.236	2.439	0.004	1.220	1.571	0.003	1.219	0.755	0.001
1.271	2.917	0.001	1.255	2.450	0.001	1.239	1.585	0.001	1.237	0.757	0.001
1.291	2.924	0.004	1.274	2.442	0.003	1.257	1.586	0.001	1.257	0.754	0.002
1.633	2.831	0.007	1.293	2.428	0.003	1.276	1.568	0.004	1.602	0.750	0.003
1.651	2.847	0.002	1.311	2.321	0.009	1.295	1.506	0.013	1.621	0.757	0.001
1.670	2.917	0.002	1.635	2.381	0.004	1.621	1.550	0.006	1.639	0.761	0.000
1.688	2.929	0.002	1.653	2.429	0.001	1.639	1.577	0.002	1.658	0.763	0.001
1.706	2.903	0.006	1.672	2.436	0.001	1.657	1.586	0.001	1.676	0.751	0.003
2.239	4.168	0.006	1.691	2.436	0.002	1.676	1.579	0.002	2.255	1.025	0.001
2.501	4.942	0.019	1.709	2.425	0.006	1.694	1.540	0.005	2.508	1.819	0.005
2.524	2.951	0.010	2.246	3.389	0.005	2.246	2.109	0.001	2.542	1.612	0.020
2.531	2.952	0.003	2.508	4.893	0.013	2.508	3.442	0.005	2.587	0.767	0.001
3.729	3.235	0.022	3.746	2.473	0.004	2.549	1.763	0.009	2.603	0.776	0.002
4.064	2.957	0.004	3.879	1.451	0.008	2.558	1.686	0.007	3.790	0.762	0.001
4.082	2.966	0.003	4.079	2.480	0.002	3.763	1.601	0.002	4.105	0.755	0.002
4.101	3.005	0.006	4.097	2.484	0.001	4.088	1.580	0.003	4.123	0.762	0.000
6.811	4.168	0.006	4.115	2.523	0.004	4.106	1.591	0.002	4.141	0.768	0.001
7.589	2.932	0.004	6.807	3.394	0.005	4.125	1.602	0.004	6.788	1.026	0.001
7.618	2.946	0.003	7.627	2.470	0.004	6.790	2.110	0.004	7.750	0.760	0.001
			7.651	2.480	0.002	7.678	1.591	0.002	7.771	0.763	0.001
						7.699	1.601	0.002			
Cation mean value ± SD	2.923 ± 0.043			2.441 ± 0.044			1.573 ± 0.025			0.756 ± 0.006	
Anion mean value ± SD	4.168			3.391 ± 0.004			2.109 ± 0.001			1.025 ± 0.001	

**Table S8.** Diffusion coefficients (D) measured for each signal (frequency) of the <sup>13</sup>C-DOSY spectra of mixtures of ILs [BMMIm][Im] and [BMMIm][2-MeIm], at different concentrations, with CO<sub>2</sub>. The colors indicate the signals from: cation in orange, anions [Im]<sup>-</sup> and [2-MeIm]<sup>-</sup> in purple, residual solvent in green, peaks unrelated to sample in gray and anion HCO<sub>3</sub><sup>-</sup> in yellow.

[BMMIm][Im] 1.0 M + CO <sub>2</sub>			[BMMIm][Im] 2.0 M + CO <sub>2</sub>			[BMMIm][2-MeIm] 1.0 M + CO <sub>2</sub>			[BMMIm][2-MeIm] 2.0 M + CO <sub>2</sub>		
Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error	Frequency (ppm)	D (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	Error
8.998	1.415	0.060	8.949	1.233	0.033	8.839	1.900	0.134	8.803	1.150	0.124
9.194	1.428	0.049	9.157	1.183	0.059	9.047	1.871	0.130	8.999	1.266	0.096
9.402	1.329	0.024	9.353	1.103	0.033	9.242	1.664	0.059	9.195	1.193	0.016
13.768	1.353	0.012	13.719	1.210	0.007	13.596	1.675	0.033	13.561	1.239	0.009
19.296	1.383	0.014	19.296	1.179	0.017	13.706	2.039	0.024	13.671	1.441	0.008
31.588	1.387	0.020	31.563	1.223	0.020	19.112	1.700	0.035	19.138	1.205	0.021
34.963	1.354	0.016	34.926	1.189	0.013	31.416	1.743	0.035	31.430	1.200	0.036
39.048	2.923	0.027	39.048	2.638	0.026	34.804	1.646	0.040	34.768	1.208	0.025
39.256	2.937	0.017	39.256	2.646	0.009	38.901	3.404	0.074	38.890	2.657	0.082
39.464	2.937	0.005	39.464	2.623	0.010	39.109	3.484	0.025	39.098	2.619	0.018
39.672	2.945	0.004	39.672	2.608	0.008	39.317	3.501	0.010	39.306	2.626	0.014
39.880	2.954	0.006	39.880	2.602	0.008	39.525	3.538	0.011	39.514	2.617	0.011
40.088	2.950	0.018	40.088	2.593	0.011	39.733	3.497	0.011	39.722	2.618	0.014
40.296	2.888	0.045	40.296	2.645	0.037	39.941	3.501	0.031	39.930	2.654	0.018
47.744	1.376	0.024	47.744	1.180	0.021	40.149	3.463	0.083	40.138	2.632	0.061
121.174	1.445	0.095	121.284	1.190	0.015	47.548	1.654	0.061	47.586	1.148	0.058
121.309	1.366	0.020	122.104	2.275	0.051	121.016	1.881	0.098	121.151	1.271	0.033
122.079	2.311	0.039	122.715	1.250	0.016	121.150	1.672	0.061	121.335	1.462	0.014
122.617	1.465	0.083	135.851	1.853	0.017	121.297	2.259	0.073	122.460	1.321	0.087
122.752	1.404	0.019	144.400	1.176	0.011	122.459	1.438	0.178	122.570	1.205	0.035
135.851	2.032	0.011	160.372	1.038	0.005	122.581	1.617	0.093	144.169	1.418	0.006
144.436	1.364	0.017				144.058	2.046	0.025	160.166	1.224	0.018
160.115	1.285	0.025				144.278	1.660	0.035			
						159.676	1.587	0.151			

Cation mean value $\pm$ SD	$1.378 \pm 0.029$	$1.192 \pm 0.346$	$1.67 \pm 0.04$	$1.217 \pm 0.028$
Anion mean value $\pm$ SD	$2.171 \pm 0.197$	$2.064 \pm 0.298$	$2.042 \pm 0.005$	$1.440 \pm 0.022$
HCO <sub>3</sub> <sup>-</sup> value	1.285	1.038	1.587	1.224