

Supporting Information for:

Intermolecular hydrogen bonds in water@IL supramolecular complexes

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1. Synthesis and characterisation of ionic liquids

Materials and instruments. High resolution mass spectrometry electrospray ionization (HRMS-ESI) data, in a positive and negative mode, were collected using a Micromass Q-ToF instrument. Samples were infused by a 100 μL syringe at a flow rate of 30 $\mu\text{L min}^{-1}$ for all samples. Typical operating conditions were: a capillary voltage of 2980 V, a sample cone voltage of 30 V, an extraction cone voltage of 3.0 V, and a desolvation gas temperature of 60 $^{\circ}\text{C}$. N_2 was used as the desolvation gas and deionized water as the solvent of the samples.

Synthesis of 1-*n*-butyl-2,3-dimethyl-imidazolium chloride (BMMI-Cl): The ionic liquid was prepared according to known procedures,⁵¹ to give a white crystalline solid. Melting point: 94-96 $^{\circ}\text{C}$. ^1H NMR (400 MHz; CDCl_3): δ 7.90 (d, 1H, $^3J = 1.9$ Hz), 7.66 (d, 1H, $^3J = 1.9$ Hz), 4.28 (t, 2H, $^3J = 7.3$ Hz), 4.07 (s, 3H), 2.85 (s, 3H), 1.81 (quint, 2H, $^3J = 7.1$ Hz), 1.39 (sex, 2H, $^3J = 7.2$ Hz), 0.96 (t, 3H, $^3J = 7.2$ Hz).

General procedure of anion exchange: The corresponding imidazolium salt (20 mmol) was dissolved in a minimum amount of water and eluted through an ion exchange resin column (Amberlite IRA 400, 100mL, basic form). Imidazole (1.36 g, 20 mmol) was added to the resulting aqueous corresponding imidazolium hydroxide solution and the water was evaporated under reduced pressure.

1-*n*-butyl-2,3-dimethyl-imidazolium imidazolate (BMMI-Im):⁵² 1-*n*-butyl-2,3-dimethyl-imidazolium imidazolate chloride (3.77 g, 20 mmol) was eluted through the column to resulting an orange semisolid (4.05 g, 92 % yield). ^1H NMR (400 MHz, D_2O) δ 7.63 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 7.02 (s, 1H), 4.00 (t, 2H, $J = 7.3$ Hz), 3.66 (s, 3H), 2.47 (s, 3H), 1.69 (quint, 2H, $^3J = 7.3$ Hz), 1.25 (sex, 2H, $^3J = 7.3$ Hz), 0.86 (t, 3H, $^3J = 7.4$). ^{13}C NMR (101 MHz, D_2O) δ 143.8, 137.3, 122.3, 121.9, 120.5, 47.7, 34.3, 30.8, 18.7, 12.7, 8.4.

1-*n*-butyl-2,3-dimethyl-imidazolium methylimidazolate (BMMI-Melm): 1-*n*-butyl-2,3-dimethyl-imidazolium imidazolate chloride (3.77 g, 20 mmol) was eluted through the column to resulting an purple crystal (4.17 g, 89 % yield).

^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$) δ ppm 7.66 (d, 1H, $^3J = 2$ Hz), 7.61 (d, 1H, $^3J = 2$ Hz), 6.50 (s, 2H), 4.07 (t, 2H, $^3J = 7.6$ Hz), 3.70 (s, 3H), 2.51 (m, 3H, H7), 2.12 (s, 3H), 1.66 (quint, 2H, $^3J = 7.2$ Hz), 1.27 (sex, 2H, $^3J = 8$ Hz), 0.90 (t, 3H, $^3J = 7.2$ Hz). ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$) δ ppm 148.8; 144.2; 123.9;

122.3; 120.9; 47.2; 34.5; 31.3; 18.9; 17.2; 13.5; 9.0. ESI-HRMS(+) (m/z) elem. anal. calc. para: $C_9H_{17}N_2^+$ 153,13862; Found: 153,1389.

1-*n*-butyl-2,3-dimethyl-imidazolium pyrazolate (BMMI-Pyr): 1-*n*-butyl-2,3-dimethyl-imidazolium imidazolate chloride (3.77 g, 20 mmol) was eluted through the column to resulting an orange semisolid (3.61 g, 82 % yield). 1H NMR (400 MHz, D_2O) δ ppm 7.57 (d, 2H, $^3J = 2.0$ Hz), 7.22 (d, 2H, $^3J = 2.1$ Hz), 7.19 (d, 1H, $^3J = 2.0$ Hz, H5), 6.27 (m, 1H, H15), 3.95 (t, 2H, $^3J = 7.3$ Hz), 3.63 (s, 3H, H6), 2.43 (s, 3H, H7), 1.64 (quint, 2H, $^3J = 7.5$ Hz), 1.21 (sex, 2H, $^3J = 7.7$ Hz), 0.82 (t, 3H, $^3J = 7.4$ Hz). ^{13}C NMR (100 MHz, D_2O) δ ppm 143.8; 124.5; 121.9; 120.5; 104.6; 34.3; 30.8; 23.3; 18.7; 12.7; 8.6. ESI-HRMS(+) (m/z) elem. anal. calc. para: $C_9H_{17}N_2^+$ 153,13862; Found: 153,1380.

Deuteration of ionic liquid

The ionic liquid (0.1 mmol or 0.5 mmol) were charged in an Eppendorf and $CDCl_3$ (0.5 mL) was added and the solution transferred to a NMR tube kept at room temperature (298 K). The 1H NMR analysis was performed after 1 hour. Deuterium incorporation was calculated using the H11 (CH_3 of butyl) signal of ionic liquid as the internal standard (Figures S7-S9). Similar procedure has been done to prepare the NMR tube to 2D analysis.

Synthesis of deuterated ketones

The correspond IL catalysts (0.2 mmol) and acetophenone (1 mmol) were charged in an Eppendorf and $CDCl_3$ (0.5 mL) was added. The reaction solution was transferred to a NMR tube kept at room temperature (298 K). The 1H NMR analyses were performed after 1 hour and 24 hours. Deuterium incorporation was calculated using the signal from ortho hydrogens of the substrate as the internal standard, as showed in Figures S10-S12.

2. NOESY analysis of BMMI-Im (different solvents)

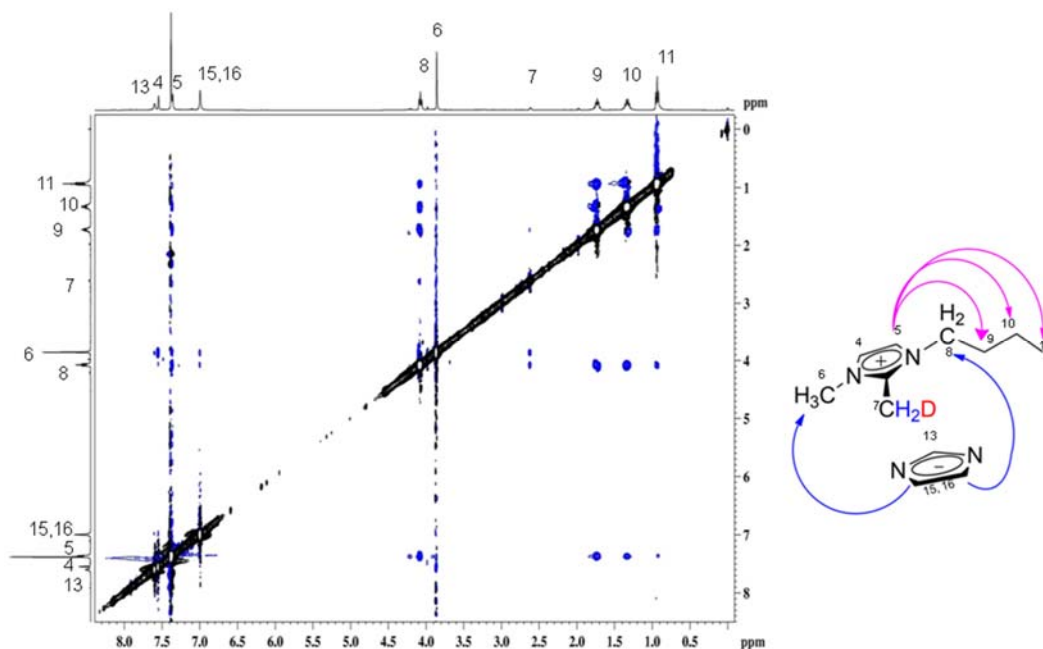


Figure S1. $^1\text{H},^1\text{H}$ -NOESY contour map of BMMI-Im in CDCl_3 ($0.2 \text{ mol}\cdot\text{L}^{-1}$), chemical shifts were referenced to TMS peak.

The NOESY counter map indicates a stronger NOE correlation due to the intramolecular interaction between the protons on the butyl substituent (even with more distance signal - H11) with H4 and H5 of the imidazolium ring. A moderate NOE correlation was observed due to the intermolecular interaction of imidazolate hydrogen (H15 and H16) with H6 and H8 of the cation.

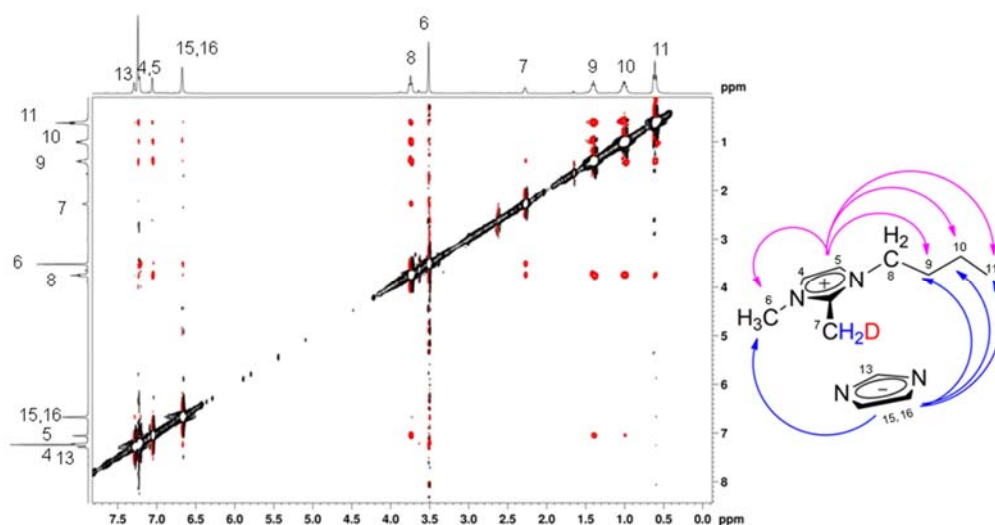


Figure S2. $^1\text{H},^1\text{H}$ -NOESY of contour map of BMMI-Im in CDCl_3 ($1 \text{ mol}\cdot\text{L}^{-1}$).

The NOESY pattern of Figure S2 indicate a stronger NOE correlation due to intermolecular interaction when compare to 0.2 mol.L^{-1} in the same solvent. Strong ion pair contact characterized by cross peaks of imidazolate hydrogen (H15, H16) with the cation hydrogen H6, H8, H9, H10, H11.

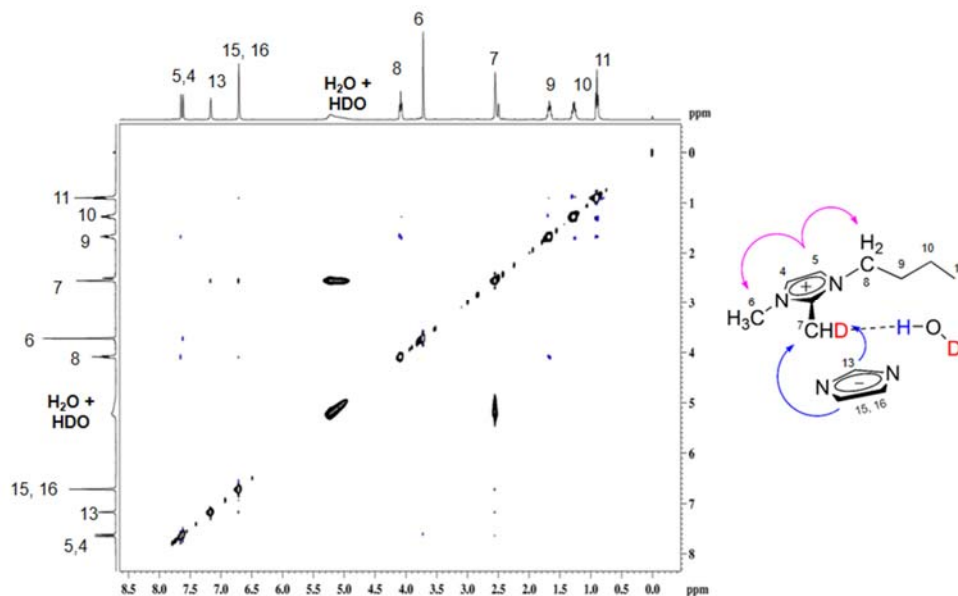


Figure S3. $^1\text{H}, ^1\text{H}$ -NOESY contour map of BMMI·Im in $[\text{D}_6]\text{DMSO}$ (0.2 mol.L^{-1}).

The NOESY indicate weaker intra and intermolecular correlation when compare to 0.2 mol.L^{-1} in the CDCl_3 , due to higher dielectric constant. Interesting to note the appearance of broad signal around 5.3 ppm, corresponding to water molecule, thereby providing evidence of water–imidazolium cation interactions.

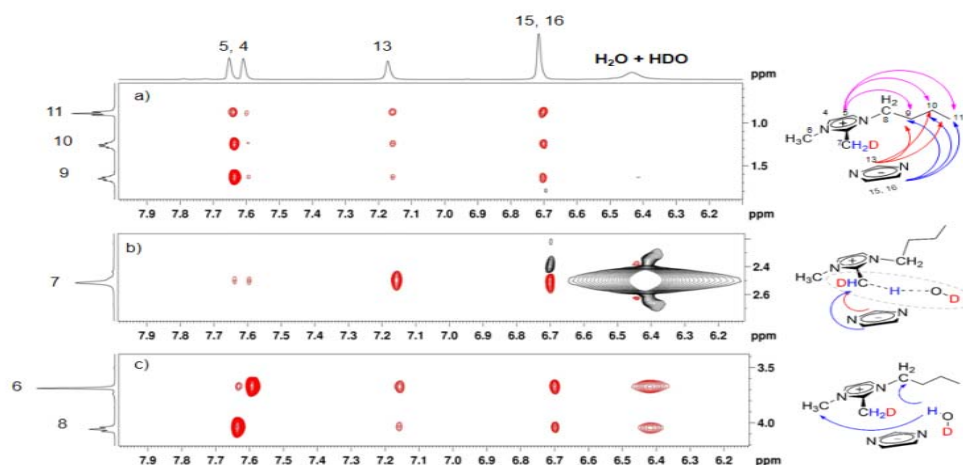


Figure S4. $^1\text{H}, ^1\text{H}$ -NOESY zoom of contour map of BMMI·Im in $[\text{D}_6]\text{DMSO}$ (1 mol.L^{-1}).

The NOESY pattern indicate stronger NOE correlation due to intermolecular interaction compare to 0.2 mol.L^{-1} in the same solvent. The HDO signal (*c.a.* 6.4 ppm) could be observed in the $^1\text{H}, ^1\text{H}$ -NOESY

experiments and the crossover peaks indicate that this species exchanges H with the C7-methyl group of the cation.

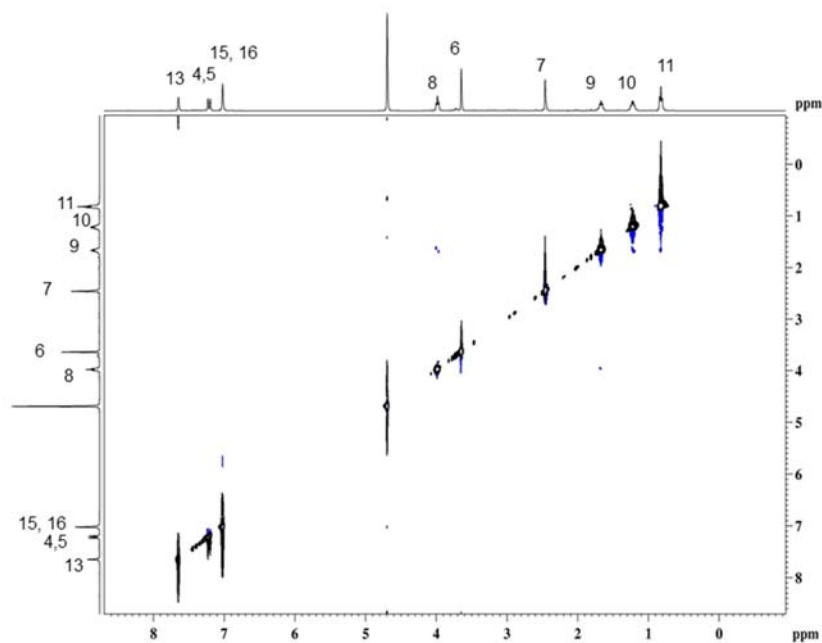


Figure S5. $^1\text{H}, ^1\text{H}$ -NOESY zoom of contour map of BMMI-Im in D_2O ($0.2 \text{ mol}\cdot\text{L}^{-1}$).

No significant NOE correlation could be detected, indicating higher solvation by the D_2O , and ion pair separated by solvent.

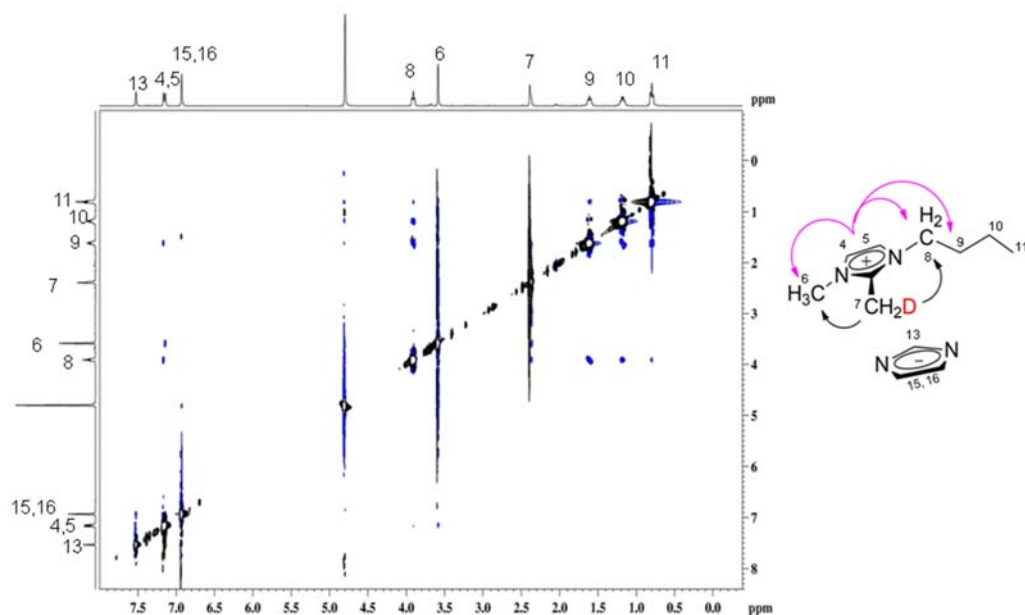


Figure S6. $^1\text{H}, ^1\text{H}$ -NOESY zoom of contour map of BMMI-Im in D_2O ($1 \text{ mol}\cdot\text{L}^{-1}$).

The NOESY counter map indicate strong intramolecular correlation into the cation and no significant intermolecular correlation.

3. H/D exchange reaction at C7 position for BMMI·X ILs

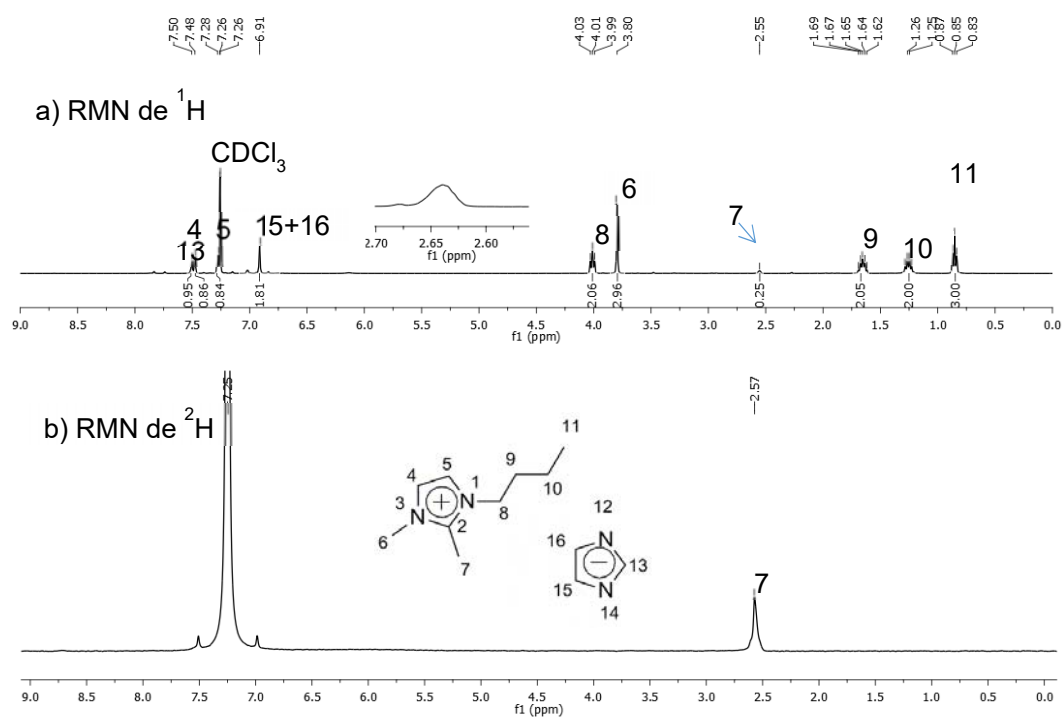


Figure S7. NMR spectrum of BMMI·Im in CDCl_3 ($0.2 \text{ mol}\cdot\text{L}^{-1}$) after 1 h: (a) ^1H NMR (400 MHz) e (b) ^2H NMR (61.4 MHz).

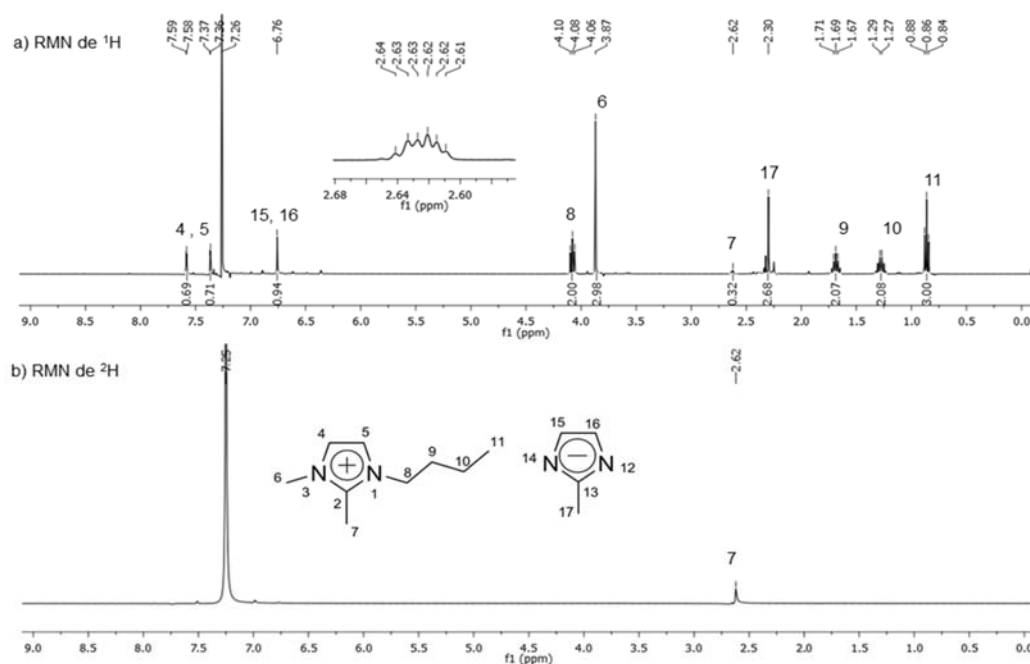


Figure S8. NMR spectrum of BMMI·MeIm in CDCl_3 ($0.2 \text{ mol}\cdot\text{L}^{-1}$) after 1 h: (a) ^1H NMR (400 MHz) e (b) ^2H NMR (61.4 MHz).

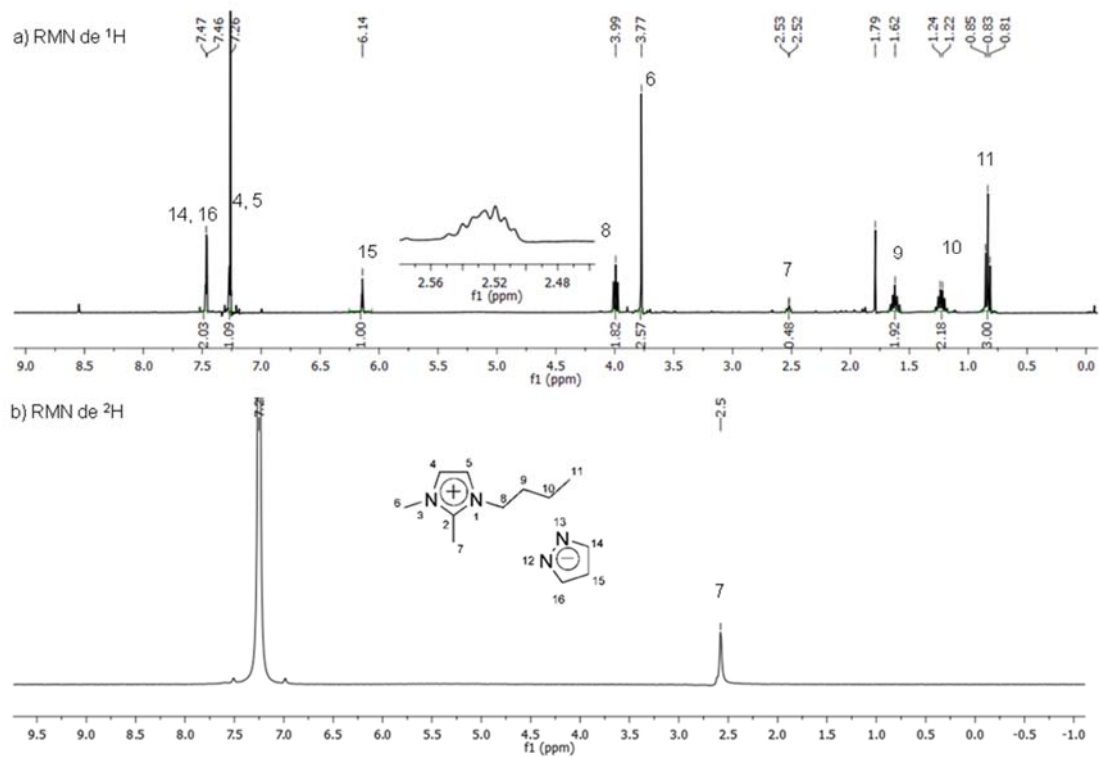


Figure S9. ^1H NMR (400 MHz) spectrum of BMMI·Pyr in CDCl_3 ($0.2 \text{ mol}\cdot\text{L}^{-1}$) after 1 h. (b) ^2H NMR (61.4 MHz).

4. H/D exchange reaction for acetophenone using BMMI-X as catalyst

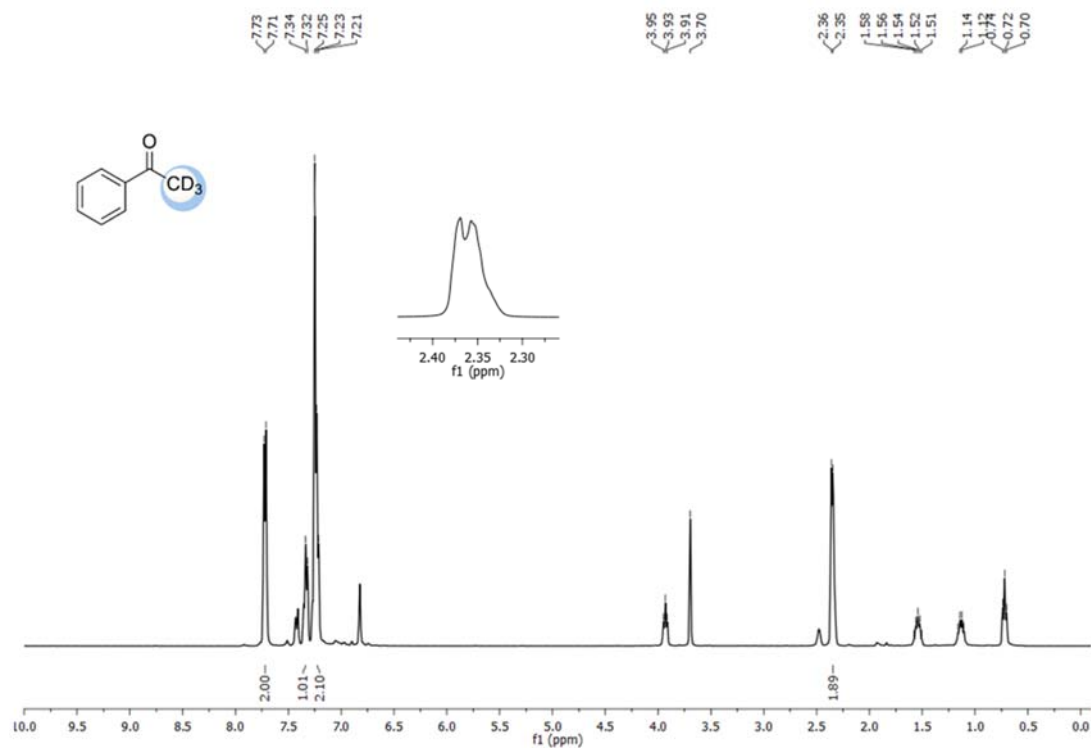


Figure S10. ^1H -NMR (400 MHz, 25 °C, CDCl_3) spectrum of deuterated acetophenone with BMMI-Im after 1 h, 36% of conversion.

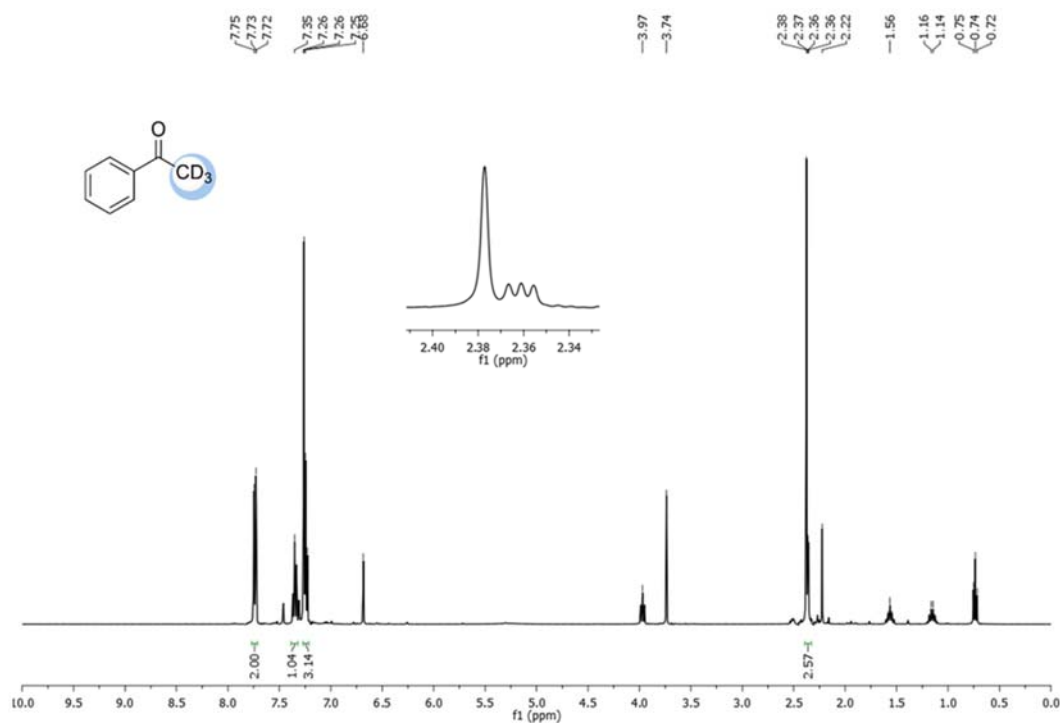


Figure S11. ^1H -NMR (400 MHz, 25 °C, CDCl_3) spectrum of deuterated acetophenone with BMMI-Melm after 1 h, 14% of conversion.

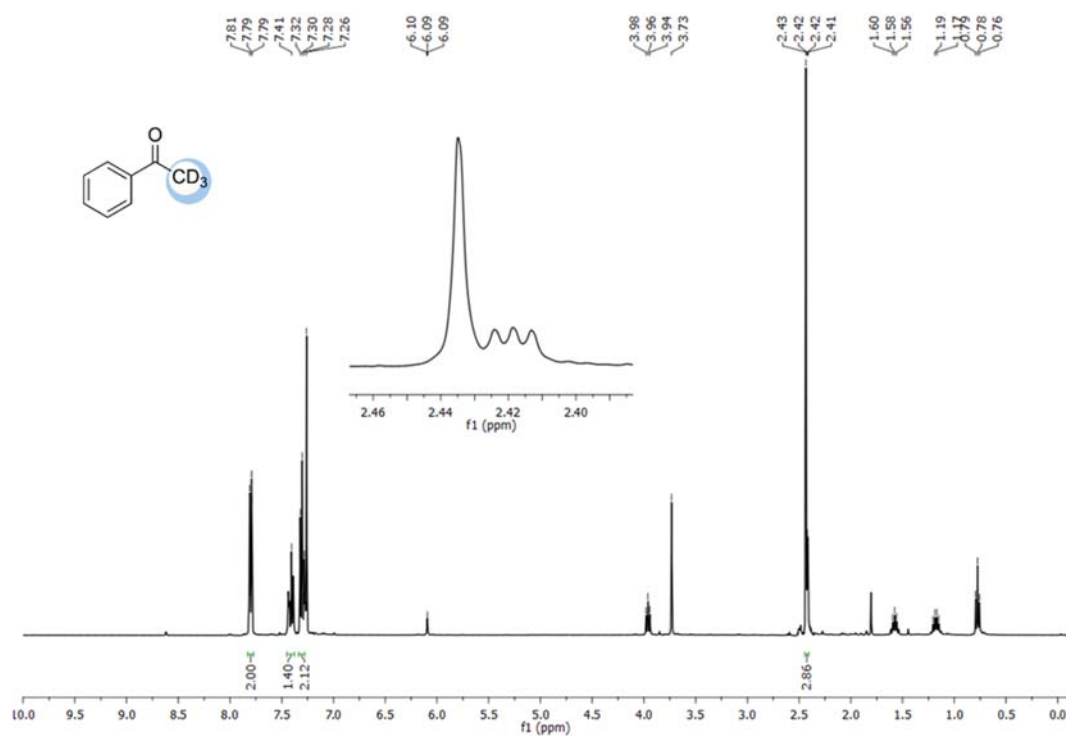


Figure S12. ¹H-NMR (400 MHz, 25 °C, CDCl₃) spectrum of deuterated acetophenone with BMMI-Pyr after 1 h, 5% of conversion.

5. DFT theoretical calculations

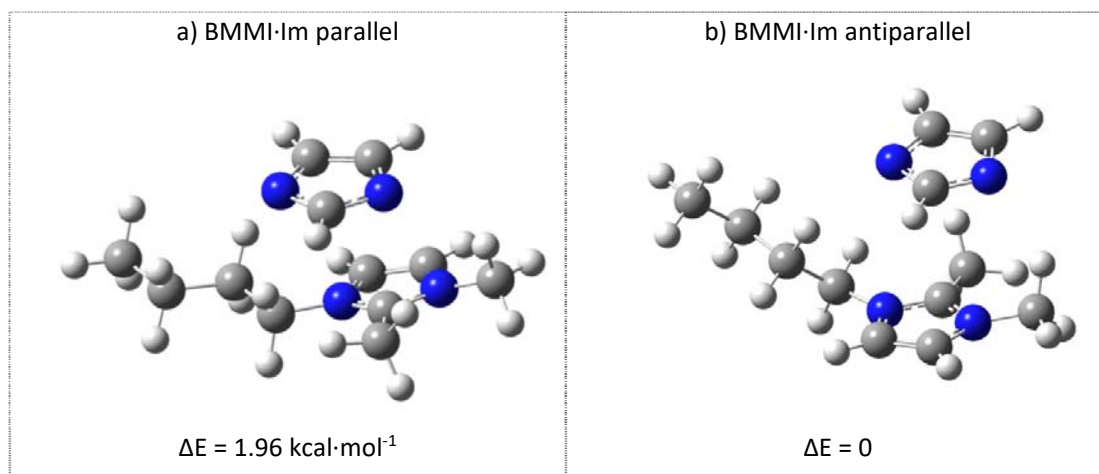


Figure S13. Optimised structure obtained by DFT calculations of the ionic pair of BMMI·Im (a) parallel configuration of imidazolium rings ($\pi^+-\pi^-$); (b) anti-parallel configuration 1.96 kcal·mol⁻¹ more stable than parallel.

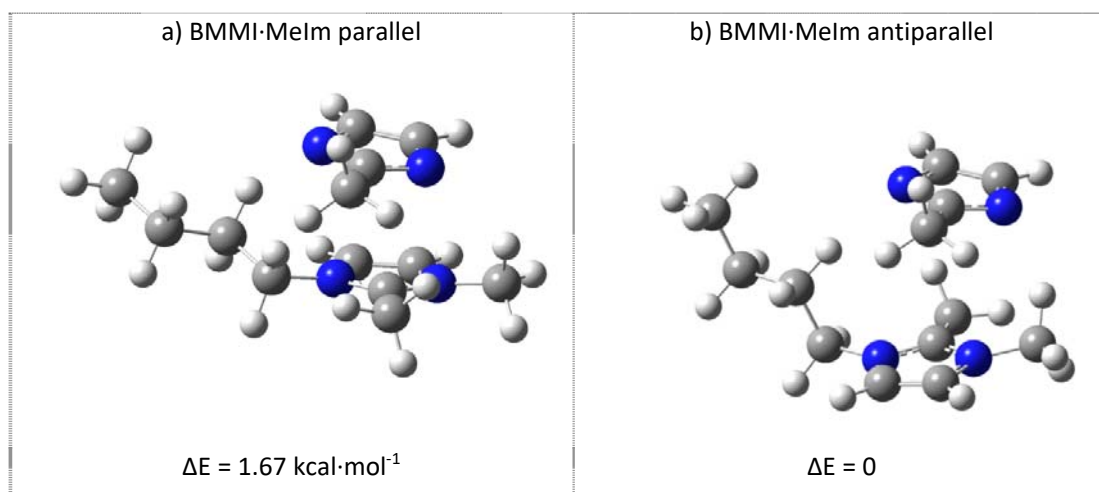


Figure S14. Optimised structure obtained by DFT calculations of the ionic pair of BMMI·Melm (a) parallel configuration of imidazolium rings ($\pi^+-\pi^-$); (b) anti-parallel configuration 1.67 kcal·mol⁻¹ more stable than parallel.

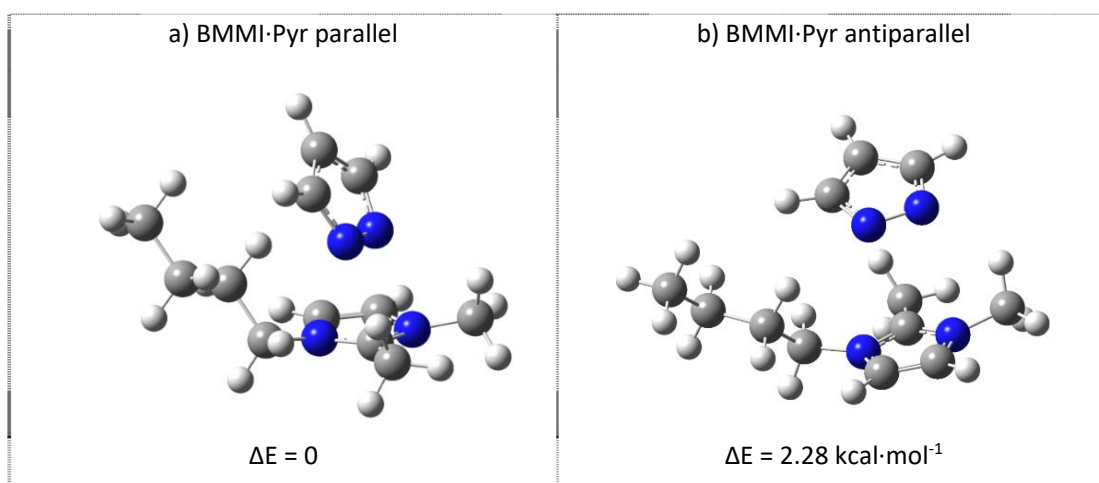


Figure S15. Optimised structure obtained by DFT calculations of the ionic pair of BMMI·Pyr (a) parallel displaced to T shape configuration of imidazolium rings ($\pi^+-\pi^-$), 2.28 kcal·mol⁻¹ more stable than anti-parallel configuration; (b) anti-parallel displaced configuration.

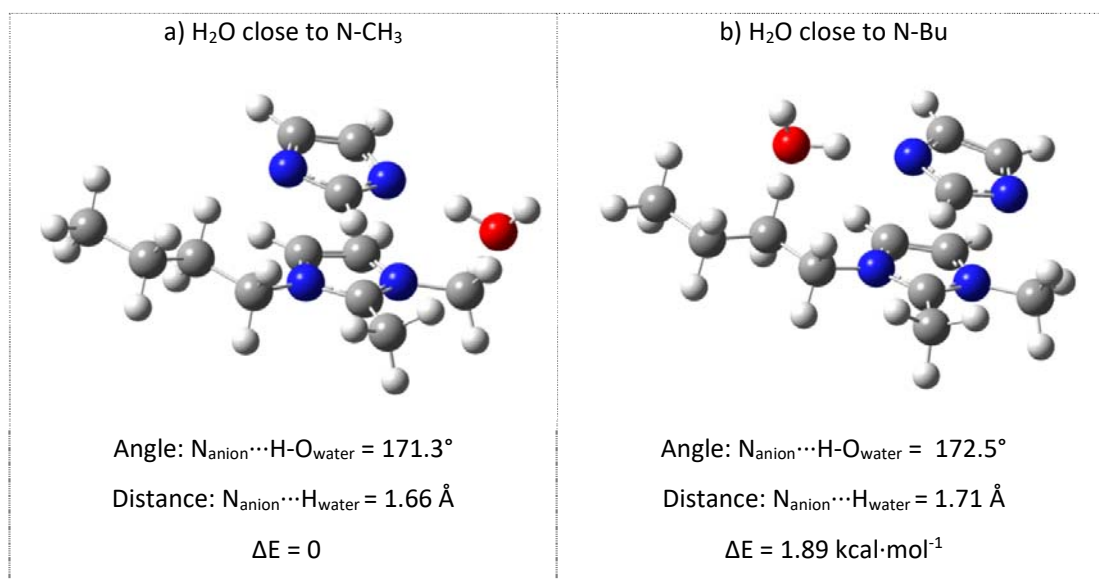


Figure S16. Optimised structure obtained by DFT calculations of [BMMI-Im]·[H₂O] complex at **parallel** configuration (a) H₂O molecule closer to N-CH₃ group of cation ring. It is 1.89 kcal·mol⁻¹ more stable than (b) H₂O molecule closer to N-Bu group of cation ring.

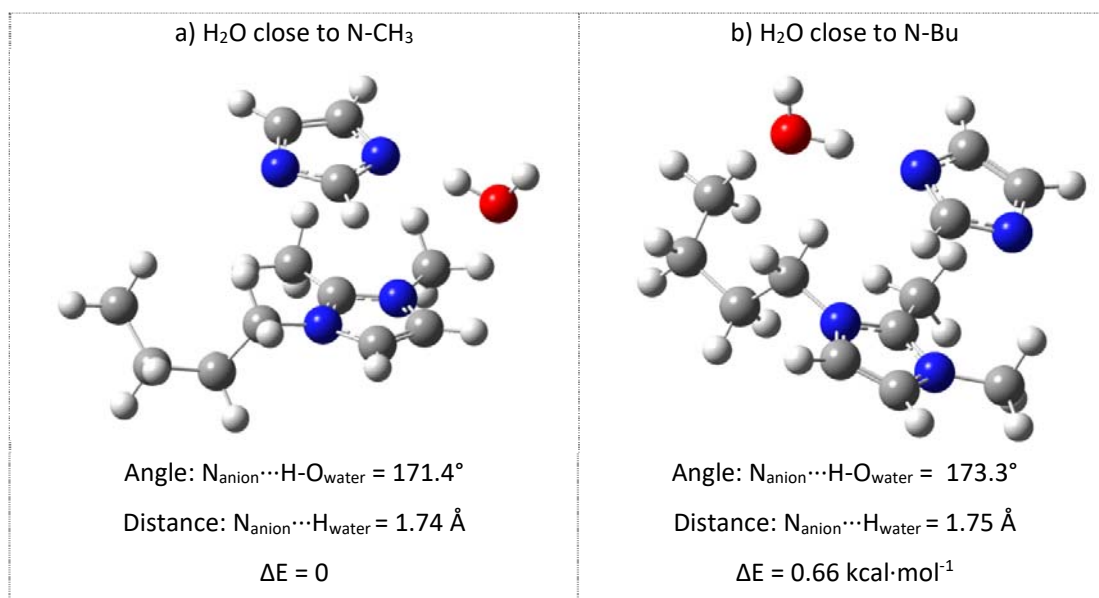


Figure S17. Optimised structure obtained by DFT calculations of [BMMI-Im]·[H₂O] complex at **anti-parallel** configuration (a) H₂O molecule closer to N-CH₃ group of cation ring. It is 0.66 kcal·mol⁻¹ more stable than (b) H₂O molecule closer to N-Bu group of cation ring.

Table A1. DFT energy optimization of the molecules separately.

Entry	Molecule	Optimized Energy (Ha) ^a
1	H ₂ O	-76.4396415
2	BMMI cation	-462.5174421
3	Im anion	-225.6471675
4	Melm anion	-264.96797297
5	Pyr anion	-225.62100392

^a Hartree (1 Ha = 627.503 kcal·mol⁻¹)

6. General Data

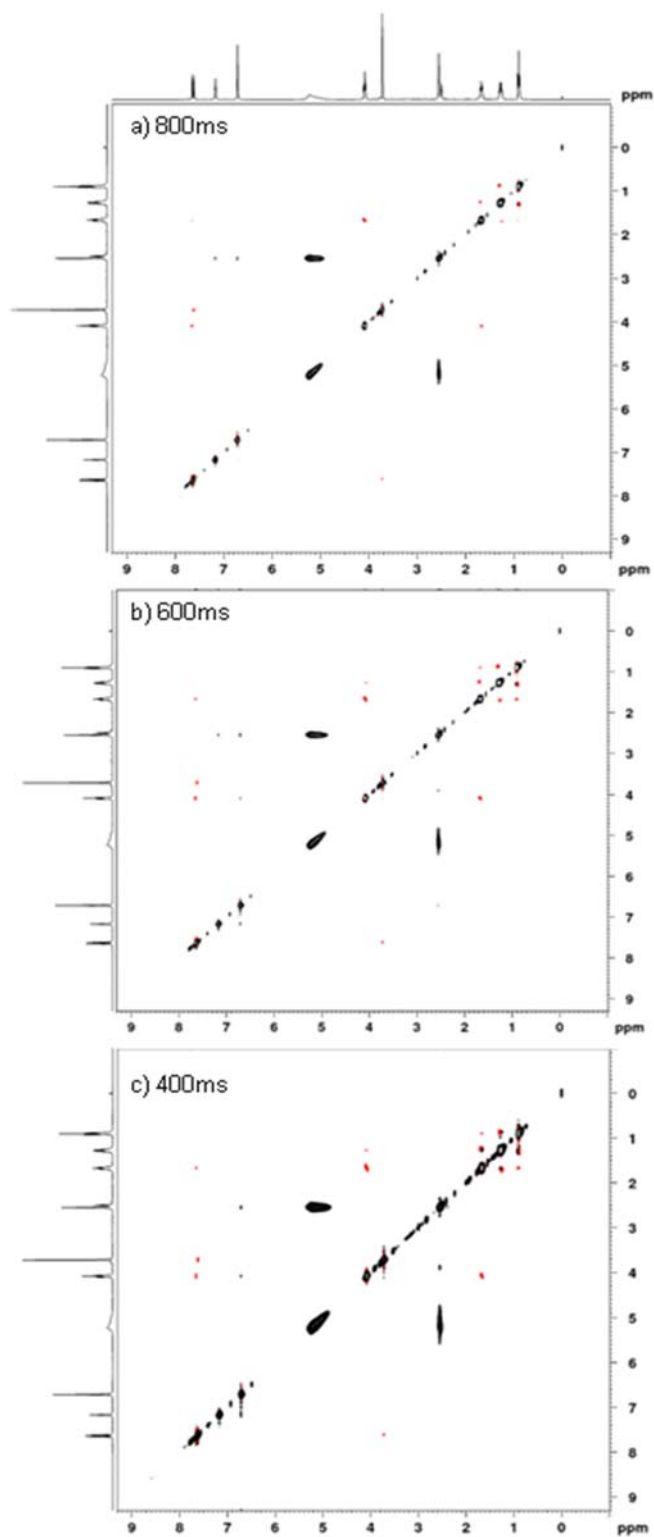


Figure S18. ^1H , ^1H -NOESY of contour map of BMMI·Im in $[\text{D}_6]\text{DMSO}$ (0.2 mol·L $^{-1}$) varying the mixing time: a) 800 ms; b) 600 ms; c) 400 ms.