Ionic Liquids as Porogens for Molecularly Imprinted Polymers: Propranaolol, a Model Study

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Electronic Supporting Information

1. Molecular modelling images of the interactions between the pre-polymerisation cluster components.
2. NMR chemical shift and chemical shift changes on addition of equivalents of the functional monomer (MAA)
3. Plot of chemical shift changes as a function of equivalents of MAA added.
4. Scatchard binding data for 1-MIPs prepared in VOC and [BMIM][PF_6]
5. TGA and DSC analysis of polymer stability.

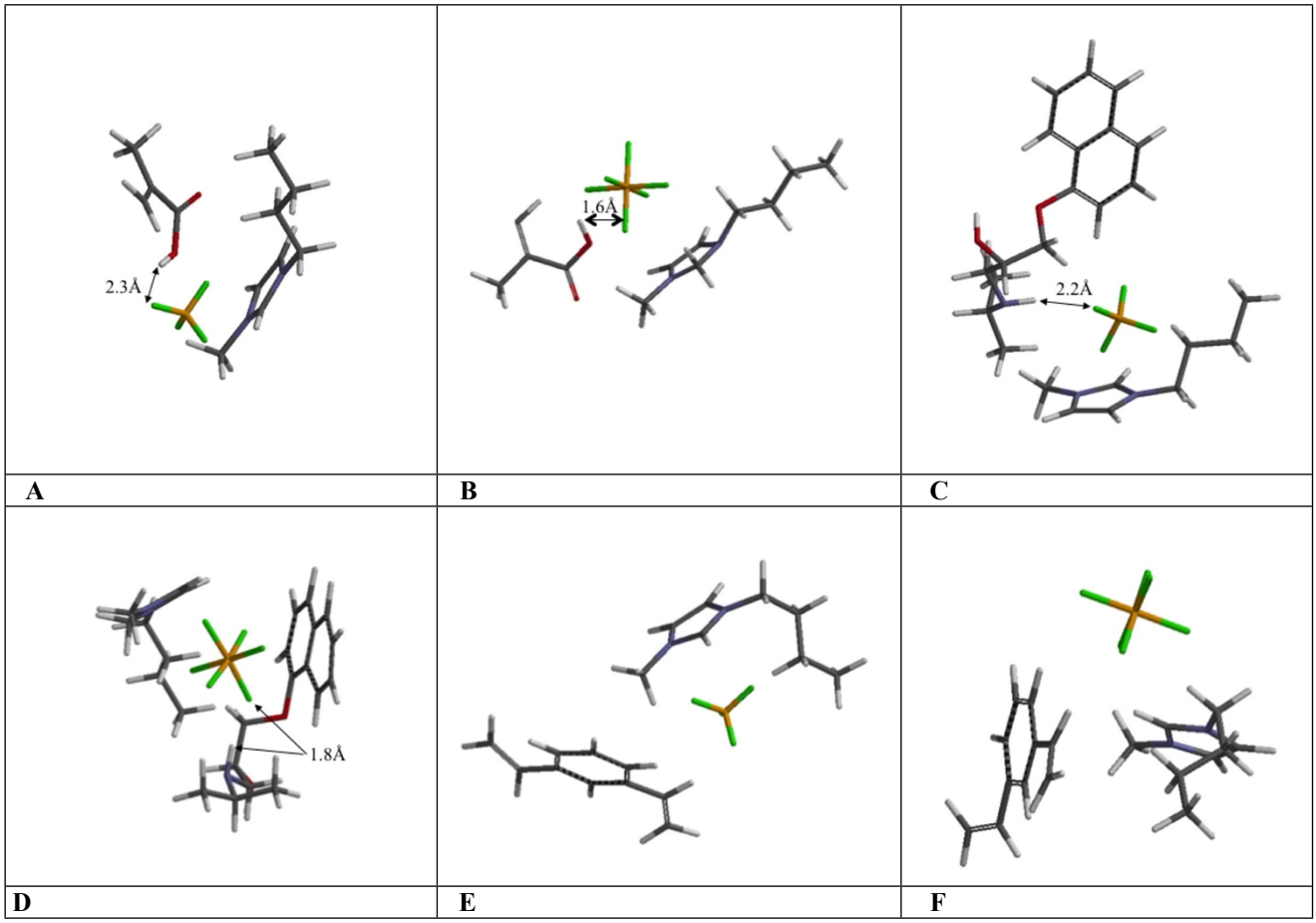

Figure S1. Energy minimised molecular modelling images of the interaction of (**A**) [BMIM][BF_4] and MAA; (**B**) [BMIM][PF_6] and MAA; (**C**) **1** and [BMIM][BF_4]; (**D**) **1** and [BMIM][PF_6]; (**E**) Modelling image of DVB and [BMIM]BF_4]; and (**F**) DVB and [BMIM][PF_6].

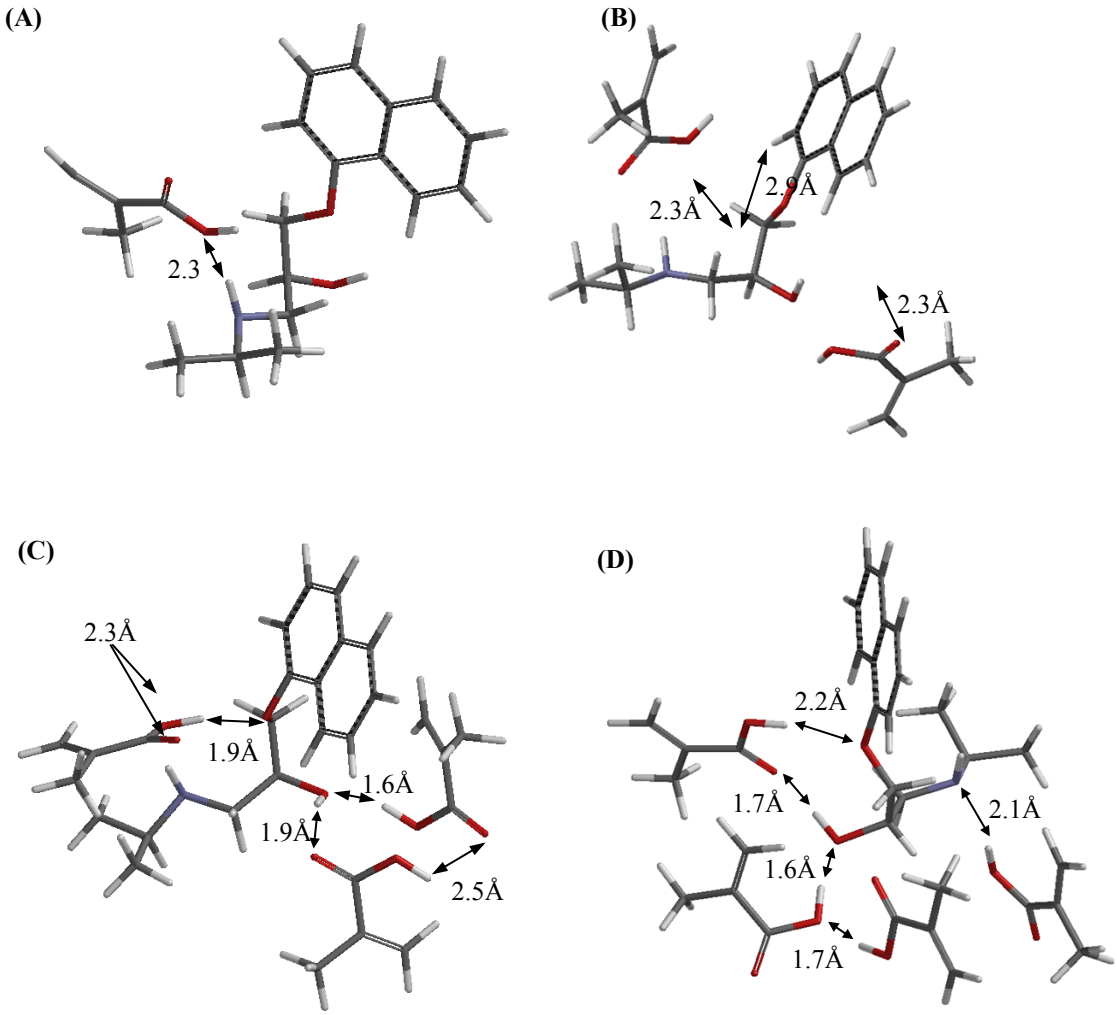

Figure S2 Modelling images of MAA and **1**. Template : monomer ratios of (**A**) 1:1, (**B**) 1:2, (**C**) 1:3 and (**D**) 1:4.

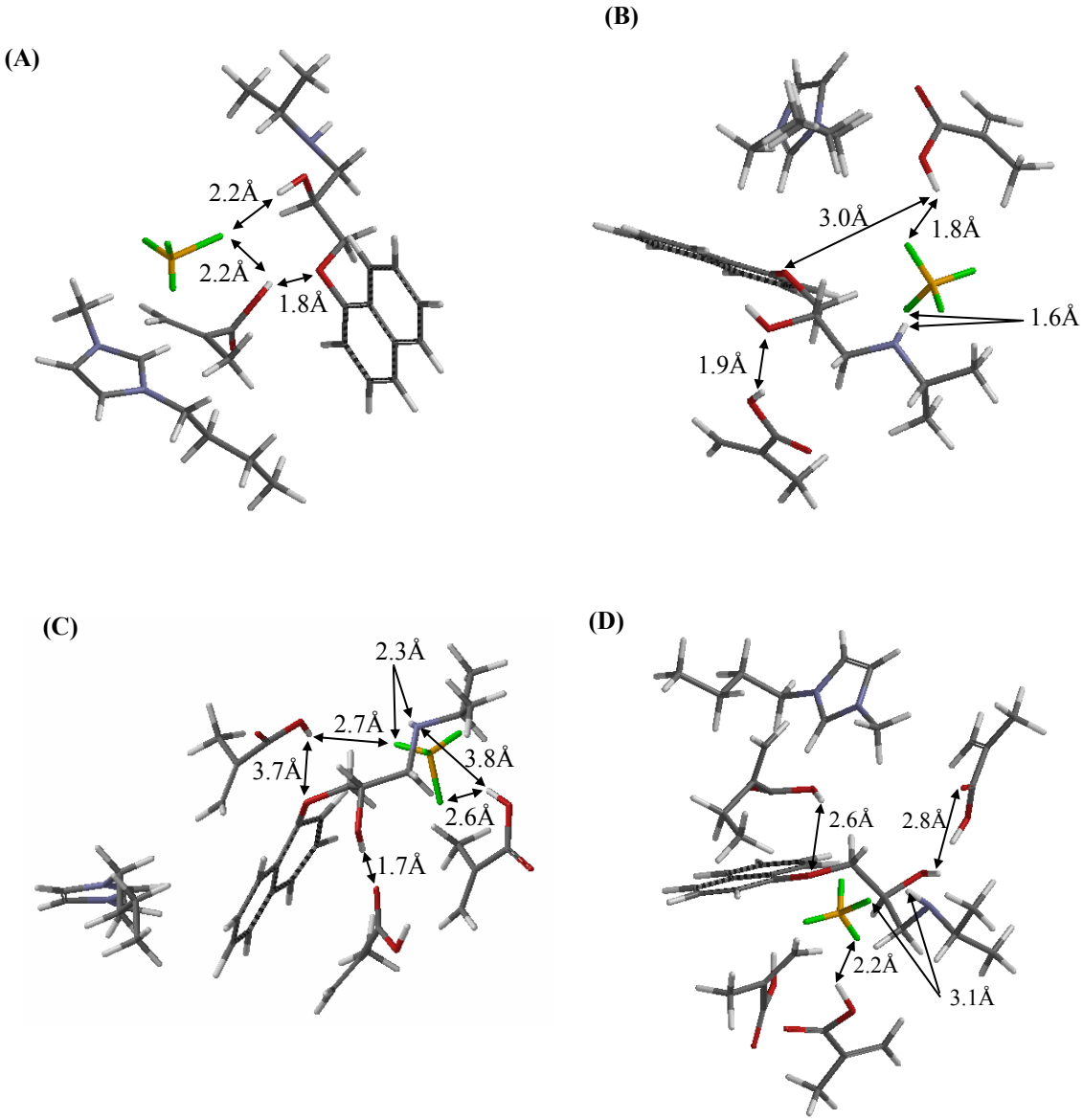

Figure S3 Modelling images of MAA, **1** and [BMIM][BF_4]. Template:monomer ratios of (**A**) 1:1, (**B**) 1:2, (**C**) 1:3 and (**D**) 1:4.

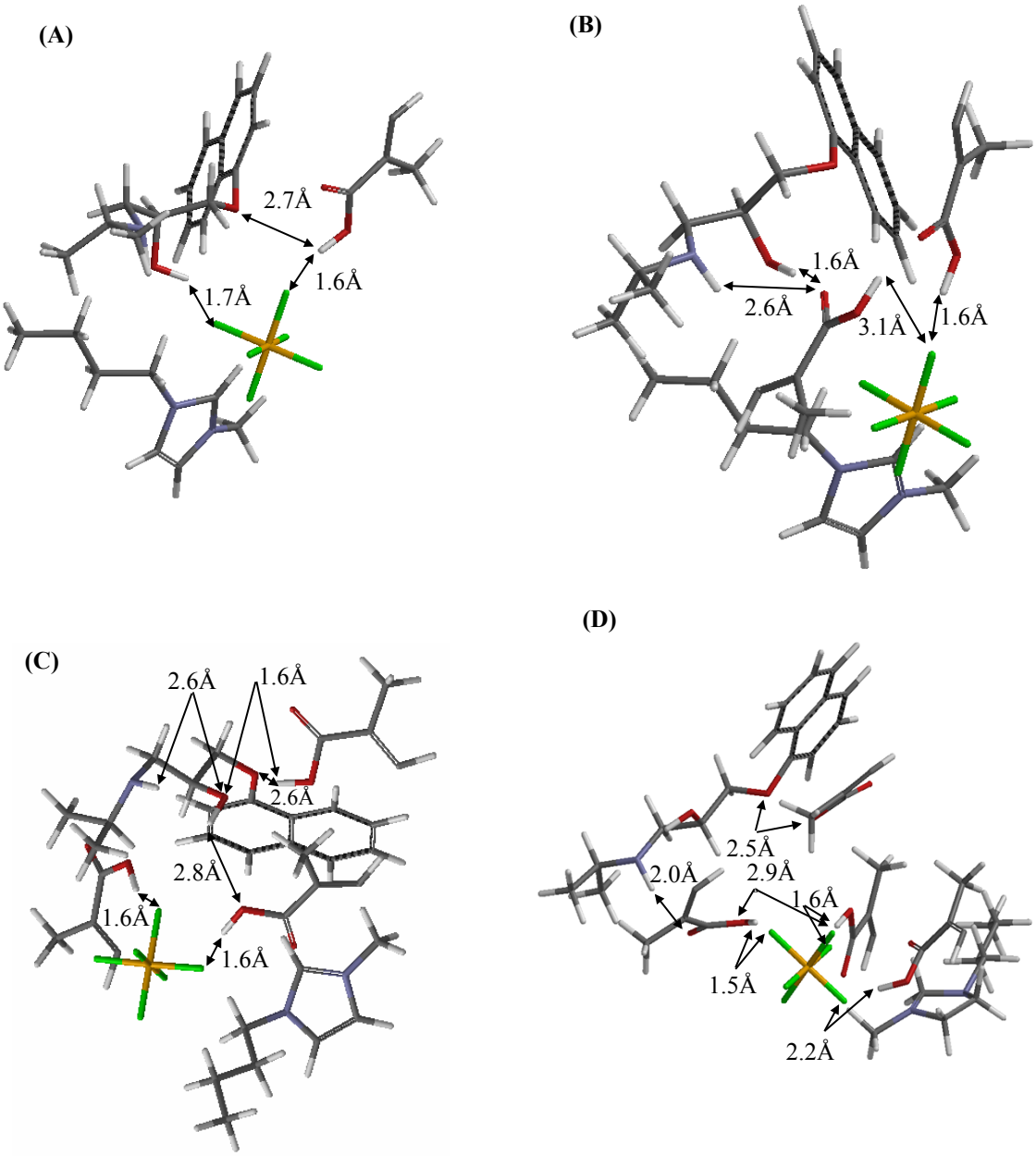

Figure S4. Modelling images of MAA, **1** and [BMIM][PF_6]. Template:monmer ratios of (**A**) 1:1, (**B**) 1:2, (**C**) 1:3 and (**D**) 1:4.

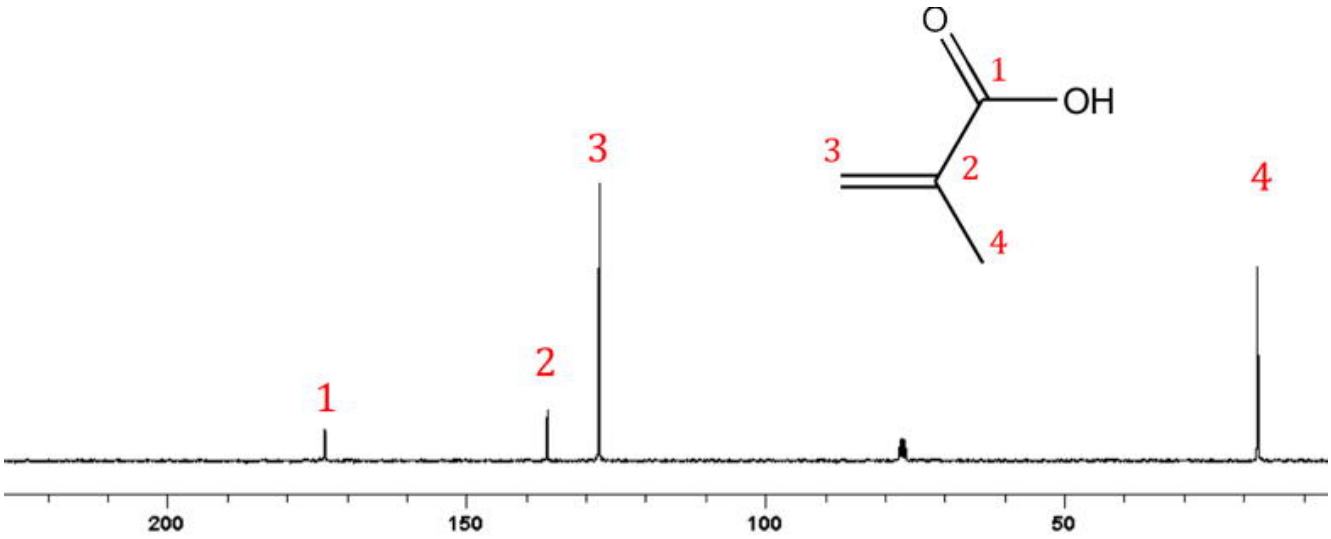

Figure S5. MAA structure, ^{13}C NMR spectrum of MAA in $CHCl_3$, with chemical shifts given in ppm.

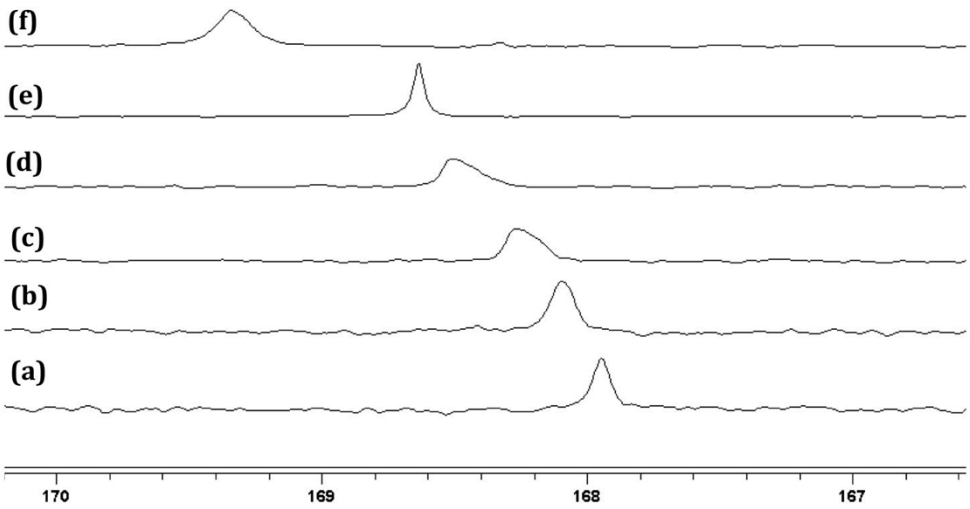

Figure S6. C1 movement in a ^{13}C NMR titration of MAA in 0.5 mL [BMIM][PF_6]. MAA additions of (**a**) 6µL, (**b**) 8 µL, (**c**) 10 µL, (**d**) 12 µl (**e**) 14 µL and (**f**) 26 µL. Shifts are in ppm.

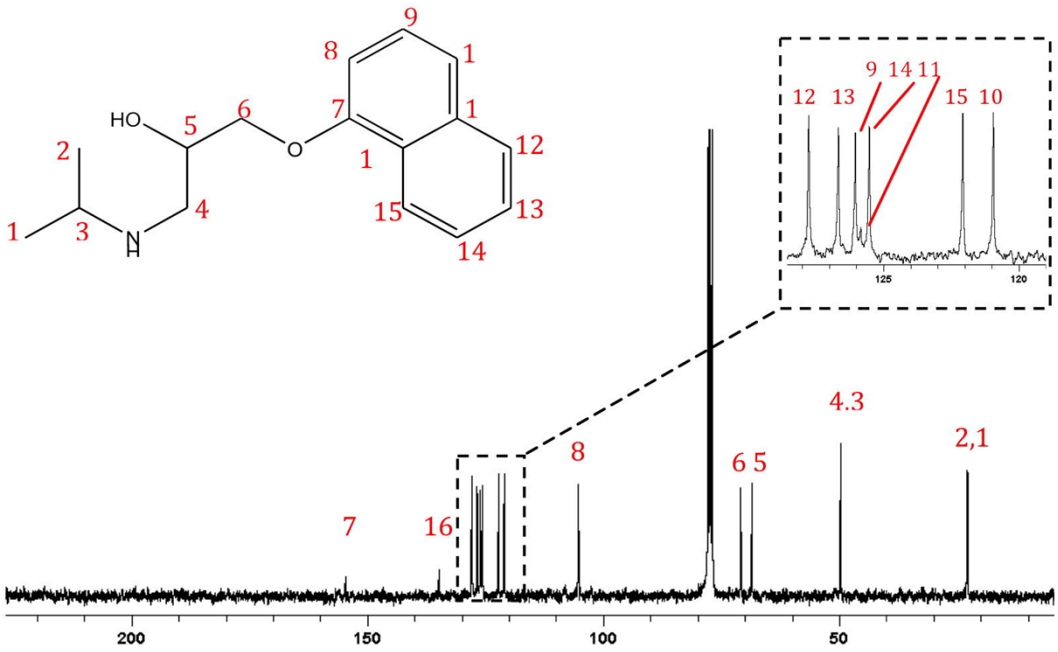

Figure S7. ^{13}C NMR spectrum of **1** with resonance assignments.

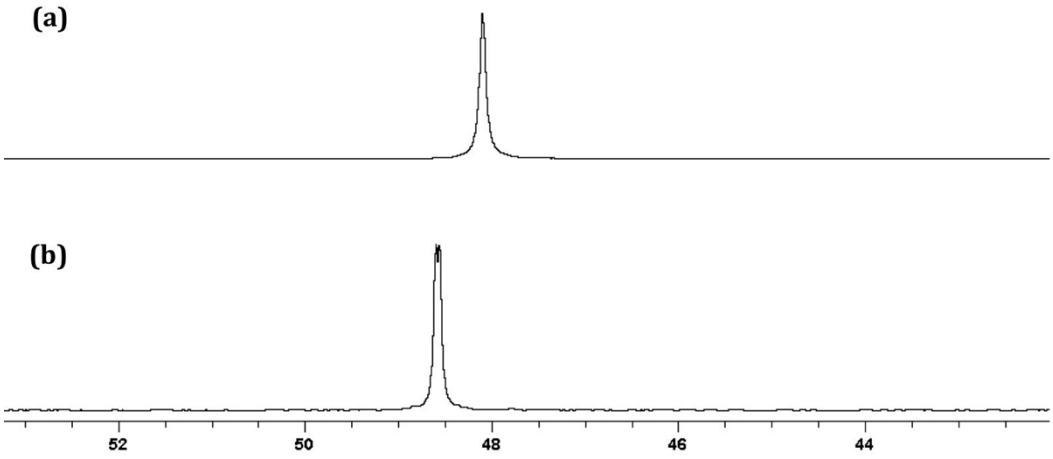

Figure S8 Partial ^{13}C NMR spectra of (**a**) 13 mg **1** in 0.5 mL [BMIM][PF_6] and (**b**) 13 mg **1** in $CHCl_3$ showing the observed C3 shifts in ppm.

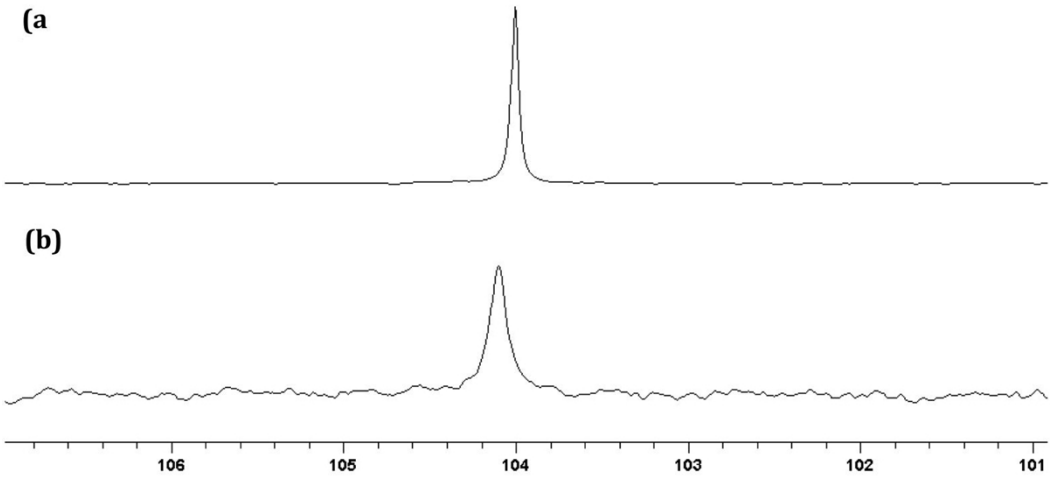

Figure S9 Partial ^{13}C NMR spectra of (**a**) 13mg **1** in 0.5mL [BMIM][PF_6] and (**b**) 13 mg **1** in $CHCl_3$ showing the observed C10 shifts in ppm.

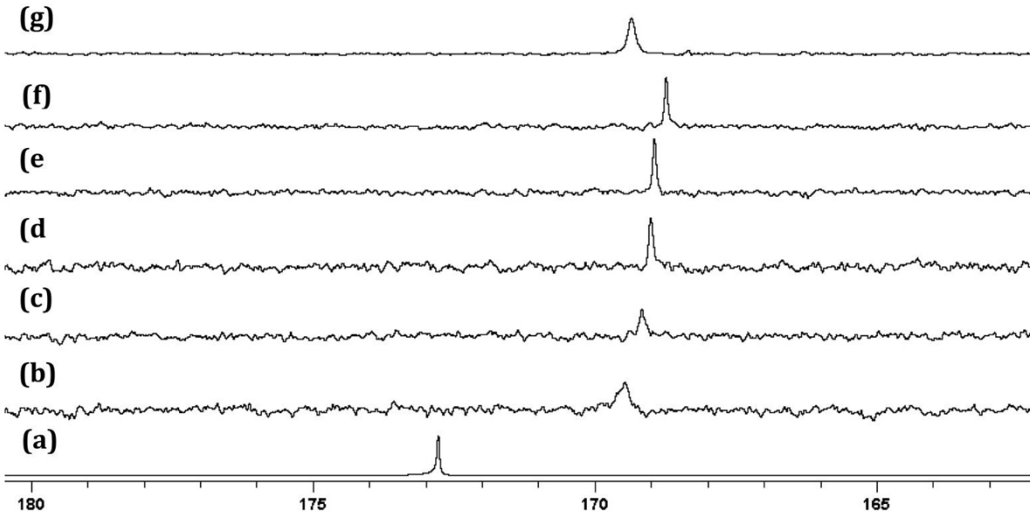

Figure S10. Partial ^{13}C NMR spectra showing C1 resonances of MAA in a titration of MAA with 13 mg **1** in 0.5 mL [BMIM][PF_6]. (**a**) MAA, (**b-g**) 13mg **1** in [BMIM][PF_6] with MAA additions of (**b**) 6 µL, (**c**) 8µL, (**d**) 10µL, (**e**) 12µL, (**f**) 14 µL and (**g**) 26 µL. Shifts are in ppm.

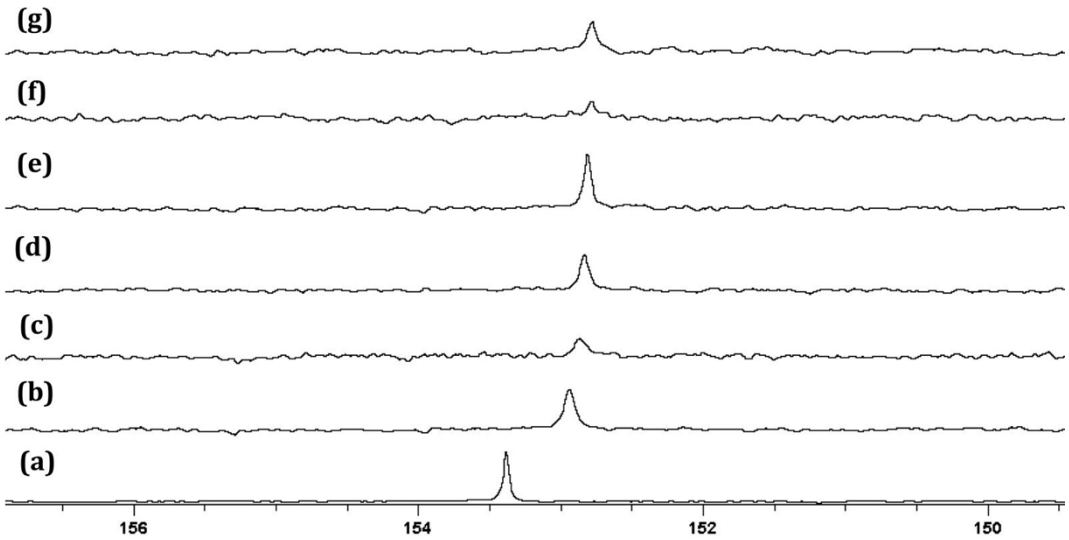

Figure S11 Partial ^{13}C NMR spectra showing C7 resonances of **1**. Solution contains 13mg **1** in [BMIM][PF_6] with MAA additions of (**a**) 0 μL MAA, (**b**) 6 μL MAA, (**c**) 8 μL MAA, (**d**) 10 μL MAA, (**e**) 12 μL MAA (**f**) 14 μL MAA and (**g**) 26 μL MAA. Shifts are in ppm.

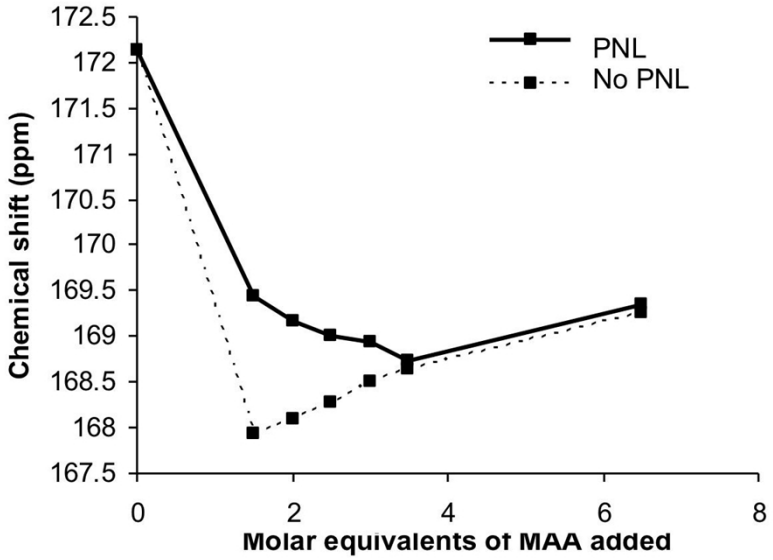

Figure S12 ^{13}C NMR shift of MAA C1 upon incremental MAA additions to [BMIM][PF_6] with and without added **1**.

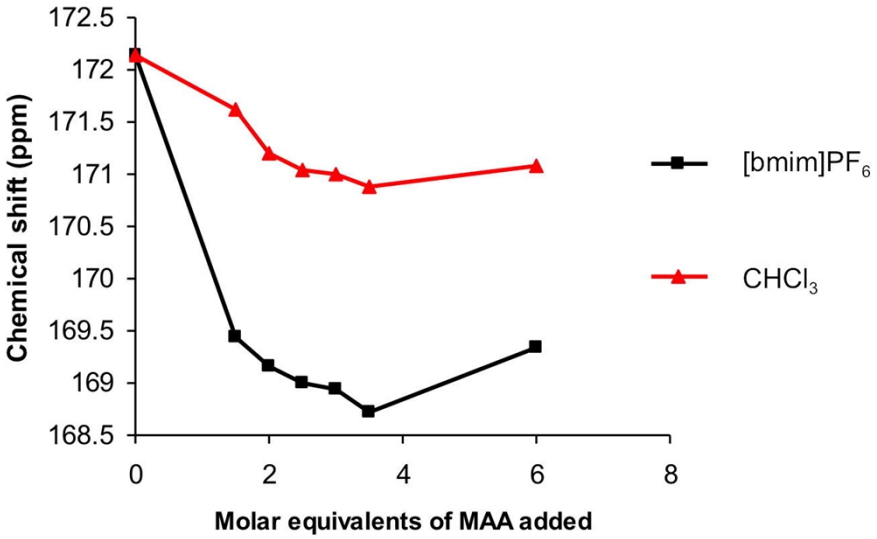

Figure S13 ^{13}C NMR shift of C1 of MAA in $CHCl_3$ and [BMIM][PF_6] in the presence of added **1**.

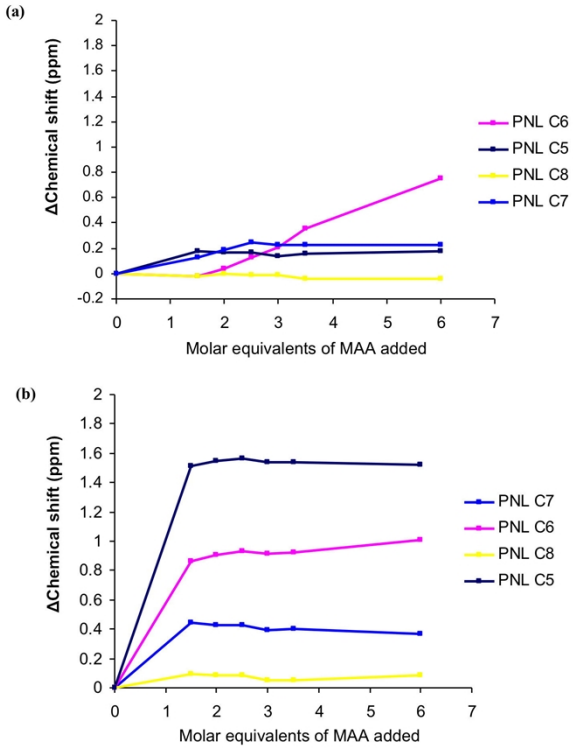

Figure S14 ^{13} C shifts of selected **1** carbon atoms in **(a)** [BMIM][PF_6] and **(b)** $CHCl_3$ upon the incremental additions of MAA.

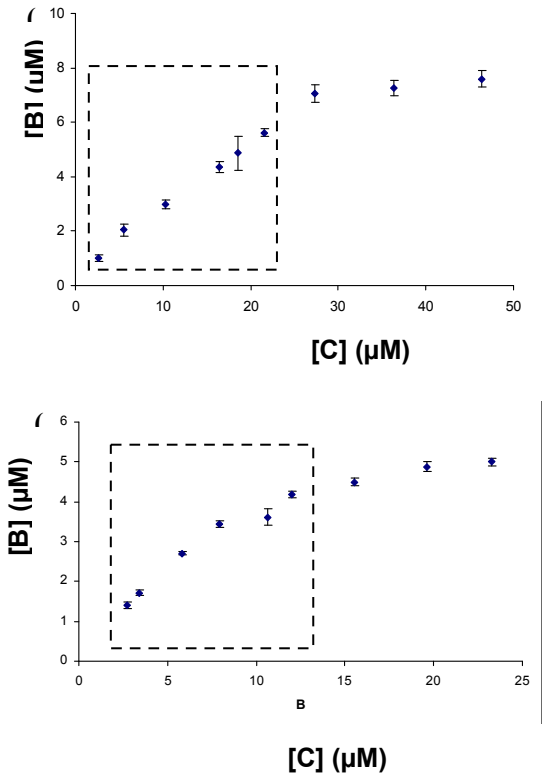

Figure S15 Saturation binding data for **1**-imprinted MIP prepared in (**a**) VOC and (**b**) [BMIM][PF_6] using 20 mg polymer in **1** solutions of various concentrations over 6 hours. The selected region indicates data used for Scatchard calculations.

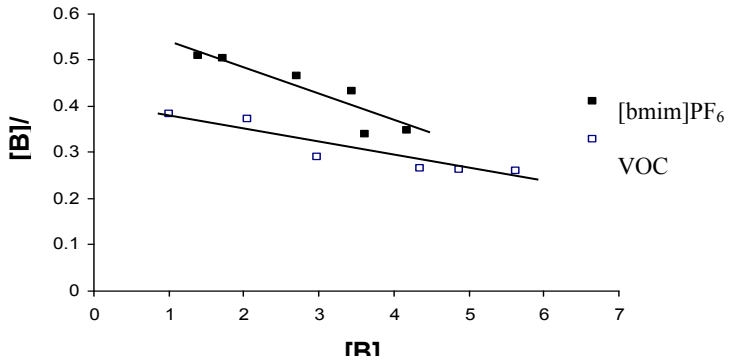

Figure S16 Scatchard analysis of VOC and [BMIM][PF_6]-prepared MIP where [B]= **1** bound and [C]= free **1** concentration.

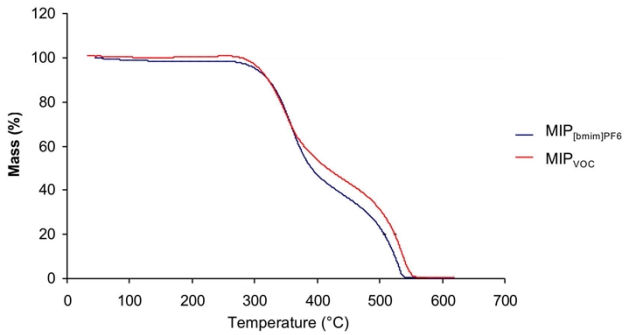

Figure S17. TGA traces of **1**-imprinted MIPs.

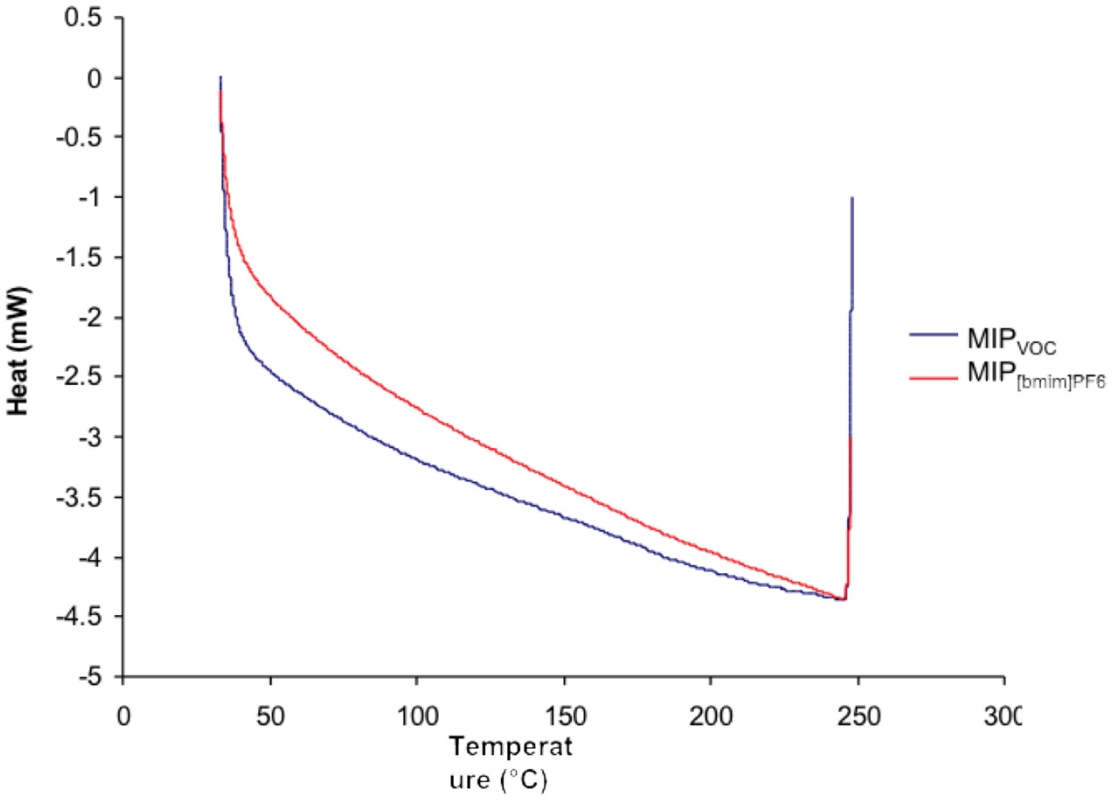

Figure S18 DSC scans of **1**-imprinted MIPs.

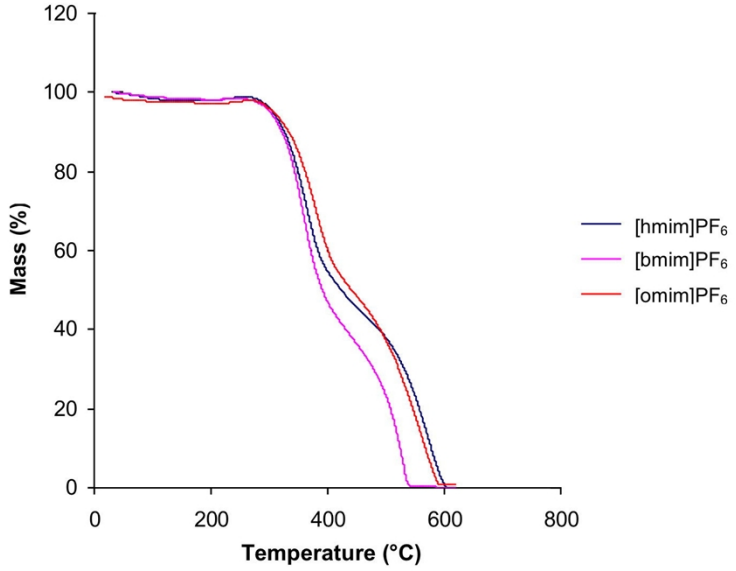

Figure S19. TGA traces of [BMIM], [HMIM] and [OMIM][PF_6]- prepared MIPs