

Electronic Supplementary Information

Decoupling manufacturing from application in additive manufactured antimicrobial materials

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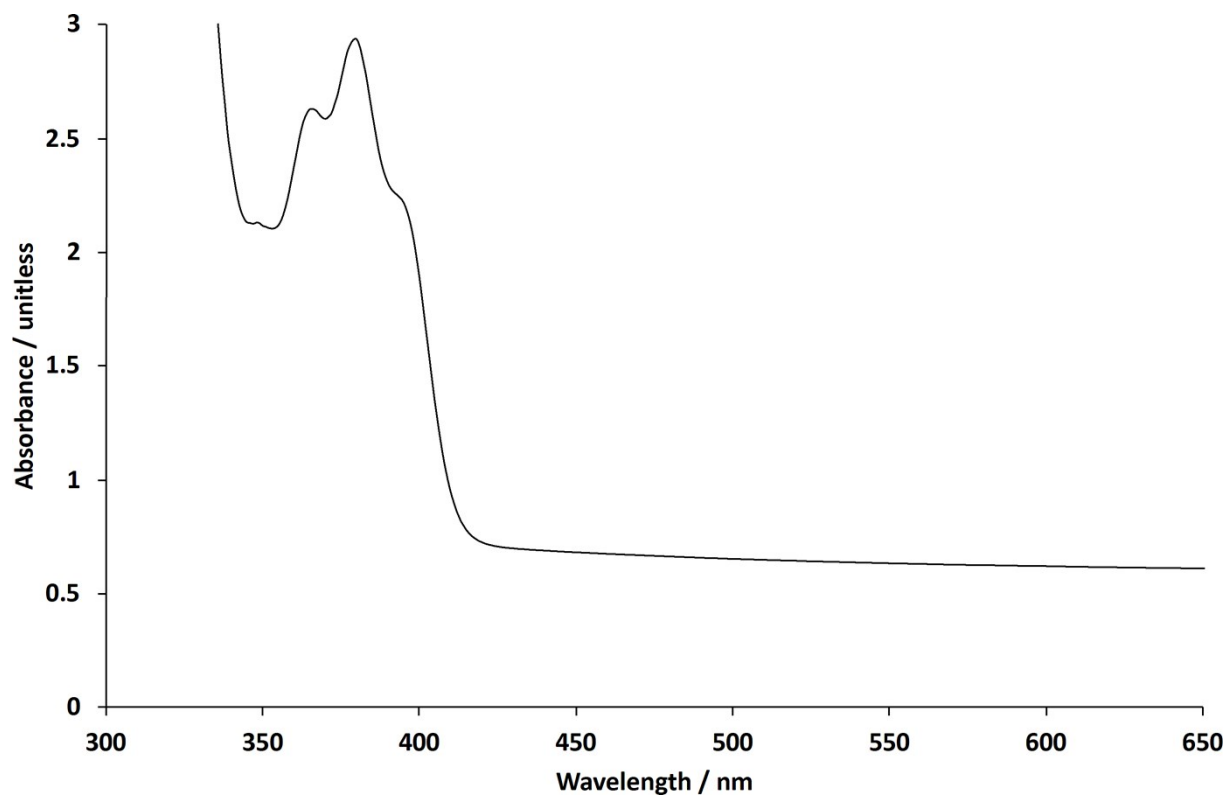


Figure S1: The transmission UV-Vis spectrum of a 3D printed **PIL1** part before post-printing UV photoreduction treatment.

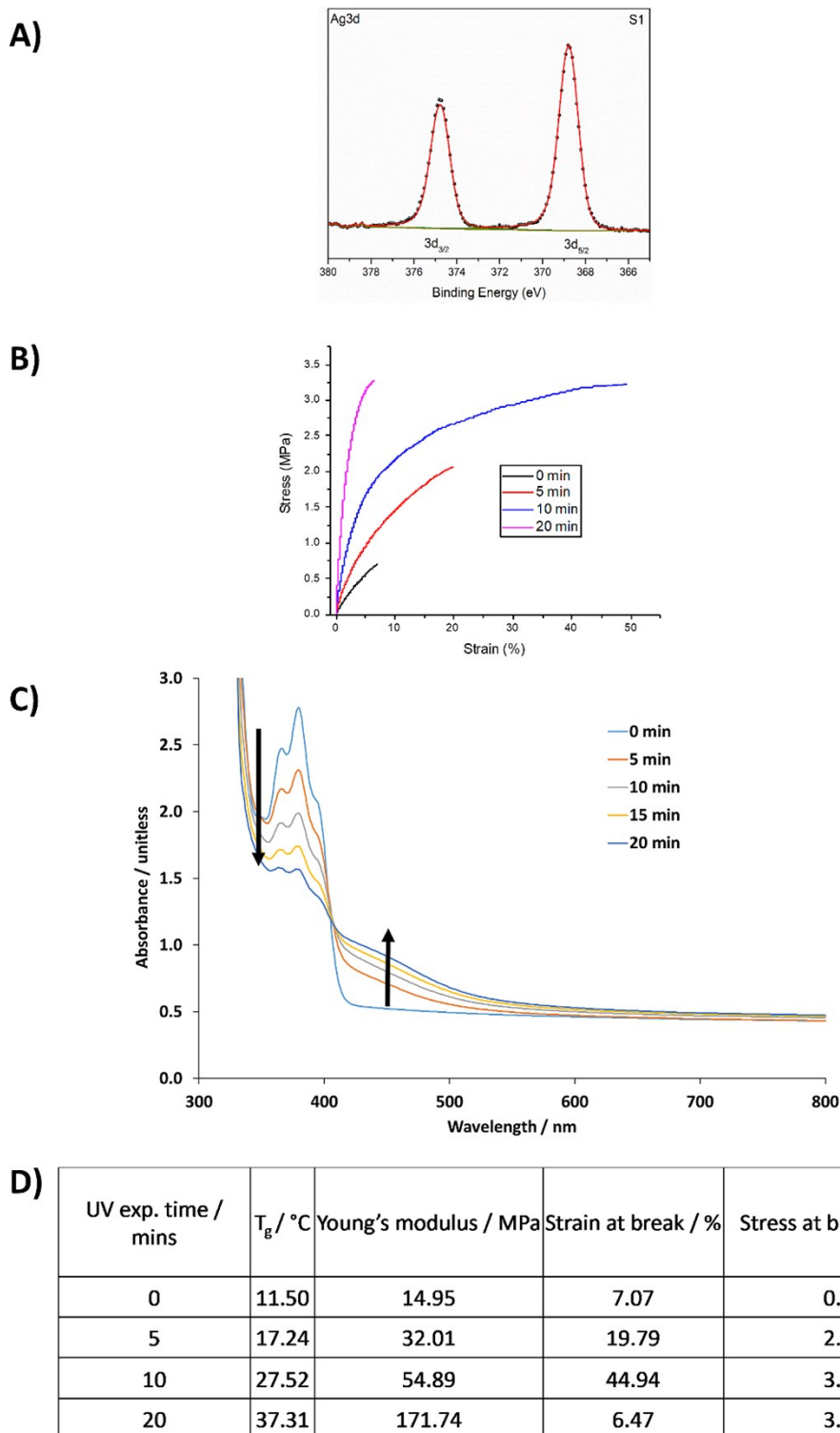


Figure S2: (A) XPS spectrum of a photoreduced **PIL1** 3D printed part XPS revealing the expected $Ag3d_{3/2}$ and $Ag3d_{5/2}$ peaks in the spectrum; (B) (Left) Stress-Strain curves for **PIL1** 3D printed parts demonstrating an increase in tensile stiffness with increasing UV exposure time; (C) UV-Visible transmission spectra of a piece of **PIL1** showing the increase in the shoulder feature at $\lambda \approx 450$ nm, which is attributed to AgNPs, with increasing post-printing UV exposure time. The absorbance of the peak features attributed to the photoinitiator ($\lambda_{max} = 380$ nm) decreased with increasing exposure time; (D) The tabulated mechanical property data for the samples.

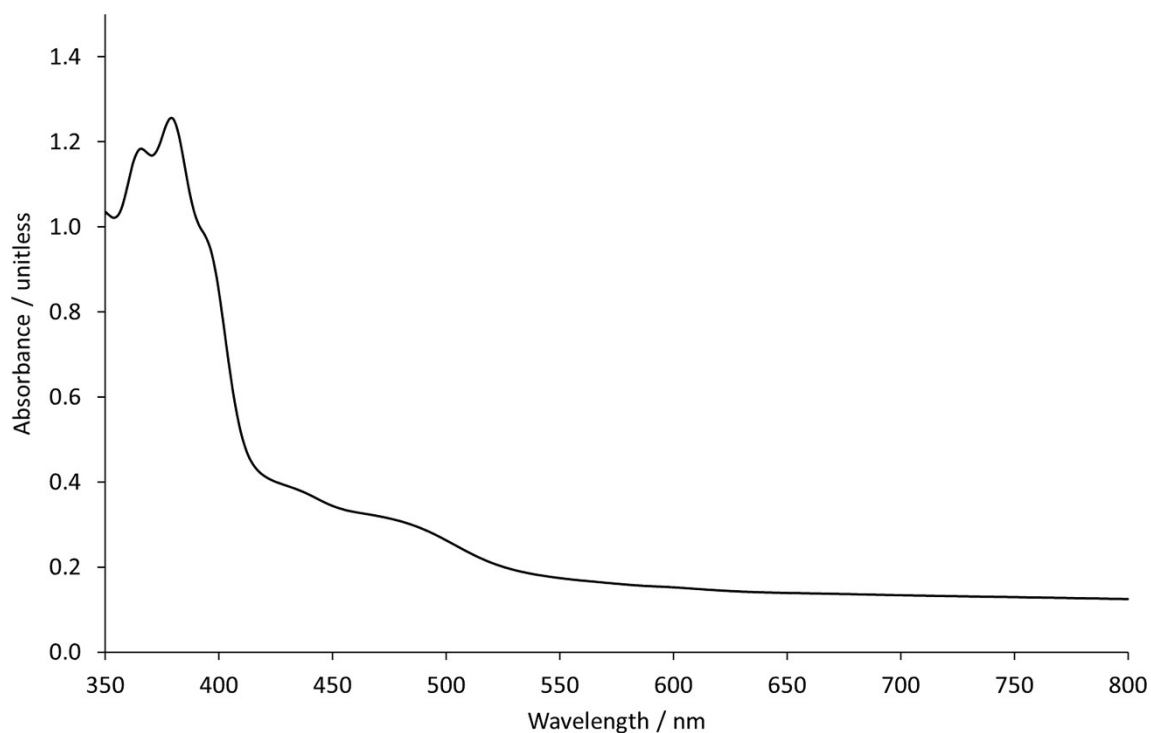


Figure S3: UV-visible spectrum of the analogous homogeneous liquid IL system, where $\text{Ag}(\text{SbF}_6)$ (~ 1 wt%) was added to 80 mol% non-polymerisable 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide, 20 mol% 1,4-BDA and 1 mol% PI and photo-reduced under UV light ($\lambda = 395$ nm) for 20 mins. The shoulder centred ~ 450 nm is attributed to a poorly resolved plasmon due to the photoreduction of Ag^+ to Ag^0 and the formation of AgNPs in the liquid IL.

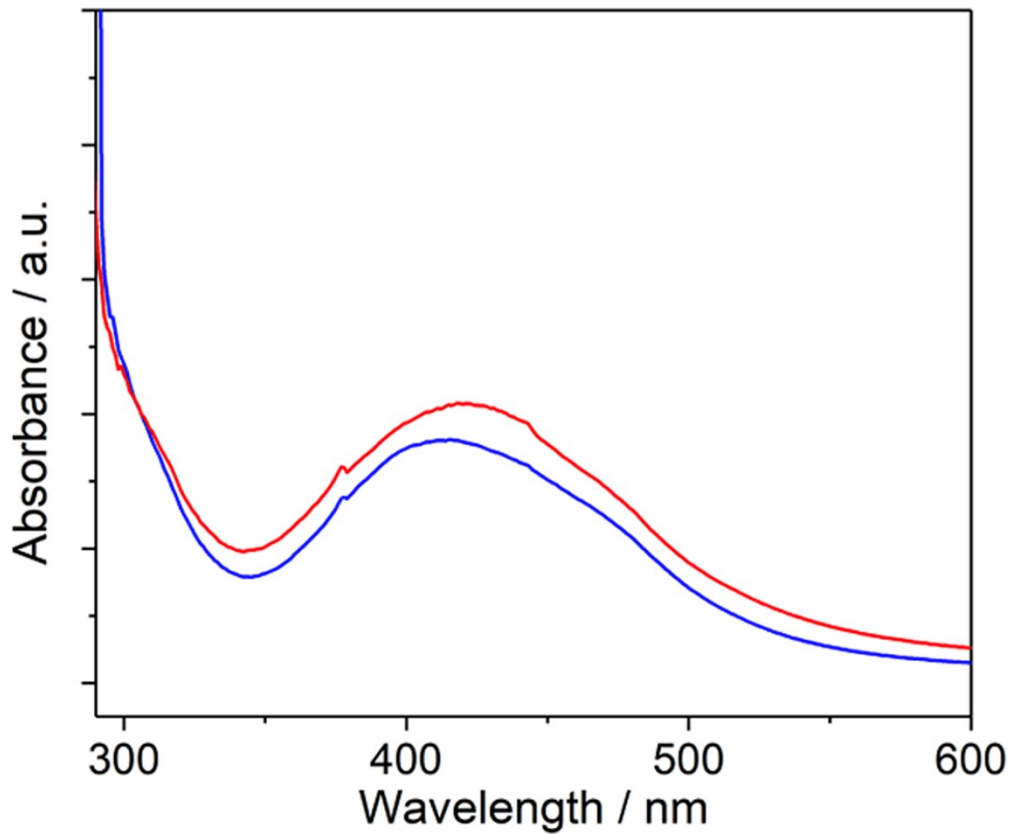


Figure S4: 3D-printed parts of **PIL2** (blue curve, BDA crosslinker) and **PIL3** (red curve, PEGDA crosslinker) showed a similar ability to stabilise AgNPs upon extended photoreduction under the same conditions. The small peak feature at ~ 380 nm is attributed to residual PI.

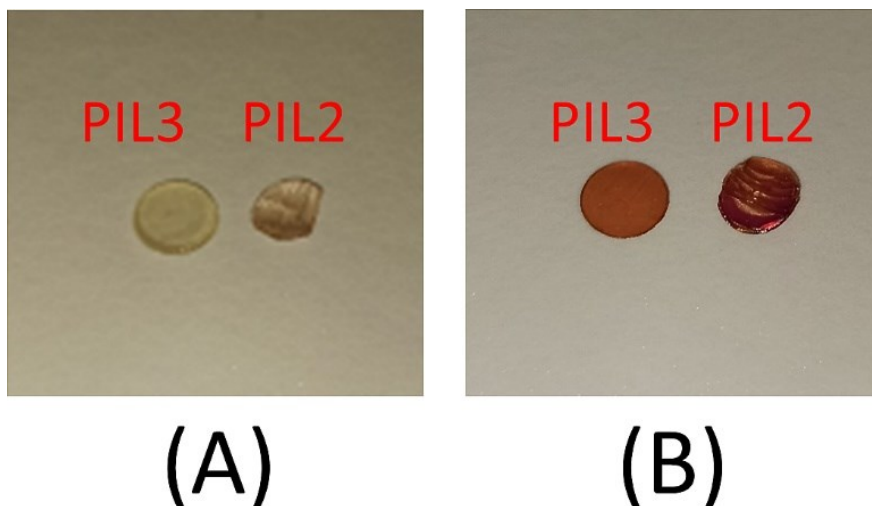


Figure S5: (A) 3D-printed parts of **PIL3** and **PIL2** before UV-exposure, further highlighting how the **PIL2** formulation deformed during 3D printing; whereas the **PIL3** formulation printed with better resolution; (B) 3D printed parts of both **PIL2** and **PIL3** formulations after 20 mins of UV exposure.

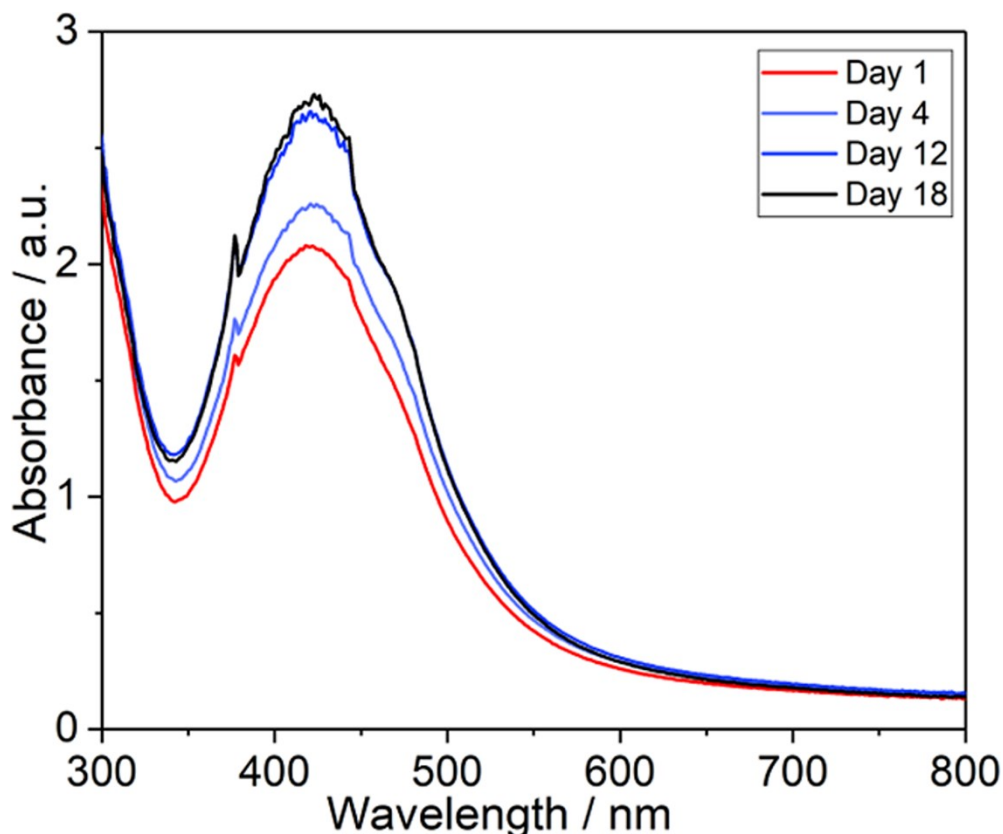


Figure S6: AgNP@PIL2 generated by post-curing photoreduction and aged under ambient light over a period of 18 days, causing an increase in the absorbance of the peak attributed to the AgNP plasmon.

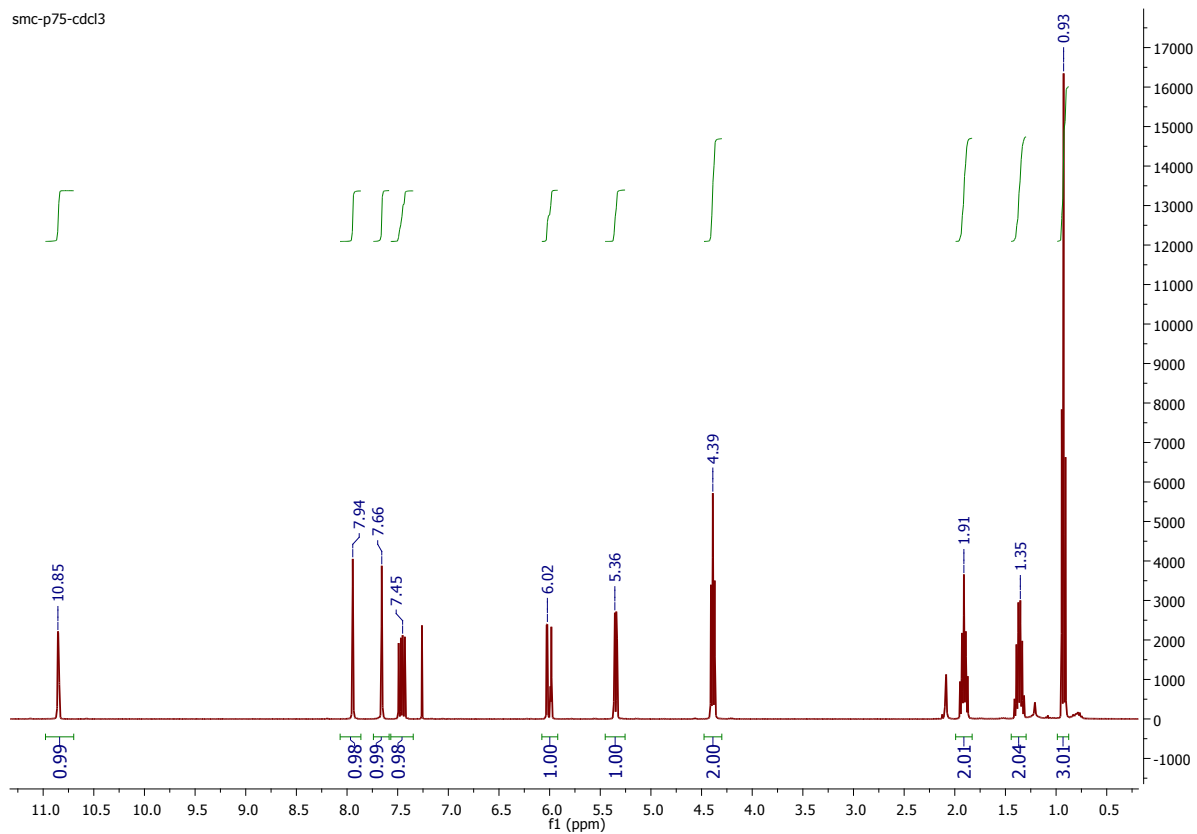
Synthesis of ionic liquids:

*1-butyl-3-vinylimidazolium bromide, [BVIM][Br] (precursor to **mIL1**):*

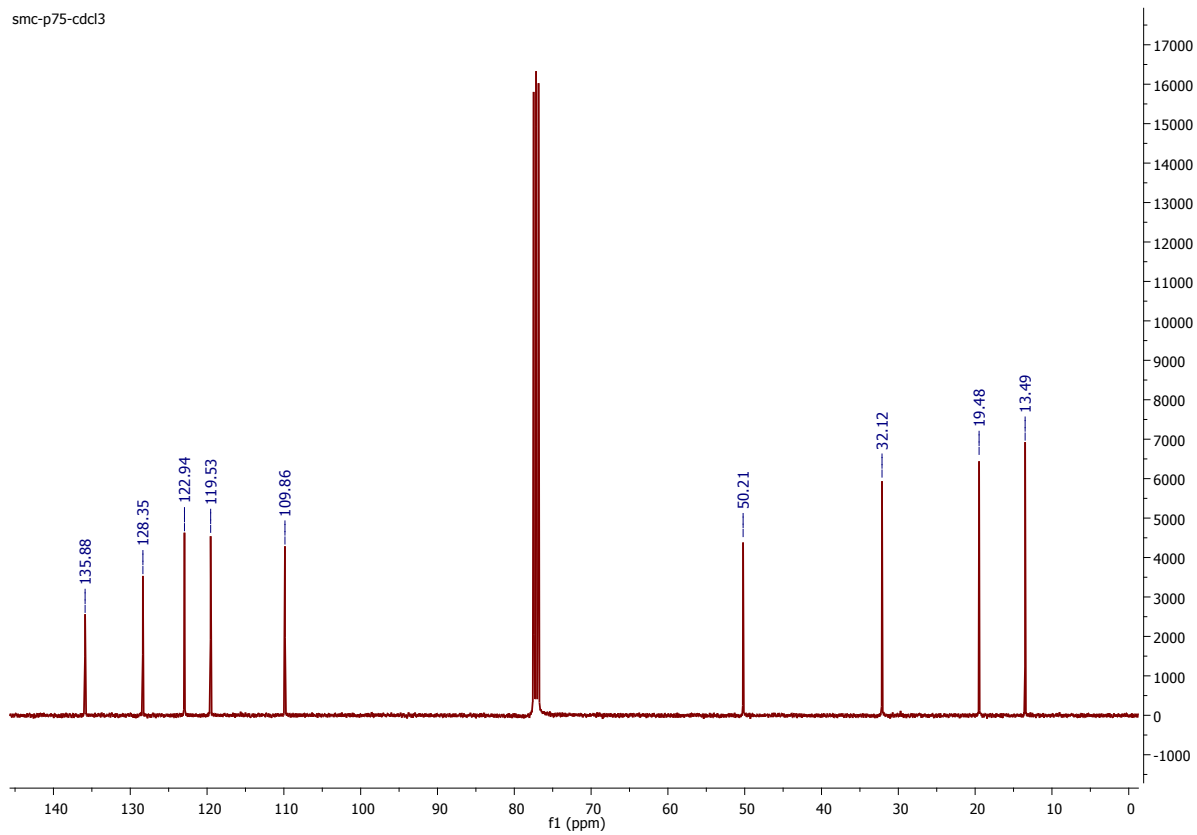
1-bromobutane (33 g, 240 mmol) dissolved in acetonitrile (10 mL) was added dropwise to a solution of 1-vinylimidazole (15 g, 160 mmol) in acetonitrile (15 mL). The resulting reaction mixture was left to react for 18 h at 40 °C. After evaporating the solvent, the crude product was then washed with diethyl ether (40 mL) four times. During the last wash the product crystallized becoming a white solid. The solid was re-dissolved in dichloromethane (5 mL) and slowly added to rapidly stirred diethyl ether (50 mL) to form a purer white solid. The solid product was dried under reduced pressure at room temperature for 6 h to afford 1-butyl-3-vinylimidazolium bromide (23.26 g, 63 %).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 10.85 (s, 1H), 7.94 (t, J = 2.0 Hz, 1H), 7.66 (t, J = 2.0 Hz, 1H), 7.45 (dd, J = 15.8, 8.4 Hz, 1H), 6.02 (dd, J = 15.8, 3.2 Hz, 1H), 5.36 (dd, J = 8.8, 3.2 Hz, 1H), 4.39 (t, J = 7.2 Hz, 2H), 1.95-1.87 (m, 2H), 1.41-1.31 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 135.9, 128.3, 122.9, 119.5, 109.9, 50.2, 32.1, 19.5, 13.5. Elemental Analysis: Calculated: C, 46.77; H, 6.54; N, 12.12; Found: C, 46.02; H, 6.13; N, 11.98.

smc-p75-cdcl3



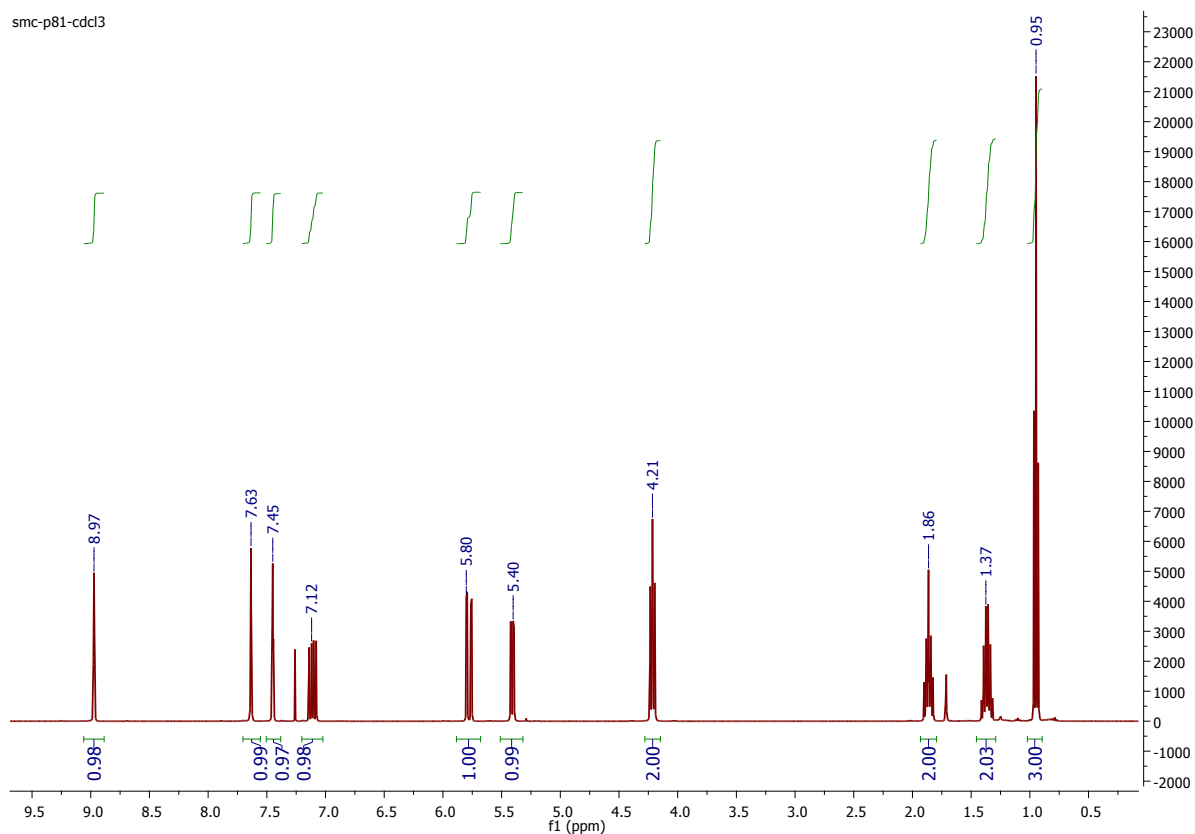
smc-p75-cdcl3

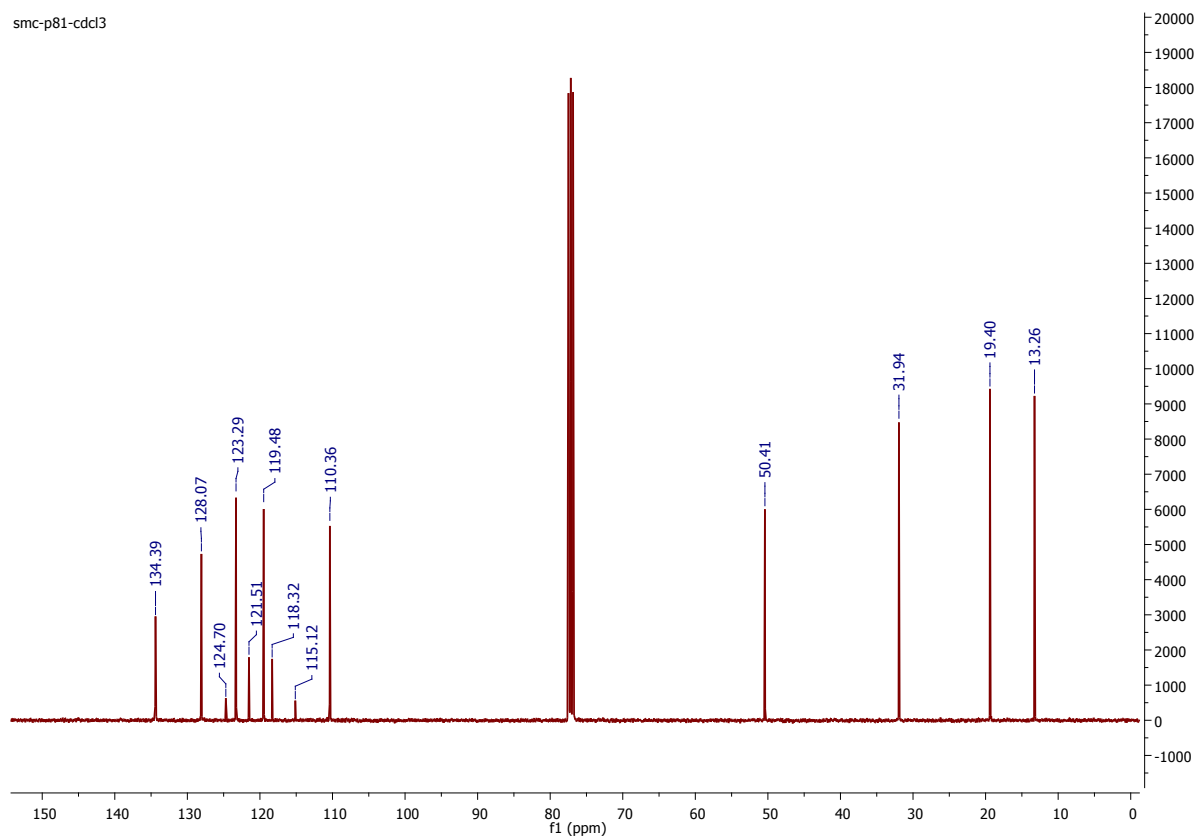


1-butyl-3-vinylimidazolium bis(trifluoromethane)sulfonimide, [BVIM][NTf₂] (**mL1**):

Lithium bis(trifluoromethane) sulfonimide (LiNTf₂) (22.35 g, 78 mmol) was dissolved in water (15 mL) and it was added dropwise to an aqueous solution (20 mL) of 1-butyl-3-vinylimidazolium bromide (15 g, 65 mmol), forming two liquid phases. The mixture was stirred rapidly for 6 h at room temperature. The phases were then separated and the aqueous phase was extracted three times with dichloromethane (50 mL). The combined organic phases were washed four times with water (75 mL) and dried over Na₂SO₄. The product was further dried under reduced pressure at 45 °C for 3 h. The yield was 77 % (21.50 g).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 8.97 (s, 1H), 7.63 (t, J = 1.6 Hz, 1H), 7.45 (t, J = 2.0 Hz, 1H), 7.12 (dd, J = 15.6, 8.4 Hz, 1H), 5.80 (dd, J = 15.2, 2.8 Hz, 1H), 5.40 (dd, J = 8.4, 2.8 Hz, 1H), 4.21 (t, J = 7.6 Hz, 2H), 1.90-1.82 (m, 2H), 1.41-1.32 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ / ppm = 134.4, 128.1, 123.3, 121.5 (q, CF₃), 119.5, 110.4, 50.4, 31.9, 19.4, 13.3. Elemental Analysis: Calculated: C, 30.63; H, 3.50; N, 9.74; Found: C, 31.47; H, 3.75; N, 9.92.





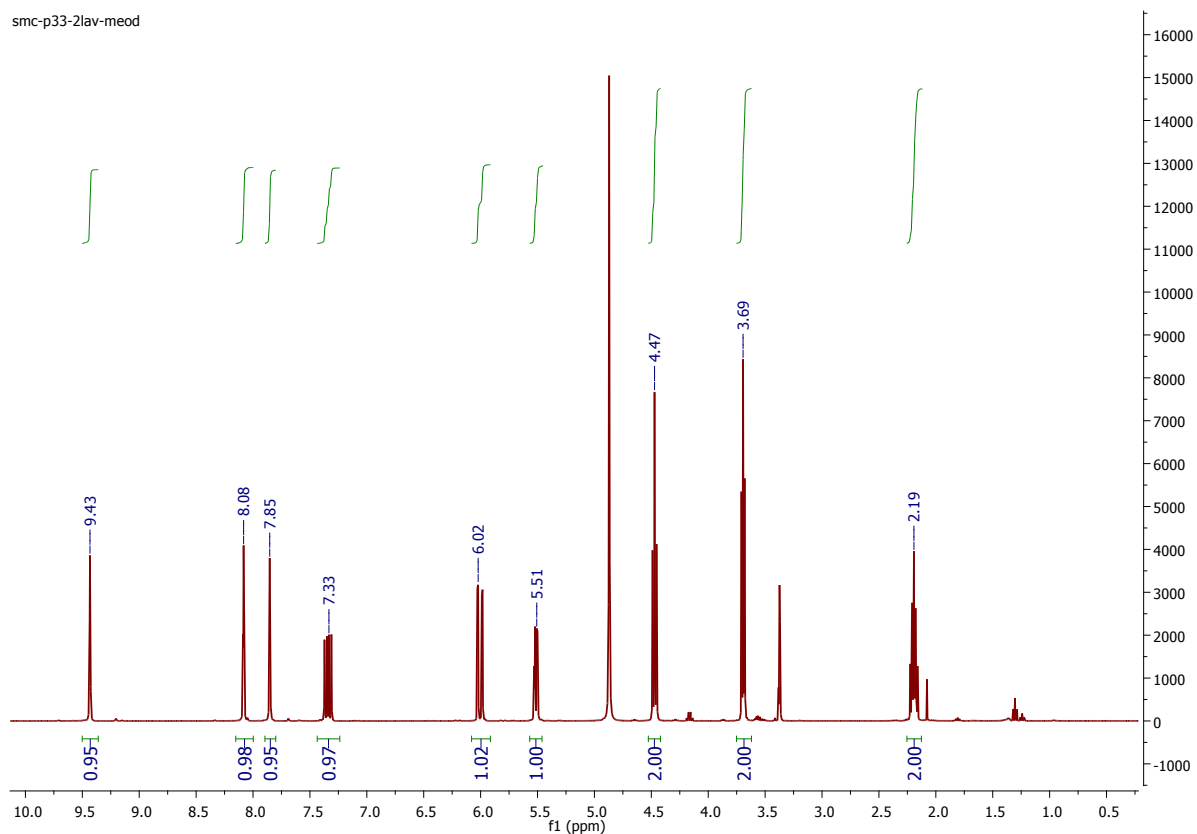
1-(3-hydroxypropyl)-3-vinylimidazolium bis(trifluoromethane)sulfonimide, [POHVIm][NTf₂] (miL2):

1-(3-hydroxypropyl)-3-vinylimidazolium bis(trifluoromethane)sulfonimide was synthesized by anion metathesis of 1-(3-hydroxypropyl)-3-vinylimidazolium bromide [POHVIm][Br] with lithium bis(trifluoromethane)sulfonimide. The full synthesis procedure for [POHVIm][Br] and [POHVIm][NTf₂]

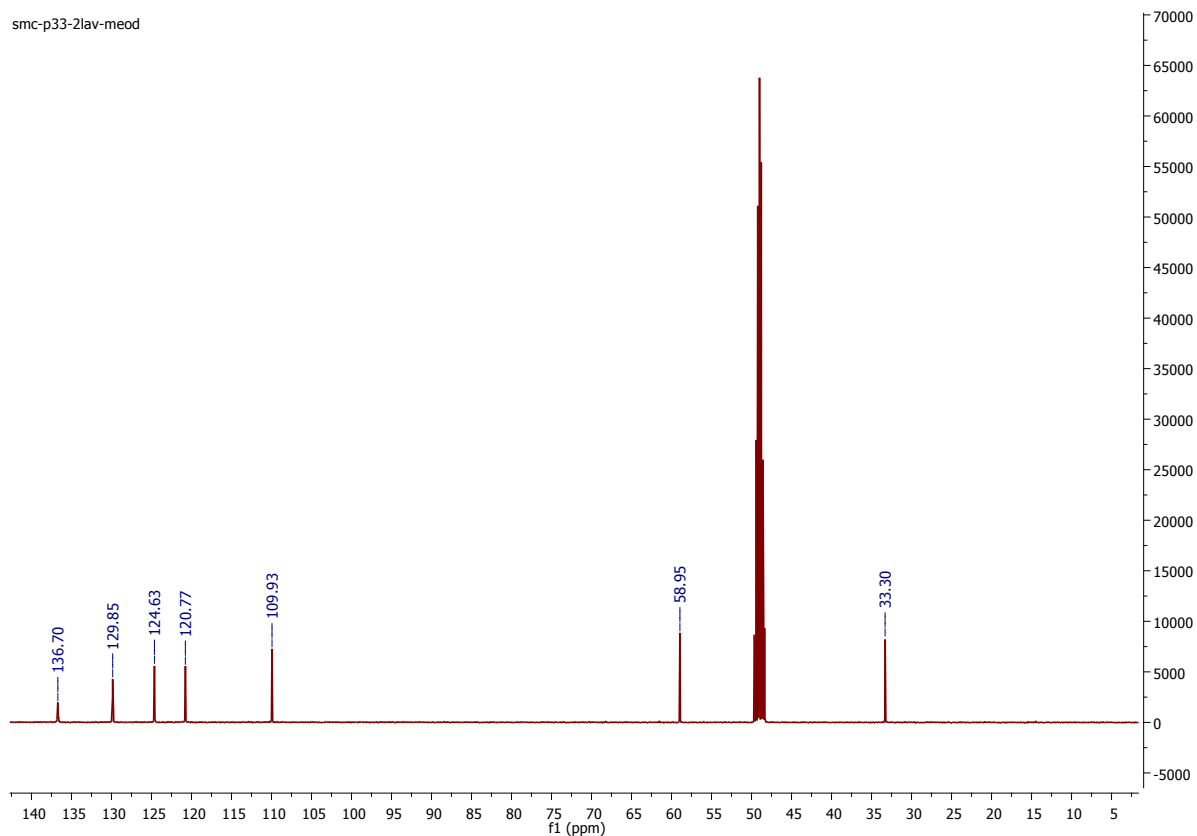
1-bromopropanol (9.13 g, 64 mmol) dissolved in acetonitrile (4 mL) was added dropwise to a solution of 1-vinylimidazole (5 g, 53 mmol) in acetonitrile (8 mL). The resulting reaction mixture was left to react for 21 h at 40 °C. After evaporating the solvent, the crude product was then washed with diethyl ether (10 mL) four times. The crude product was re-dissolved in dichloromethane (2 mL) and slowly added to rapidly stirred diethyl ether (15 mL) to form a white solid. The solid product was dried under reduced pressure at room temperature for 6 h to afford 1-(3-hydroxypropyl)-3-vinylimidazolium bromide (7.66 g, 62 %).

¹H NMR (400 MHz, CD₃OD): δ / ppm = 9.43 (s, 1H), 8.08 (t, J = 1.6 Hz, 1H), 7.85 (t, J = 2.0 Hz, 1H), 7.33 (dd, J = 15.6, 8.8 Hz, 1H), 6.02 (dd, J = 15.6, 2.4 Hz, 1H), 5.51 (dd, J = 8.8, 2.8 Hz, 1H), 4.47 (t, J = 6.8 Hz, 2H), 3.69 (t, J = 5.6 Hz, 2H), 2.22-2.16 (m, 2H); ¹³C NMR (101 MHz, CD₃OD): δ / ppm = 136.7, 129.8, 124.6, 120.8, 109.9, 58.9, 48.5, 33.3. Elemental Analysis: Calculated: C, 41.22; H, 5.62; N, 12.02; Found: C, 41.65; H, 5.95; N, 12.17.

smc-p33-2lav-meod



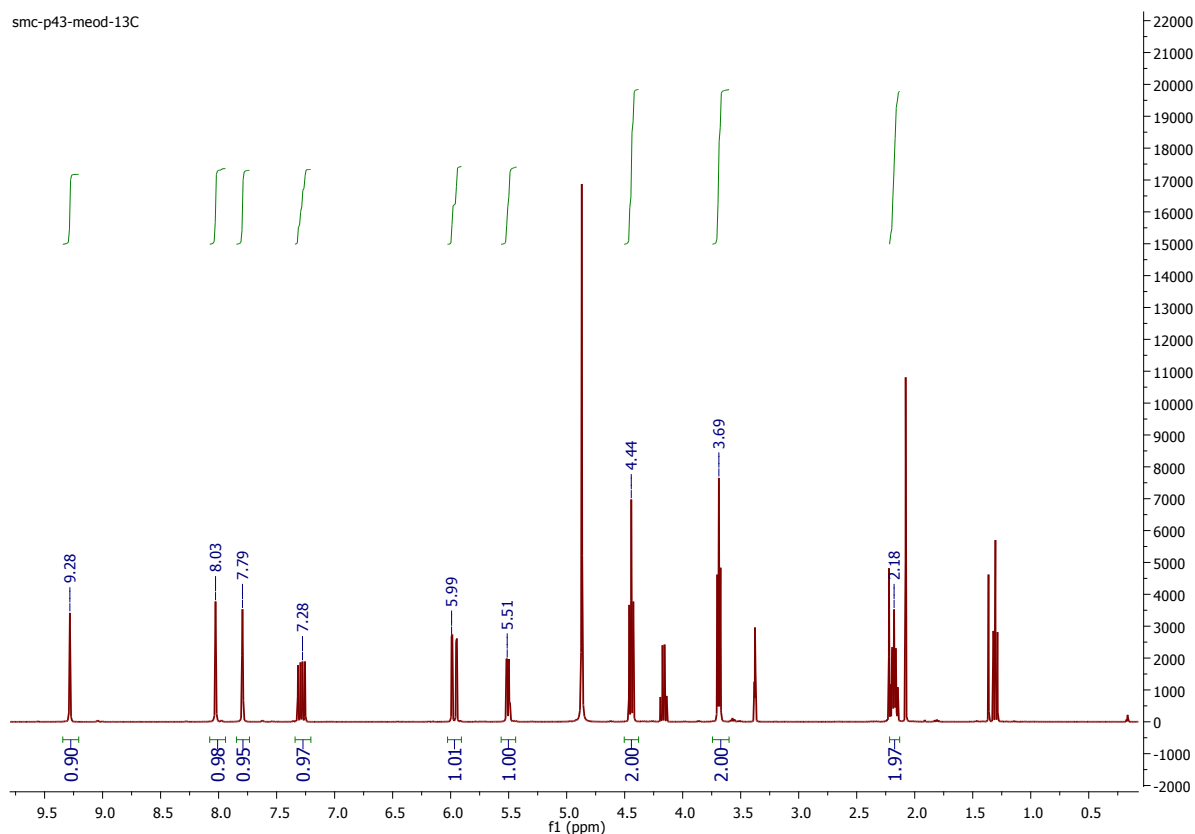
smc-p33-2lav-meod



Then, LiNTf_2 (6.46 g, 22.7 mmol) was dissolved in water (8 mL) and it was added dropwise to an aqueous solution (10 mL) of 1-(3-hydroxypropyl)-3-vinylimidazolium bromide (3.50 g, 15.1 mmol). The mixture formed two liquid phases. The mixture was stirred rapidly for 6 h at room

temperature. The phases were then separated and the aqueous phase was extracted four times with dichloromethane (25 mL). The combined organic phases were washed four times with water (10 mL) and dried over Na₂SO₄. The product was further dried under reduced pressure at 45 °C for 3 h. The yield was 90 % (5.86 g).

¹H NMR (400 MHz, CD₃OD): δ / ppm = 9.28 (s, 1H), 8.03 (t, J = 1.6 Hz, 1H), 7.79 (t, J = 2.0 Hz, 1H), 7.28 (dd, J = 15.6, 8.8 Hz, 1H), 5.99 (dd, J = 15.6, 2.8 Hz, 1H), 5.51 (dd, J = 8.4, 2.4 Hz, 1H), 4.44 (t, J = 7.2 Hz, 2H), 3.69 (t, J = 6 Hz, 2H), 2.21-2.15 (m, 2H); ¹³C NMR (101 MHz, CD₃OD): δ / ppm = 136.5, 129.7, 124.6, 122.8 (q, CF₃), 120.7, 109.9, 61.5, 58.9 33.2. Elemental Analysis: Calculated: C, 27.72; H, 3.02; N, 9.7; Found: C, 24.5; H, 2.67; N, 8.73.



smc-p43-meod-13C

