

Electronic Supplementary Information

On the way to greener and sustainable ionic liquids by naturally occurring and nature-inspired pyridinium structures

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Material and Methods

NMR spectra were acquired at room temperature on an Advance DRX 400 Spectrometer (Bruker, Billerica, MA, USA). HRMS was recorded on an LTQ-Orbitrap-XL (Thermo Scientific, Dreieich, Germany) equipped with a HESI source (Thermo Scientific, Dreieich, Germany) in positive mode.

Experimental Data

S1: Synthesis of 1-methylnicotinamide iodide ($[C_1CONH_2Py][I]$)

2 g of nicotinamide were dissolved in 20 mL MeOH followed by the addition of 3 mole equivalents of MeI. The reaction vessel was sealed and left for 72h at room temperature without stirring. After 72h, yellow crystals had formed which were removed by filtration, washed with cold MeOH and dried in vacuo. The product was obtained as pale-yellow crystals (3.55 g, 82%).

Melting point 207-209°C (Lit. 207-211°C¹). HRMS, $C_7H_9IN_2O$, calculated m/z 137.0709 $[M-I]^+$, found m/z 137.0712, $\Delta m/z$ 2.19 ppm. 1H -NMR (400 MHz, D_2O) δ = 4.39 (s, 3H), 8.08-8.12 (dd, $^3J = 8.1, 6.1$ Hz, 1H), 8.79-8.81 (d, $^3J = 8.2$ Hz, 1H), 8.88-8.90 (d, $^3J = 6.1$ Hz, 1H), 9.20 (s, 1H) ppm. ^{13}C -NMR (101 MHz, D_2O) δ = 48.63, 128.03, 133.48, 143.59, 145.15, 147.28, 165.77 ppm.

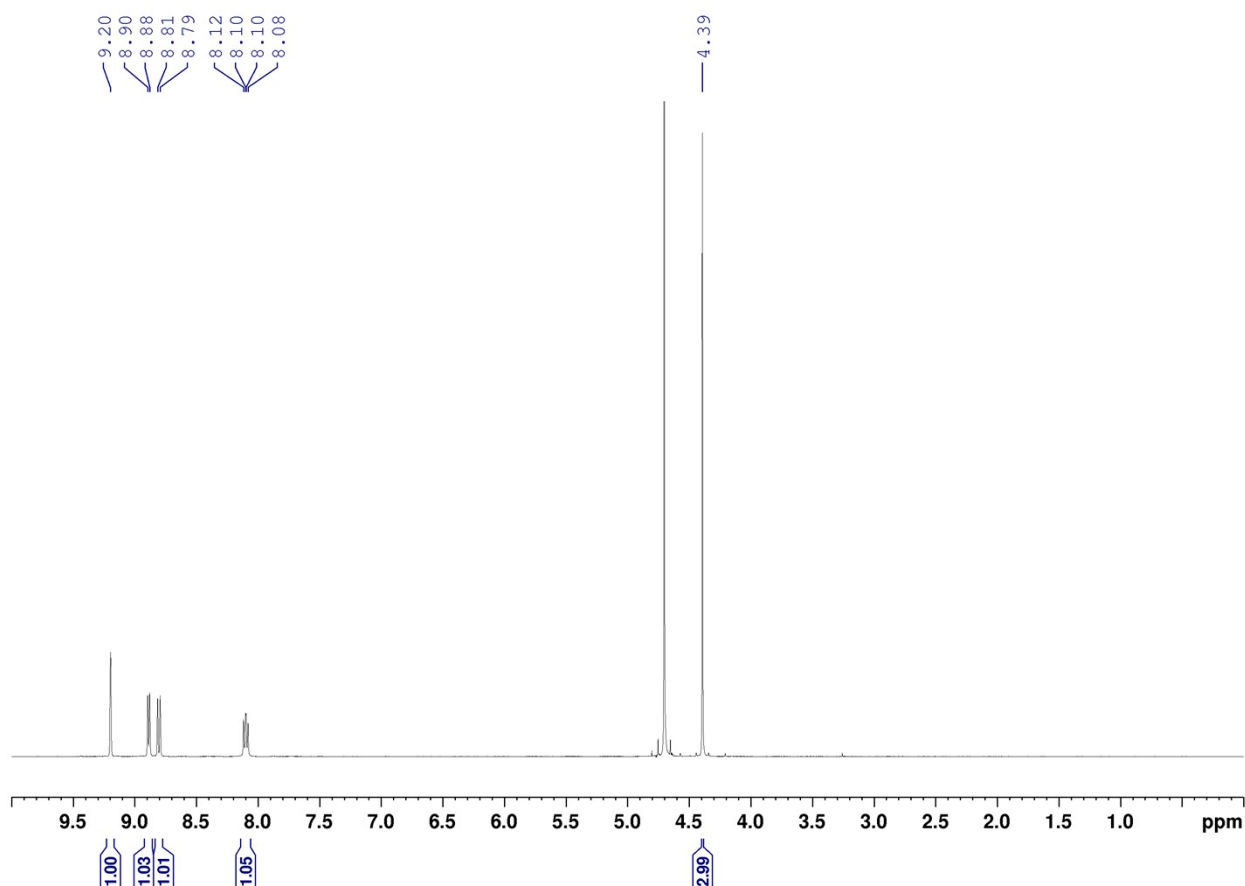


Figure S1: 1H -NMR spectrum of $[C_1CONH_2Py][I]$ in D_2O .

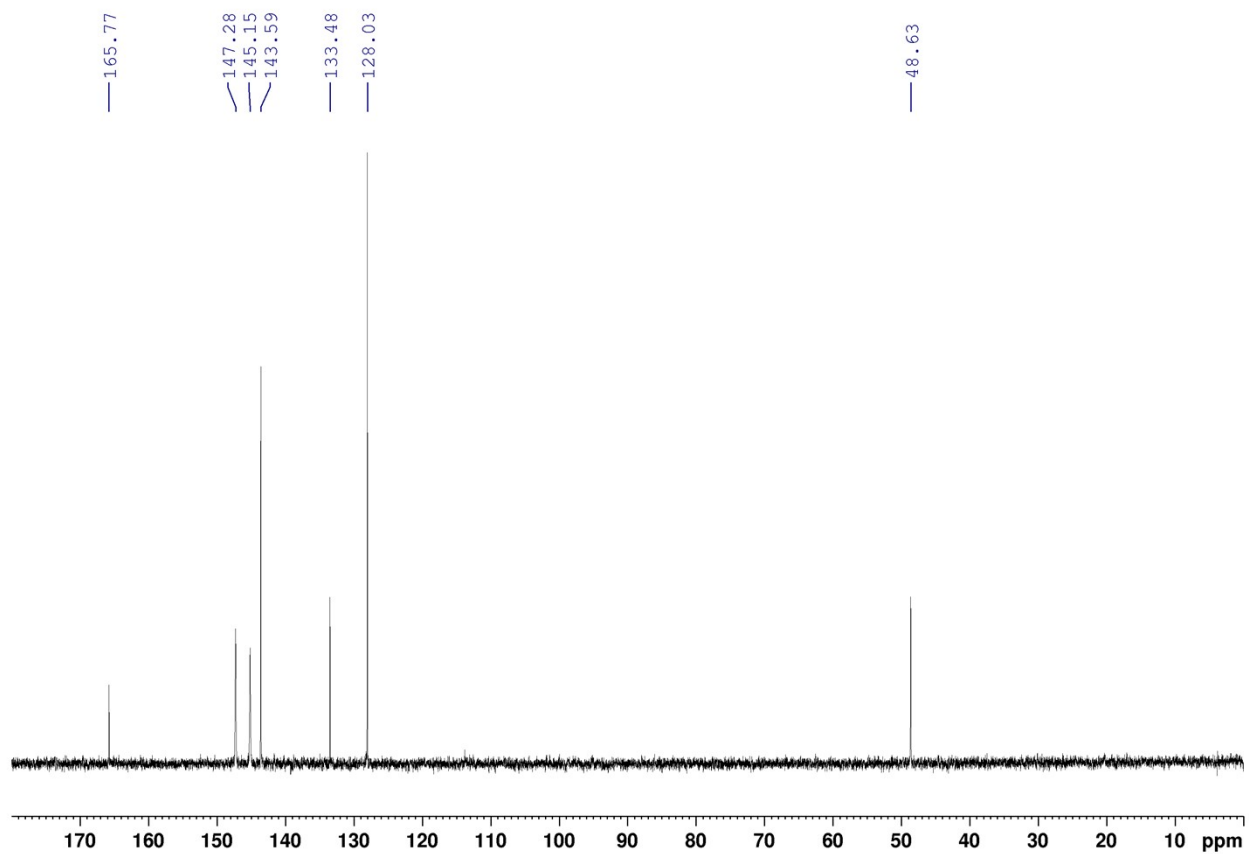


Figure S2: ^{13}C -NMR spectrum of $[\text{C}_1\text{CONH}_2\text{Py}][\text{I}]$ in D_2O .

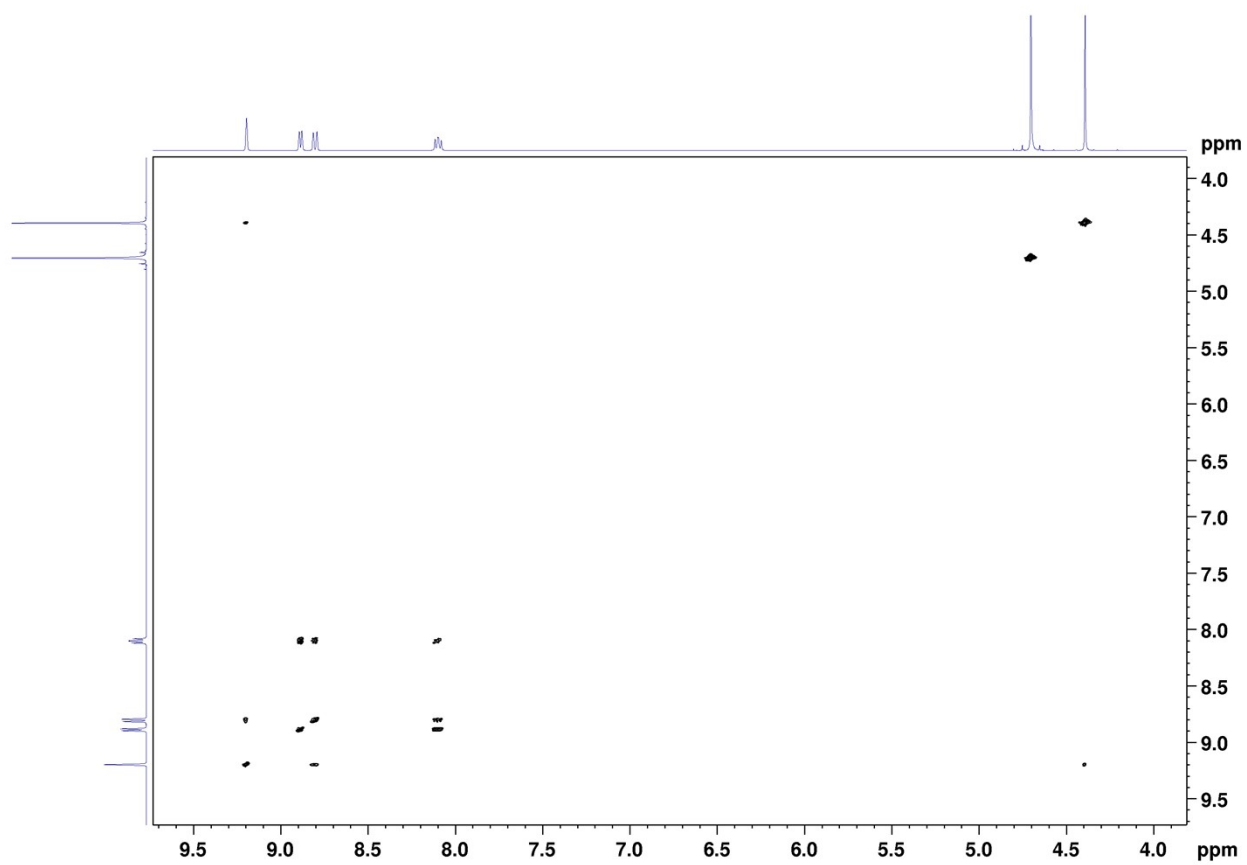


Figure S3: COSY spectrum of [C₁CONH₂Py][I] in D₂O.

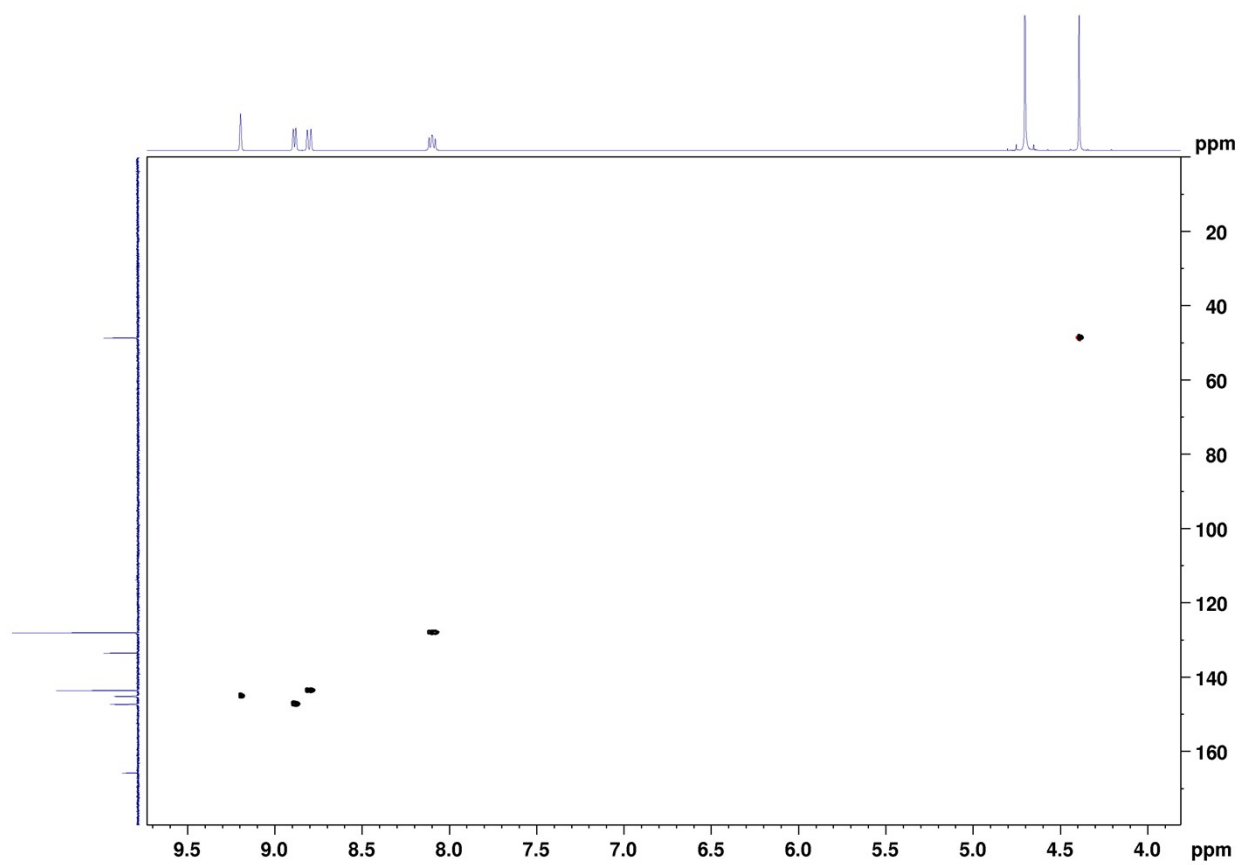


Figure S4: HSQC spectrum of $[C_1CONH_2Py][I]$ in D_2O .

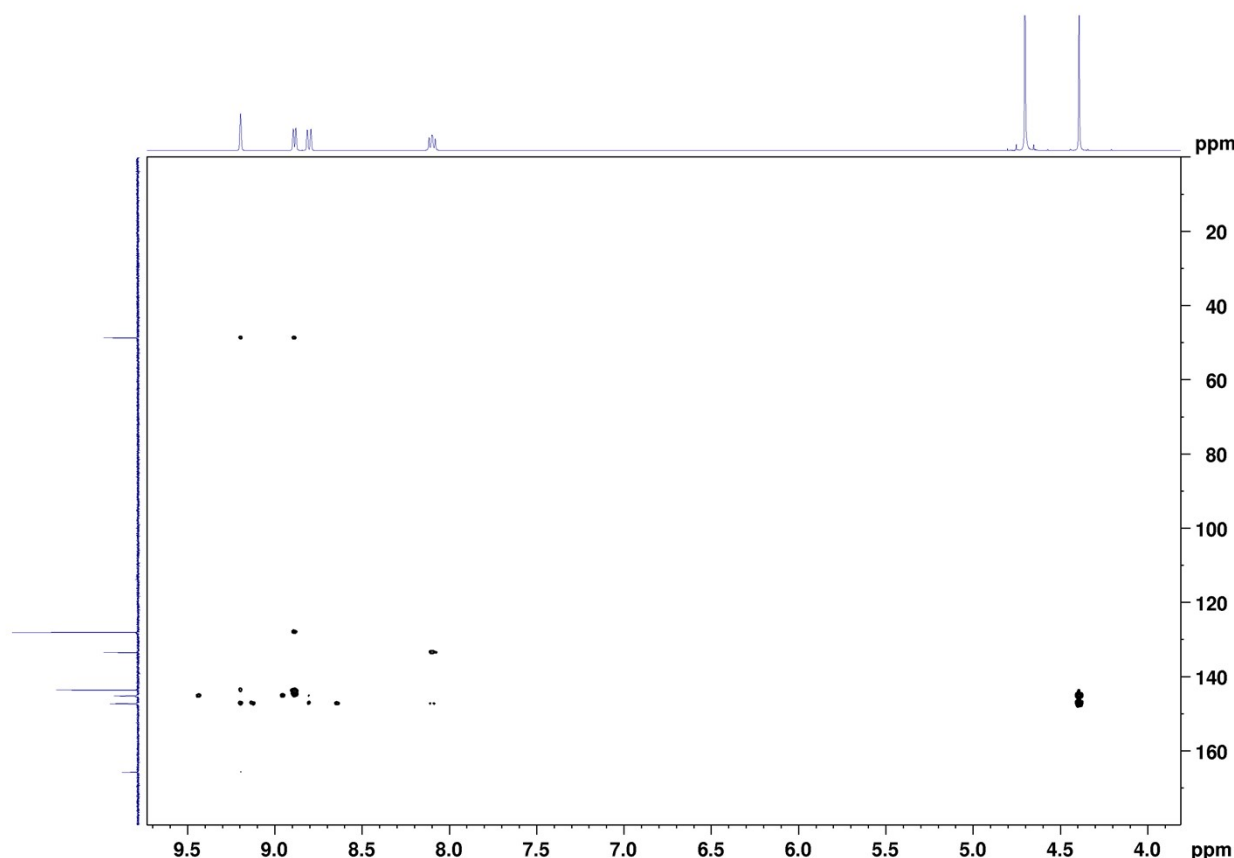


Figure S5: HMBC spectrum of $[C_1CONH_2Py][I]$ in D_2O .

S2: Synthesis of 1-methylnicotinium iodide ($[C_1mPyrPy][I]$)

The synthesis of $[C_1mPyrPy][I]$ has already been reported by Heckel et al. and was performed according to the literature with minor modifications.² 10 g of S-nicotine were dissolved in 65 mL acetic acid. After the solution cooled down to room temperature 2 mole equivalents of MeI were added and the sealed reaction vessel was left without stirring for 72h at room temperature. After 72h the solvent and MeI were removed by rotary evaporation, 150 mL Et_2O were added, and residual acetic acid and S-nicotine were filtered off with the Et_2O . The remaining solid was treated with saturated Na_2CO_3 solution until pH 8 was reached. Thereafter, the aqueous layer was removed by rotary evaporation and the residue was extracted with 3x 200 mL $CHCl_3$ for 2h under reflux. The organic extracts were combined, dried with Na_2SO_4 and evaporated under vacuum. The obtained solids were recrystallized from acetone yielding 6.33 g (34%) of orange crystals of $[C_1mPyrPy][I]$.

Melting point 165-166°C (Lit. 165-165.5°C³). HRMS, $C_{11}H_{17}IN_2$, calculated m/z 177.1386 $[M-I]^+$, found m/z 177.1387, Δ m/z 0.56 ppm. 1H -NMR (400 MHz, D_2O) δ = 1.69-1.79 (m, 1H), 1.83-1.90 (m, 2H), 2.10 (s, 3H), 2.25-2.32 (m, 1H), 2.33-2.40 (q, 3J = 9.3 Hz, 1H), 3.07-3.12 (m, 1H), 3.41-3.46 (t, 3J = 8.5 Hz, 1H), 4.28 (s, 3H), 7.91-7.95 (dd, 3J = 8.1 Hz, 6.1 Hz, 1H), 8.37-8.39 (d, 3J = 8.2 Hz, 1H), 8.60-8.62 (d, 3J = 6.1 Hz, 1H), 8.63 (s, 1H) ppm. ^{13}C -NMR (101 MHz, D_2O) δ = 21.98, 33.50, 39.12, 48.10, 56.31, 67.28, 127.93, 143.15, 144.05, 144.15, 144.26 ppm. ^{15}N -NMR (41 MHz, D_2O) δ = -176.97, -318.68 ppm.

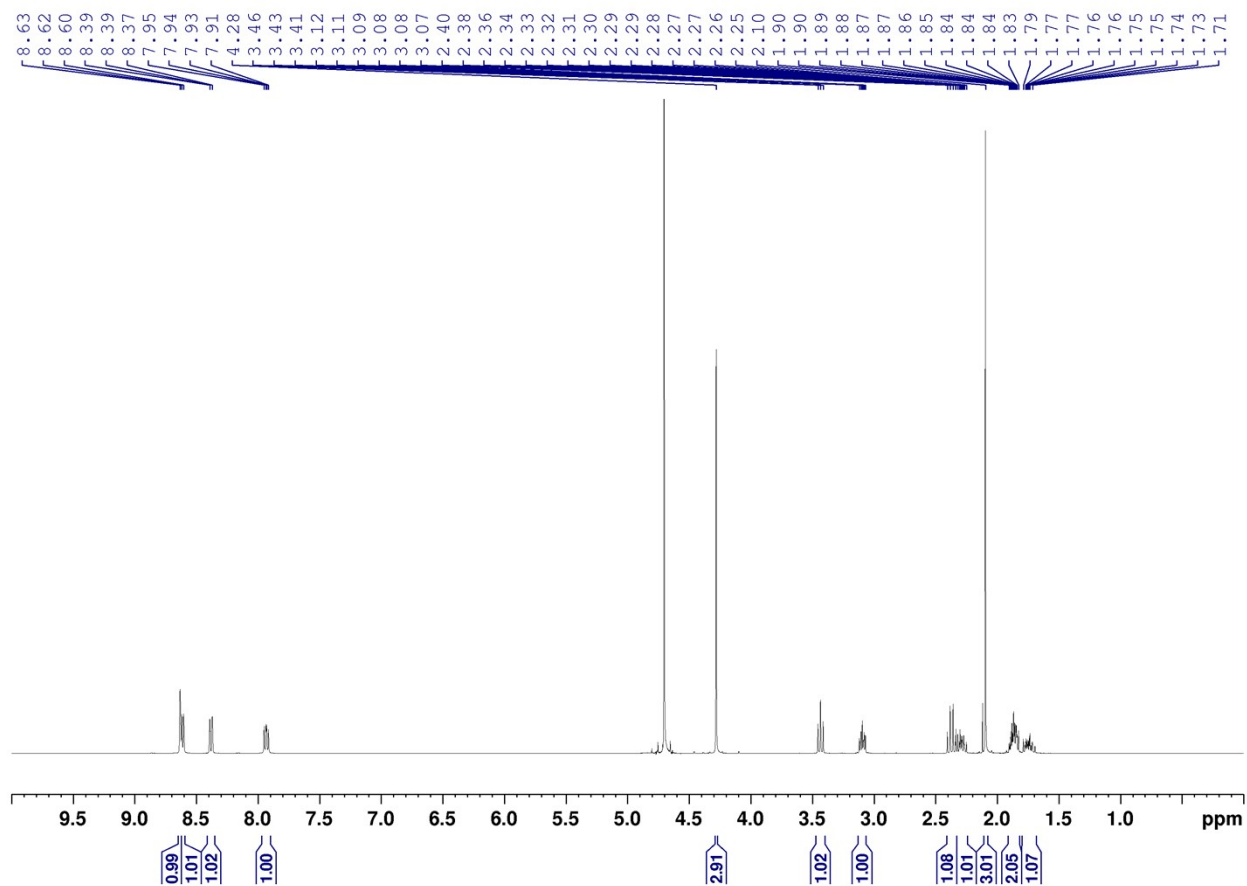


Figure S6: $^1\text{H-NMR}$ spectrum of $[\text{C}_1\text{mPyrPy}][\text{I}]$ in D_2O .

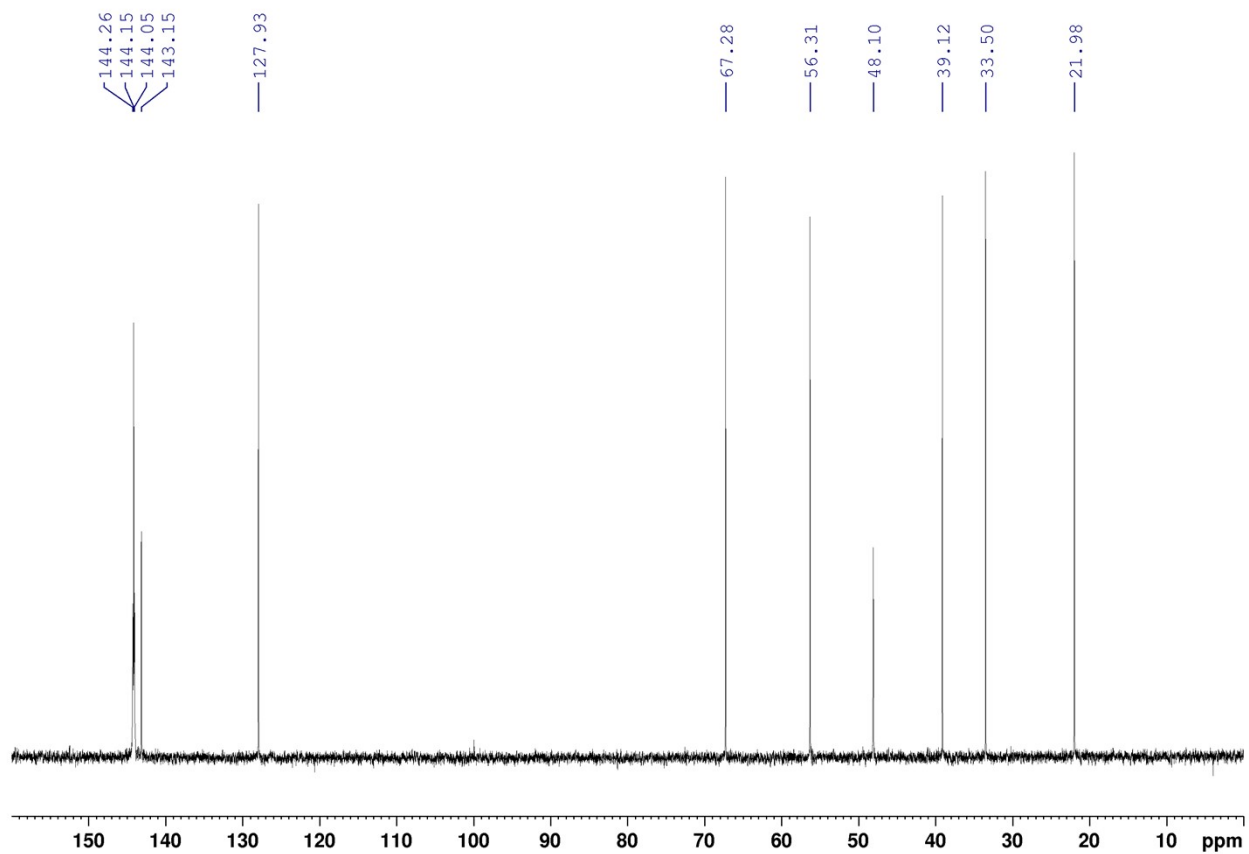


Figure S7: ^{13}C -NMR spectrum of $[\text{C}_1\text{mPyrPy}][\text{I}]$ in D_2O .

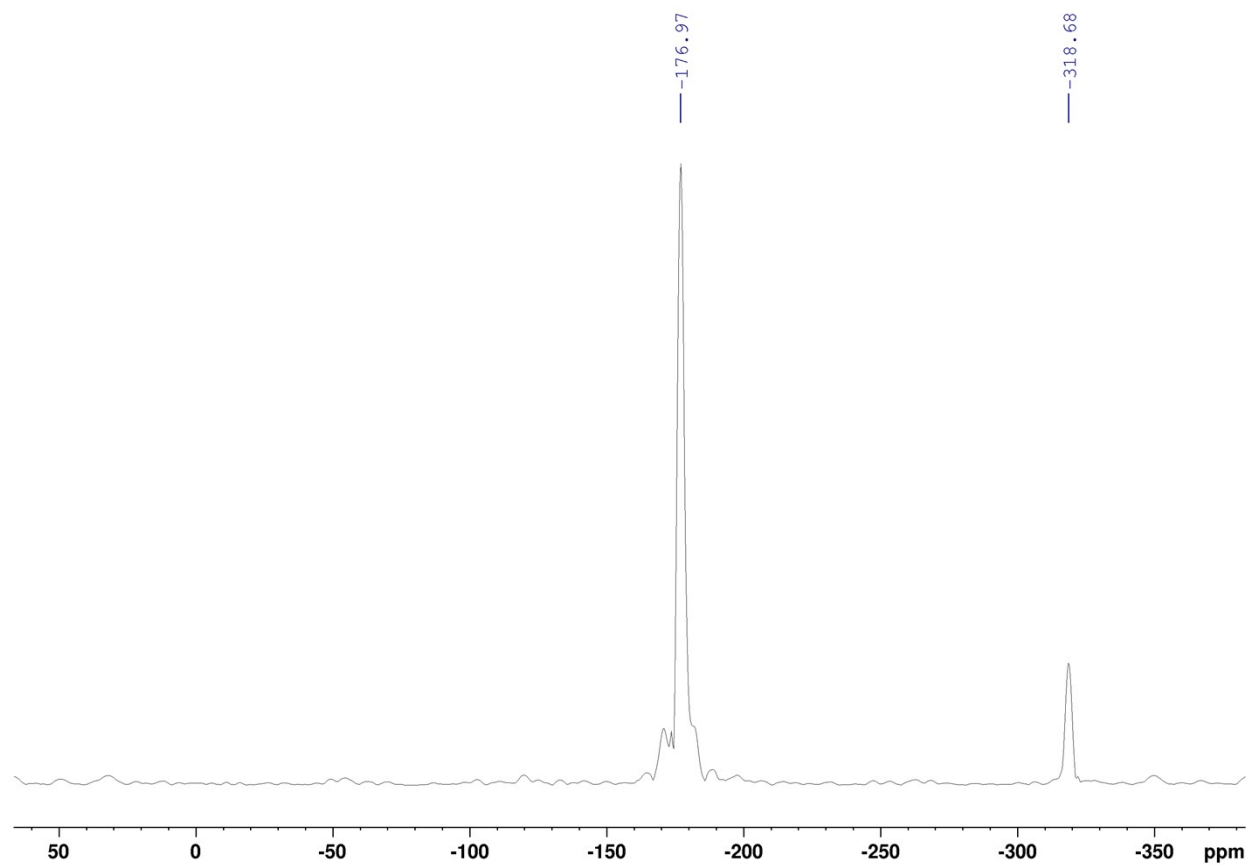


Figure S8: ^{15}N -NMR spectrum of $[\text{C}_1\text{mPyrPy}][\text{I}]$ in D_2O .

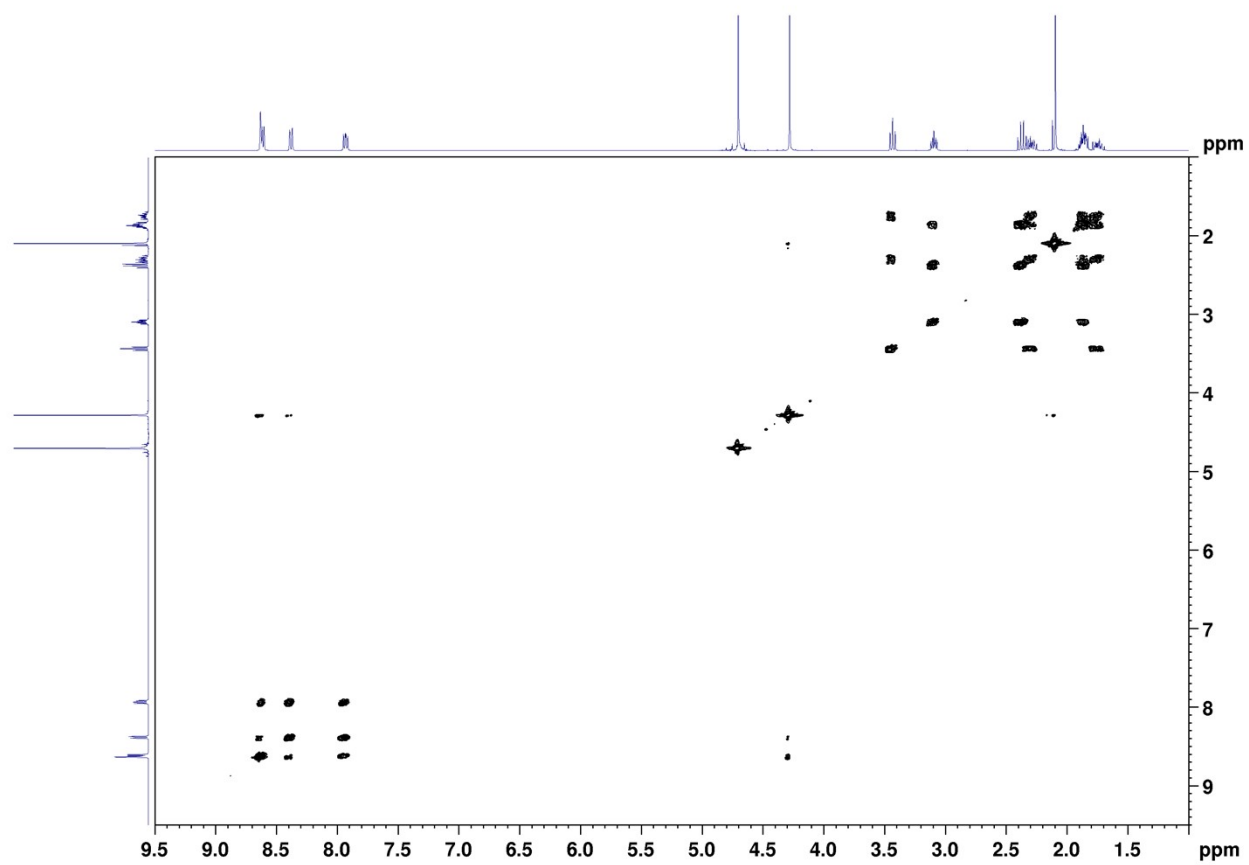


Figure S9: COSY spectrum of [C₁mPyrPy][I] in D₂O.

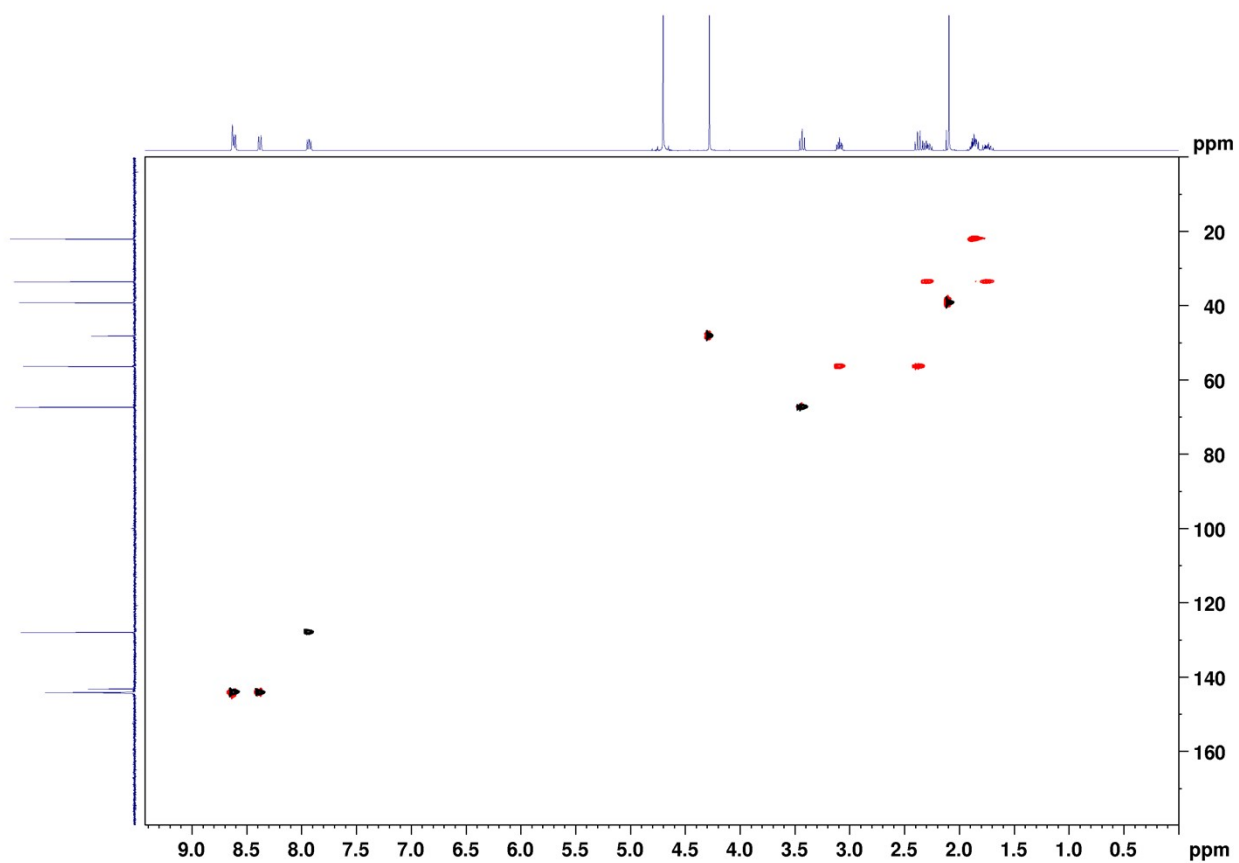


Figure S10: HSQC spectrum of $[C_{1m}PyrPy][I]$ in D_2O .

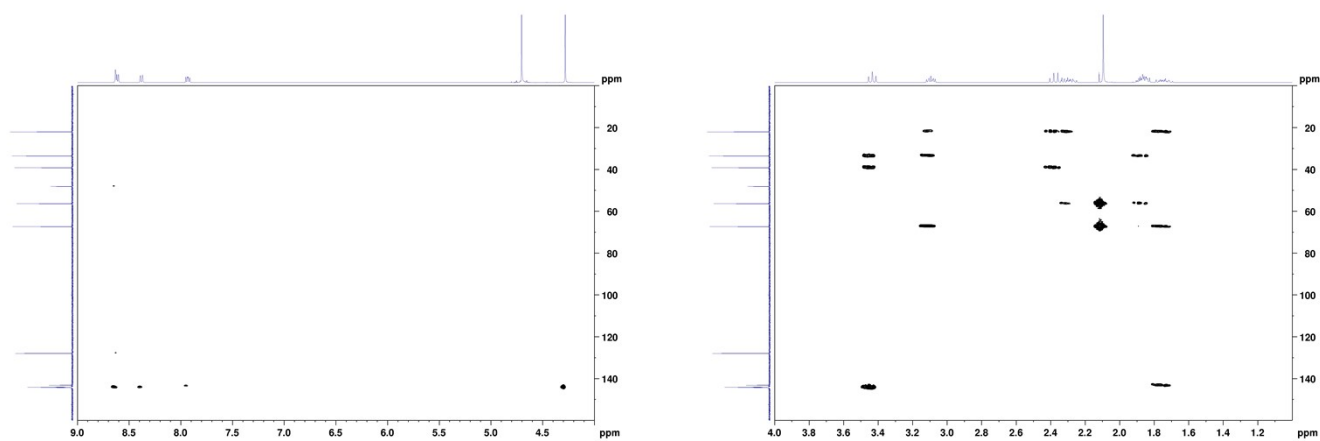


Figure S11: HMBC spectrum of $[C_{1m}PyrPy][I]$ in D_2O .

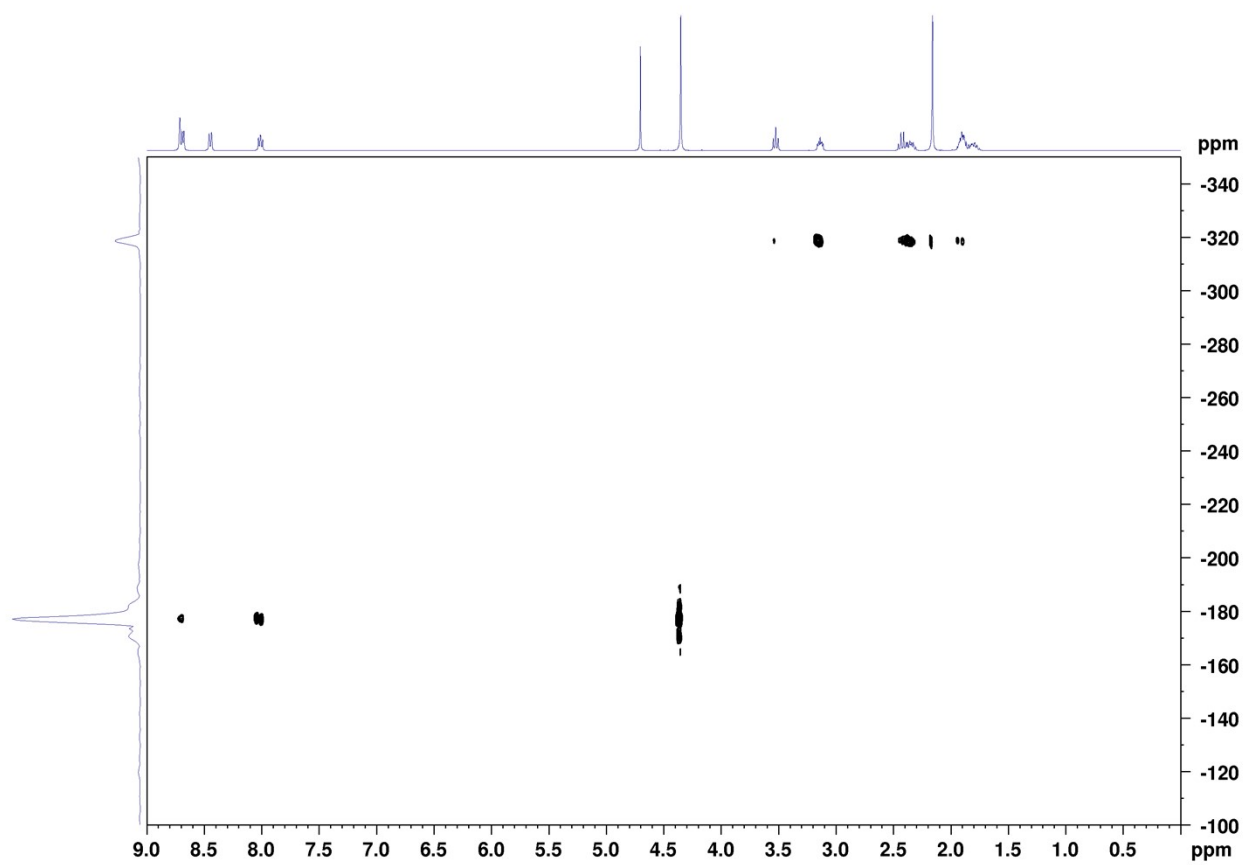


Figure S12: ^1H - ^{15}N -HMBC spectrum of $[\text{C}_1\text{mPyrPy}][\text{I}]$ in D_2O .

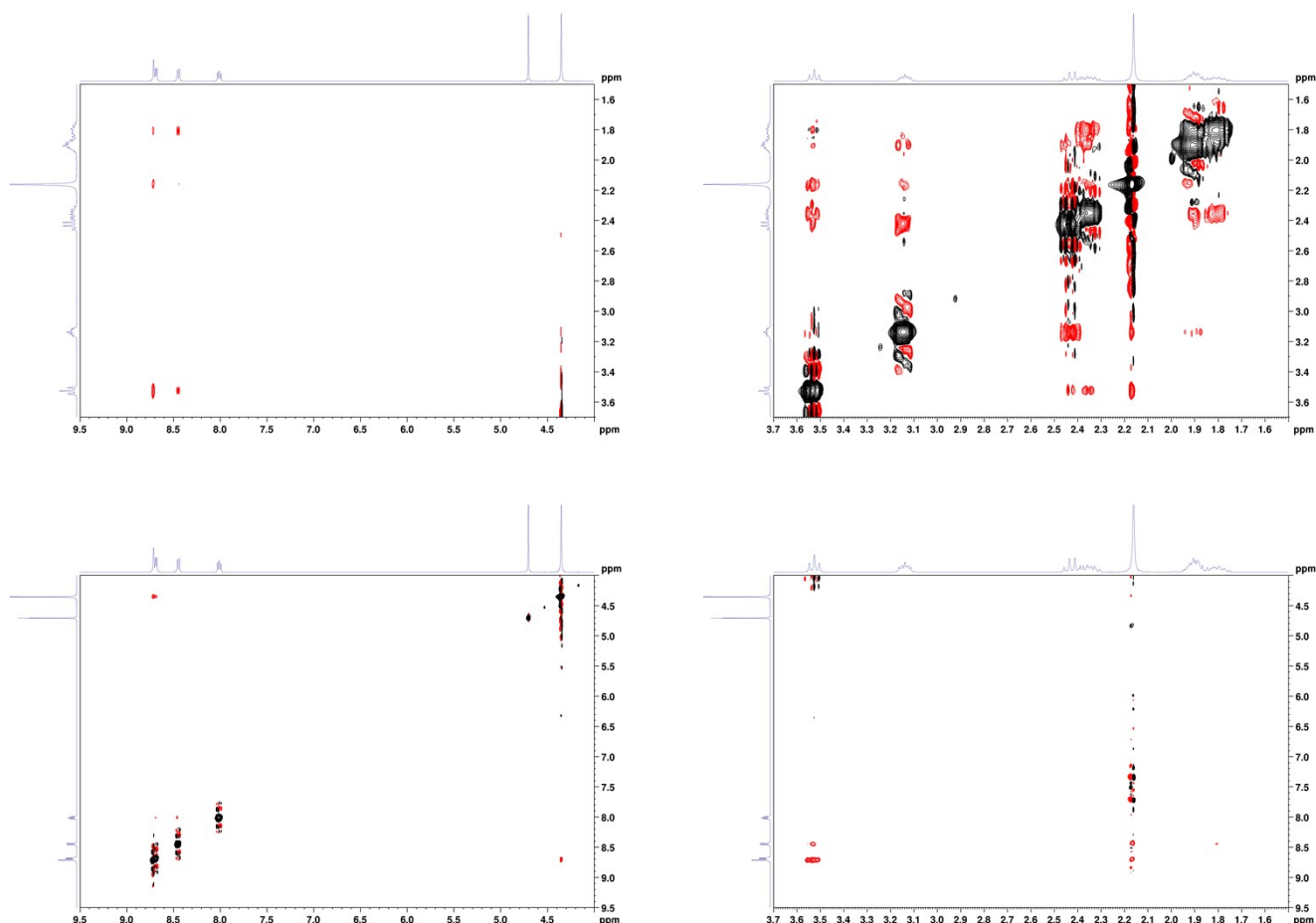


Figure S13: NOESY spectrum of $[C_1mPyrPy][I]$ in D_2O .

S3: Synthesis of 1,1'-dimethylnicotinium diiodide ($[C_1mC_1PyrPy][I_2]$)

To 1 g S-nicotine 10 mole equivalents of MeI were added in a sealed reaction vessel and left without stirring for 72h at room temperature. After evaporation of residual MeI, the solids were washed with Et_2O and recrystallized from MeOH- Et_2O yielding 1.72 g (62%) of pale-yellow crystals.

Melting point 214-215°C. HRMS, $C_{12}H_{20}I_2N_2$, calculated m/z 96.0808 $[M-I_2]^{2+}$, found m/z 96.0811, $\Delta m/z$ 3.12 ppm. 1H -NMR (400 MHz, D_2O) δ = 2.30-2.38 (m, 2H), 2.63-2.69 (m, 2H), 2.84 (s, 3H), 3.15 (s, 3H), 3.72-3.80 (m, 1H), 3.84-3.90 (m, 1H), 4.40 (s, 3H), 4.97-5.02 (t, $^3J = 9.7$ Hz, 1H), 8.15-8.19 (dd, $^3,^3J = 6.1$ Hz, 8.2 Hz, 1H), 8.76-8.78 (d, $^3J = 8.3$ Hz, 1H), 8.93-8.94 (d, $^3J = 6.1$ Hz, 1H), 9.14 (s, 1H) ppm. ^{13}C -NMR (101 MHz, D_2O) δ = 18.99, 26.10, 45.47, 48.82, 51.00, 67.15, 74.50, 128.75, 130.28, 147.19, 147.41 ppm. ^{15}N -NMR (41 MHz, D_2O) δ = -173.95, -305.02 ppm.

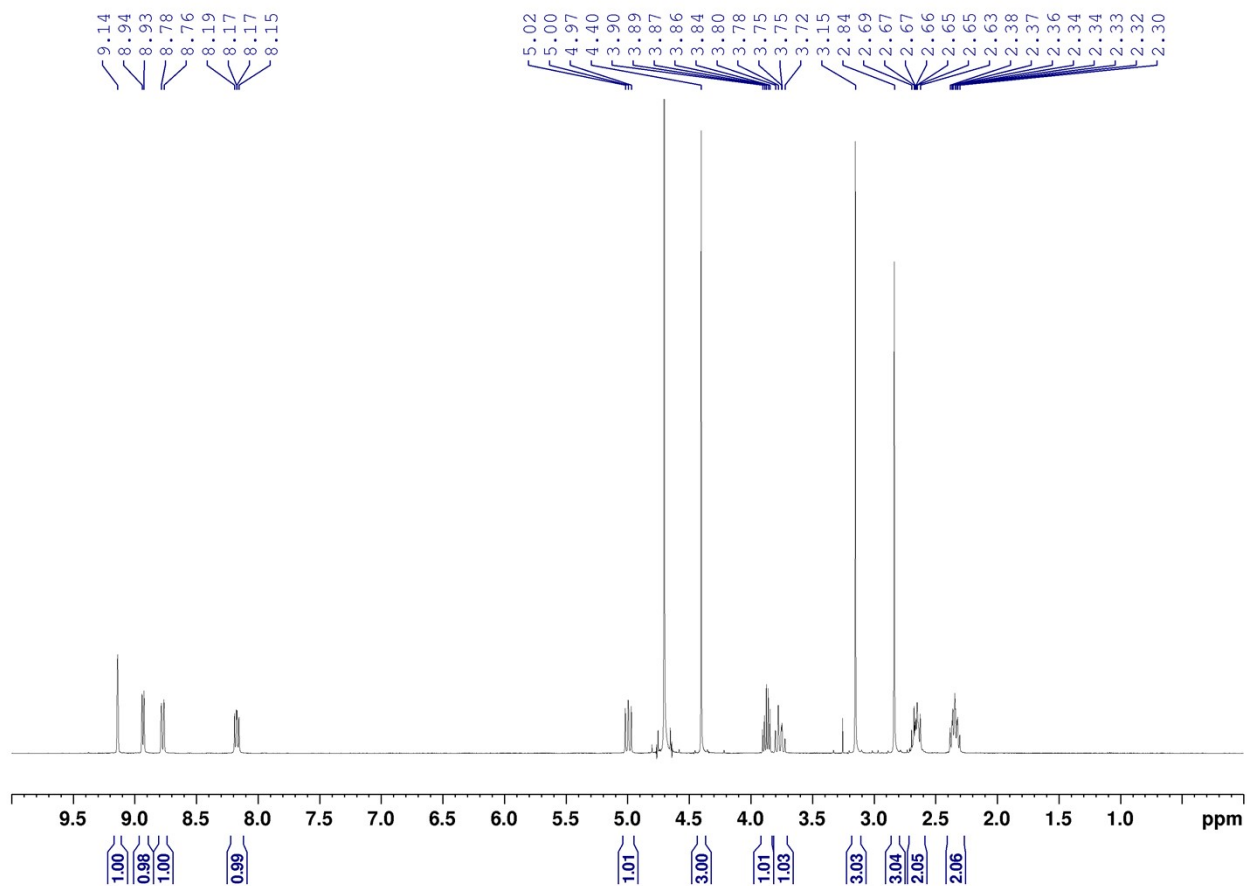


Figure S14: ¹H-NMR spectrum of [C₁mC₁PyrPy][I]₂ in D₂O.

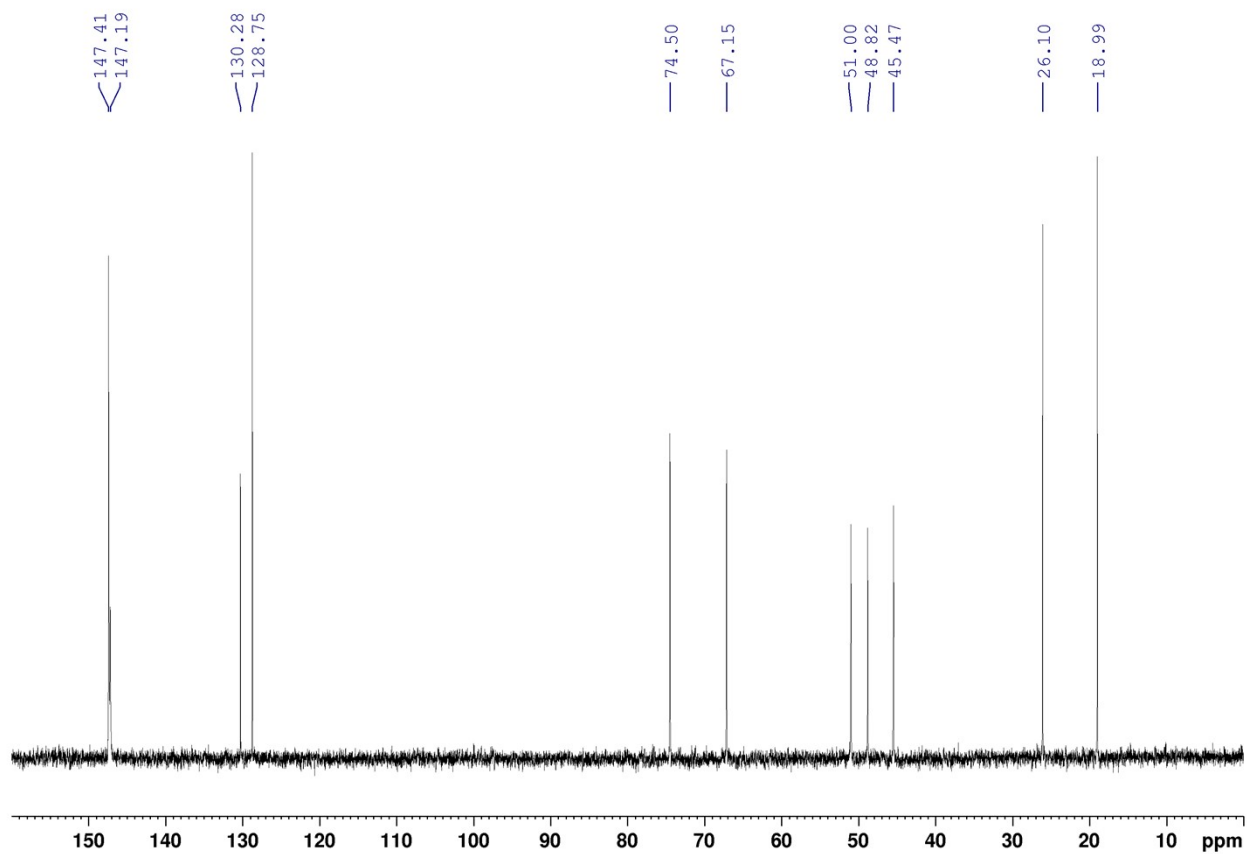


Figure S15: ^{13}C -NMR spectrum of $[\text{C}_1\text{mC}_1\text{PyrPy}][\text{I}]_2$ in D_2O .

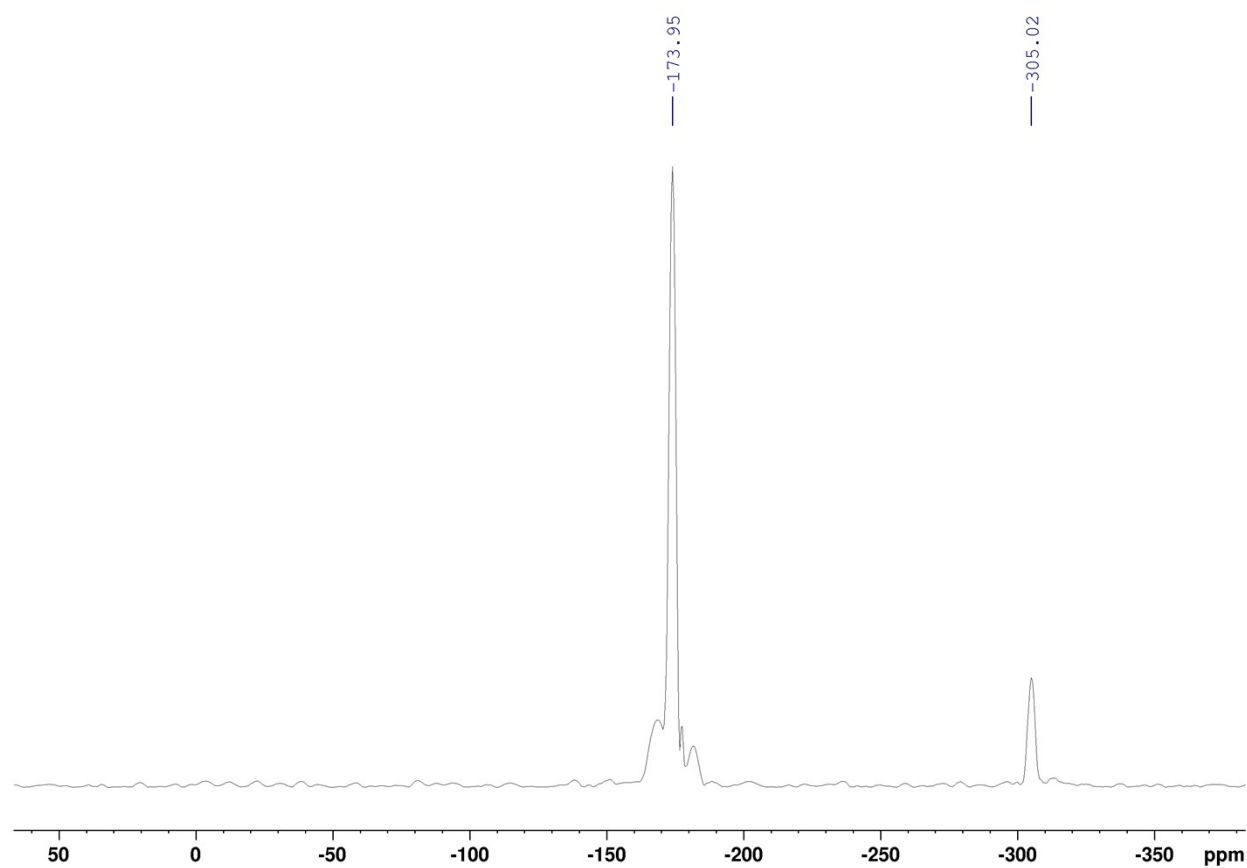


Figure S16: ^{15}N -NMR spectrum of $[\text{C}_1\text{mC}_1\text{PyrPy}][\text{I}]_2$ in D_2O .

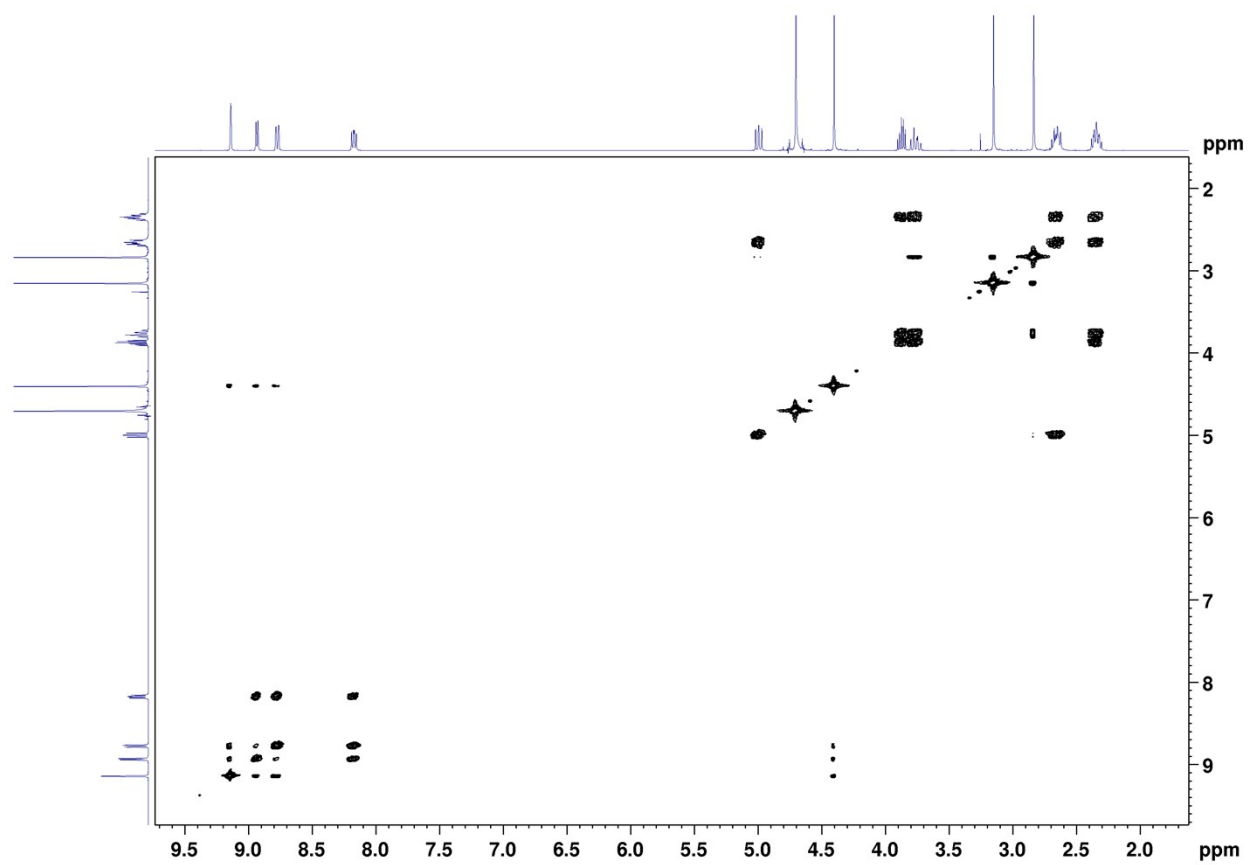


Figure S17: COSY spectrum of $[C_1mC_1PyrPy][I]_2$ in D_2O .

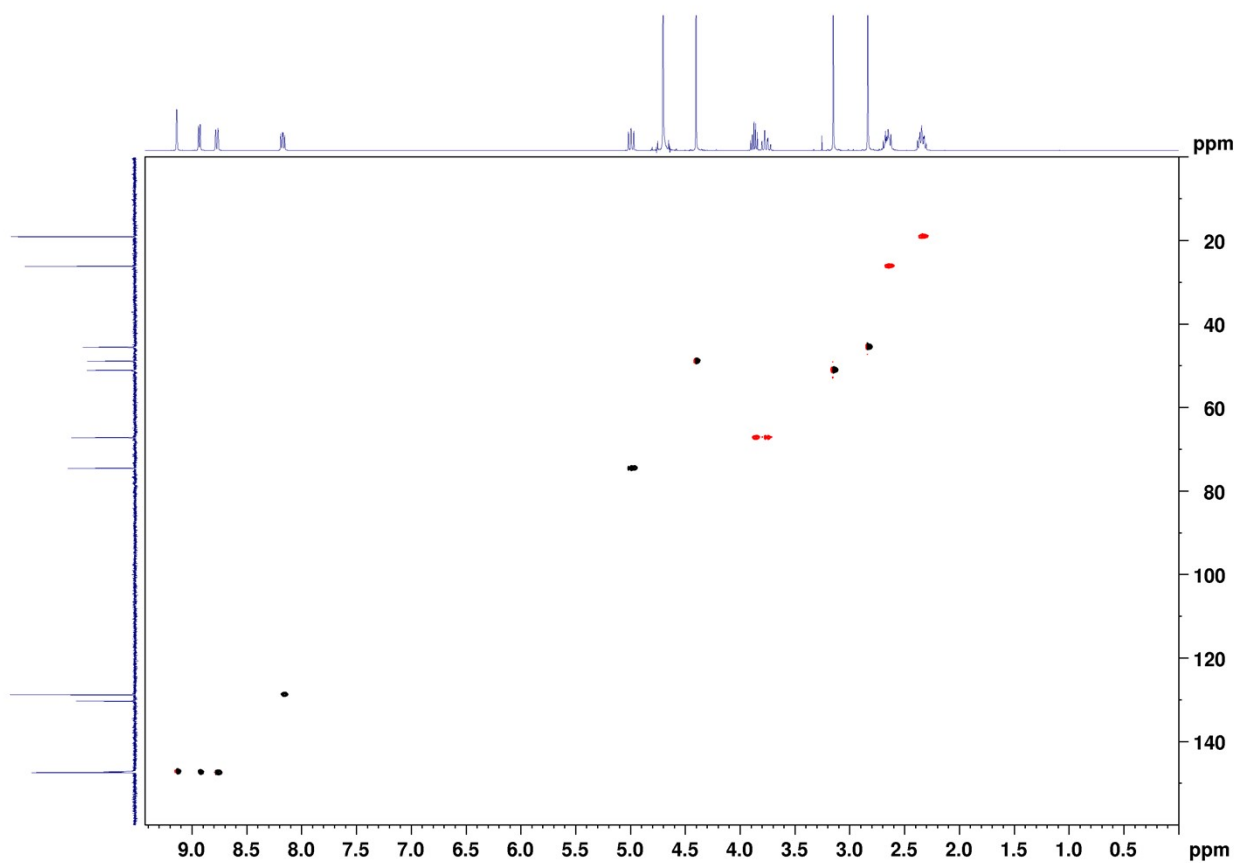


Figure S18: HSQC spectrum of $[C_1mC_1PyrPy][I]_2$ in D_2O .

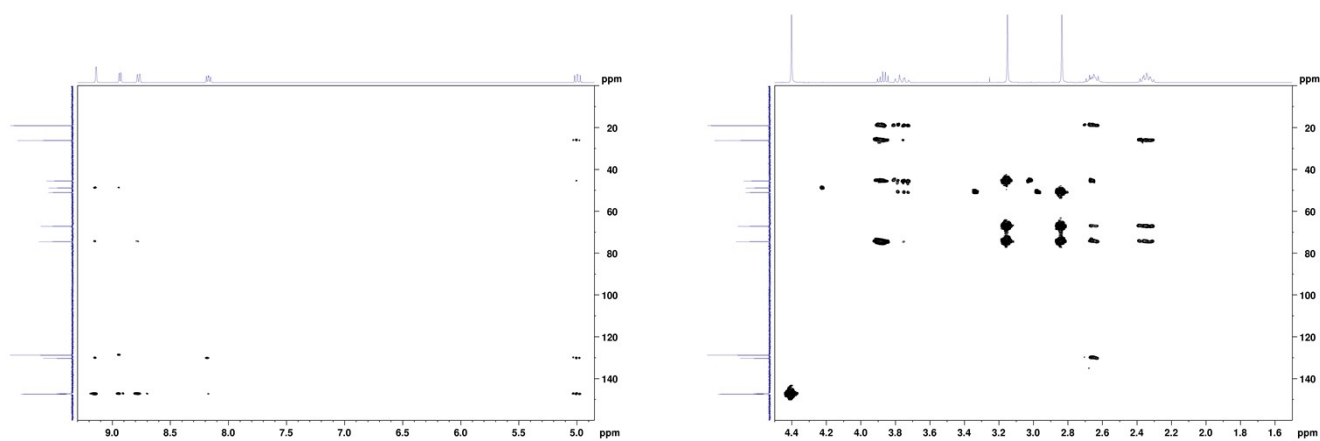


Figure S19: HMBC spectrum of $[C_1mC_1PyrPy][I]_2$ in D_2O .

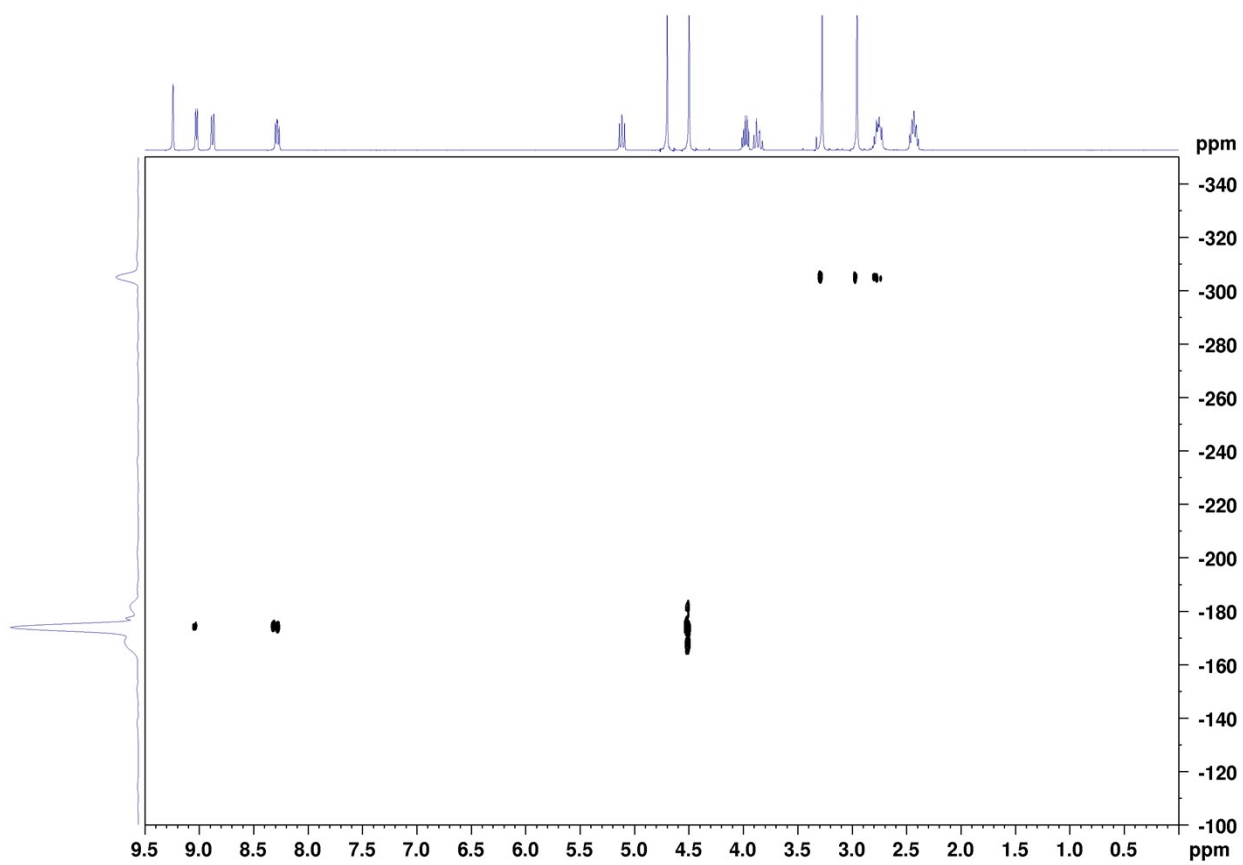


Figure S20: ^1H - ^{15}N -HMBC spectrum of $[\text{C}_1\text{mC}_1\text{PyrPy}][\text{I}]_2$ in D_2O .

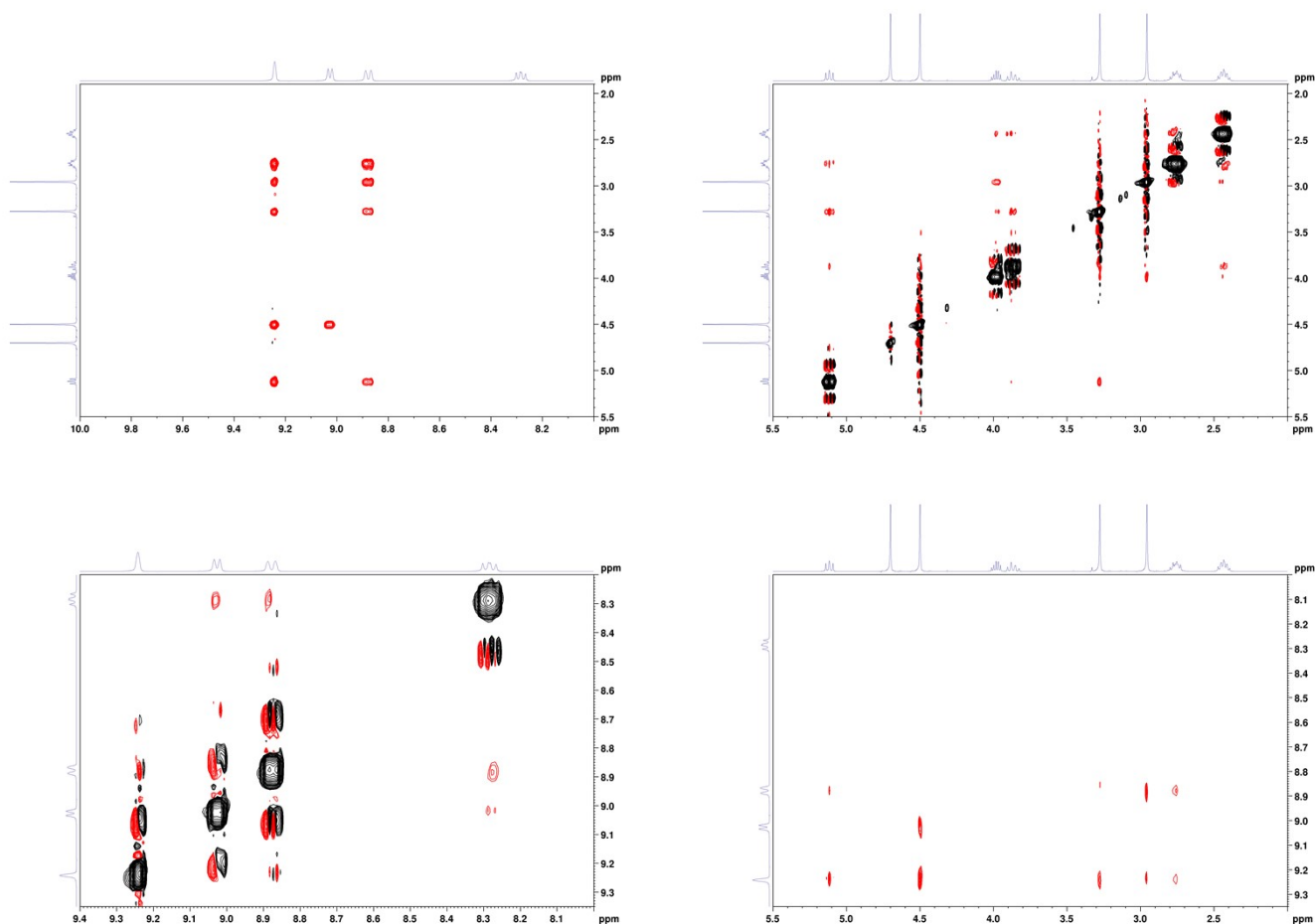


Figure S21: NOESY spectrum of $[C_1mC_1PyrPy][I]_2$ in D_2O .

References

- 1 S. L. Johnson and K. W. Smith, *J. Org. Chem.*, 1977, **42**, 2580–2589.
- 2 T. Heckel, A. Winkel and R. Wilhelm, *Tetrahedron Asymmetry*, 2013, **24**, 1127–1133.
- 3 J. I. Seeman and J. F. Whidby, *J. Org. Chem.*, 1976, **41**, 3824–3826.