Electronic Supplementary Information for

Controlling dual-positively charged pyrazolium ionic liquids for efficient catalytic conversion of CO_2 into carbonates under mild conditions

Jean Damascene Ndayambaje [1, 2], Irfan Shabbir [1,2], Qianmeng Zhao [1,2], Li Dong [1], Qian Su *[1], Weiguo Cheng *[1]

[1] CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190 (P. R. China)

[2] University of Chinese Academy of Sciences, Beijing 100049 (P. R. China)

* **Corresponding authors.**

E-mail address:

wgcheng@ipe.ac.cn (W.C);

qsu@ipe.ac.cn (Q.S)

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1. Additional experimental procedures

1.1. Materials

1-Methyl Pyrazole (≥98.0%), acetonitrile (≥99.0%), ethyl acetate (≥99.0%), propylene oxide (≥99.0%), other epoxides, and different side chain lengths analytical reagents were supplied by Aladdin Chemical Reagent Co. All purity of chemicals was the Analytical reagent. CO_2 was purchased from Beijing Analytical Instrument Factory with a purity of 99.99%, and all reagents were employed in this work without further purification.

1.2. Synthesis of DPzILs with different alkyl chain lengths

In order to synthesize dicationic pyrazolium ionic liquids, a cost-effective approach involves a one-step process. Different side chain lengths, including 1,2-Dibromoethane, 1,2-Dibromobutane, 1,2-Dibromohexane, 1,2-Dichloroethane, 1,2-Dichlorobutane, 1,2-Dichlorohexane, 1,2-Diiodoethane, 1,2-Diiodoebutane and 1,2-Diiodohexane (0.05 mol each), were mixed with 1-methyl pyrazole (0.05 mol) in 18 mL acetonitrile and stirred the above mixture for 1 hour at room temperature. Then the mixture is agitated at 80 °C for 48 hours under nitrogen protection. When the reaction was completed, the remaining solvent was evaporated using a rotary evaporator (EYELA, N-1300), and the resulting residue was subsequently washed with ethyl acetate (10 mL x 3) to remove impurities using a Benchtop High-Speed centrifuge (TG16-WS).

Finally, the obtained DPzIL was dried for 24 hours at 60 °C in a vacuum oven to produce pure DPzIL. These DPzILs with the alkyl chain lengths were named 2,2'-(hexane-1,6-dial)-bis(1-methylpyrazolium) diiodide ([DMPz-6]I_2), 2,2'-(butane-1,4-dial)-bis(1-methylpyrazolium) diiodide ([DMPz-4]I_2), 2,2'-(ethane-1,2-dial)-bis(1-methylpyrazolium) diiodide ([DMPz-2]I_2), 2,2'-(hexane-1,6-dial)-bis(1-methylpyrazolium) dibromide ([DMPz-6]Br_2), 2,2'-(butane-1,4-dial)-bis(1-methylpyrazolium) dibromide ([DMPz-4]Br_2), 2,2'-(ethane-1,2-dial)-bis(1-methylpyrazolium) dibromide ([DMPz-2]Br_2), 2,2'-(hexane-1,6-dial)-bis(1-methylpyrazolium) dichloride ([DMPz-6]Cl_2), and 2,2'-(butane-1,4-dial)-bis(1-methylpyrazolium) dichloride ([DMPz-4]Cl_2).

1.3. Cycloaddition reaction of CO_2 with epoxides into cyclic carbonates

The cycloaddition reaction was performed in a 25 mL high-pressure microreactor (reaction kettle). Epoxide (0.02 mol) and a certain amount of catalyst (30–500 mg) is added to the reaction kettle. Increase the reactor pressure to half the intended CO_2 pressure (1–20 bar) just at room temperature and start heating the reactor. Then, when the reactor temperature reaches the desired temperature (40–120 °C) for 1–15 h, the pressure is increased to the final expected CO_2, and the valve is kept open to ensure that the reactor pressure does not change during the whole reaction. After the reaction was finished, the reactor was cooled to room temperature, and the extra CO_2 was gradually released. Products are separated from the mixed solution by a benchtop high-Speed Centrifuge within 4 minutes at 8000 rotation speeds (TG16-WS) and analyzed by gas chromatography (GC). The catalyst is then dried in a vacuum and used for the next recycling.

1.4. Characterization techniques of DPzIL catalysts

The catalysts were subjected to analysis of ^{1}H and ^{13}C NMR using a Bruker AVANCE III 600 MHz spectrometer, with deuterated reagents in the form of DMSO-d_6 and tetramethylsilane (TMS) as an internal standard. The molecular weights of the catalysts were ascertained through the utilization of Electrospray ionization-mass spectrometry of impact HD (Bruker, Germany) in the presence of acetonitrile as the solvent. Both positive and negative ion modes were utilized for conducting the ESI-MS analysis. The chemical composition of catalysts was analyzed using the Fourier transform infrared spectrum of the Thermo Nicolet 380 spectrometer. KBr was employed as a reference to verify the presence of corresponding groups. A resolution of 4 cm^{-1} and 64 transmittance scans was used to cover the spectral range of 4000 to 400 cm^{-1}. The Vario EL Cube elemental analyzer (CHNS Mode) was utilized to examine the elemental compositions (C/H/N). The thermal decomposition temperature of the catalysts was detected through thermogravimetric analysis using DTG-60H under a nitrogen atmosphere. The temperature programming was set at 10 °C min-1 to achieve 600 °C. The study employed gas chromatography (GC) to conduct analyses, utilizing a GC-7890A instrument manufactured by Agilent Technologies, equipped with a flame ionization detector. The GC-mass spectrometry (GCMS-QP2020) technique is employed to qualitatively detect reaction product components and identify associated product chemical structures.

1.5. Computational details

Density functional theory (DFT) calculations performed by the Gaussian 09 program package [1] were employed to investigate the interactions of PO and catalysts. The geometries for all structures were optimized using the B3LYP functional method combined with 6-311++G(d,p) basis set (B3LYP/6-311++G(d,p)). Vibration frequency calculations were performed to confirm the stationary points, where no imaginary frequencies were obtained. Then, Noncovalent interactions (NCI)) were further analyzed for noncovalent interactions [2, 3] using Multiwfn [4] and visual molecular dynamics (VMD).[5] All the reported bond lengths and angles are conveyed in angstroms (Å) and degrees (◦), respectively.

2. NMR spectra of DPzILs catalysts

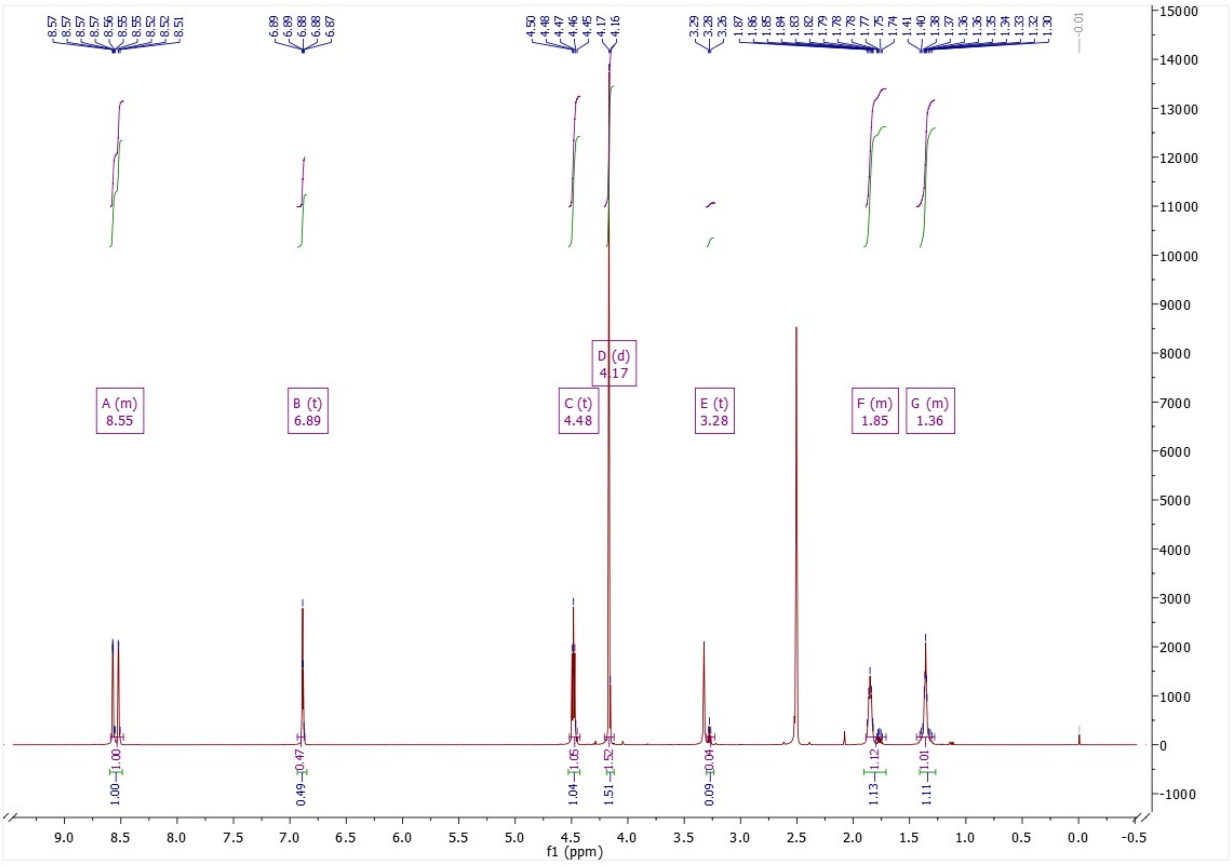

Figure S1. ^{1}H NMR spectrum of [DMPz-6]I_2

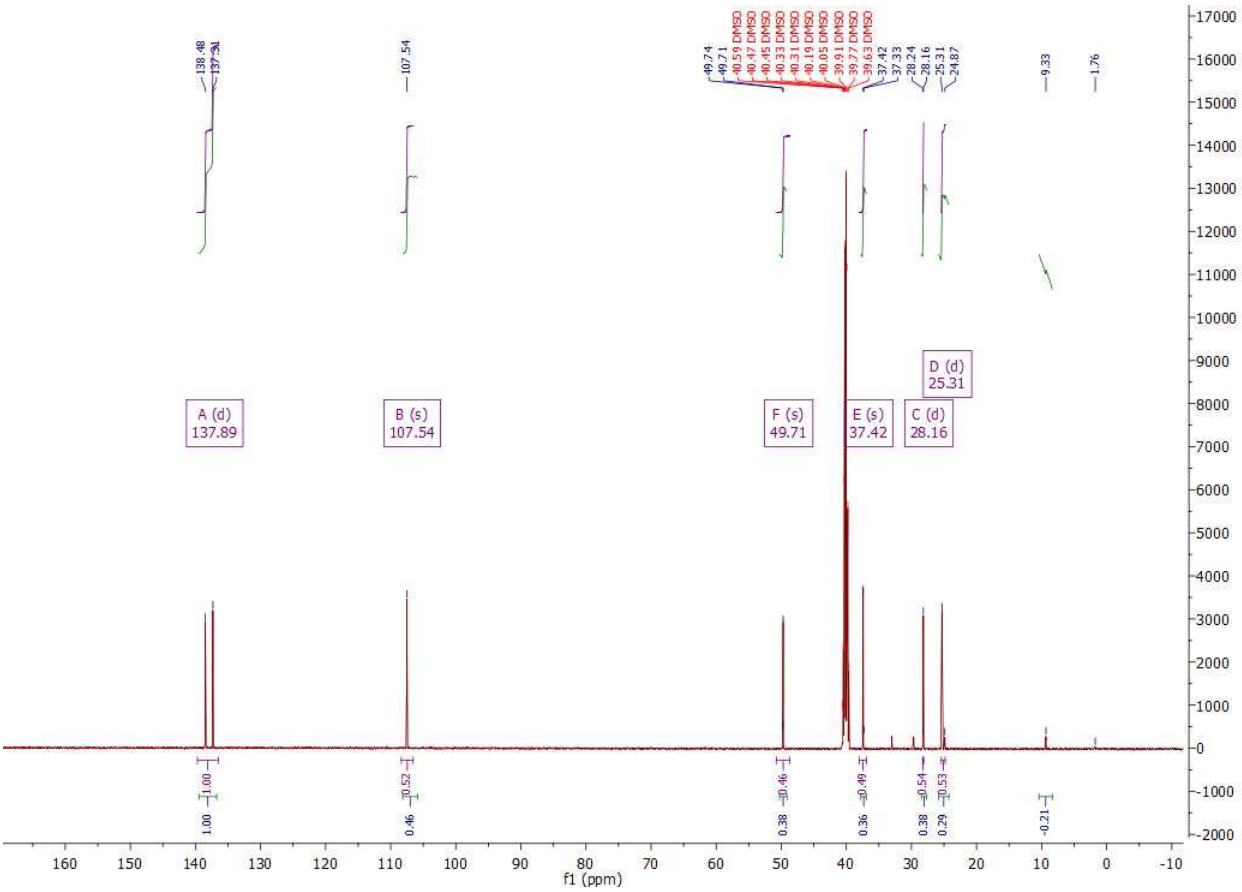

Figure S2. ^{13}C NMR spectrum of $[DMPz\text{-}6]I_2$

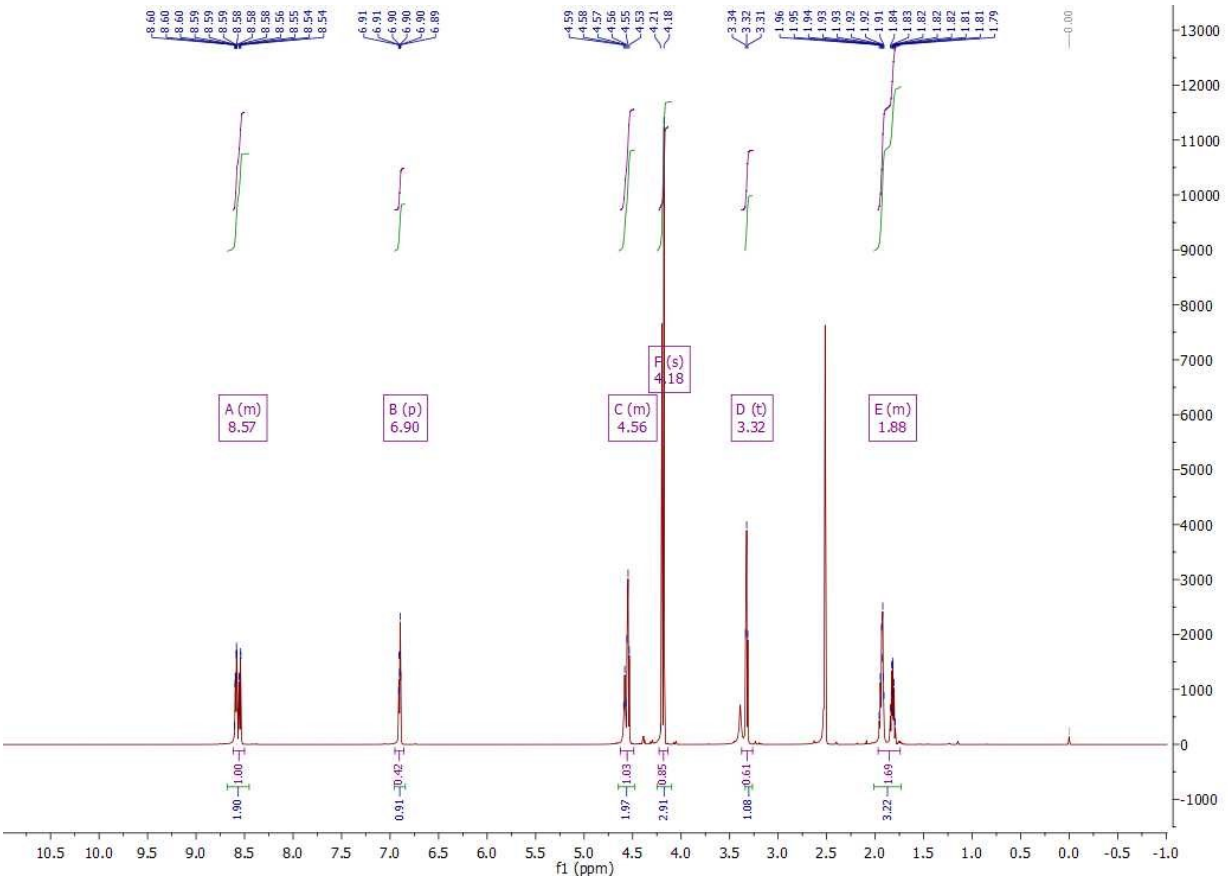

Figure S3. ^{1}H NMR spectrum of [DMPz-4]I_2

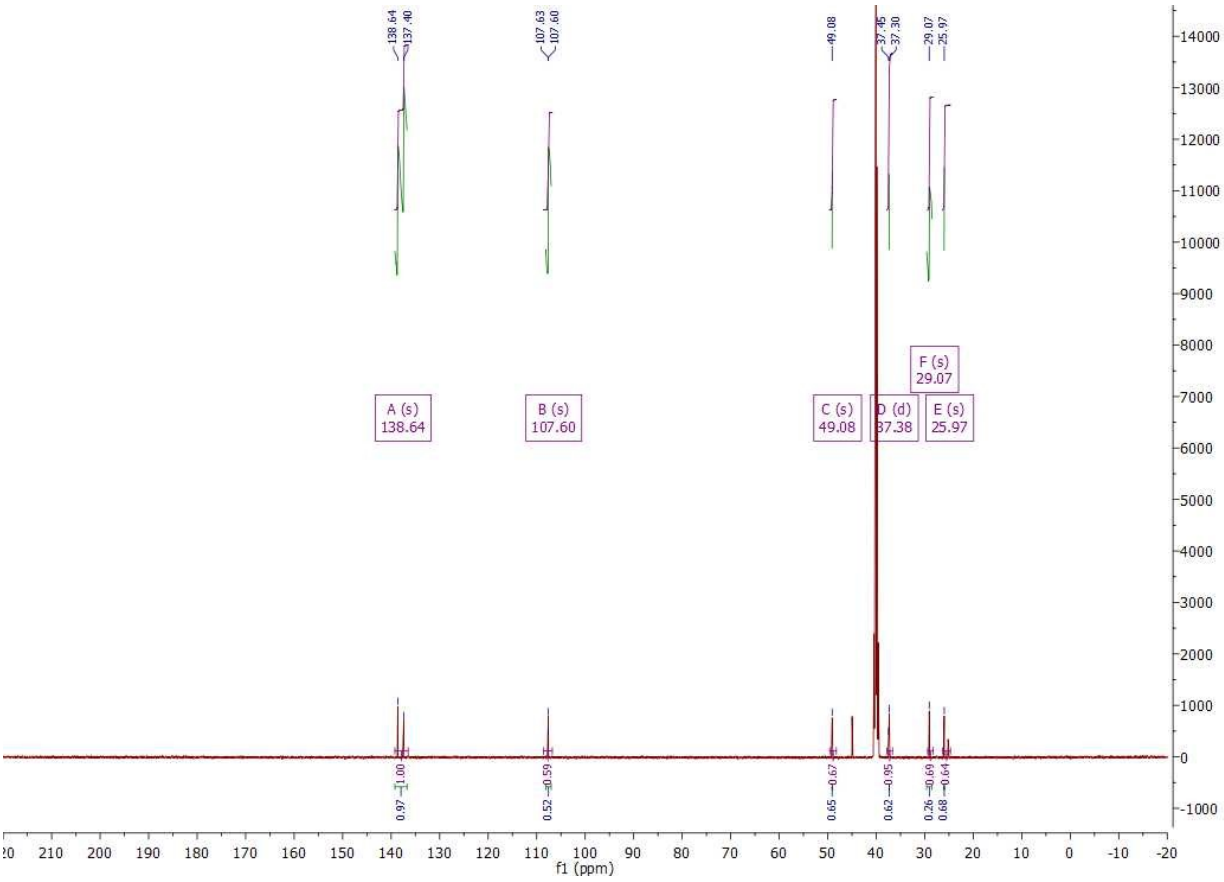

Figure S4. ^{13}C NMR spectrum of [DMPz-4]I_2

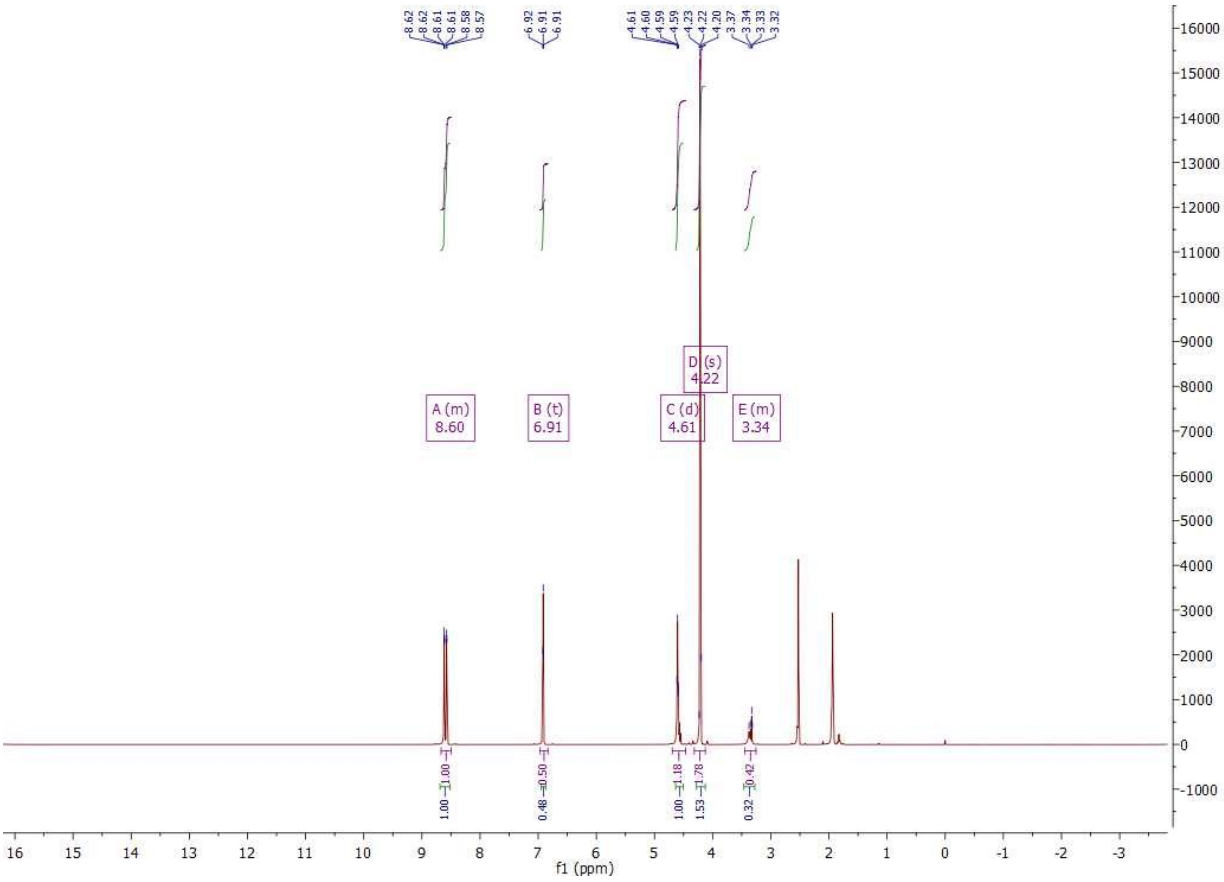

Figure S5. ^{13}H NMR spectrum of [DMPz-2]I_2

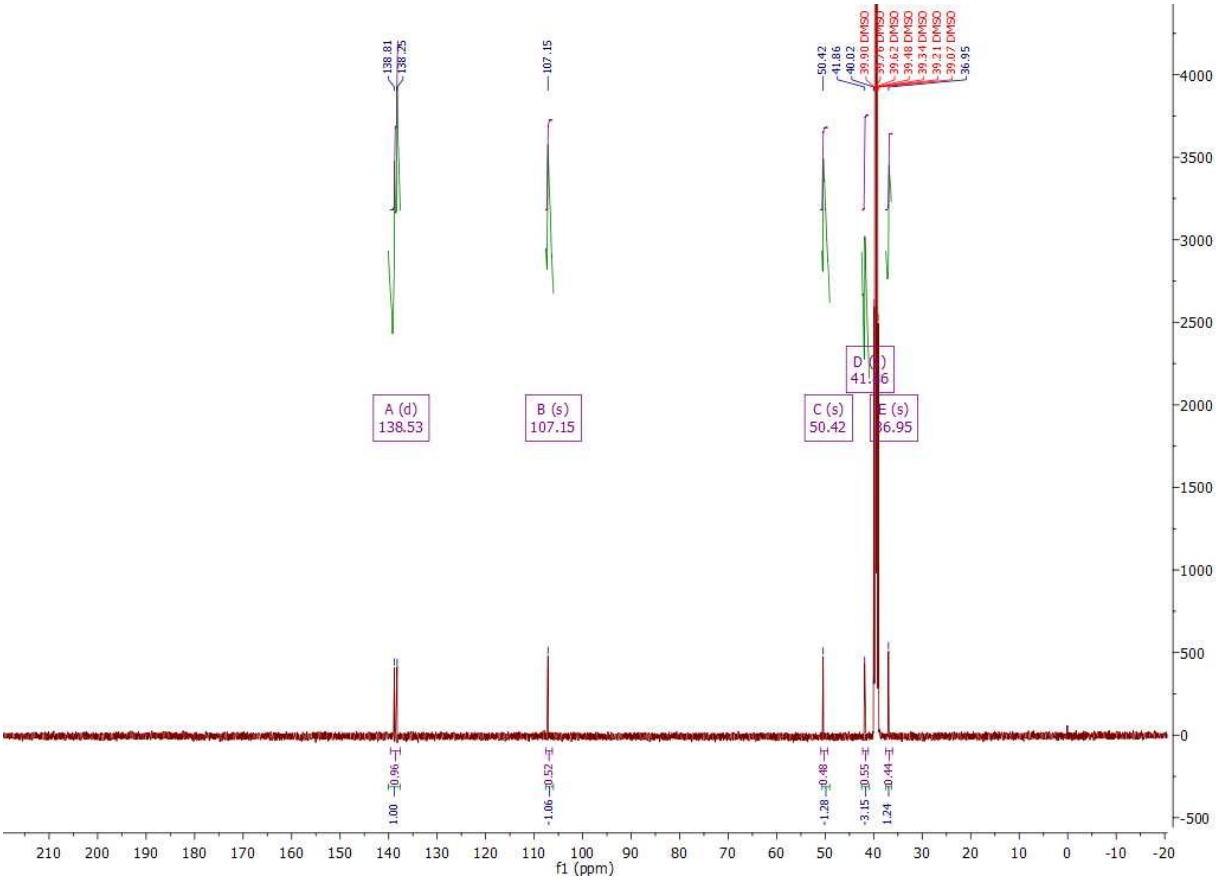

Figure S6. ^{13}C NMR spectrum of [DMPz-2]I_2

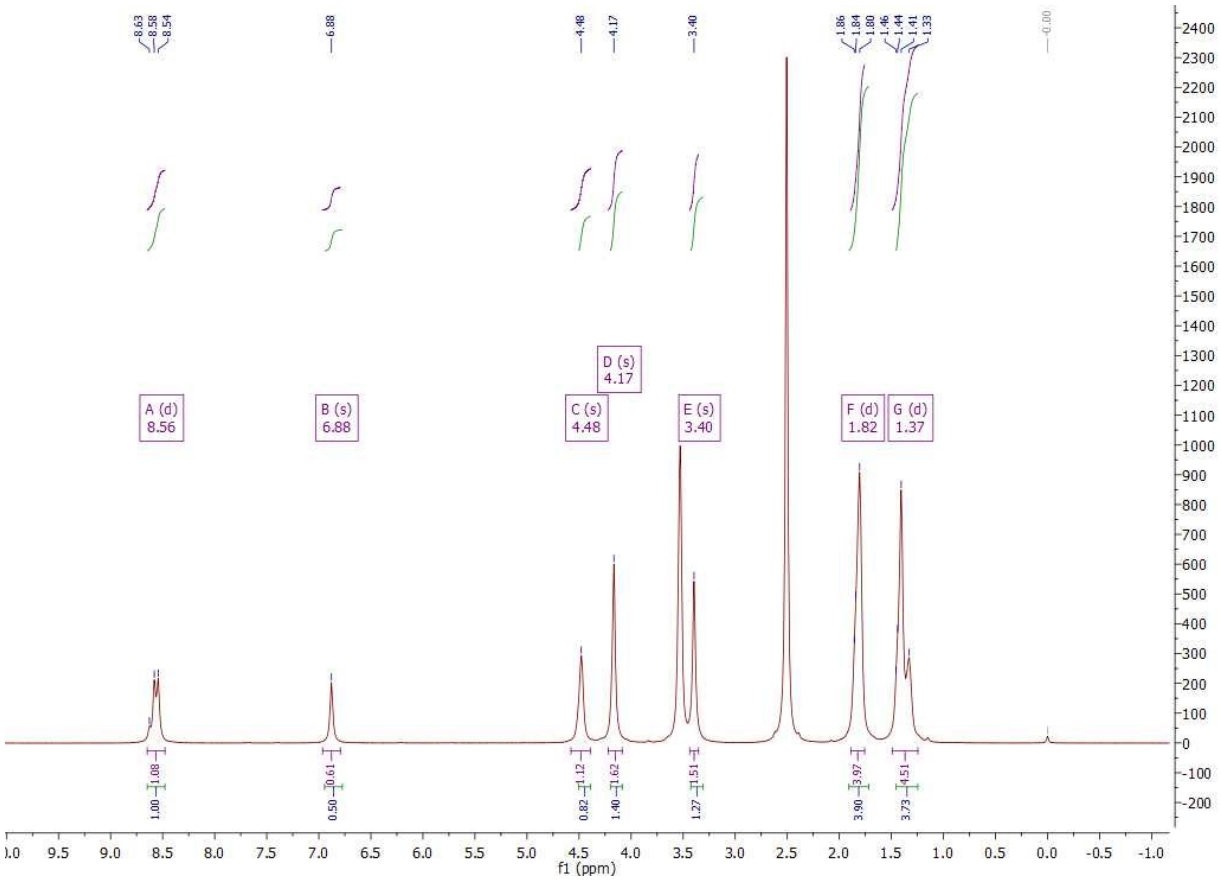

Figure S7. ^{1}H NMR spectrum of [DMPz-6]Br_2

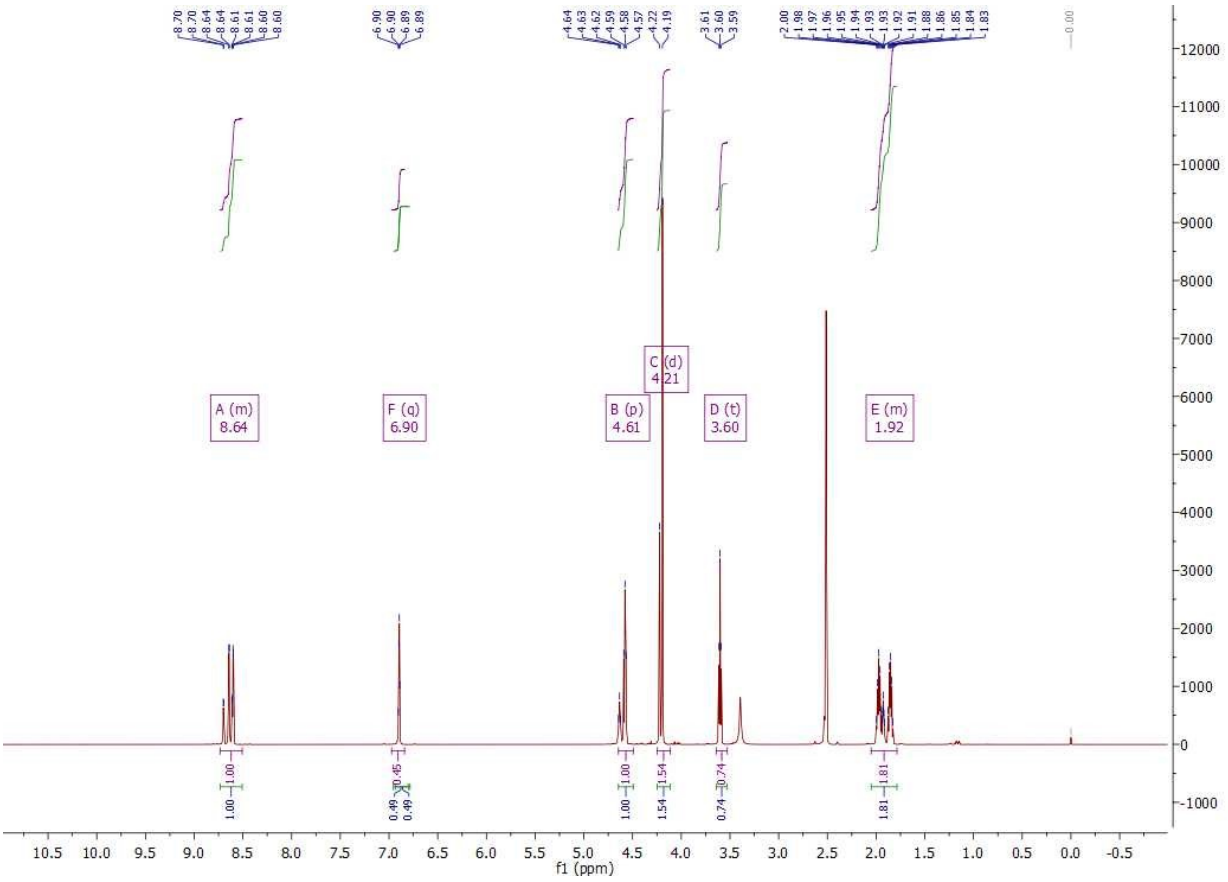

Figure S8. ^{13}C NMR spectrum of [DMPz-6]Br_2

Figure S9. ^{1}H NMR spectrum of [DMPz-4]Br_2

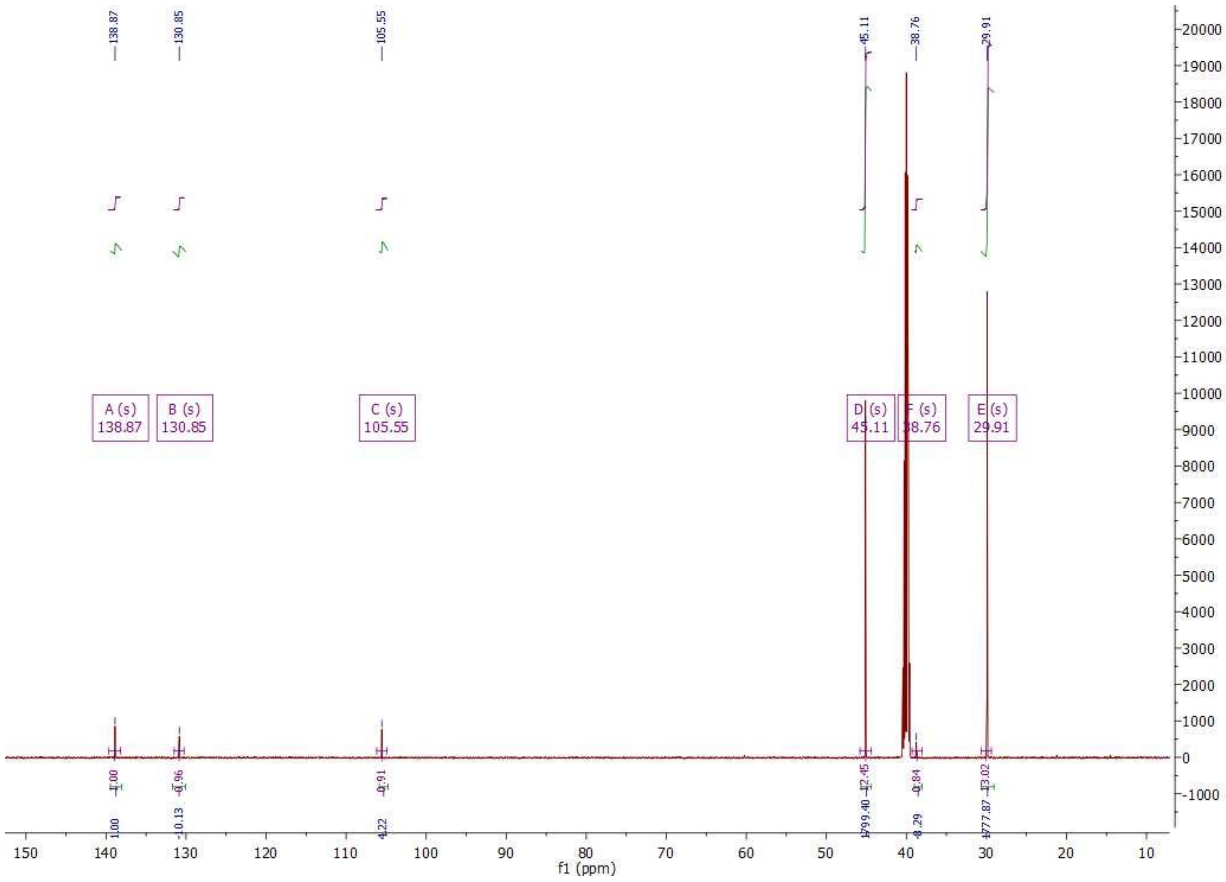

Figure S10. ^{13}C NMR spectrum of [DMPz-4]Br_2

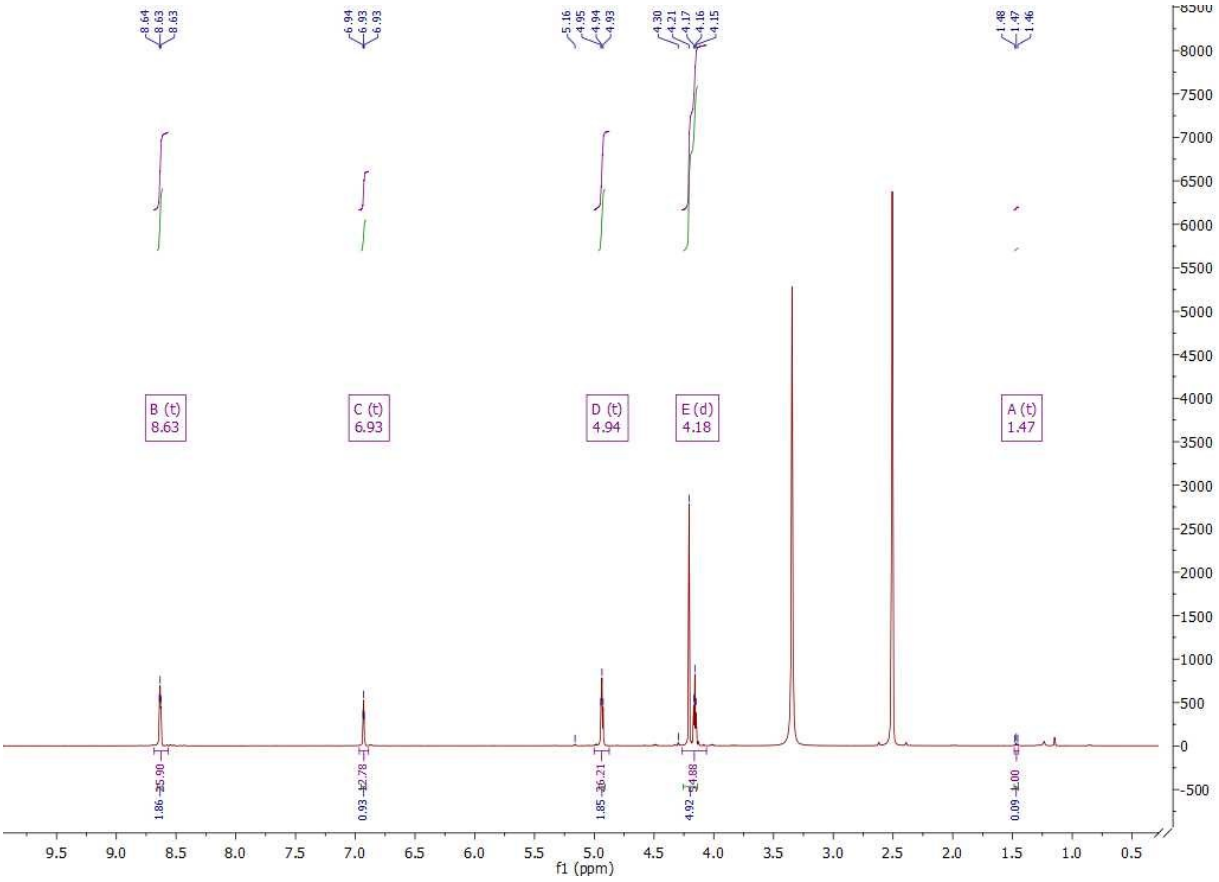

Figure S11. ^{1}H NMR spectrum of [DMPz-2]Br_2

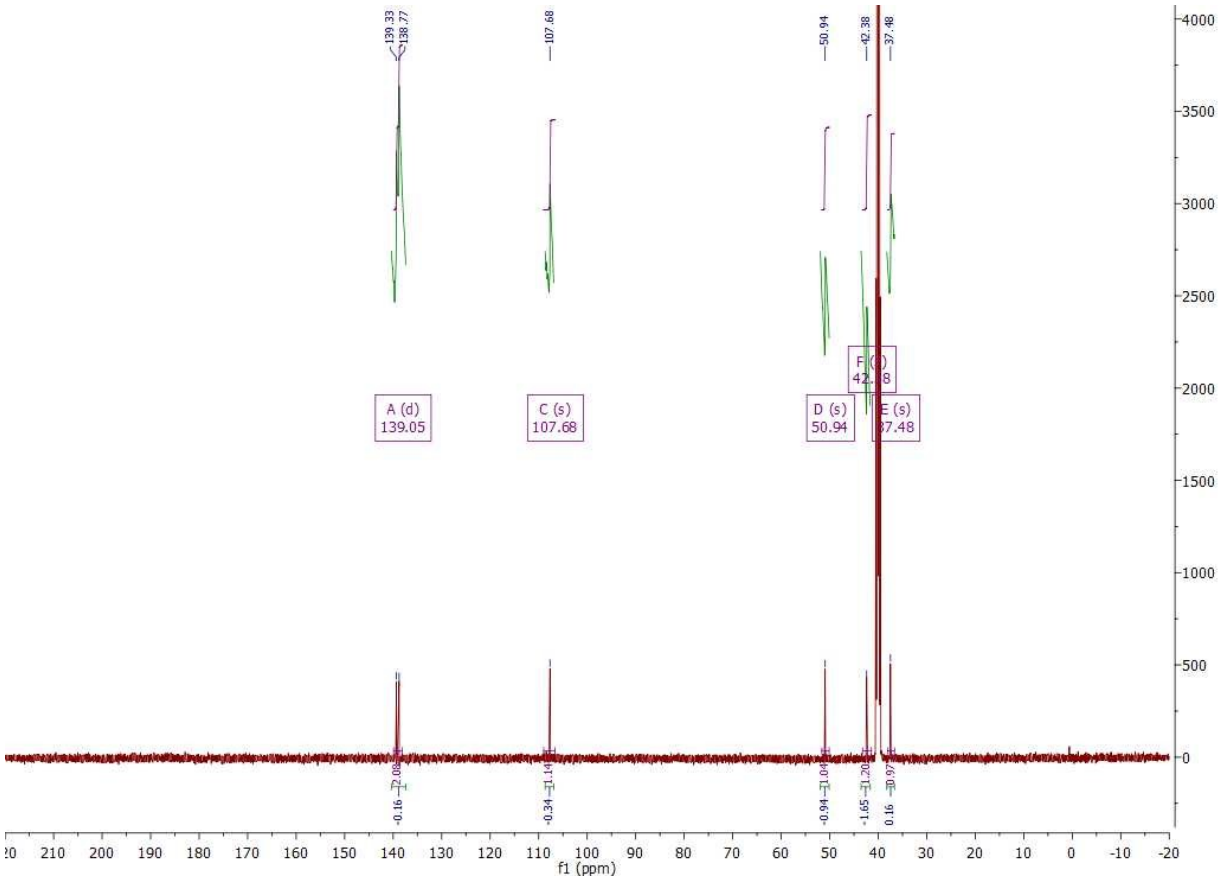

Figure S12. ^{13}C NMR spectrum of [DMPz-2]Br_2

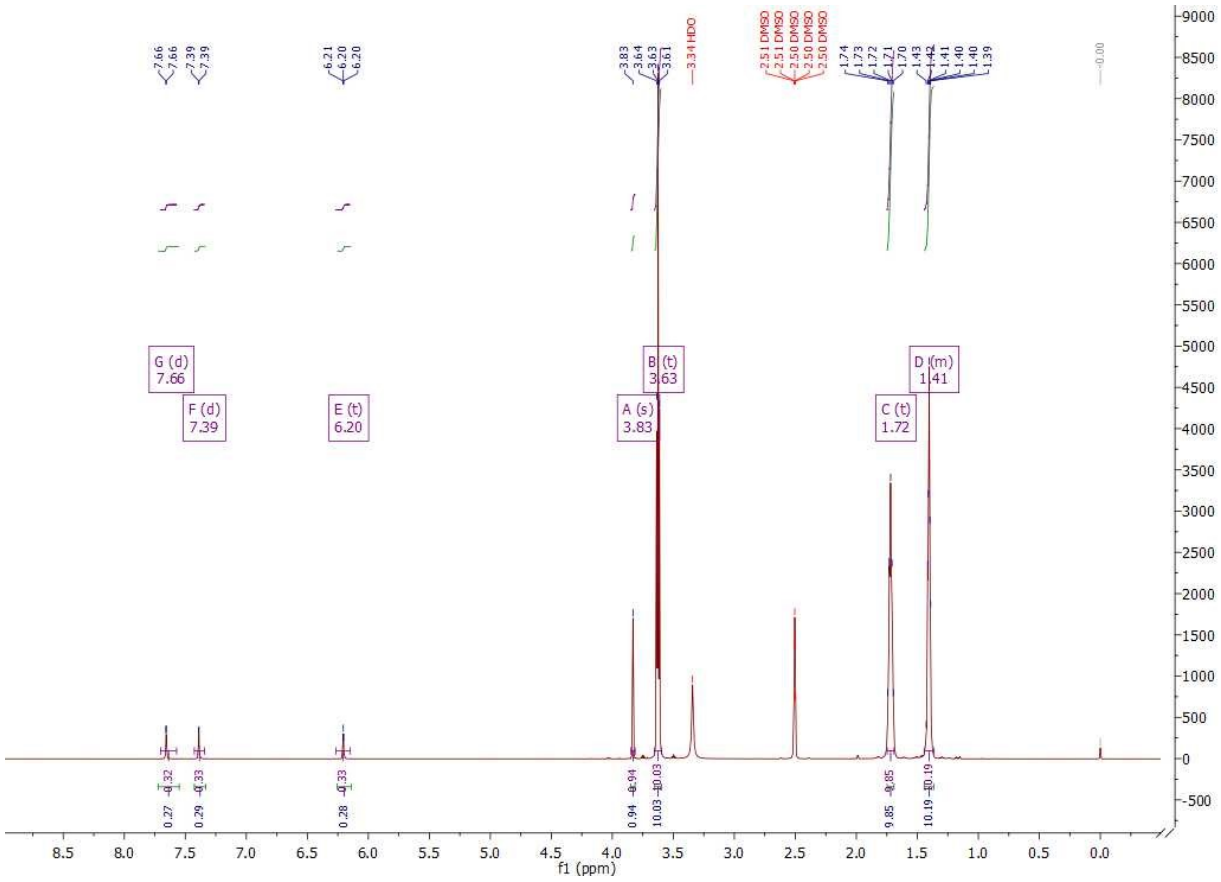

Figure S13. ^{1}H NMR spectrum of [DMPz-6]Cl_2

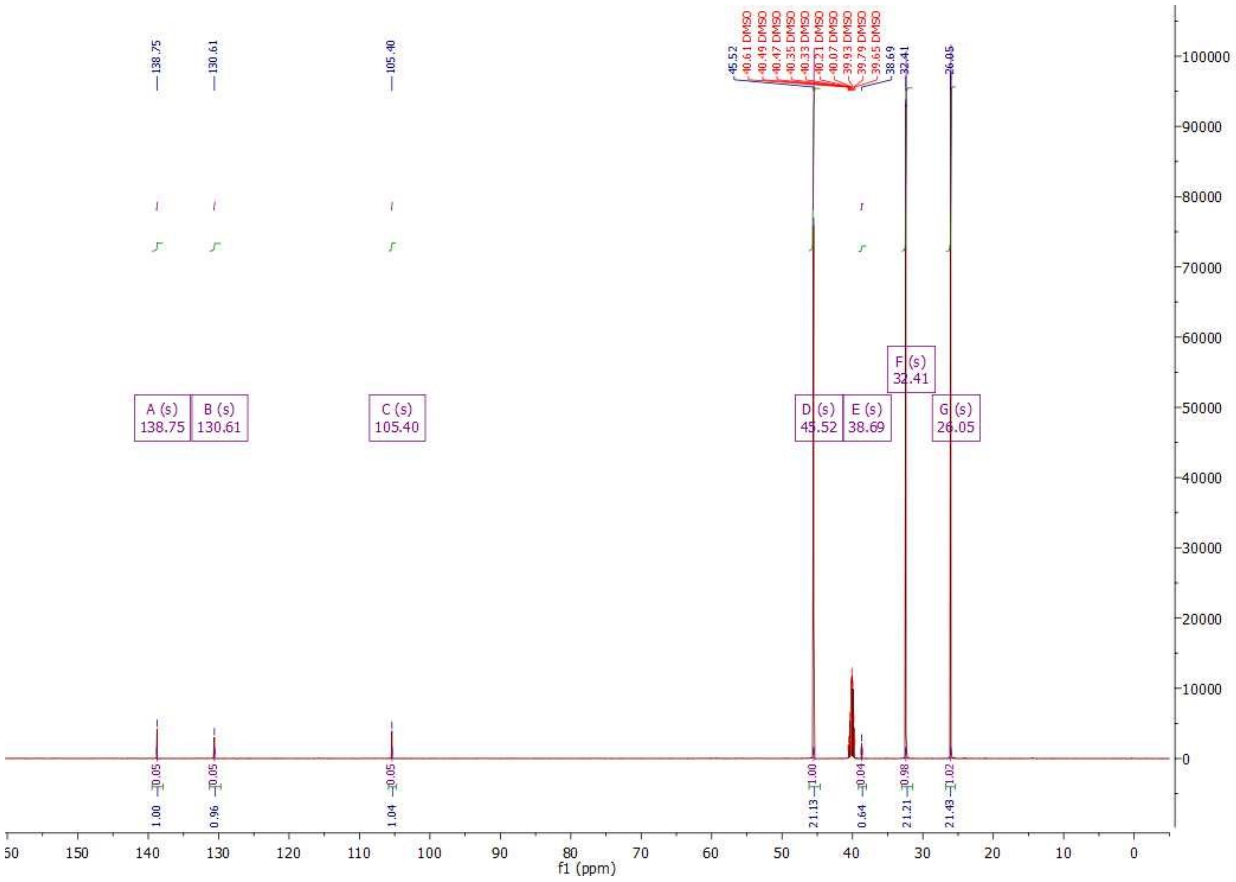

Figure S14. ^{13}C NMR spectrum of [DMPz-4]Cl_2

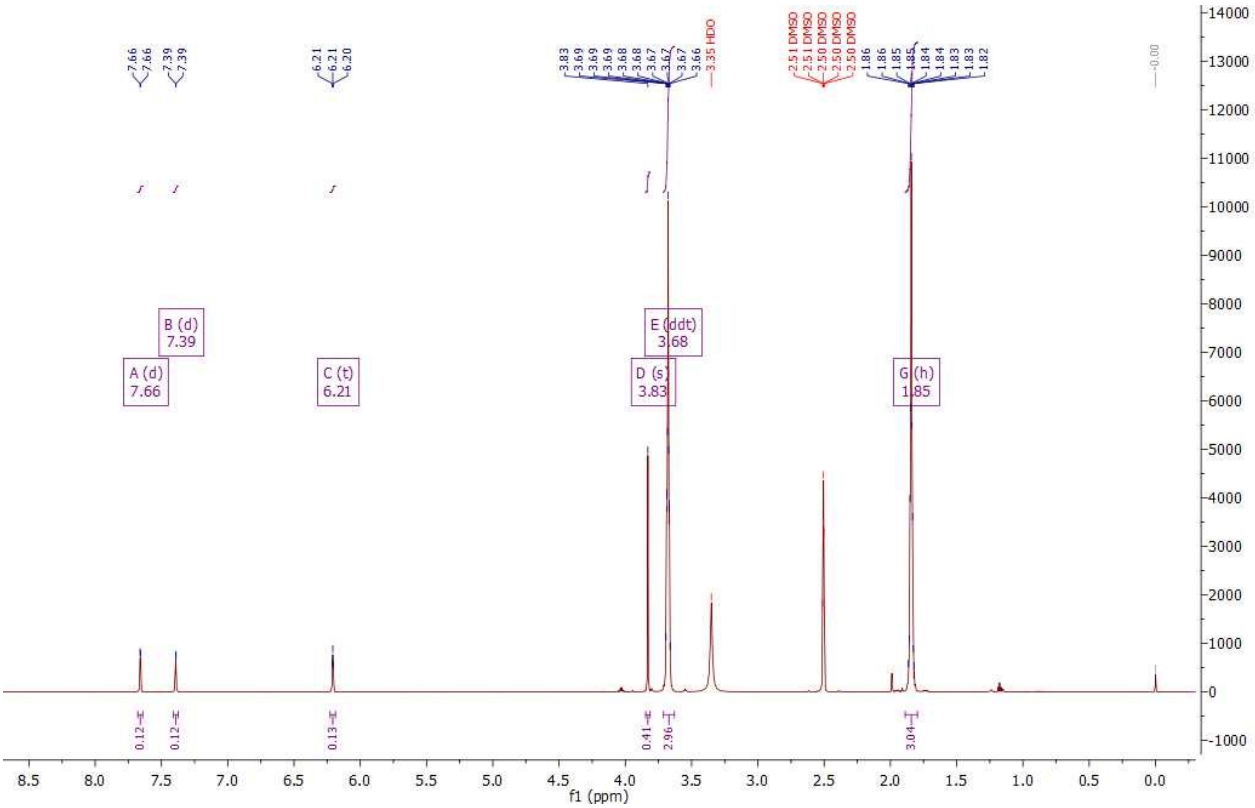

Figure S15. ^{1}H NMR spectrum of $[DMPz\text{-}4]Cl_2$

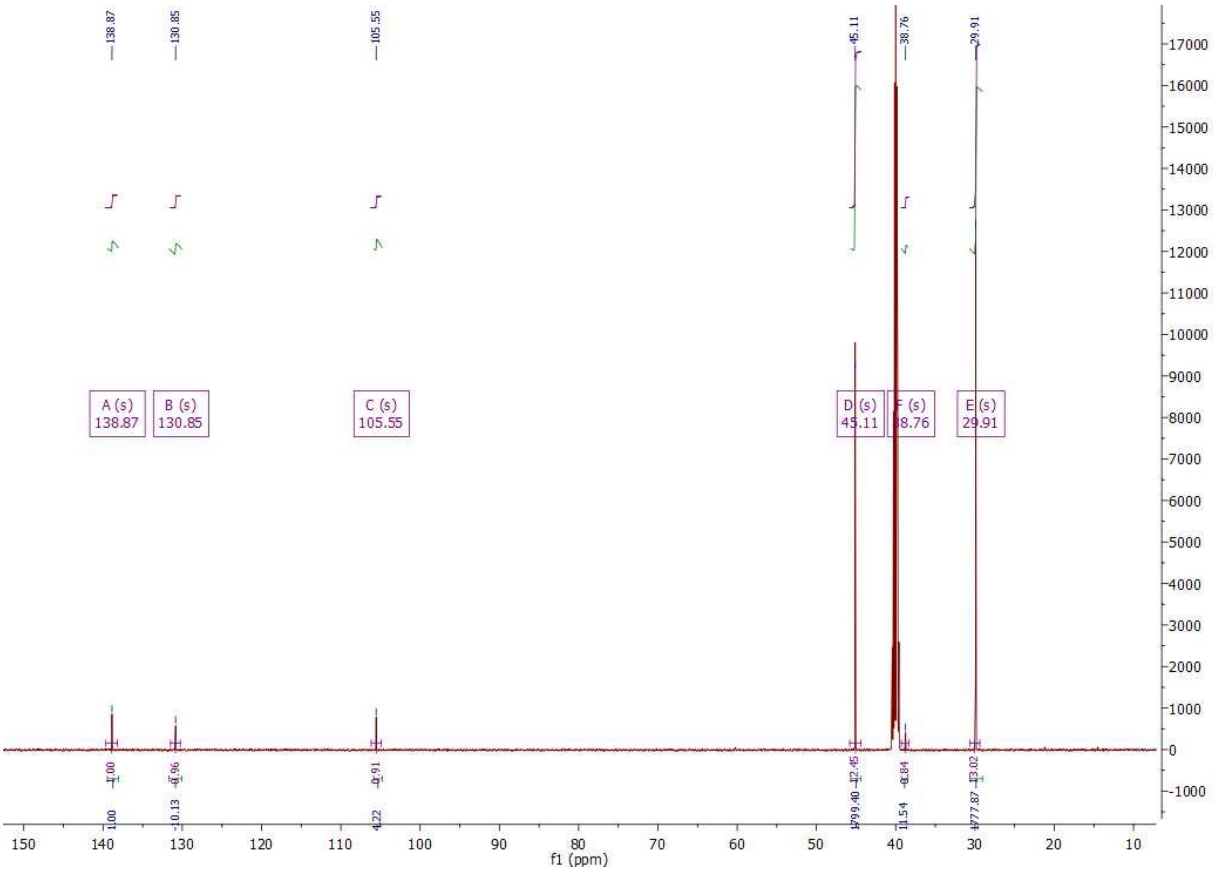

Figure S16. ^{13}C NMR spectrum of $[DMPz\text{-}4]Cl_2$

3. ESI-MS spectra of DPzILs catalysts

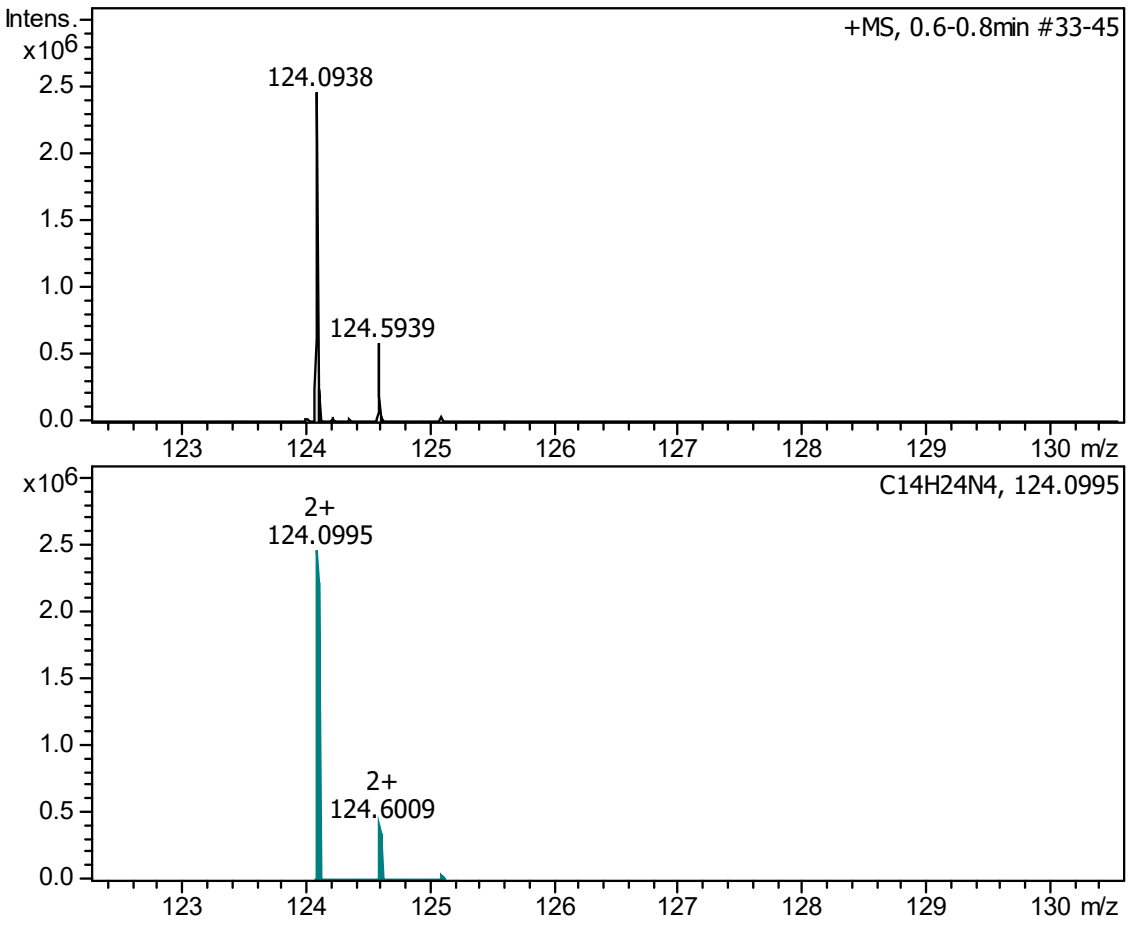

Figure S17. [DMPz-6]I_2-Positive mode, $[C_7H_{12}N_2]^{2+}$:

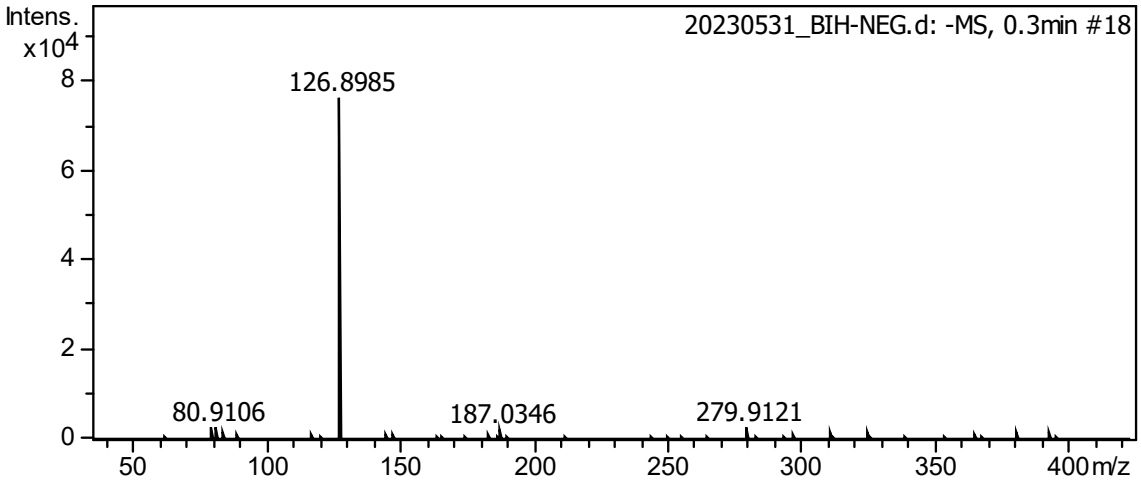

Figure S18. [DMPz-6]I_2-Negative mode, $[I^-]$:

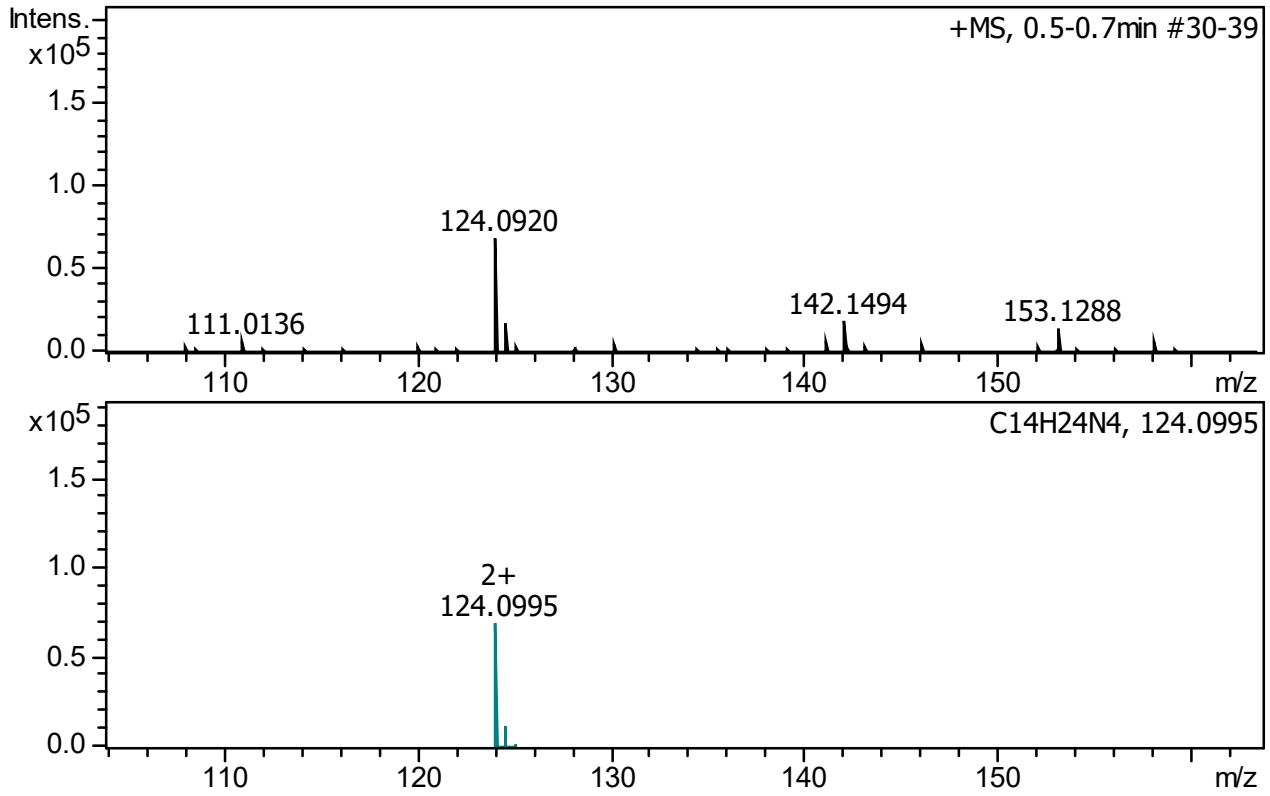

Figure S19. [DMPz-6]Br_2-Positive mode, $[C_7H_{12}N_2]^{2+}$:

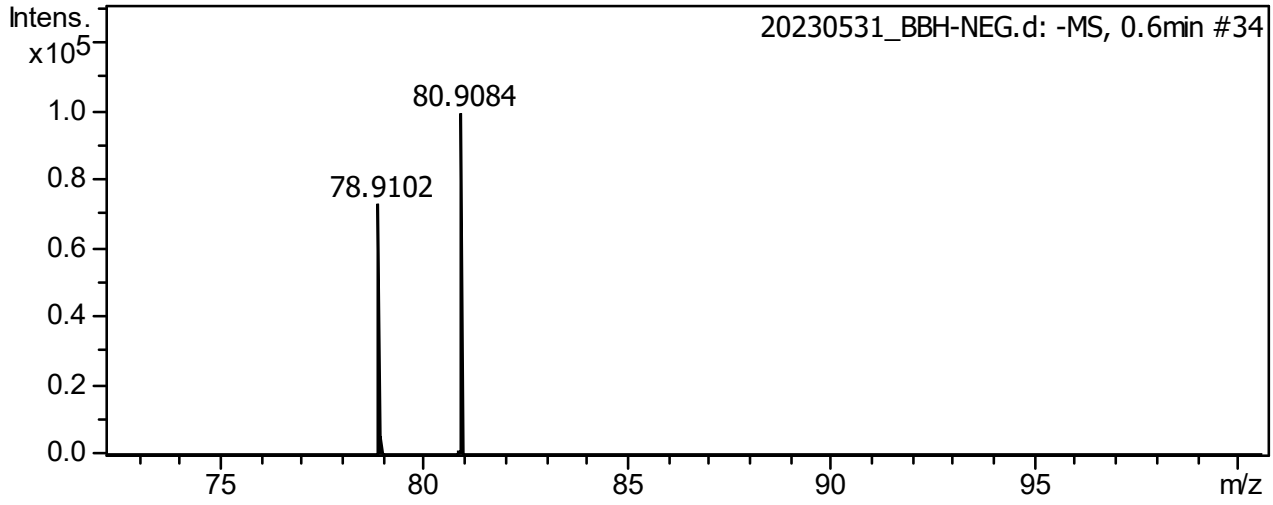

Figure S20. [DMPz-6]Br_2-Negative mode, $[Br^-]$.

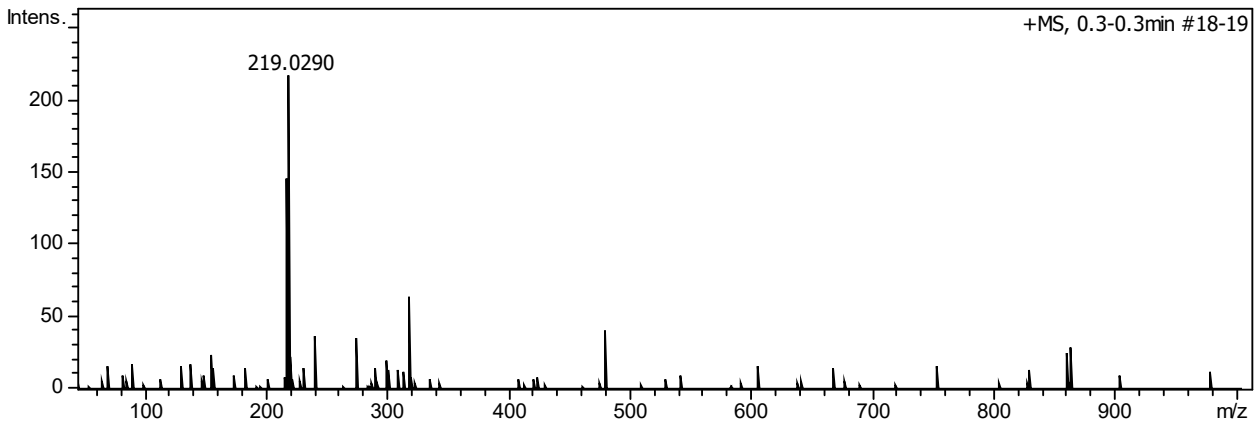

Figure S21. [DMPz-4]I_2-Positive mode, $[C_{12}H_{20}N_4]^+$.

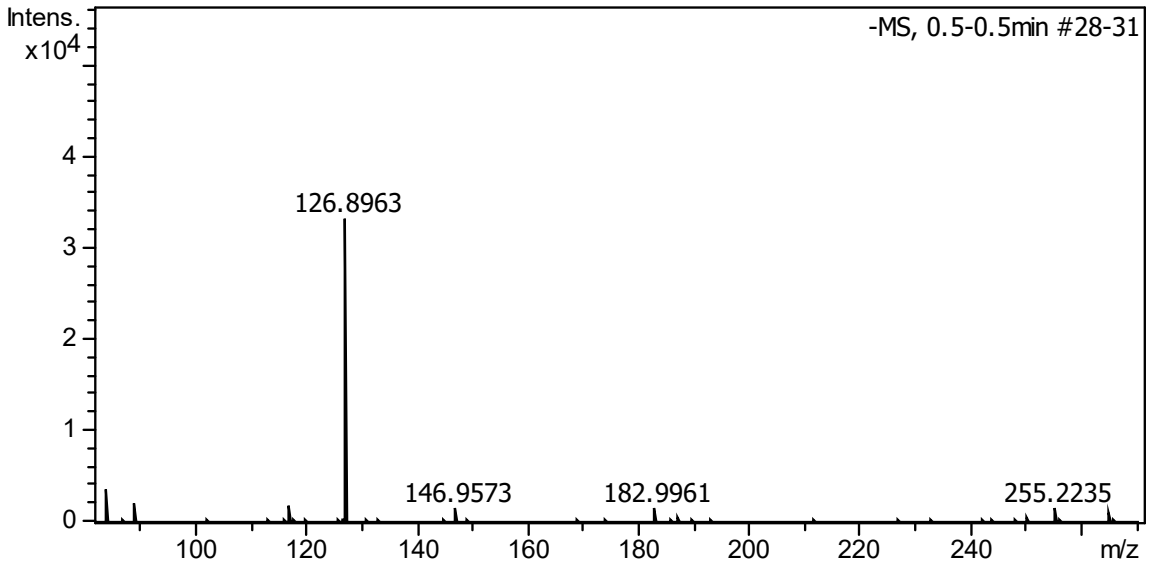

Figure S22. [DMPz-4]I_2-Negative mode, $[I^-]$.

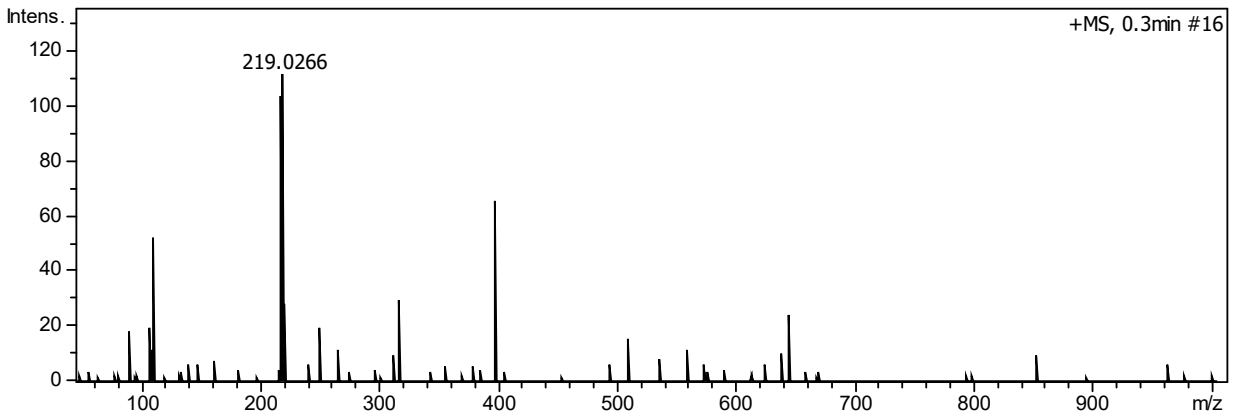

Figure S23. [DMPz-4]Br_2-Positive mode, $[C_{12}H_{20}N_4]^+$:

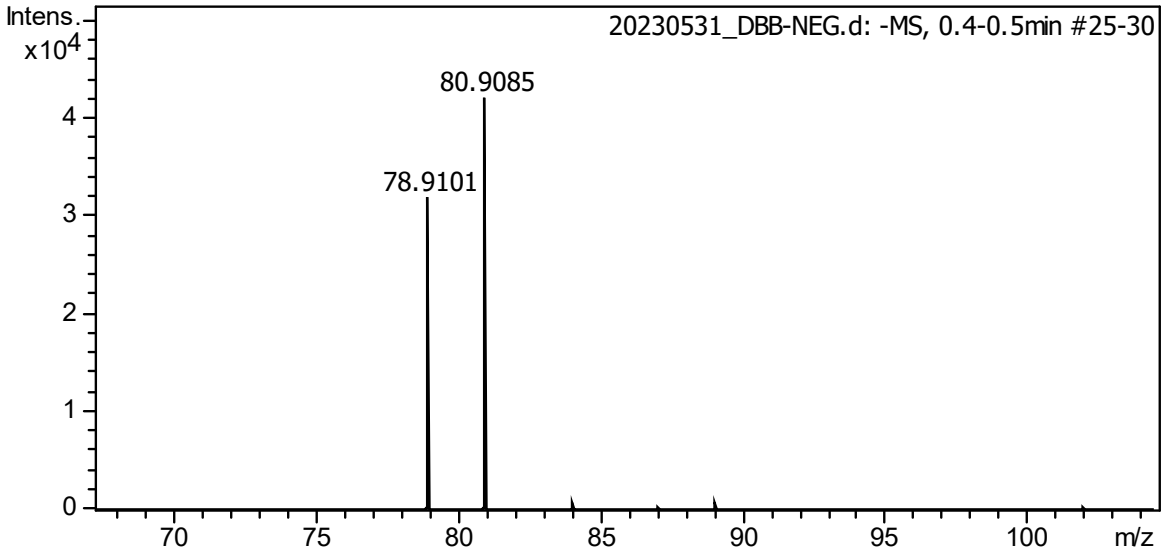

Figure S24. [DMPz-4]Br_2-Negative mode, $[Br^-]$.

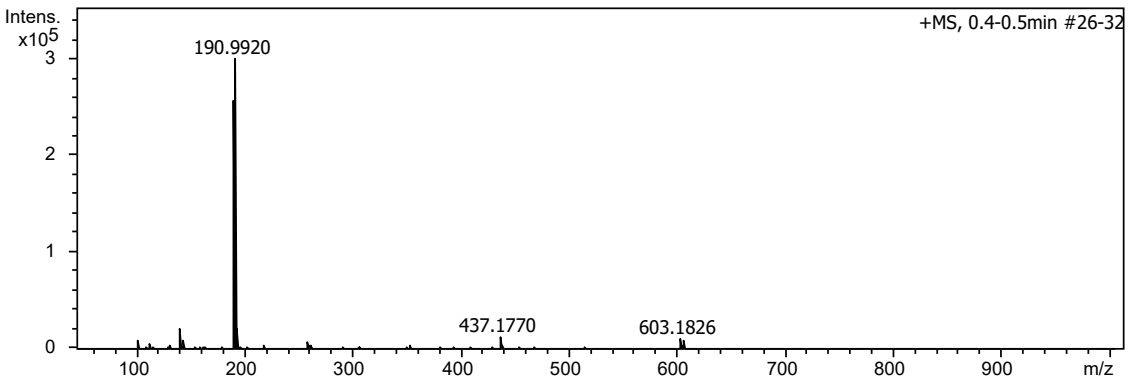

Figure S25. [DMPz-2]Br_2-Positive mode, $[C_{10}H_{16}N_4]^+$.

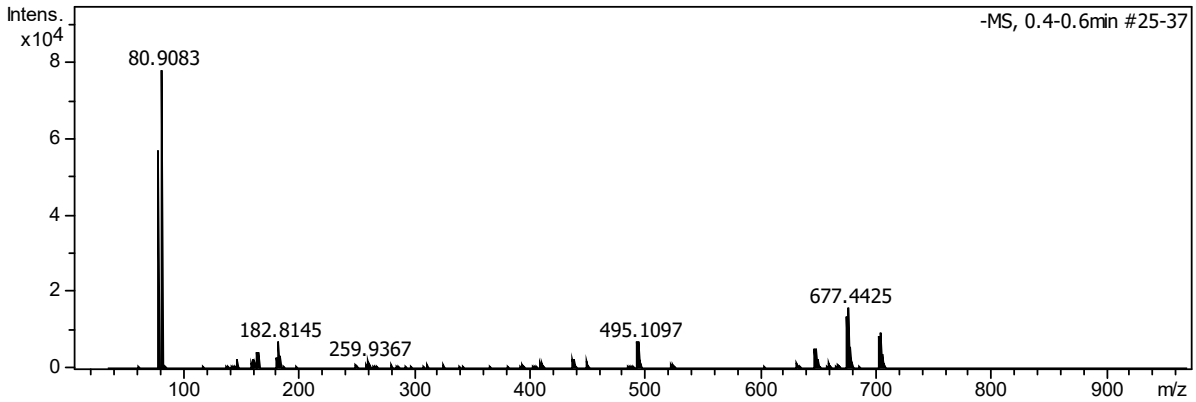

Figure S26. [DMPz-2]Br_2-Negative mode, $[Br^-]$.

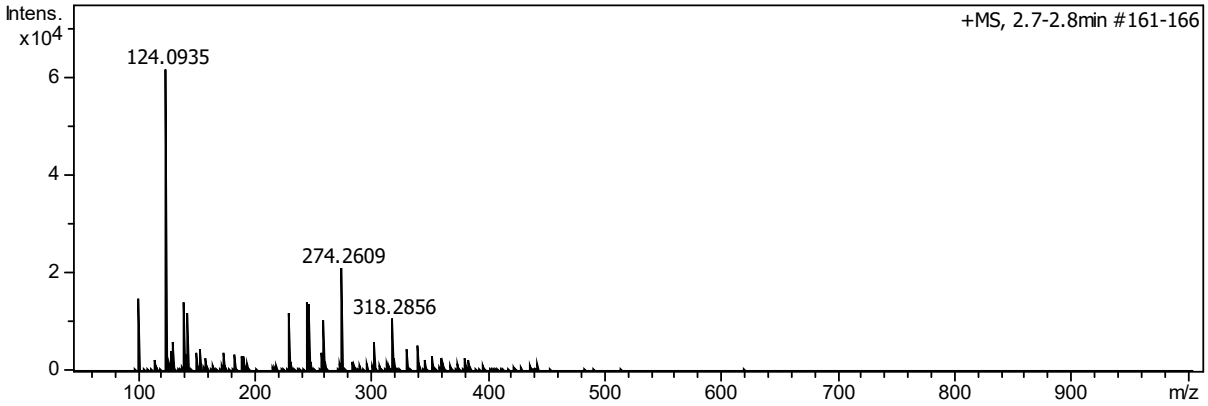

Figure S27. [DMPz-6]Cl_2-Positive mode, $[C_7H_{12}N_2]^{2+}$.

4. TGA curves of DPzILs catalysts

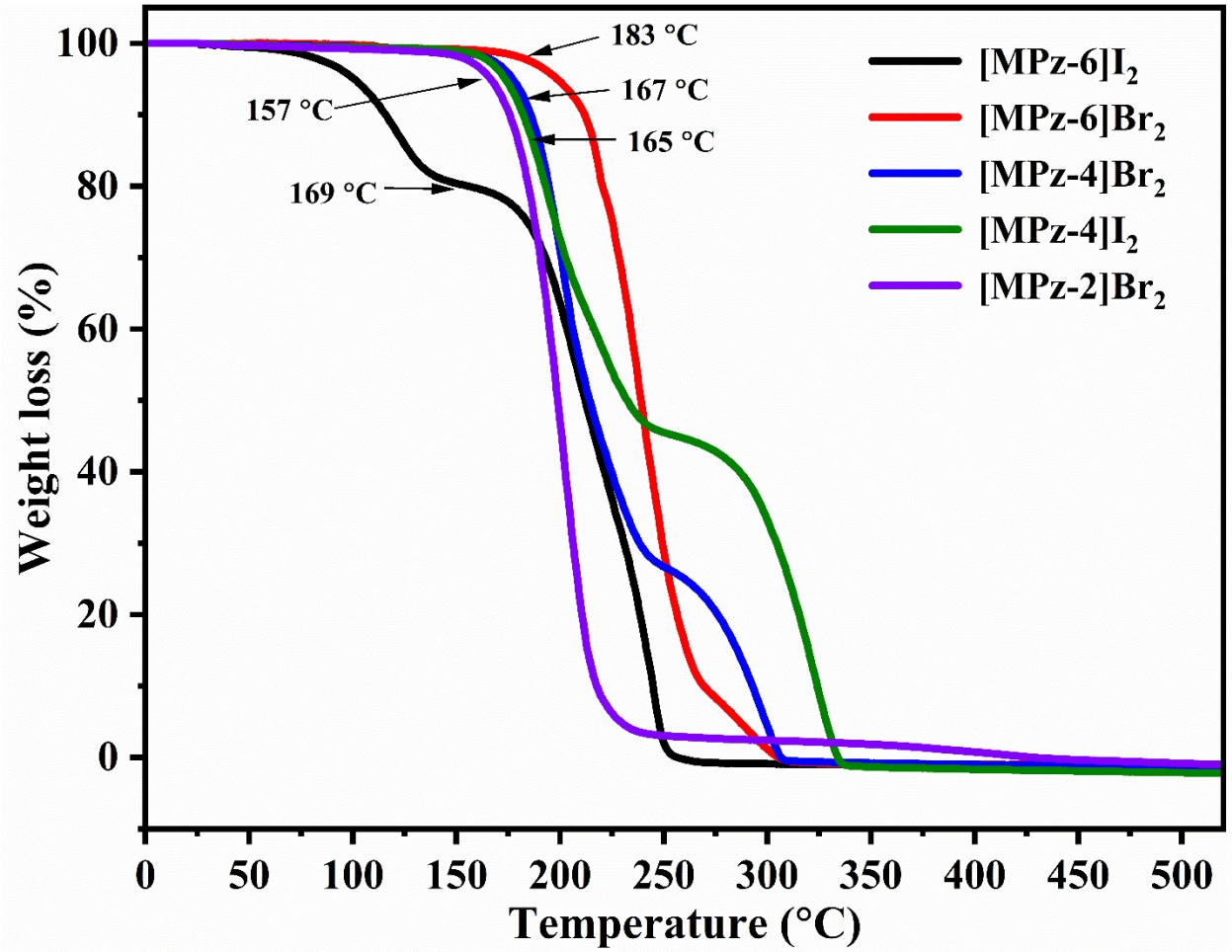

Figure S28. TGA curves for five selected DPzILs

5. FTIR spectrum of fresh and reused [DMPz-6]I_2

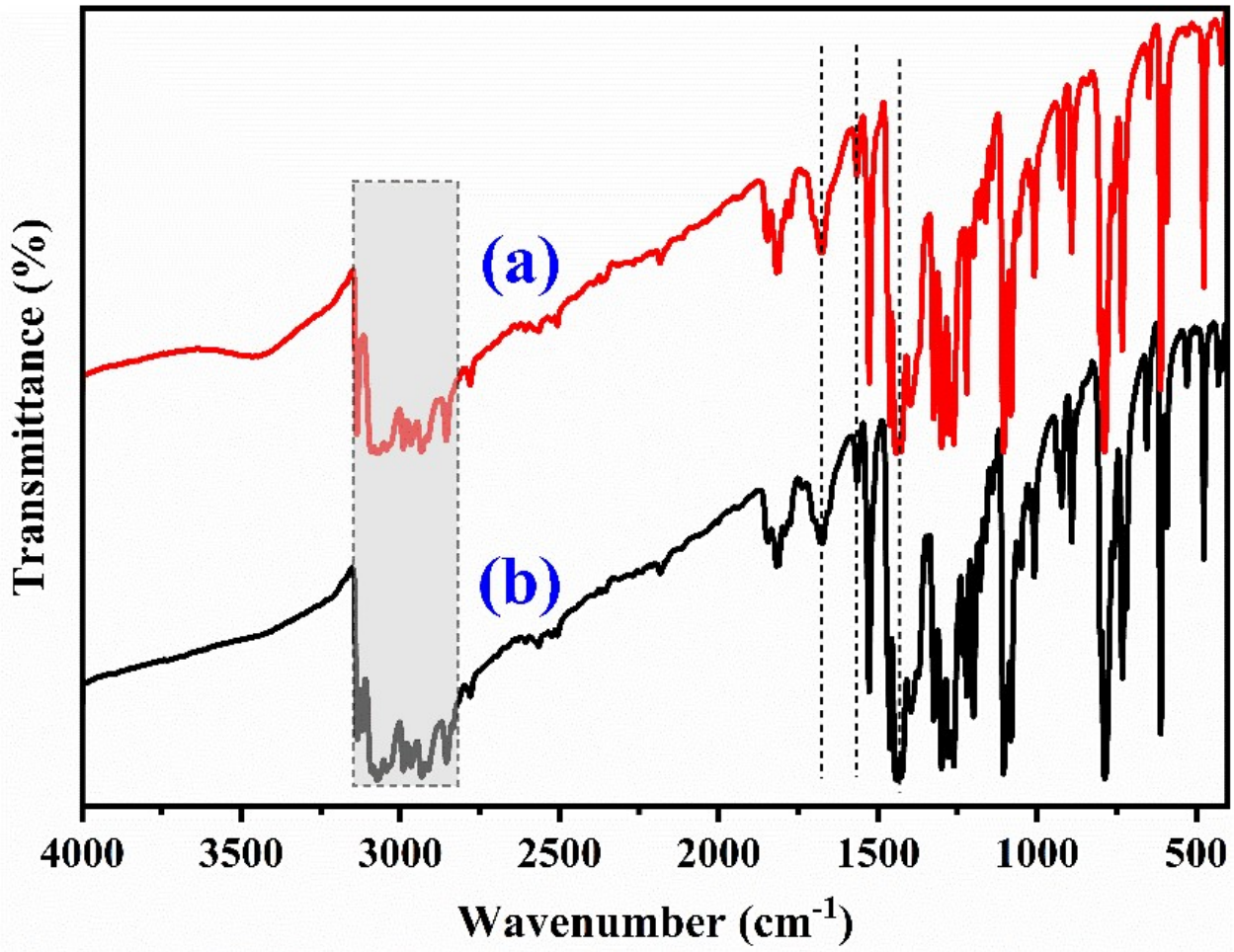

Figure S29. FT-IR spectra of fresh and 5 times reused [DMPz-6]I_2

6. Optimized geometries of DPzILs and PO

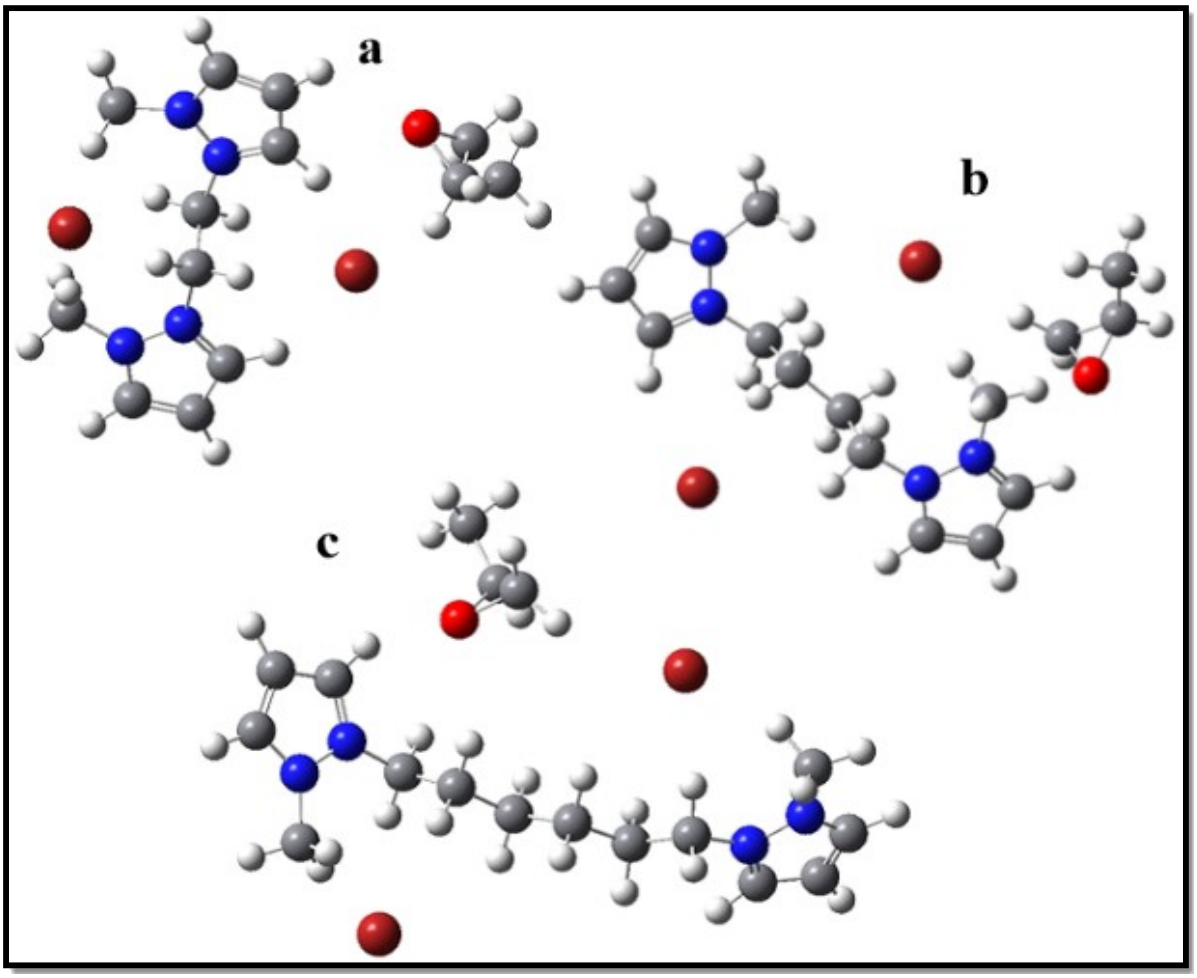

Figure S30. Optimized geometries for DPzILs and PO computed at the B3LYP/6-311++G (d,p) set level: (a) [DMPz-2]Br_2-PO (b) [DMPz-4]Br_2-PO, (c) [DMPz-6]Br_2-PO.

Table S1. C/N/H Elemental analysis of synthesized dicationic pyrazolium ILs

Catalyst	C [wt.%]	N [wt.%]	C/N molar ratio	C/N theoretical molar ratio
[DMPz-6]I_2	68.43	23.43	3.41	3.5
[DMPz-6]Br_2	66.86	21.61	3.60	3.5
[DMPz-4]I_2	30.17	11.27	3.12	3.0
[DMPz-4]Br_2	35.35	12.64	3.02	3.0
[DMPz-2]I_2	22.02	10.33	2.49	2.5
[DMPz-2]Br_2	26.88	10.46	2.48	2.5

References

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