Carboxylic Acid Functionalized *ortho*-Linked Oxacalix[2]benzene[2] pyrazine: Synthesis, Structure, Hydrogen Bond and Metal Directed Self-Assembly

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Crystal Structure and New Compound's Characterization

Comments of Structure of **9:**

For the crystal structure compound **9**, high R factors are associated with the crystal quality. During the refinement, restraints OMIT, DFIX, ISOR, EADP, EXYZ were used. Due to the highly disordered nature of the ligands **3'** in the structure of **9**, some of the hydrogen atoms in ligands **3'** are not located/ fixed, which are also not included in the formula.

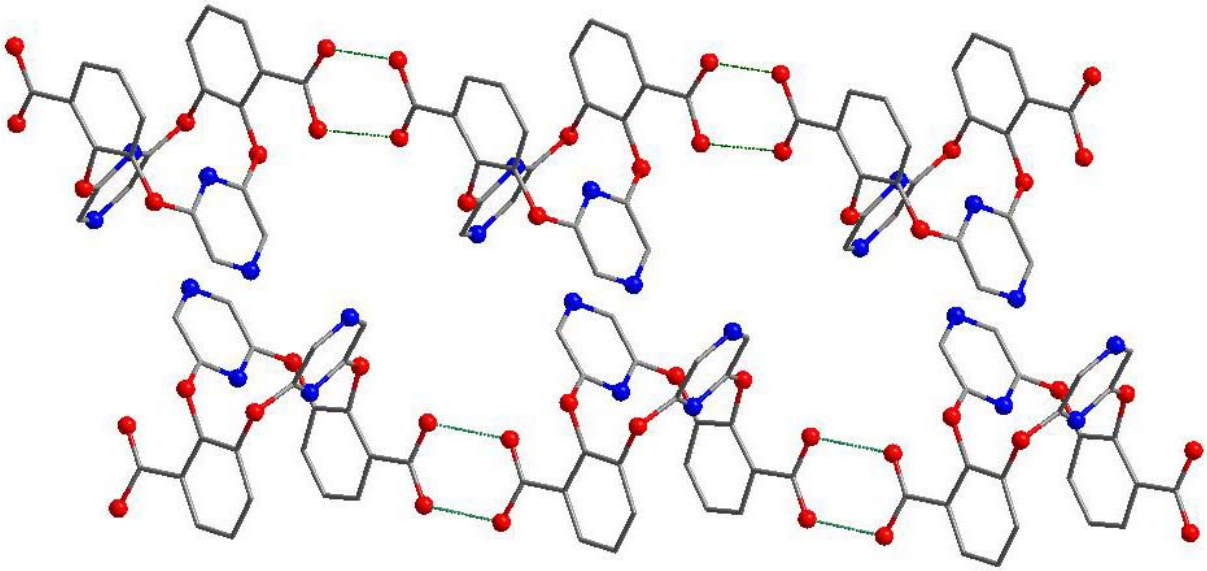


Figure S1 An isomeric pair of hydrogen-bonded supramolecular polymeric chains of **3** obtained in methanol. Color code: O (red), N (blue), and C (gray).

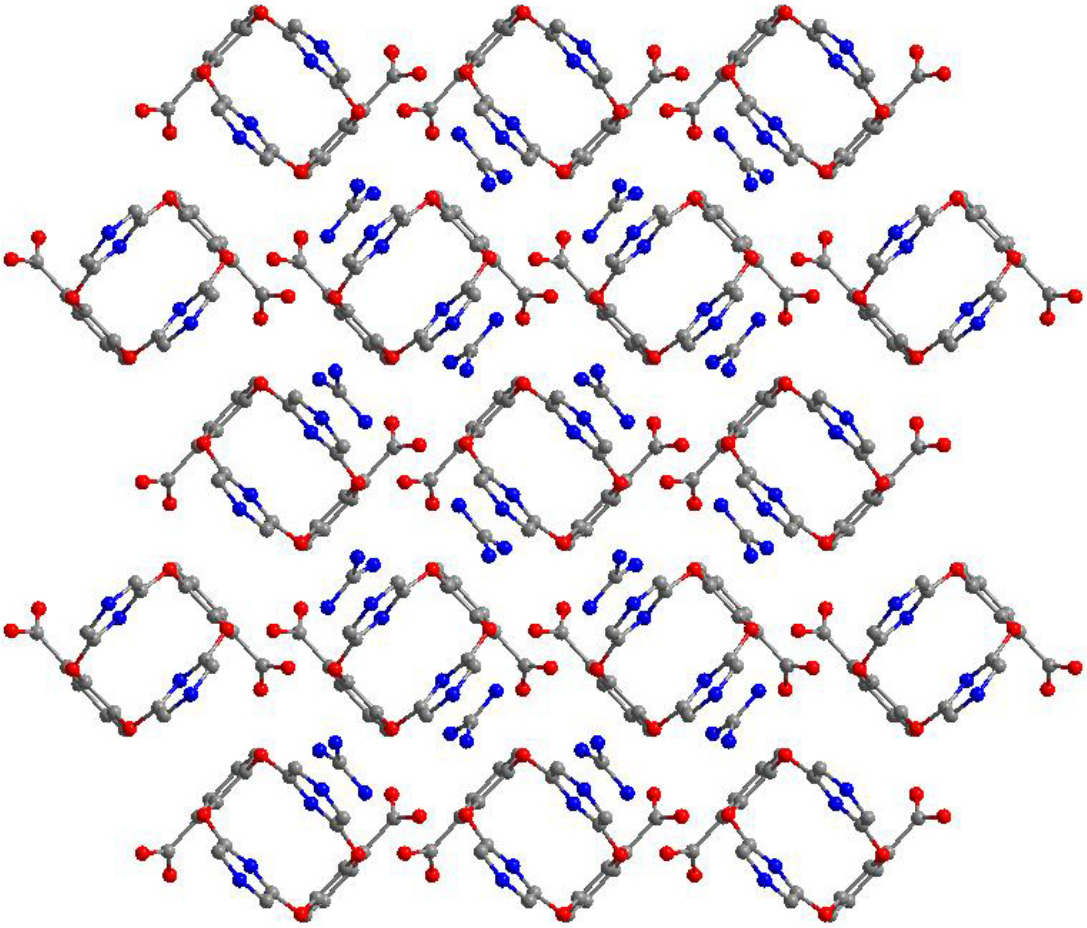
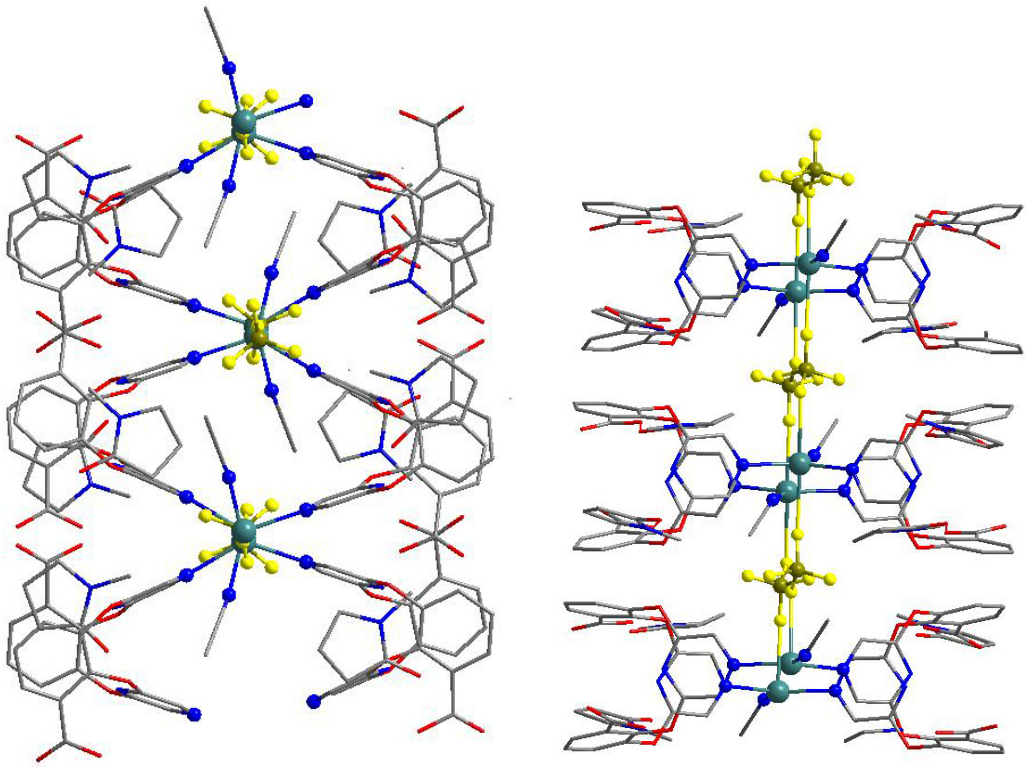


Figure S2 Packing diagram of guanidinium salt of the isomeric pair of **3** viewed along c axe. Color code: O (red), N (blue), and C (gray).



a b

Figure S3 Packing diagram of complex **7** viewed along c (a) and b (b) axes. Color code: Ag (green), O (red), N (blue), C (gray), B (brown) and F (yellow).

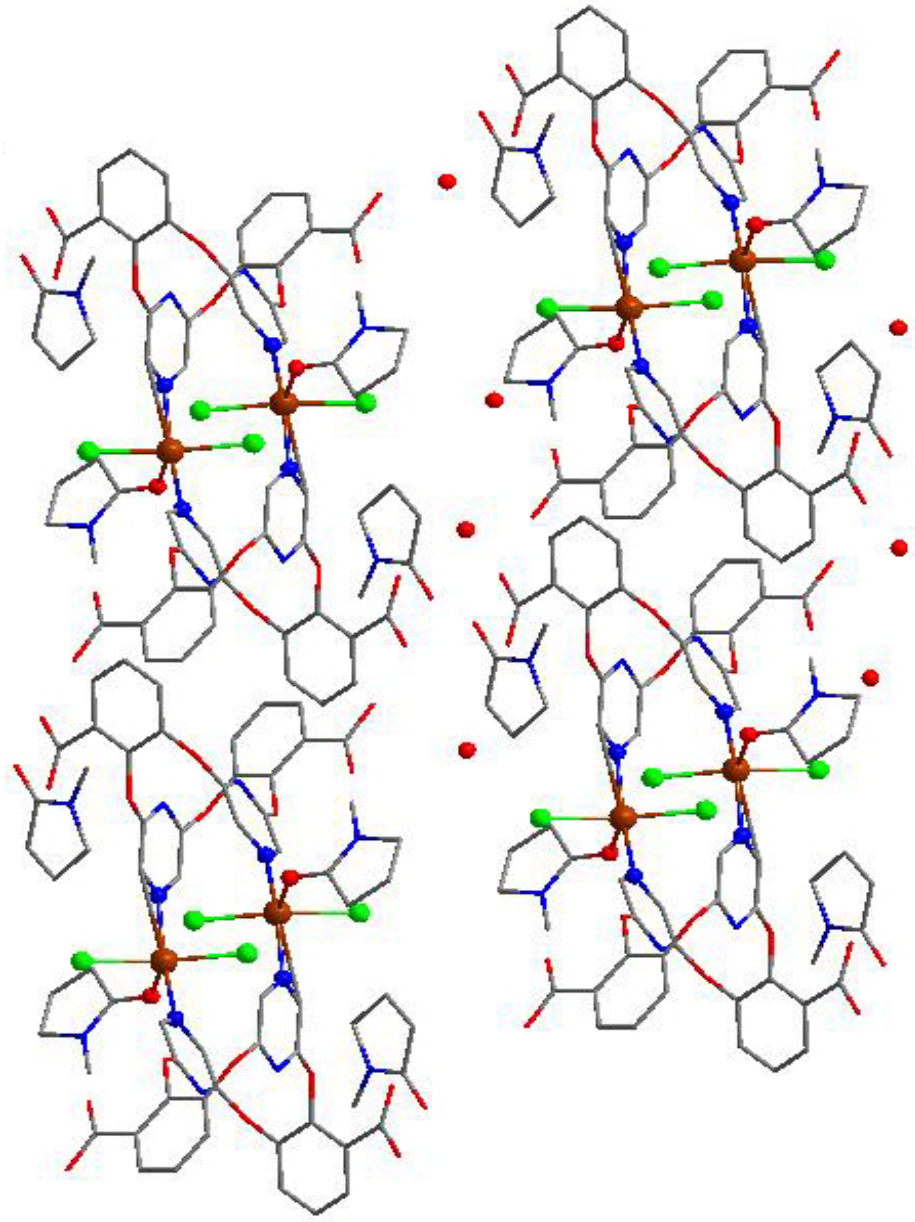


Figure S4 Packing diagram of complex **8** viewed along a axe. Color code: Cu (deep red), O (red), N (blue), C (gray) and Cl (green).

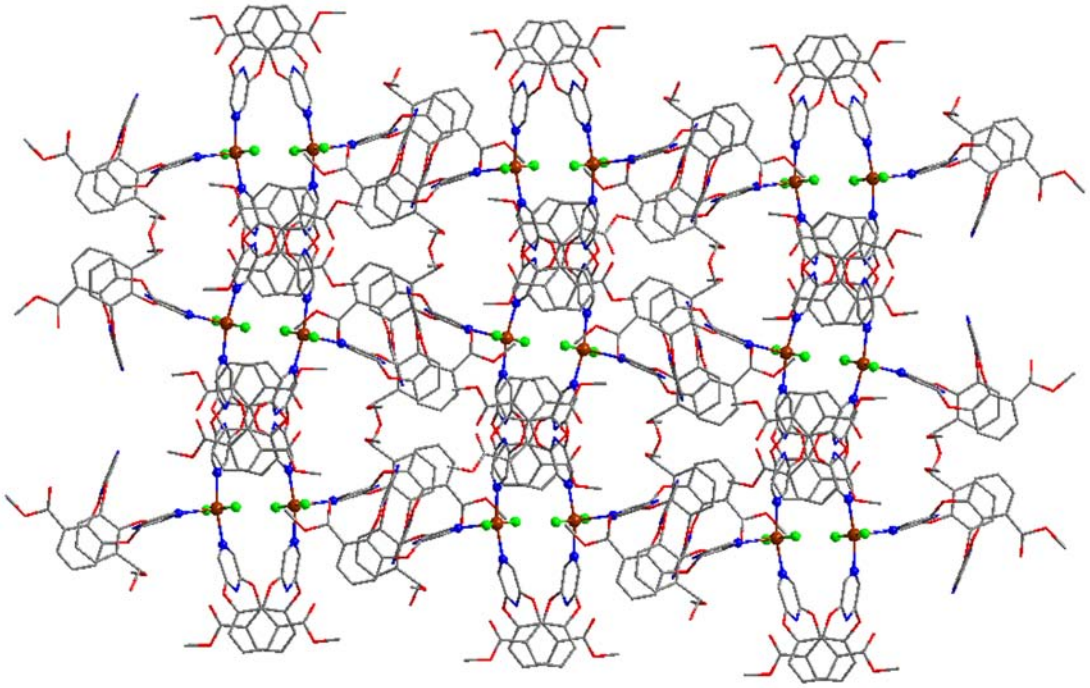


Figure S5 Packing diagram of complex **9** viewed along b axe. Color code: Cu (deep red), O (red), N (blue), C (gray) and Cl (green).

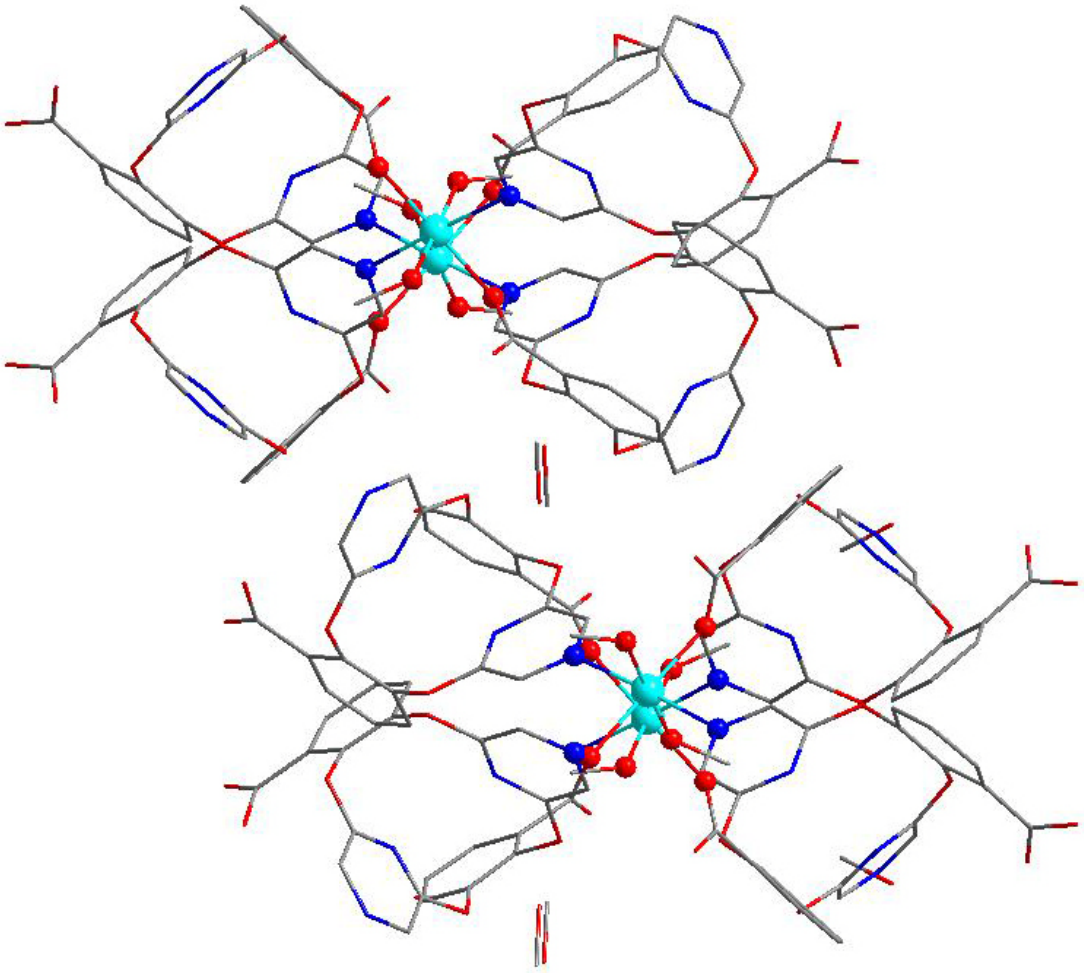


Figure S6 Packing diagram of complex **10** viewed along c axe. Color code: Zn (green), O (red), N (blue) and C (gray).

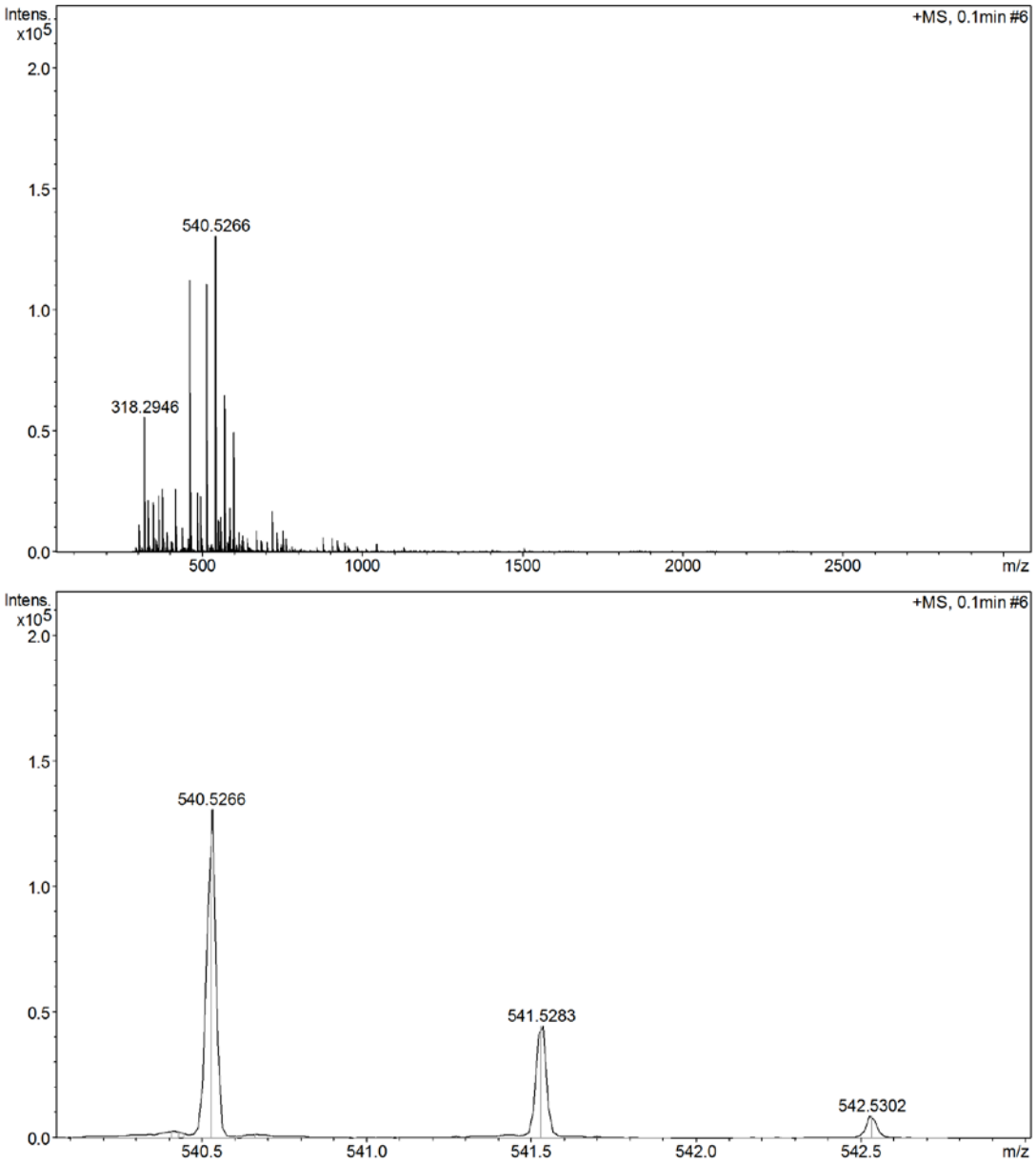


Figure S7 HRMS spectrum of 1:1 adducts of **3** and pyridine in solution.

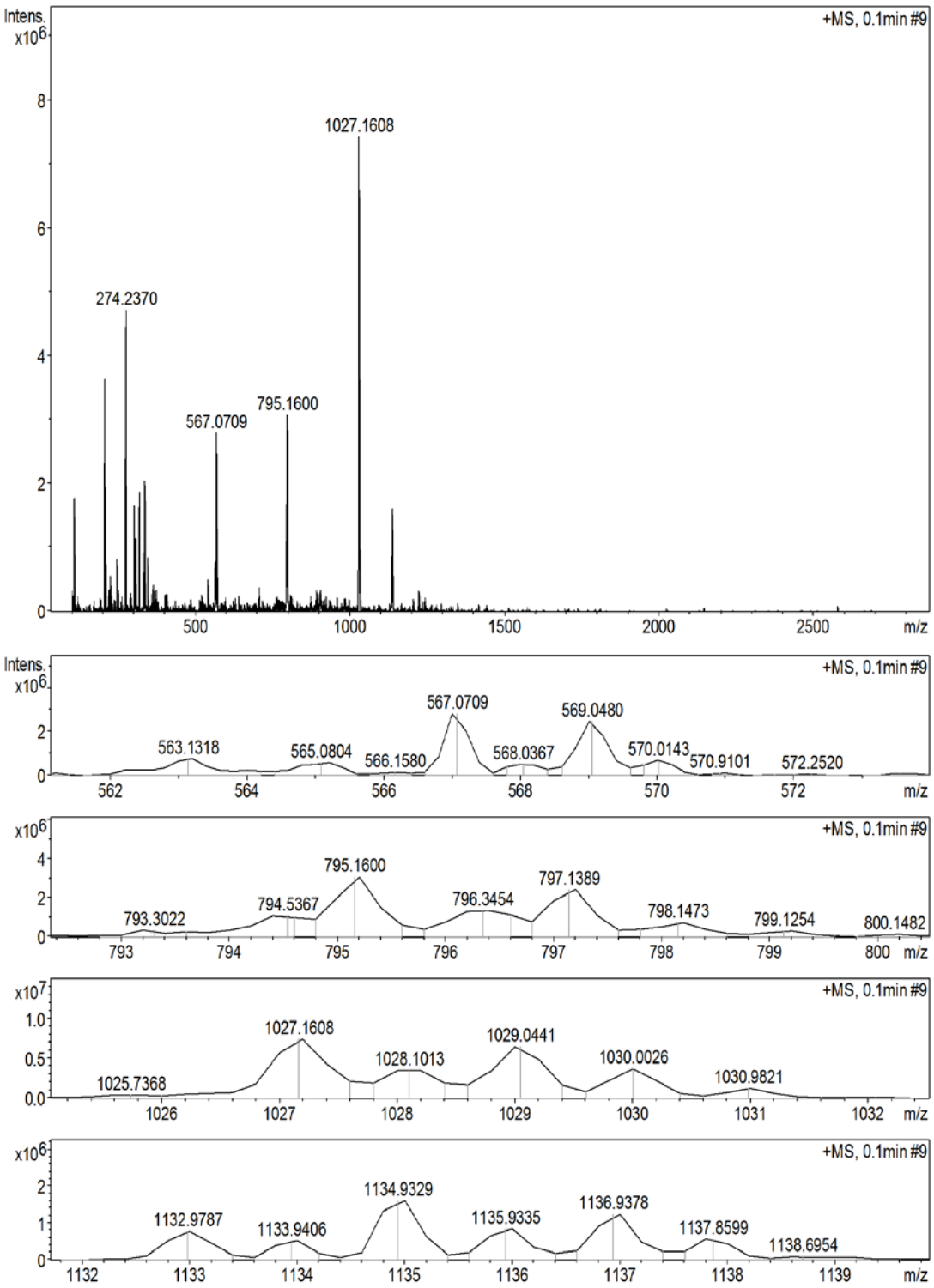


Figure S8 HRMS spectrum of $[Ag_2(\mathbf{3})_2.2\mathbf{ACN}]$ in NMP solution. Signals at m/z 567.1, 795.2, 1027.2 and 1035.0 can be assigned to $[Ag(\mathbf{3})]^{1+}$ or $[Ag_2(\mathbf{3})_2]^{2+}$,$[Ag_2(\mathbf{3}^-).3\mathbf{ACN}]^+$,$[Ag(\mathbf{3})_2]^+$ and $[Ag_2(\mathbf{3}^-).\mathbf{NMP}]^+$, respectively.

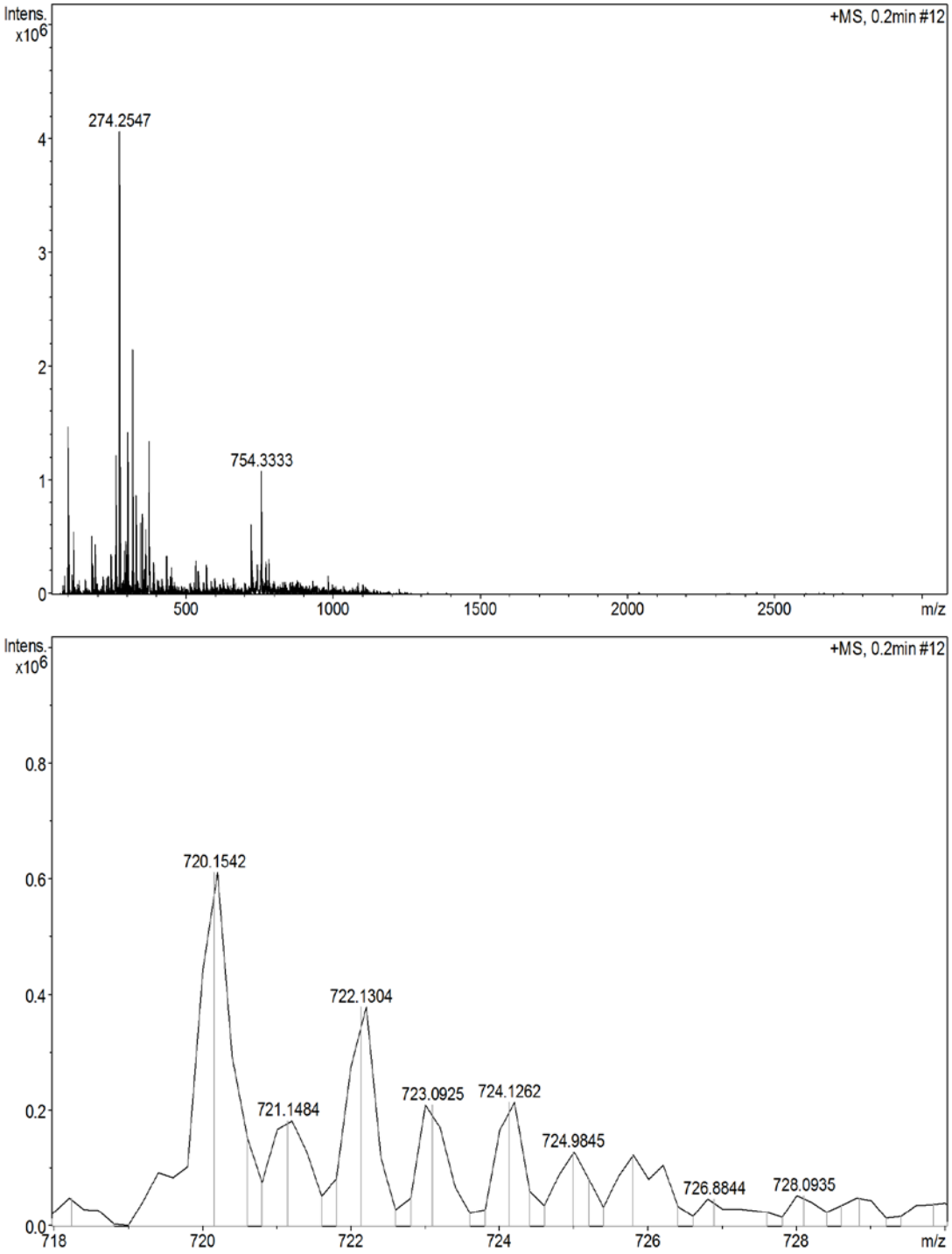


Figure S9 HRMS spectrum of $[Cu_2(\mathbf{3})_2Cl_4].2NMP$ in NMP solution. Only signal at 720.2 could be assigned to $[Cu(\mathbf{3}^-).2NMP]^+$ ~~or~~ ~~$[Cu_2(\mathbf{3}^-)_2.4NMP]^{2+}$~~, other signals remains to be correctively assigned.

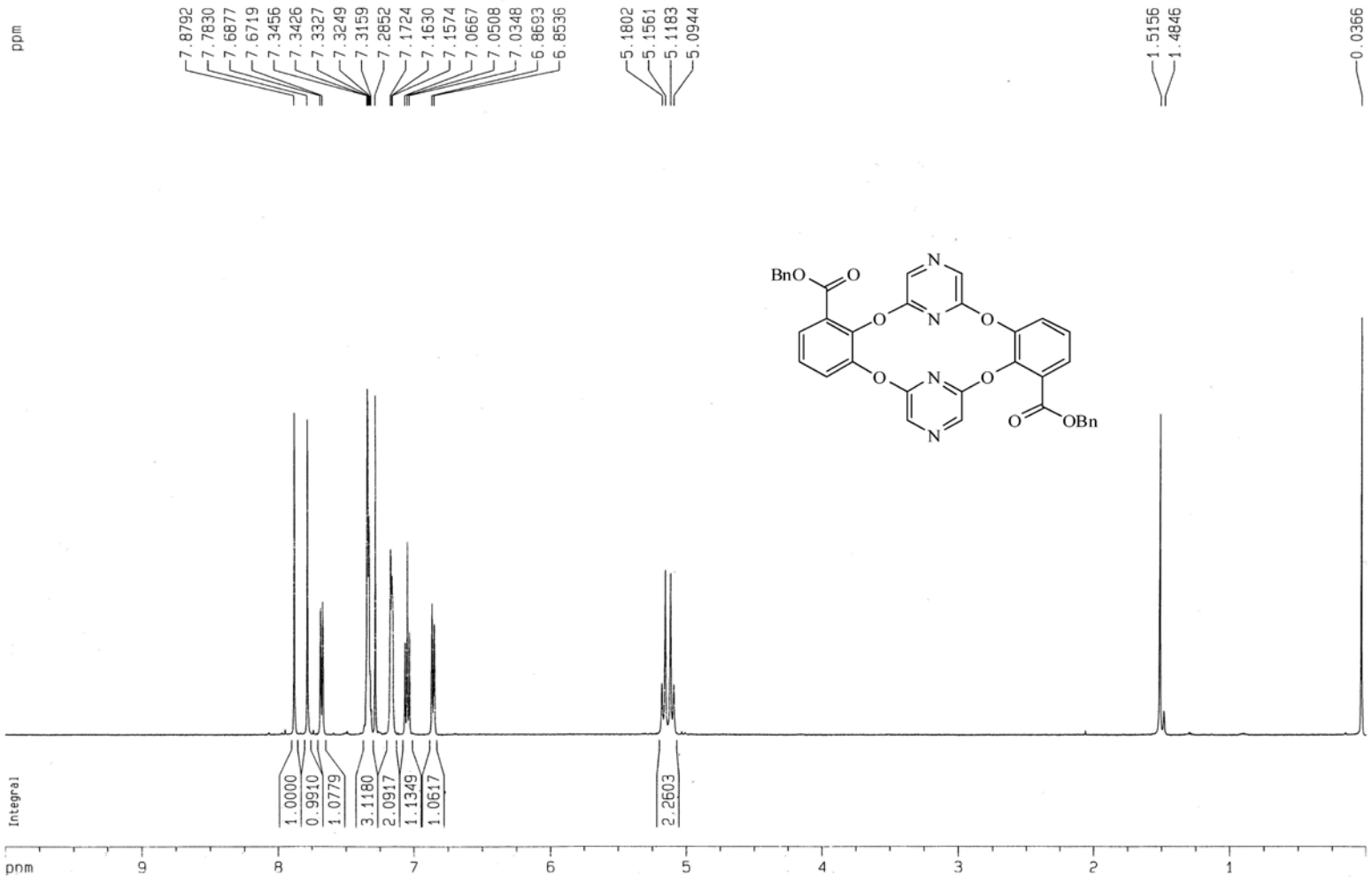


Figure S10 ^{1}H NMR spectrum of the isomeric **6** in $CDCl_3$.

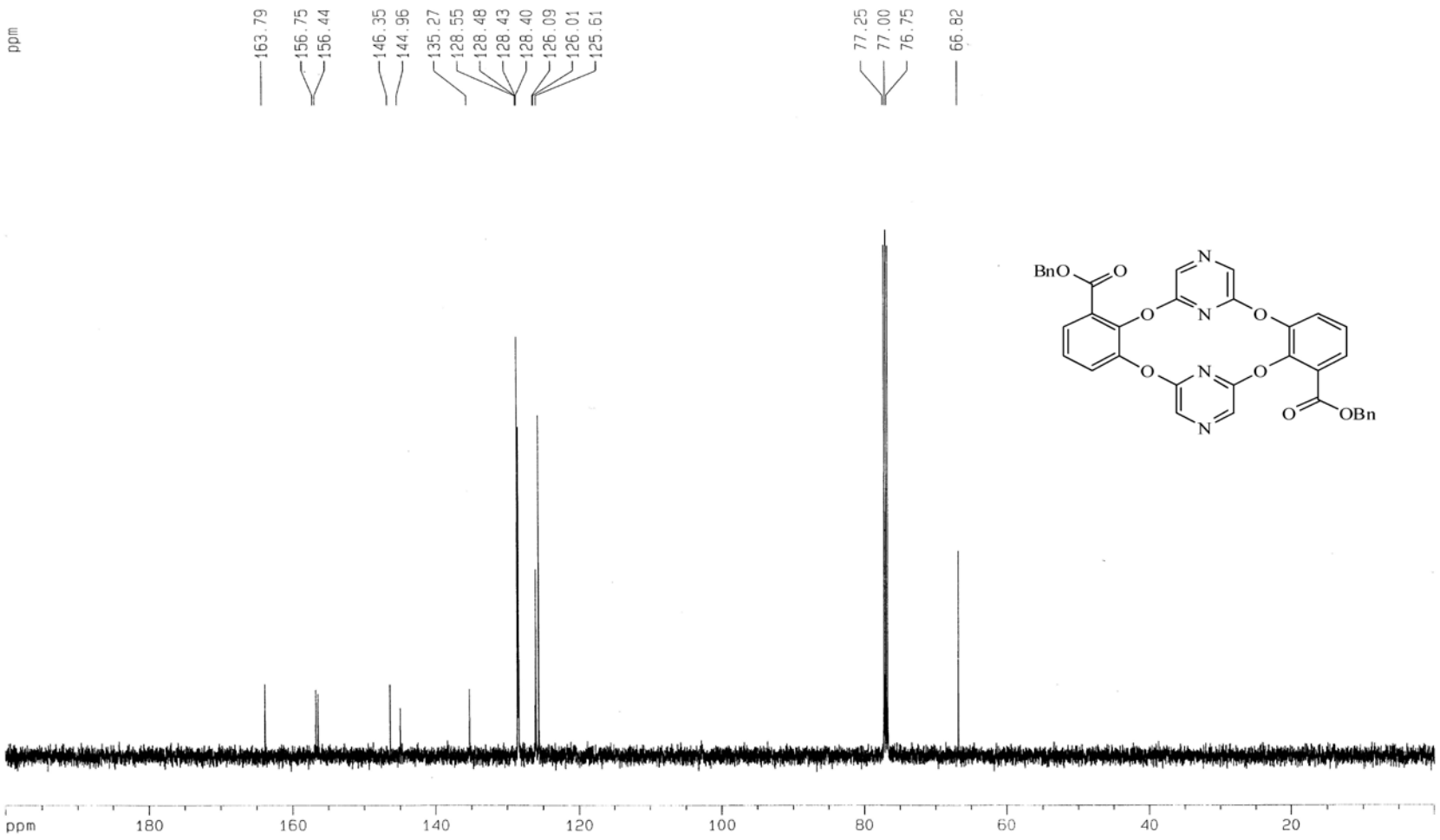


Figure S11 ^{13}C NMR spectrum of the isomeric **6** in $CDCl_3$.

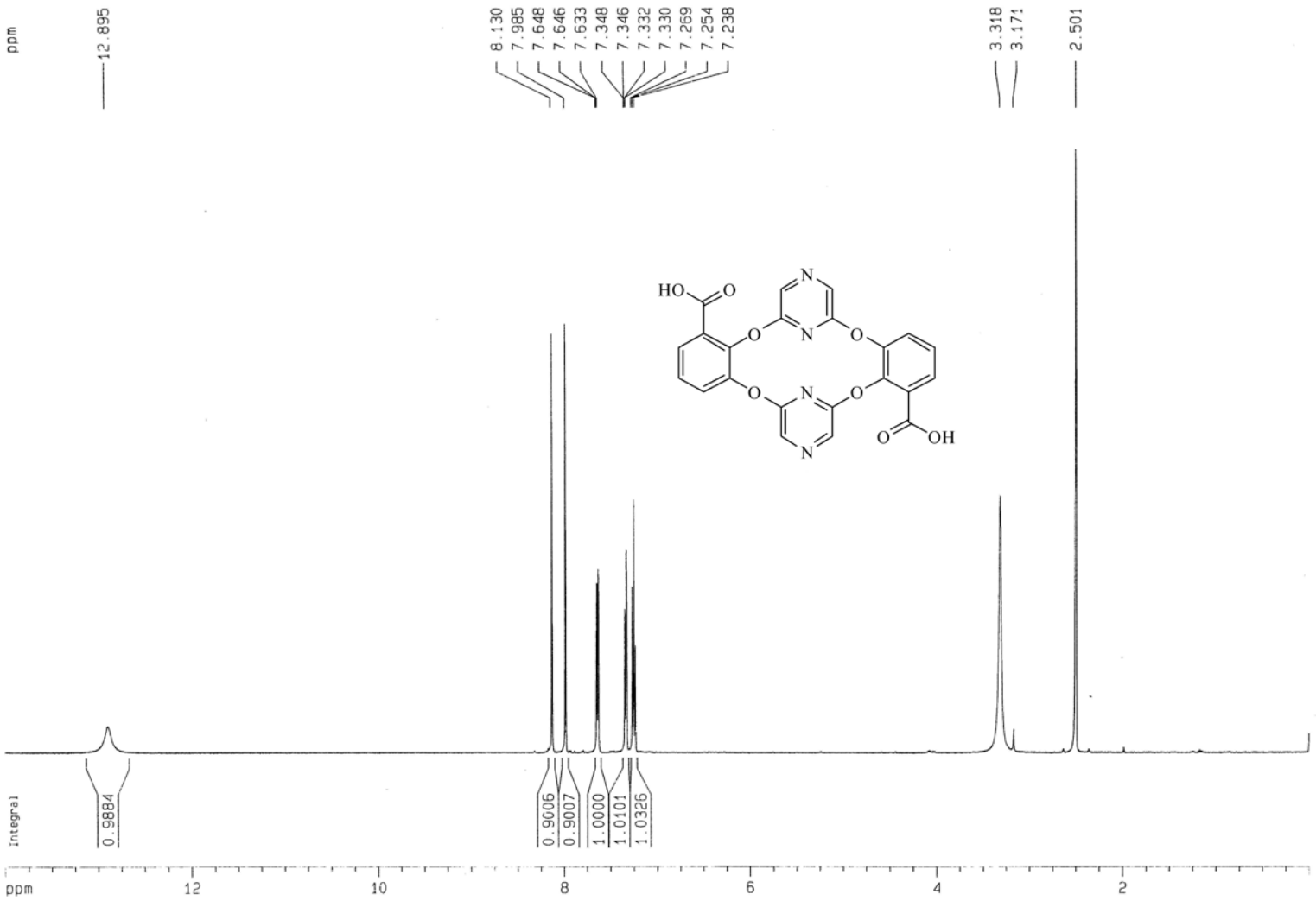


Figure S12 ^{1}H NMR spectrum of the isomeric **3** in DMSO-d_6.

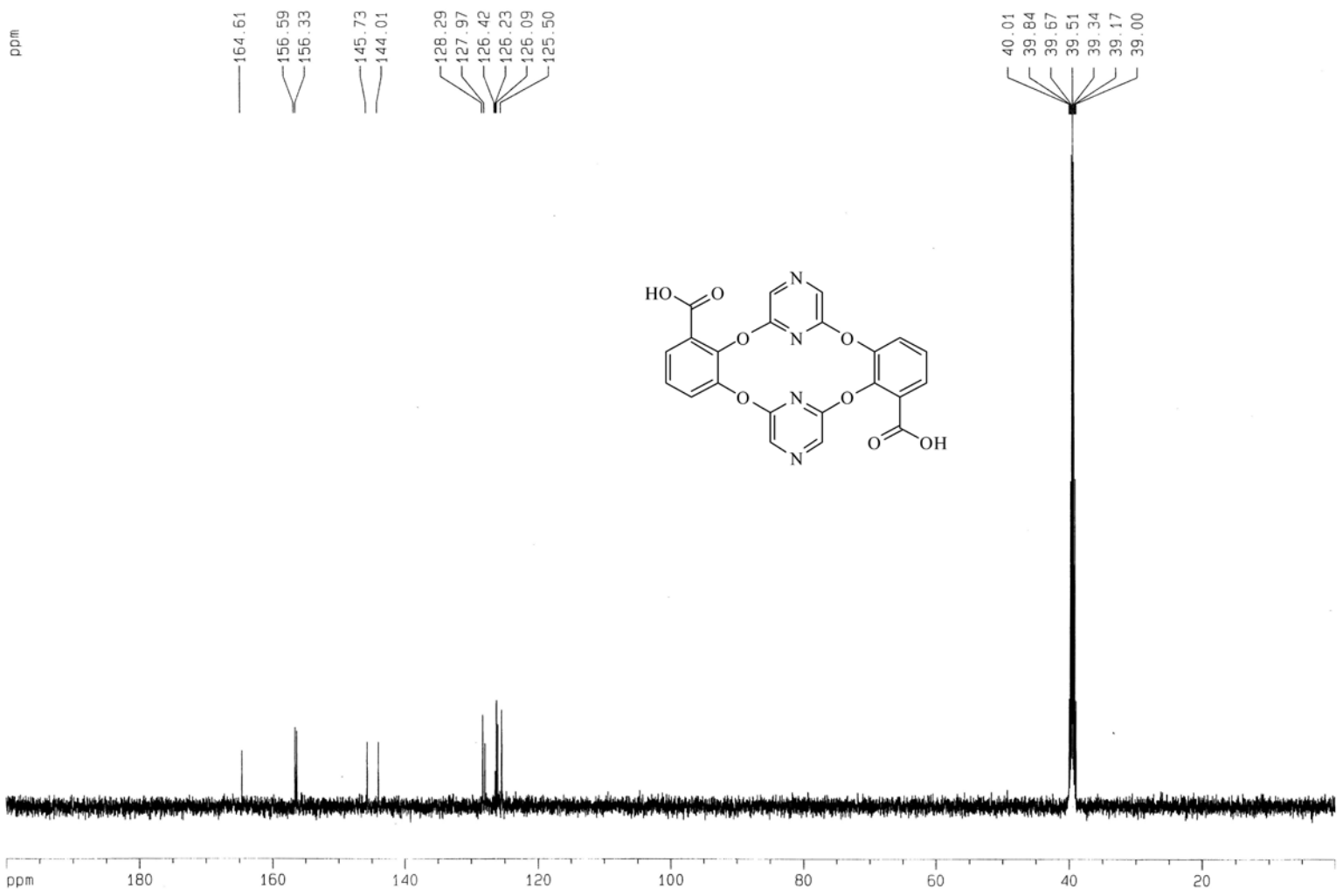


Figure S13 ^{13}C NMR spectrum of the isomeric **3** in DMSO-d_6.

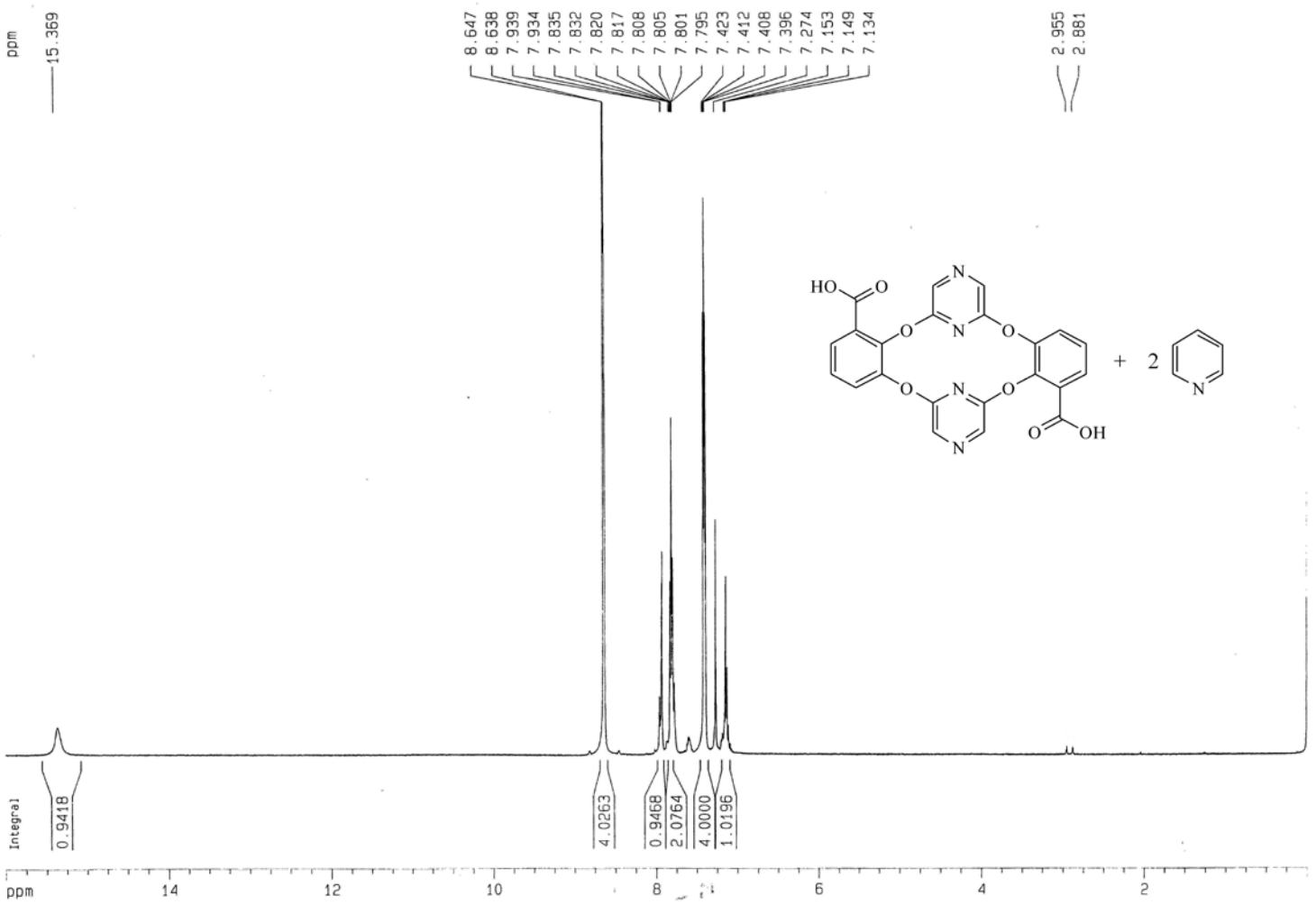


Figure S14 ^{1}H NMR spectrum of the isomer **3** and pyridine in $CDCl_3$.

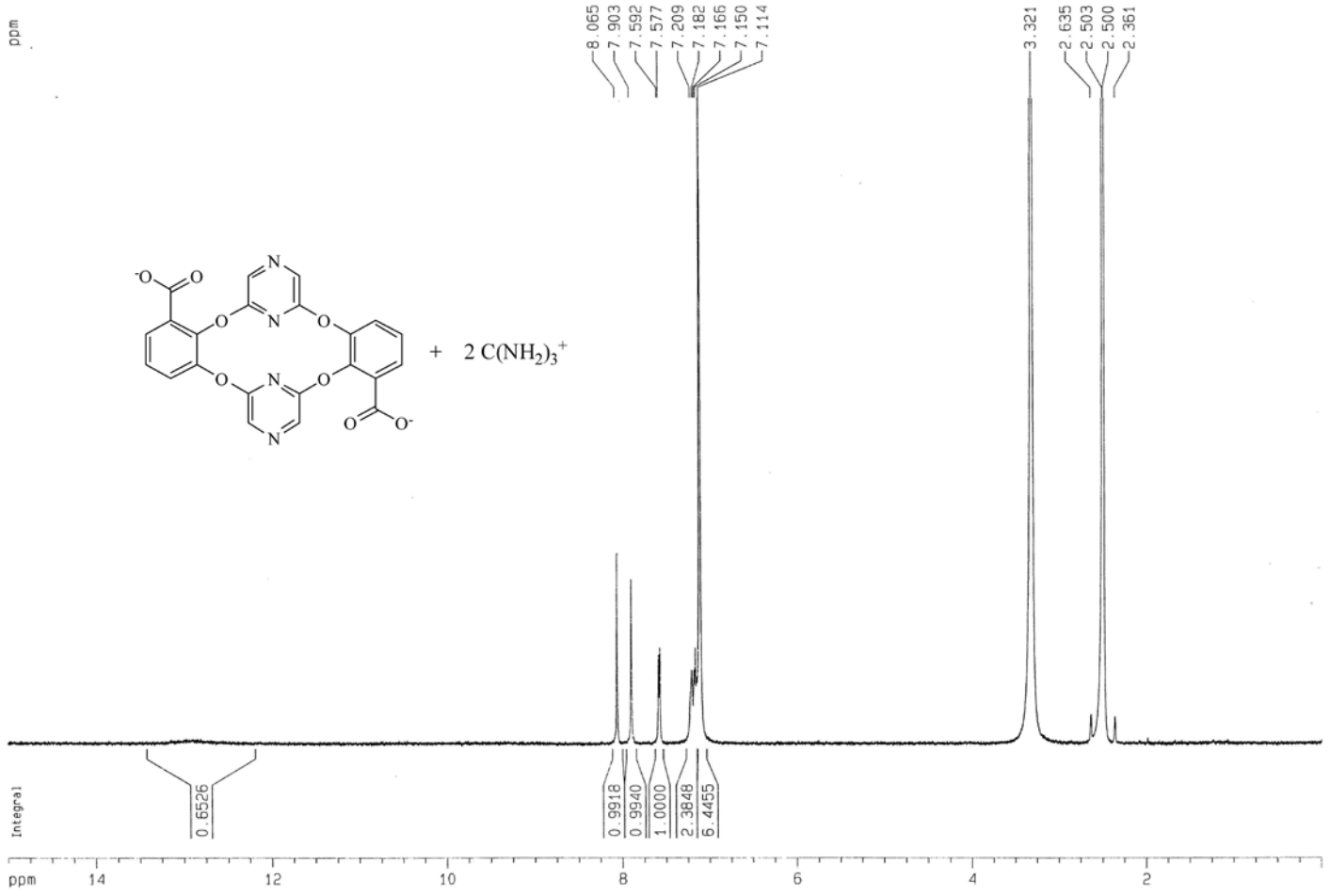


Figure S15 ^{1}H NMR spectrum of the guanidinium salt of isomeric **3** in DMSO-d_6.

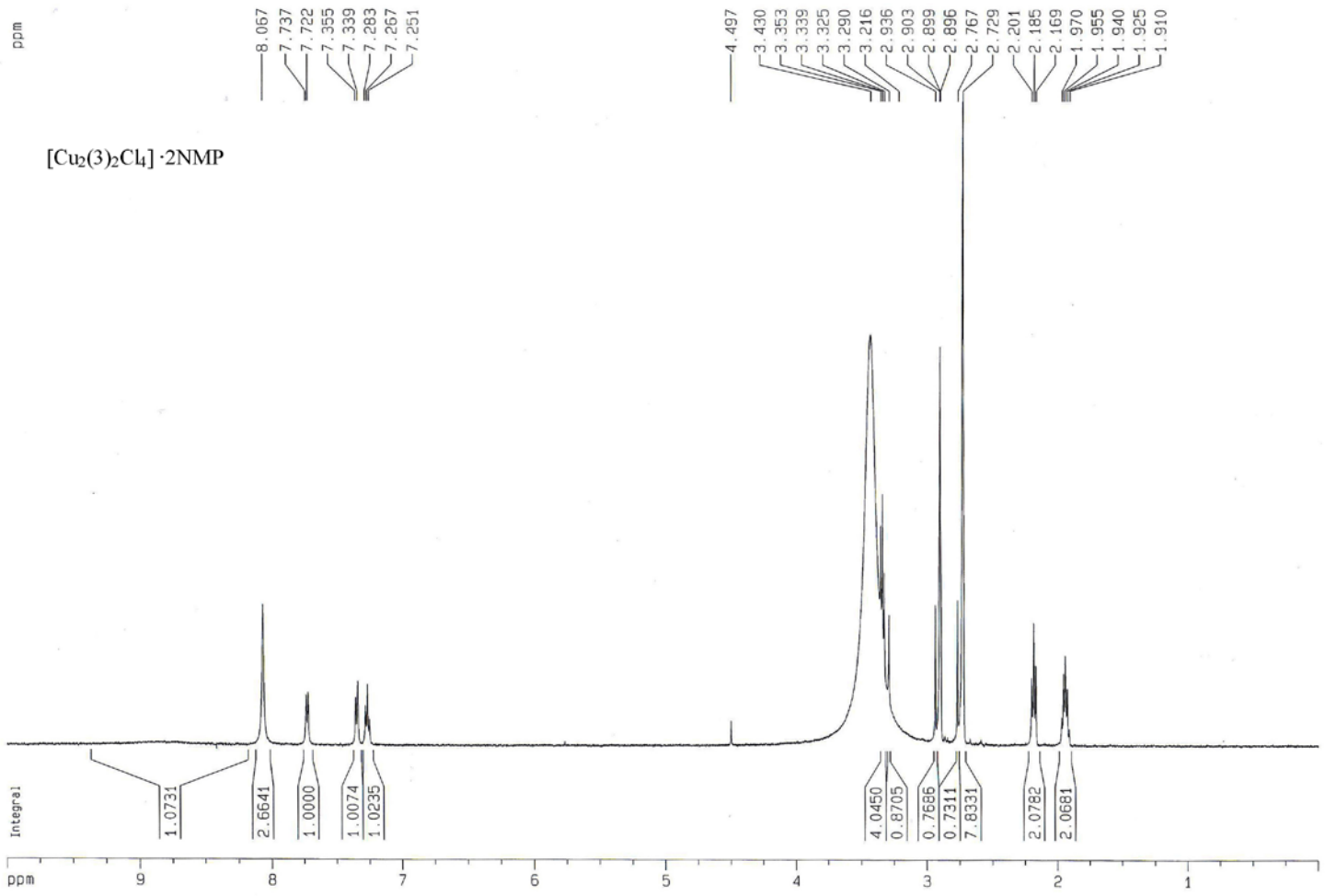


Figure S16 ^{1}H NMR spectrum of $[Cu_2(\mathbf{3})_2Cl_4]$.2NMP in DMF-d_7.