Supporting information

Reaction of Dichloromethane with Pyridine Derivatives under Ambient Conditions

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* New characterization data for previously reported compounds.

(1) General Experimental

Materials and Instrumentation. Anhydrous pyridine, thionyl chloride, and paraformaldehyde were 99.8, 99, and 95 %, respectively. Other pyridine derivatives were typically 98% or better and used as received. Dichloromethane (ACS certified) and acetonitrile (HPLC grade) were used as received. DMSO-d_6 and D_2O were 99.9% D. Mass spectral data were acquired using a high-resolution (30,000) Thermo LTQ-Orbitrap Discovery hybrid mass spectrometry instrument equipped with an electrospray ionization source operating in the positive mode. The mass spectrometer was externally calibrated prior to data acquisition allowing accurate mass measurements for M^{2+} ions to be obtained within 3 ppm.

(2) Additional Compound Characterization (3a)

(2.1) 1,1'-methylenebispyridinium dichloride (3a).

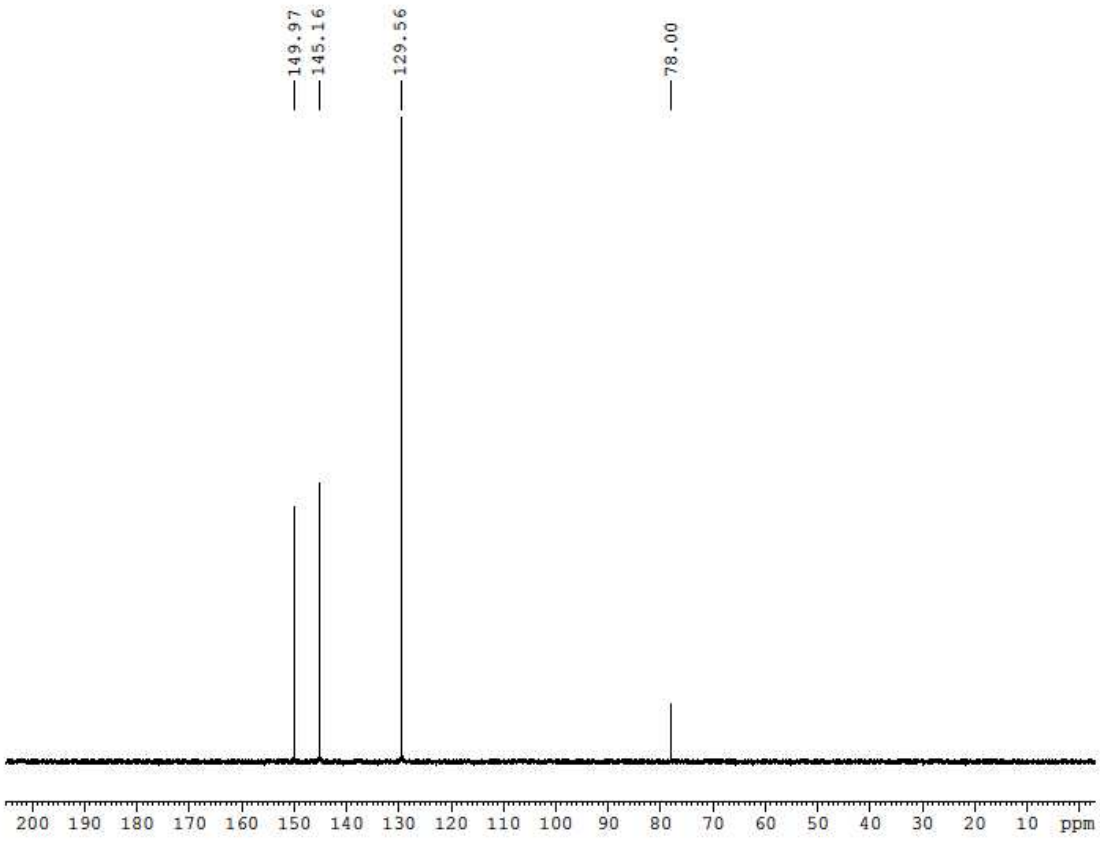

Figure S1. Carbon NMR spectrum of compound **3a** in D_2O.

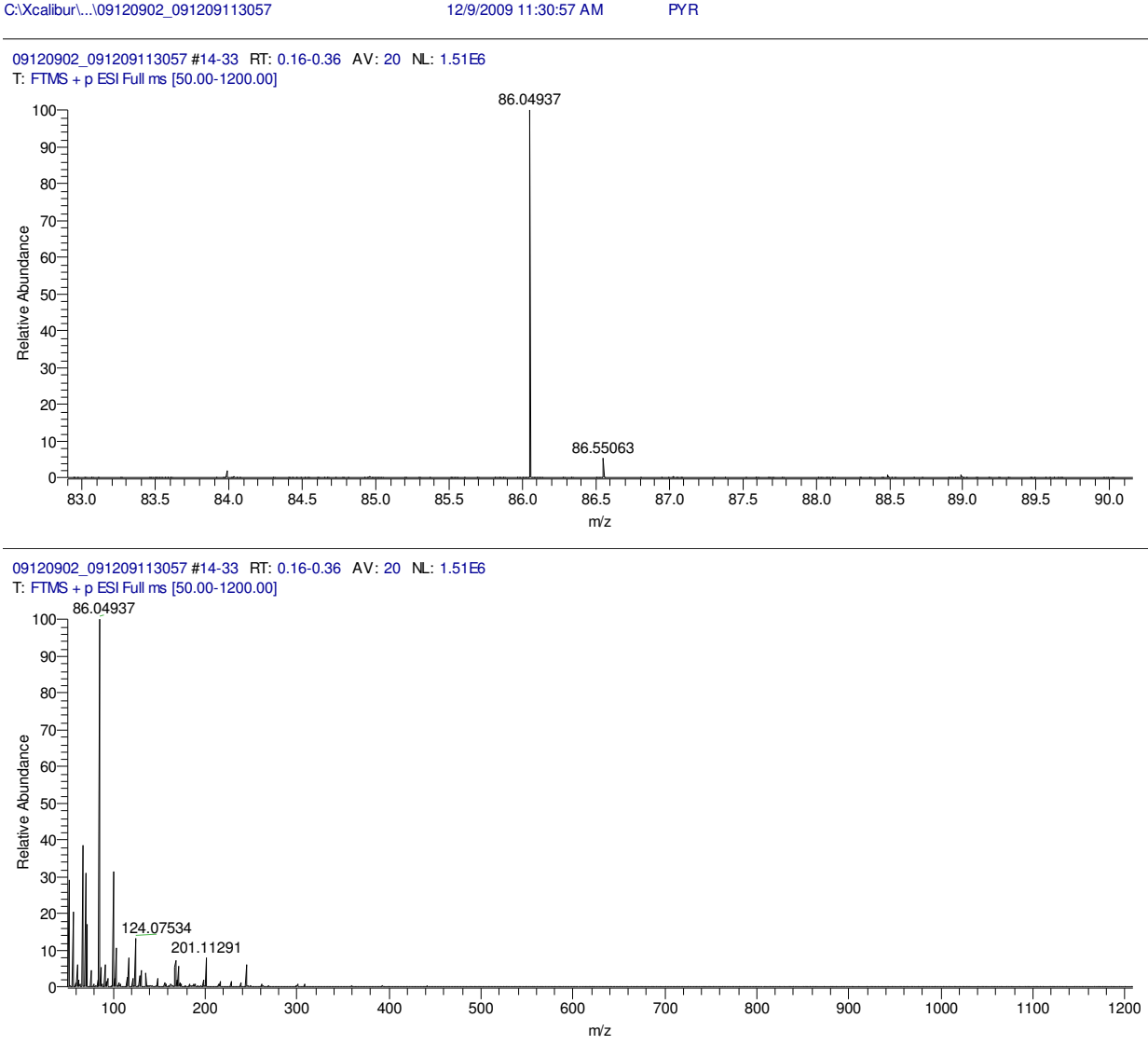

Figure S2. ESI (positive mode) HRMS of compound **3a**, showing the peak for the M^{2+} ion without Cl^- counterions.

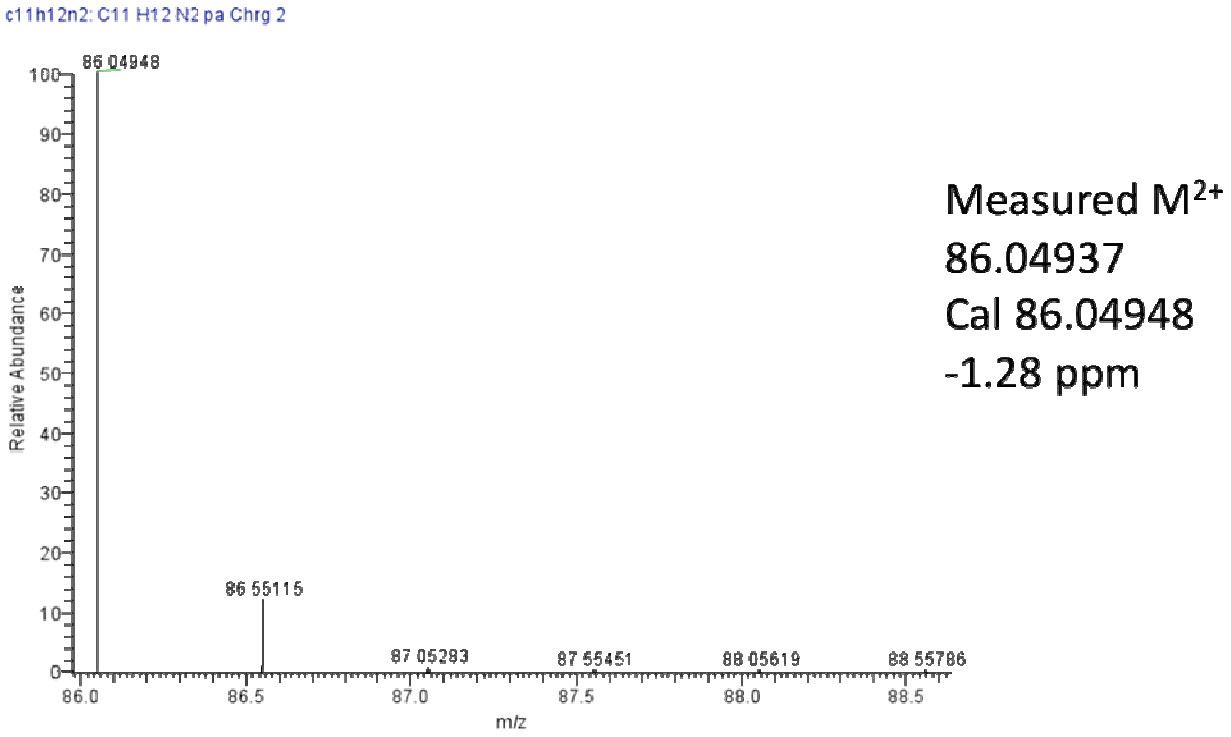

Figure S3. Calculated ESI (positive mode) HRMS spectrum for compound **3a**, M^{2+} ion without Cl^- counterions.

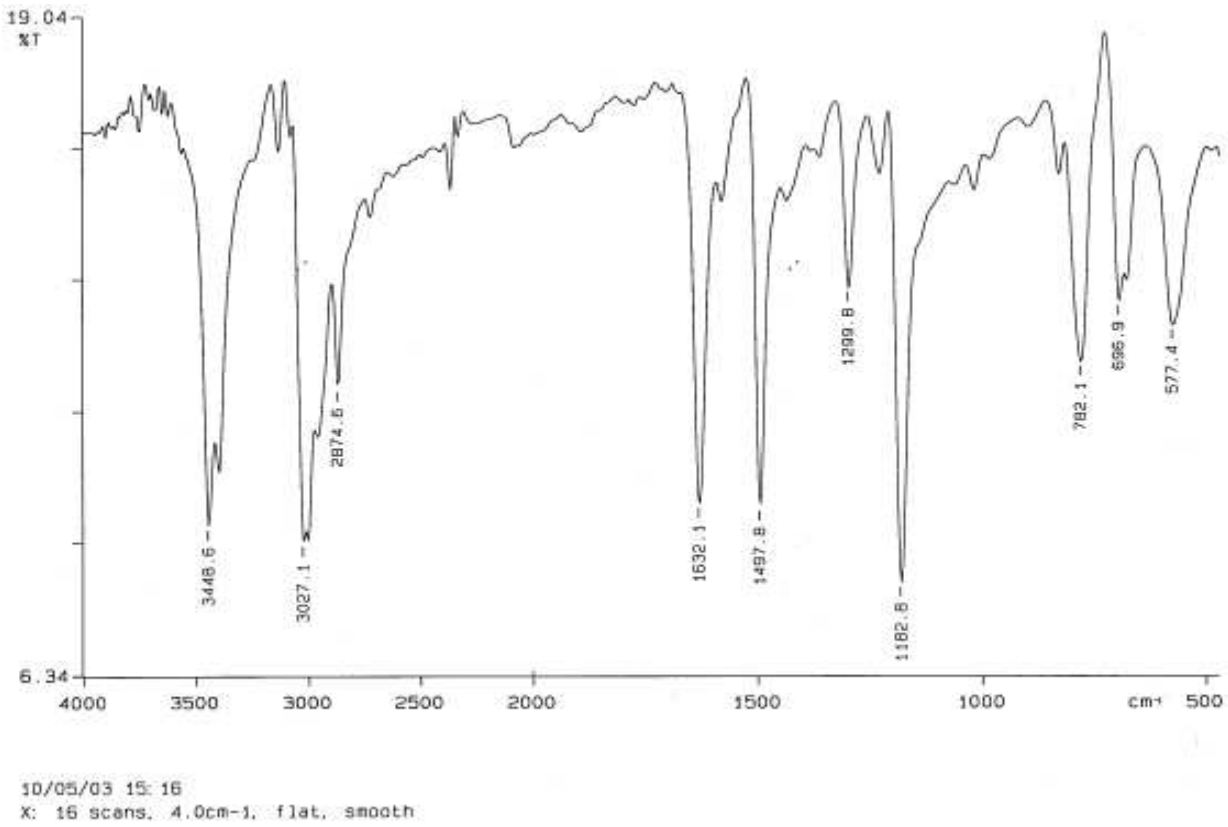

Figure S4. IR spectrum (KBr pellet) of compound **3a** showing vibrations at 3027 cm^{-1} (=C-H), 2874 cm^{-1} (-C-H), 1632 and 1497 cm^{-1} (C=C), 1182 cm^{-1} (C-N).

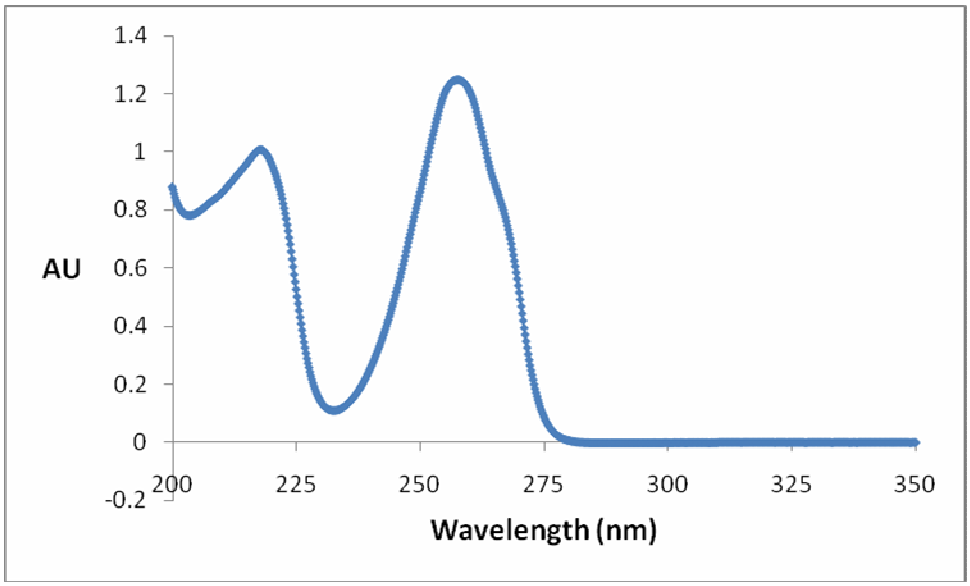

Figure S5. UV-Visible spectrum of **3a** in H_2O.

(2.2) 1-Chloromethylpyridinium chloride (2a).

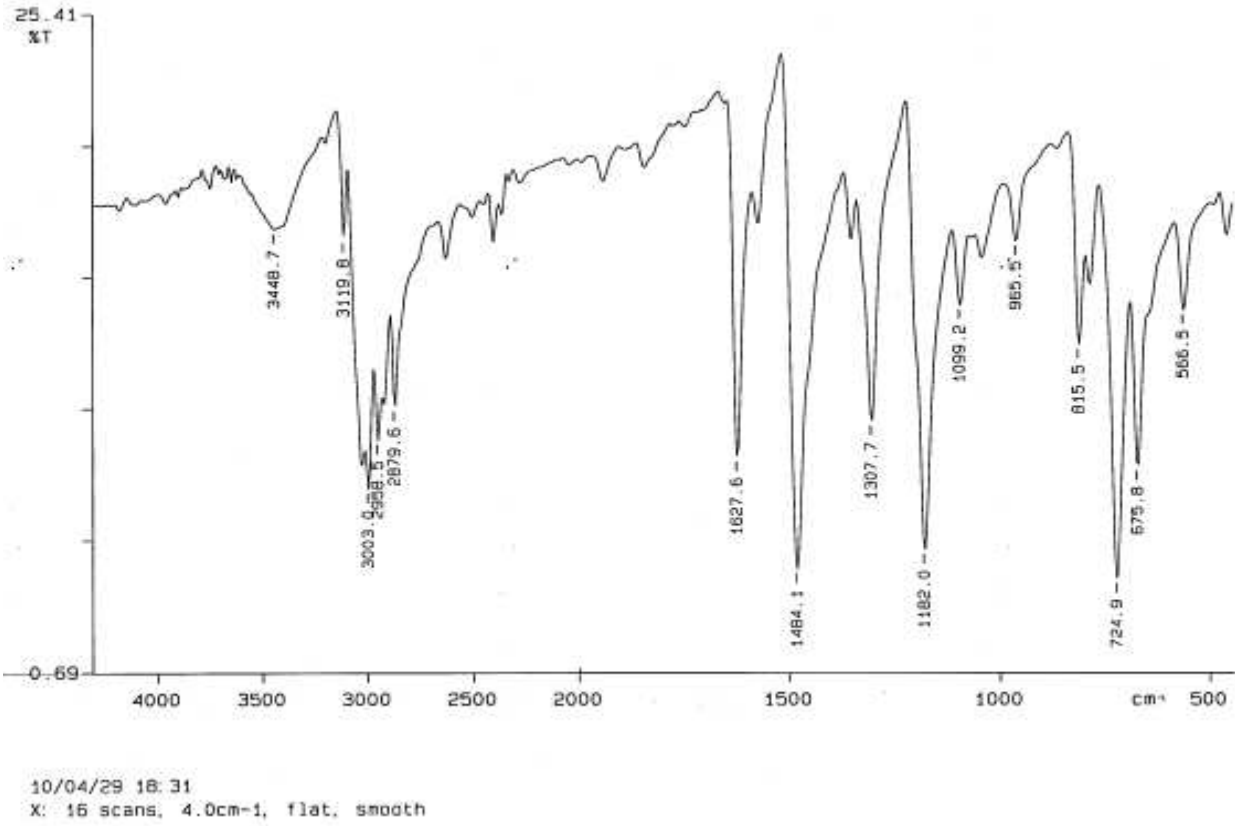

Figure S6. IR spectrum (KBr pellet) of compound **2a** showing vibrations at 3003 cm^{-1} (=C-H), 2958 cm^{-1} (-C-H), 1627 and 1484 cm^{-1} (C=C), 1182 cm^{-1} (C-N), 1307 and 725 cm^{-1} (C-Cl).

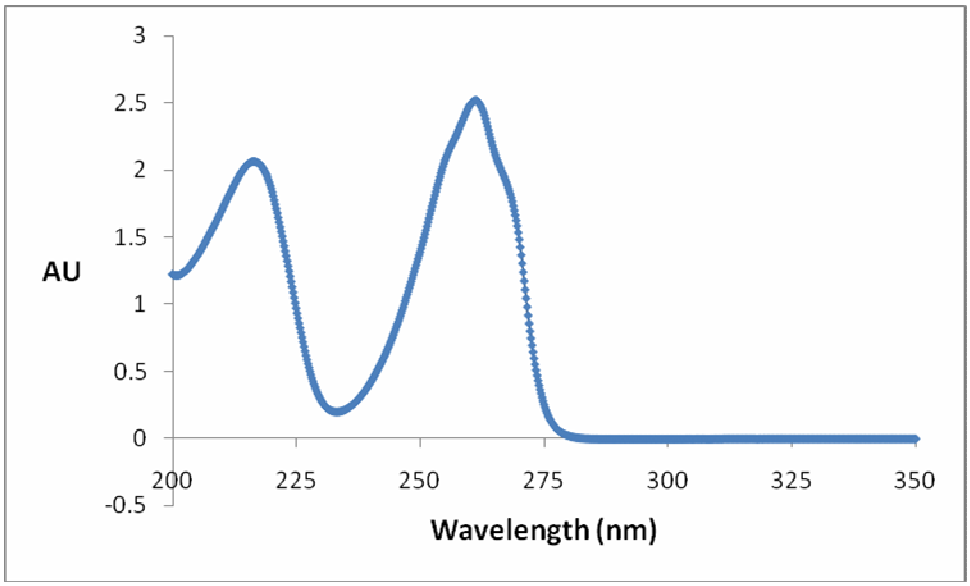

Figure S7. UV-Visible spectrum of **2a** in H_2O.

(2.3) 1-Chloromethyl-4-(dimethylamino)pyridinium chloride (2b).

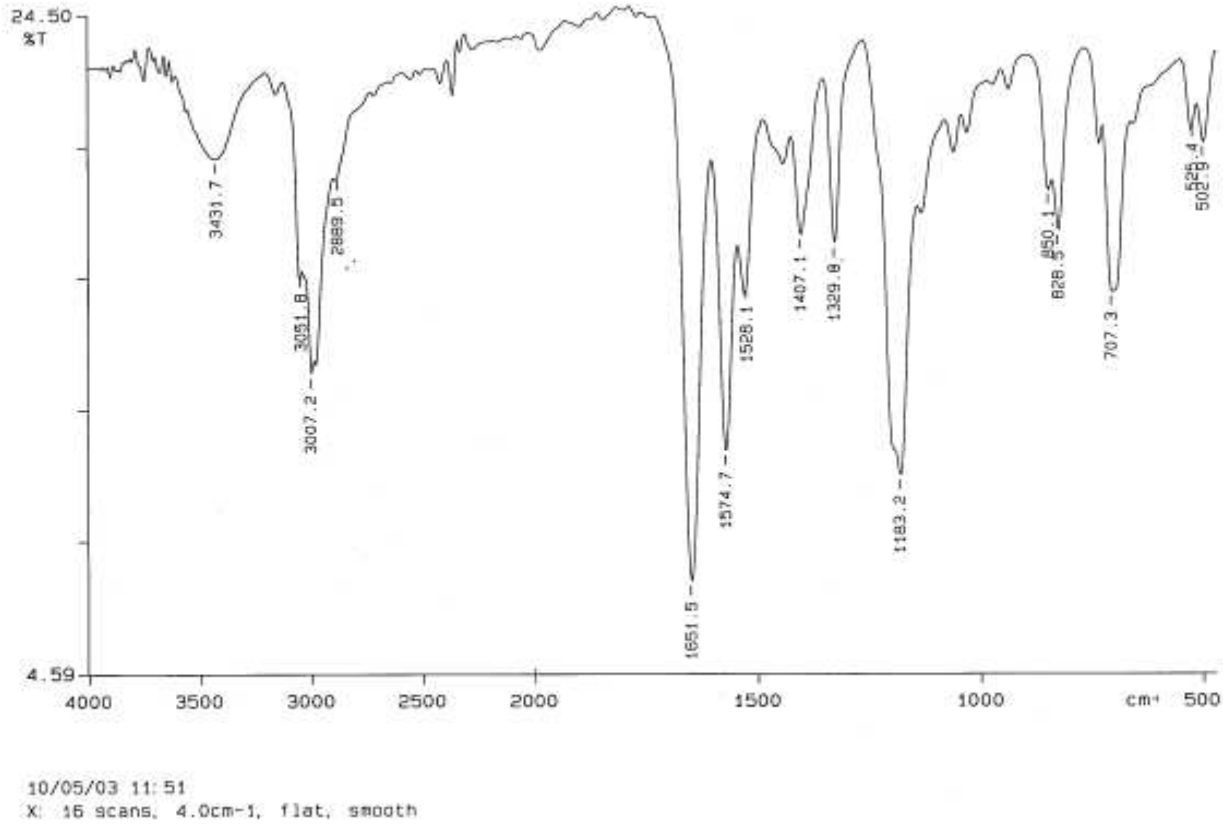

Figure S8. IR spectrum (KBr pellet) of compound **2b** showing vibrations at 3007 cm^{-1} (=C-H), 2889 cm^{-1} (-C-H), 1651 cm^{-1} (C=C), 1183 cm^{-1} (C-N), 1329 and 707 cm^{-1} (C-Cl).

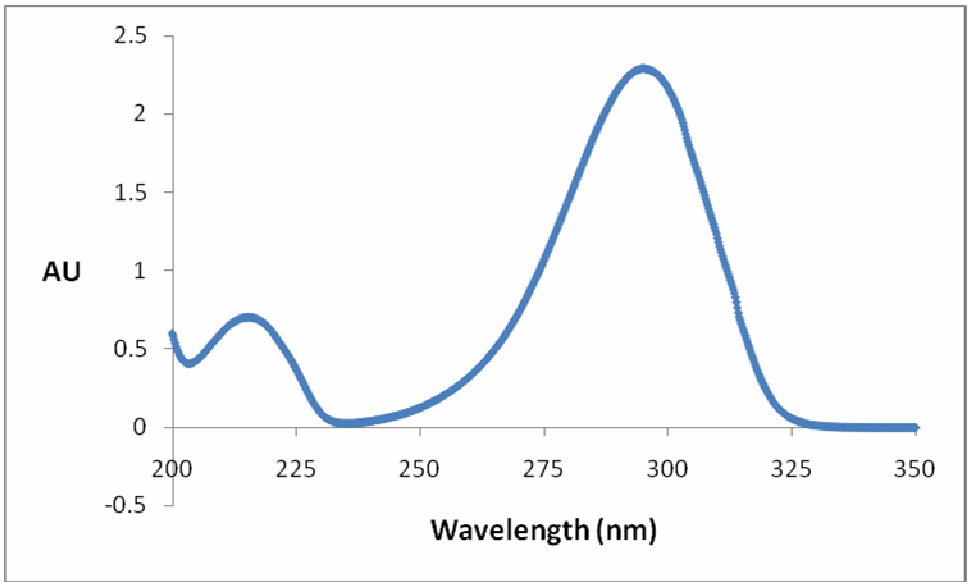

Figure S9. UV-Visible spectrum of **2b** in H_2O.

(3) New Compound Characterization (3b-f)

(3.1) 1,1'-methylenebis(4-dimethylaminopyridinium) dichloride (3b).

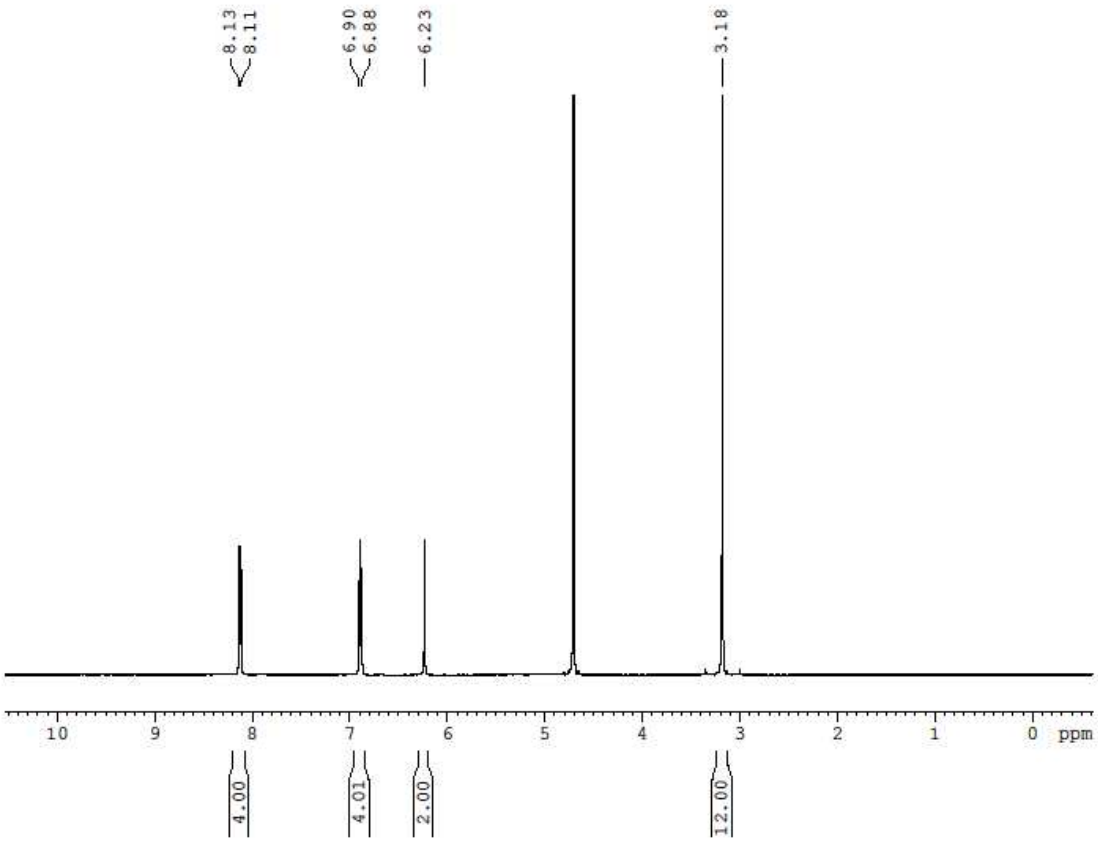

Figure S10. Proton NMR spectrum of compound **3b** in D_2O.

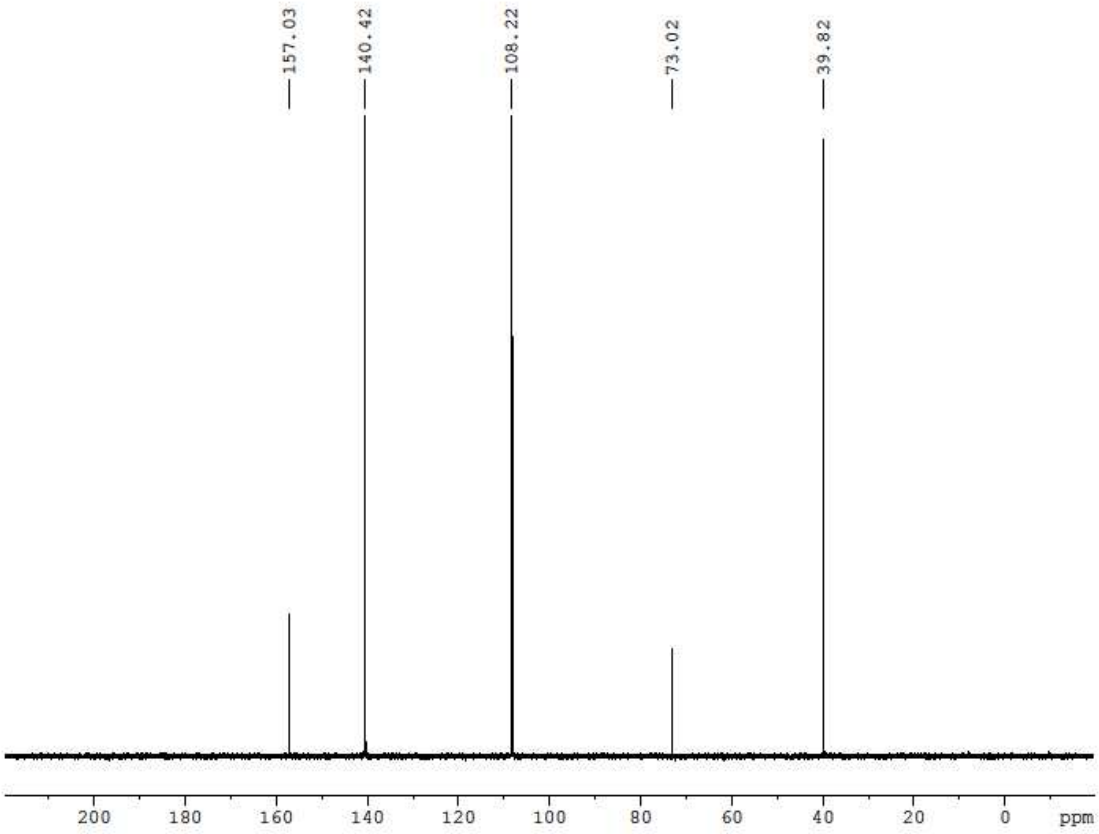

Figure S11. Carbon NMR spectrum of compound **3b** in D_2O.

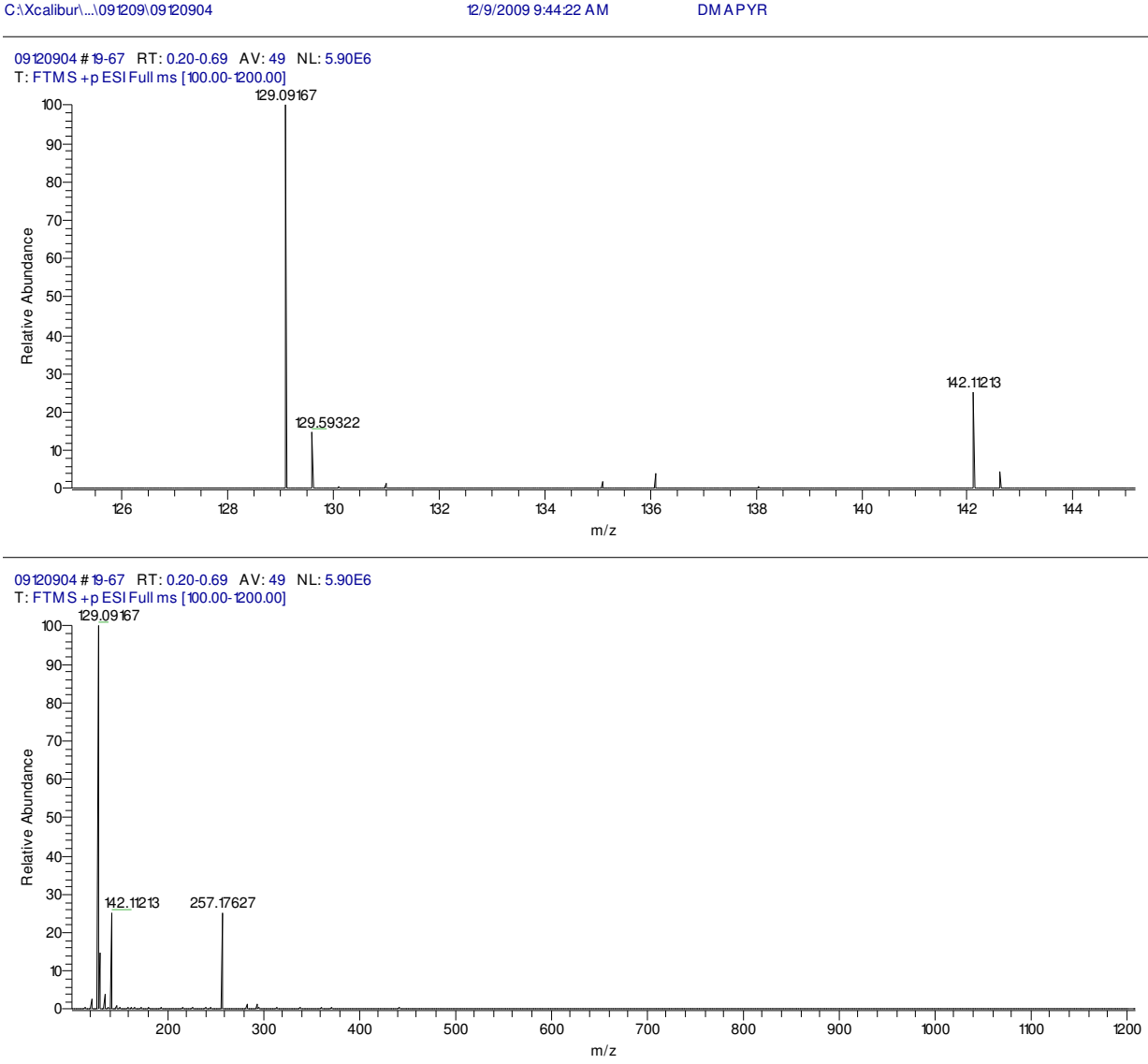

Figure S12. ESI (positive mode) HRMS of compound **3b**, showing the peak for the M^{2+} ion without Cl^- counterions.

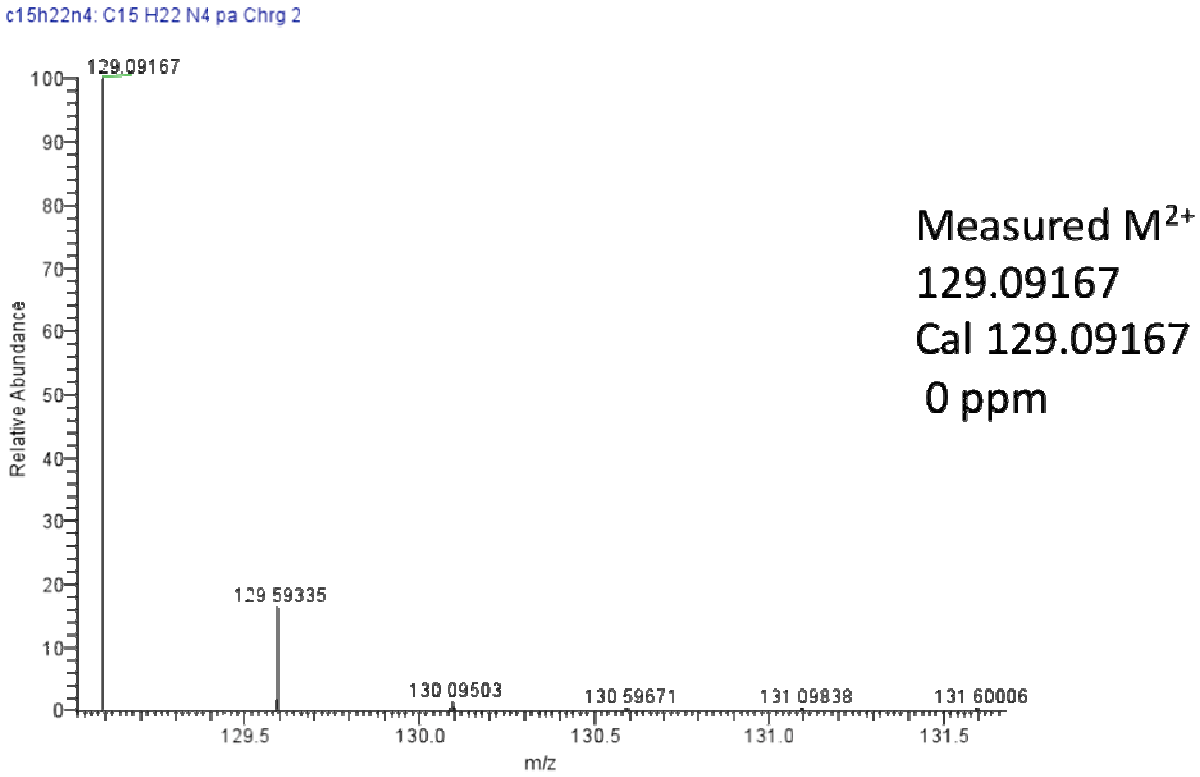

Figure S13. Calculated ESI (positive mode) HRMS spectrum for compound **3b**, M^{2+} ion without Cl^- counterions.

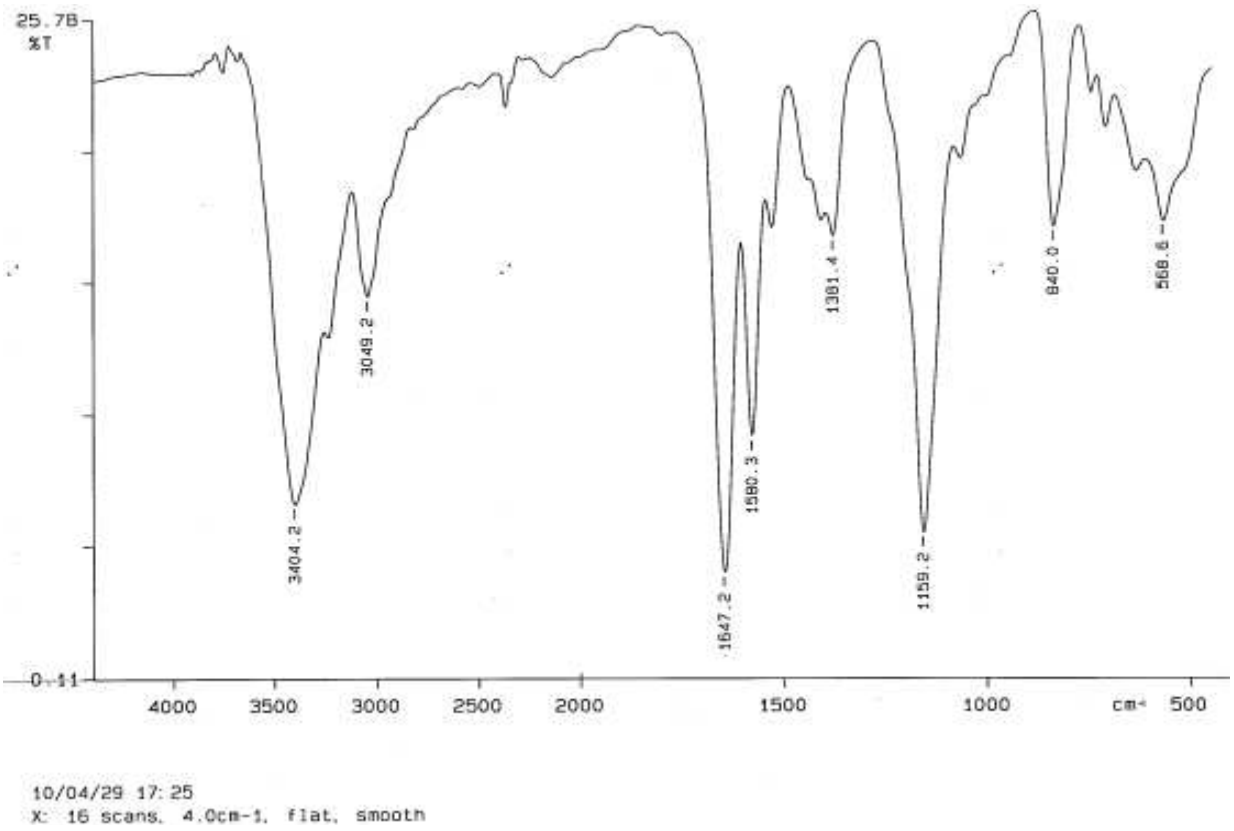

Figure S14. IR spectrum (KBr pellet) of compound **3b** showing vibrations at 3049 cm^{-1} (=C-H), ~2950 cm^{-1} (-C-H, small shoulder), 1647 cm^{-1} (C=C), 1159 cm^{-1} (C-N).

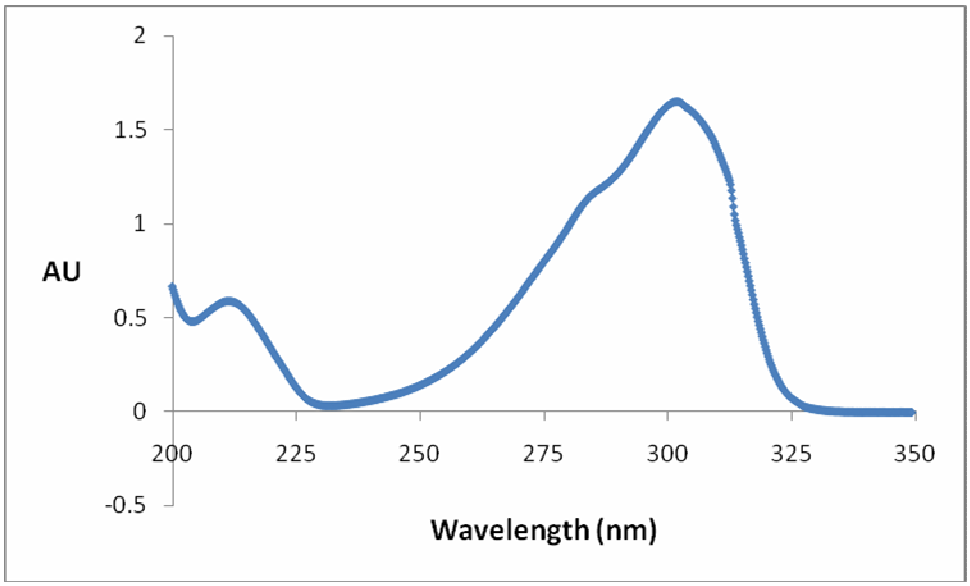

Figure S15. UV-Visible spectrum of **(3b)** in H_2O.

(3.2) 1, 1'-Methylenebis(4-t-butylpyridinium) dichloride (3c).

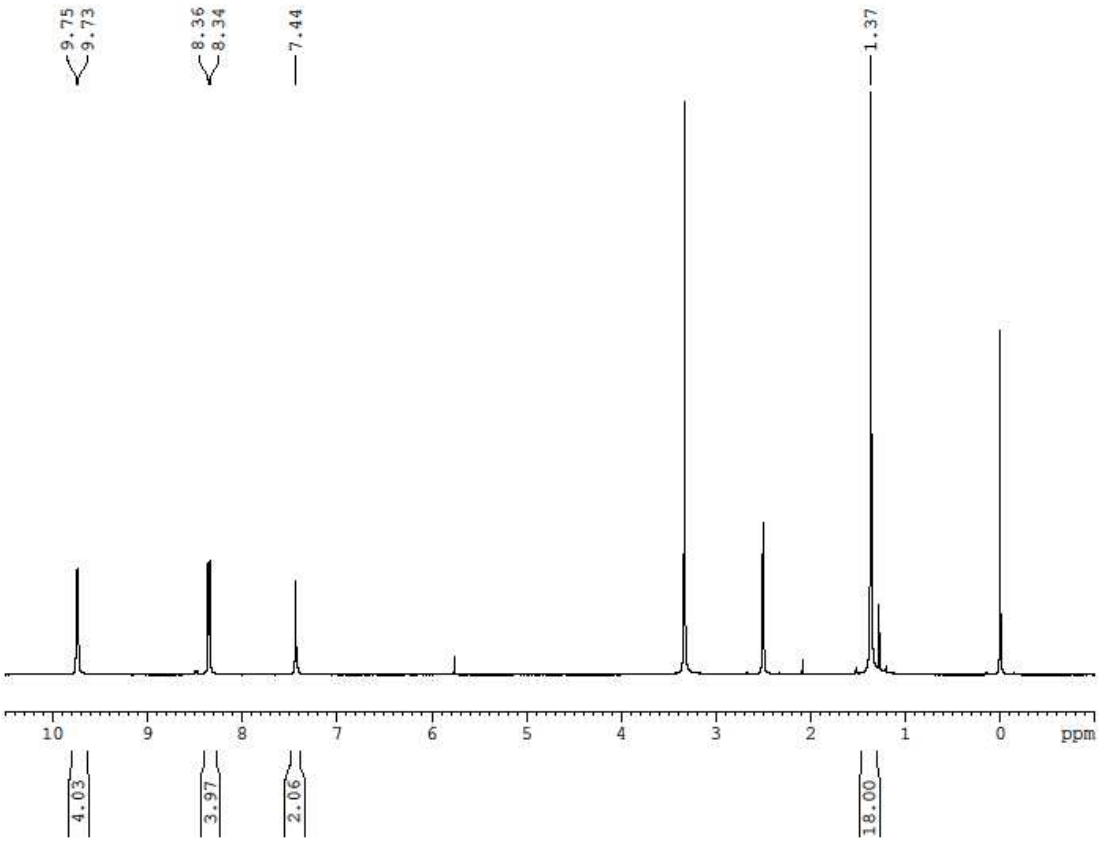

Figure S16. Proton NMR spectrum of compound **3c** in DMSO-d_6. The peaks at 2.5 and 3.4 ppm are DMSO and H_2O respectively.

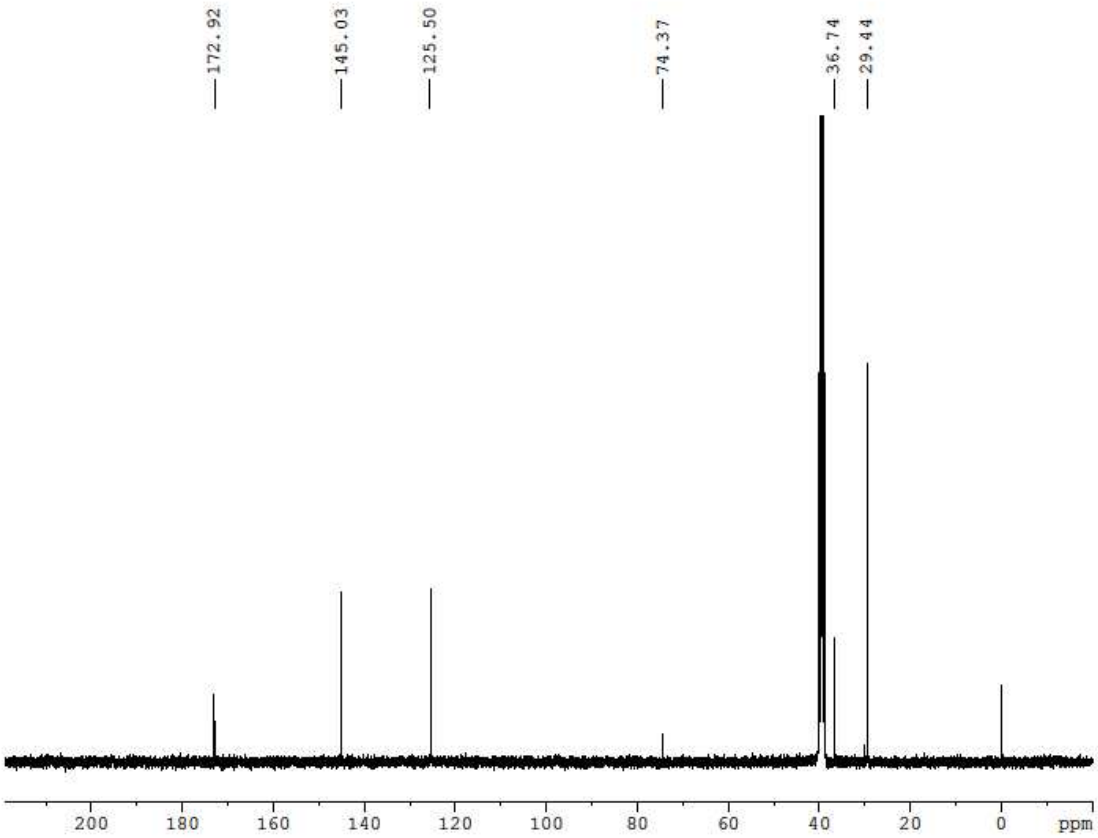

Figure S17. Carbon NMR spectrum of compound **3c** in DMSO-d_6.

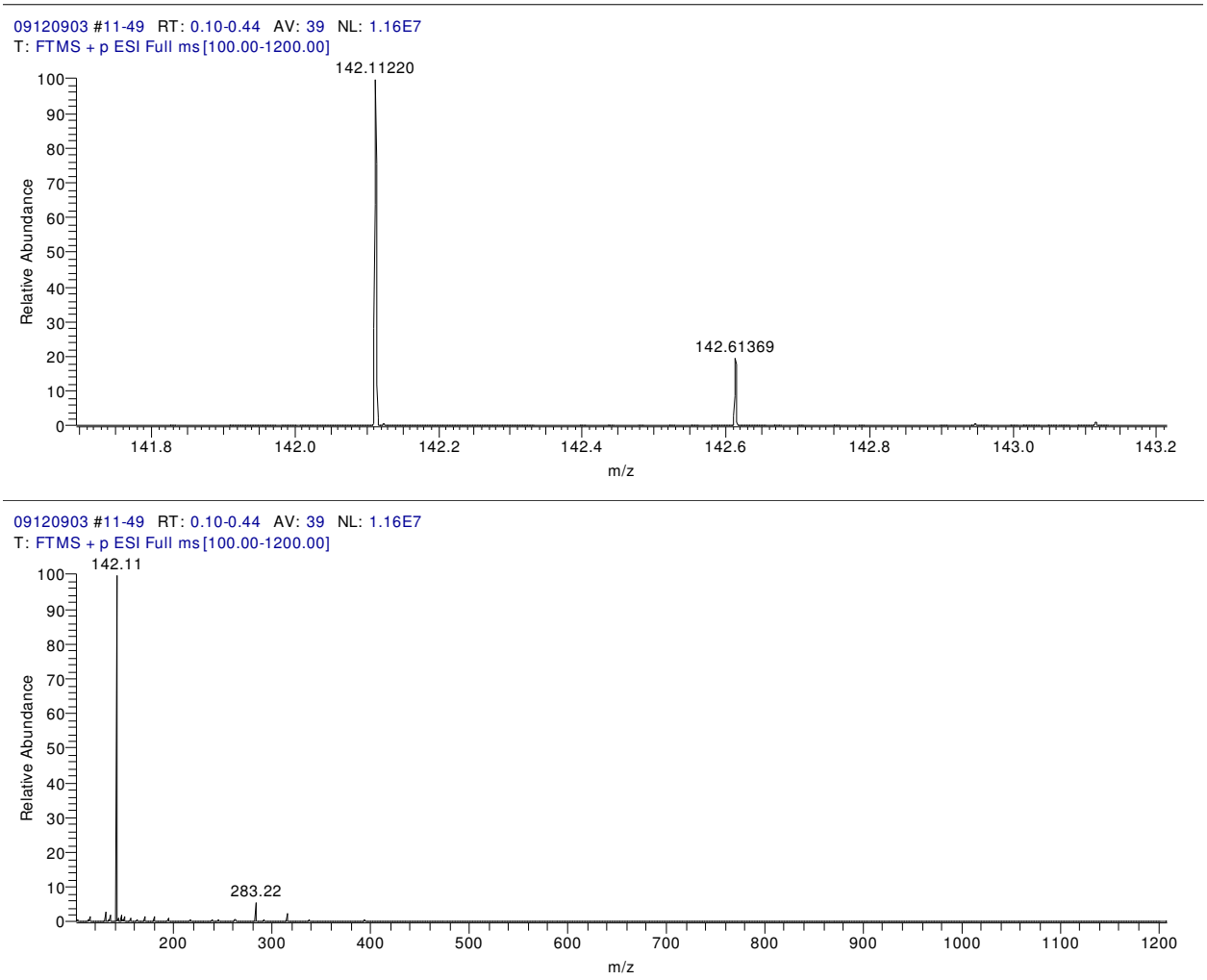

Figure S18. ESI (positive mode) HRMS of compound **3c**, showing the peak for the M^{2+} ion without Cl^- counterions.

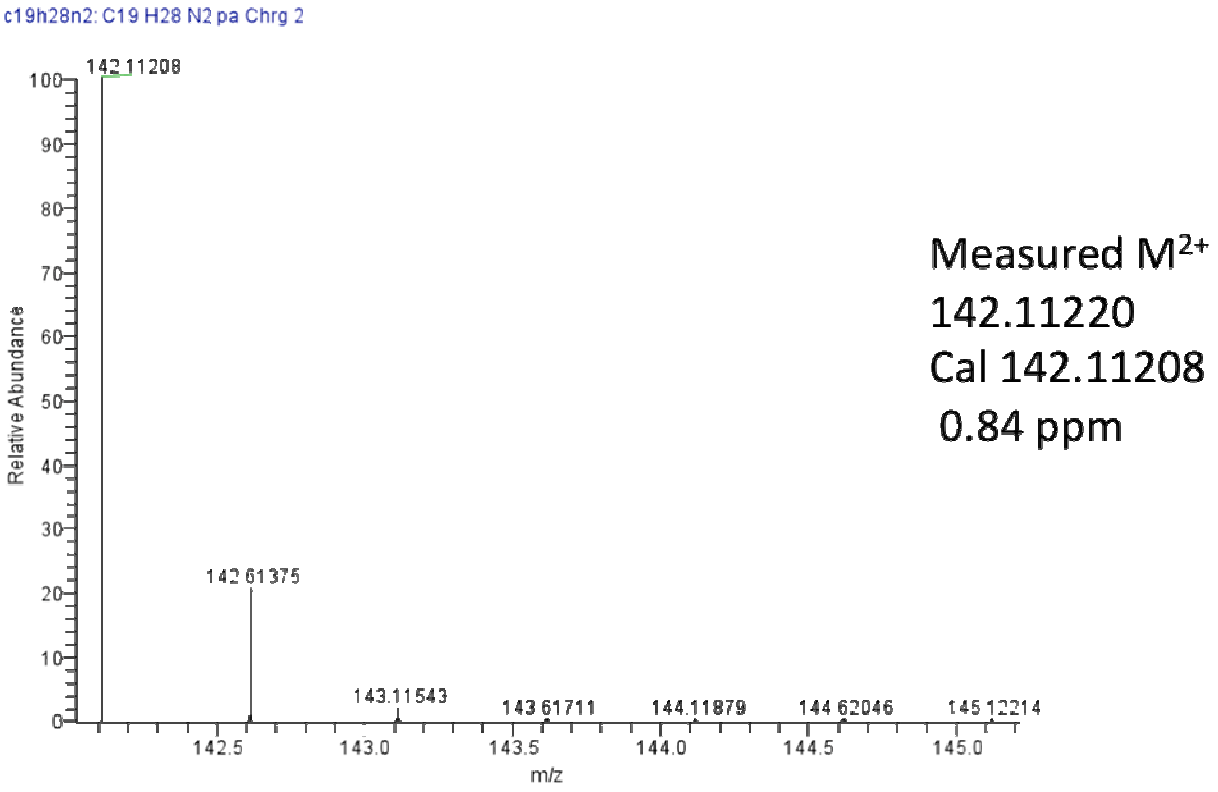

Figure S19. Calculated ESI (positive mode) HRMS spectrum for compound **3c**, M^{2+} ion without Cl^- counterions.

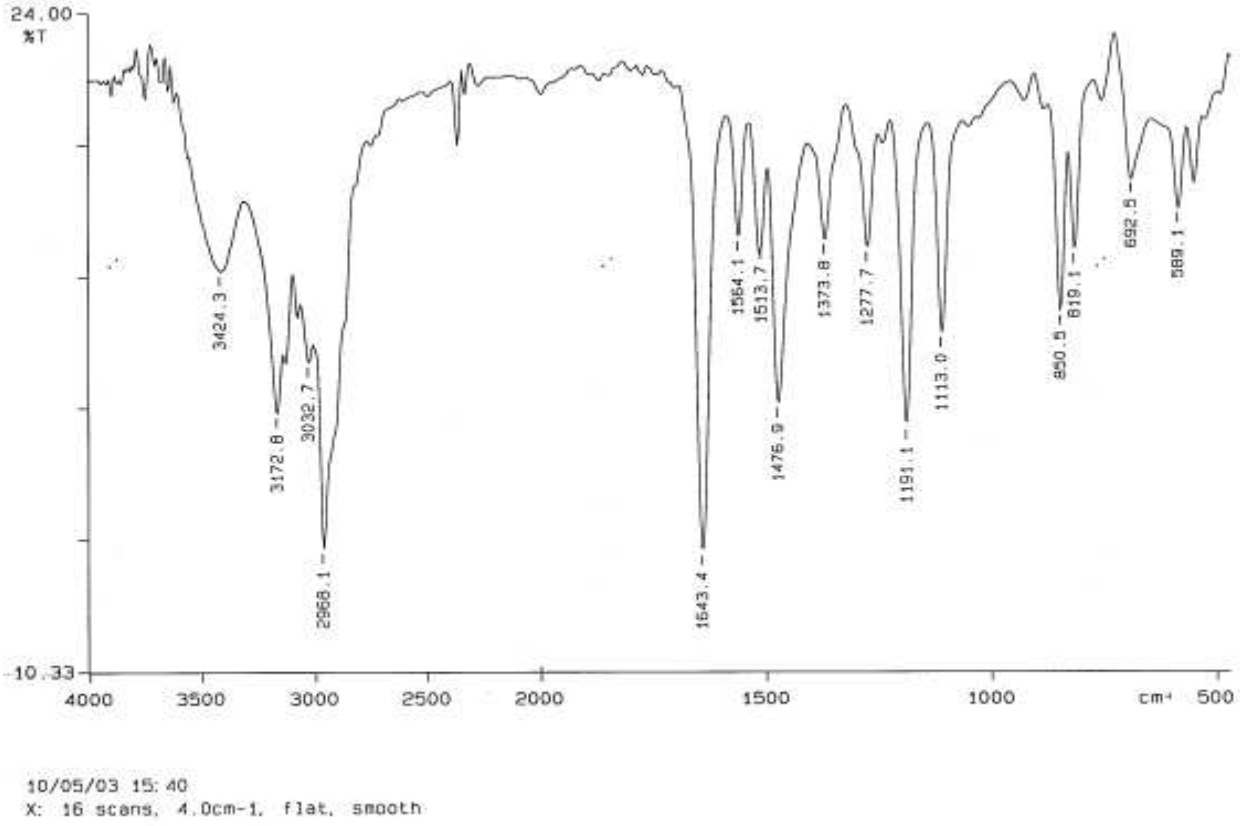

Figure S20. IR spectrum (KBr pellet) of compound **3c** showing vibrations at 3032 cm^{-1} (=C-H), 2968 cm^{-1} (-C-H), 1643 and 1476 cm^{-1} (C=C), 1191 cm^{-1} (C-N).

(3.3) 1, 1'-Methylenebis(4-aminopyridinium) dichloride (3d).

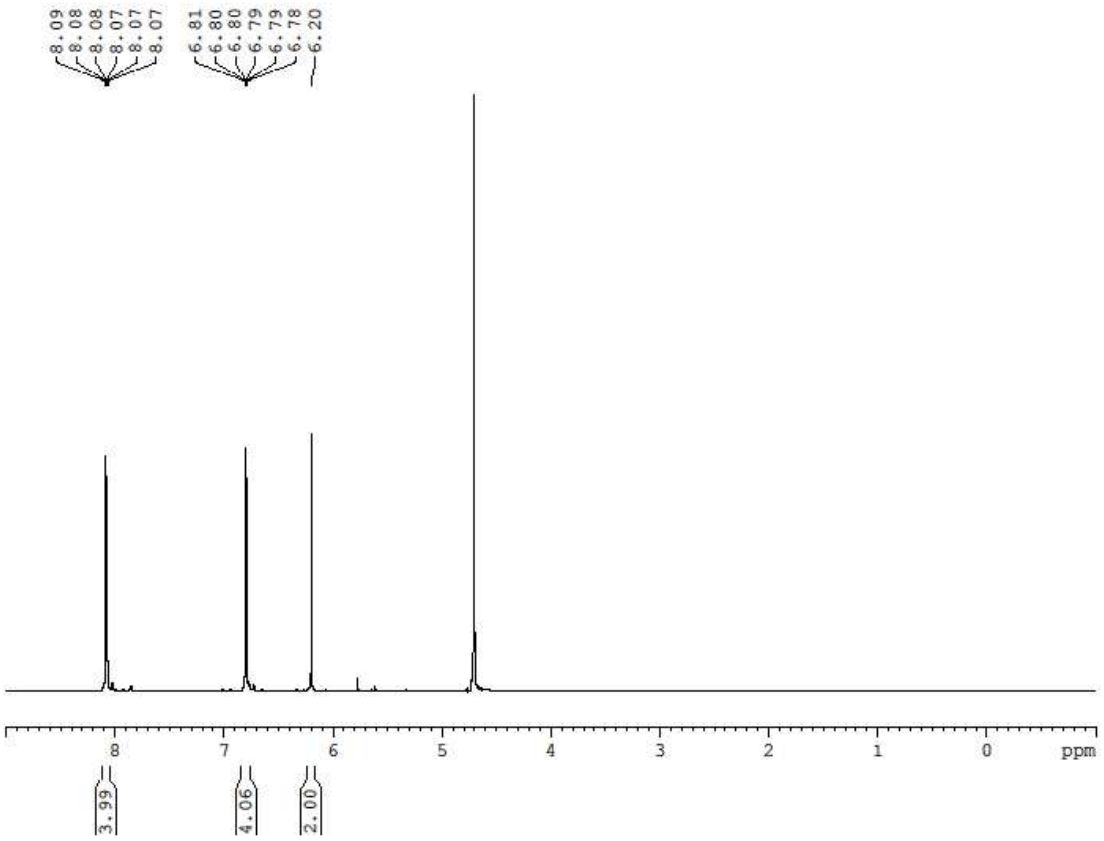

Figure S21. Proton NMR spectrum of compound **3d** in D_2O.

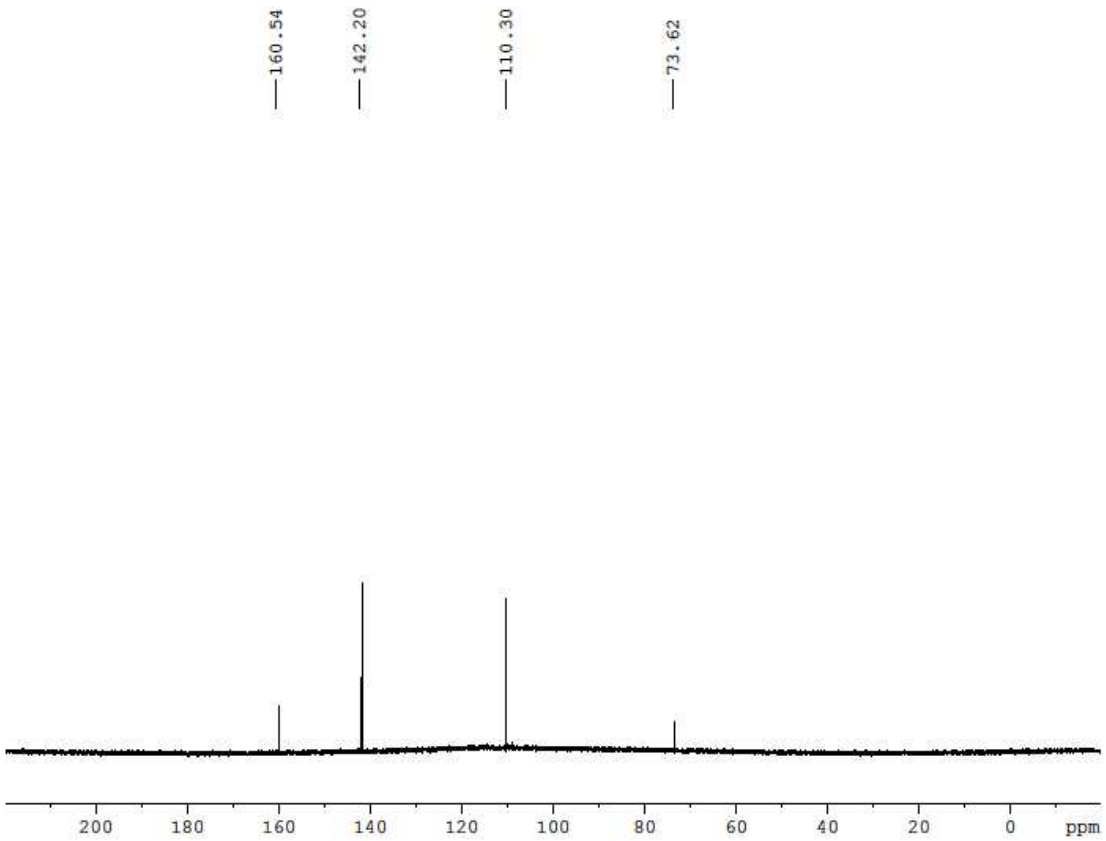

Figure S22. Carbon NMR spectrum of compound **3d** in D_2O.

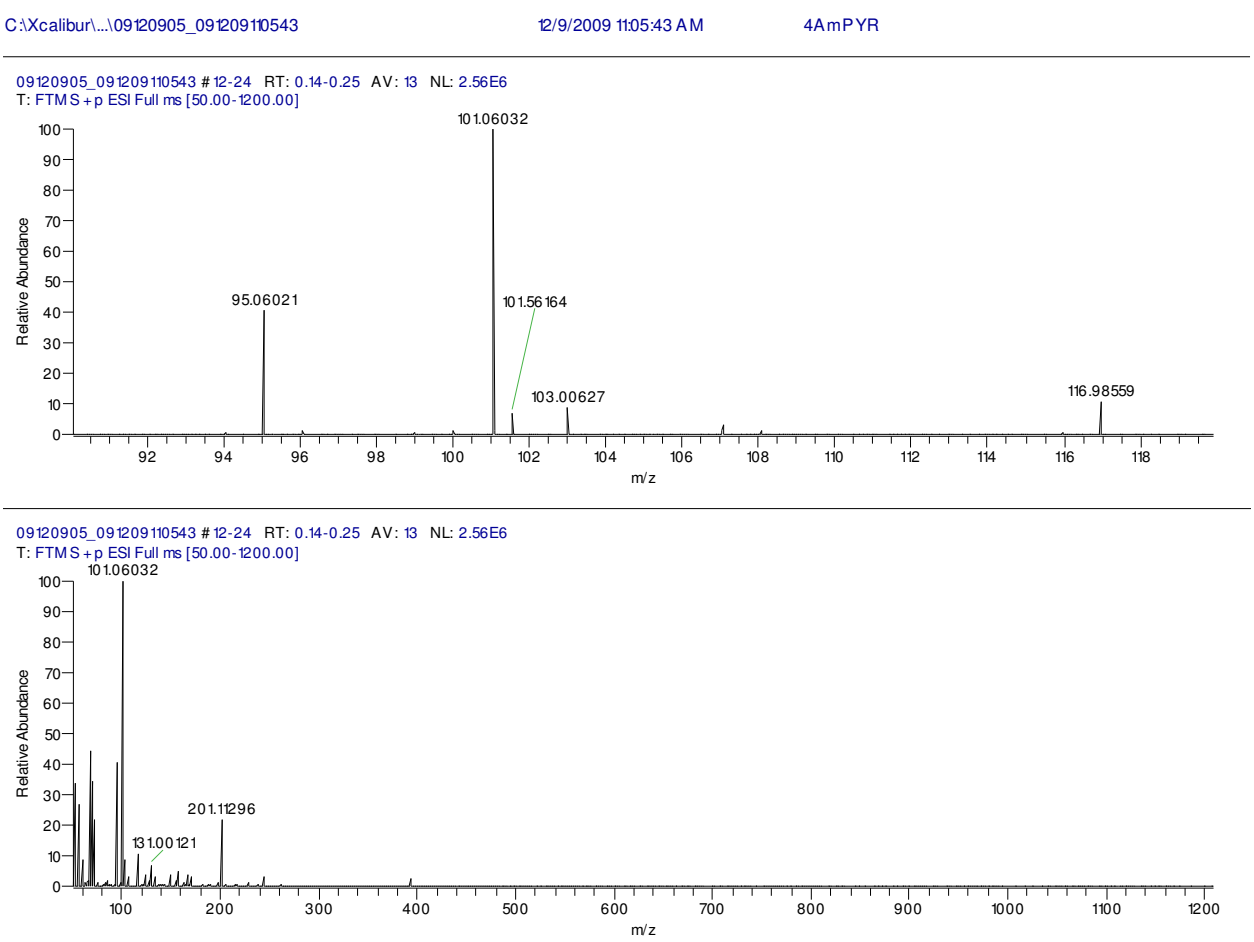

Figure S23. ESI (positive mode) HRMS of compound **3d**, showing the peak for the M^{2+} ion without Cl^- counterions.

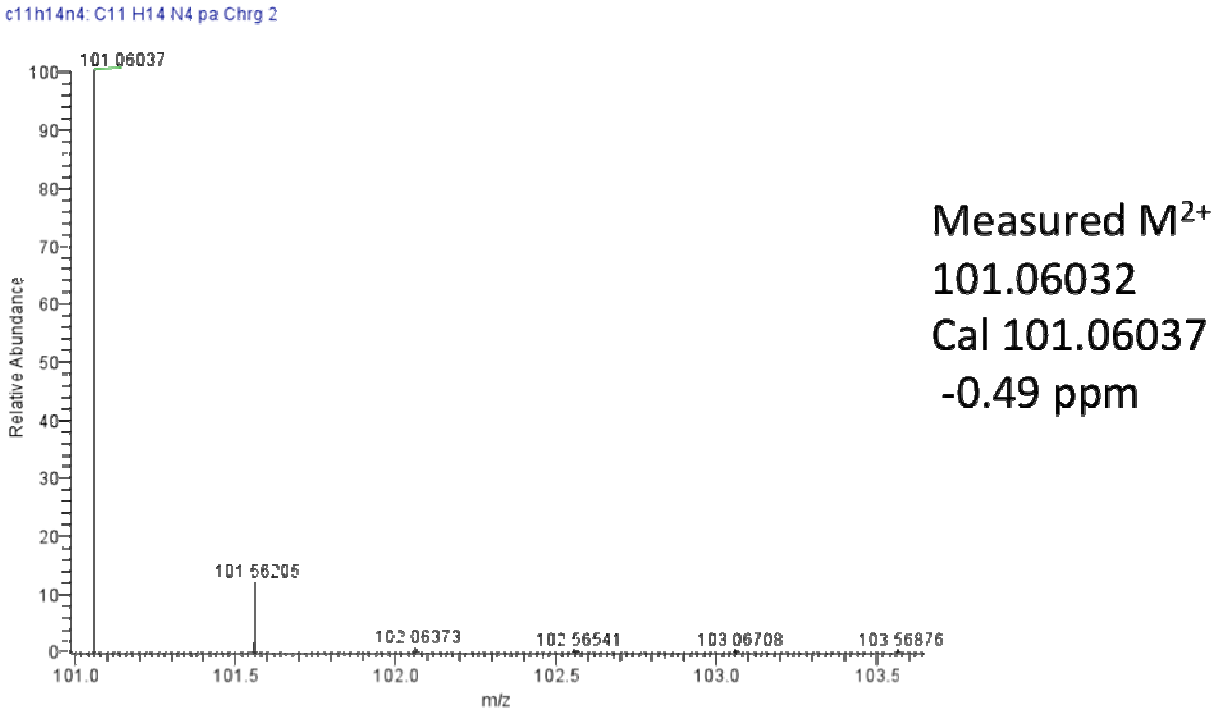

Figure S24. Calculated ESI (positive mode) HRMS spectrum for compound **3d**, M^{2+} ion without Cl^- counterions.

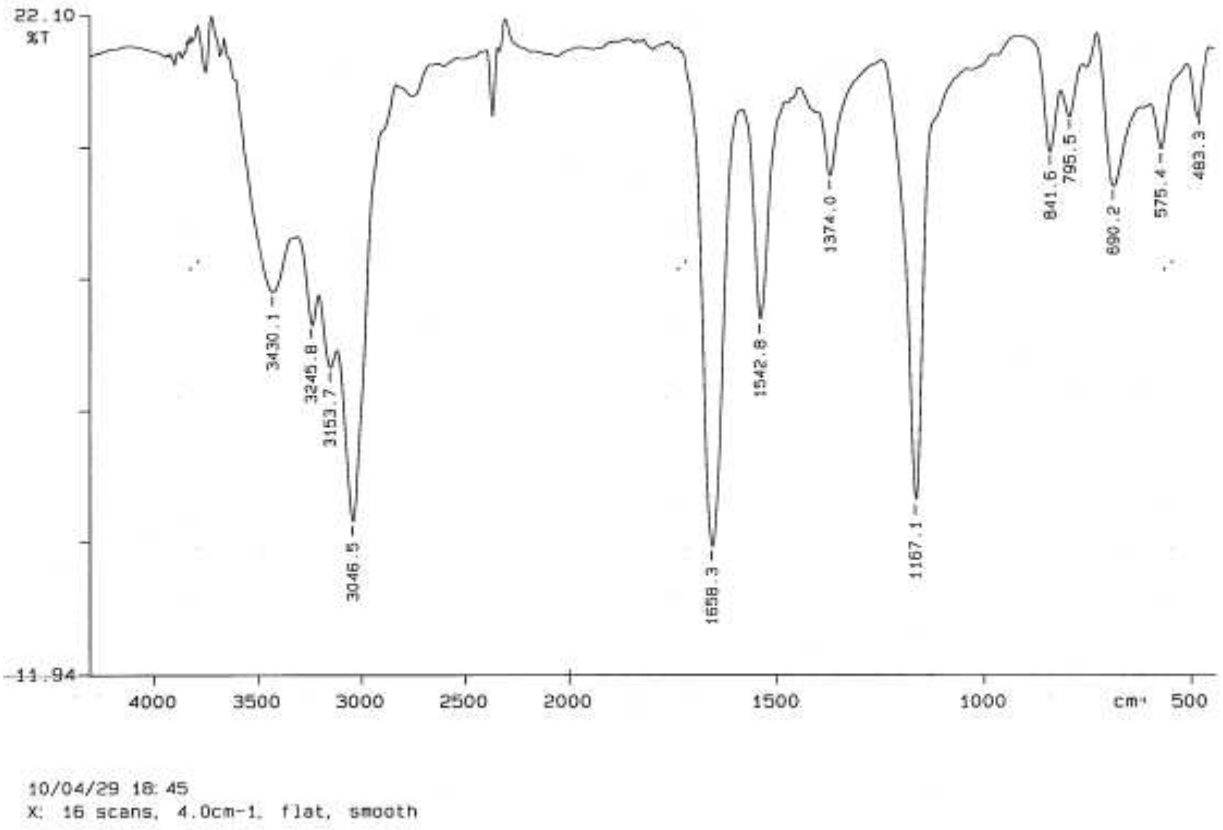

Figure S25. IR spectrum (KBr pellet) of compound **3d** showing vibrations at 3245 and 3153 (NH_2), 3046 cm^{-1} (=C-H), 1658 and 1542 cm^{-1} (C=C), 1167 cm^{-1} (C-N).

(3.4) 1, 1'-Methylenebis(3-aminopyridinium) dichloride (3e).

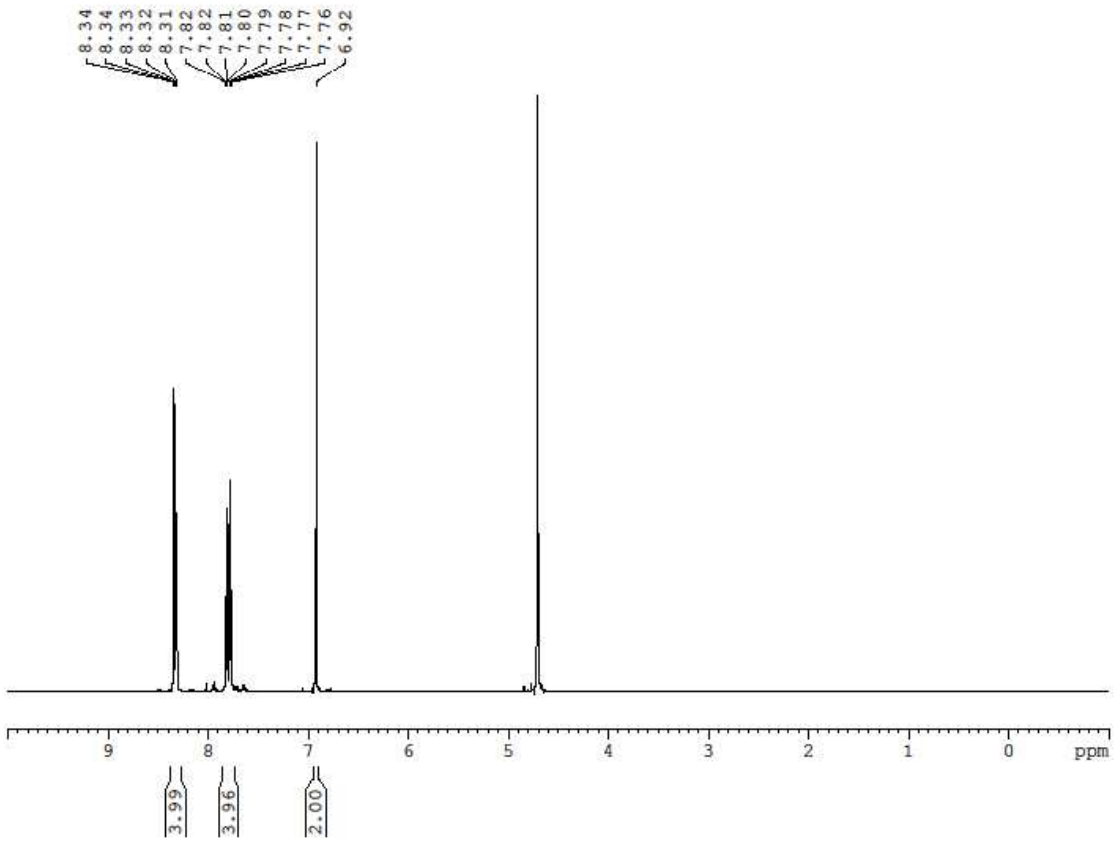

Figure S26. Proton NMR spectrum of compound **3e** in D_2O.

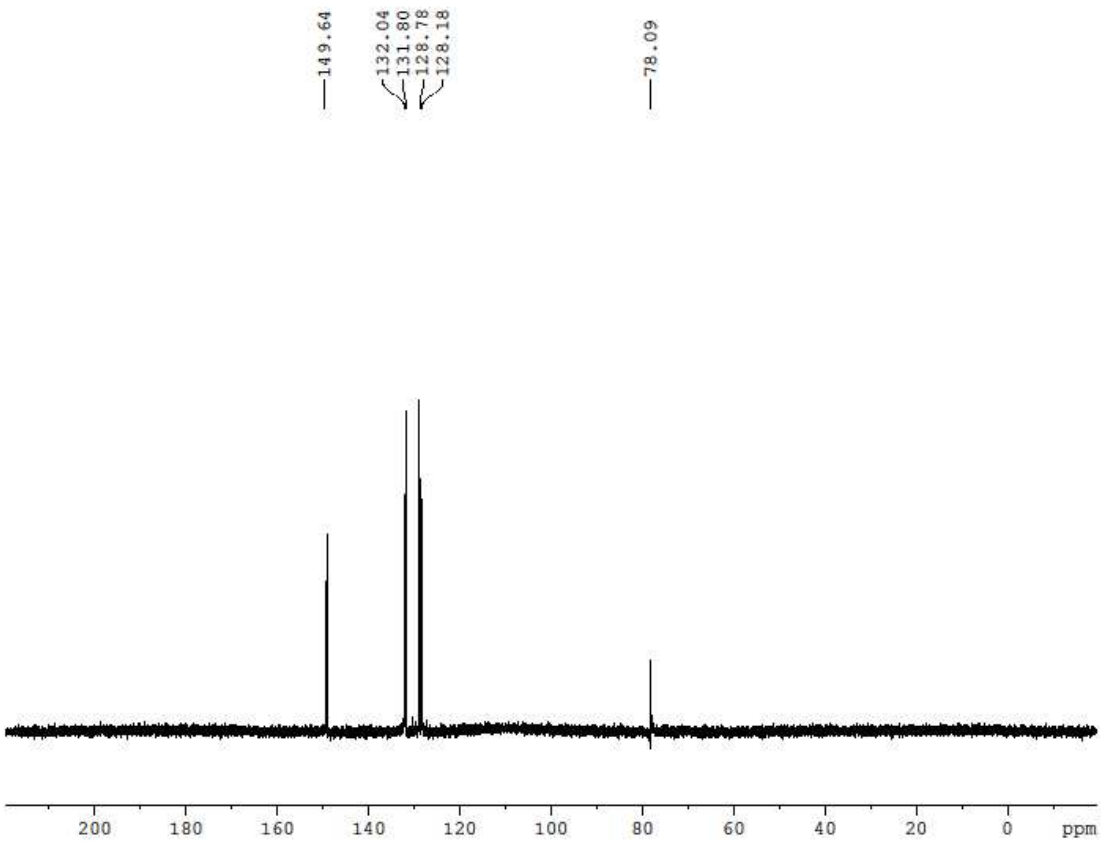

Figure S27. Carbon NMR spectrum of compound **3e** in D_2O.

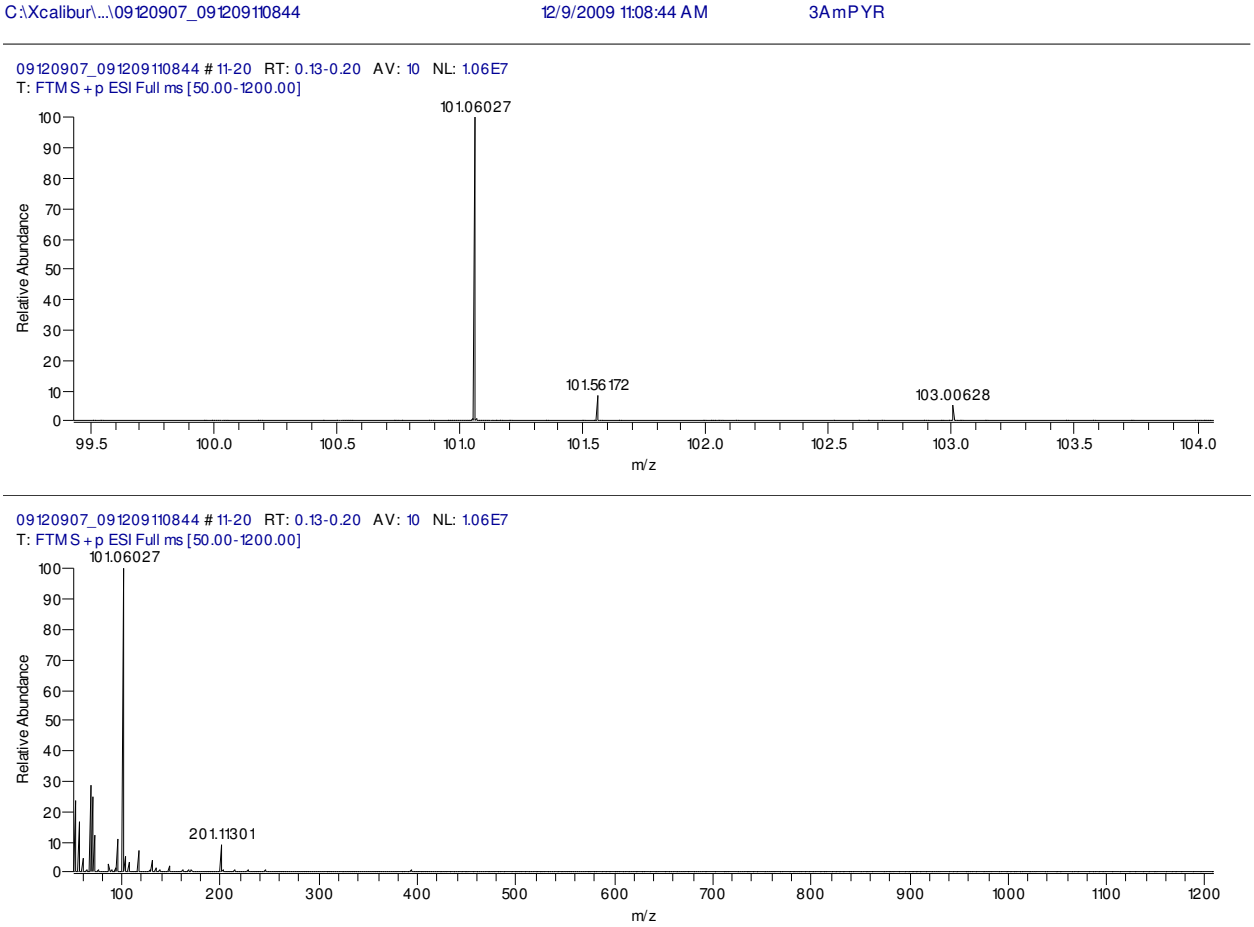

Figure S28. ESI (positive mode) HRMS of compound **3e**, showing the peak for the M^{2+} ion without Cl^- counterions.

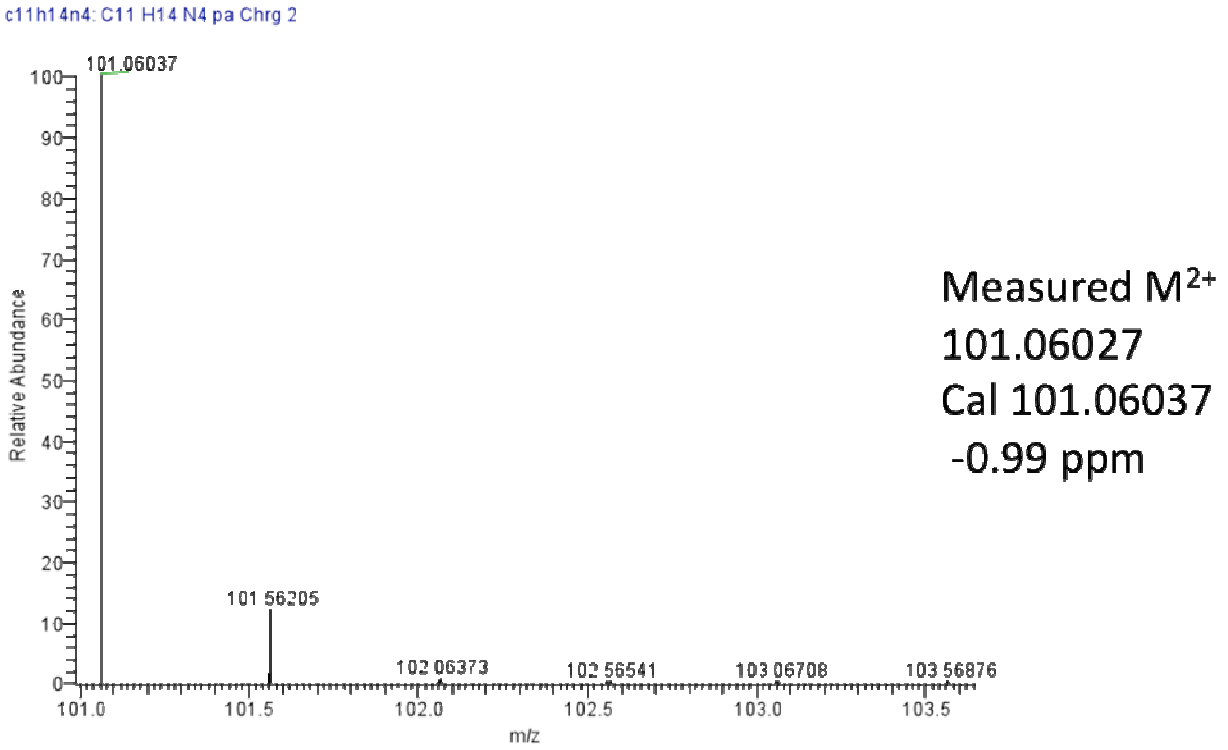

Figure S29. Calculated ESI (positive mode) HRMS spectrum for compound **3e**, M^{2+} ion without Cl^- counterions.

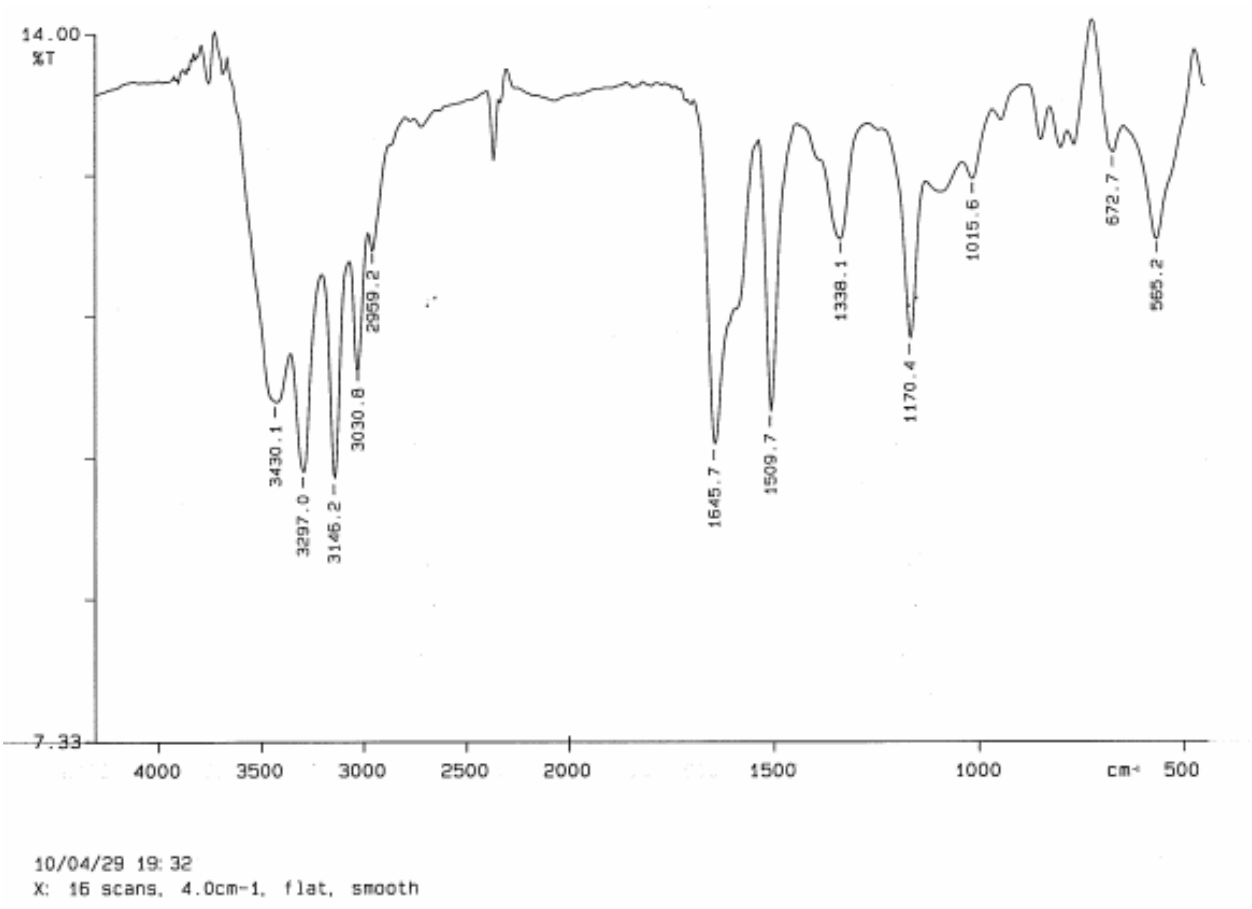

Figure S30. IR spectrum (KBr pellet) of compound **3e** showing vibrations at 3297 and 3146 cm^{-1} (NH_2) 3030 cm^{-1} (=C-H), 2959 cm^{-1} (-C-H), 1645 and 1509 cm^{-1} (C=C), 1170 cm^{-1} (C-N).

(3.5) 1, 1'-Methylenebis(4-γ-pyridylpyridinium) dichloride (3f).

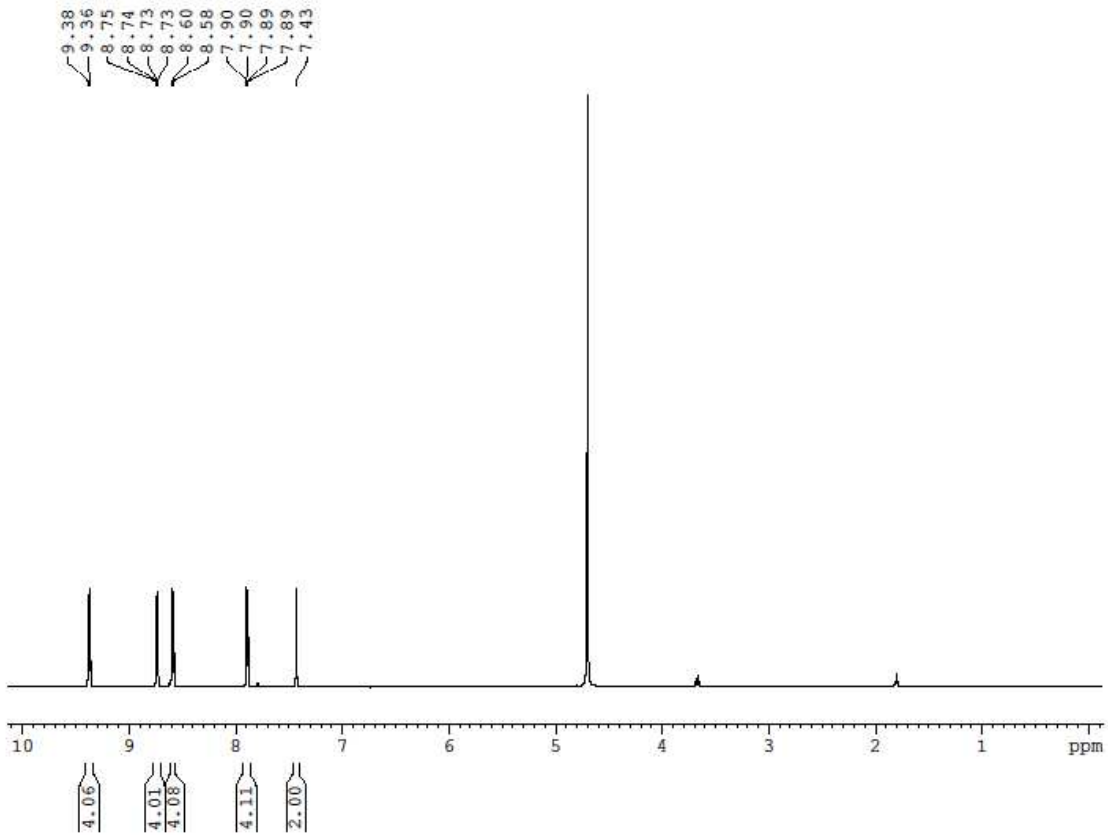

Figure S31. Proton NMR spectrum of compound**3f** in D_2O. Peaks at 1.76 and 3.60 ppm are residual solvent peaks (THF).

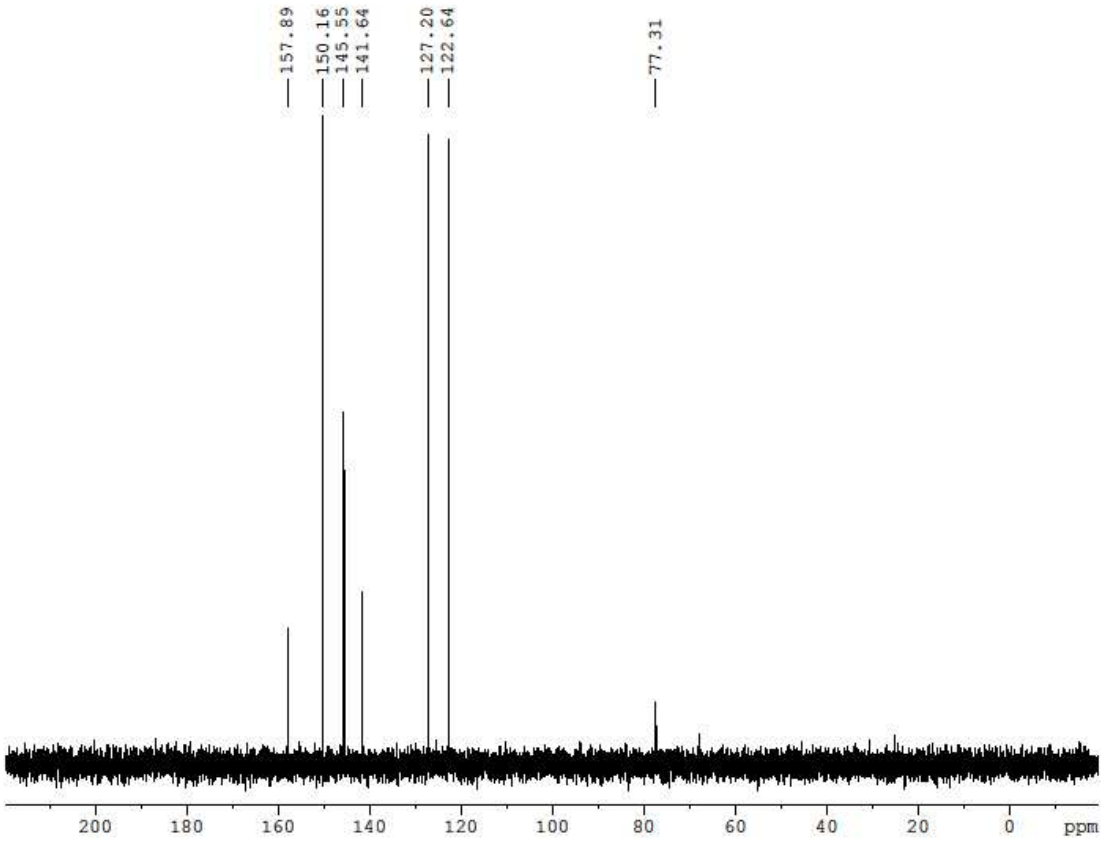

Figure S32. Carbon NMR spectrum of compound **3f** in D_2O.

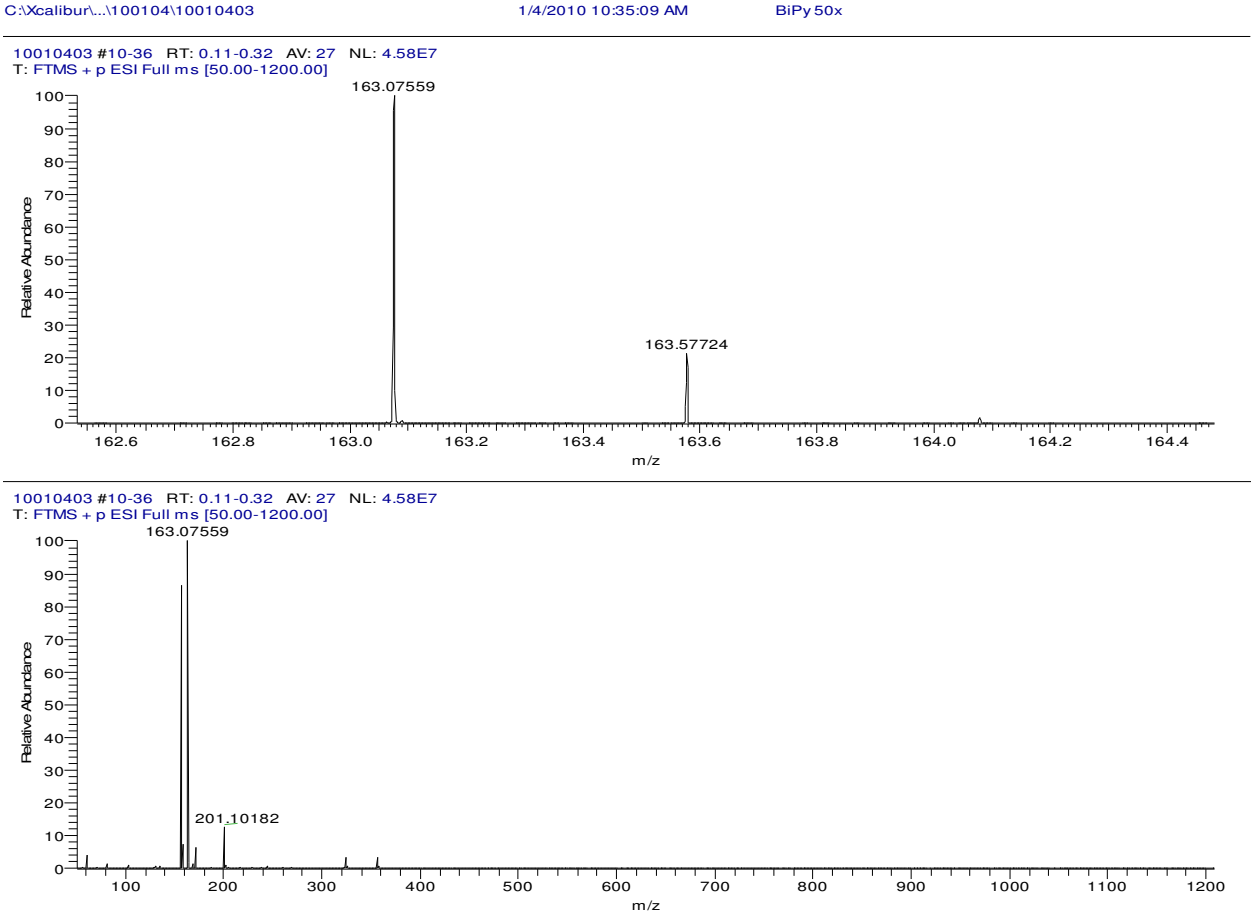

Figure S33. ESI (positive mode) HRMS of compound **3f**, showing the peak for the M^{2+} ion without Cl^- counterions.

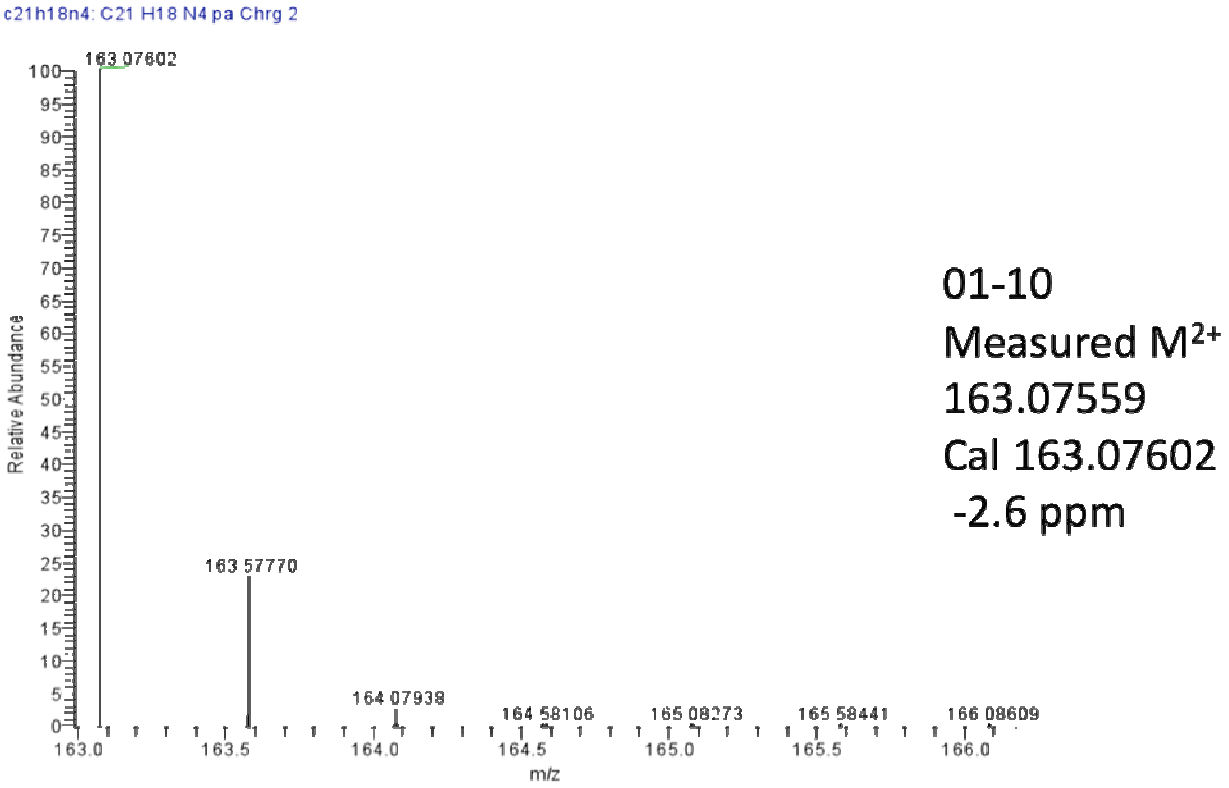

Figure S34. Calculated ESI (positive mode) HRMS spectrum for compound **3f**, M^{2+} ion without Cl^- counterions.

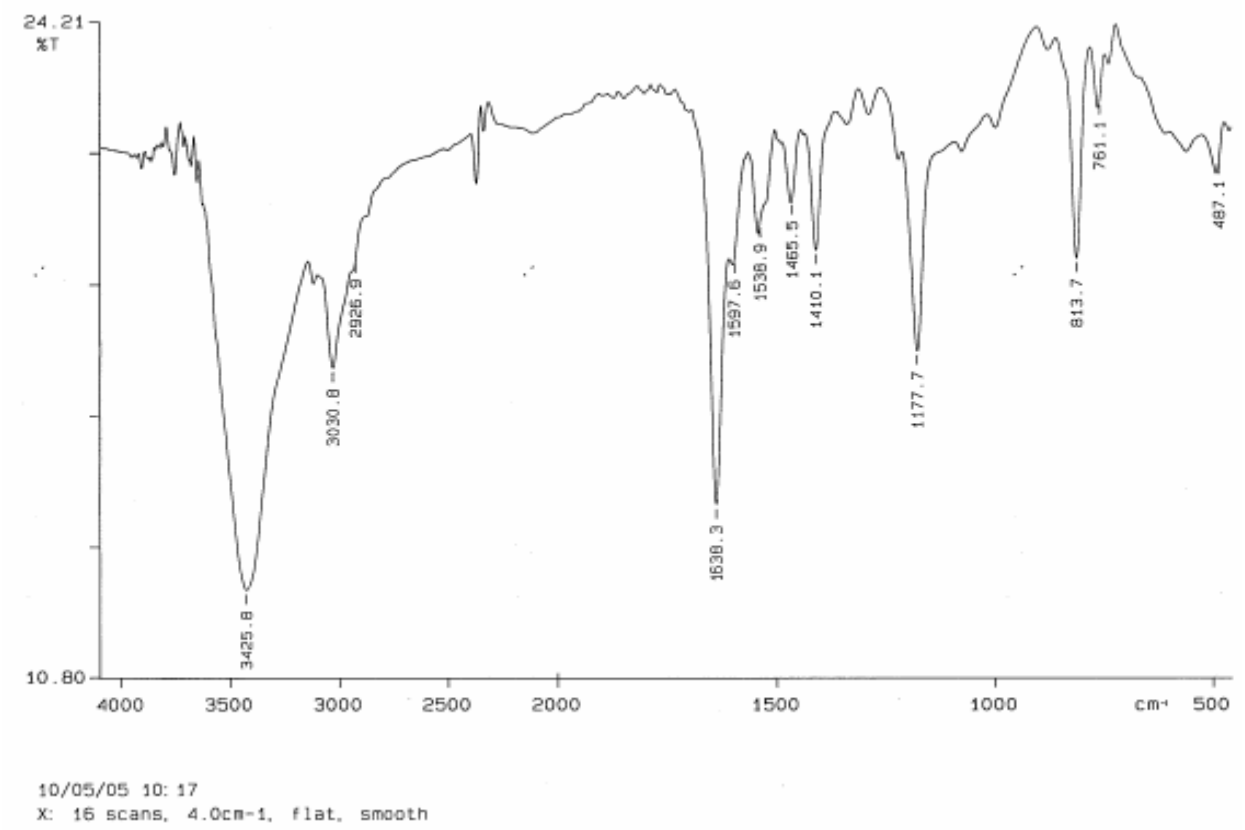

Figure S35. IR spectrum (KBr pellet) of compound **3e** showing vibrations at 3030 cm^{-1} (=C-H), 2926 cm^{-1} (-C-H), 1638 and 1538 cm^{-1} (C=C), 1177 cm^{-1} (C-N).

(4) Kinetic Plots and Calculations

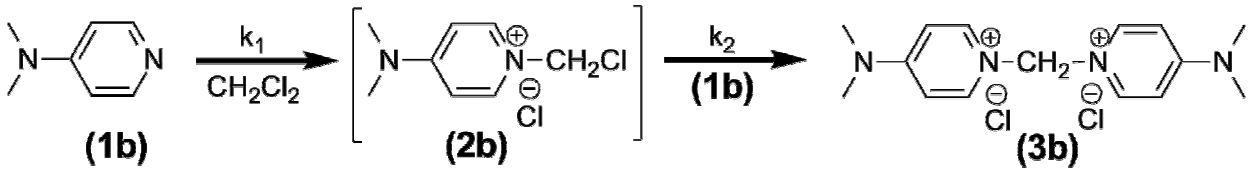

Figure S36. Proposed mechanism for the reaction of DCM and DMAP.

(4.1) Kinetic plots for the overall process 2(1b) + DCM → 3b runs 1-4.

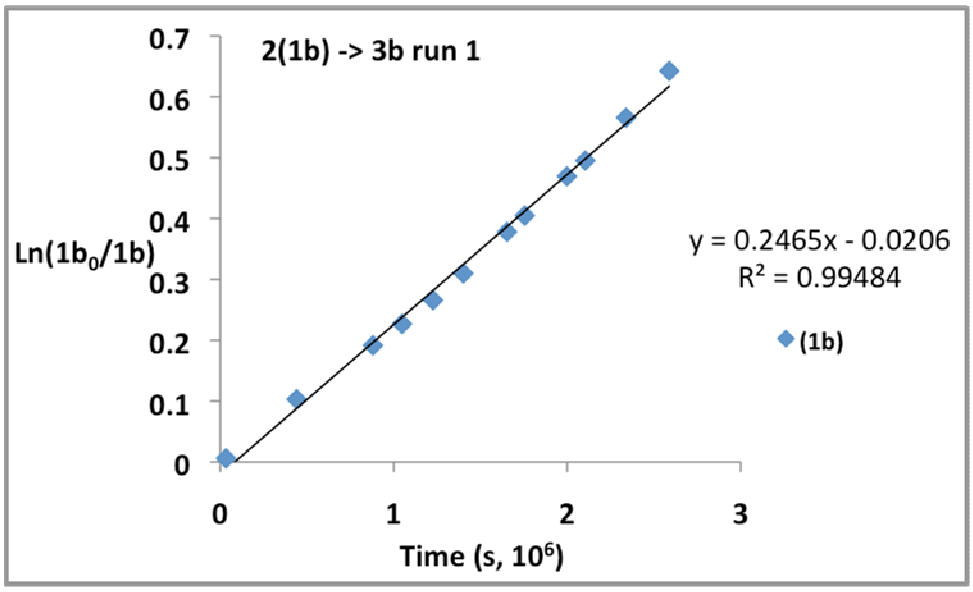

Figure S37. Pseudo 1st order kinetic plot for the reaction 2**(1b) + DCM (excess) → 3b** run 1. The slope of the plot is used to calculate the 2nd order rate constant k_1.

Since in the overall process intermediate **2b** is not isolated or observed we estimate $k_2 >> k_1$ and that the observed rate constant is approximately equal to the 2nd order rate constant for the first step.

Slope = $2k_1*[DCM]_0$

k_1 = slope/$2[DCM]_0$ initial concentration of DCM is 5.04 M

k_1 (run 1) = 2.47 x 10^{-8} $M^{-1}s^{-1}$

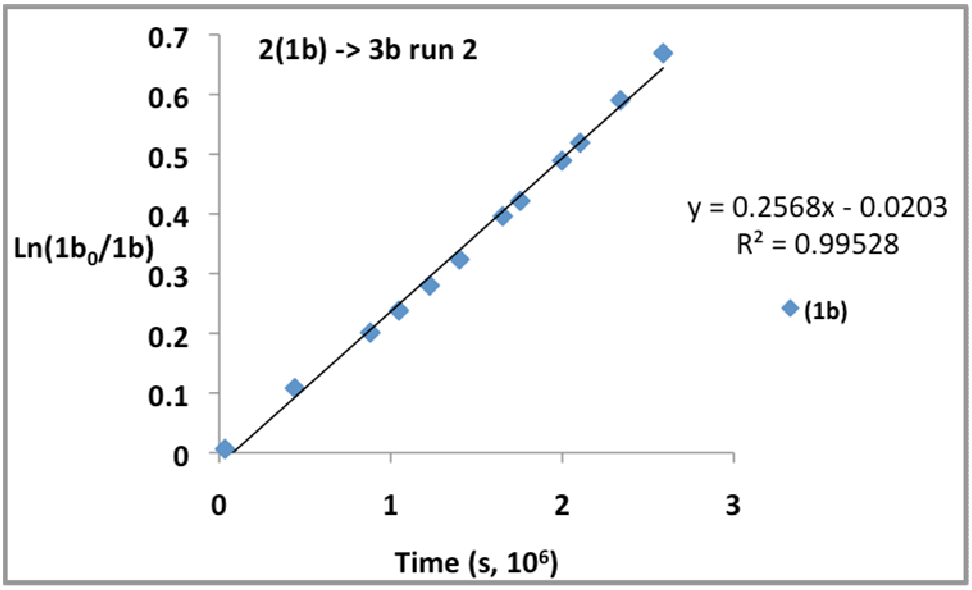

Figure S38. Pseudo 1st order kinetic plot for the reaction **2(1b) + DCM (excess) → 3b** (run 2). The slope of the plot is used to calculate the 2nd order rate constant k_1.

k_1 (run 2) = 2.57 x 10^{-8} $M^{-1}s^{-1}$

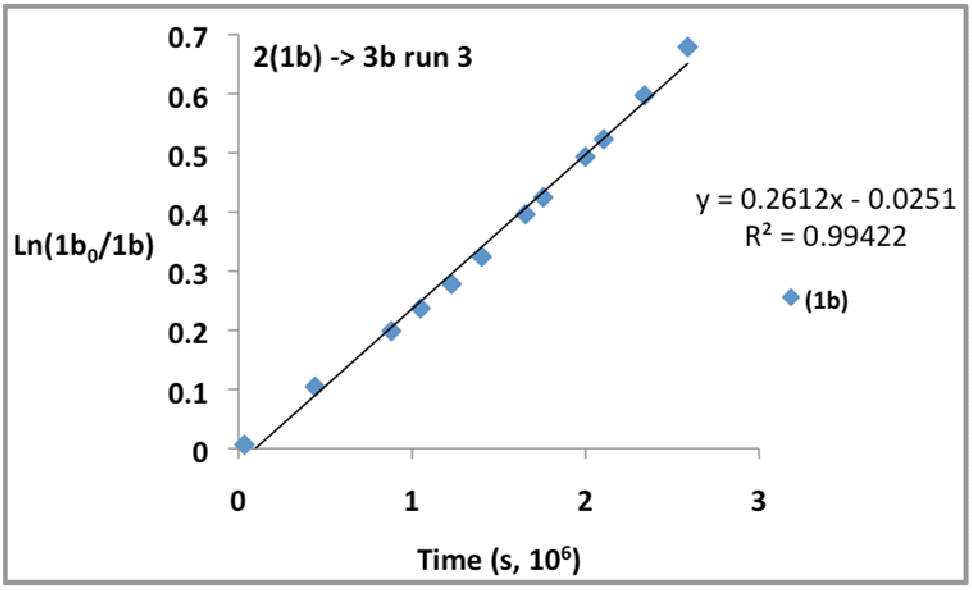

Figure S39. Pseudo 1st order kinetic plot for the reaction **2(1b) + DCM (excess) → 3b** (run 3). The slope of the plot is used to calculate the 2nd order rate constant k_1.

k_1 (run 3) = 2.61 x 10^{-8} $M^{-1}s^{-1}$

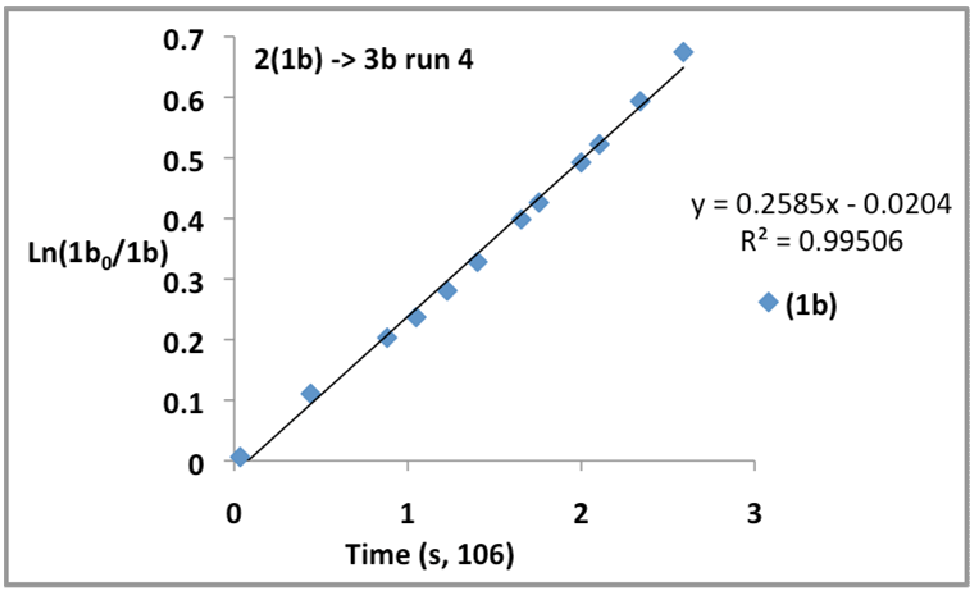

Figure S40. Pseudo 1st order kinetic plot for the reaction **2(1b) + DCM (excess) → 3b** (run 4). The slope of the plot is used to calculate the 2nd order rate constant k_1.

k_1 (run 4) = 2.54 x 10^{-8} $M^{-1}s^{-1}$

k_1 (ave) = 2.56(± 0.06) x 10^{-8} $M^{-1}s^{-1}$

(4.2) Kinetic plots for the second step reaction 1b + 2b → 3b runs 1-4.

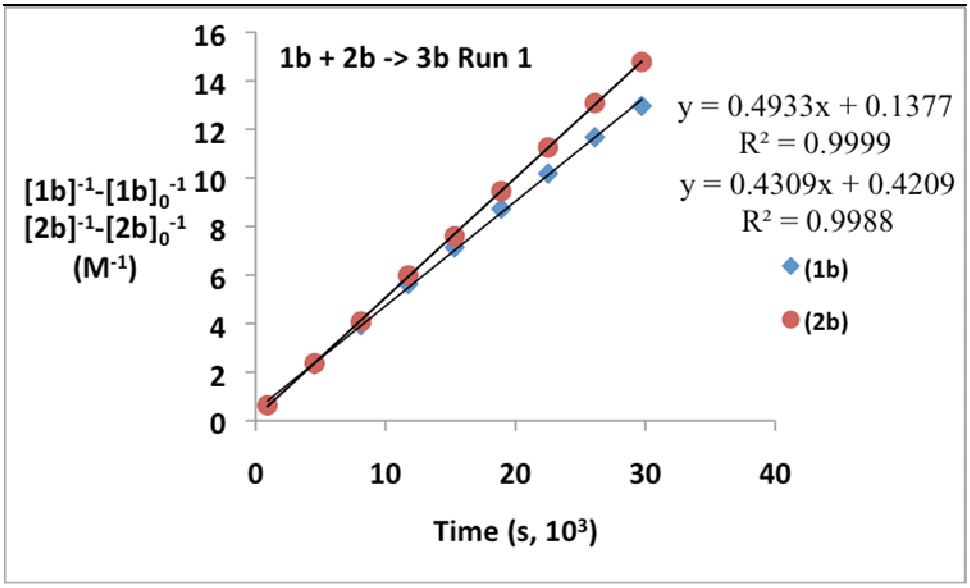

Figure S41. 2nd order kinetic plot for the reaction **1b + 2b → 3b** (run 1). The slope of the plot is the 2nd order rate constant for the second step reaction. The slope in terms of both **1b** and intermediate **2b** are shown.

$k_{2(\mathbf{1b})}$ (run 1) = 4.31 x 10^{-4} $M^{-1}s^{-1}$

$k_{2(\mathbf{2b})}$ (run 1) = 4.93 x 10^{-4} $M^{-1}s^{-1}$

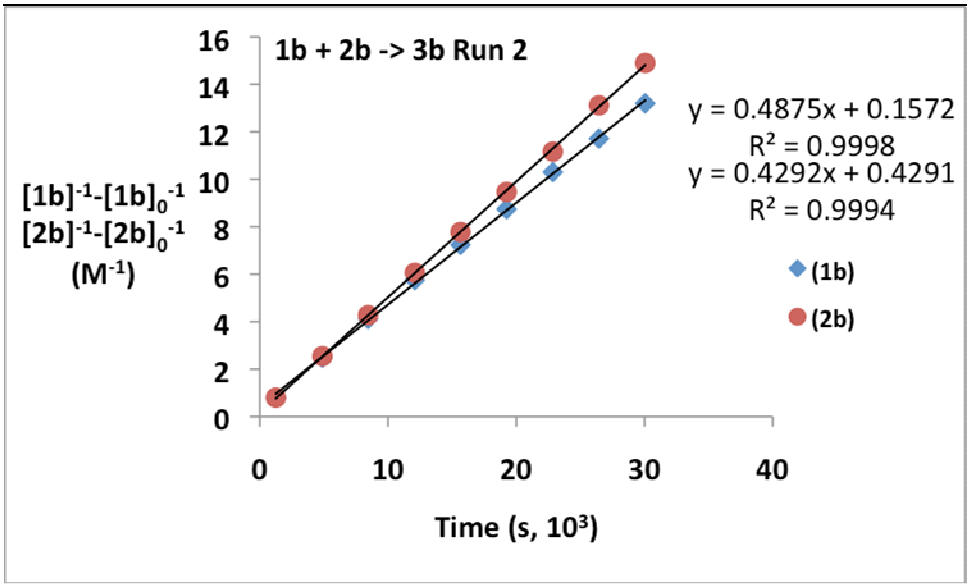

Figure S42. 2nd order kinetic plot for the reaction **1b + 2b → 3b** (run 2). The slope of the plot is the 2nd order rate constant for the second step reaction. The slope in terms of both **1b** and intermediate **2b** are shown.

$k_{2(\mathbf{1b})}$ (run 2) = 4.29 x 10^{-4} $M^{-1}s^{-1}$
$k_{2(\mathbf{2b})}$ (run 2) = 4.88 x 10^{-4} $M^{-1}s^{-1}$

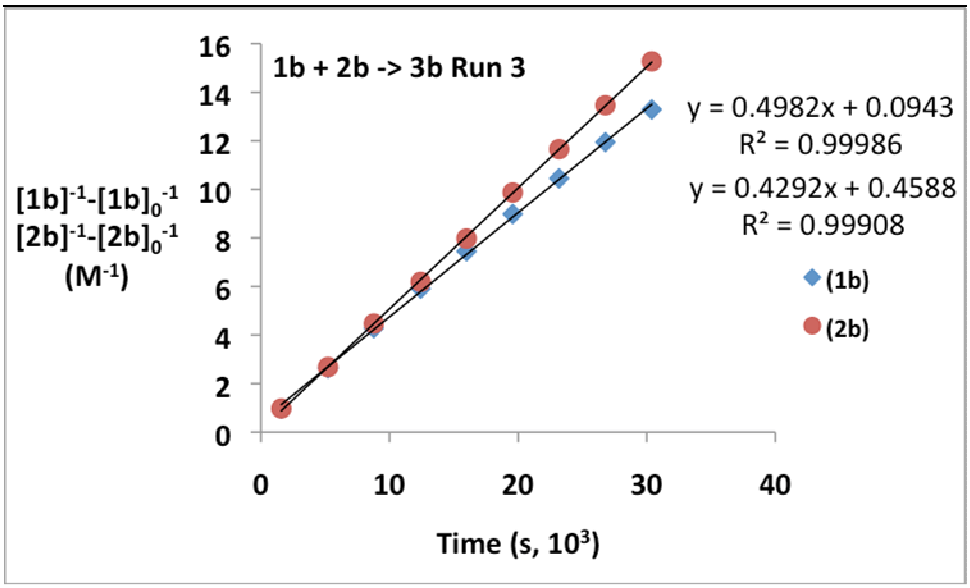

Figure S43. 2nd order kinetic plot for the reaction **1b + 2b → 3b** (run 3). The slope of the plot is the 2nd order rate constant for the second step reaction. The slope in terms of both **1b** and intermediate **2b** are shown.

$k_{2(\mathbf{1b})}$ (run 3) = 4.29 x 10^{-4} $M^{-1}s^{-1}$
$k_{2(\mathbf{2b})}$ (run 3) = 4.98 x 10^{-4} $M^{-1}s^{-1}$

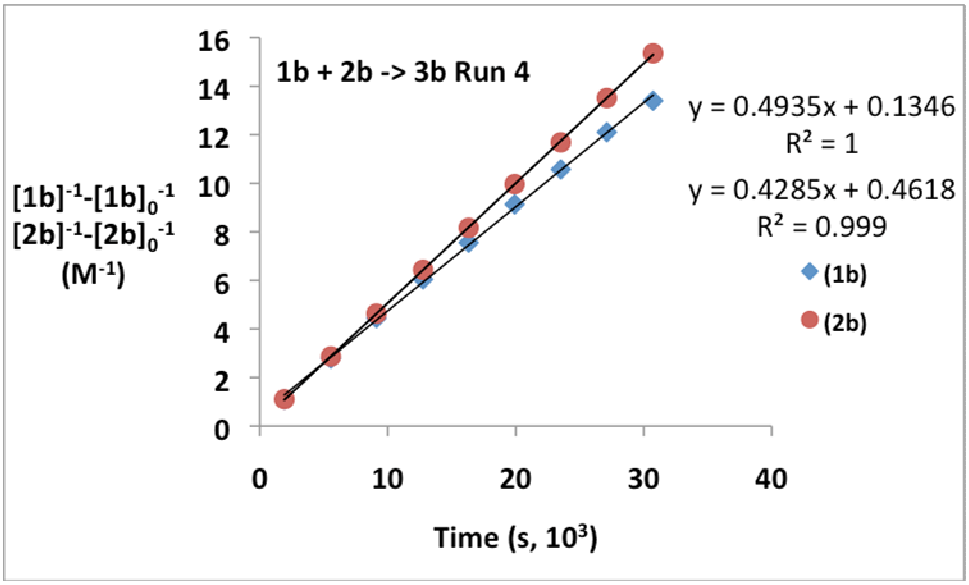

Figure S44. 2nd order kinetic plot for the reaction **1b + 2b → 3b** (run 4). The slope of the plot is the 2nd order rate constant for the second step reaction. The slope in terms of both **1b** and intermediate **2b** are shown.

$k_{2(\mathbf{1b})}$ (run 4) = 4.29 x 10^{-4} $M^{-1}s^{-1}$

$k_{2(\mathbf{2b})}$ (run 4) = 4.94 x 10^{-4} $M^{-1}s^{-1}$

$k_{2(\mathbf{1b})}$ (ave) = 4.29(±0.01) x 10^{-4} $M^{-1}s^{-1}$

$k_{2(\mathbf{2b})}$ (ave) = 4.93(±0.04) x 10^{-4} $M^{-1}s^{-1}$

Reaction rate comparison between the 1st and 2nd step.

$k_{2(\mathbf{1b})}/k_1$ = ~17,000

$k_{2(\mathbf{2b})}/k_1$ = ~20,000

Intermediate concentration [2b] at the steady state.

Based on the steady state approximation: $k_1[\mathbf{1b}][DCM]_o = k_2[\mathbf{1b}][\mathbf{2b}]$.

$(k_1/k_{2(\mathbf{1b})})[5.04]_o = [\mathbf{2b}]$ = 2.9 x 10^{-4} M at steady state

$(k_1/k_{2(\mathbf{2b})})[5.04]_o = [\mathbf{2b}]$ = 2.5 x 10^{-4} M at steady state

[**2b**] = 2.9 x 10^{-4} M at steady state

(4.3) Full ^{1}H NMR spectra for the overall reaction and for the 2nd step reaction

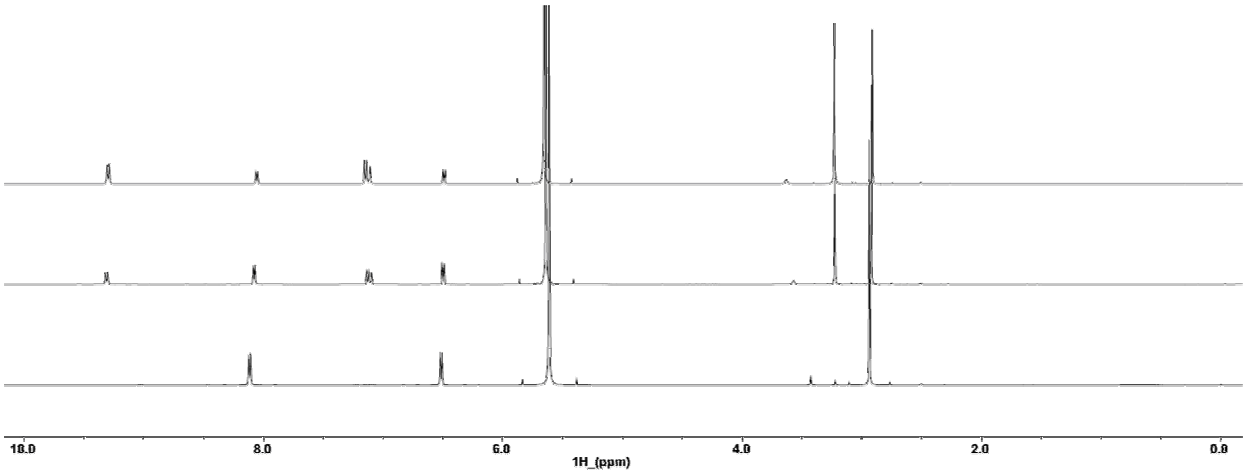

Figure S45. 400 MHz proton NMR spectra for the overall reaction between DMAP and DCM to form **3b**.

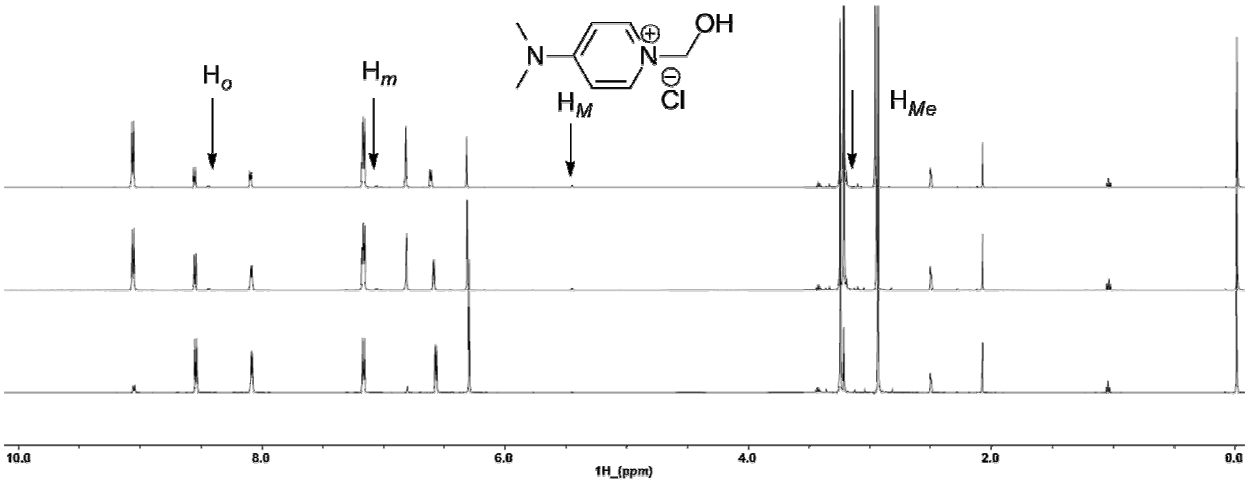

Figure S46. 600 MHz proton NMR spectra for the second step reaction, highlighting the small side reaction; a possible structure for the byproduct is given. The subscripts *o* and *m* refer to aromatic hydrogens *ortho* and *meta* to the ring nitrogen respectively, M refers to methylene protons and Me refers to methyl protons. Peaks at 1 and 3.4 ppm and 2 ppm are due to residual ethanol and acetone wash solvents respectively.