SUPPLEMENTARY INFORMATION

Hydrophobic 1-Allyl-3-alkylimidazolium Dicyanamide Ionic Liquids with Low Densities

Qinghua Zhang, Xiangyuan Ma, Shimin Liu, Benqun Yang, Liujin Lu, and Youquan Deng*

Center for Green Chemistry and catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
**Corresponding author. Email:ydeng@licp.cas.cn, Fax:+86-931-4968116*

General Considerations. Except that the N-alkylimidazole including 1-hexylimidazole, 1-octylimidazole, 1-decylimidazole, 1-dodecylimidazole, and 1-tetradecylimidazole) were prepared according to the reported method[1], all other regents with the purity of analytical grade were received commercially and were used without further purification. 1-Allyl-3-alkyl-imidazolium ([ARIm], R= n-butyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl.) chlorides were prepared via the quaternization reaction of N-alkylimidazole (1.0 equiv, including 1-vinylimidalole, 1-butylimidazole, 1-hexylimidazole, 1-octylimidazole, 1-decylimidazole, 1-dodecylimidazole, and 1-tetradecylimidazole) with 3-chloropropene (1.1 equiv) in a round bottom flask at 60 ^{o}C for 3 days, followed by removal of volatile components. The counter-ion exchanges of the resulting 1-Allyl-3-alkyl-imidazolium chlorides (1.0 equiv) with the sodium dicyanamide (1.1 equiv) were performed in the cold distilled water at room temperature for 24 h. The synthetic details about these ILs were described below.

Characterization and Instruments. To ensure that the effect of the water on the ILs' properties was reduced as low as possible, each IL was further treated in a vacuum (pressure 10^{-2}-10^{-3} mbar) at 80 ^{o}C for 12 hour before every test.

Water content: The water content in ILs was determined by means of a Karl-Fischer titration (Metrohm 831 KF coulometer).

Content of the Halogen ion: The content of bromide or chloride ion was determined by a Mettler–Toledo Seven Muliti meter with a Cl^- or Br^- selective electrode.

NMR and IR: ^{1}H and ^{13}C NMR spectra were measured by a Bruker AMX-400 NMR spectrometer in the D_6-acetone or $CDCl_3$ solutions. Chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. IR spectra were recorded on a Thermo Nicolet 5700 FT-IR spectrophotometer. The phase transitions and the measurements of the specific heat capacity were performed with Mettler–Toledo DSC822e calorimeter and calibrated using indium and zinc.

Phase transitions and thermal stability: The DSC data were evaluated by using the Mettler–Toledo STARe software version 7.01. The samples were sealed in 40 μL aluminum pan and a pinhole at the top of the pan for the sake of the sample exposing to a flowing N_2 (50 mL min^{-1}) atmosphere using an empty pan as the reference. DSC traces were typically scanned from 100 to -100 °C at speed of 10 °C min^{-1}, and then followed the heating process at the same speed. The decomposition temperature (T_d) was recorded with 5% of mass loss by Pyris Diamond Perkin-Elmer TG/DTA at scan rate of 10 °C min^{-1} under a N_2 atmosphere (flow rate = 100 mL min^{-1}) and each IL was heated from room temperature to 800 °C.

XPS: X-Ray Photoelectron Spectroscopy (XPS) analysis was performed on a VG ESCALAB 210 instrument with Mg Ka source (1253.6 eV) and calibrated versus the C 1s peak at 285.0 eV. A thin layer of the IL was deposited on a polycrystalline gold substrate.

Viscosity, density, surface tension, and refractive index: The viscosity and density of each IL at different temperatures were measured on a Stabinger Viscosimeter SVM 3000/GR. The surface tensions of each IL at different temperatures were determined with a Tensiometer (Shang Hai Solon Tech co., ltd.) with a Wilhelmy Slide method. Measurements of refractive indices of each IL at different temperatures were conducted with a WAY-2s Abbe refractometer (Shanghai Precision & Scientific Instrument Co.), calibrated by the refractive indices of deionized water.

Conductivity and electrochemical stability: The ion conductivity was measured by a Mettler–Toledo Seven Muliti meter. Cyclic voltammetry was conducted using a CHI 660A Electrochemical Work Station. The working electrode was a glassy carbon electrode (3 mm diameter), the auxiliary electrode was a platinum wire and a Ag/AgCl electrode was used as a reference. The cyclic voltammogram of the ILs responses exhibited in 0.1M acetonitrile solution to ascertain the accessible electrochemical window at a scan rate of 0.05V.s^{-1} in the potential versus Ag/AgCl electrode.

Synthetic details of the ILs:

Take the synthesis of [AC$_8$Im]DCA as an example: A mixture of 1-octylimidazole (90g, 0.50 mol) and 3-chloropropene (42g, 0.55 mol) in ethanol (100 mL) was stirred at 60℃ for 3 days. After removal of the volatile components, the mixtures were washed with the absolute ethyl ether for three times to remove the unreacted reagents, and the resulting 1-allyl-3-octylimidazolium chloride ([AOIm]Cl) could be obtained as a pale yellow viscous liquid with the yield of *ca.* 90%. Then, to a solution of the obtained [AC$_8$Im]Cl (115g, 0.45 mol) in distilled water (100 mL), the aqueous solution containing the sodium dicyanamide (44.5g, 0.5mol) was added under vigorous stirring at room temperature, and the reaction mixture was stirred for 24 h. After the reaction was finished, the crude product was extracted from water by adding CH_2Cl_2 (50 mL*3), and the combined extracts were washed with the deionized water until no residual chloride ion in the washed water were detected by a Mettler–Toledo Seven Muliti meter with a chloride ion selective electrode. The final product [AC$_8$Im]DCA was dried in a vacuum (pressure 10^{-2}-10^{-3} mbar) for more than 12 hours at 80 ^{o}C, and 122g (*ca.* 85% yield) of the desired product was obtained as a pale yellow viscous liquid. The product was analytically pure as determined by ^{1}H and ^{13}C NMR spectroscopy; spectra are provided below.

Synthesis of [AC$_n$Im]DCA (n= 4, 6, 10, 12, 14): The same procedure as that described above for the synthesis of [AC$_8$Im]DCA was followed, except N-alkylimidazole (N-RIm, R = n-butyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, respecitively, 0.50 mol) was used instead of 1-octylimidazole (90g, 0.50 mol). The product [AC$_n$Im]DCA was obtained as a pale yellow viscous hydrophobic liquid with the yield of *ca.* 81-93%, and was analytically pure as determined by ^{1}H and ^{13}C NMR spectroscopy; spectra are provided below; spectra are provided below.

Synthesis of [VC$_8$Im]DCA and [VC$_{10}$Im]DCA: A mixture of 1-vinylimidalole (0.50 mol) and 1-bromooctane (0.55 mol) in ethanol (100 mL) was stirred at 70 ^{o}C for 3 days. After removal of the volatile components, the mixtures were washed with the absolute ethyl ether for three times to remove the unreacted reagents, and the resulting 1-vinyl-3-octylimidazolium bromide ([VC$_8$Im]Br) could be obtained as a pale yellow viscous liquid with the yield of *ca.* 84%. Then, to a solution of the obtained [VC$_8$Im]Br (0.2 mol) in distilled water (100 mL), the aqueous solution containing the sodium dicyanamide (0.22mol) was added under vigorous stirring at room temperature, and the reaction mixture was stirred for 24 h. After the reaction was finished, the crude product was extracted from water by adding CH_2Cl_2 (50 mL*3), and the combined extracts were washed with the deionized water until no residual bromide ion in the washed water were detected by a Mettler–Toledo Seven Muliti meter with a bromide ion selective electrode. The final product [VC_8Im]DCA was dried in a vacuum (pressure 10^{-2}-10^{-3} mbar) for more than 12 hours at 80 ^{o}C, and 122g (*ca.* 85% yield) of the desired product was obtained as a pale yellow viscous liquid. The product was analytically pure as determined by ^{1}H and ^{13}C NMR spectroscopy; spectra are provided below. The same procedure was used for the synthesis of [VC_{10}Im]DCA, and the 88%.yield was obtained.

Synthesis of [AVIm]DCA: The same procedure as that described above for the synthesis of [AC_8Im]DCA was followed, except 1-vinylimidalole was used instead of 1-octylimidazole. The product [AVIm]DCA was obtained as a pale yellow hydrophilic liquid with the yield of *ca.* 83%, and was analytically pure as determined by ^{1}H and ^{13}C NMR spectroscopy; spectra are provided below.

References

1. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.*, **1996**, *35*, 1168.

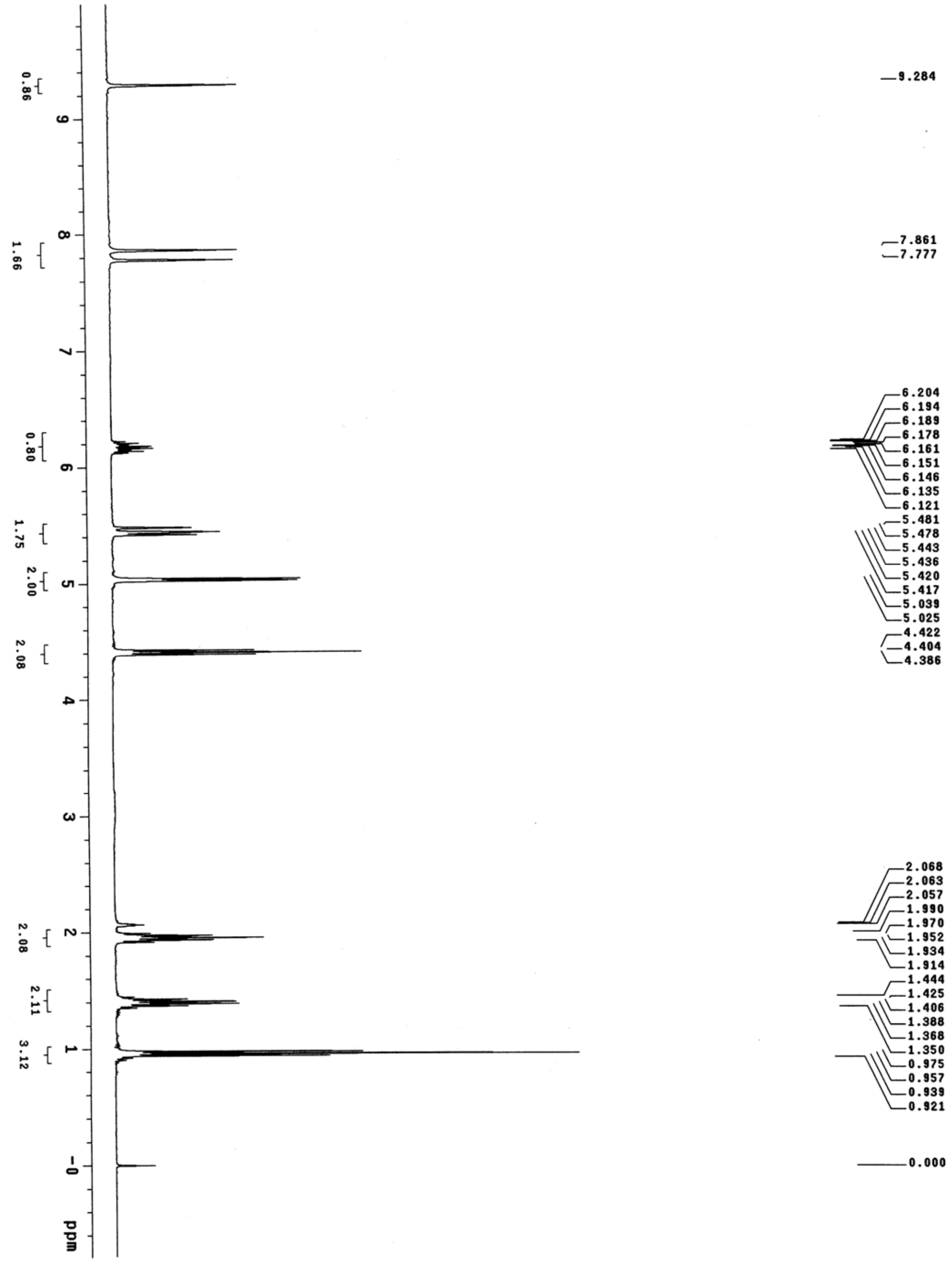

Fig. S1 ^{1}H-NMR spectrum of [AC_4Im]DCA (D_6-acetone)

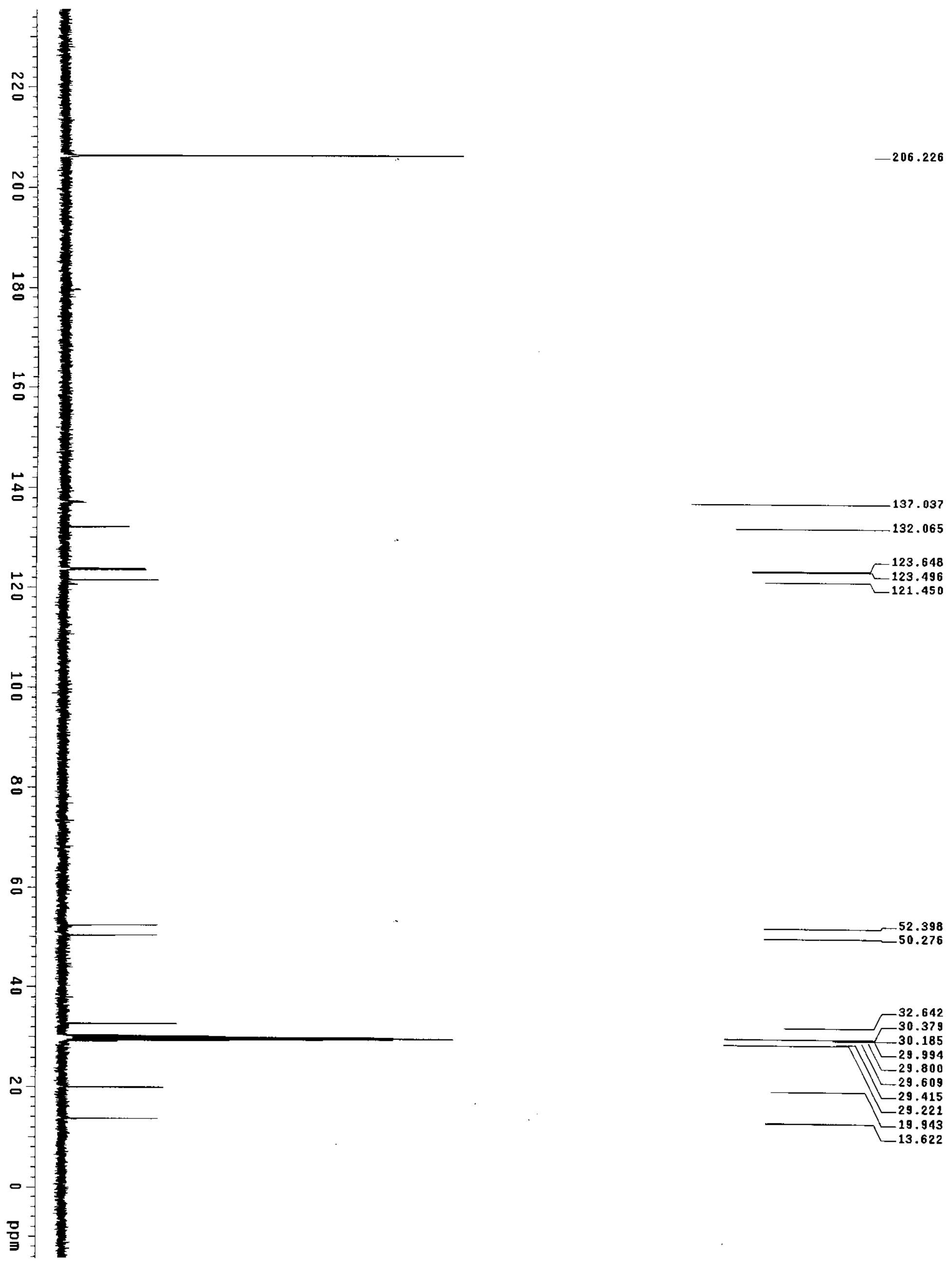

Fig. S2 ^{13}C-NMR spectrum of [AC$_4$Im]DCA (D$_6$-acetone)

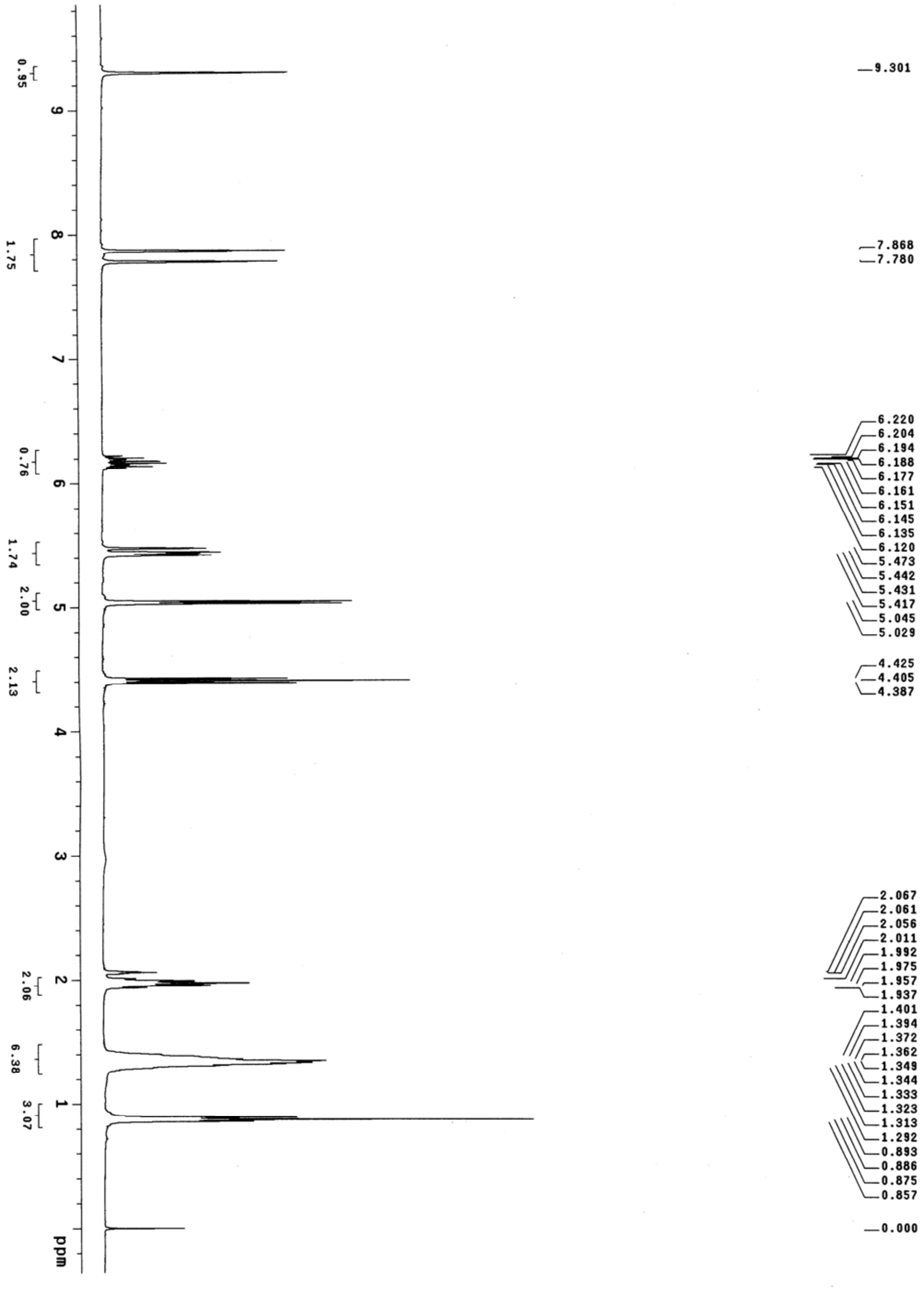

Fig. S3 ^{1}H-NMR spectrum of [AC$_6$Im]DCA (D$_6$-acetone)

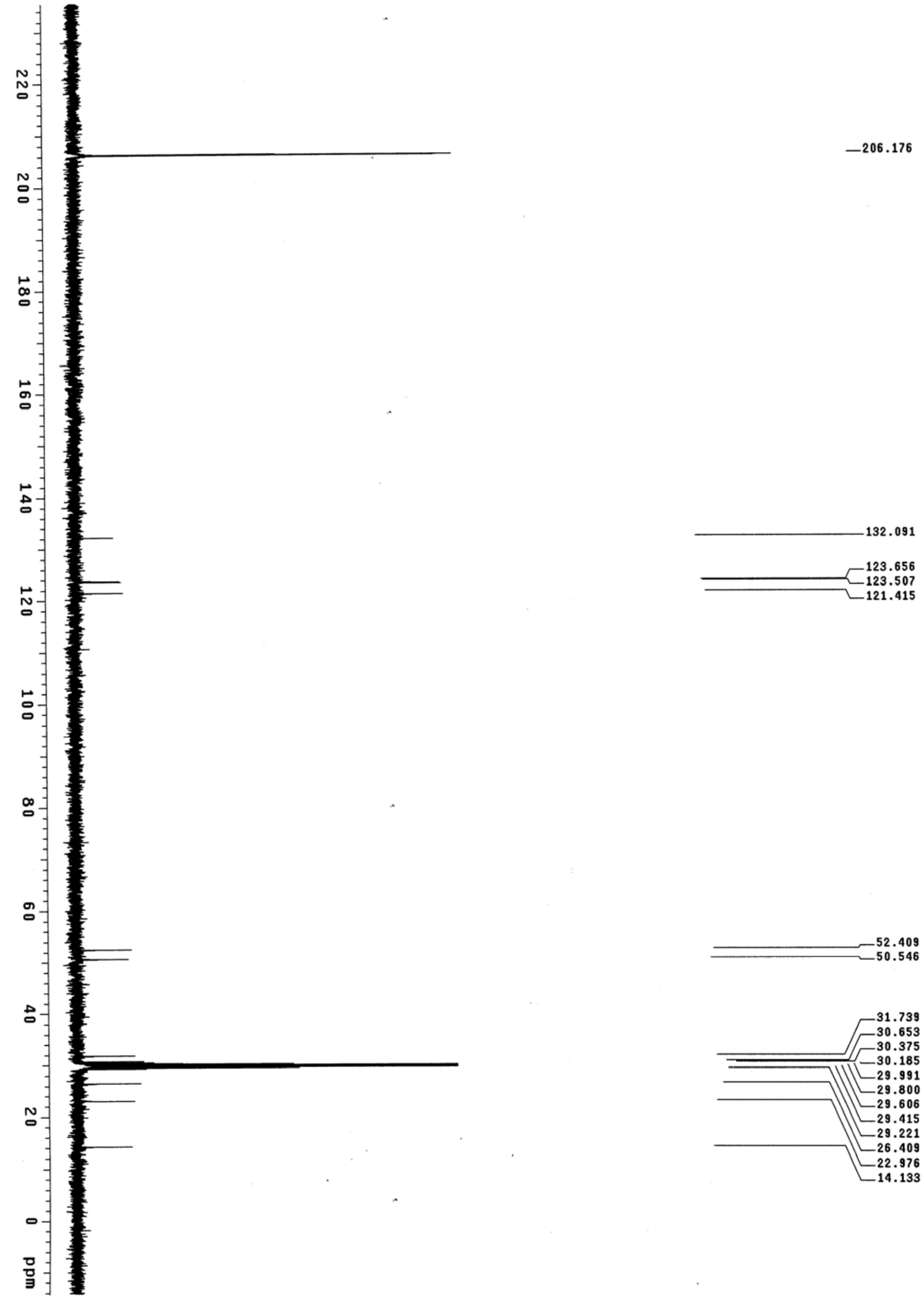

Fig. S4 ^{13}C-NMR spectrum of [AC$_6$Im]DCA (D$_6$-acetone)

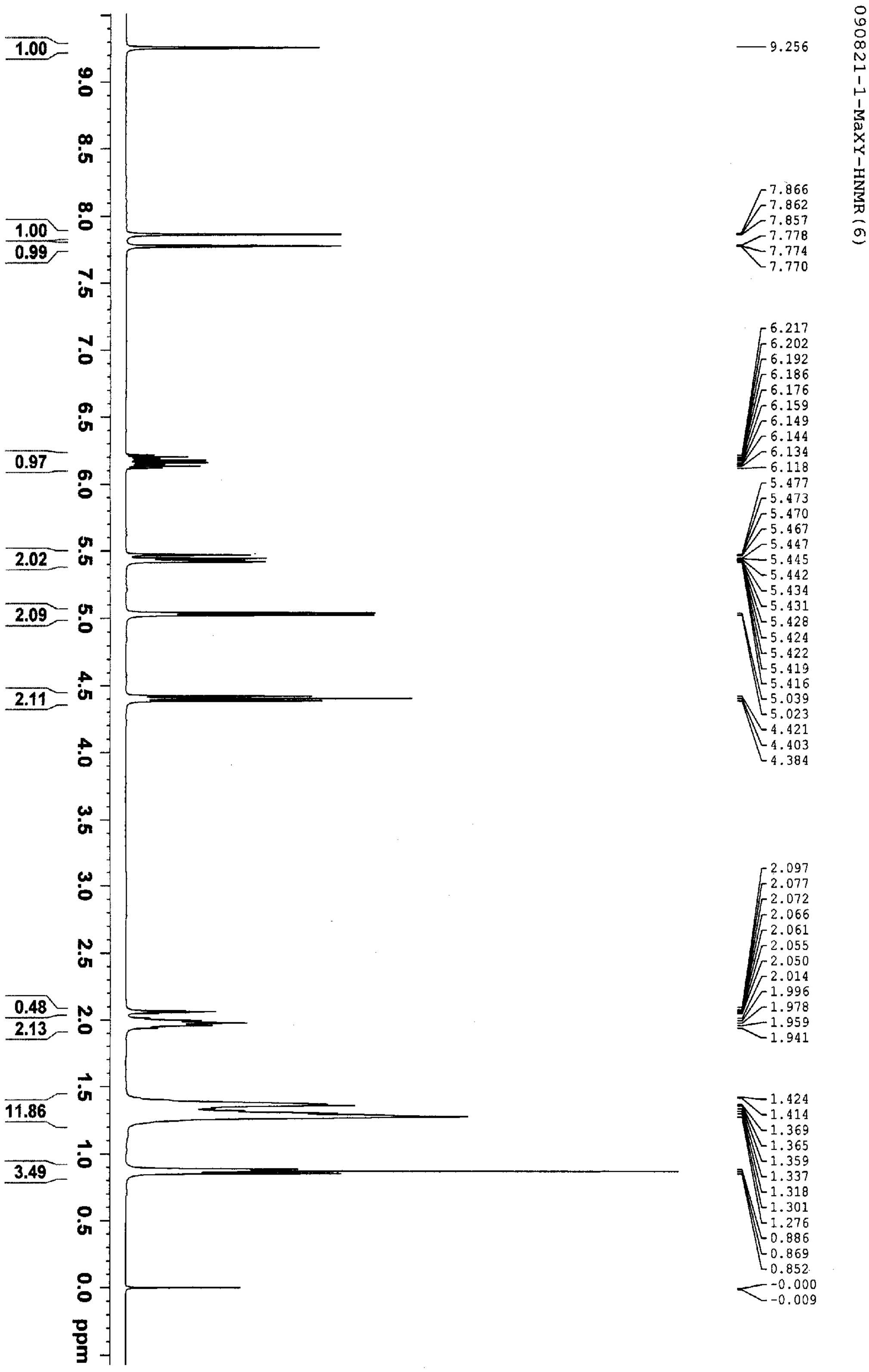

Fig. S5 ^{1}H-NMR spectrum of [AC$_8$Im]DCA (D$_6$-acetone)

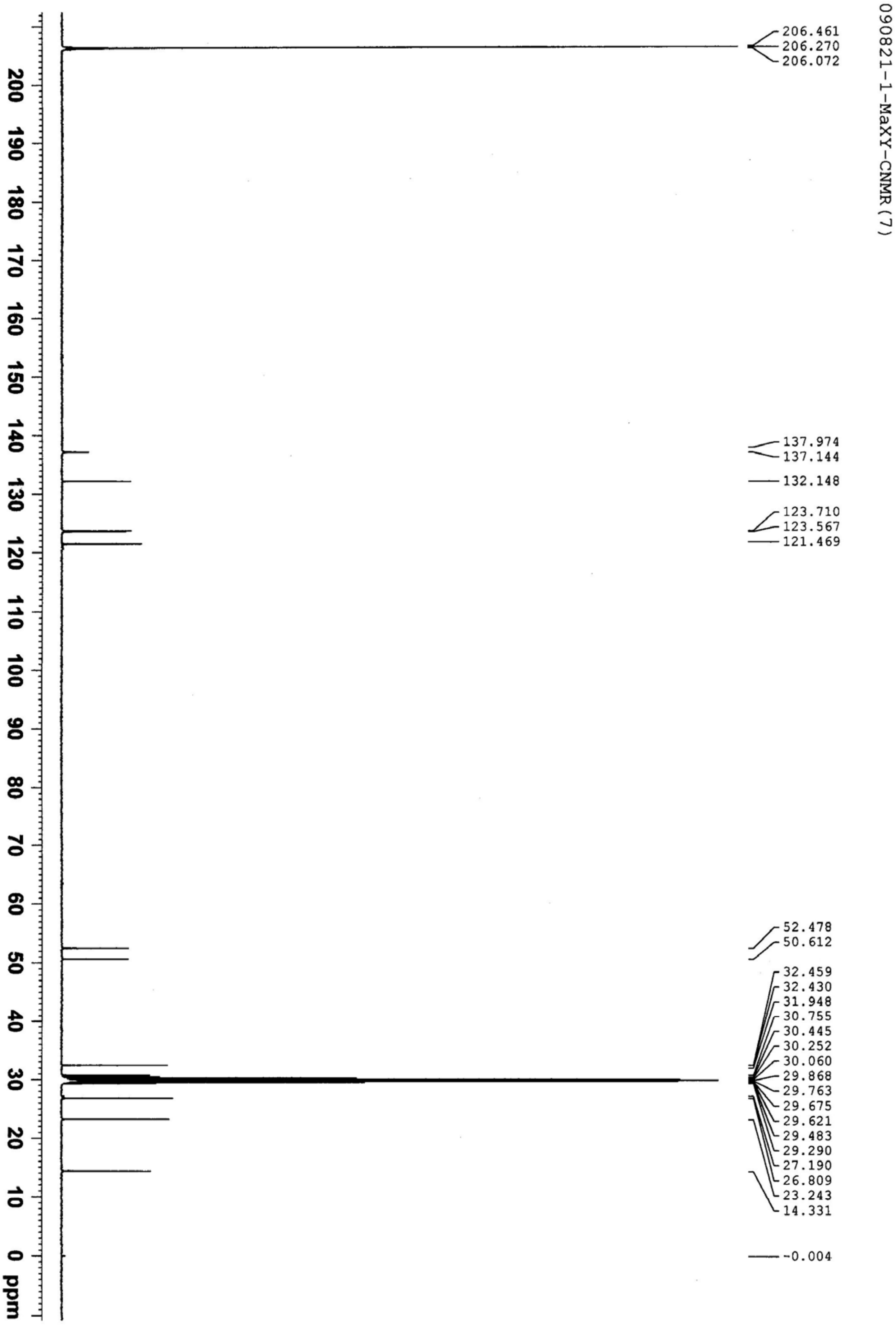

Fig. S6 ^{13}C-NMR spectrum of [AC$_8$Im]DCA (D$_6$-acetone)

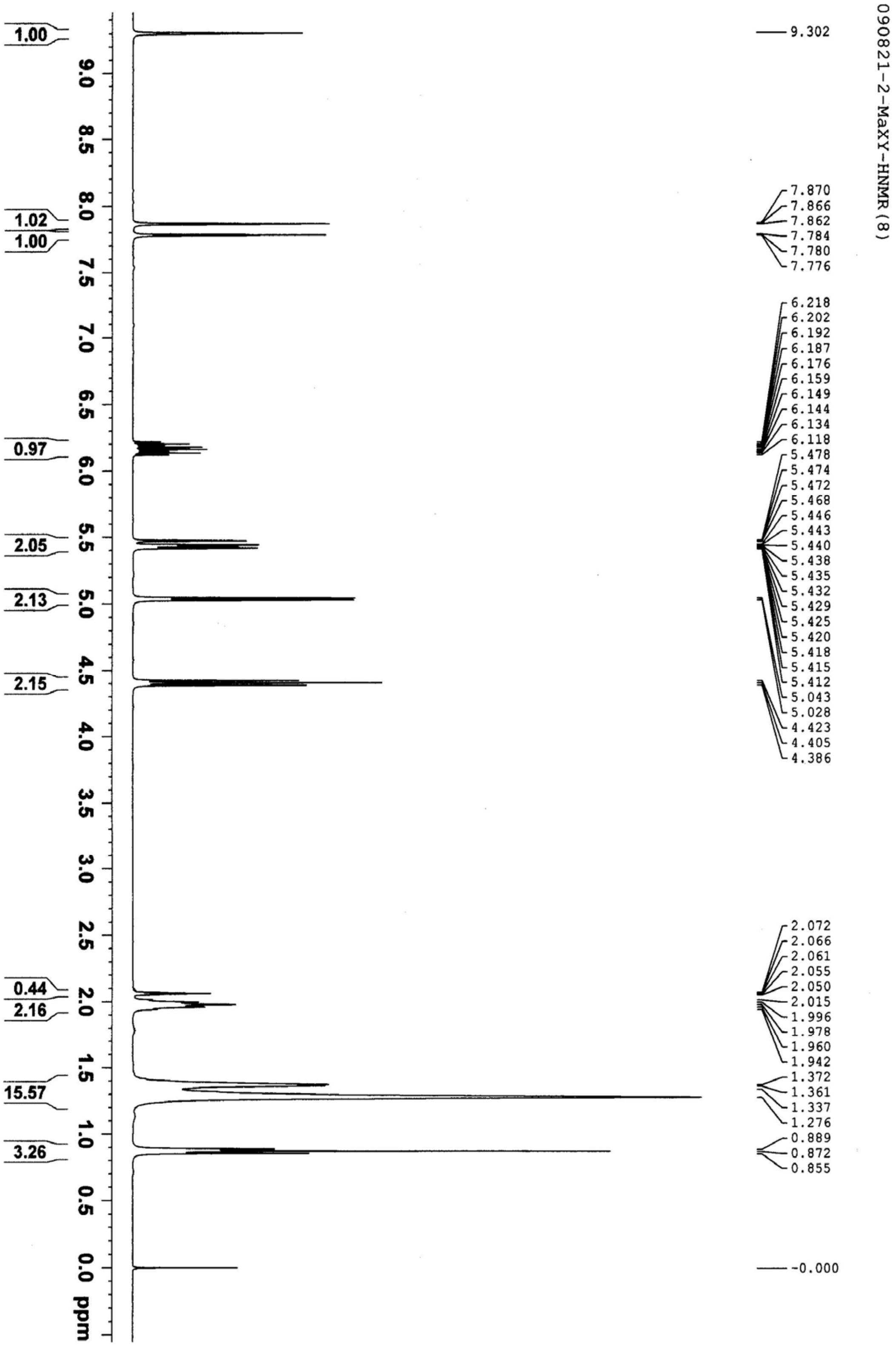

Fig. S7 ^{1}H-NMR spectrum of [AC$_{10}$Im]DCA (D$_6$-acetone)

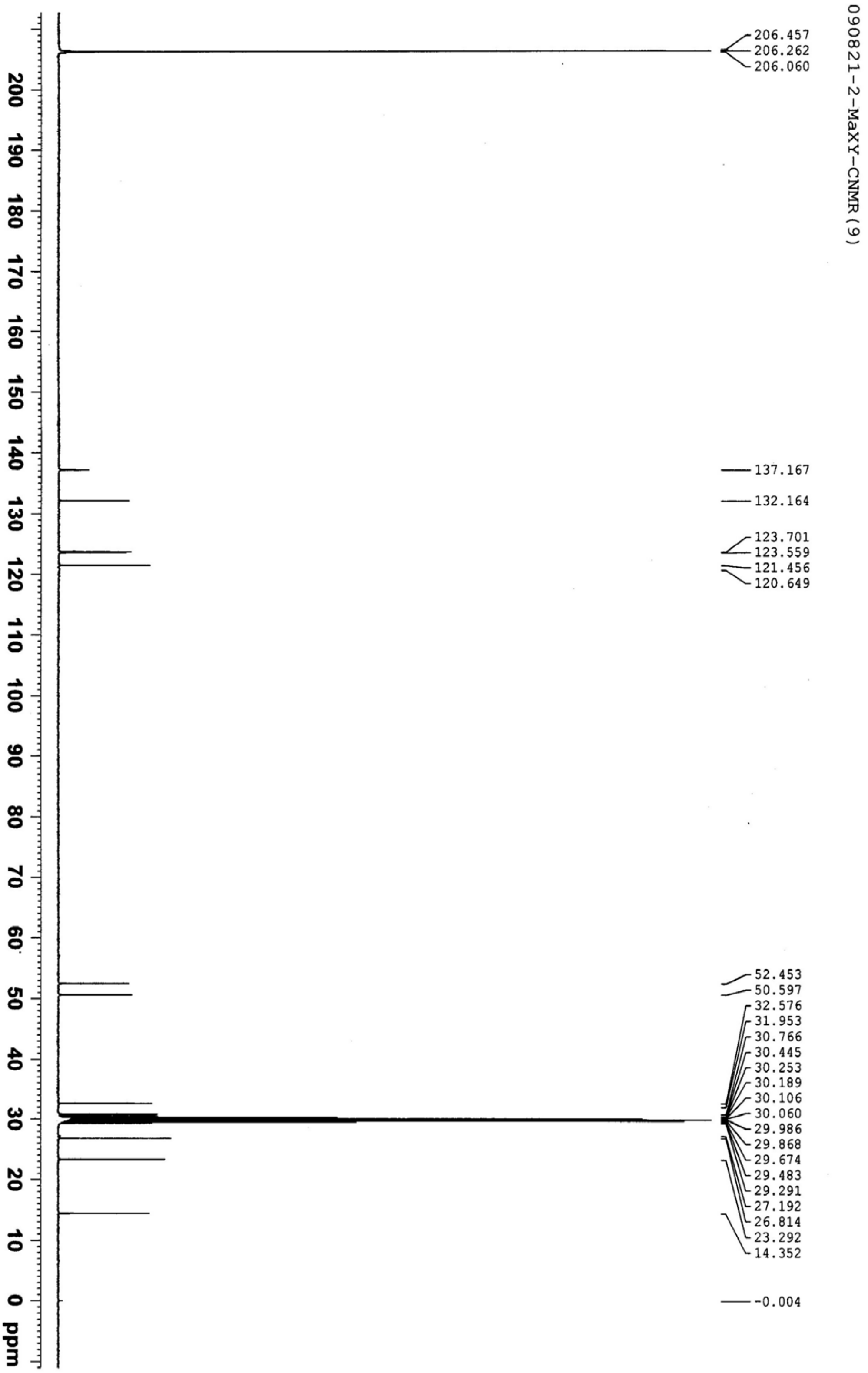

Fig. S8 ^{13}C-NMR spectrum of [AC$_{10}$Im]DCA (D$_6$-acetone)

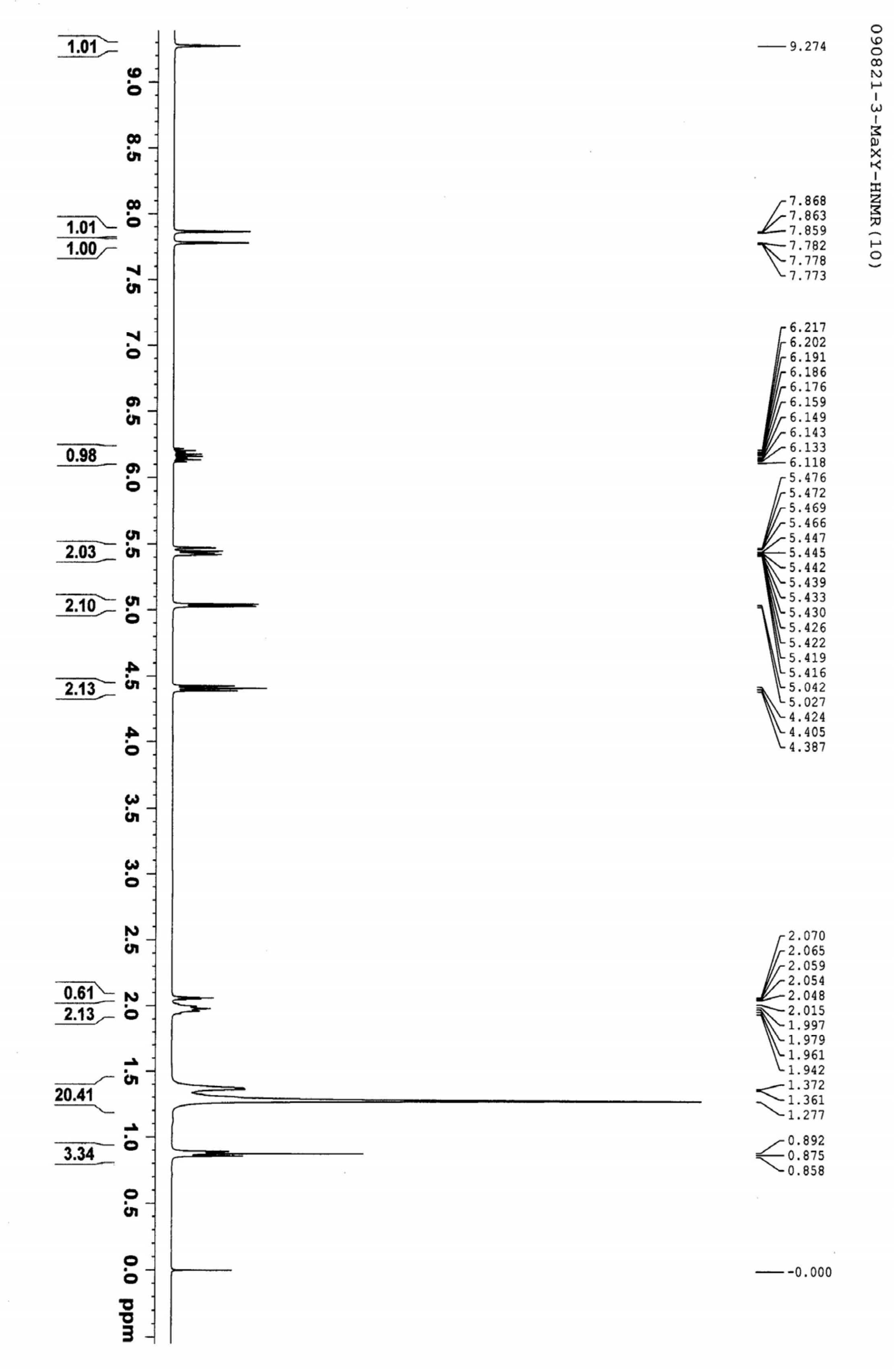

Fig. S9 ^{1}H-NMR spectrum of [AC$_{12}$Im]DCA (D$_6$-acetone)

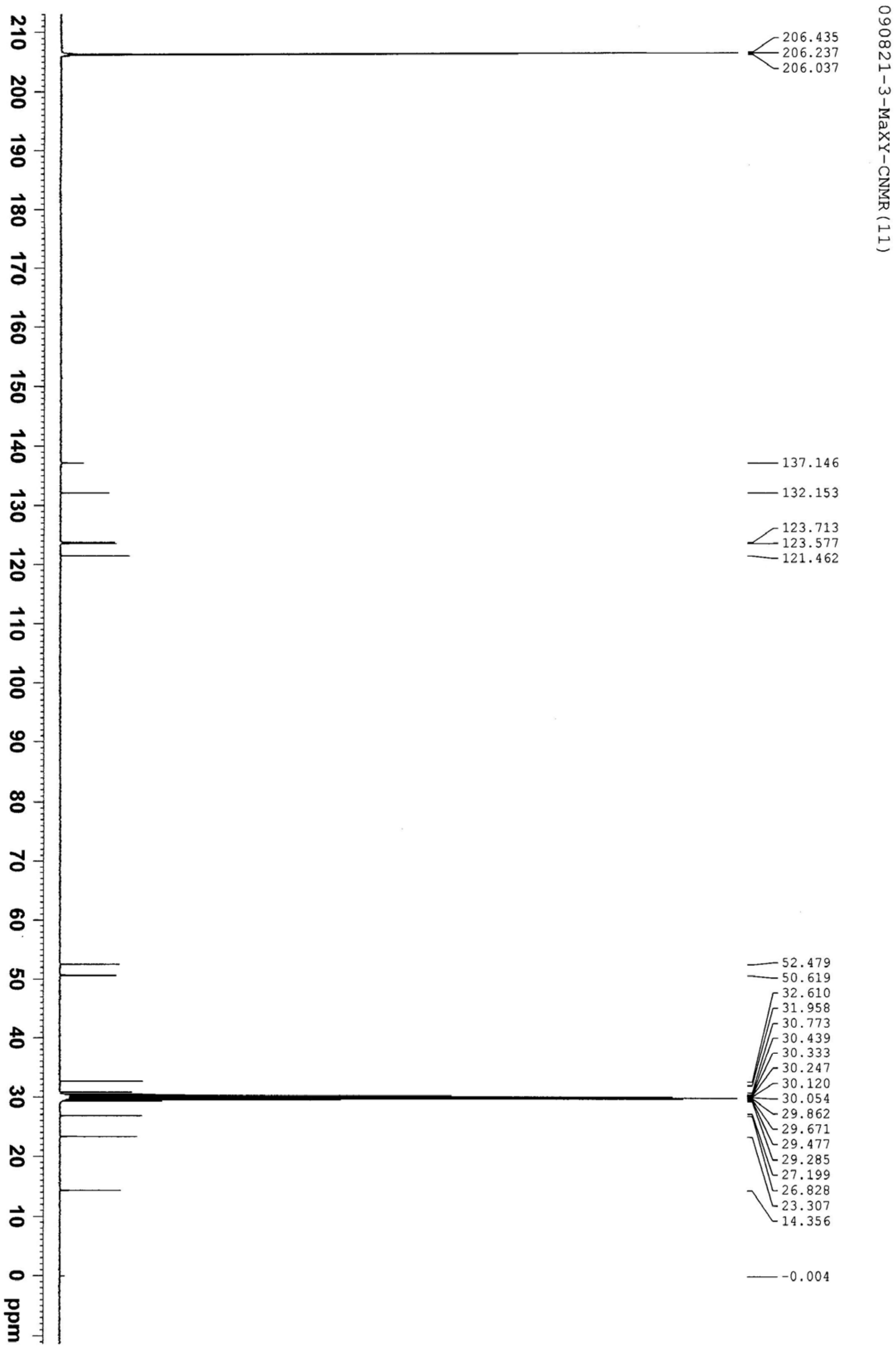

Fig. S10 ^{13}C-NMR spectrum of [AC$_{12}$Im]DCA (D$_6$-acetone)

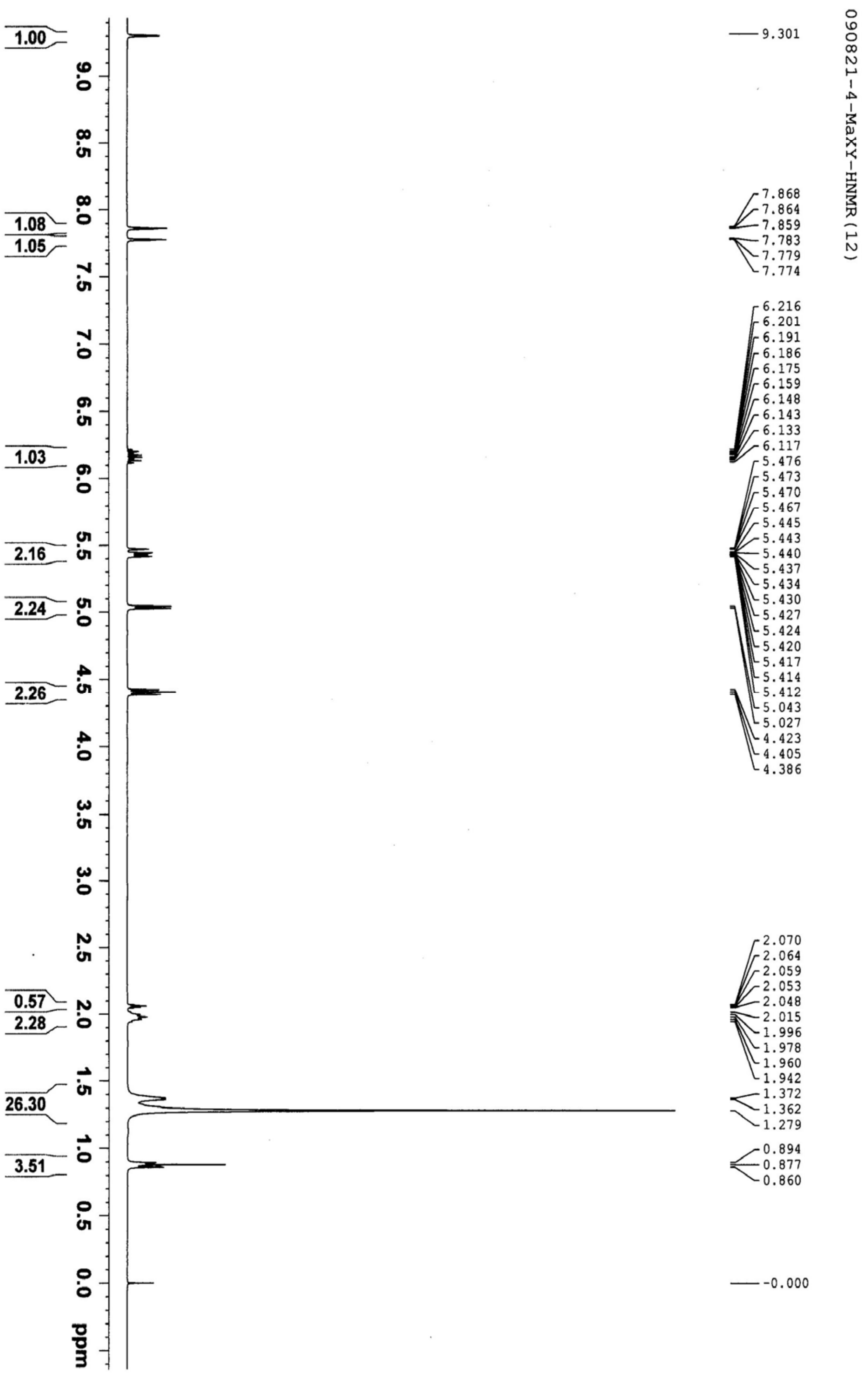

Fig. S11 ^{1}H-NMR spectrum of [AC$_{14}$Im]DCA (D$_6$-acetone)

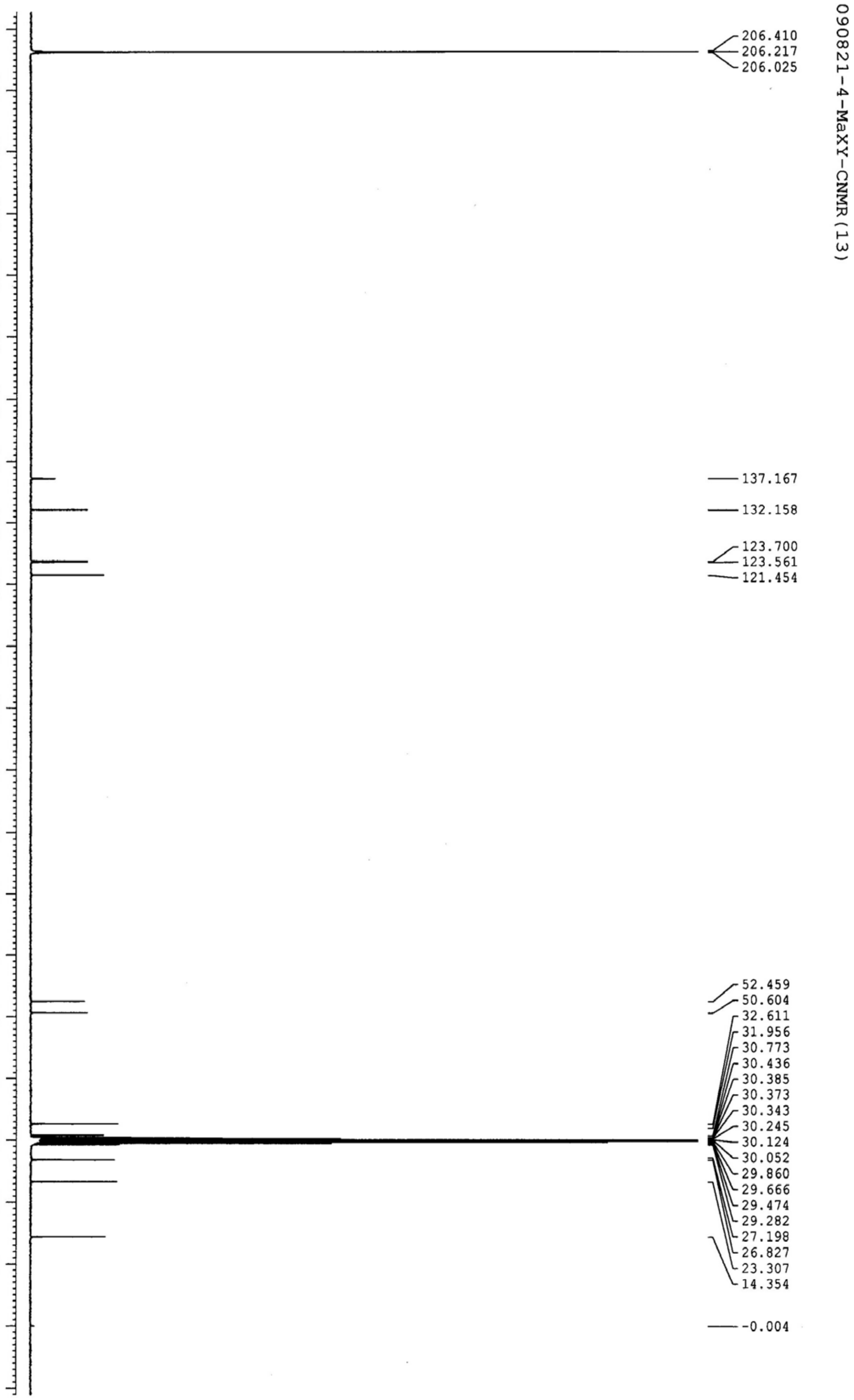

Fig. S12 ^{13}C-NMR spectrum of [AC$_{14}$Im]DCA (D$_6$-acetone)

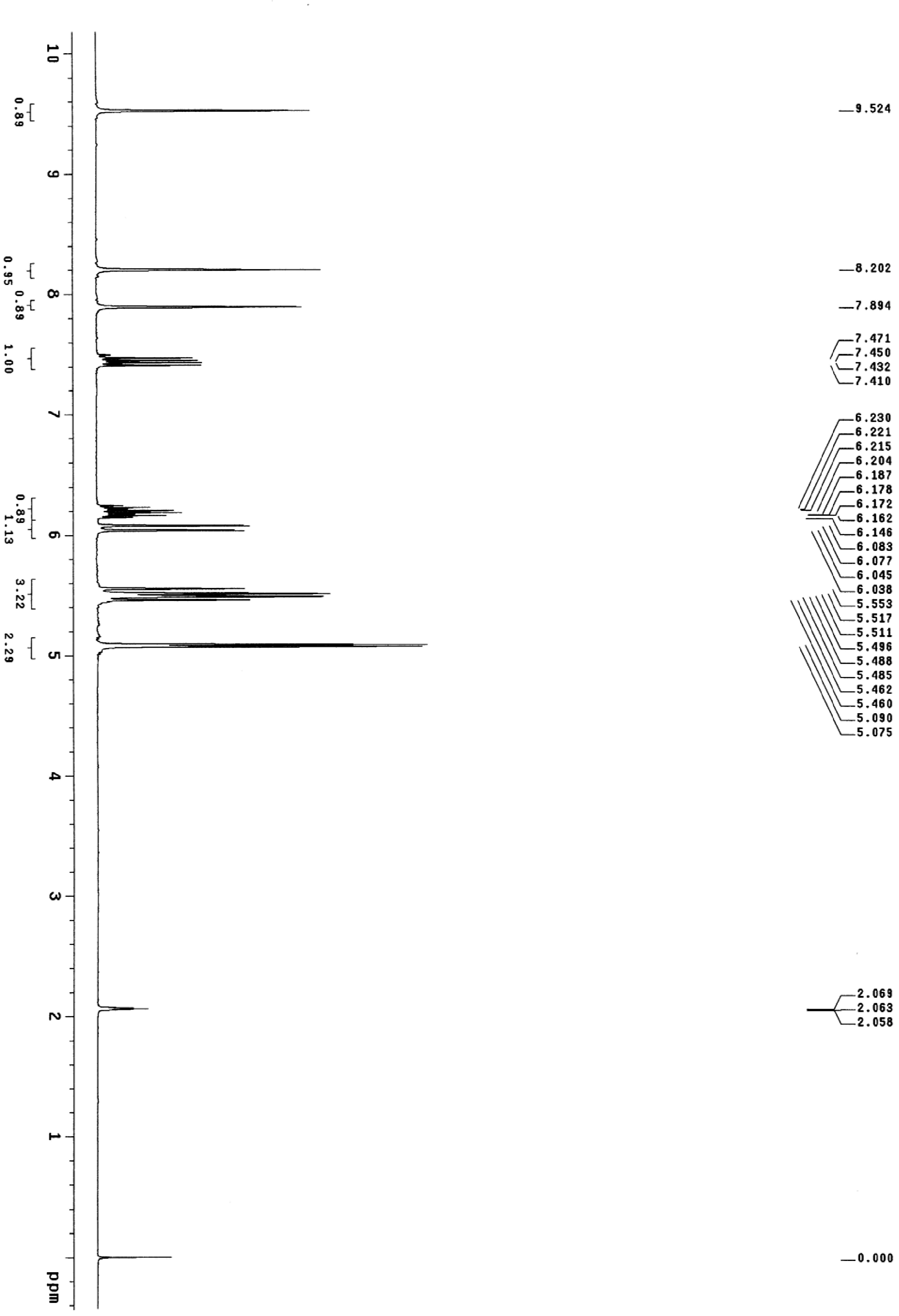

Fig. S13 ^{1}H-NMR spectrum of [AVIm]DCA (D_6-acetone)

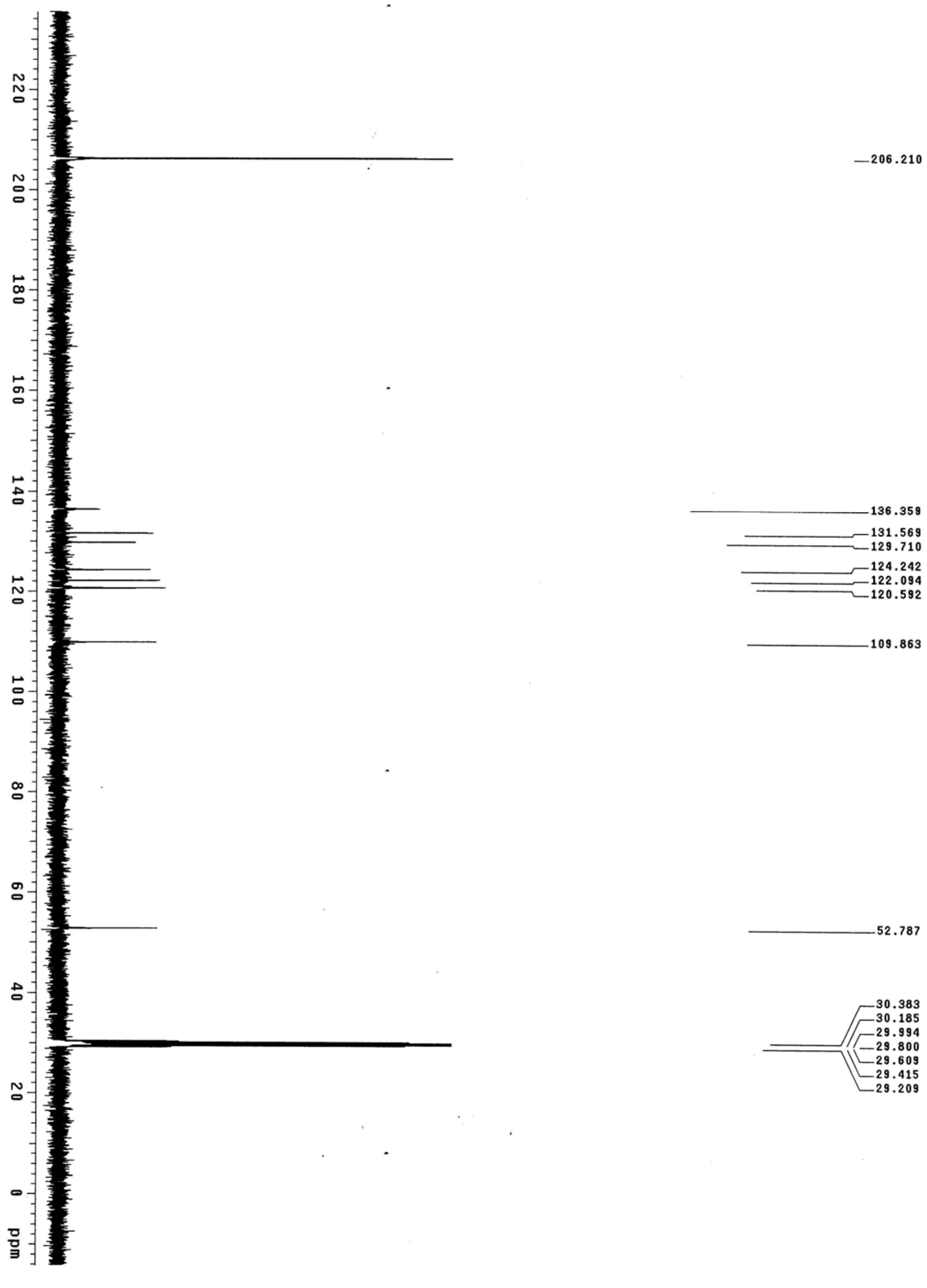

Fig. S14 ^{13}C-NMR spectrum of [AVIm]DCA (D$_6$-acetone)

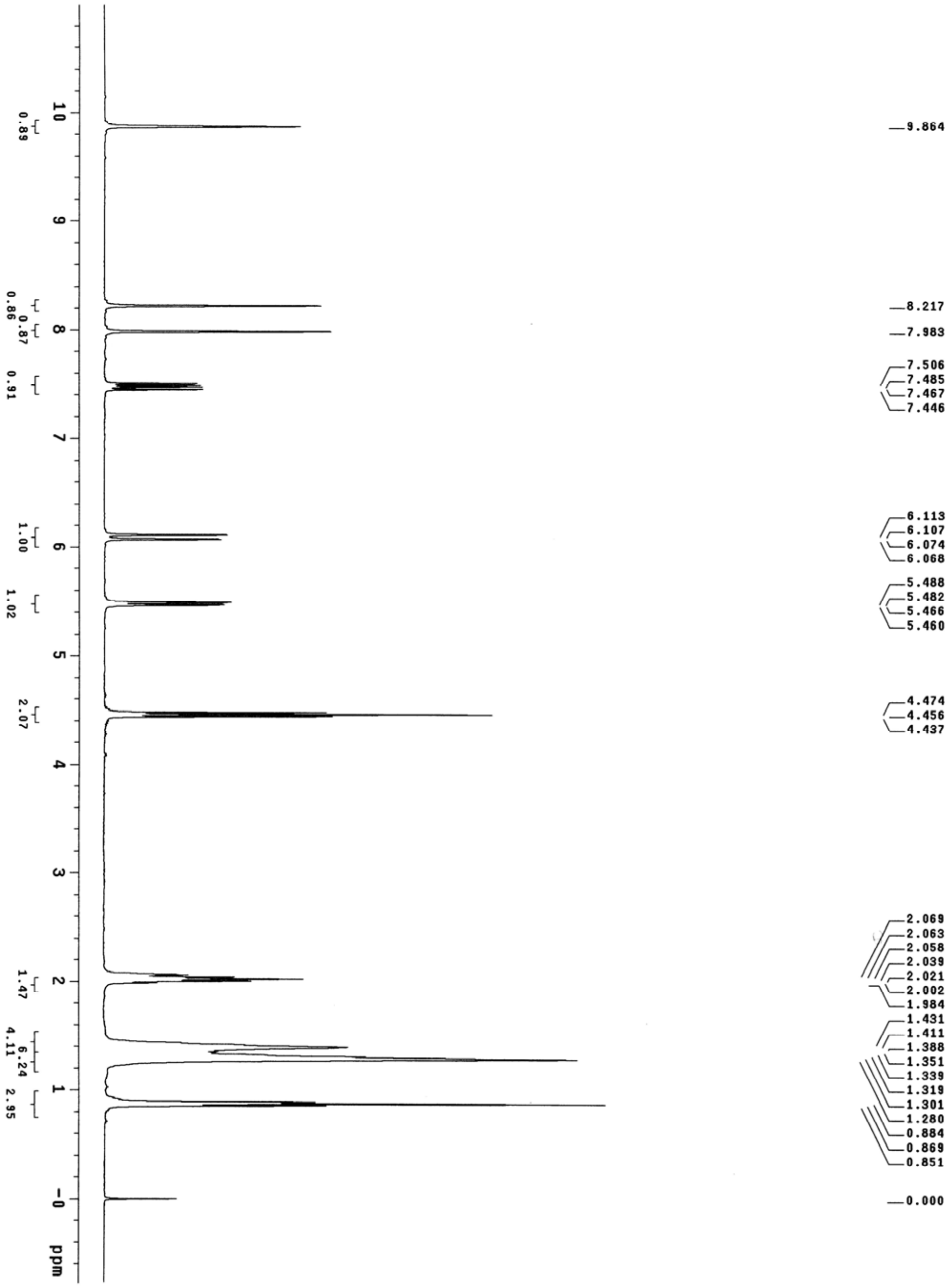

Fig. S15 ^{1}H-NMR spectrum of [VC$_8$Im]DCA (CDCl$_3$)

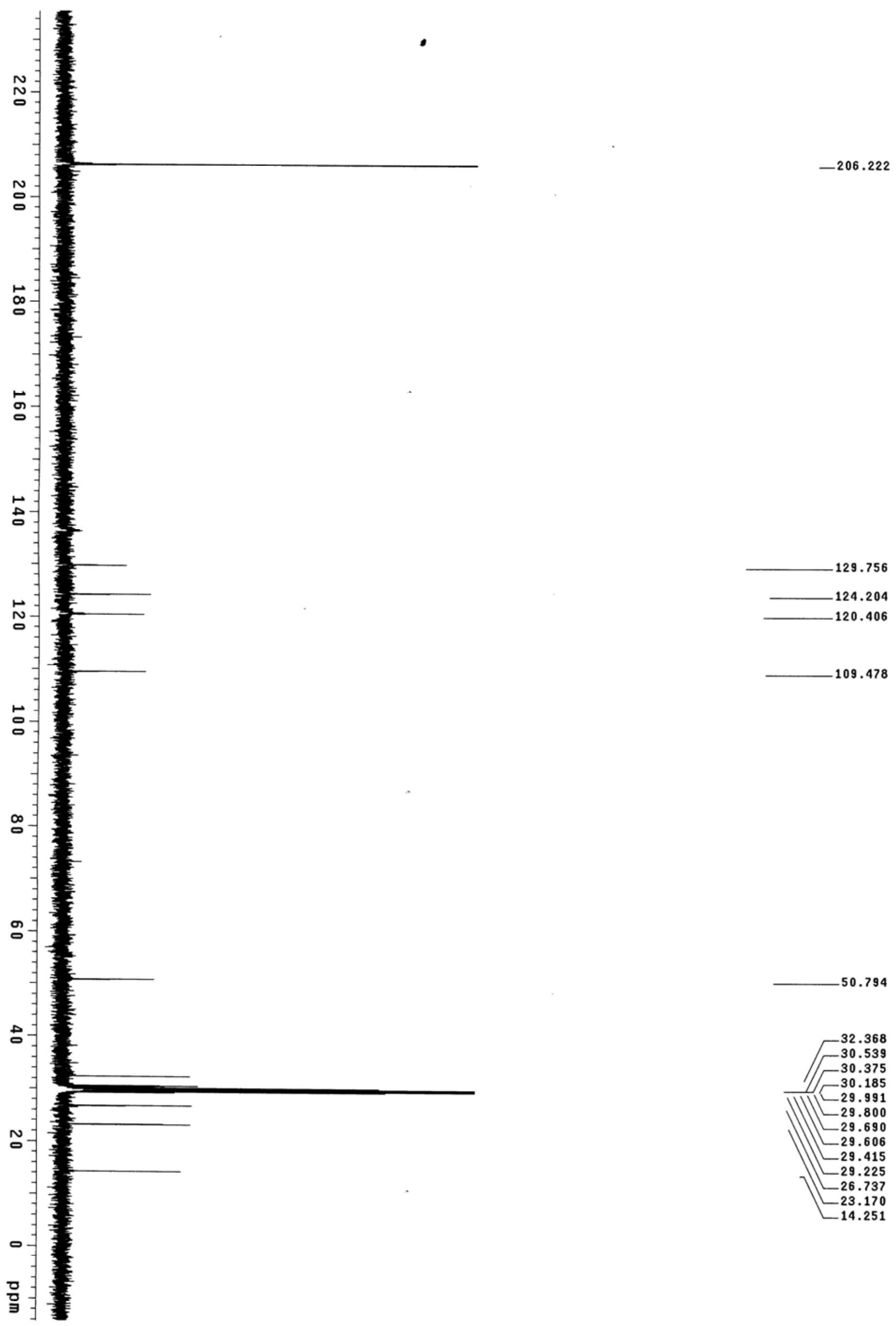

Fig. S16 ^{13}C-NMR spectrum of [VC$_8$Im]DCA (D$_6$-acetone)

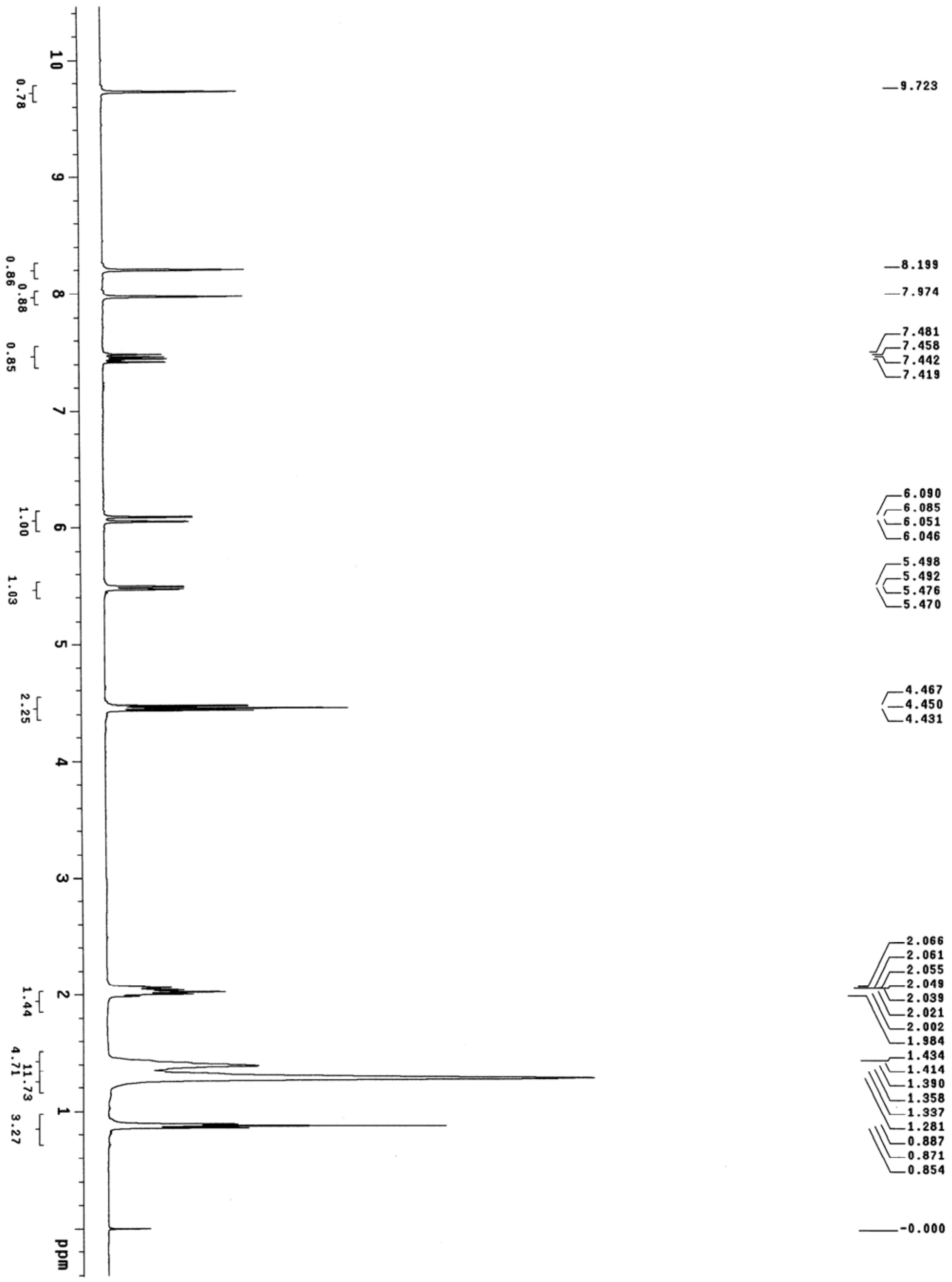

Fig. S17 ^{1}H-NMR spectrum of [VC$_{10}$Im]DCA (CDCl$_3$)

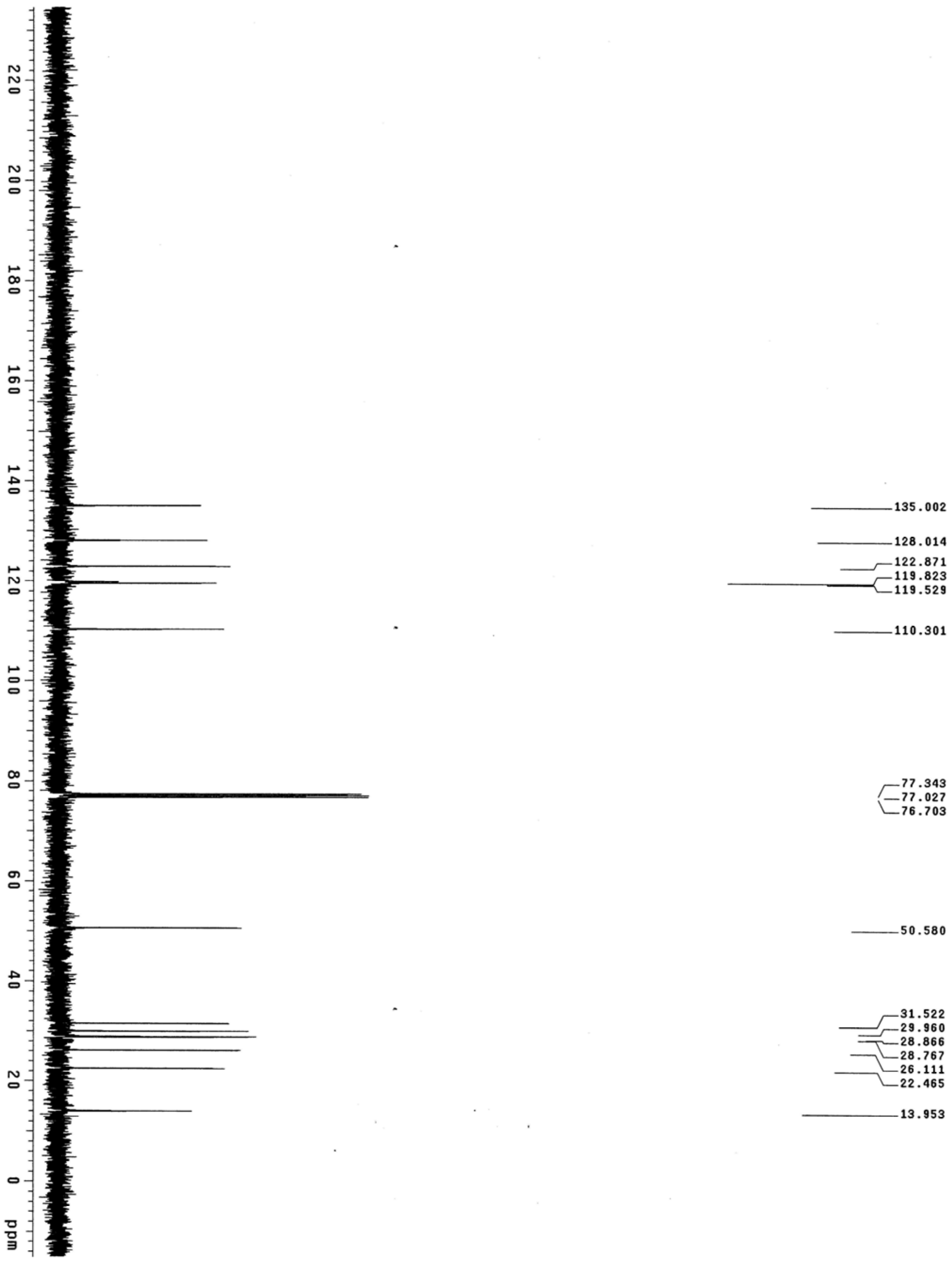

Fig. S18 ^{13}C-NMR spectrum of [VC$_{10}$Im]DCA (CDCl$_3$)

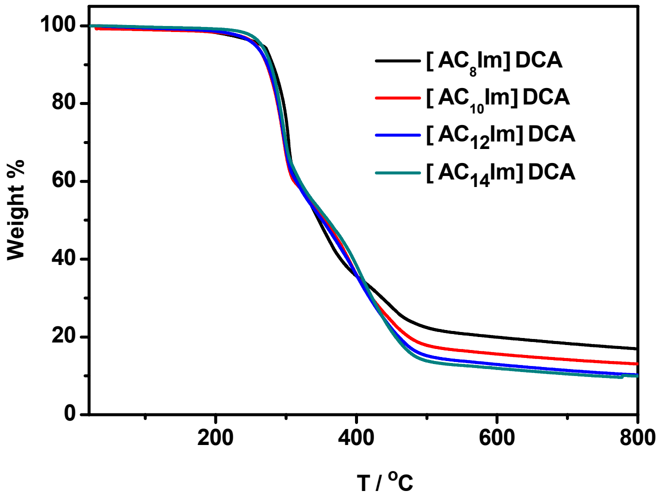

Fig. S19 TGA traces of four [AC$_n$Im]-based dicyanamide salts

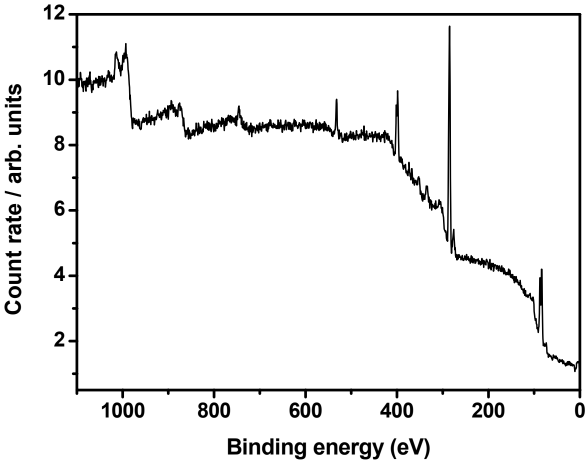

Fig. S20 Survey spectrum of [AC$_8$Im]DCA

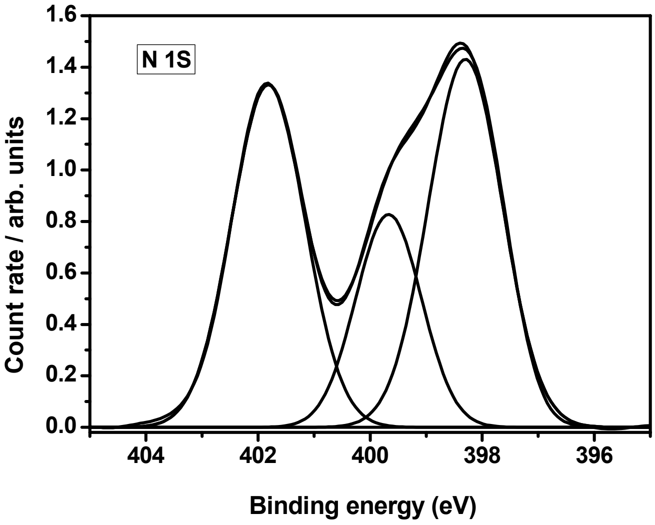

Fig. S21 High-resolution spectra dealing with the N 1s photoemission of [A C_8Im]DCA

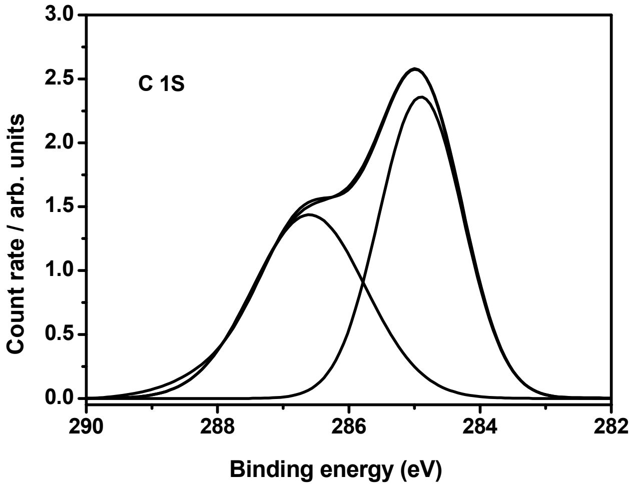

Fig. S22 High-resolution spectra dealing with the C 1s photoemission of [A C_8Im]DCA

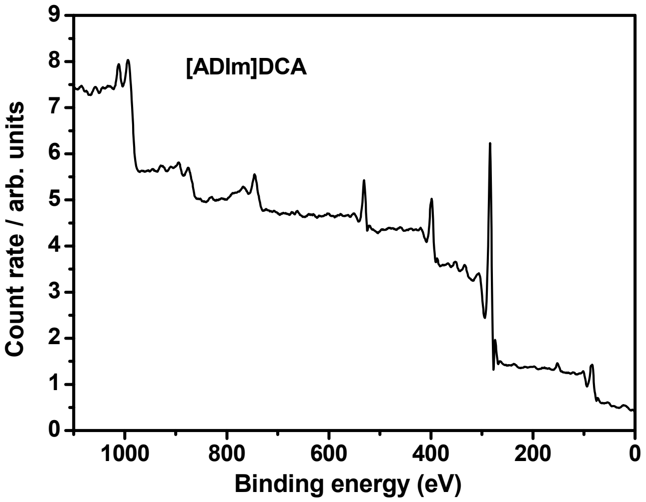

Fig. S23 Survey spectrum of [A C_{10}Im]DCA

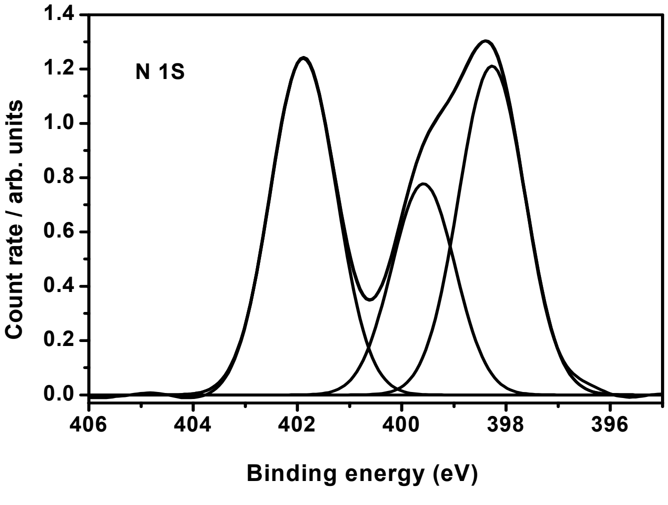

Fig. S24 High-resolution spectra dealing with the N 1s photoemission of [A C_{10}Im]DCA

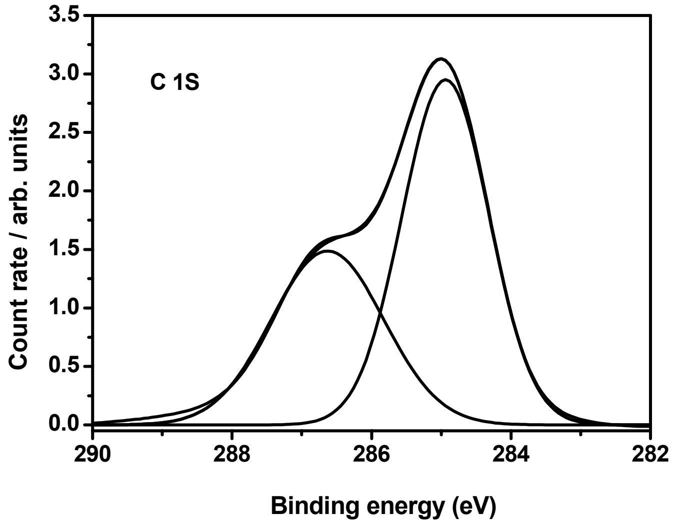

Fig. S25 High-resolution spectra dealing with the C 1s photoemission of $[AC_{10}Im]DCA$

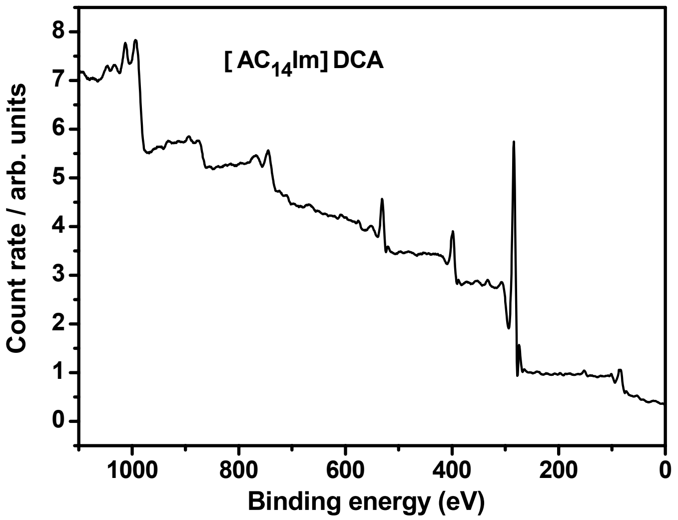

Fig. S26 Survey spectrum of $[AC_{14}Im]DCA$

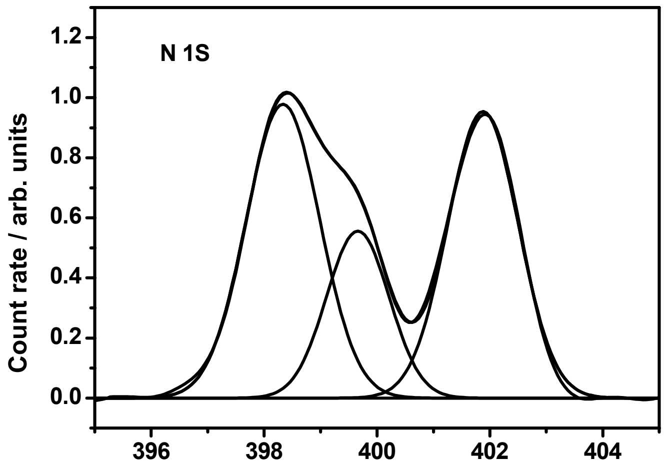

Fig. S27 High-resolution spectra dealing with the N 1s photoemission of $[A\ C_{14}Im]DCA$

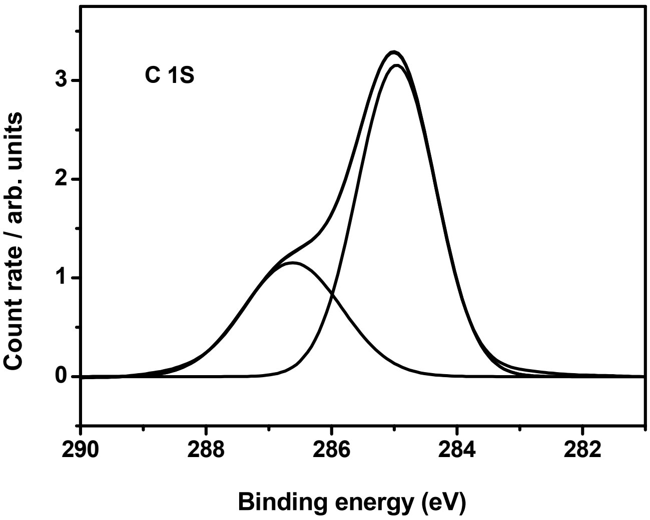

Fig. S28 High-resolution spectra dealing with the C 1s photoemission of [A C_{14}Im]DCA

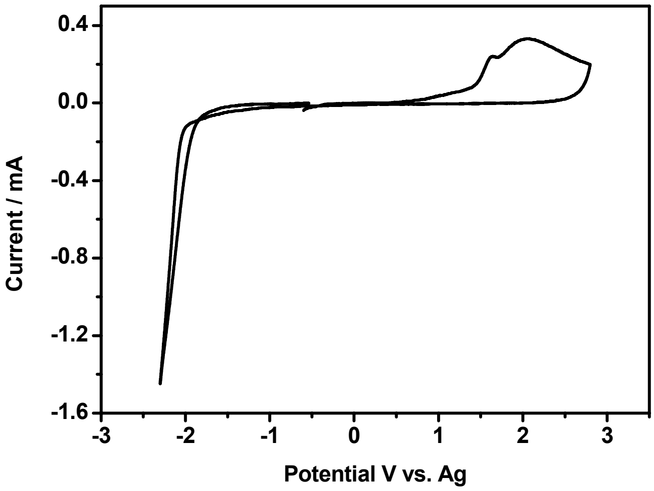

Fig. S29 Cyclic voltammogram of [AOIm]DCA; GC working electrode.