Electronic Supplementary Information

Thiacalix[4]arene-cinnamaldehyde derivative: ICT-induced preferential nanomolar detection of Ag+ among different transition metal ions

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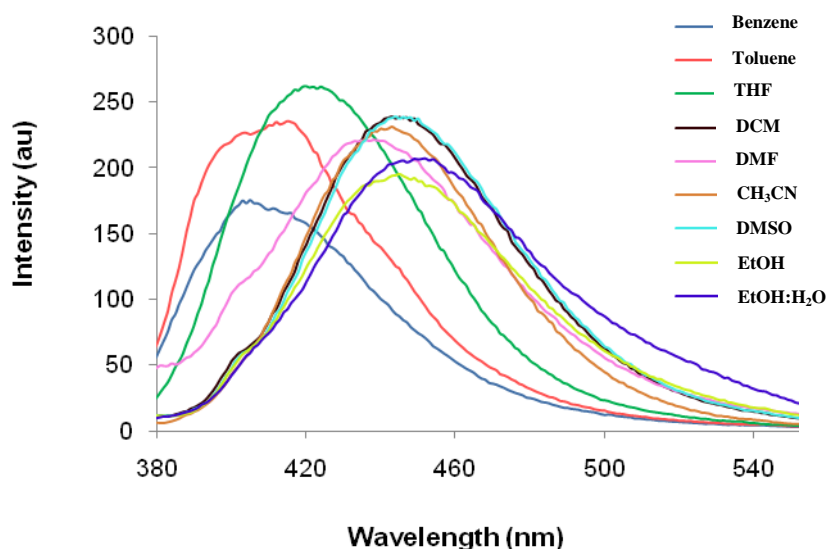Fax: 091-(183)-2258820; Tel: 091-(183)-2258802-9 Extn. 3205;
E-mail: mksharmaa@yahoo.co.in

Figure S1. Fluorescence spectra of **3** (1×10^{-6} M) in various solvents; λex = 360 nm. In non-polar solvents like benzene and toluene receptor **3** shows unresolved emission spectra corresponding to both delocalized excited (DE) state at short wavelength (402 nm) and twisted intramolecular charge transfer (TICT) state at longer wavelength (414 nm). Any increase in polarity of the solvents did not affect the position of delocalized excited band. However, delocalized excited band in polar solvent appears as a shoulder on the main emission band. In comparison to delocalized excited band, TICT band shows a large red shift while moving from non-polar to polar solvents. For example, in THF a red shift of TICT band (4 nm) was observed in comparison to non-polar solvents, while the presence of delocalized excited band is hardly observed as in this case the delocalized excited band goes underneath the envelop of the TICT emission band. Further, by increasing the polarity of the solvents from THF to ethanol:water (9:1) mixture, we observed a continuous red shift (418 to 450 nm) of the TICT emission band.
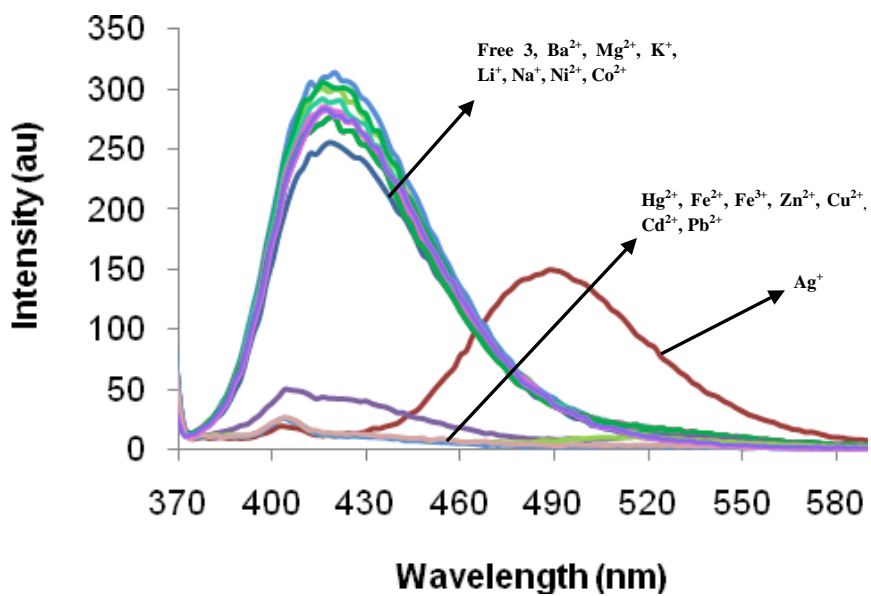
Figure S2. Fluorescence spectra of **3** (1×10^{-6} M) in the presence of various metal ions (30 μM each) in THF; λex = 360 nm.
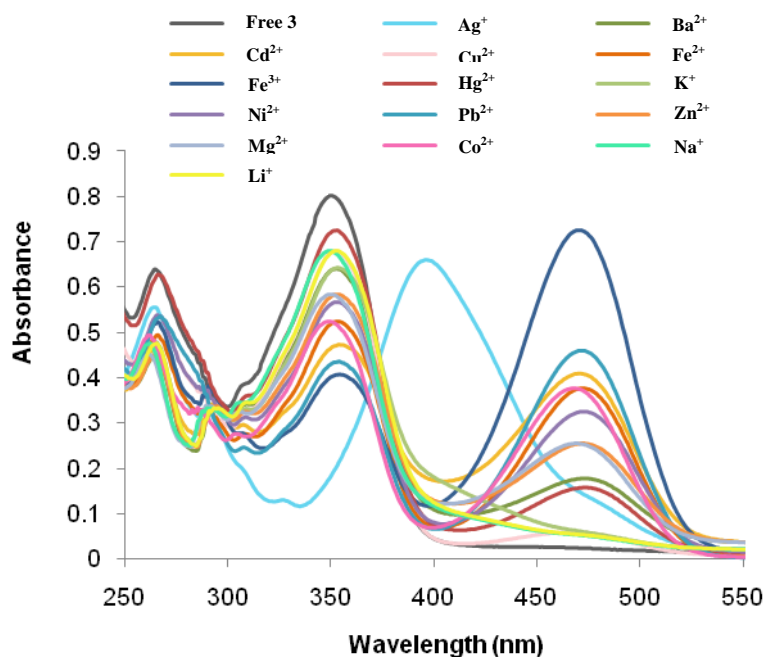
Figure S3. UV-vis spectra of **3** (1×10^{-5} M) in the presence of various metal ions (1 equiv each) in THF.

Calculations for quantum yield:

Fluorescence quantum yield[1] was determined using optically matching solutions of naphthalene ($\Phi_{fr} = 0.23$ in ethanol) as standard at an excitation wavelength of 360 nm and quantum yield is calculated using the equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1-10^{-A_sL_s}}{1-10^{-A_rL_r}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Φ_{fs} and Φ_{fr} are the radiative quantum yields of sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference respectively, Ds and Dr the respective areas of emission for sample and reference. L_s and L_r are the lengths of the absorption cells of sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

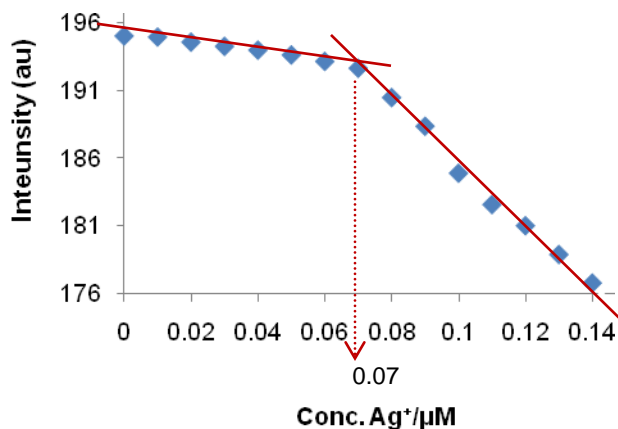## Calculations for detection limit:

Figure S5. Figure showing the fluorescence intensity at 418 nm as a function of Ag⁺ ions concentration.

To determine the detection limit, fluorescence titration of compound **3** with silver ions was carried out by adding aliquots of silver solution of micromolar concentration and the fluorescence intensity as a function of Ag^+ ions added was then plotted. From this graph the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **3** gave the detection limit.

Equation used for calculating detection limit (DL):

DL   = $C_L \times C_T$

C_L = Conc. of Ligand; C_T = Conc. of Titrant at which change observed.
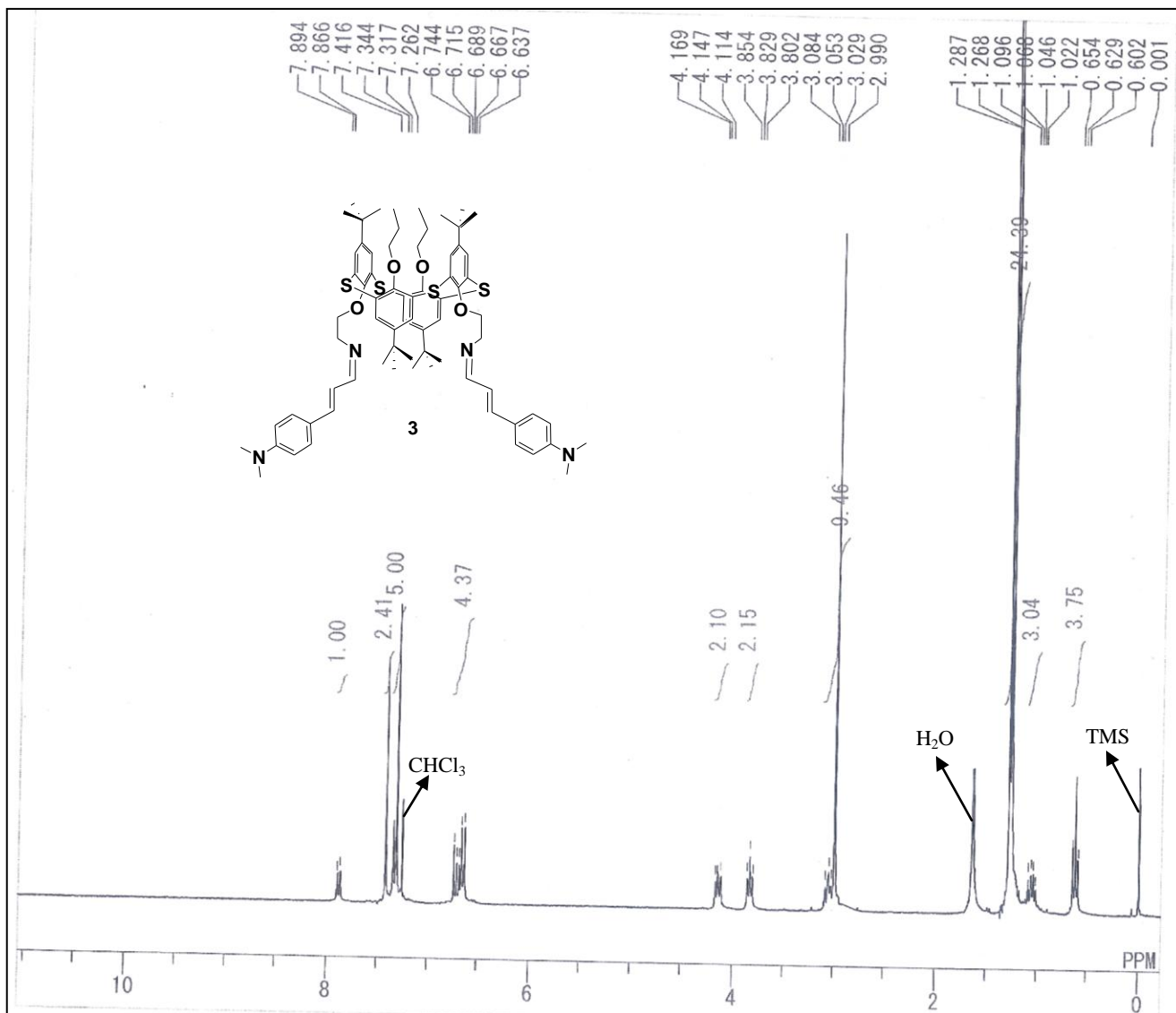
Thus;

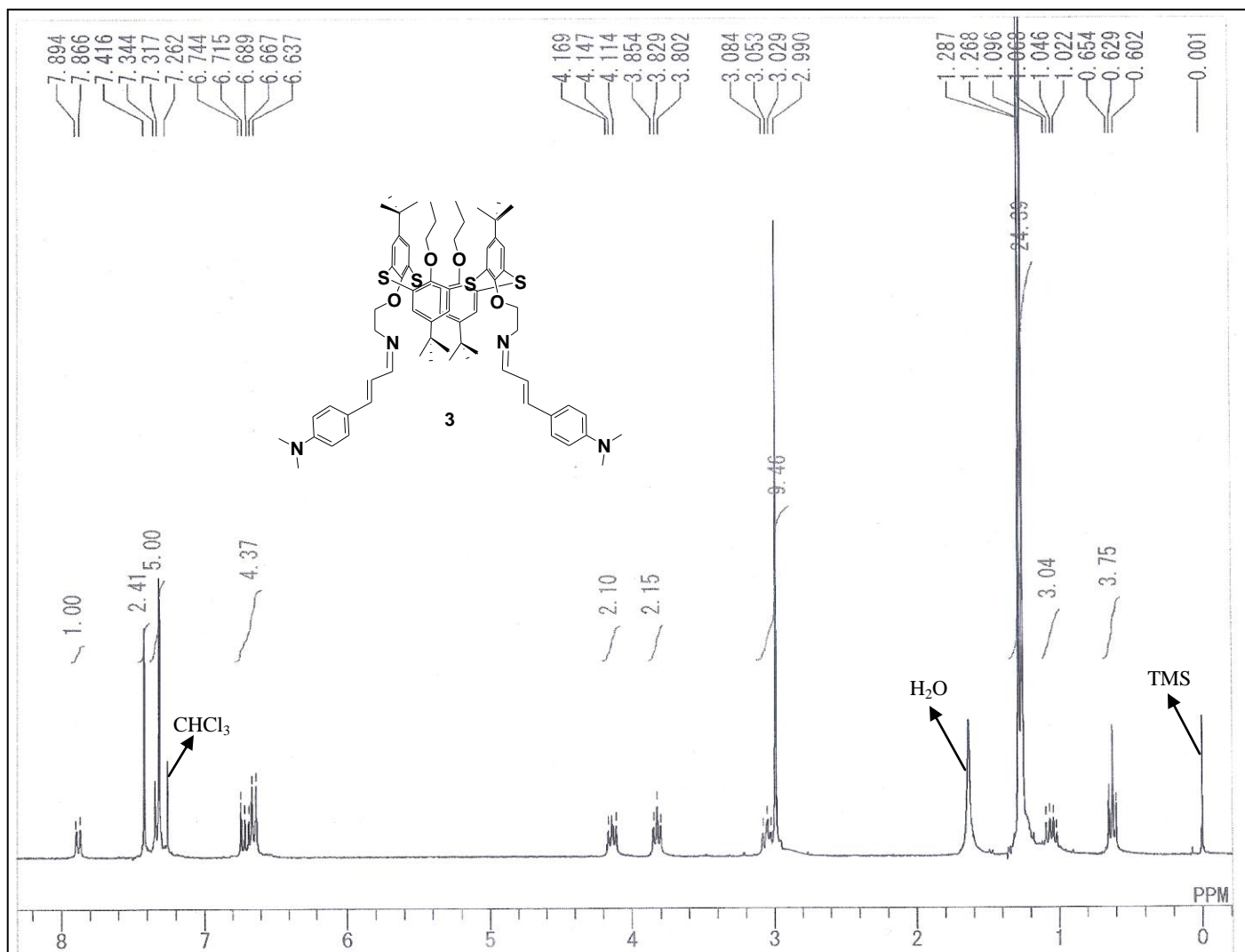DL = 1×10^{-6} × 0.07×10^{-6} = 0.07×10^{-6} = 7×10^{-8}

                 or

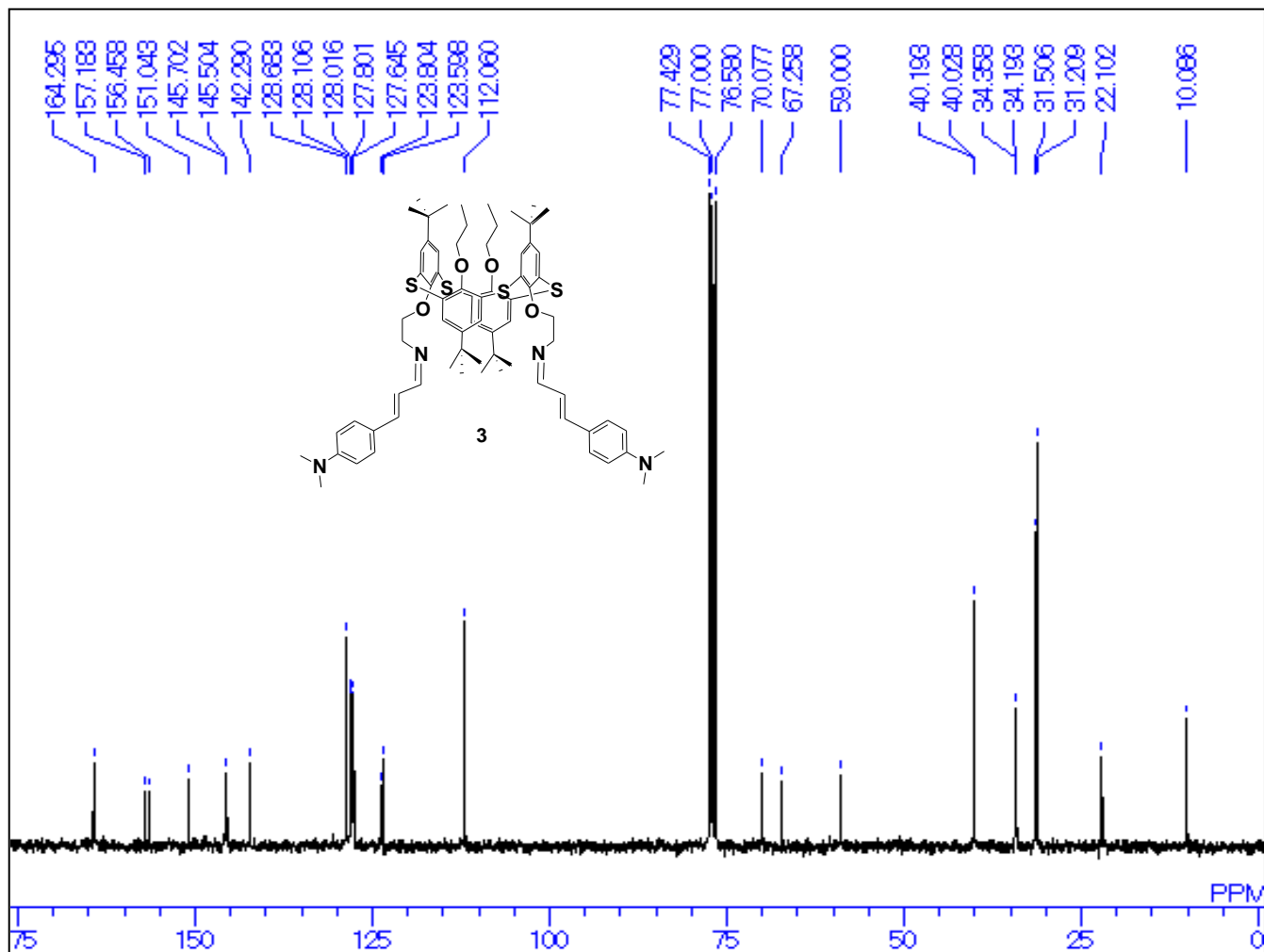   = 70×10^{-9} = 70 nanomolar
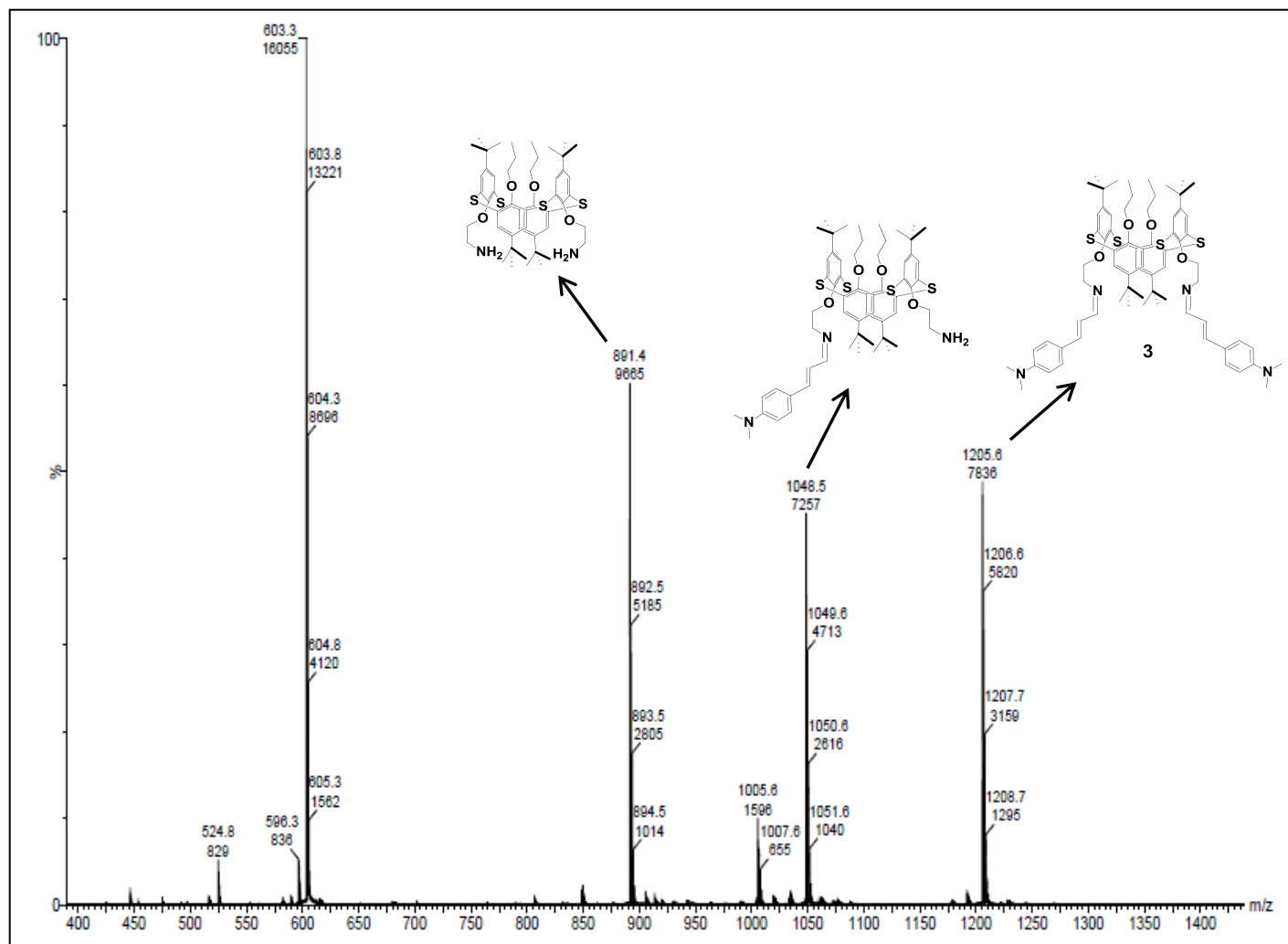
^{1}H NMR spectrum of receptor **3** (11-0 ppm).

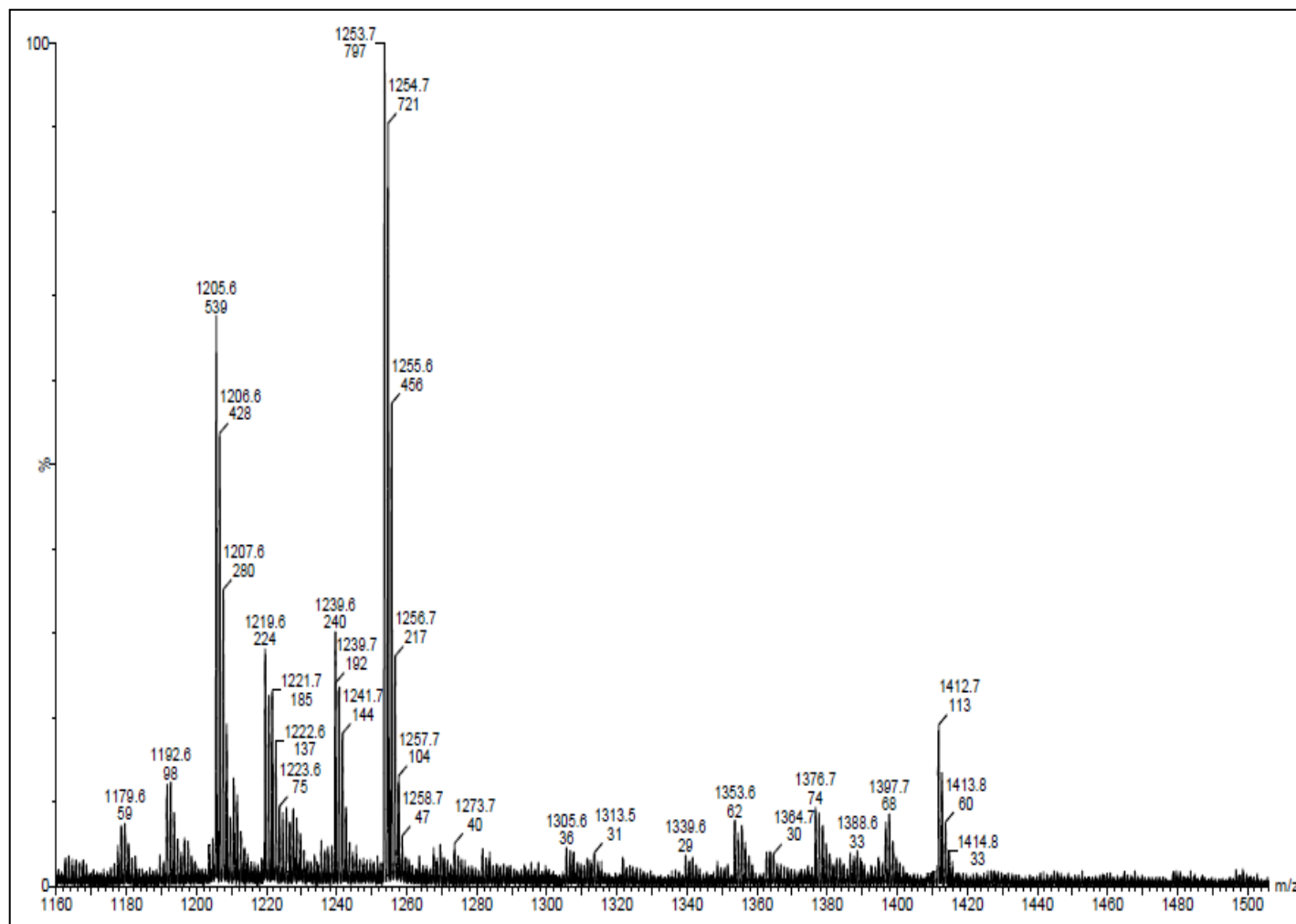^{1}H NMR spectrum of receptor **3** (expanded).
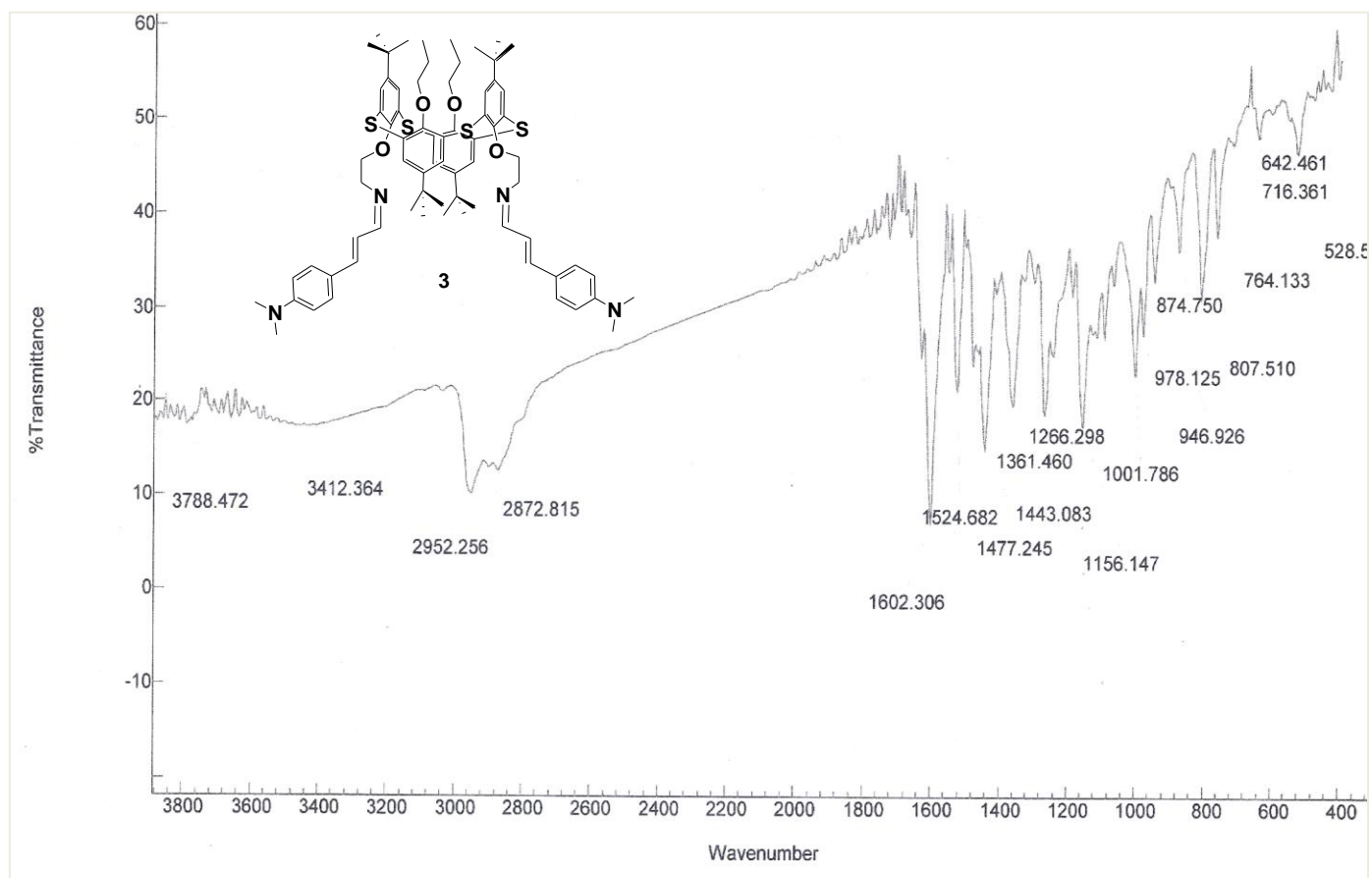
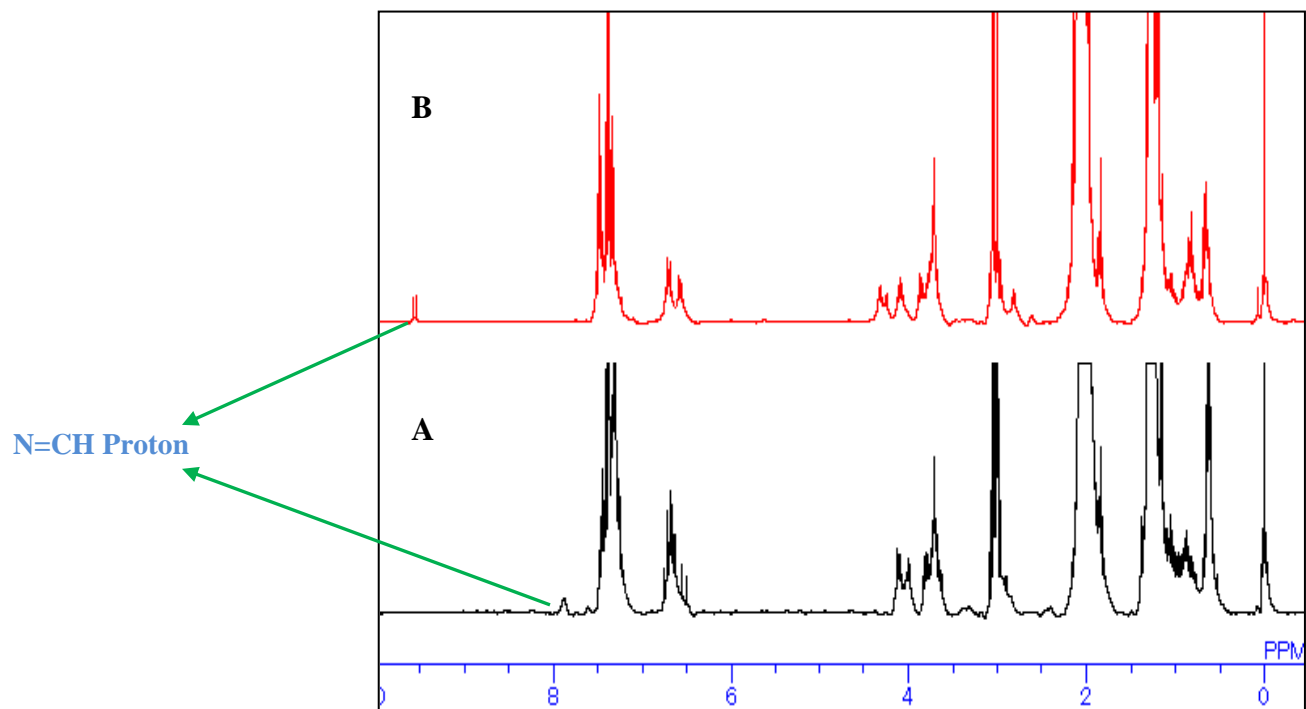^{13}C NMR spectrum of compound **3**.

Mass spectrum of receptor **3**.

Mass spectrum of receptor **3**.AgClO$_4$ complex

IR spectrum of compound **3**.
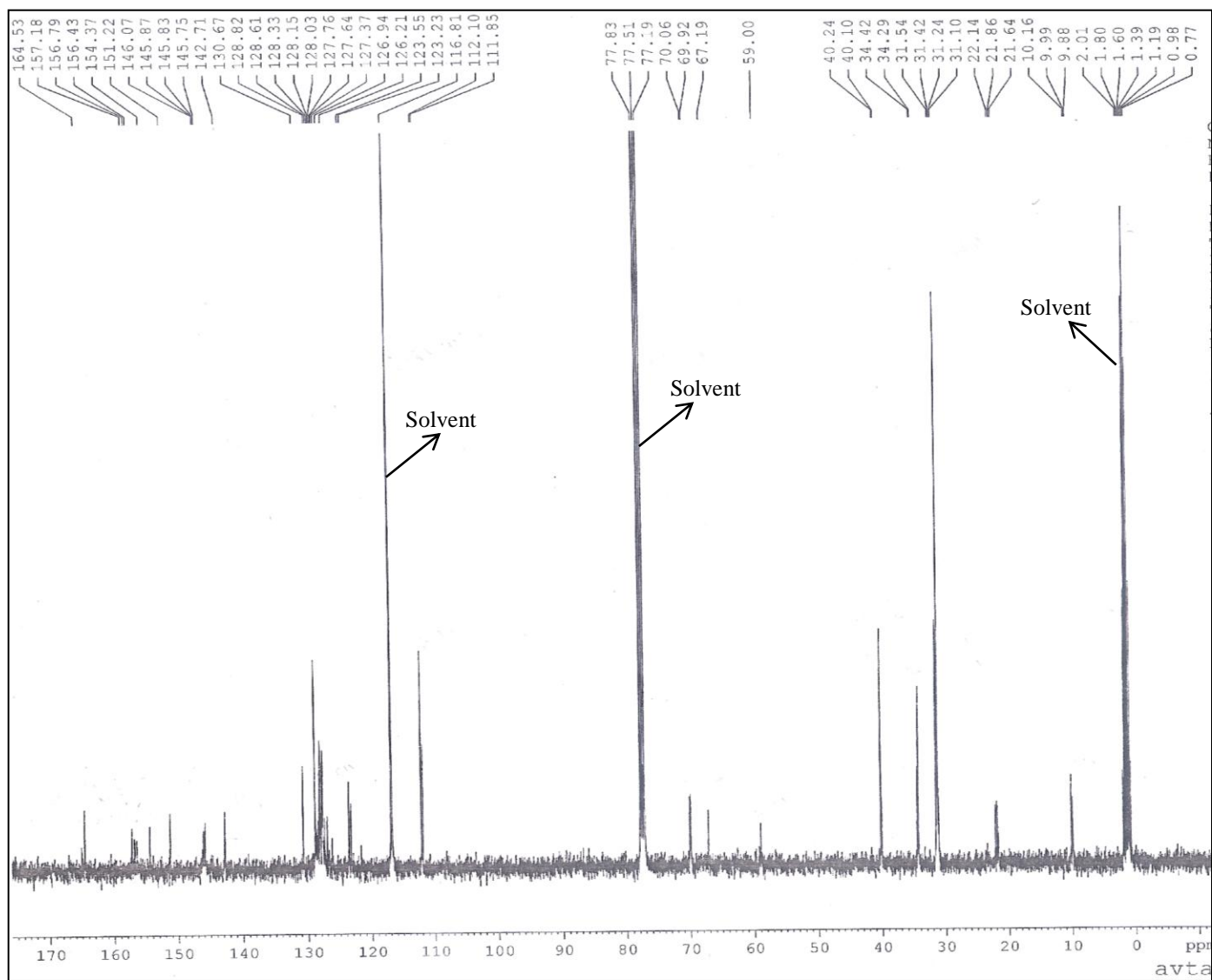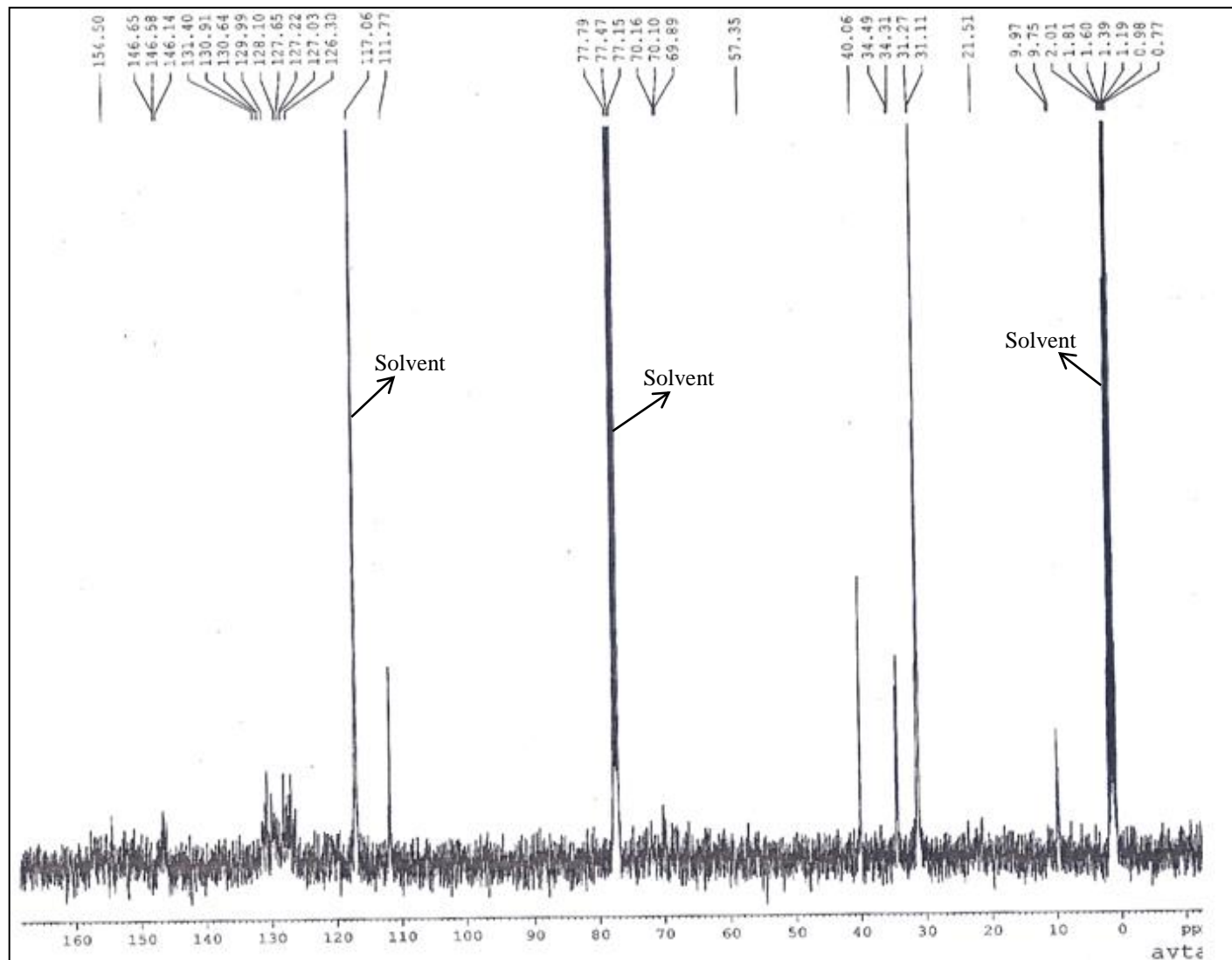
^{1}H NMR spectra of **3** in CDCl$_3$/CD$_3$CN (8:2). (**A**) Free ligand (**B**) in presence of 1.0 equiv of silver perchlorate.
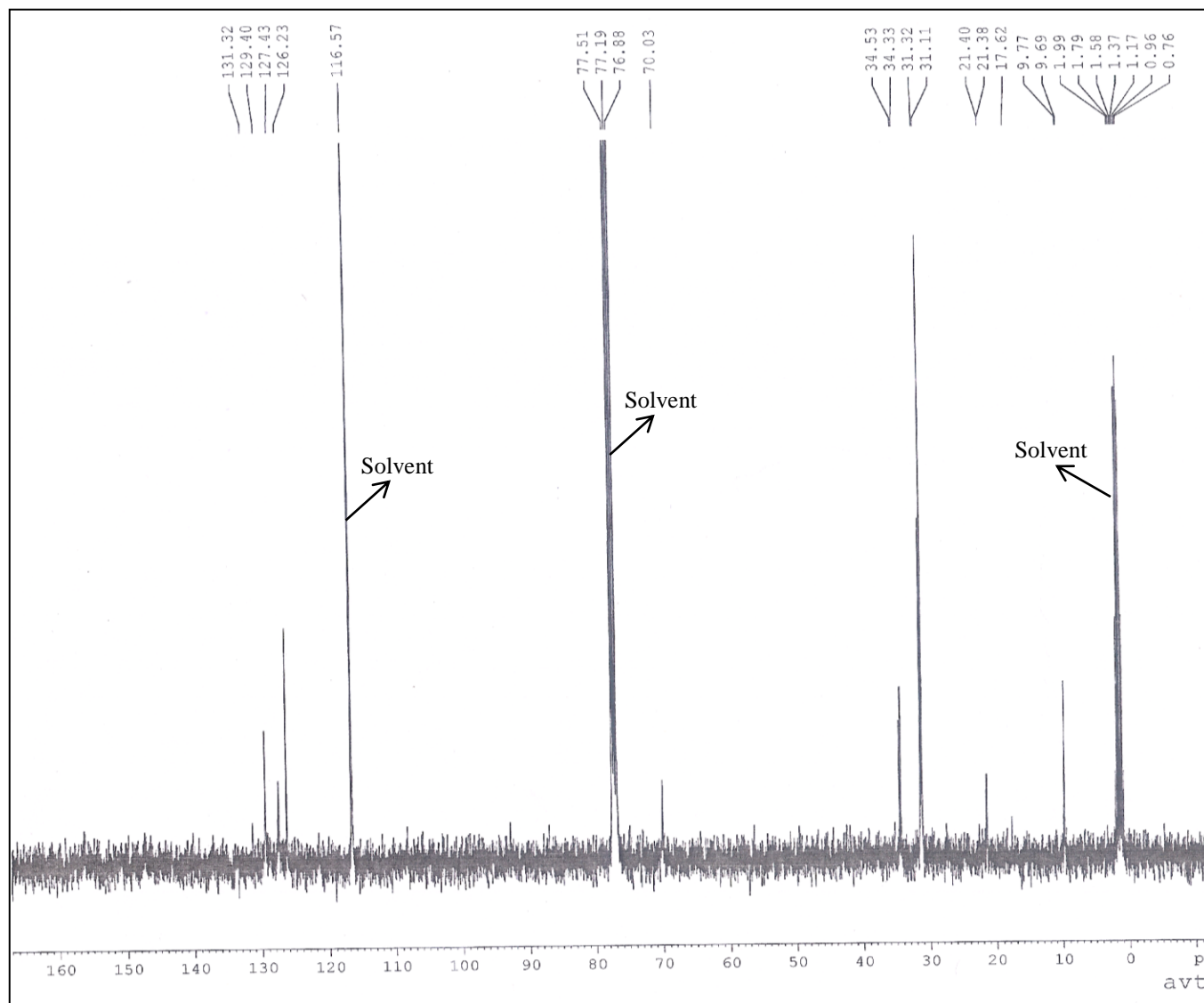
^{13}C NMR spectrum of compound **3** in CHCl$_3$:CH$_3$CN (8:2).

^{13}C NMR spectrum of compound **3** in CHCl$_3$:CH$_3$CN (8:2) in the presence of 1.0 equiv of silver perchlorate.

^{13}C NMR spectrum of compound **1** in CHCl$_3$:CH$_3$CN (8:2).

^{13}C NMR spectrum of compound **1** in CHCl$_3$:CH$_3$CN (8:2) in the presence of 1.0 equiv of silver perchlorate

Solvent

Solvent

Solvent
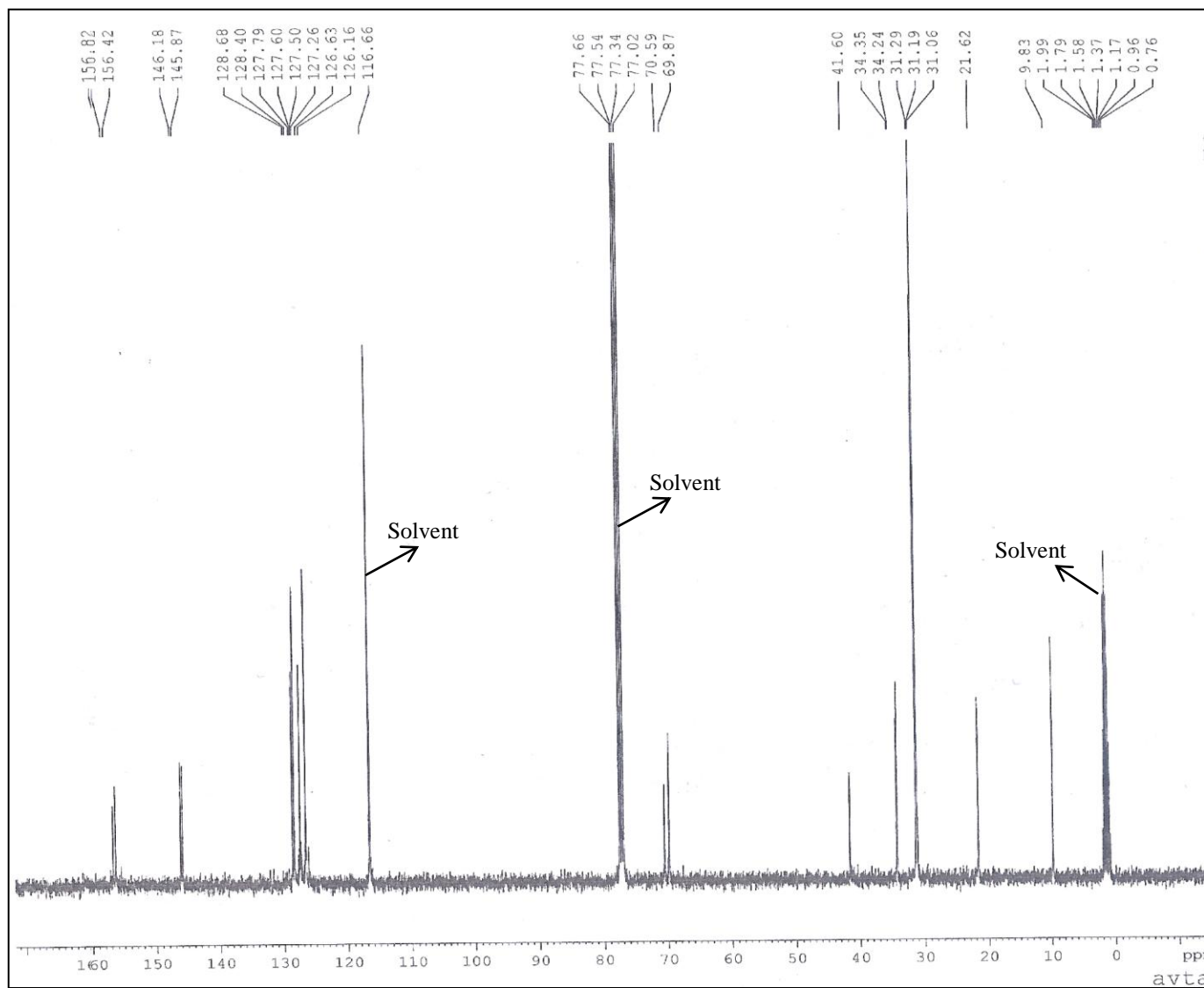
References

1. Deams, J. N.; Grosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.