

Green synthesis of CuO nanoparticles using *Lantana camara* flower extract and their potential catalytic activities towards the aza-Michael reaction

Rakesh Chowdhury,¹ Aslam Khan² and Md. Harunar Rashid^{*,1}

¹Department of Chemistry, Rajiv Gandhi University, Rono Hills
Doimukh 791 112 (Arunachal Pradesh)

²King Abdullah Institute for Nanotechnology, King Saud University, Riyadh 11451, Saudi
Arabia

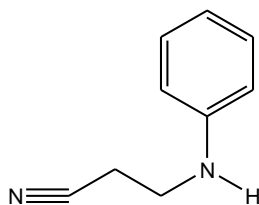
*Corresponding Author E-mail: harunar.rashid@rgu.ac.in

Characterization of the products

The synthesized CuO was characterized by different spectroscopic, microscopic and diffractometric techniques. X-ray diffraction (XRD) study of the dried powder samples was carried out on a X'Pert Pro (Panalytical) powder X-ray diffractometer using Cu k_{α} radiation with a wavelength of 0.154 nm at an accelerating voltage of 40 kV with 35 mA current. For scanning electron microscopic (SEM) study, a small amount of the dry powder samples were spread on a carbon tape pasted on an aluminum stub and then sputter-coated with platinum to minimize the charging effect. The micrographs were then recorded in a field emission scanning electron microscope (FESEM) (JEOL 7600F) at an accelerating voltage of 5 kV. For transmission electron microscopic (TEM) studies, a drop of an aqueous suspension of individual powder sample was cast on a carbon-coated copper grid. The excess solutions were soaked with a tissue paper followed by drying in air. The micrographs were then recorded in a high-resolution JEOL electron microscope (JEM 2100EM) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analyses of the dried powder samples were performed in Thermo Fisher Scientific, UK makes ESCALB Xi⁺ X-ray photoelectron spectrometer using Al k_{α} radiations with an incident energy of 1486.61 eV. The

instrument was operated at 15 kV and 300 W at ambient temperature under ultrahigh vacuum. The charging effect on the sample was corrected by setting the binding energy of the carbon (C-1s) at 284.6 eV and this carbon peak was used as a reference position for scaling all the other peaks. The nitrogen (N₂) gas adsorption-desorption isotherms of the CuO NPs were recorded at 77 K (Quantachrome Nova 1000 Instrument) after degassing the powder samples at 120 °C for 2 h in an inert atmosphere. Brunauer-Emmett-Teller (BET) specific surface areas and pore diameters of the samples were determined from the adsorption-desorption isotherms following the well-known Barrett-Joyner-Halenda (BJH) method. ¹H and ¹³C NMR spectra were recorded in a JNM ECS 400 MHz NMR spectrophotometer (JEOL) using tetramethylsilane (TMS) as the internal standard. Chemical shift values are expressed in ppm. Coupling constants are expressed in Hertz.

3-Phenylamino-propionitrile

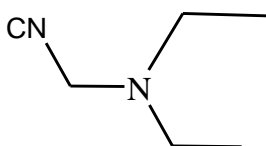


Physical appearance: Brown colored solid

^1H NMR (CDCl_3 , 400 MHz): δ 7.18 (*t*, 2H, $J=7.2$ Hz), 6.72 (*t*, 1H, $J=7.6$ Hz), 6.57 (*d*, 2H, $J=8$ Hz), 3.46 (*t*, 2H, $J=6.40$ Hz), 2.57 (*t*, 2H, $J=6.4$ Hz) ppm.

^{13}C NMR (CDCl_3 , 125 MHz): 146.25, 129.89, 119.32, 118.48, 113.62, 40.12, 19.724 ppm.

Diethyl-isocyanomethyl-amine:

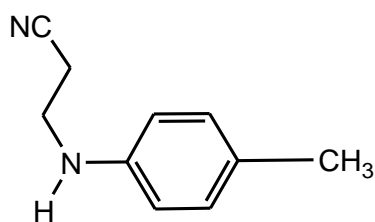


Physical appearance: Light brown colored semisolid

^1H NMR (CDCl_3 , 400 MHz): δ 2.764 (*t*, $J=6.8$, 2H), 2.510 (*q*, $J=7.2$ Hz, 4H), 2.404 (*t*, $J=7.2$ Hz, 2H), 1.001 (*t*, $J=7.2$ Hz, 6H) ppm.

^{13}C NMR (CDCl_3 , 125 MHz): 119.176, 48.409, 46.49, 15.97, 11.928 ppm.

3-*p*-Tolylamino-propionitrile:

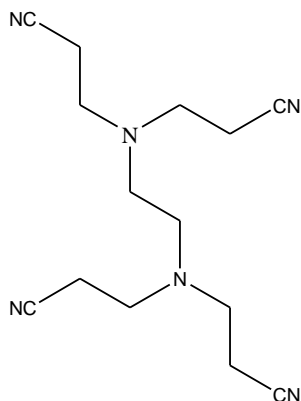


Physical appearance: Brown colored solid

¹H NMR (CDCl₃, 400 MHz): δ 7.0125 (*d*, *J*=8.4 Hz, 2H), 6.540 (*d*, *J*=8.4 Hz, 2H) 3.491 (*t*, *J*=6.4 Hz, 2H), 2.613 (*t*, *J*=6.4 Hz, 2H), 2.224 (*s*, 3H) ppm.

¹³C NMR (CDCl₃, 125 MHz): 143.74, 130.14, 128.22, 118.59, 113.48, 40.06, 20.41, 18.07 ppm.

3-[[2-[Bis-(2-cyano-ethyl)-amino]-ethyl]-(2-cyano-ethyl)-amino]-propionitrile:

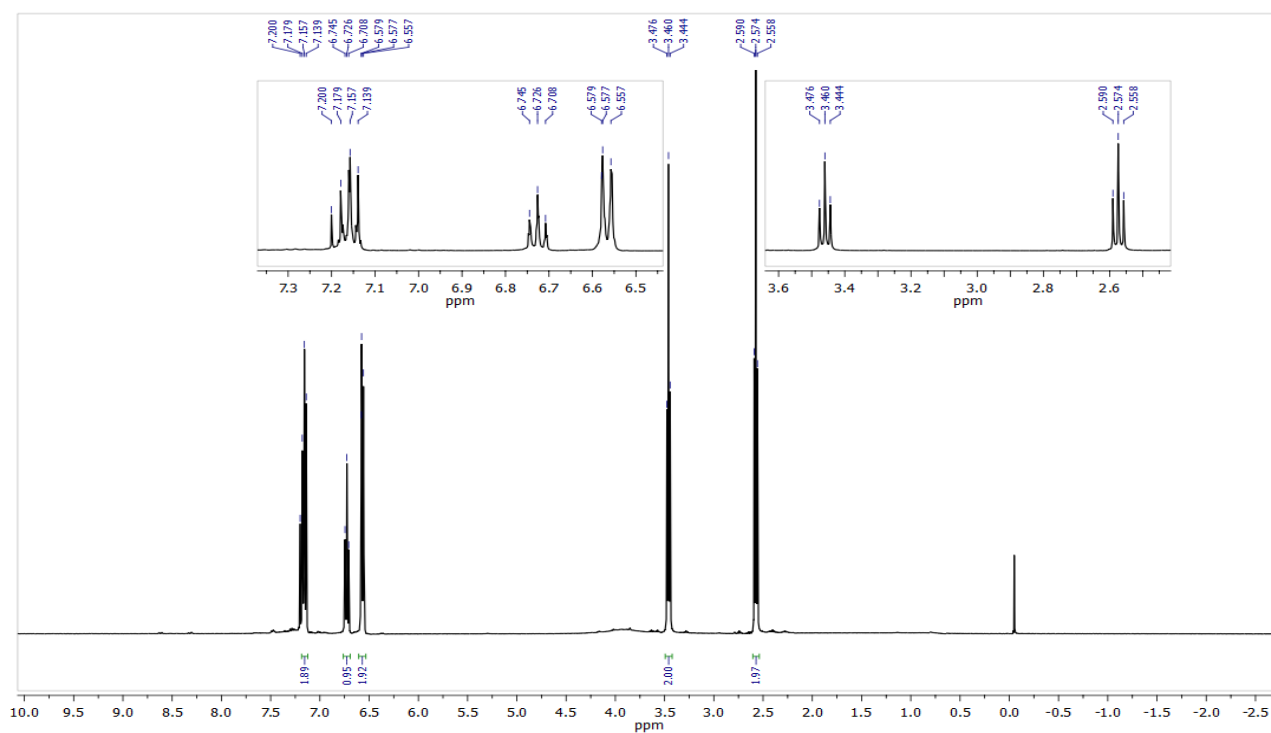


Physical appearance: Brown colored solid.

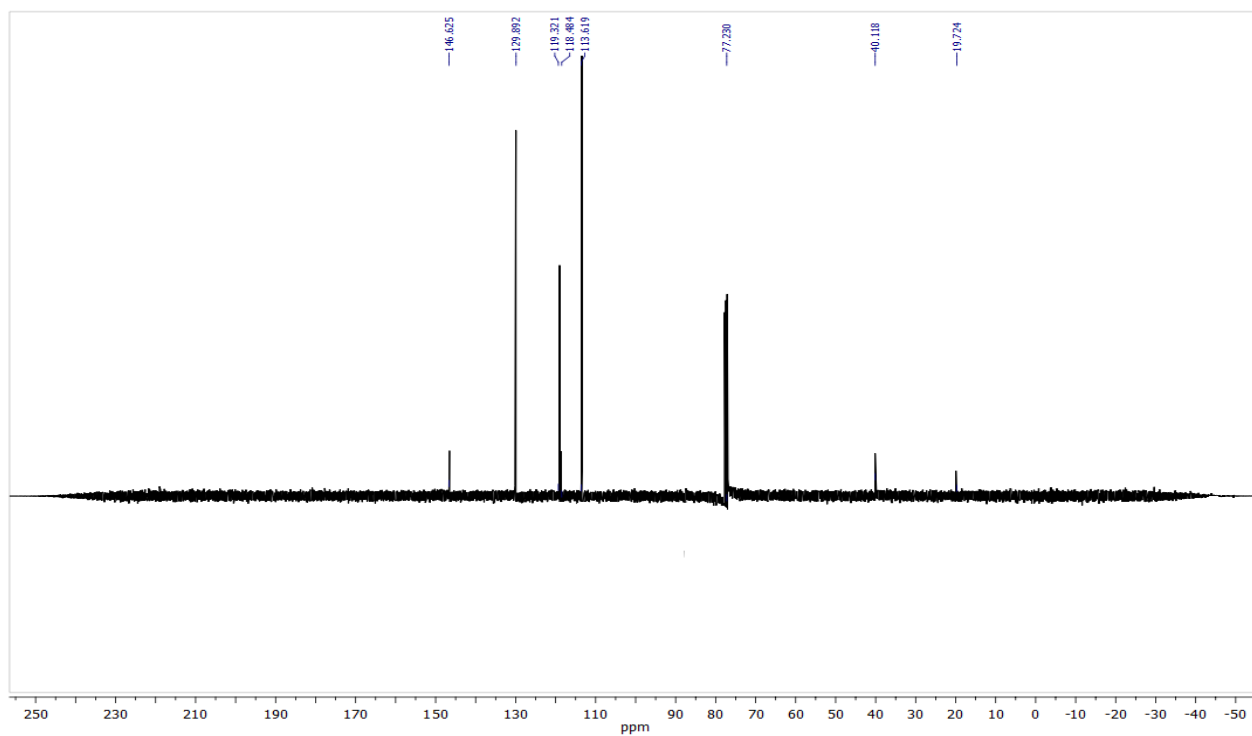
¹H NMR (CDCl₃, 400 MHz): δ 2.901 (*t*, 8H, *J*=6.4 Hz), 2.719 (*s*, 4H), 2.505 (*t*, 8H, *J*=6.8 Hz) ppm.

¹³C NMR CDCl₃, 125 MHz): 118.84, 53.06, 50.22, 17.31 ppm.

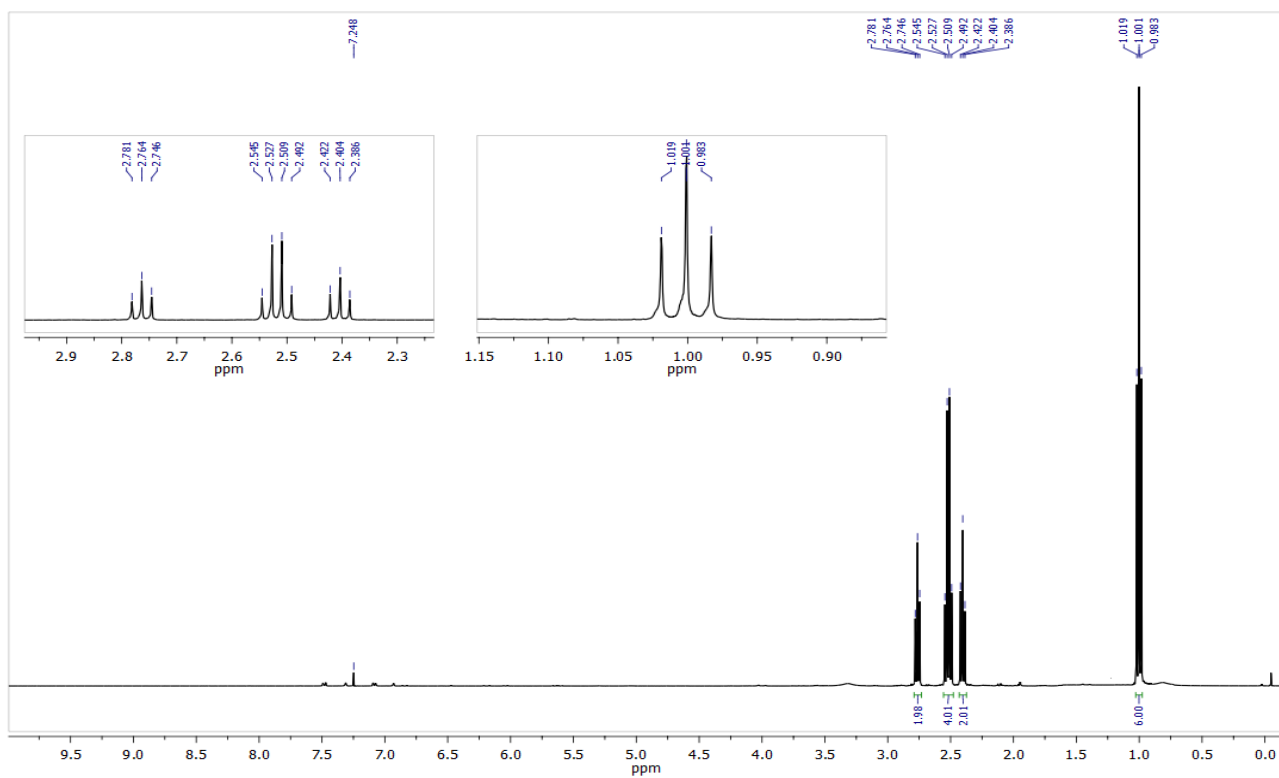
^1H and ^{13}C NMR of isolated products



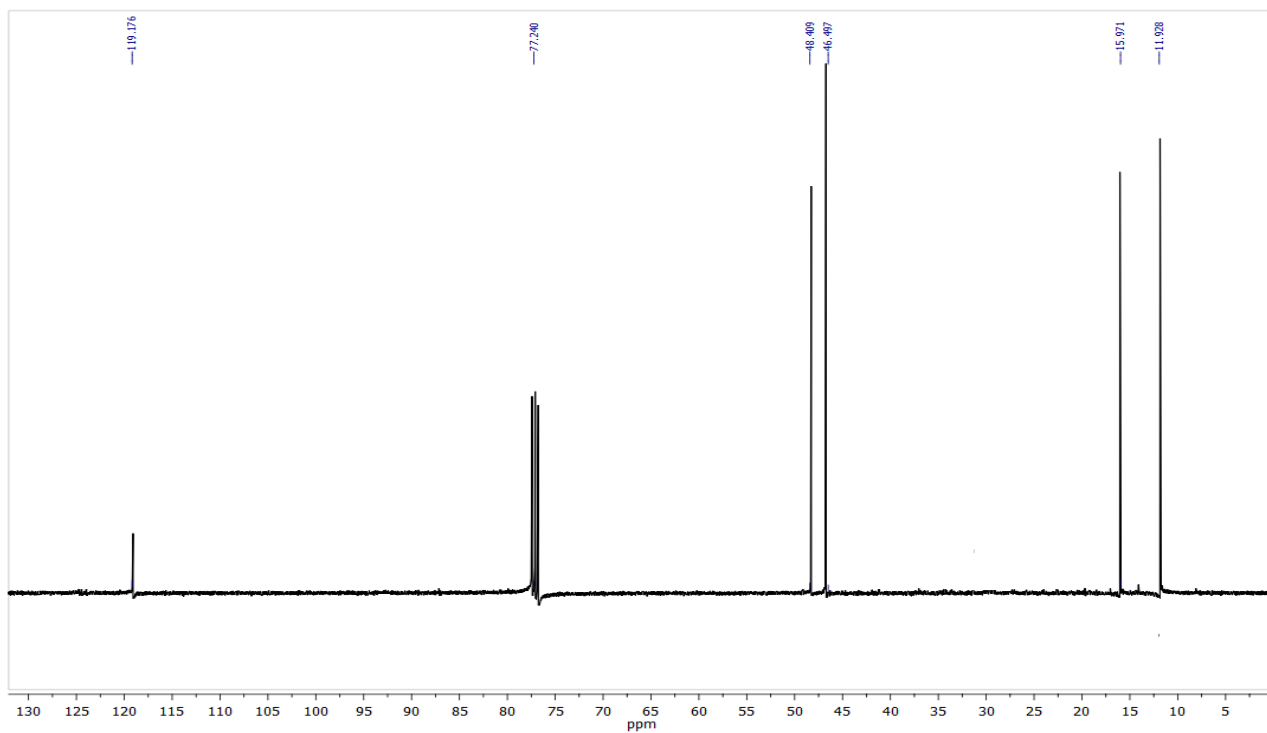
^1H NMR spectra of 3-phenylamino-propionitrile



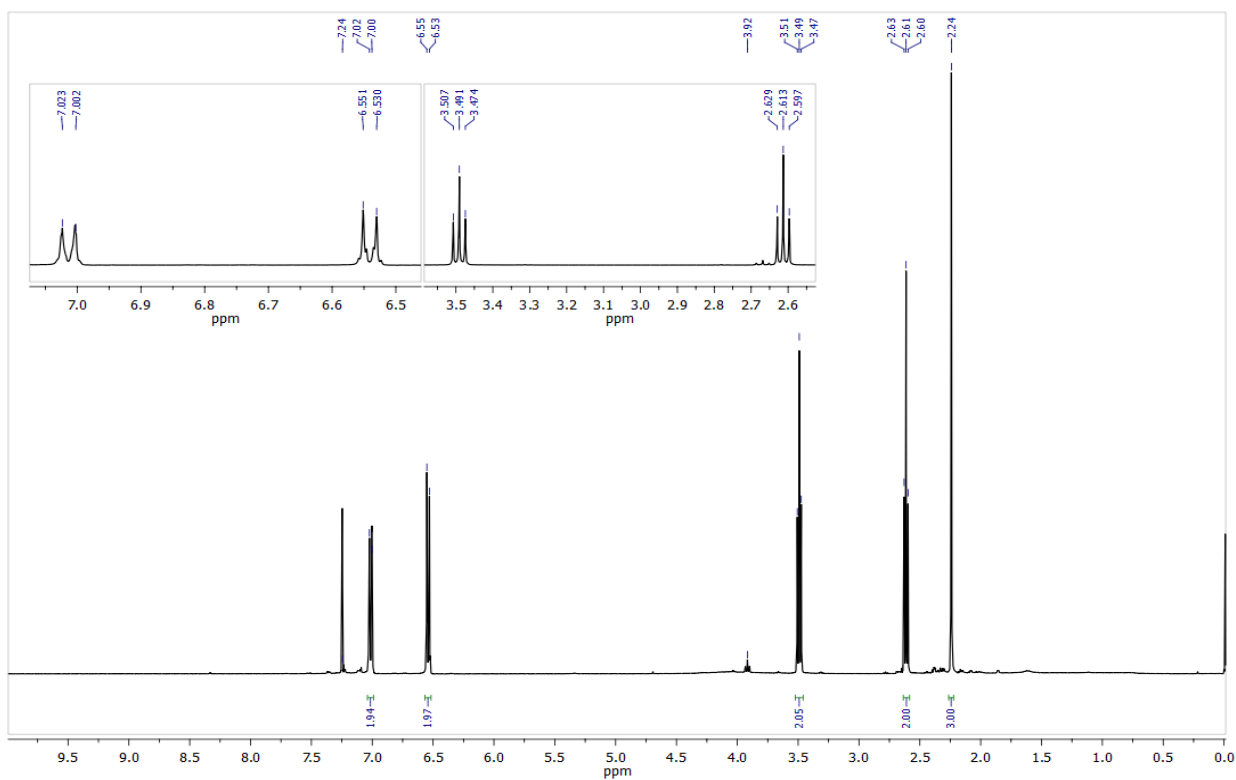
^{13}C NMR spectra of 3-phenylamino-propionitrile



¹H NMR spectra of diethyl-isocyanomethyl-amine



¹³C NMR spectra of diethyl-isocyanomethyl-amine



¹H NMR spectra of 3-p-tolylamino-propionitrile

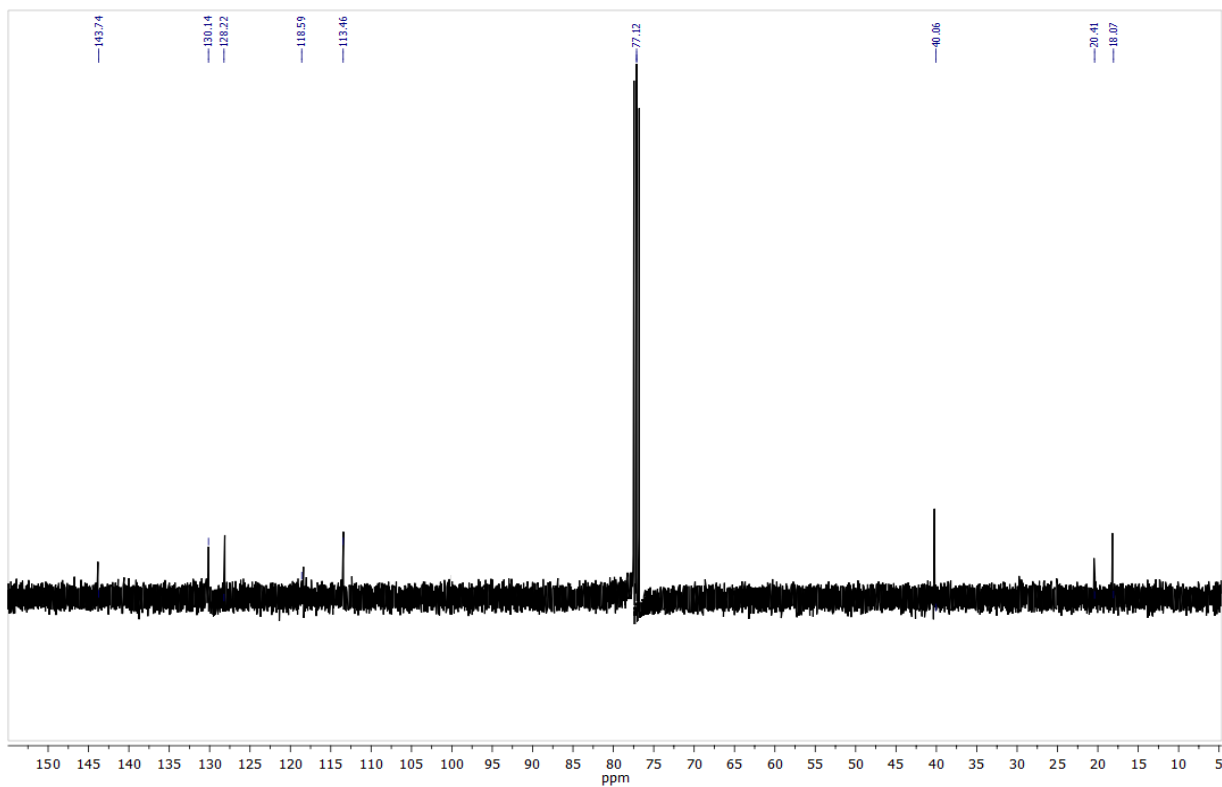
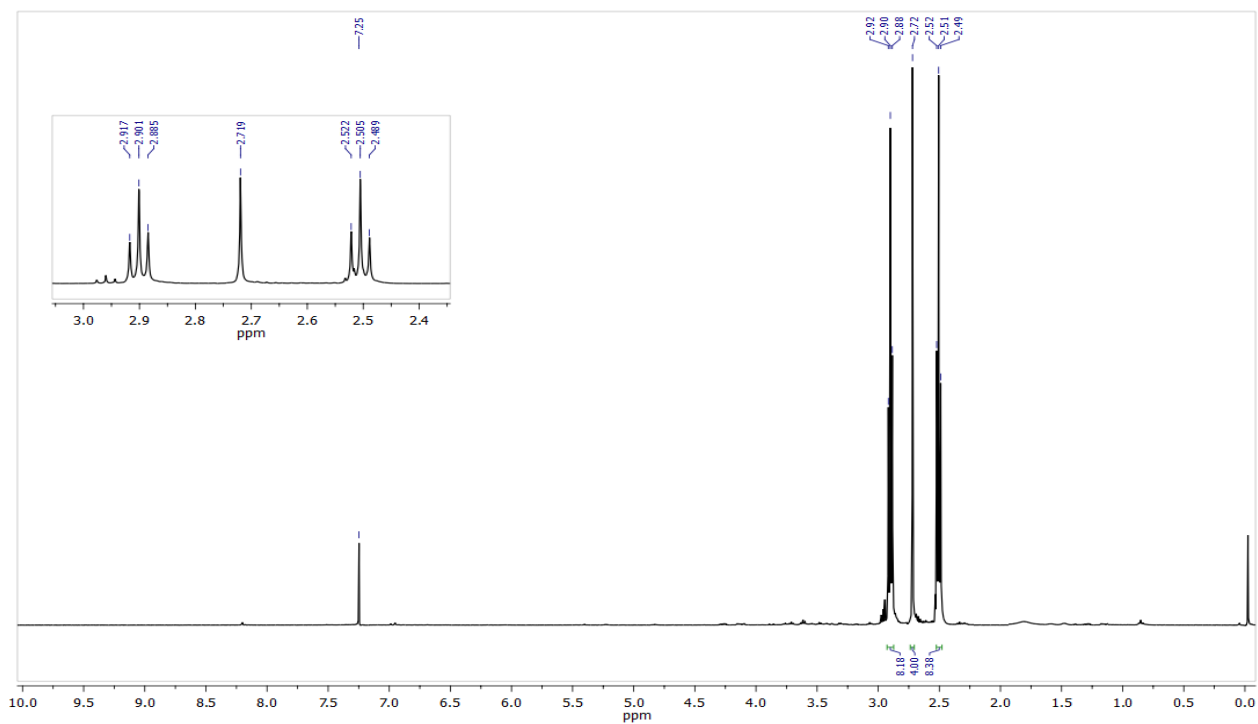
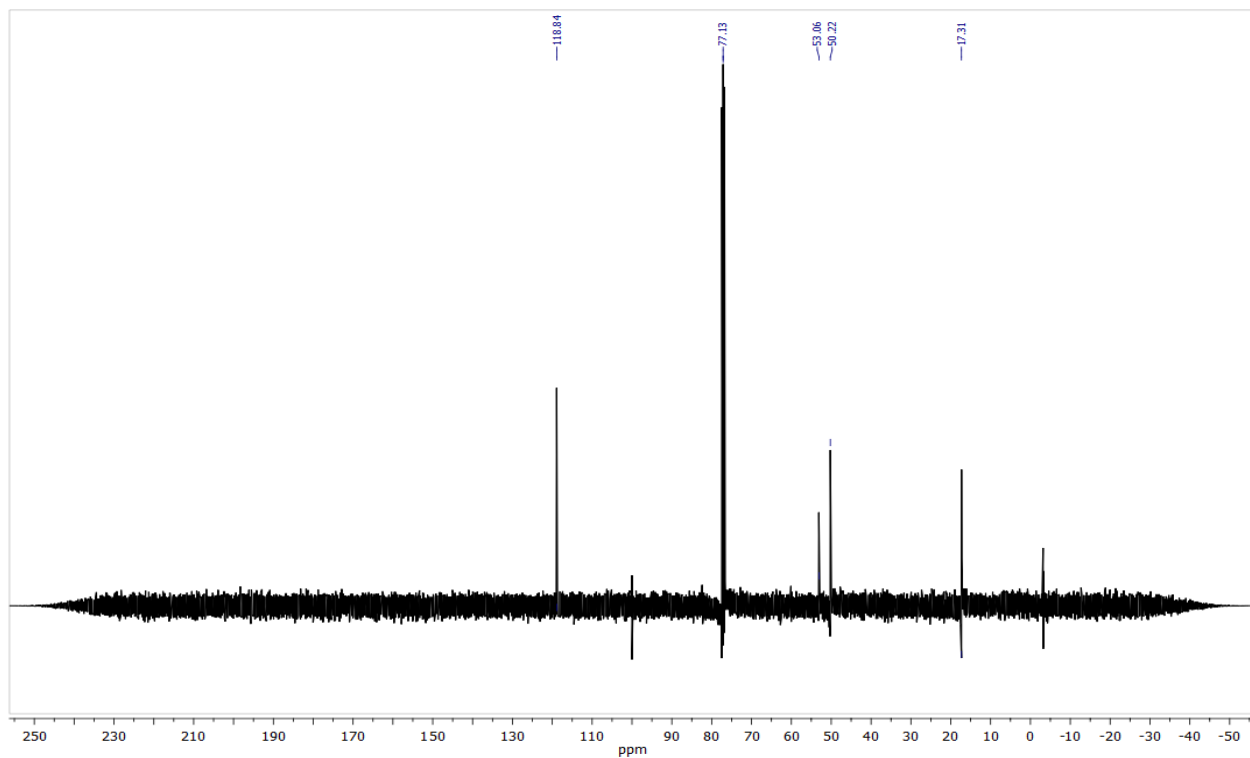


Figure. ¹³C NMR spectra of 3-p-tolylamino-propionitrile



¹H NMR spectra of 3-[[2-[bis-(2-cyano-ethyl)-amino]-ethyl]-(2-cyano-ethyl)-amino]-propionitrile



¹³C NMR spectra of 3-[[2-[Bis-(2-cyano-ethyl)-amino]-ethyl]-(2-cyano-ethyl)-amino]-propionitrile