Supporting Information

Gold nanoparticles stabilized on nanocrystalline magnesium oxide as an active catalyst for reduction of nitroarenes in aqueous medium at room temperature

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General remarks

NAP-MgO (commercial name: NanoActive™ Magnesium Oxide Plus), was purchased from Nano Scale Materials, Inc. (Manhattan, USA). All chemicals were purchased from commercial sources, and were used as received. All solvents used for experiments were dried using standard procedures (except water), and distilled prior to use. Transmission Electron Microscope (JEOL JEM-2100 in ISSP, Univ. Tokyo) operating at 200 kV was used to obtain a bright field image for Au catalysts. The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku diffractometer with Cu Kα radiation. XPS (X-ray photoelectron spectra) were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The FT-IR (Fourier Transformation-Infrared) spectra were recorded on a Perkin–Elmer spectrophotometer. Energy dispersive X-ray (EDX) spectroscopy was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. An inductively coupled plasma optical emission spectrometer (ICP-OES, Intrepid II XDL, Thermo Jarrel Ash) was used for determining the gold content in the catalyst. Measurements of Au- L_{III} edge extended X-ray absorption fine structure (EXAFS) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK－IMSS－PF). The measurements were made in a fluorescence mode. Spectra were measured at BL-7C. The electron storage ring was operated at 2.5 GeV and 450 mA. Synchrotron radiation from the storage ring was monochromatized by a Si(111) channel cut crystal. Ionization chamber, which was used as detector for incident X-ray (I_0) was filled with N_2 (100 %) gas. The fluorescence yield was detected using a Lytle detector filled with Ar gas. The EXAFS raw data were analyzed with UWXAFS analysis package [1] including background subtraction program AUTOBK [2] and curve fitting program FEFFIT [3]. The amplitude reducing factor, S_0^2 was fixed at 0.95. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code [4]. ATOMS [5] was used to obtain FEFF input code for crystalline materials.After the evacuation at 473 K for 8 hours, the amounts of nitrogen adsorption for the samples were measured at liquid nitrogen temperatures with Autosorb-1C (Quantachrome). The surface area values were determined with a multi-plot BET method. UV-visible spectrophotometric studies were performed on a Hitachi U-2910 spectrophotometer.^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on an Avance 300 (300 MHz for ^{1}H-NMR and ^{13}C-NMR) spectrometer in $CDCl_3$ or d_6-DMSO solvent using TMS as an internal standard. Mass spectral studies were carried out on a Waters 2695 Photoiodide array Detector instrument. GC-MS analysis was carried out in a Hewlett

Packard 6890 series GC system using a HP-IMS column of 15m X 0.25 mm X 0.25 µm. GC analyses were performed on a Shimadzu 2014 Gas Chromatograph using column BP-01(30m X 0.25mm X 1.0 µm). ACME SILICA GEL was used for column chromatography purposes using ethyl acetate/hexanes as eluting agents, and thin layer chromatography was performed on Merck precoated silica-gel 60-F254 plates.

Plots of $\ln C_t/C_0$ vs time for supported gold catalysts corresponding to 100% conversion of 4-nitrophenol to 4-aminophenol

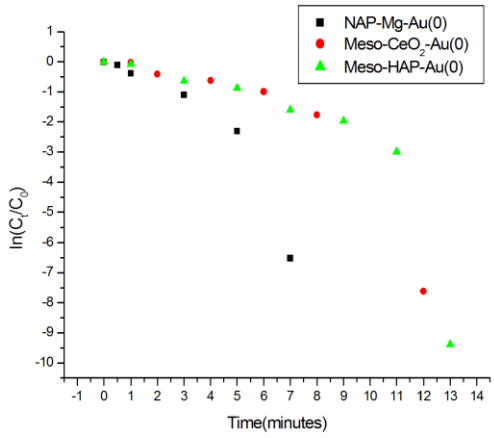


Fig.1 Plot of ln (C_t/C_0) versus time for the reduction of 4-nitrophenol with supported gold catalysts corresponding to 100% conversion.

TEM images of meso-HAP-Au(0) and meso-CeO_2-Au(0)

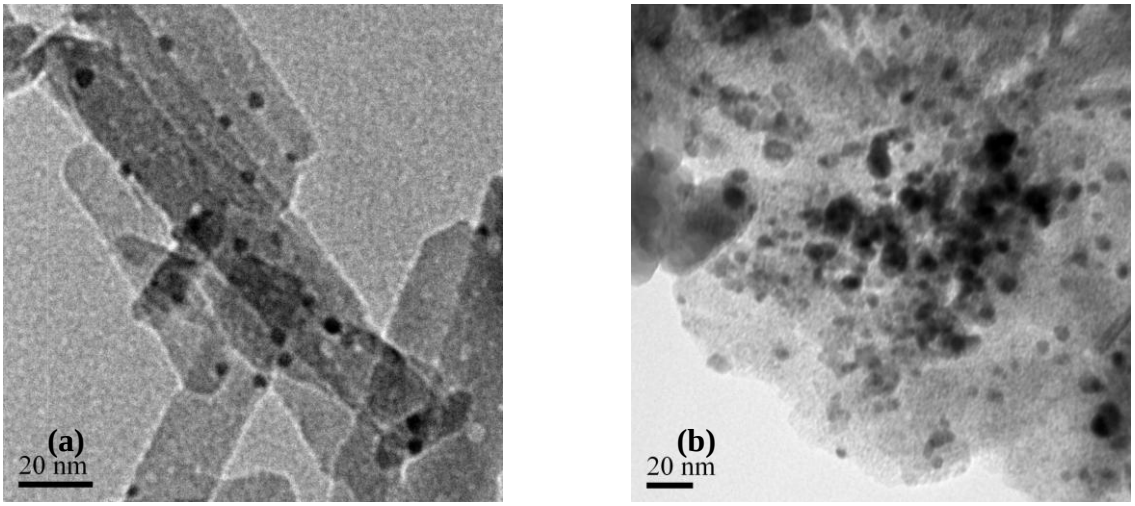


Fig. 2 Bright Field Transmission Electron Micrograph (TEM) images of (a) meso-HAP-Au(0)(HAP: Hydroxyapatite) and (b) meso-CeO_2-Au(0).

EXAFS studies of supported gold catalysts

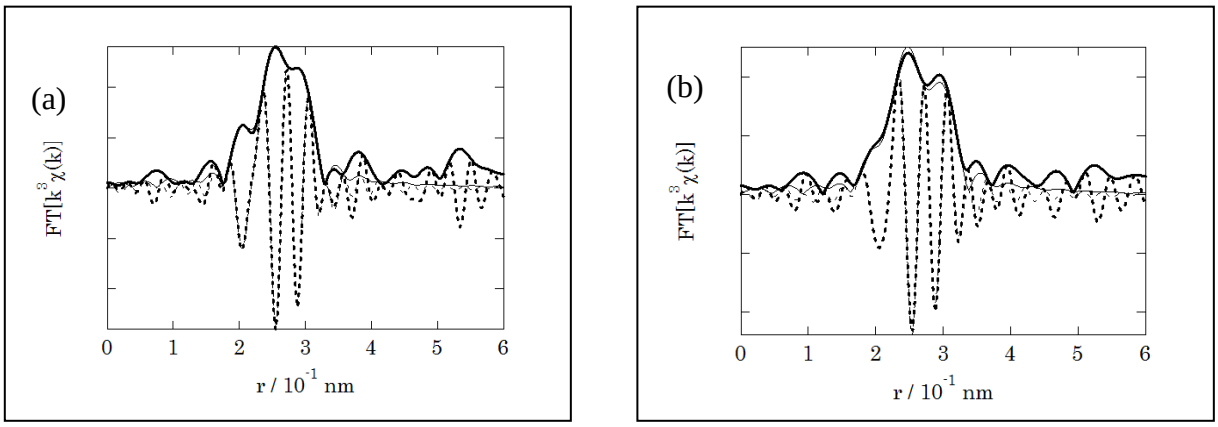


Fig.3 k^3-weighted Fourier transform of Au-LIII edge EXAFS for (a) meso-HAP-Au(0) and (b) meso-CeO_2-Au(0). Amplitude: solid curves; imaginary part: dotted curves; observed data: thick curves; fitting data: thin curves

Table1 Summary of the EXAFS fitting results for Au catalysts

	Au-Au R (10^{-1}nm)	CN	DW (10^{-5}nm^2)	Δk (10 nm^{-1})	Δr (10^{-1}nm)	ΔE_0(eV)	R_f (%)
Au foil	2.857±0.019	11.4±0.5	8.0±0.2	3.0-16.0	1.0-3.0	0.5±0.5	0.46
Meso HAP-Au(0)	2.851±0.013	9.2±0.7	8.6±0.5	3.0-12.0	1.0-3.2	3.7±0.7	0.78
Meso CeO_2-Au(0)	2.850±0.007	9.5±1.0	9.1±0.8	3.0-11.0	1.0-3.2	4.4±1.0	1.19

Measurements of Au- L_{III} edge extended X-ray absorption fine structure (EXAFS) were carried out in order to characterize the coordination states of Au catalysts. From these measurements and summary table for EXAFS fitting results, it was found that both meso HAP-Au(0) and meso CeO_2-Au(0) exhibit Au-Au metallic bonding with slightly reduced coordination numbers as Au foil, indicative of Au metallic nanoparticles.

Spectroscopic characterization of the products

Aniline (Table 4, Entry 1): Colourless liquid, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.35 (s, 2H), 6.36-6.43(m, 2H), 6.60-6.67(m, 1H), 6.97-7.05(m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 114.578, 117.748, 128.741, 146.158. GC-MS: m/z = 93

2-Aminophenol (Table 4, Entry 2): Off-white solid, 99%. ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 4.49(bs, 2H), 6.36-6.42(m, 1H), 6.51-6.65(m, 3H), 8.95(bs, 1H); ^{13}C NMR (300 MHz, d_6-DMSO, ppm): δ 114.797, 114.963, 117.005, 119.975, 136.789, 144.381. ESI-MS: m/z = 110 (M+H). $^{+}$

3-Aminophenol (Table 4, Entry 3): Greyish white solid, 99%. ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 4.82(bs, 2H), 5.94(d, *J*= 7.932 Hz, 1H), 6.01-6.04(m, 2H), 6.76(t, *J*=8.120 Hz, 1H), 8.92(bs, 1H); ^{13}C NMR (300 MHz, d_6-DMSO, ppm): δ 101.018, 103.470, 105.567, 129.456, 149.527, 157.873. ESI-MS: m/z = 110 (M+H). $^{+}$

4-Aminophenol (Table 4, Entry 4): Greyish white solid, 98%. ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 4.00(bs, 2H), 6.31-6.39(m, 4H), 8.95(bs, 1H); ^{13}C NMR (300 MHz, d_6-DMSO, ppm): δ 115.389, 115.488, 140.261, 148.229. ESI-MS: m/z = 110 (M+H). $^{+}$

2-Nitroaniline (Table 4, Entry 5): Yellow solid, 78%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.11(bs, 2H), 6.67(t, *J*=7.554 Hz, 1H), 6.80(d, *J*=9.065 Hz, 1H), 7.33(t, *J*=7.554 Hz, 1H), 8.09(d, *J*=9.065 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 116.853, 118.720, 126.083, 132.131, 135.602, 144.677. ESI-MS: m/z = 139 (M+H) $^{+}$.

***o*-Phenylenediamine (minor product of Table 4, Entry 5):** Greyish white solid, 15%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.29(bs, 4H), 6.62-6.74(m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 116.196, 119.705, 134.202. ESI-MS: m/z = 147 (M+K) $^{+}$.

***m*-Phenylenediamine (Table 4, Entry 6):** Off-white solid, 98%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.53(s, 4H), 6.00(s, 1H), 6.09(dd, *J*= 7.932 Hz, 2.077 Hz, 2 H), 6.90(t, *J*= 7.743 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 101.817, 105.808, 130.041, 147.408. ESI-MS: m/z = 109 $(M+H)^+$.

4-Nitroaniline (Table 4, Entry 7): Yellow solid, 74%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.40(bs, 2H), 6.61(d, *J*= 9.065 Hz, 2H), 8.06(d, *J*= 9.065 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$ + d_6-DMSO , ppm): δ 111.584, 125.113, 135.703, 153.884. ESI-MS: m/z = 139 $(M+H)^+$.

***p*-Phenylenediamine (minor product of Table 4, Entry 7):** Grey solid, 21%. ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 3.69(bs, 4H), 6.50(s, 4H); ^{13}C NMR (300 MHz, d_6-DMSO , ppm): δ 115.307, 138.607. ESI-MS: m/z = 109 $(M+H)^+$.

2-Fluoroaniline (Table 4, Entry 8): Colourless liquid, 77%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.63(bs, 2H), 6.58-6.68(m, 2H), 6.84-6.97(m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 114.766, 116.746, 118.199, 124.192, 134.257, 153.022. ESI-MS: m/z = 112 $(M+H)^+$.

2-Chloroaniline (Table 4, Entry 9): Colourless liquid, 68%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.97(bs, 2H), 6.57-6.75(m, 2H), 6.95-7.10(m, 1H), 7.15-7.30(m, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 115.563, 118.530, 118.699, 127.293, 128.931, 142.635. ESI-MS: m/z = 128 $(M+H)^+$.

4-Chloroaniline (Table 4, Entry 10): White solid, 81%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.57(bs, 2H), 6.56(d, *J*= 9.065 Hz, 2H), 7.06(d, *J*= 9.065 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 116.116, 122.910, 128.968, 144.883. ESI-MS: m/z = 128 $(M+H)^+$.

4-Bromoaniline (Table 4, Entry 11): Off-white solid, 85%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.60(bs, 2H), 6.53(d, *J*= 9.065 Hz, 2H), 7.20(d, *J*=9.065 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 109.793, 116.542, 131.725, 145.308. ESI-MS: m/z = 172 $(M)^+$.

2-Iodoaniline (Table 4, Entry 12): Grey solid, 55%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.07(bs, 2H), 6.44-6.50(m, 1H), 6.74(dd, *J*= 9.065 Hz, 1.511Hz, 1H), 7.10-7.16(m, 1H), 7.63(dd, *J*= 9.065 Hz, 1.511Hz, 1H). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 84.105, 114.562, 119.917, 129.225, 138.914, 146.641. ESI-MS: m/z = 220 $(M+H)^+$.

4-Iodoaniline (Table 4, Entry 13): Greyish-white solid, 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.63(bs, 2H), 6.44(d, *J*= 8.687 Hz, 2H), 7.39(d, *J*= 8.687 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 87.330, 117.159, 137.687, 145.926. ESI-MS: m/z = 220 $(M+H)^+$.

2-Chloro- 5-fluoroaniline (Table 4, Entry 14): Greyish-white solid, 74%.^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 5.10(bs, 2H), 6.55-6.62(m, 1H), 6.78-6.82(m, 1H), 7.21-7.30(m, 1H); ^{13}C NMR (300 MHz, d_6-DMSO, ppm): δ 105.006, 106.121, 119.786, 131.726, 147.505, 157.873. ESI-MS: m/z = 146 $(M+H)^+$.

2-Bromo- 5-chloroaniline (Table 4, Entry 15): Greyish-white solid, 78%. ^{1}H NMR (300 MHz, d_6-DMSO, ppm): δ 5.39(s, 2H), 6.47(dd, *J*= 7.743 Hz, 2.077 Hz, 1H), 6.56-6.59(m, 1H), 7.00(t, *J*=7.932 Hz, 1H); ^{13}C NMR (300 MHz, d_6-DMSO, ppm): δ 116.743, 119.713, 123.333, 133.795, 137.314, 151.327. ESI-MS: m/z = 207 $(M+H)^+$.

4-Aminobenzonitrile (Table 4, Entry 16): Off-white solid, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.20(bs, 2H), 6.63(d, *J*= 9.065 Hz, 2H), 7.38(d, *J*= 9.065 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 99.697, 114.302, 120.178, 133.649, 150.493. ESI-MS: m/z = 119 $(M+H)^+$.

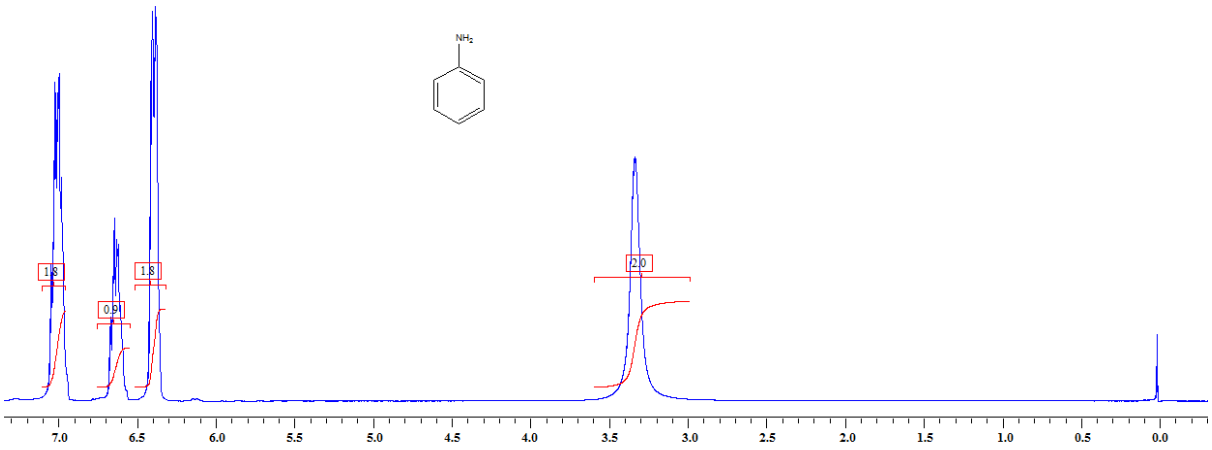
***p*-Toluidine (Table 4, Entry 17):** White solid, 88%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ2.22(s, 3H), 3.47(bs, 2H), 6.56(d, *J*= 8.309 Hz, 2H), 6.93(d, *J*= 7.932, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 20.102, 114.913, 127.190, 129.401, 143.627. ESI-MS: m/z = 108 $(M+H)^+$.

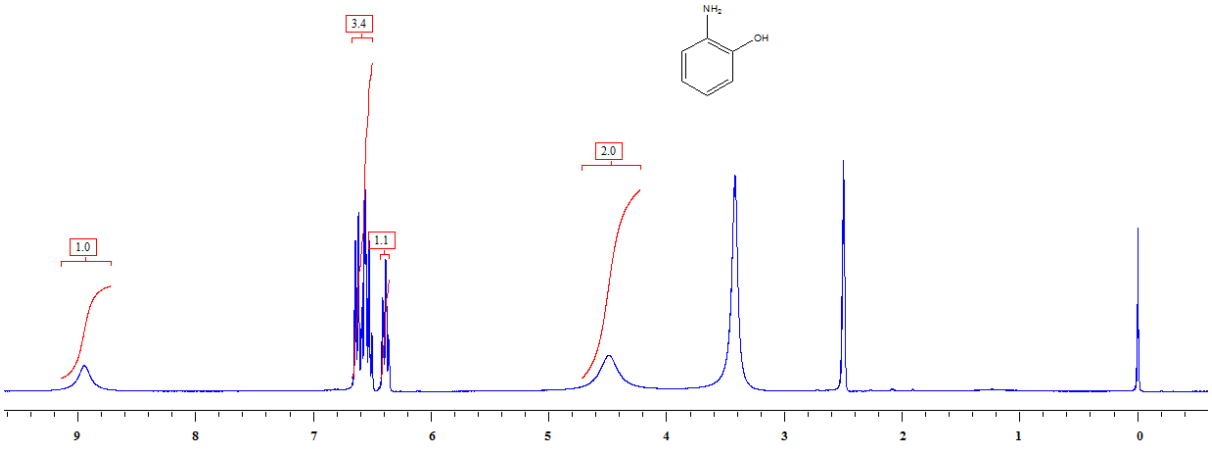
***p*-Anisidine (Table 4, Entry 18):** Grey solid, 91%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.37(bs, 2H), 3.75(s, 3H), 6.63(d, *J*= 8.876 Hz, 2H), 6.72(d, 8.876 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 55.623, 114.709, 116.399, 139.810, 152.703. ESI-MS: m/z = 124 $(M+H)^+$.

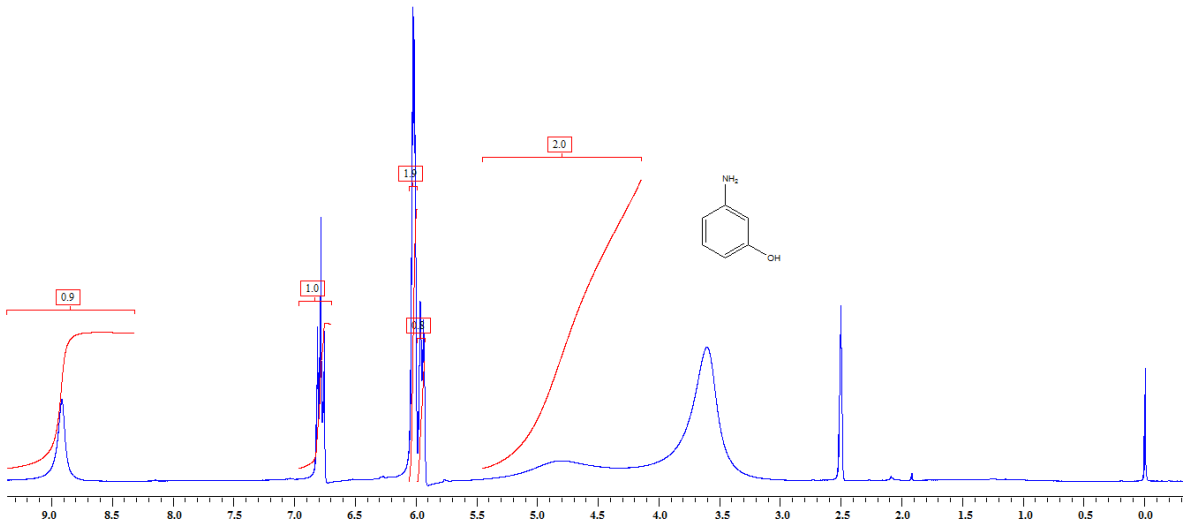
Methyl 4-aminobenzoate (Table 4, Entry 19): White solid, 80%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.84(s, 3H), 4.17(bs, 2H), 6.61(d, *J*= 8.687 Hz, 2H), 7.82(d, *J*= 8.687 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 51.480, 113.644, 119.390, 131.461, 150.904, 167.125. ESI-MS: m/z = 152 $(M+H)^+$.

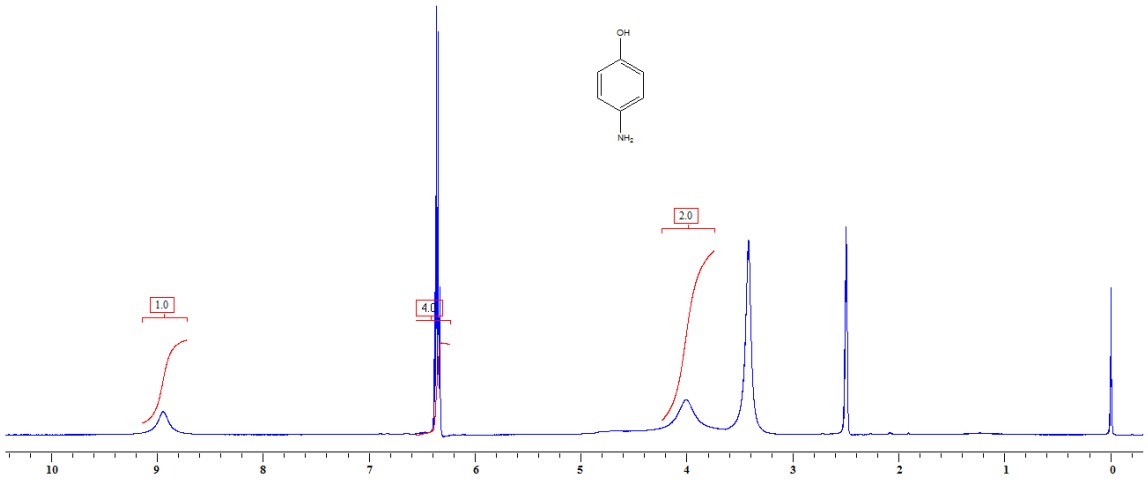
3-Vinylaniline (Table 4, Entry 20): Colourless liquid, 81%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.53(bs, 2H), 5.15(d, *J*= 10.575 Hz, 1H), 5.63(d, *J*= 17.374 Hz, 1H), dd(*J*=7.554, 2.266 Hz, 1H), 6.54-6.63(m, 2H), 6.77(d, *J*= 7.554 Hz, 1H), 7.04(t, *J*= 8.309 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 112.965, 113.867, 115.058, 116.921, 129.663, 137.314. ESI-MS: m/z = 120 $(M+H)^+$.

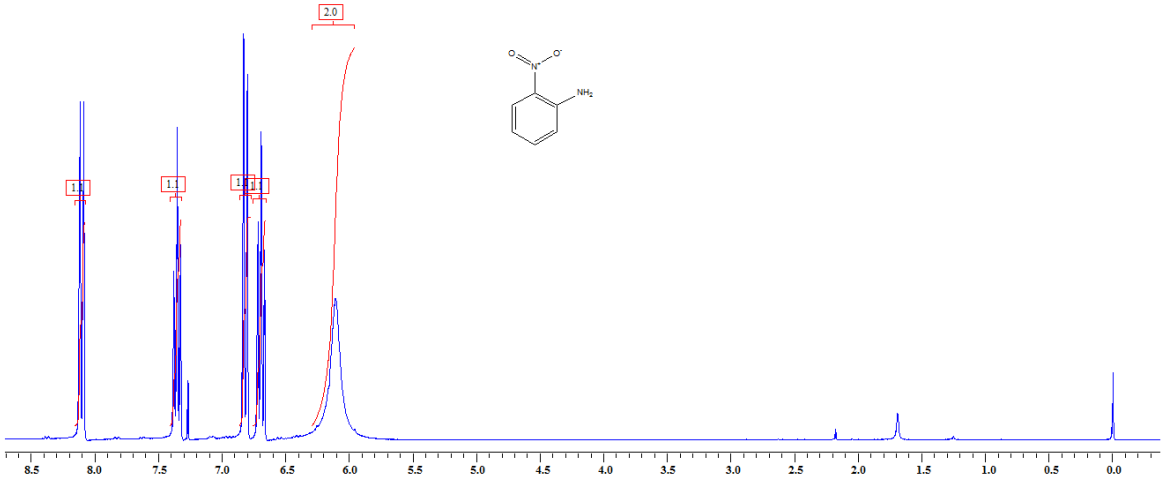
^{1}H NMR spectra of the products

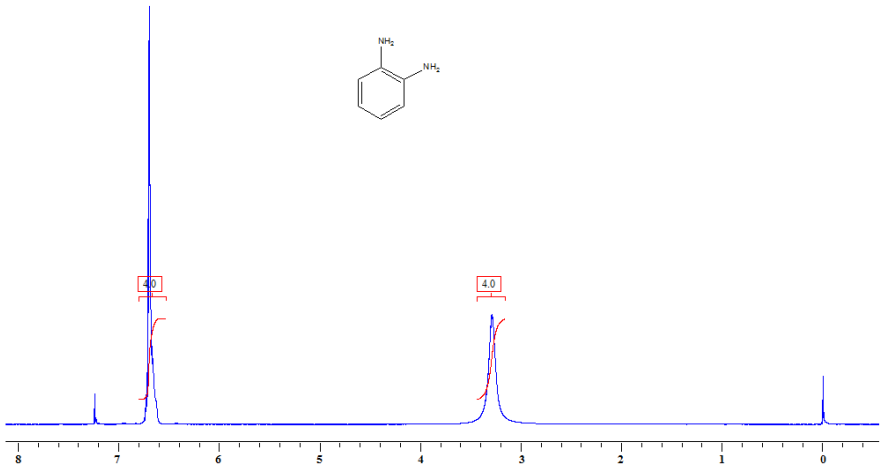


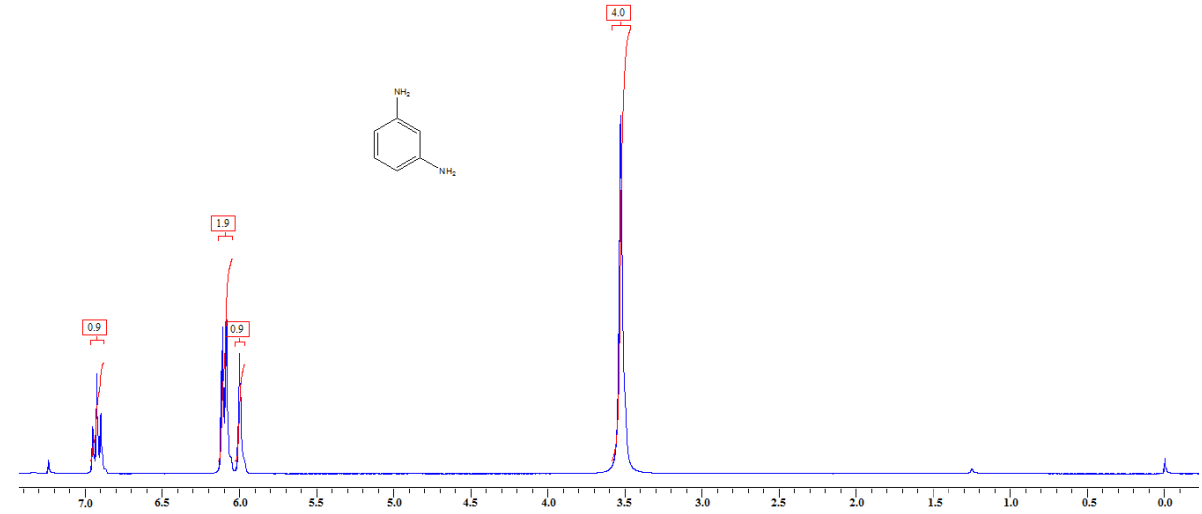


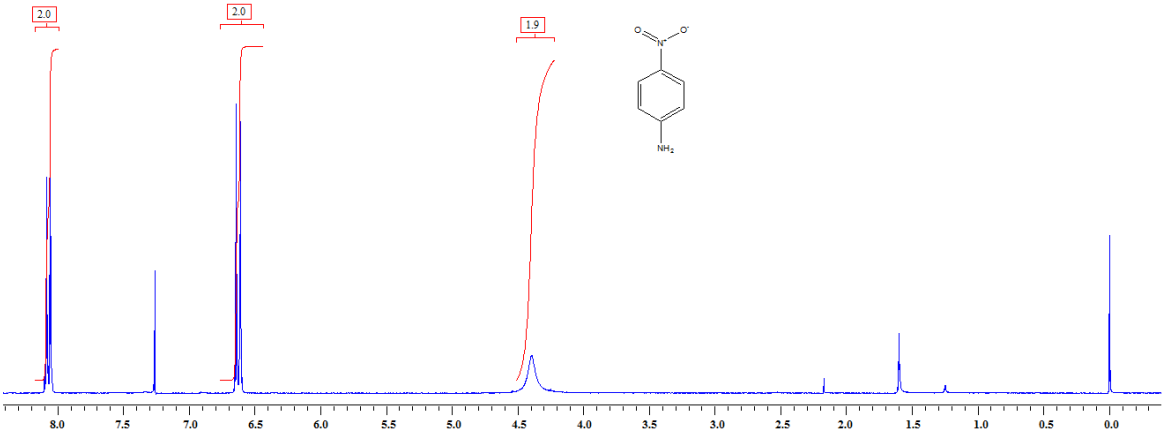


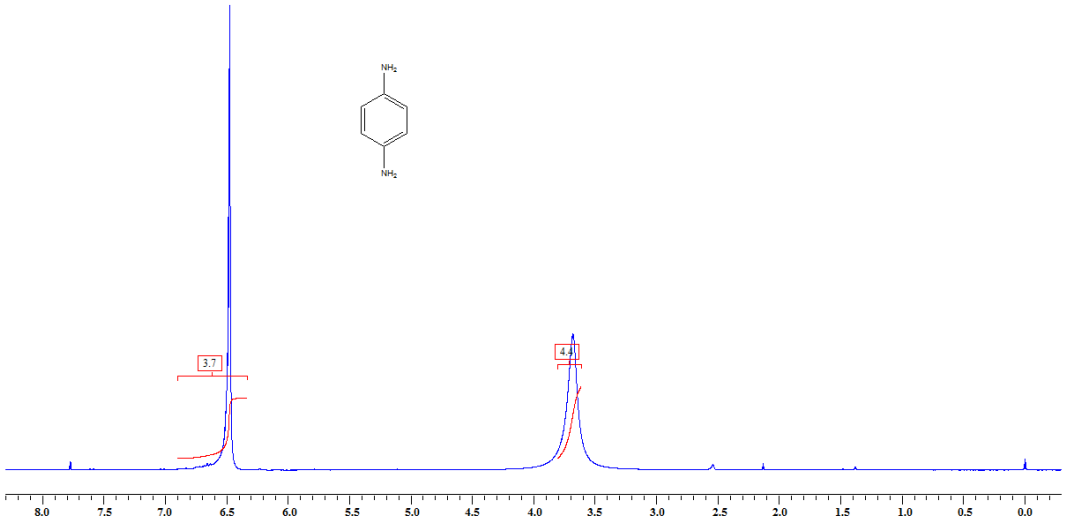


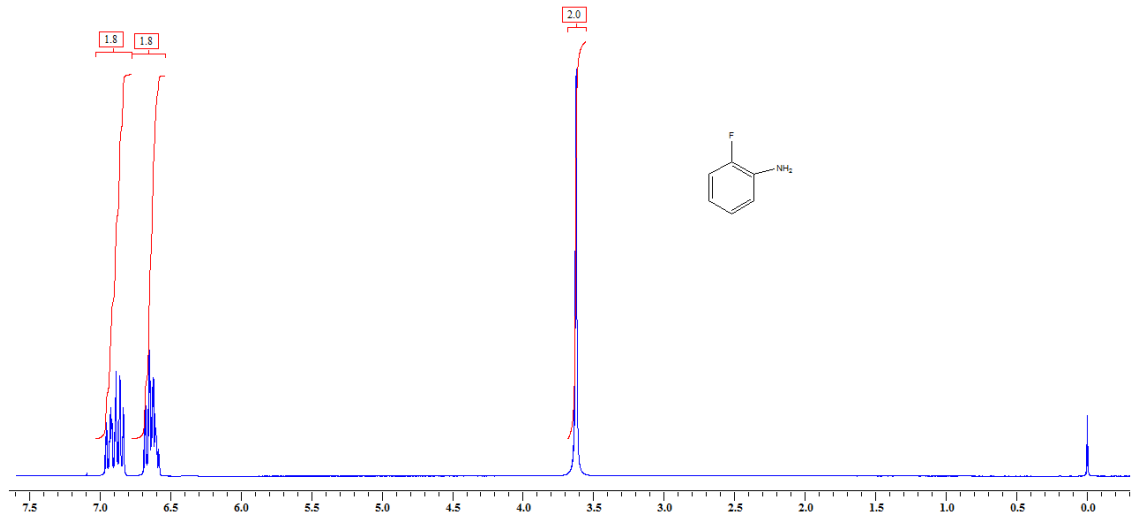


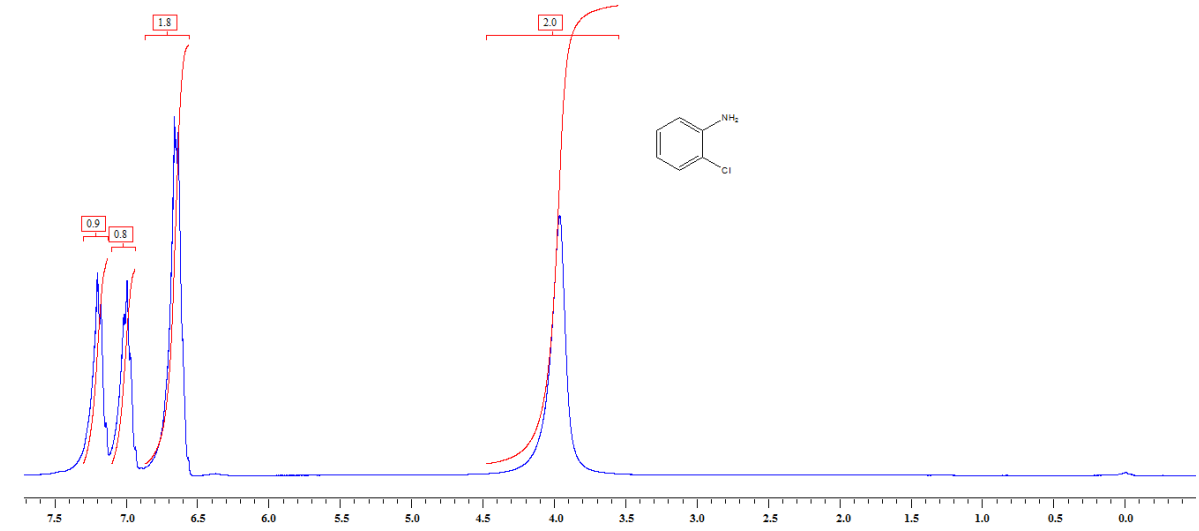


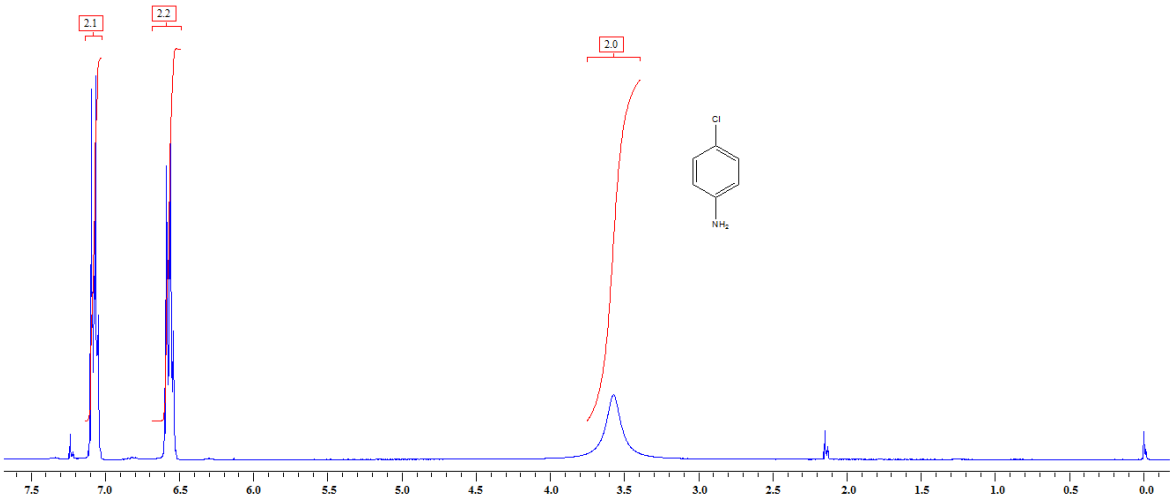


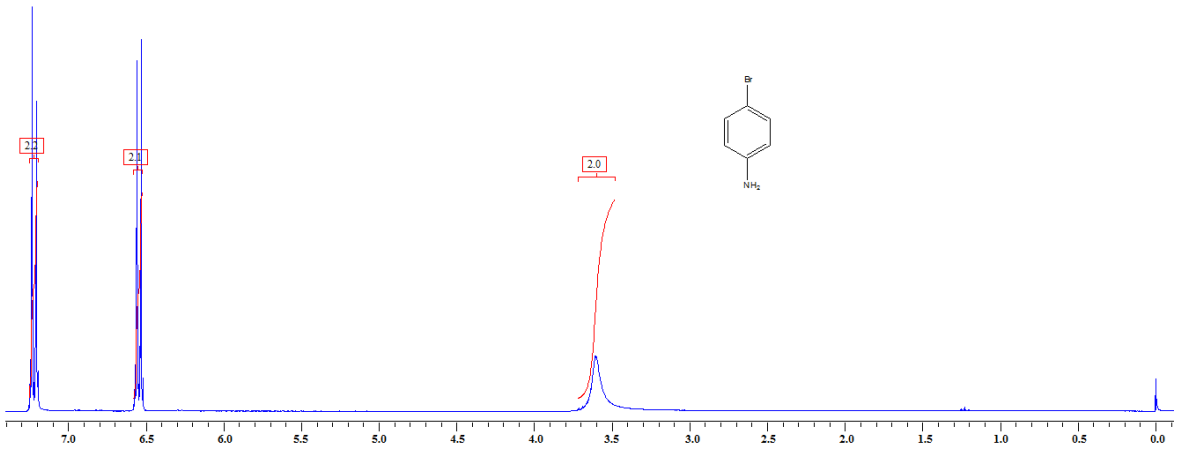


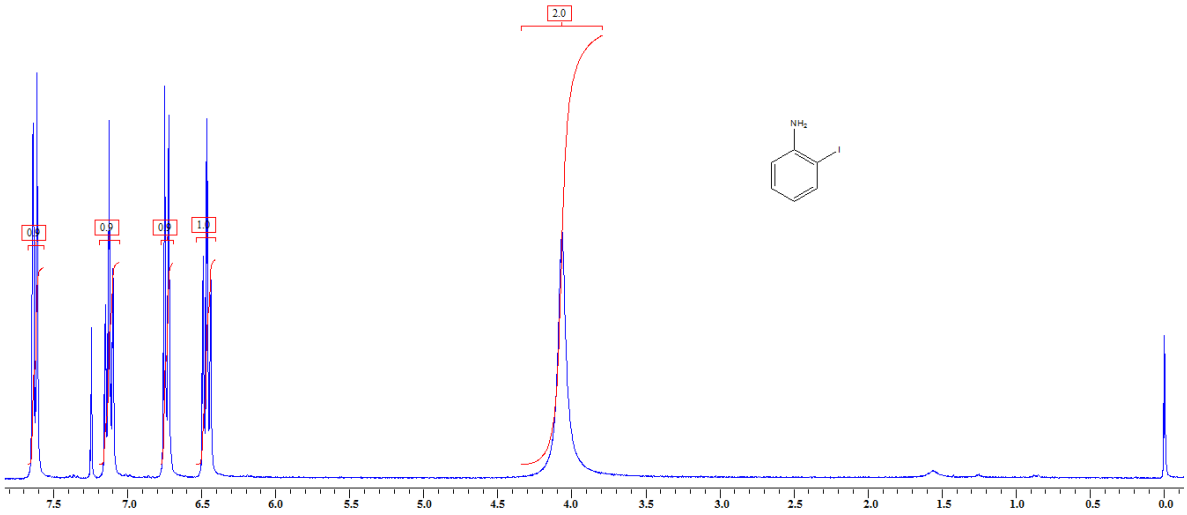


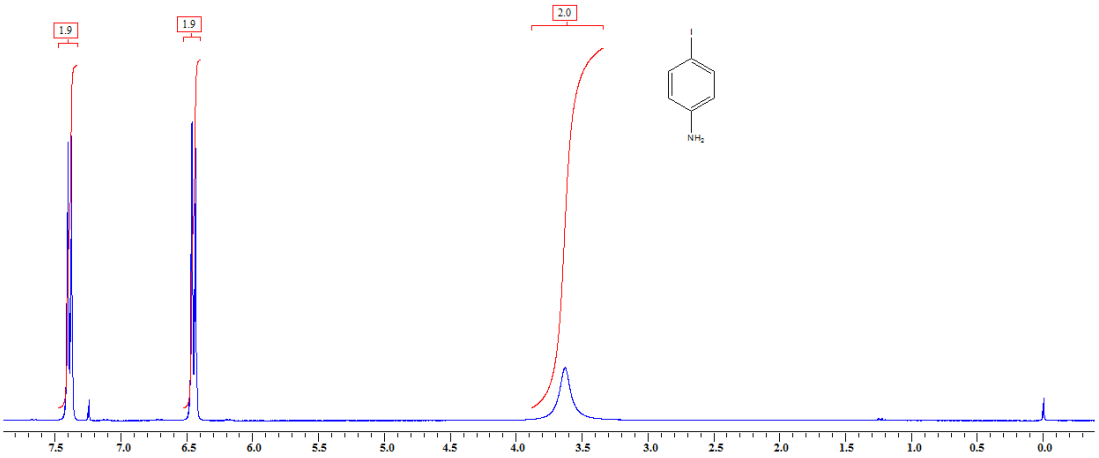


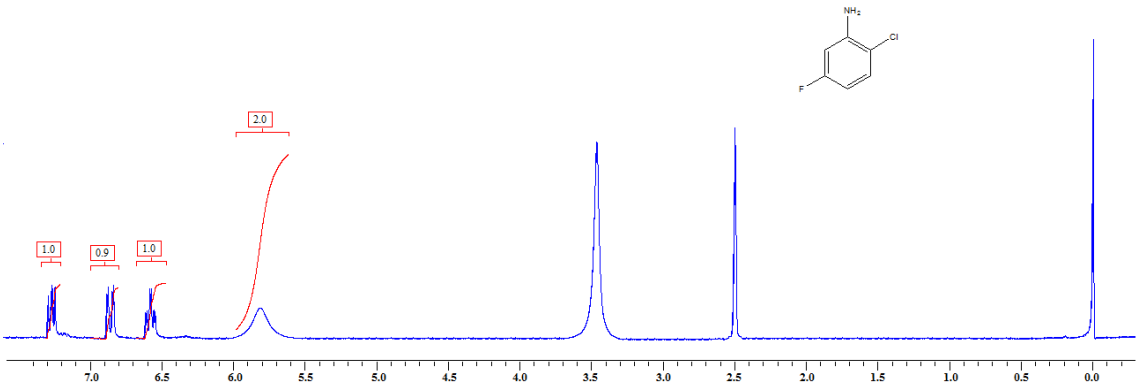


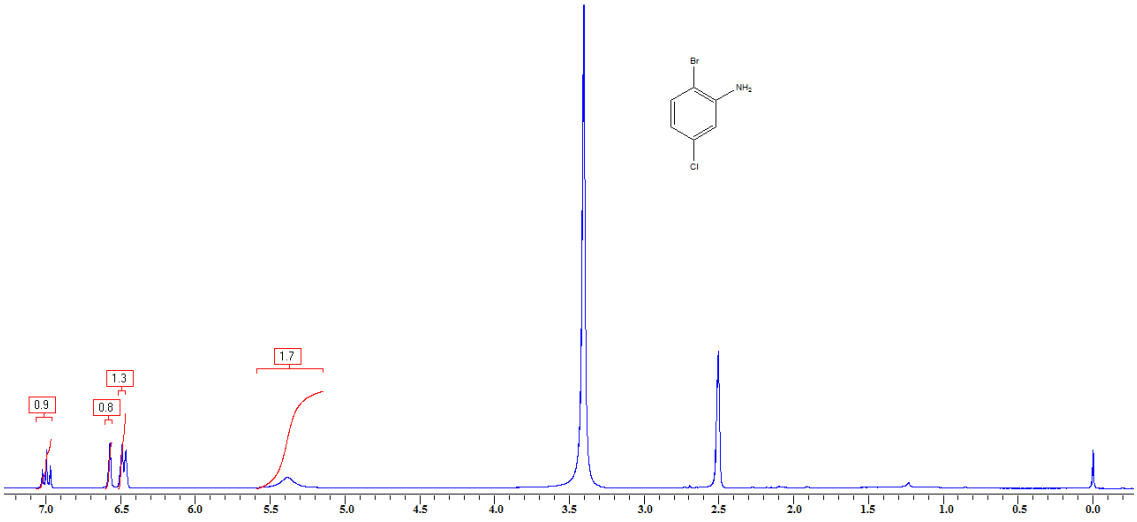


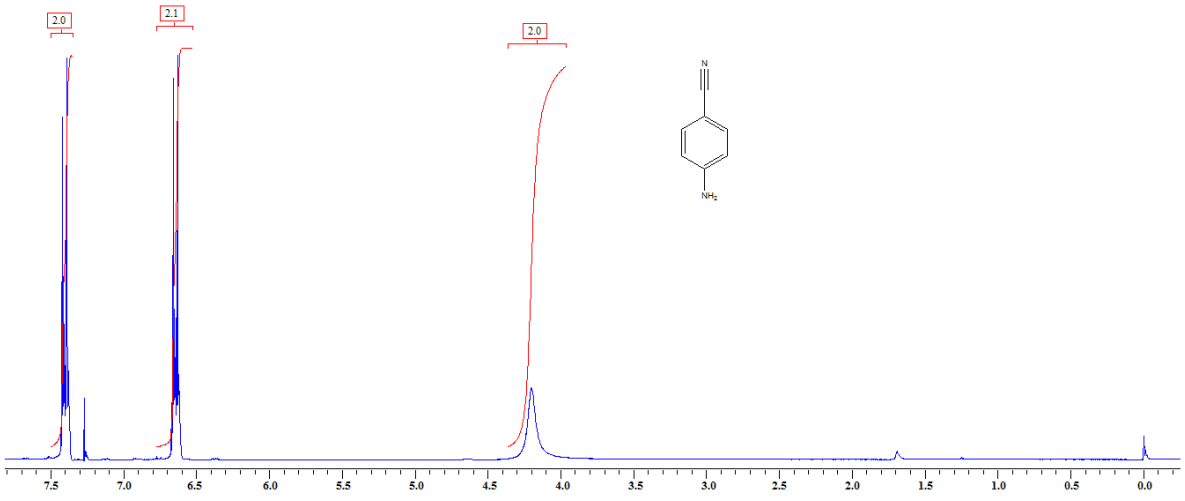


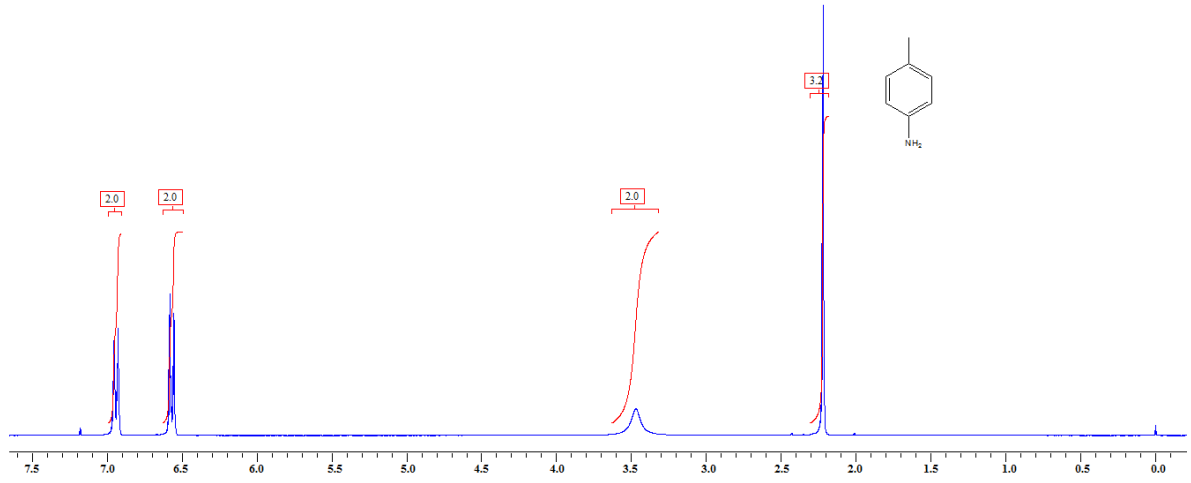


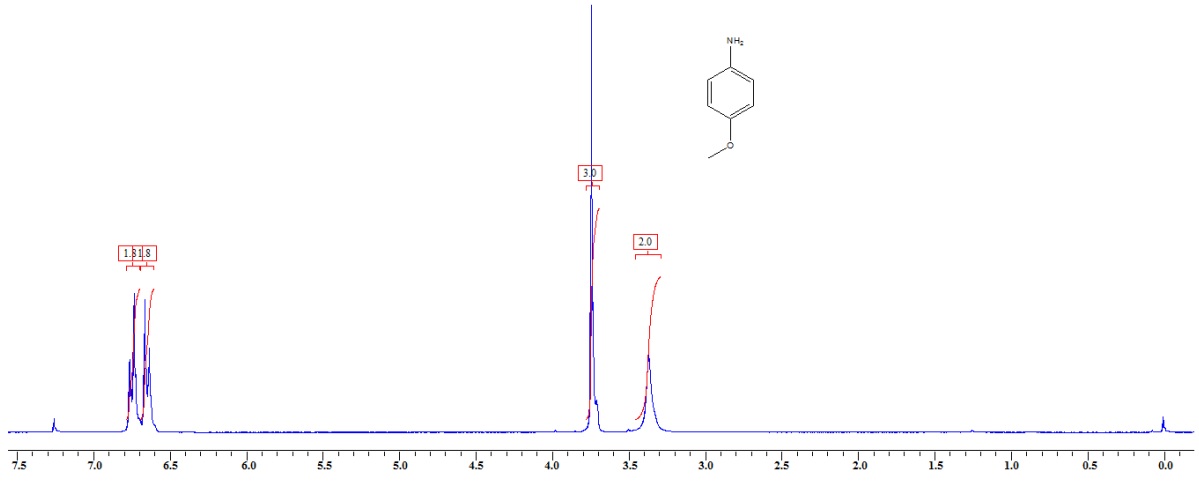


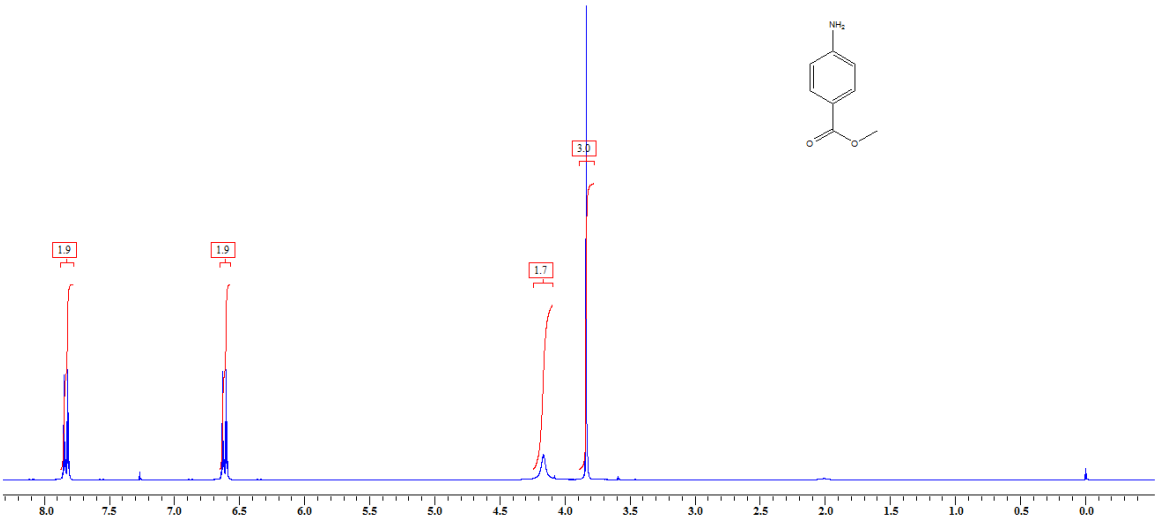


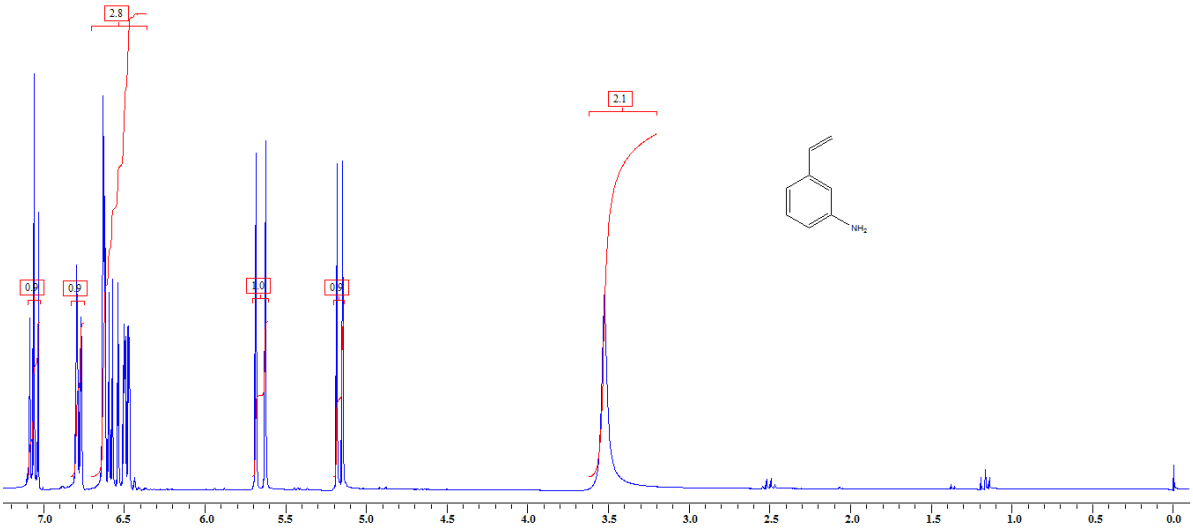












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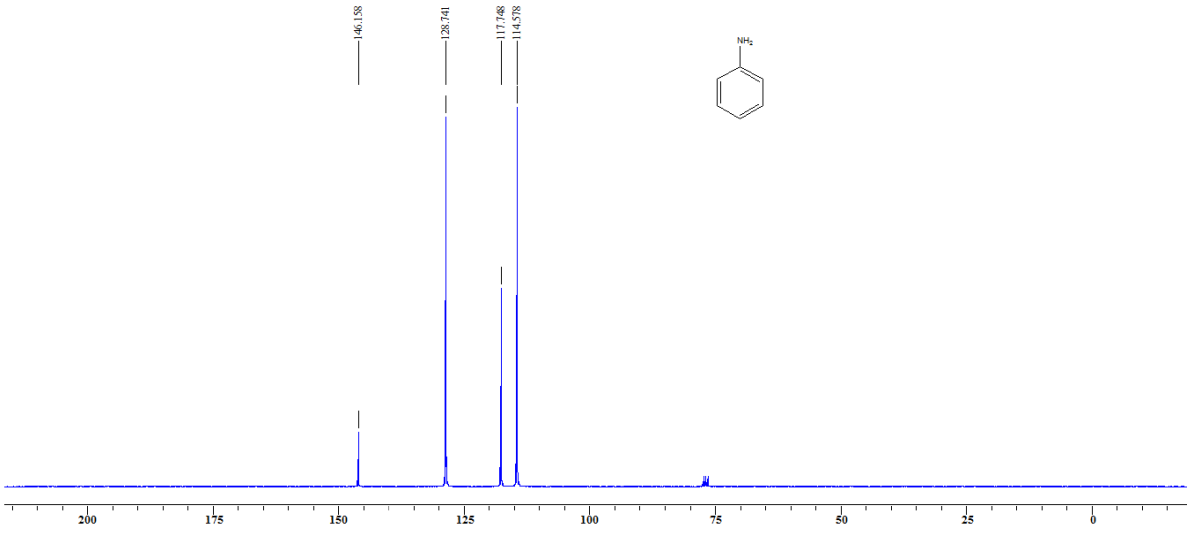

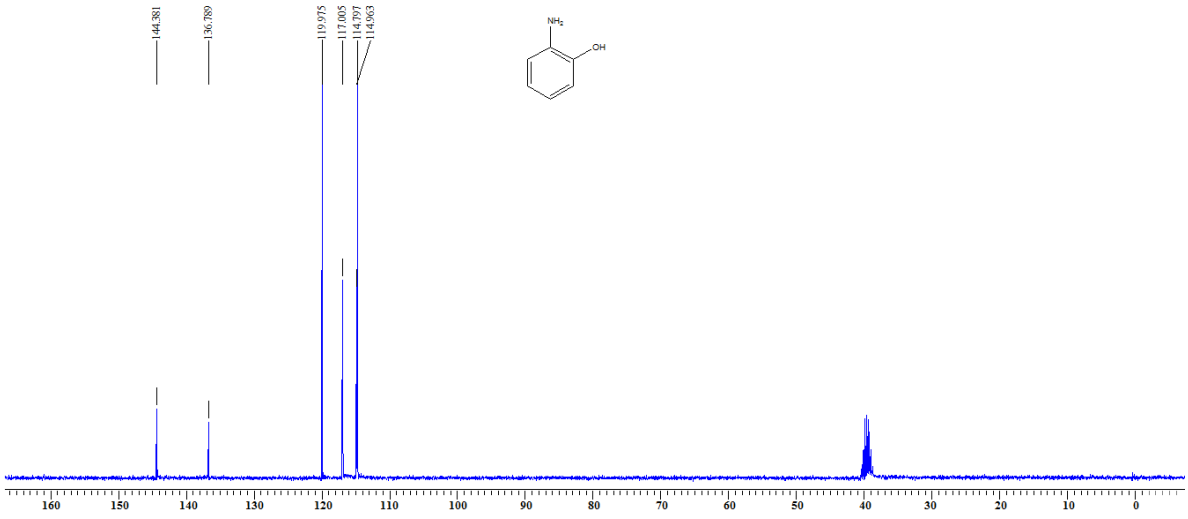

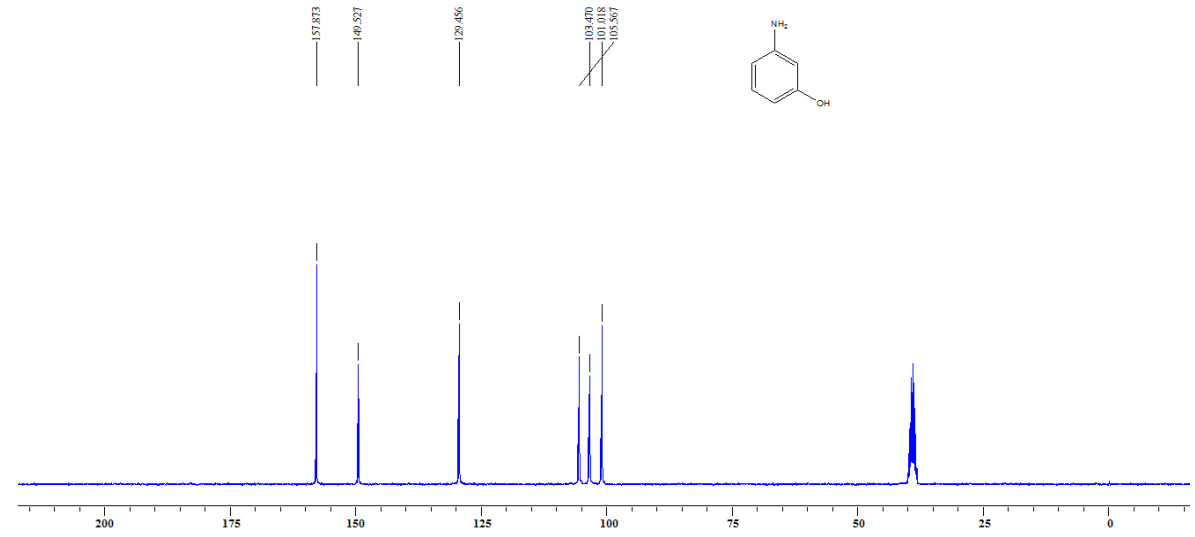

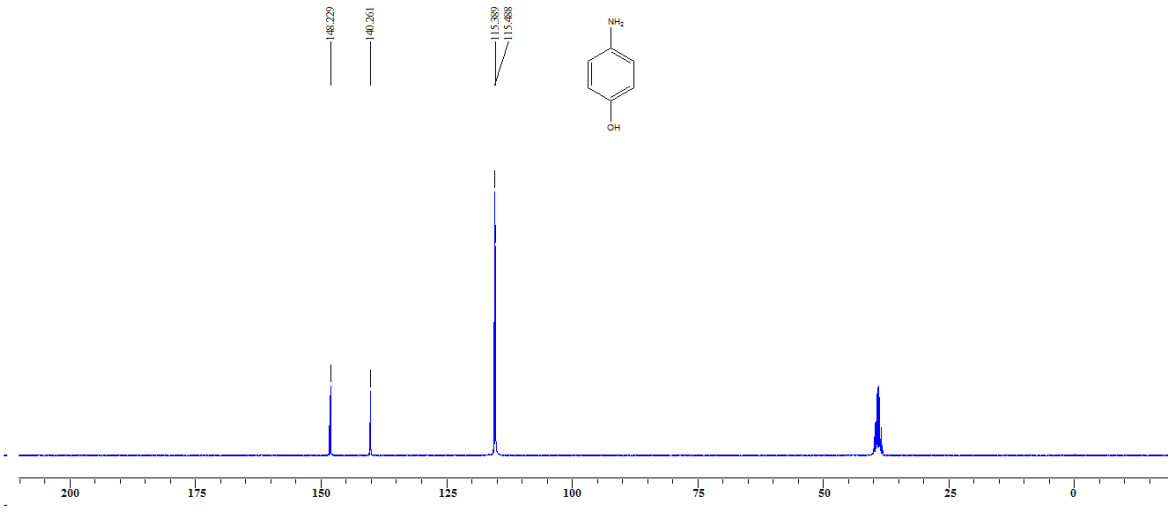

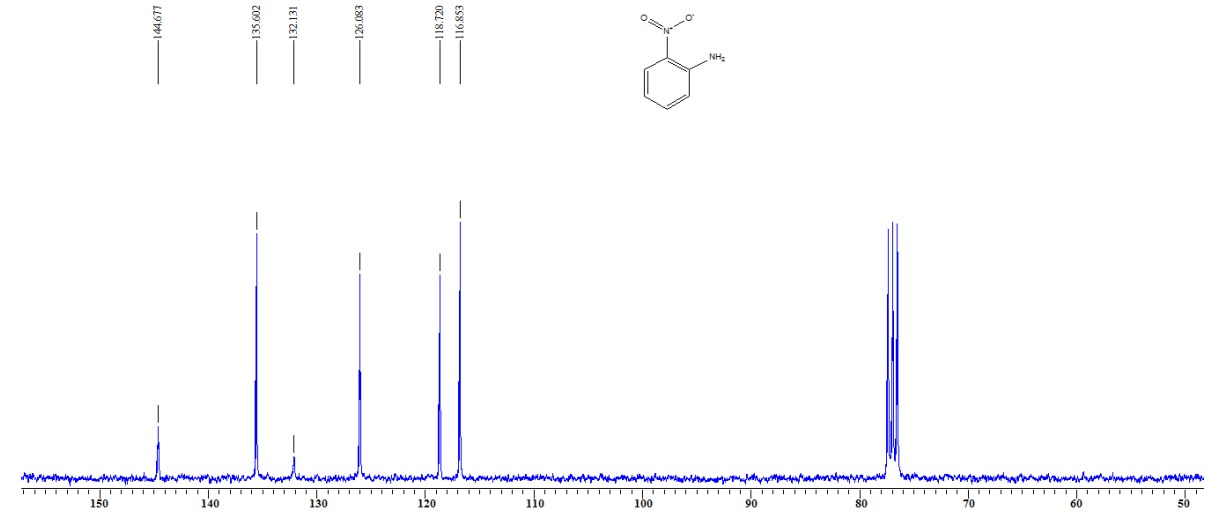

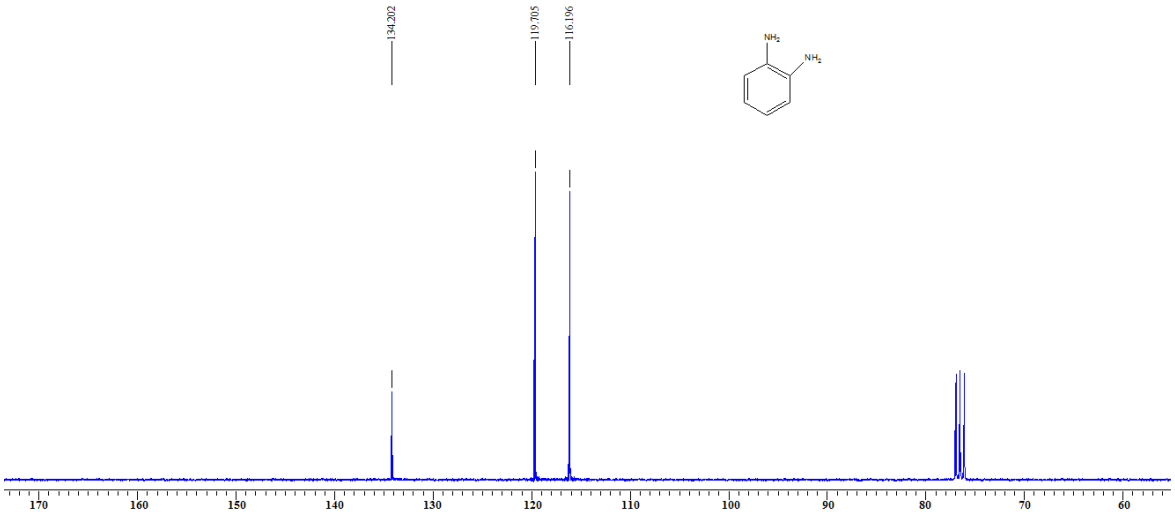

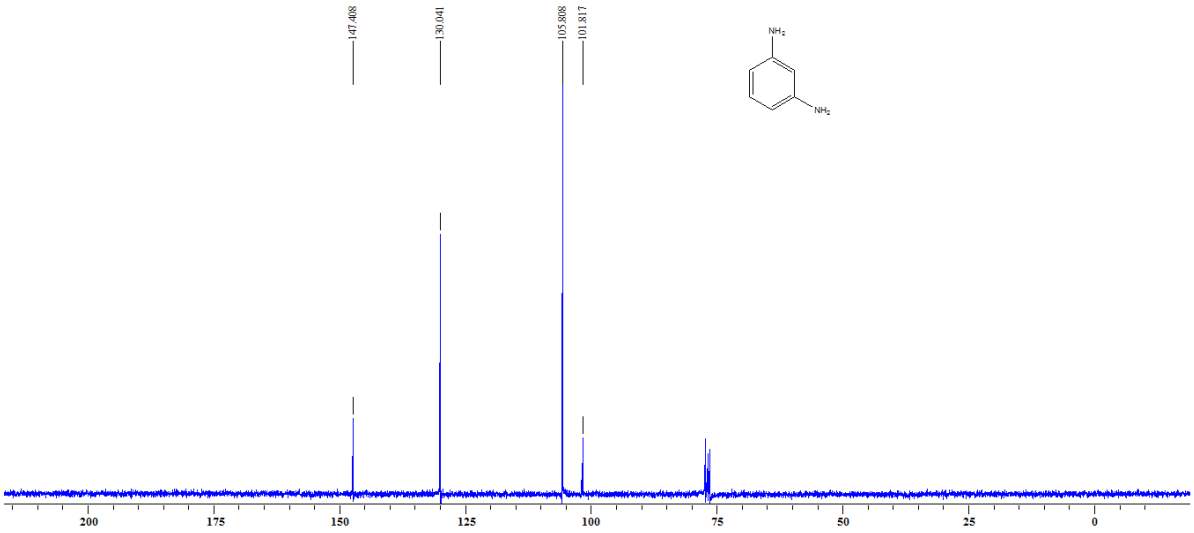

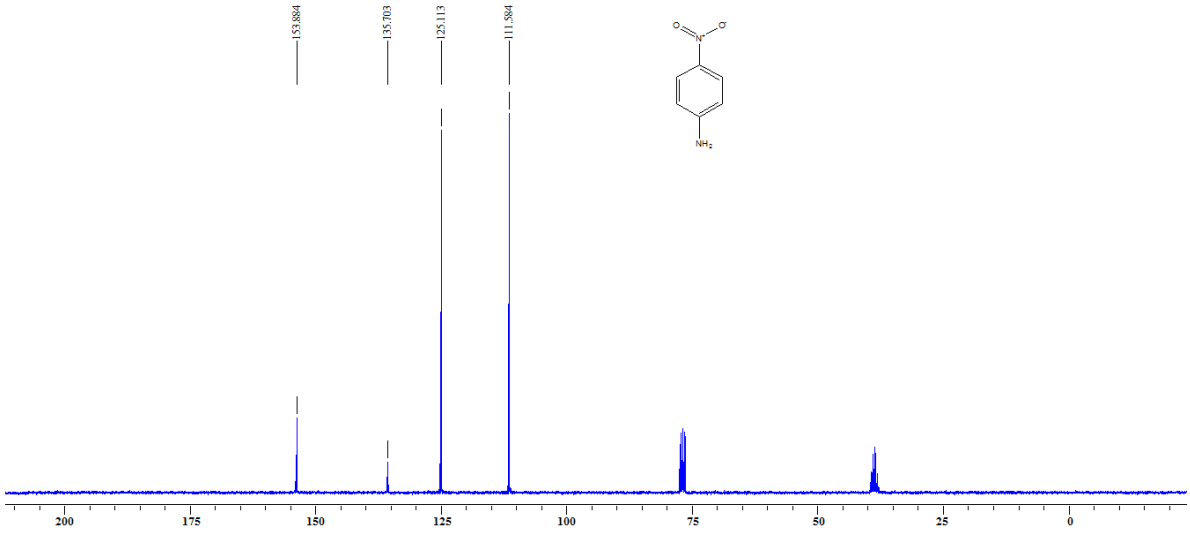

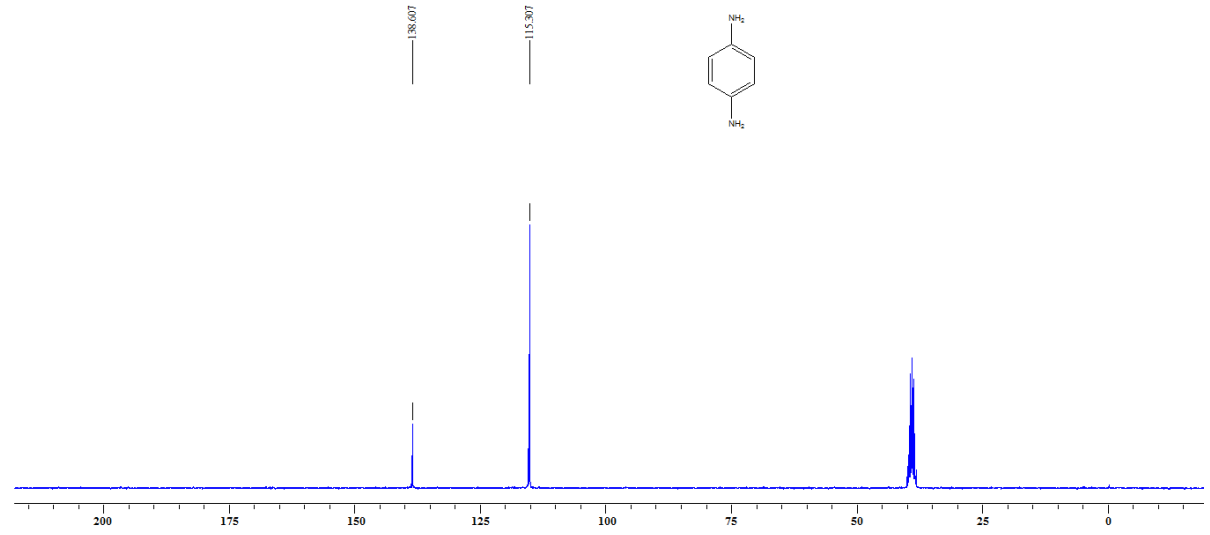

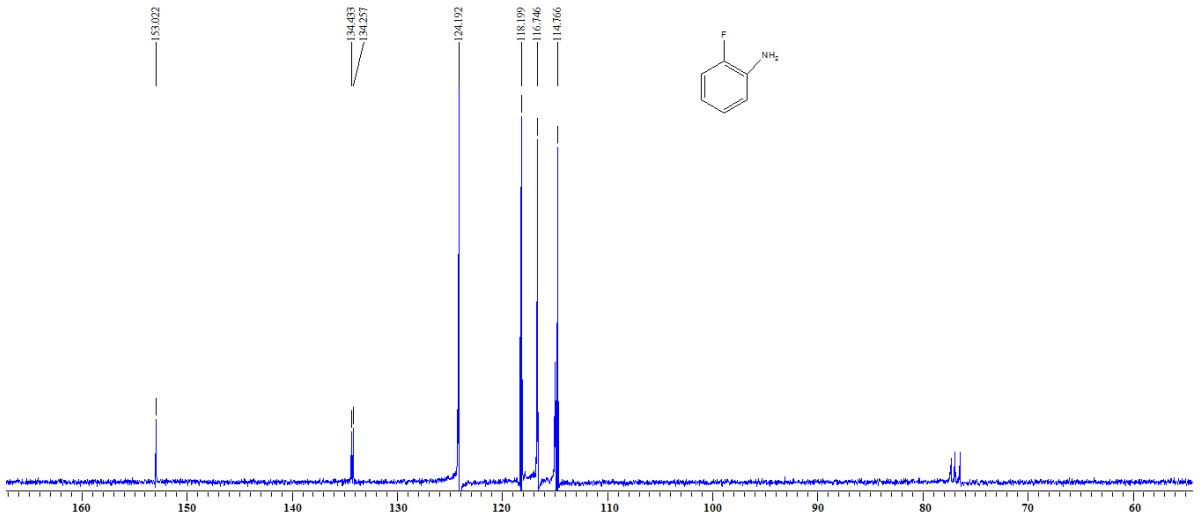

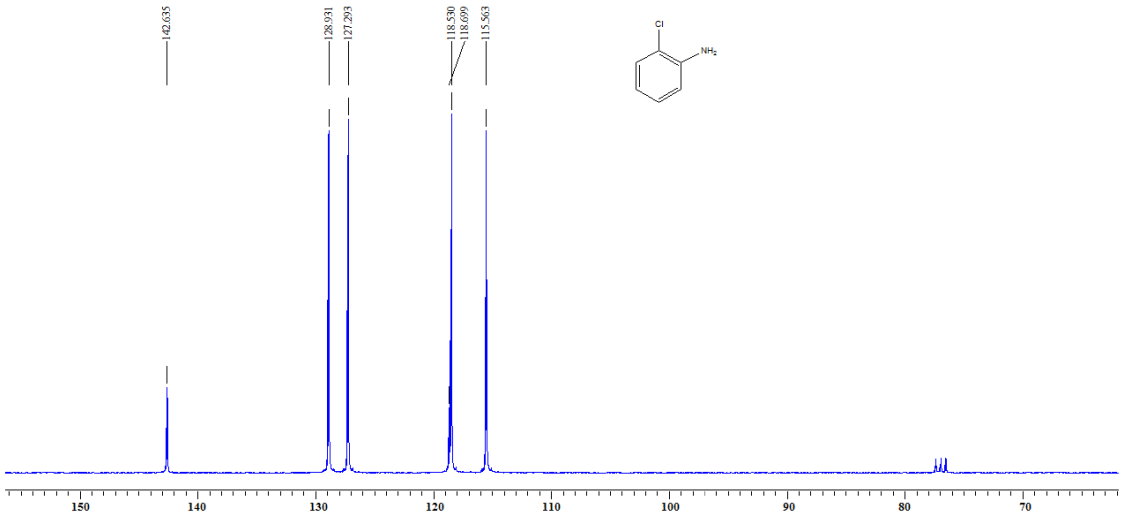

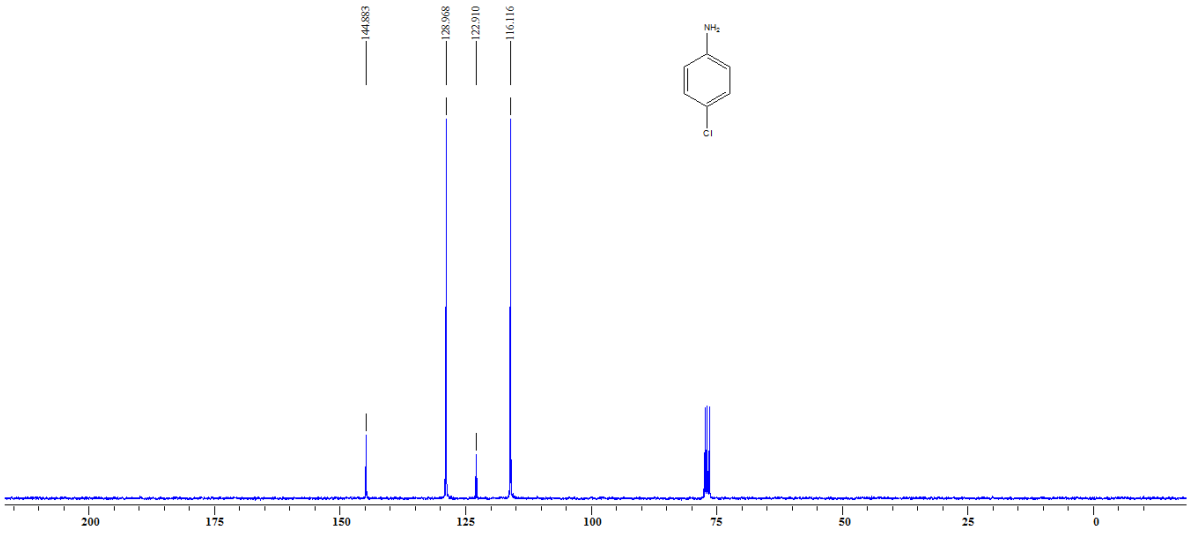

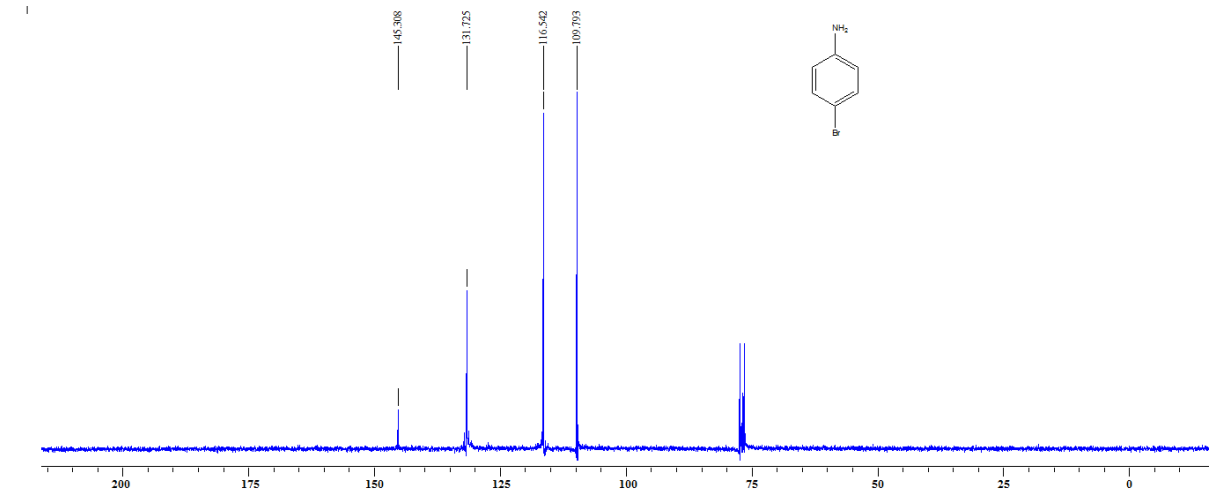

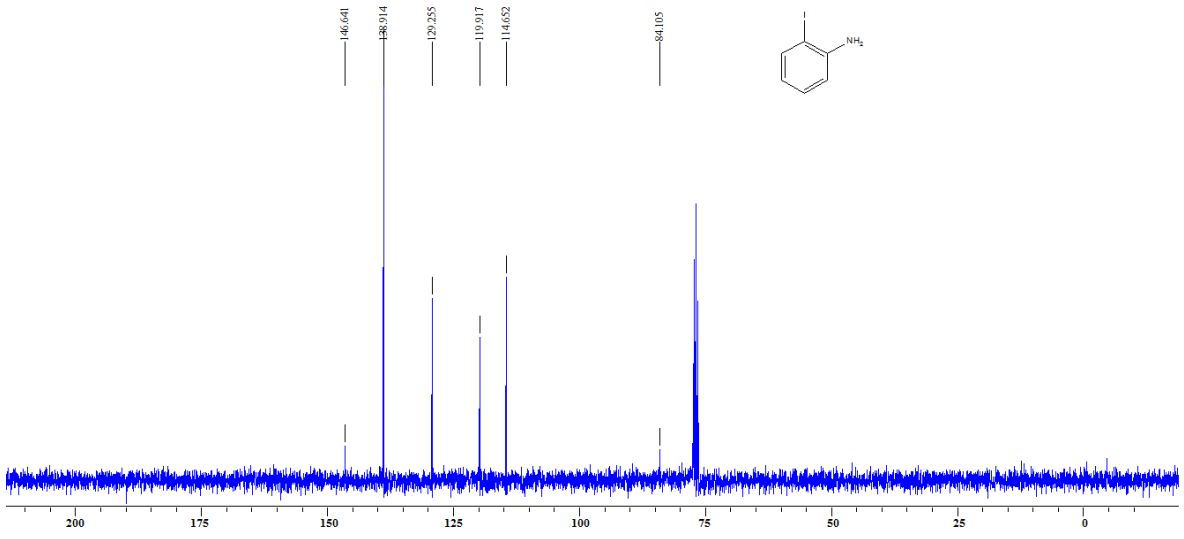

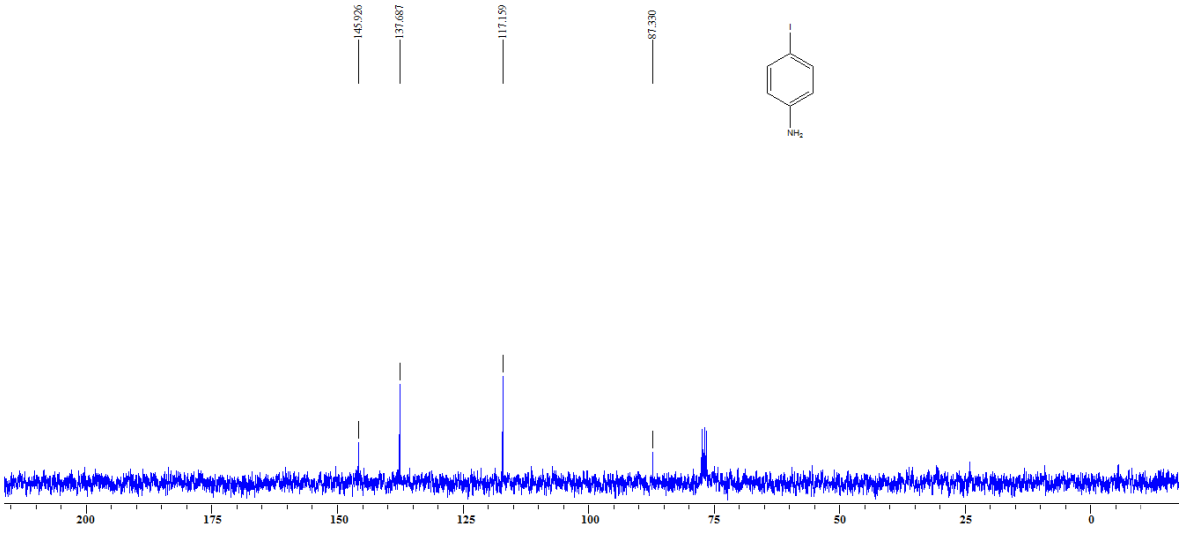

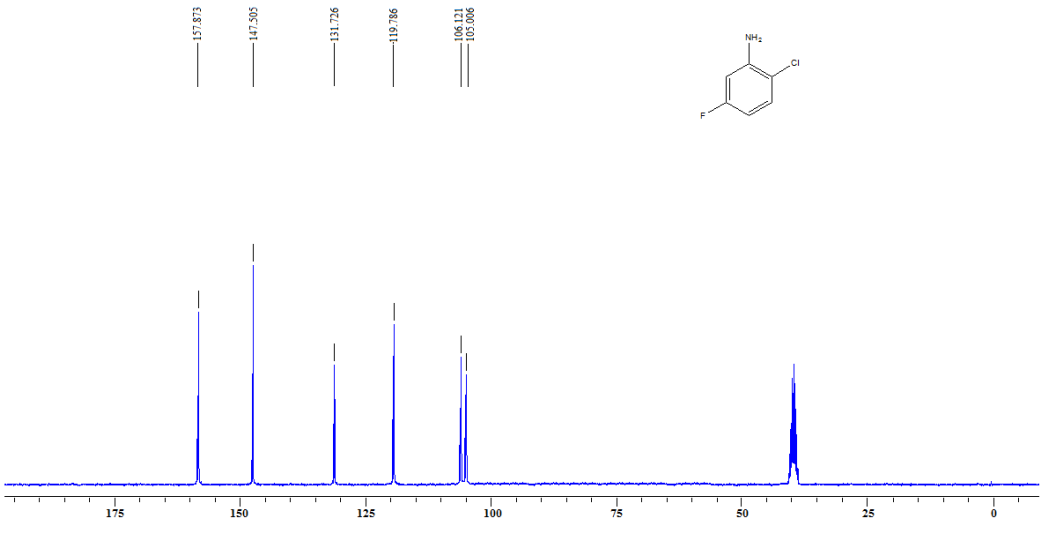

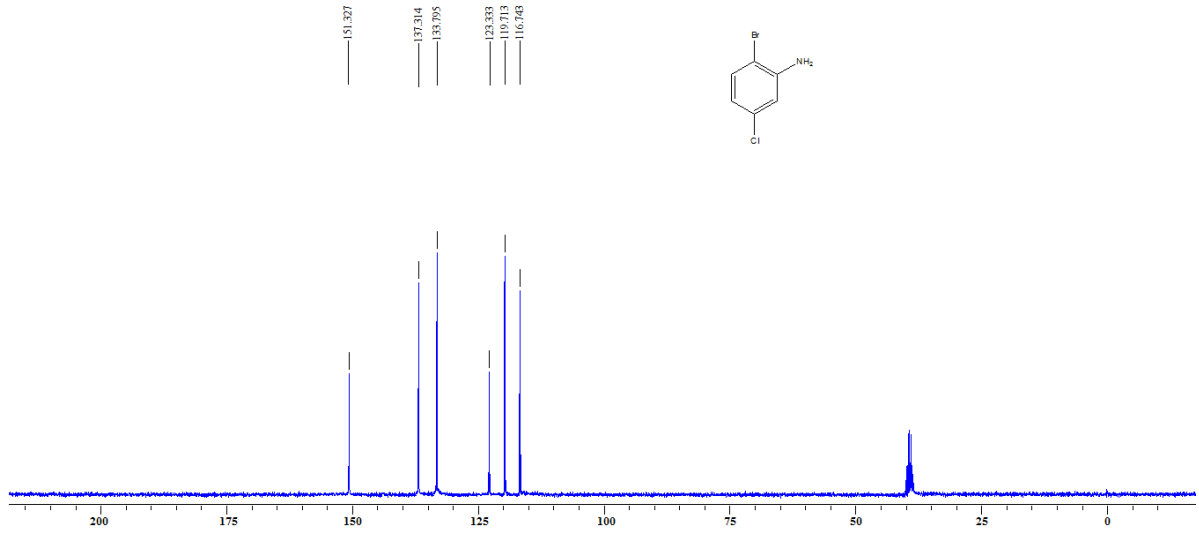

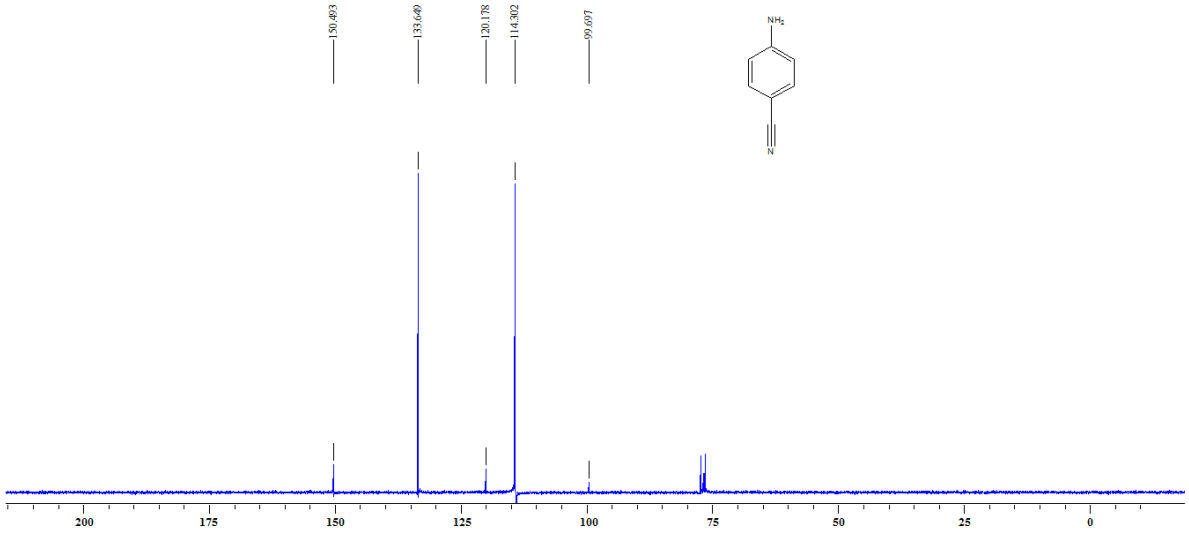

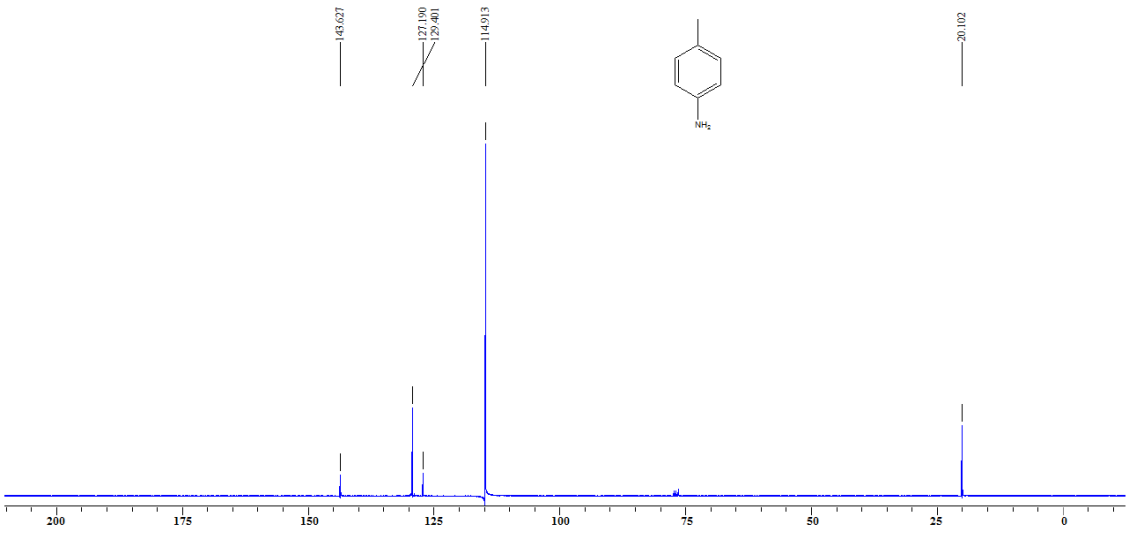

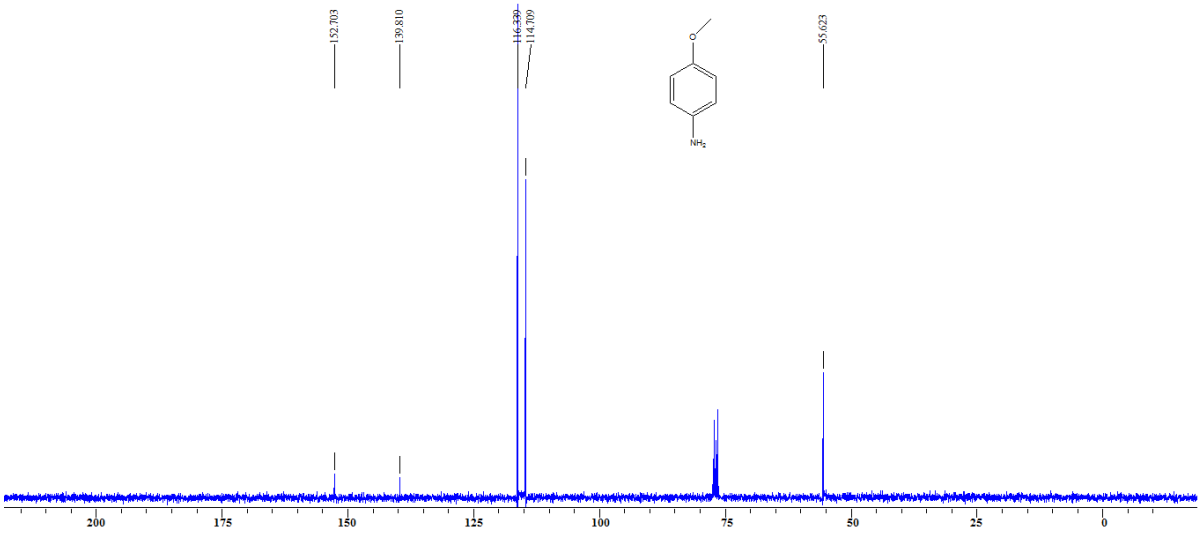

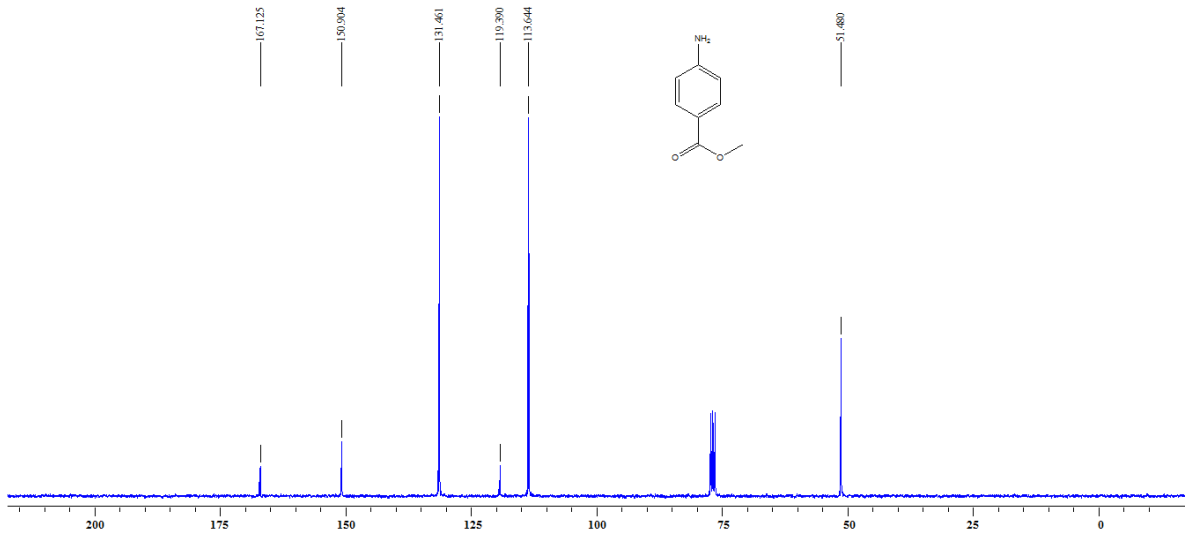

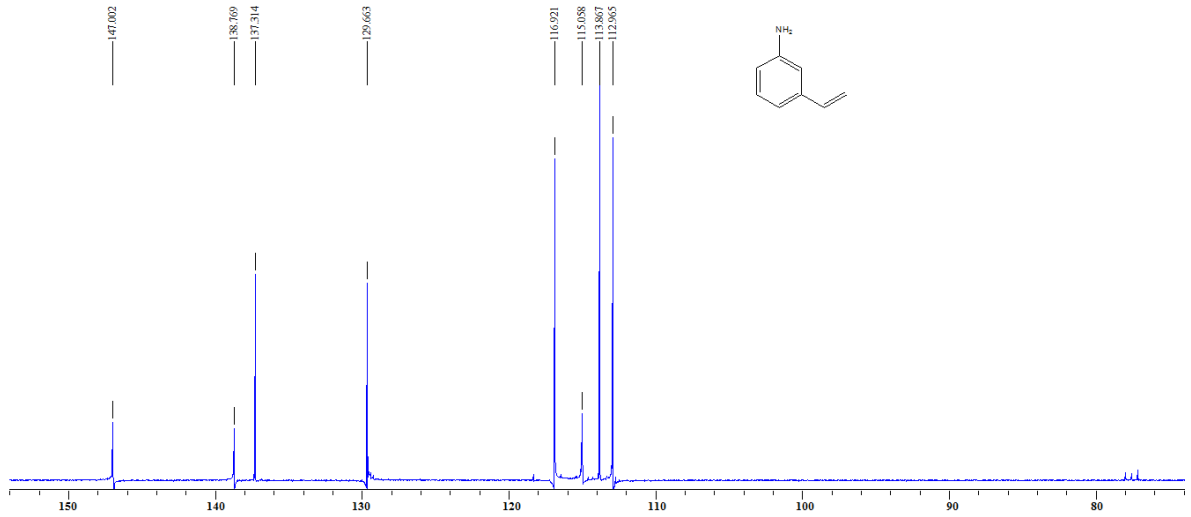

References

1. E. A. Stern, M. Newville, B. Ravel, Y. Yacoby and D. Haskel, *Physica B*, 1995, **208-209**, 117**.**

2. M. Newville, P. Livins, Y. Yacoby, E. A. Stern and J. J. Rehr, *Phys. Rev. B*, 1993, **47**, 14126.

3. A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B*, 1998, **58**, 7565.

4. A. L. Ankudinov, A. I. Nesvizhskii, and J. J. Rehr, *Phys. Rev. B*, 2003, **67**, 115120 .

5. B. Ravel, *J. Synchrotron Rad*., 2001, **8**, 314.