

*Supporting Information*

**Cobalt Nanoclusters Coated by N-Doped Carbon for  
Chemoselective Nitroarene Hydrogenation and  
Tandem Reactions in Water**

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## 1. GENERAL INFORMATION.

All reagents and solvents were purchased from commercial suppliers and used without further purification.

**X-ray Powder Diffraction (XRD).** The X-ray Diffraction measurements were acquired with a HTPhilips X'Pert MPD diffractometer equipped with a PW3050 goniometer using Cu Ka radiation and a multisampling handler.

**High-Resolution HAADF.** High-Resolution HAADF images and XEDS studies were performed in a double aberration-corrected Titan Themis 60-300 TEM/STEM microscope operated at 200 kV. This instrument is equipped with a monochromated, high brightness, XFEG electron source and a high sensitivity XEDS Super-X system, which integrates the signal coming from 4 detectors allowing a total solid angle of 0.9 sr. The acquisition of XEDS maps was carried out using an electron probe less than 0.5 nm, beam current of 60-70 pA, convergence angle of 19 mrad and 20 keV of range. The STEM images were recorded under analogous conditions employing an annular dark field detector with a collection range of 50-200 mrad. In this sense, more than 200 particles were measured by using an image analyzer software (ImageJ). Then, relative frequency distributions with a gaussian fitting were set up on size values in order to estimate the average particle size for each material.

**X-ray photoelectron spectra (XPS).** X-ray photoelectron spectra of the catalysts were recorded with a SPECS spectrometer equipped with a Phoibos 150MCD-9 multichannel analyzer using non-monochromatic MgK $\alpha$  (1253.6 eV) irradiation. Spectra were recorded using an analyzer pass energy of 30 eV and an X-ray power of 100W and under an operating pressure of 10<sup>-9</sup> mbar.

Peak intensities were calculated after nonlinear Shirley-type background subtraction and corrected by the transmission function of the spectrometer and Gaussian-Lorentzian curves were used for peak fitting. During data processing of the XPS spectra, binding energy (BE) values were referenced to the C1s peak (284.5 eV). Casa XPS software was used for spectra treatment.

**Temperature-programmed reduction (TPR).** Micromeritics Auto- Chem 2910 catalyst characterization system with a thermal conductivity detector (TCD) was used. Prior to each experiment, about 40 mg of sample was pretreated at room temperature in flowing He (10 mL/min) for 20 min. The sample was treated by heating from 25 °C to 600 °C at a rate of 5 °C/min in a flow of 10 vol% H<sub>2</sub> in Ar. The total gas flow rate was 50 mL/min.

**Raman Spectroscopy.** Raman spectra were recorded with 785 nm laser excitation on a Renishaw in Raman Spectrometer ("Refelx") equipped with a CCD detector. The laser power

on the sample was between 5 and 50% and a total of 20 acquisitions were taken for each spectrum.

**Thermogravimetric analysis (TGA).** It was carried out in a Mettler Toledo TGA/SDTA 851 apparatus, using a heating rate of 10 °C/min in an air stream until a temperature of 800 °C was reached.

**Nuclear magnetic resonance (NMR).** <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker 300 spectrometer and the chemical shifts are reported in ppm relative to residual proton solvents signals. Data for <sup>1</sup>H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublets, bs = broad signal), coupling constant and integration. Data for <sup>13</sup>C NMR spectra are reported in chemical shift (δ, ppm).

**Gas Chromatography.** GC analyses were acquired on Agilent gas chromatograph equipped with an HP5 capillary column (30m x 250 μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 50:1, and inlet and detector temperatures of 250 °C and 300 °C, respectively. Helium was used as carrier gas with a constant flow rate of 2 mL/min. The temperature program used for all the analyses is 80.0 °C, 2 min; 10 °C/min to 160 °C, 14°C/min to 300, 5 min.

**GC/MS.** GC/MS analyses were acquired on Agilent 6890 Network gas chromatograph coupled to a Agilent 5973 Network mass selective detector equipped with an Agilent HP5-M5 capillary column (30m x 250 μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 60:1, and inlet and detector temperatures of 250 °C and 280 °C, respectively. Helium was used as carrier gas with a constant flow rate of 1.2 mL/min. The temperature program used for all the analyses is as follows: 50.0 °C, 2 min; 30 °C/min to 280°C, 15 min.

**ATR-FTIR.** A PIKE Technologies Horizontal ATR (HATR) accessory was used for the FTIR measurements. The ATR prism consists of Zinc Selenide with 4 mm thick and 80 mm length being the angle of incidence of 45 °C. The total number of reflections with these values is 10. Spectra were recorded using a Bruker 70V spectrometer using a DTGS detector and acquiring at 4 cm<sup>-1</sup> resolution. In a typical experiment, nitrobenzene or 3-nitrostyrene were adsorbed on the catalyst surface of Co@NC-800 by wet impregnation via ethanolic solution. For that, 50 mg of the reactant were dissolved in 3 mL of ethanol and stirred with 100 mg of **Co@NC-800** for 30 minutes under N<sub>2</sub> atmosphere. After that, the solvent was evacuated in vacuum in an inert atmosphere and the material with the pre-adsorbed probe molecule was mixed with KBr and pressed in a flat plate for the analysis.

**X-ray Absorption Spectroscopy (XAS).** X-ray Absorption Spectroscopy experiments at the Co K-edge (7709 eV) were performed at CLAESS beamline of the ALBA Spanish synchrotron (Cerdanyola del Vallès, Spain).<sup>[1]</sup> The white beam was monochromatized using a Si (111) double crystal cooled with liquid nitrogen; harmonic rejection was performed using two Rh-coated silicon mirrors. The samples were pressed into 13 mm pellets and placed in a multi-purpose cell allowing in-situ experiments. The spectra were collected in transmission mode using ionization chambers filled with an appropriate amount of gases as detectors. A metallic cobalt foil was used as a reference for data alignment, which was located between I<sub>1</sub> and I<sub>2</sub> ionization chambers. Several spectra were collected for each sample to ensure the reproducibility of the spectra and a good signal-to-noise ratio. Data reduction and extraction of  $\chi(k)$  were performed using IFEFFIT package.<sup>[2]</sup>

## 2. EXPERIMENTAL PROCEDURES.

### A. Synthesis of Co@NC-T catalysts

Cobalt(II) nitrate hexahydrate (Sigma-Aldrich  $\geq 98\%$ , 35.3 mg, 0.119 mmol) and 2,2':6',2''-terpyridine (abcr, 97%, 57.2 mg, 0.238 mmol) (Co:terpyridine = 1:2 molar ratio) were stirred in ethanol (40 mL) during 10 minutes at room temperature. Then, carbon powder (696 mg) (VULCAN® XC72R, Cabot Corporation Prod. Code XVC72R; CAS No. 1333-86-4) was added to the solution and the resulting mixture was left to stir at room temperature overnight. After that, the ethanol was removed *in vacuo*. The final solid obtained was dried at 60 °C for 12 hours, after which it was ground to a fine powder. Then, the ground powder was transferred into a quartz reactor and placed in a vertical oven. The oven was purged by evacuating to ca. 5 mbar and then flushed with nitrogen for three times. Then, the sample was pyrolyzed with a ramp rate of 25 °C/min and held at 400, 500, 600, 700 or 800 °C for 2 h under nitrogen flow. Finally, the sample was cooled down to room temperature. During the whole process nitrogen was constantly passed through the oven. The obtained catalyst was denoted as **Co@NC-T**, where T represents the pyrolysis temperature. For comparison, the analog catalyst was also prepared but in the absence of tpy ligand using Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(acac)<sub>2</sub>·H<sub>2</sub>O as cobalt sources and changing the nitrogenated ligand (1,10-phenanthroline and ethylenediaminetetraacetic acid).

### B. Nitroarene Hydrogenation

The chemoselective hydrogenation of nitroarenes was performed in a 7 mL reaction glass vial fitted with a septum cap. 0.5mmol of the reactant, 100 $\mu$ L of internal standard (hexadecane), 3 mL of water and 30 mg of powder **Co@NC-T** (1% Co) were added to the batch reactor. The reaction vial was then placed into a 300 mL autoclave, purged with hydrogen three times and

finally pressurized to 10 bar. The reaction mixture was left to stir for 14h at 100 °C. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Then, the catalyst was filtered and the product was extracted with ethyl acetate. Aliquots were analyzed during different times by gas chromatography and by GC–MS. Finally, the ethyl acetate was rotaevaporated and the product was also characterized by NMR.

Gram-scale reaction: To a 40 mL reactor equipped with a stir bar, pressure gauge, sample extraction probe, gas bubbling probe and gas outlet on the benchtop was added 200 mg of **Co@NC-800** followed by nitrobenzene (1 mmol, 1.196 g) and 20 mL of water. The reactor was purged several times with N<sub>2</sub> to remove oxygen and it was pressurized to 10 bar with H<sub>2</sub> (the total pressure was maintained during the reaction). The reaction mixture was left to stir for 20 h at 100°C. After cooling the reaction mixture to room temperature, the reactor was slowly depressurized. The catalyst was filtered, the product was extracted with ethyl acetate and the internal standard (hexadecane) was added before been analyzed by gas chromatography.

### C. Synthesis of amines though reductive amination.

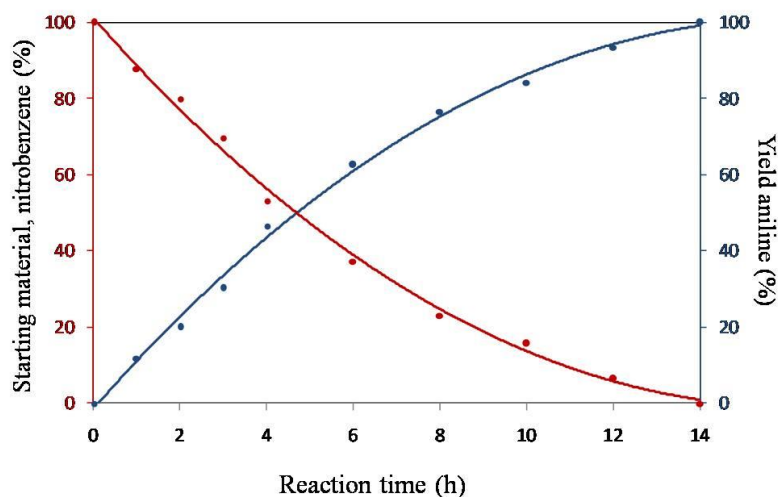
A coupling process through a reductive amination reaction was performed in a 7 mL reaction glass vial fitted with a septum cap. 0.5 mmol of the nitroarene, 2 equivalents of benzaldehyde (1 mmol), 100µL of internal standard (hexadecane), 3 mL of water and 30 mg of powder **Co@NC-800** (1% Co) were added to the batch reactor. The reaction vial was then placed into a 300 mL autoclave, purged with hydrogen three times and finally pressurized to 30 bar. The reaction mixture was left to stir for 14h at 100 °C. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Then, the catalyst was filtered and the product was extracted with ethyl acetate. Aliquots were analyzed during different times by gas chromatography and by GC–MS. Finally, all obtained products were isolated by column chromatography on silica gel (n-hexane/ethyl acetate 9:1) and the products were also characterized by NMR. (Table 3, products 2a-2e).

### D. Synthesis of oxindolines

Moreover, a second coupling process was performed in a 7 mL reaction glass vial fitted with a septum cap by adding 2 equivalents of 2-carboxybenzaldehyde (1mmol) to the mixture previously described (0.5 mmol of the nitroarene, 100µL of internal standard (hexadecane), 3 mL of water and 30 mg of powder **Co@NC-800** (1% Co)). The reaction vial was then placed into a 300 mL autoclave, purged with hydrogen three times and finally pressurized to 30 bar. The reaction mixture was left to stir for 14h at 100 °C. After cooling the reaction mixture to room temperature, the autoclave was slowly depressurized. Then, the catalyst was filtered and

the product was extracted with ethyl acetate. Aliquots were analyzed during different times by gas chromatography and by GC-MS. Finally, all obtained products were isolated by column chromatography on silica gel (hexane/ethyl acetate 3:1) and the products were also characterized by NMR. (Table 4, products 3a-3e).

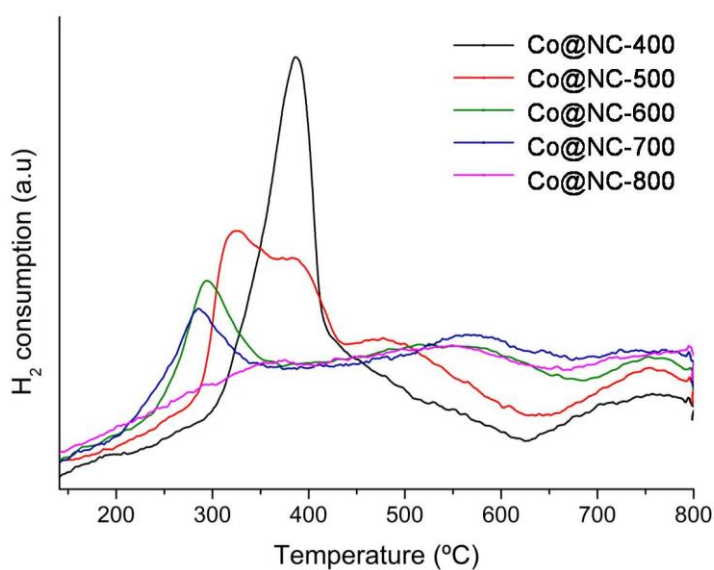
### 3. KINETIC STUDY



**Figure S1.** Kinetic profile of the hydrogenation of nitrobenzene to aniline catalyzed by **Co@NC-800** under optimized reaction conditions.

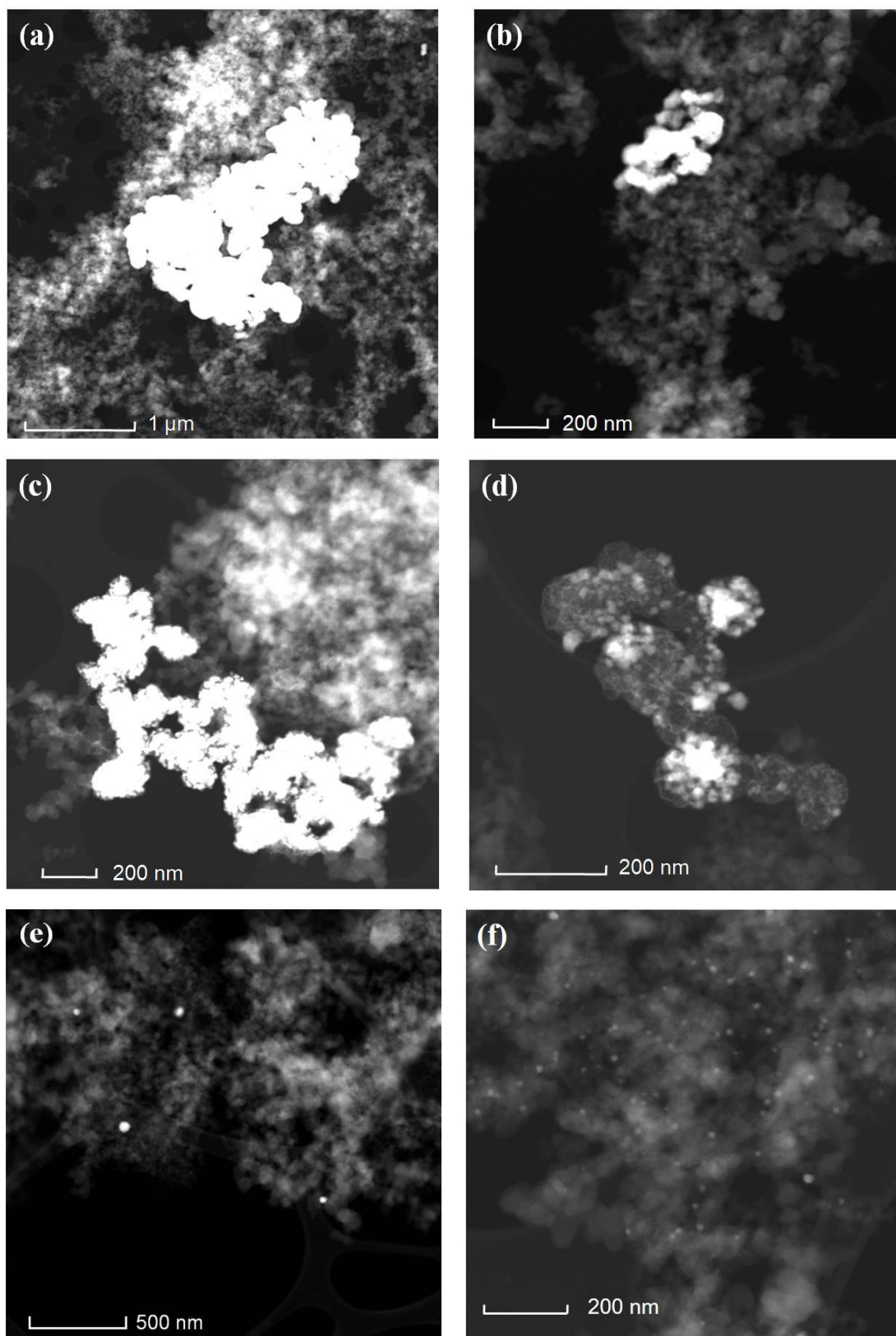
### 4. CHARACTERIZATION OF THE CATALYSTS

#### A. Temperature Programmed Reduction (TPR)



**Figure S2.** TPR analysis of **Co@NC-T** samples.

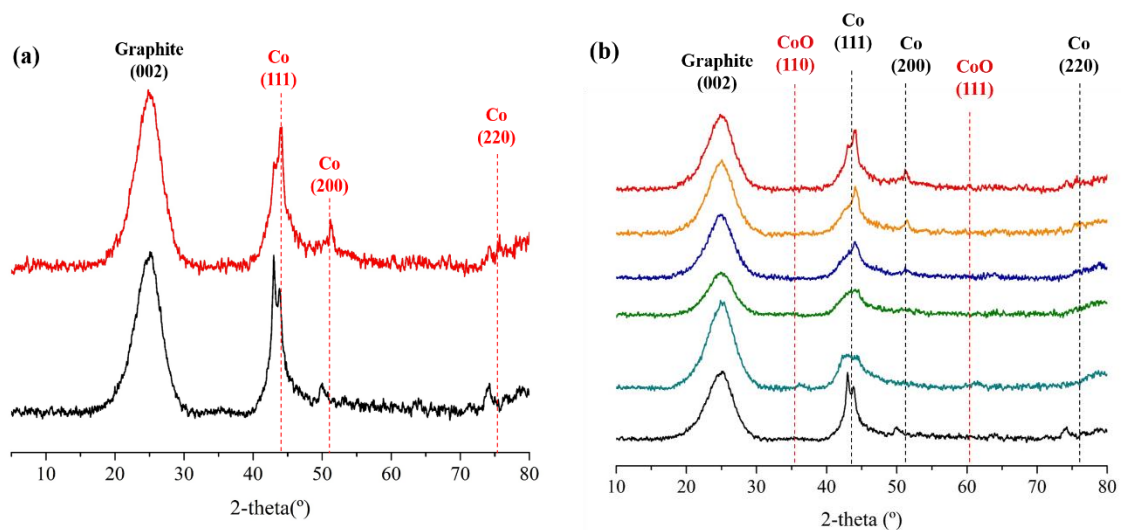
**B. Scanning transmission electron microscopy (STEM).**



**Figure S3.** STEM images of (a) Co@NC-400, (b) Co@NC-500, (c) Co@NC-600, (d) Co@NC-700, (e) Co@NC-800 and (f) Co@C-800.



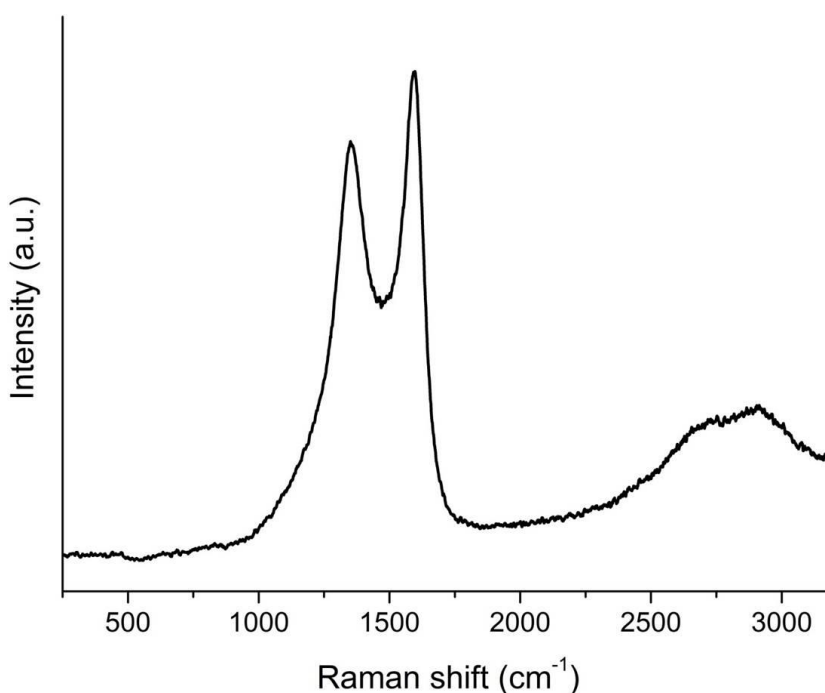
### C. X-ray Powder Diffraction (XRPD).



**Figure S4.** XRD patterns of (a) Carbon support (black) and Co@NC-800 (red), (b) Carbon support (black), Co@NC-400 (clear blue), Co@NC-500 (green), Co@NC-600 (blue), Co@NC-700 (orange) and Co@NC-800 (red).

### D. Raman spectroscopy

Raman spectroscopy (Figure S5) shows that the graphitic carbon structure from the support is maintained in the final material. Both G (at  $1590\text{ cm}^{-1}$ ) and D (at  $1350\text{ cm}^{-1}$ ) bands can be observed, which are related to in-plane vibration of the  $\text{sp}^2$  carbon atoms and due to a defect-induced non-perfect crystalline structure of the material, respectively.<sup>3</sup>



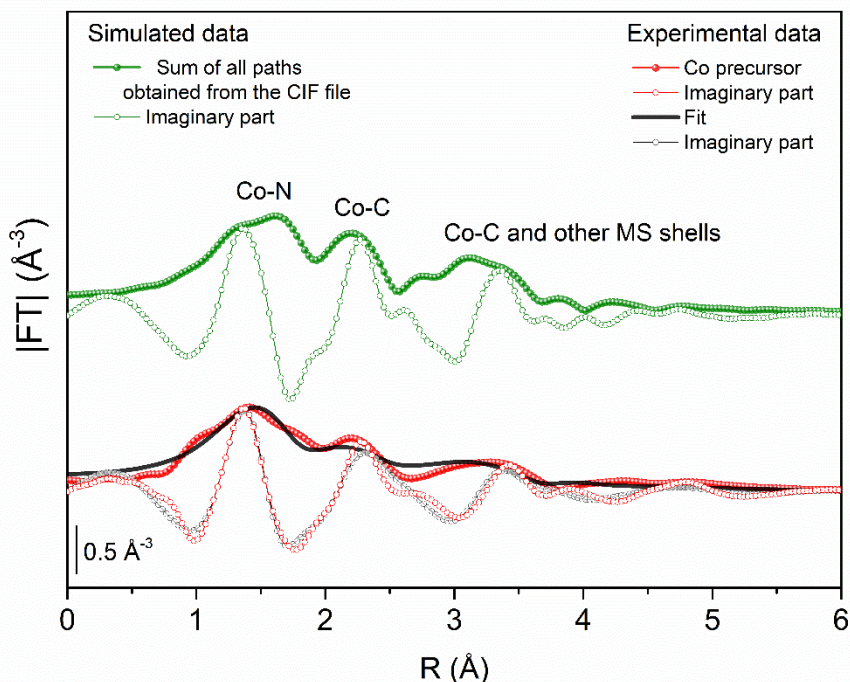
**Figure S5.** Raman spectrum of Co@NC-800.

## E. X-ray Absorption Spectroscopy (XAS)

**Table S1.** Summary of optimized parameters by fitting the Co K-edge EXAFS data.<sup>[a]</sup>

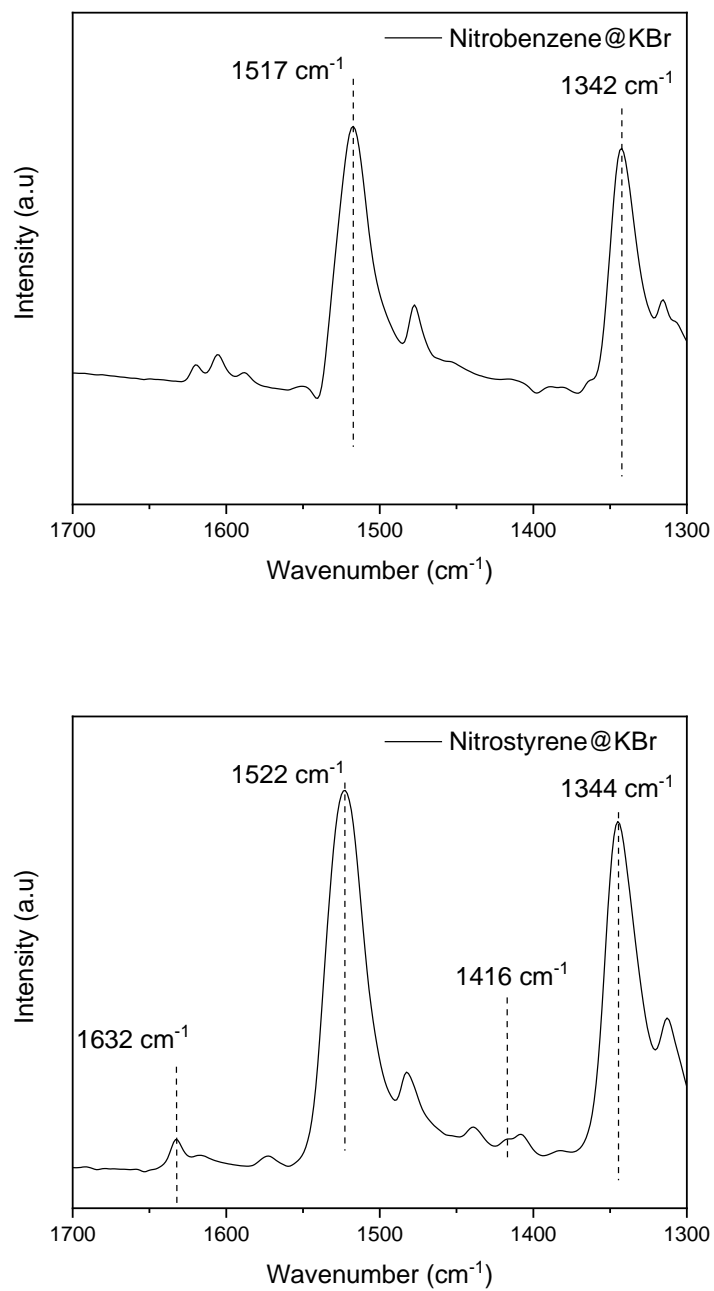
| Sample       | N                | Path  | R (Å)         | $\sigma^2$ (Å <sup>2</sup> ) | $\Delta E_0$ (eV) | r-factor (%) |
|--------------|------------------|-------|---------------|------------------------------|-------------------|--------------|
| Co foil      | 12               | Co-Co | 2.495 ± 0.001 | 0.0063 ± 0.0001              | 7.6 ± 0.2         | 0.0004       |
| Co precursor | 3 <sup>[b]</sup> | Co-N  | 1.950 ± 0.009 | 0.0081 ± 0.0013              | 0.7 ± 0.7         | 0.0049       |
|              | 3 <sup>[b]</sup> | Co-N  | 2.127 ± 0.012 | 0.0080 ± 0.0022              |                   |              |
|              | 5.4 ± 0.6        | Co-C  | 2.874 ± 0.014 | 0.0084 ± 0.0047              |                   |              |
| Co@NC-800    | 2.1 ± 1.2        | Co-N  | 1.928 ± 0.025 | 0.0090 ± 0.0088              | 0.5 ± 1.5         | 0.0083       |
|              | 5.9 ± 0.6        | Co-Co | 2.499 ± 0.008 | 0.0063 ± 0.0011              |                   |              |

<sup>[a]</sup>The fits were performed up to the second coordination shell over FT of the  $k^2$ -weighted  $\chi(k)$  functions performed in the  $\Delta k = 2.2$ -12.2 Å<sup>-1</sup> and  $\Delta R = 1.2$ -2.8 Å intervals. Non-optimized parameters (or fixed<sup>[b]</sup>) are recognizable by the absence of the corresponding error bar.  $S_0^2 = 0.76$ .  $N_{\text{Co-Co}}$  equal to  $5.9 \pm 0.6$  corresponds to cobalt nanoclusters ranging from 0.8-0.9 nm.<sup>4</sup>



**Figure S6.**  $k^2$ -weighted  $|FT|$  of Co precursor (red dots) and alternative curve-fitting (black line) adopting a CIF file obtained from the single-crystal structure. The green line represents the sum of all paths generated by FEFF when using the CIF of the complex as a model. The imaginary parts are also reported for comparison.

## F. ATR-FTIR study




**Figure S7.** FTIR spectra of nitrobenzene (up) and nitrostyrene (down) on KBr.


## 5. COMPARISON WITH REPORTED CATALYSTS.

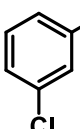
**Table S2.** Comparison of **Co@NC-800** activity for nitrobenzene hydrogenation with other reported catalysts.


| Entry     | Catalyst                              | Substrate/<br>Metal | T<br>(°C)  | Solvent                            | t<br>(h)  | H <sub>2</sub><br>(bar) | Conversion<br>(%) | Ref              |
|-----------|---------------------------------------|---------------------|------------|------------------------------------|-----------|-------------------------|-------------------|------------------|
| 1         | Co-L/C                                | 100                 | 110        | THF-H <sub>2</sub> O               | 6         | 50                      | 91                | 5                |
| 2         | Co <sub>3</sub> O <sub>4</sub> /NGr@C | 100                 | 110        | THF-H <sub>2</sub> O               | 12        | 50                      | >99               | 6                |
| 3         | Co@C/CNT                              | 12.5                | 110        | EtOH                               | 12        | 30                      | 98                | 7                |
| 4         | Co@C/SiO <sub>2</sub>                 | 20                  | 110        | EtOH-H <sub>2</sub> O              | 15        | 50                      | >99               | 8                |
| 5         | Co@C                                  | 20                  | 100        | Toluene                            | 10        | 7-11                    | 95                | 9                |
| 6         | Co/CoO@C                              | 10                  | 120        | THF-H <sub>2</sub> O               | 4         | 30                      | 95                | 10               |
| 7         | Co-Mo-S                               | 30                  | 150        | Toluene                            | 7         | 11                      | >99               | 11               |
| 8         | Co@NC                                 | 24                  | 110        | EtOH                               | 3         | 30                      | 99                | 12               |
| 9         | CoC@C                                 | 20                  | 120        | Toluene                            | 3         | 7-11                    | 95                | 13               |
| 10        | Co-L7/C                               | -                   | 110        | EtOH- H <sub>2</sub> O             | 8         | 50                      | >99               | 14               |
| 11        | Co/N-C-800-BT                         | -                   | 110        | H <sub>2</sub> O                   | 1.5       | 3.5                     | >99               | 15               |
| 12        | Co@mesoNC                             | 150                 | 110        | EtOH                               | 2         | 30                      | 73                | 16               |
| 13        | Co@N-SiC                              | 50                  | 100        | EtOH- H <sub>2</sub> O             | 20        | 40                      | >99               | 17               |
| 14        | CoOx@NC                               | 10                  | 110        | H <sub>2</sub> O                   | 5         | 50                      | 100               | 18               |
| 15        | Co@CN-800                             | 4.1                 | 70         | H <sub>2</sub> O                   | 2         | 20                      | >99               | 19               |
| 16        | CMK-3-CoPc-WII                        | 15.8                | 40         | MeTHF-H <sub>2</sub> O             | 24        | 20                      | >99               | 20               |
| 17        | CoSAs/NC                              | 260                 | 110        | EtOH-H <sub>2</sub> O              | 8         | 30                      | 99.7              | 21               |
| 18        | Co-MA-800                             | 14.7                | 120        | THF-H <sub>2</sub> O               | 18        | 40                      | >99               | 22               |
| 19        | CN1meso-Co                            | 71.8                | 100        | Propanol-Et <sub>3</sub> N         | 14        | 15                      | >99               | 23               |
| 20        | FeS <sub>2</sub> /NSC                 | 43.5                | 120        | H <sub>2</sub> O                   | 5         | 20                      | 99                | 24               |
| 21        | FeS <sub>2</sub>                      | 1.2                 | 120        | THF-H <sub>2</sub> O               | 18        | 50                      | 100               | 25               |
| 22        | Fe <sub>2</sub> P@C                   | -                   | 120        | THF-H <sub>2</sub> O               | 12        | 50                      | >99               | 26               |
| 23        | Fe/rGO-N                              | 88.6                | 120        | THF-H <sub>2</sub> O               | 2         | 30                      | >99               | 27               |
| 24        | Fe@SiCN                               | 10                  | 120        | Et <sub>3</sub> N-H <sub>2</sub> O | 20        | 60                      | >99               | 28               |
| 25        | Fe <sub>2</sub> O <sub>3</sub> /nGr@C | 22                  | 120        | THF-H <sub>2</sub> O               | 12        | 50                      | 95                | 29               |
| 26        | Ni/CeO <sub>2</sub> -CAS              | 24.3                | 210        | EtOH                               | 7         | 20                      | 99.5              | 30               |
| 27        | Ni-N-C-700                            | 79.3                | 120        | EtOH                               | 10        | 30                      | 99                | 31               |
| <b>28</b> | <b>Co@NC-800</b>                      | <b>98.2</b>         | <b>100</b> | <b>H<sub>2</sub>O</b>              | <b>14</b> | <b>10</b>               | <b>&gt;99</b>     | <b>This work</b> |
| <b>29</b> | <b>Co@NC-800</b>                      | <b>69</b>           | <b>70</b>  | <b>H<sub>2</sub>O</b>              | <b>14</b> | <b>10</b>               | <b>&gt;99</b>     | <b>This work</b> |


## 6. CHARACTERIZATION OF CATALYTIC PRODUCTS.


 **Aniline (1a).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.25 (t,  $J$  = 7.8 Hz, 2H), 6.86 (t,  $J$  = 7.8 Hz, 1H), 6.75 (d,  $J$  = 7.5 Hz, 2H), 3.69 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.6, 129.4, 118.6, 115.2. The spectra are in accordance with the literature.<sup>19</sup> GC-MS: calculated for  $\text{C}_6\text{H}_7\text{N}$  93.2. Found: 93.2.

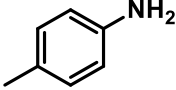
 **2-fluoroaniline (1b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.04-6.95 (m, 2H), 6.84-6.73 (m, 2H), 3.72 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 153.37, 134.49, 124.52, 118.71, 116.98, 115.14.  $\delta$  = 153.4 ( $^1J_{\text{FC}}$  238,3 Hz), 134.5 ( $^2J_{\text{FC}}$  13,0 Hz), 124.5 ( $^4J_{\text{FC}}$  3,5 Hz), 118.7 ( $^3J_{\text{FC}}$  7,1 Hz), 117.0 ( $^3J_{\text{FC}}$  3,6 Hz), 115.1 ( $^2J_{\text{FC}}$  18,2 Hz). The spectra are in accordance with the literature.<sup>19</sup> GC-MS: calculated for  $\text{C}_6\text{H}_6\text{NF}$  111.2. Found: 111.3

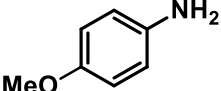
 **3-chloroaniline (1c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.01-6.95 (m, 1H), 6.66-6.58 (m, 2H), 6.48-6.45 (m, 1H), 3.63 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.6, 134.9, 130.3, 118.5, 115.0, 113.2. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for  $\text{C}_6\text{H}_6\text{NCl}$  127.5. Found: 127.4.

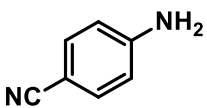
 **4-bromoaniline (1d).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.15 (d,  $J$  = 8.8 Hz, 2H), 6.47 (d,  $J$  = 8.8 Hz, 2H), 3.57 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.5, 132.0, 116.8, 110.2. The spectra are in accordance with the literature.<sup>32</sup> GC-MS: calculated for  $\text{C}_6\text{H}_6\text{NBr}$  172.0. Found: 172.0.

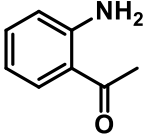
 **2-iodoaniline (1e).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.65 (d,  $J$  = 8.0 Hz, 1 H), 7.15 (t,  $J$  = 8.0 Hz, 1 H), 6.77 (d,  $J$  = 8.0 Hz, 1 H), 6.49 (t,  $J$  = 8.0 Hz, 1 H), 4.01 (br s, 2 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 146.8, 139.0, 129.3, 120.0, 114.7, 84.2. The spectra are in accordance with the literature.<sup>33</sup> GC-MS: calculated for  $\text{C}_6\text{H}_6\text{NI}$  219.0. Found: 219.0.

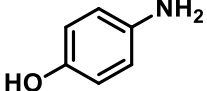
 **2-ethylaniline (1f).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.10-7.04 (m, 2H), 6.78 (t,  $J$  = 8.1 Hz, 1H), 6.71 (d,  $J$  = 8.1 Hz, 1H), 3.56 (br s, 2H), 2.55 (q,  $J$  = 7.0 Hz, 2H), 0.91 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 143.9, 128.4, 128.2, 126.8, 118.9, 115.5, 23.7, 13.0. The spectra are in accordance with the literature.<sup>34</sup> GC-MS: calculated for  $\text{C}_7\text{H}_9\text{N}$  121.2. Found: 121.2.

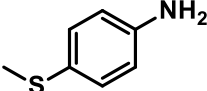
 **4-methylaniline (1g).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 6.90 (d, *J* = 8.1 Hz, 2H), 6.53 (d, *J* = 8.1 Hz, 2H), 3.51 (br s, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 143.8, 129.8, 127.8, 115.3, 20.4. The spectra are in accordance with the literature.<sup>35</sup> GC-MS: calculated for C<sub>7</sub>H<sub>9</sub>N 107.2. Found: 107.3.

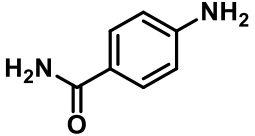
 **4-methoxyaniline (1h).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.77 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 4.03 (br s, 2H), 3.78 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 150.9, 131.6, 119.8, 113.8, 51.6. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub> 153.2. Found: 153.2.

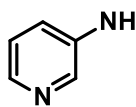
 **4-aminobenzonitrile (1i).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.33 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.13 (br s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 150.5, 133.8, 120.2, 114.5, 100.1. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for C<sub>7</sub>H<sub>6</sub>N<sub>2</sub> 118.1. Found: 118.2.


 **2'-aminoacetophenone (1j).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.73-7.70 (m, 1H), 7.30-7.24 (m, 1H), 6.68-6.62 (m, 2H), 6.31 (br s, 2H), 2.58 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 200.7, 150.3, 134.4, 132.0, 118.3, 117.2, 115.7, 27.8. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for C<sub>8</sub>H<sub>9</sub>NO 135.2. Found: 135.3.

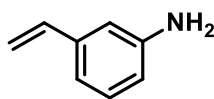
 **4-Aminophenol (1k).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 8.33 (s, 1H), 6.47 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 8.6 Hz, 2H), 4.37 (br s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 148.2, 140.6, 115.5, 115.2. The spectra are in accordance with the literature.<sup>32</sup> GC-MS: calculated for C<sub>6</sub>H<sub>7</sub>NO 109.1. Found: 109.1.

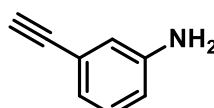
 **4-(methylsulfanyl)aniline (1l).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.10 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 3.50 (br s, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 145.1, 131.1, 125.9, 115.8, 18.8. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for C<sub>7</sub>H<sub>9</sub>NS 139.2. Found: 139.2.

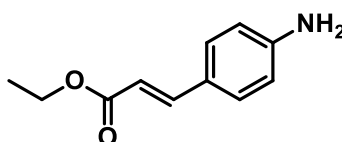
 **4-Aminobenzamide (1m).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.57 (d, *J* = 8.7 Hz, 2H), 7.50 (br s, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 5.58 (br s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 168.0, 151.6, 129.1, 121.0, 112.4. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O 136.2. Found: 136.2.

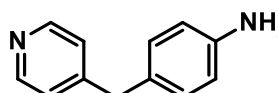
 **Pyridine-3-amine (1n).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.01-7.94 (m, 2H), 7.00-6.96 (m, 1H), 6.90-6.86 (m, 1H), 3.69 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 142.7, 139.9, 137.5, 123.7, 121.4. The spectra are in accordance with the literature.<sup>35</sup> GC-MS: calculated for  $\text{C}_5\text{H}_6\text{N}_2$  94.1. Found: 94.2.

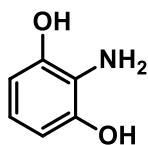
 **5-amino-furfuryl alcohol (1o).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.32-7.29 (m, 1H), 6.53-6.50 (m, 1H), 5.54 (br s, 1H), 4.52 (s, 2H), 3.22 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.5, 156.3, 117.9, 115.1, 61.3. The spectra are in accordance with the literature. GC-MS: calculated for  $\text{C}_5\text{H}_7\text{NO}_2$  113.1. Found: 113.1.

 **3-vinylaniline (1p).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.14 (t,  $J$  = 7.8 Hz, 1H), 6.85 (d,  $J$  = 7.8 Hz, 1H), 6.77 (s, 1H), 6.71-6.61 (m, 2H), 5.73 (d,  $J$  = 17.6, 1H), 5.23 (d,  $J$  = 10.9, 1H). 3.51 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.5, 138.7, 137.0, 129.4, 117.0, 114.8, 113.6, 112.8. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for  $\text{C}_8\text{H}_9\text{N}$  119.2. Found: 119.2.

 **3-Ethynylaniline (1q).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.15-7.10 (m, 1H), 6.93 (d,  $J$  = 7.8 Hz, 1H), 6.83 (s, 1H), 6.67 (d,  $J$  = 7.8 Hz, 1H) 3.70 (br s, 2H), 3.06 (s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.3, 129.3, 122.8, 122.5, 118.3, 115.9, 84.0, 76.6. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for  $\text{C}_8\text{H}_7\text{N}$  117.1. Found: 117.1.

 **Ethyl (2E)-3-(4-aminophenyl)-2-propenoate (1r).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.64-7.58 (d,  $J$  = 15.9 Hz, 1H), 7.35 (m, 2H), 6.65 (m, 2H), 6.27-6.22 (d,  $J$  = 15.9 Hz, 1H) 4.25 (q,  $J$  = 7.1 Hz, 2H), 3.96 (br s, 2H), 1.33 (t,  $J$  = 7.1 Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.7, 148.7, 144.8, 129.9, 124.8, 114.8, 113.8, 60.1, 14.4. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for  $\text{C}_{11}\text{H}_{13}\text{NO}_2$  191.2. Found: 191.2.

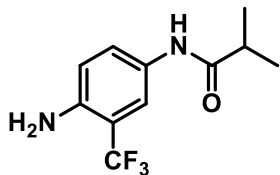
 **4-(4-pyridinylmethyl)aniline (1s).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.39 (d,  $J$  = 6.1 Hz, 2H), 7.01 (d,  $J$  = 6.1 Hz, 2H), 6.88 (d,  $J$  = 8.5 Hz, 2H), 6.57 (d,  $J$  = 8.5 Hz, 2H), 3.78 (br s, 2H), 3.55 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.9, 149.7, 145.0, 129.9, 188.8, 124.1, 115.5, 40.4. The spectra are in accordance with the literature.<sup>11</sup> GC-MS: calculated for  $\text{C}_{12}\text{H}_{12}\text{N}_2$  184.2. Found: 184.2.



**2-amino-1,3-benzenediol (1t).**  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  = 8.84 (br s, 2H), 6.30-6.22 (m, 3H), 3.84 (br s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

145.4, 124.3, 116.4, 107.1. The spectra are in accordance with the literature.<sup>36</sup>

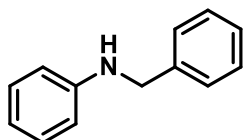
GC-MS: calculated for  $\text{C}_6\text{H}_7\text{NO}_2$  125.1. Found: 125.1.



**N-[4-amino-3-(trifluoromethyl)phenyl]-2-methyl-propanamide**

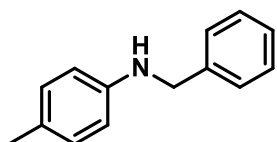
**(1u).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.64 (s, 1H) 7.73 (d,  $J$  = 2.6 Hz, 1H), 7.42 (dd,  $J$  = 8.8, 2.6 Hz, 1H), 6.79 (d,  $J$  = 8.8 Hz, 1H), 5.32 (br s, 2H), 2.51 (dt,  $J$  = 13.3, 6.6 Hz, 1H), 1.08 (d,  $J$  = 6.7 Hz,

6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 175.2, 142.5 ( $^3J_{\text{FC}}$  2.3 Hz), 128.8, 125.5 ( $^3J_{\text{FC}}$  1.4 Hz), 125.4 ( $^1J_{\text{FC}}$  270 Hz), 117.6, 117.4 ( $^2J_{\text{FC}}$  5.7 Hz), 110.8 ( $^2J_{\text{FC}}$  29.9 Hz), 35.2, 19.9. The spectra are in accordance with the literature.<sup>37</sup> GC-MS: calculated for  $\text{C}_{11}\text{H}_{14}\text{NOF}_3$  247.1. Found: 247.1.



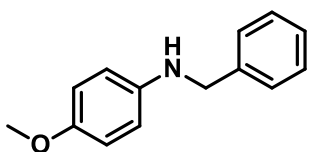
**N-Benzylaniline (2a).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.45-7.33 (m, 5H), 7.26-7.21 (m, 2H), 6.77 (t,  $J$  = 8.8 Hz, 1H), 6.70 (d,  $J$  = 8.8 Hz, 2H), 4.38 (s, 2H), 4.07 (br s, 1H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{13}\text{H}_{13}\text{N}$  183.3. Found: 183.2.



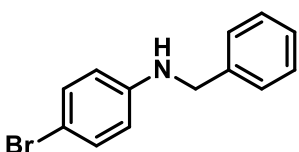
**Benzyl-*p*-tolyl-amine (2b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.38-7.25 (m, 5H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 6.56 (d,  $J$  = 8.8 Hz, 2H), 4.31 (s, 2H), 3.90 (br s, 1H), 2.23 (s, 3H).  $^{13}\text{C}$ -NMR (75 MHz,

$\text{CDCl}_3$ ):  $\delta$  = 145.9, 139.7, 129.3, 128.7, 127.6, 127.3, 126.8, 112.9, 48.7, 20.5. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{14}\text{H}_{15}\text{N}$  197.3. Found: 197.3.



**N-Benzyl-4-methoxyaniline (2c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.29-7.19 (m, 5H), 6.70 (d,  $J$  = 8.8 Hz, 2H), 6.55 (d,  $J$  = 8.8 Hz, 2H), 4.22 (s, 2H), 3.67 (s, 3H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  =

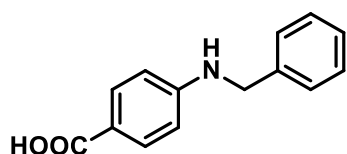
152.5, 142.0, 139.4, 128.6, 127.7, 127.2, 114.9, 114.5, 55.8, 49.5. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{14}\text{H}_{15}\text{NO}$  213.3. Found: 213.3.



**N-Benzyl-4-bromoaniline (2d).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.36-7.28 (m, 5H), 7.23 (d,  $J$  = 4.4 Hz, 2H), 6.56 (d,  $J$  = 4.4 Hz, 2H), 4.31 (s, 2H), 4.00 (br s, 1H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.6,

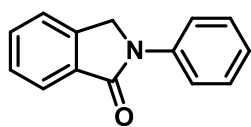
138.9, 129.0, 128.7, 127.4, 127.3, 122.1, 113.9, 48.3. The spectra are in accordance with the literature.<sup>39</sup> GC-MS: calculated for  $\text{C}_{13}\text{H}_{12}\text{NBr}$  262.2. Found: 262.2.





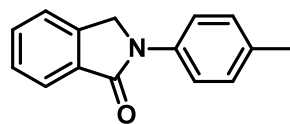
**4-(Benzylamino)benzoic acid (2e).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.93-7.91 (m, 2H), 7.39-7.28 (m, 5H), 6.61 (d,  $J$  = 8.8 Hz, 2H), 4.41 (s, 2H), 4.07 (br s, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.6, 138.9, 129.0, 128.7, 127.4, 127.3, 122.1, 113.9, 48.3.

The spectra are in accordance with the literature.<sup>39</sup> GC-MS: calculated for  $\text{C}_{14}\text{H}_{13}\text{NO}_2$  227.3. Found: 227.3.



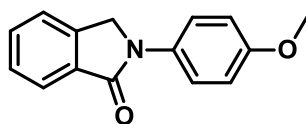
**Phenylisoindolin-1-one (3a).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.95 (d,  $J$  = 7.6 Hz, 1 H), 7.90 (d,  $J$  = 7.6 Hz, 2 H), 7.62-7.43 (m, 5 H), 7.21 (m, 1 H), 4.90 (s, 2 H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.5, 140.1, 139.5,

133.3, 132.1, 129.2, 128.4, 124.5, 124.2, 122.6, 119.5, 50.8. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{14}\text{H}_{11}\text{NO}$  209.2. Found: 209.2.



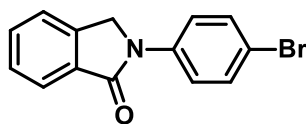
**2-(p-Tolyl)isoindolin-1-one (3b).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 (d,  $J$  = 8 Hz, 1 H), 7.66 (d,  $J$  = 8.4 Hz, 2 H), 7.53-7.50 (m, 1 H), 7.45 (d,  $J$  = 8 Hz, 2 H), 7.17 (d,  $J$  = 8.4 Hz, 2 H), 4.78 (s, 2 H), 2.29

(s, 3 H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.4, 140.2, 136.7, 134.2, 133.4, 131.9, 129.7, 128.4, 124.1, 122.6, 119.7, 50.9, 20.9. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{15}\text{H}_{13}\text{NO}$  223.3. Found: 223.3.



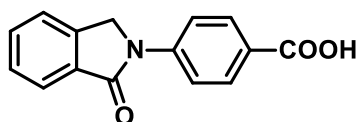
**2-(4-Methoxyphenyl)isoindolin-1-one (3c).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 (d,  $J$  = 7.2 Hz, 1 H), 7.67 (d,  $J$  = 8.8 Hz, 2 H), 7.52-7.42 (m, 3 H), 6.90 (d,  $J$  = 7.2 Hz, 2 H), 4.76 (s, 2 H), 3.77 (s,

3 H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 167.3, 156.7, 140.2, 133.3, 132.7, 131.8, 128.4, 124.1, 122.6, 121.6, 114.4, 55.5, 51.2. The spectra are in accordance with the literature.<sup>38</sup> GC-MS: calculated for  $\text{C}_{15}\text{H}_{13}\text{NO}_2$  239.3. Found: 239.3.



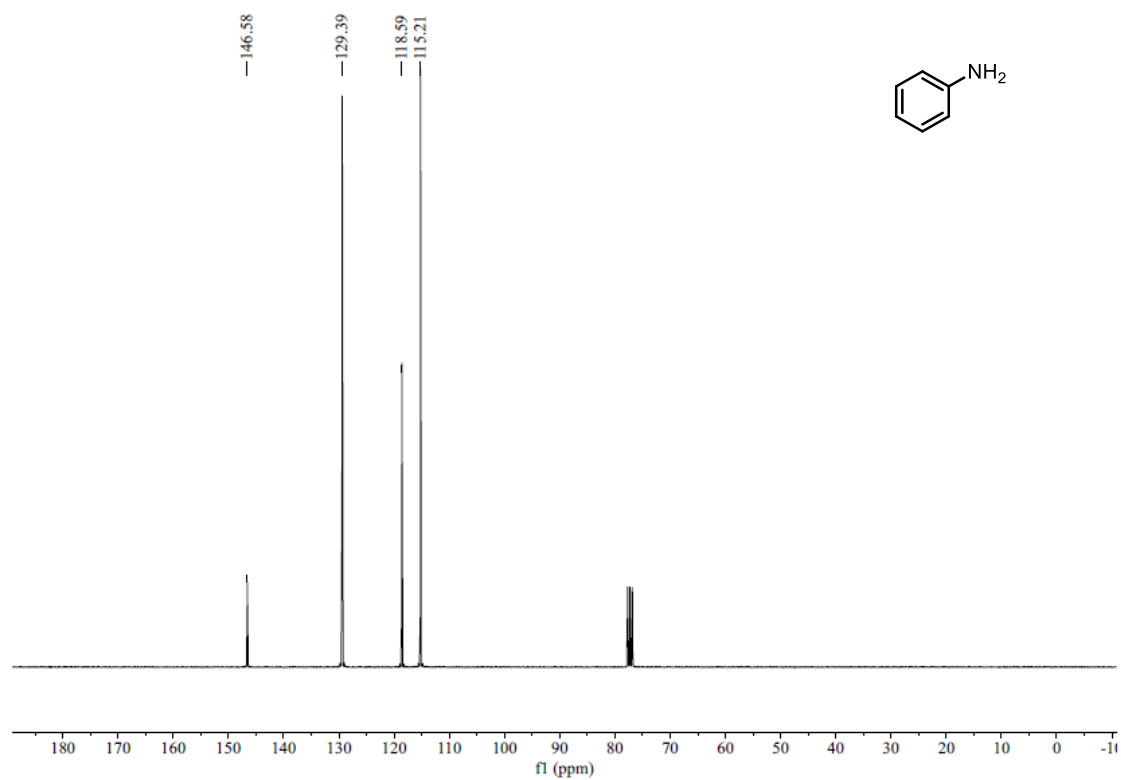
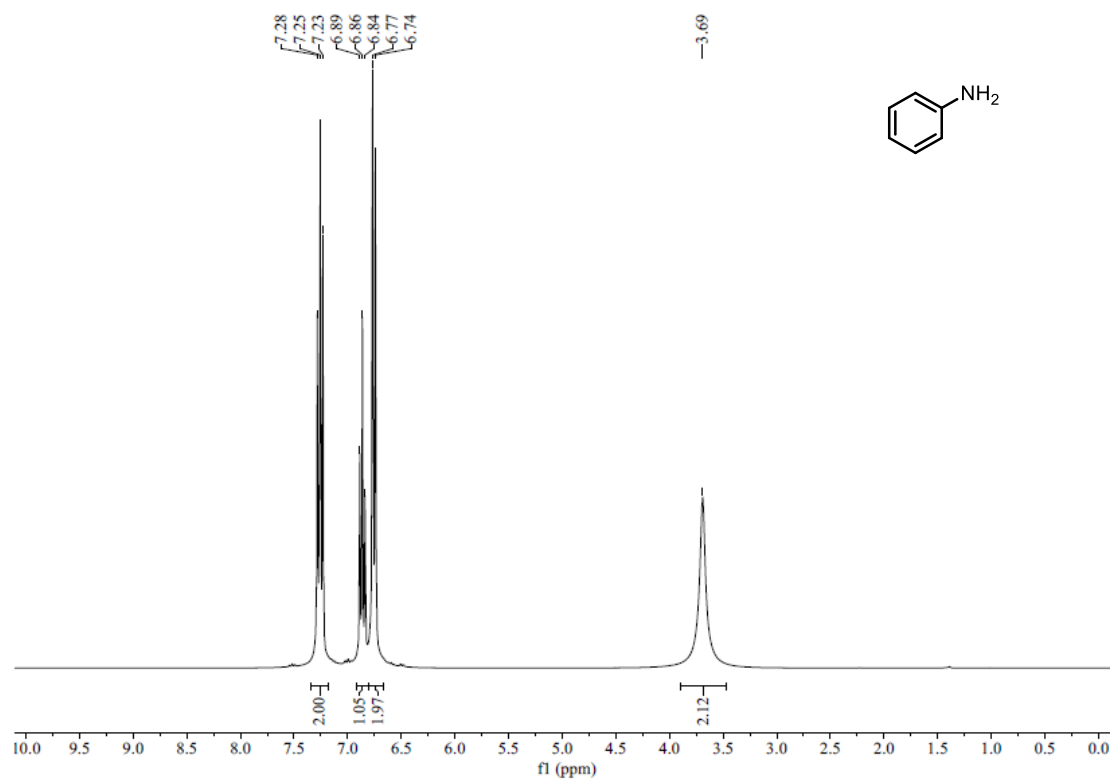
**2-(4-Bromophenyl)isoindolin-1-one (3d).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.95 (d,  $J$  = 8.4 Hz, 1H), 7.82 (d,  $J$  = 7.2 Hz, 2H), 7.66 – 7.61 (m, 1H), 7.57-7.54 (m, 4H), 4.86 (s, 2H).  $^{13}\text{C-NMR}$  (75 MHz,

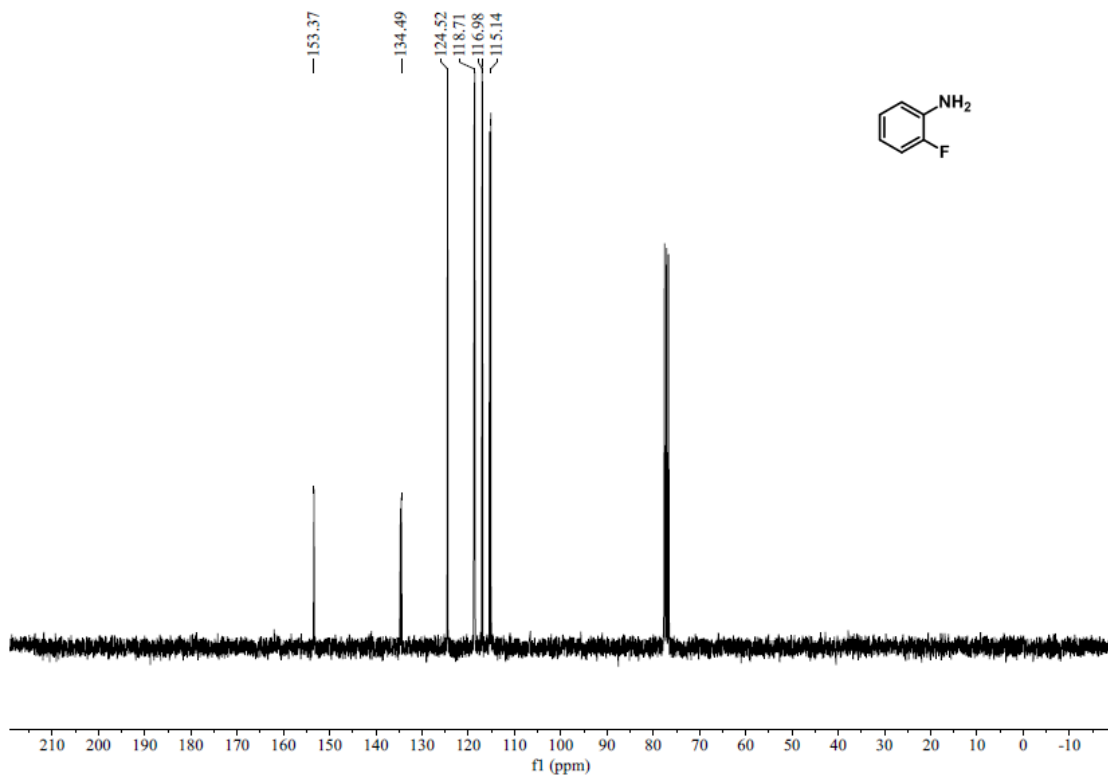
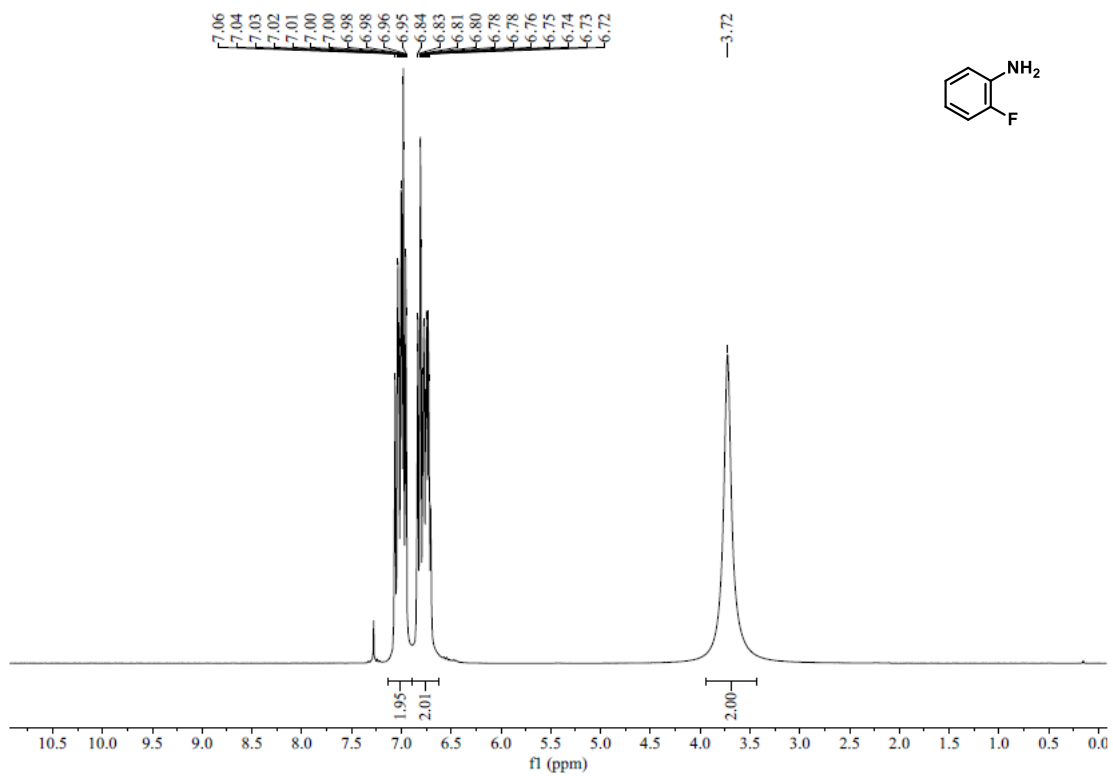
$\text{CDCl}_3$ ):  $\delta$  = 167.6, 160.0, 158.3, 139.9, 138.6, 132.1, 128.6, 124.3, 122.7, 120.8, 117.3, 116.7, 50.6. The spectra are in accordance with the literature.<sup>40</sup> GC-MS: calculated for  $\text{C}_{14}\text{H}_{10}\text{NOBr}$  289.1. Found: 289.2.

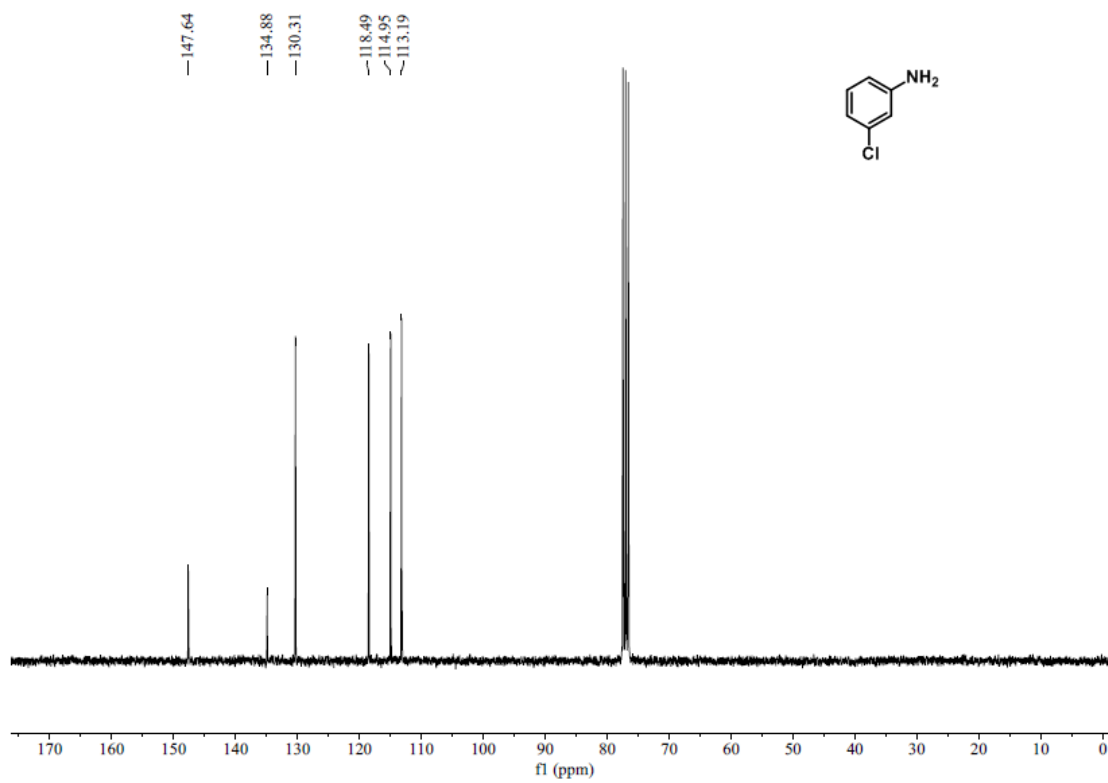
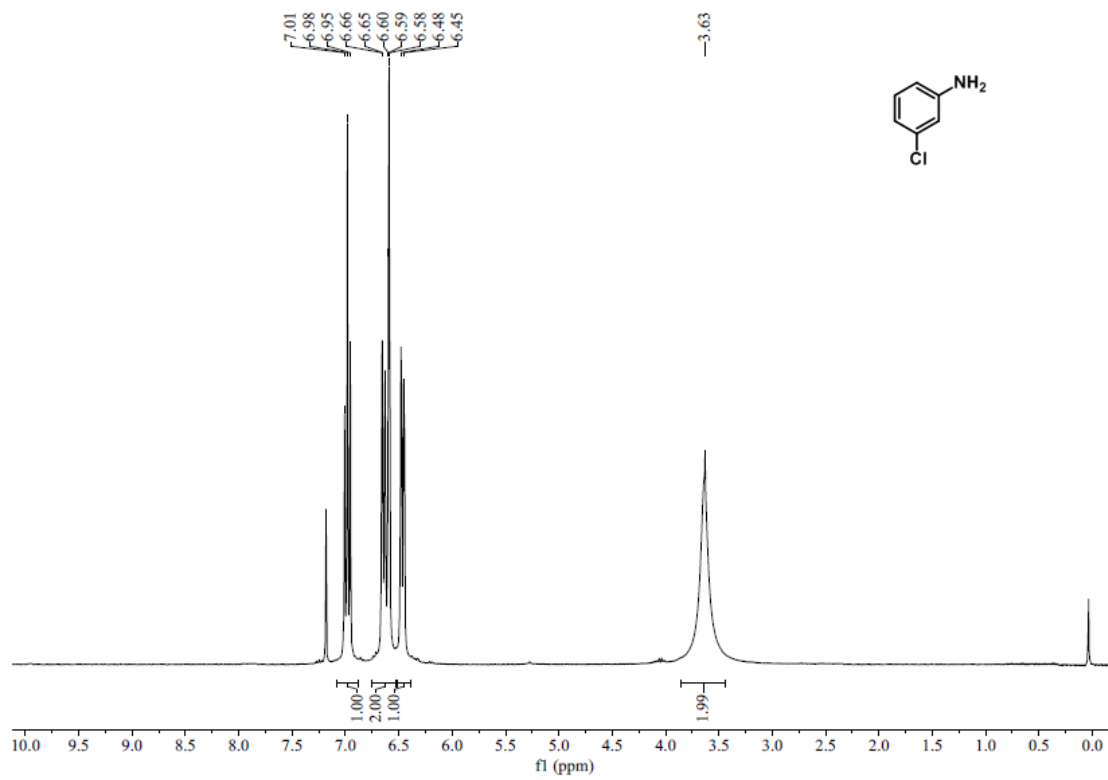


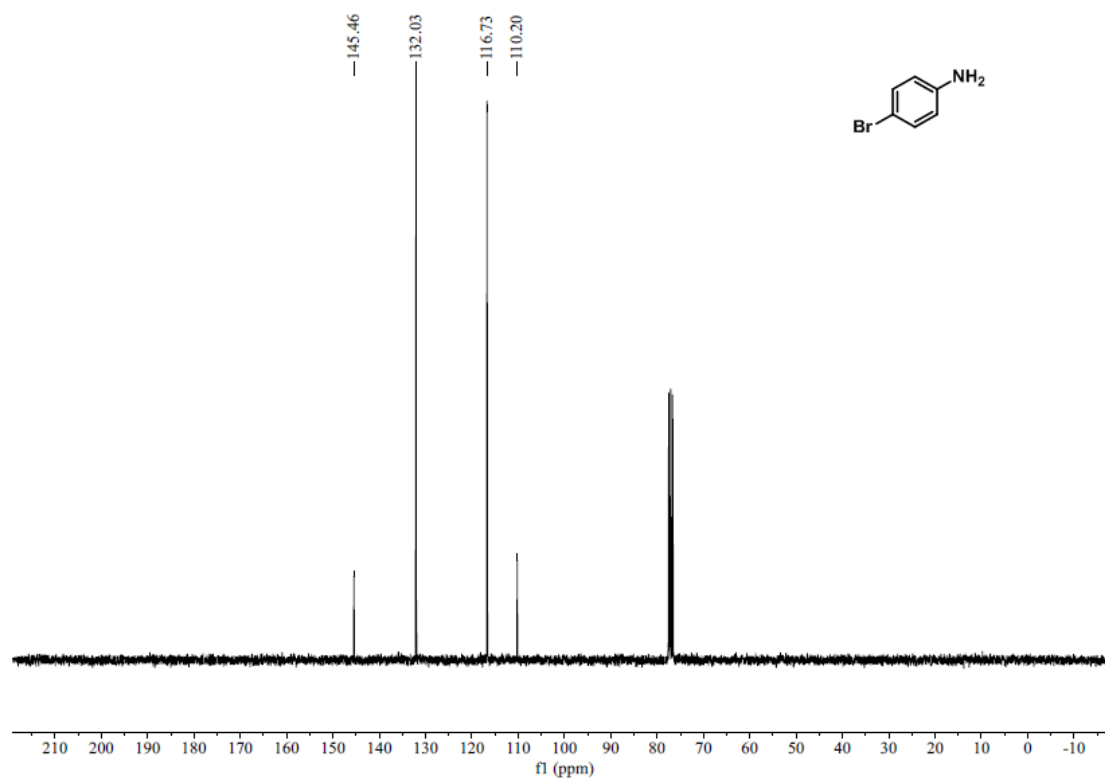
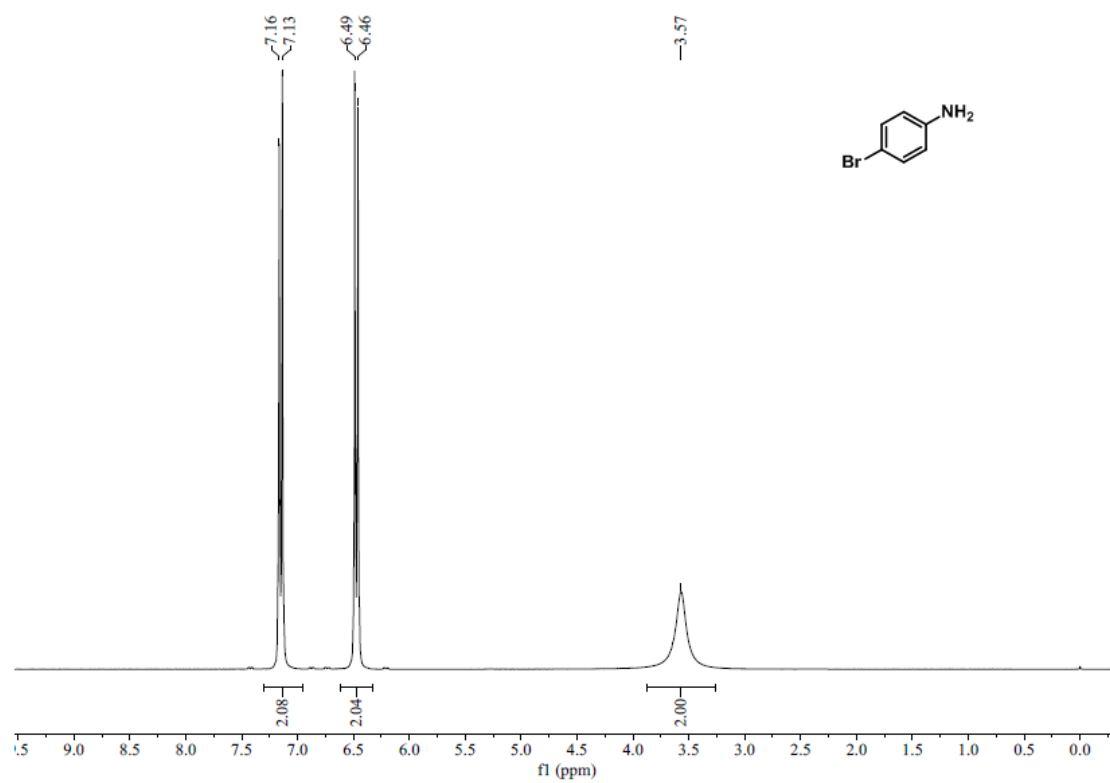
**4-(1-Oxoisindolin-2-yl)benzoic acid (3e).**  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 12.91 (s, 1H), 8.07 (d,  $J$  = 8.8 Hz, 2H), 8.01 (d,  $J$  = 8.8 Hz, 2H), 7.82 (d,  $J$  = 7.6 Hz, 1H), 7.72 (t,  $J$  = 7.6 Hz,

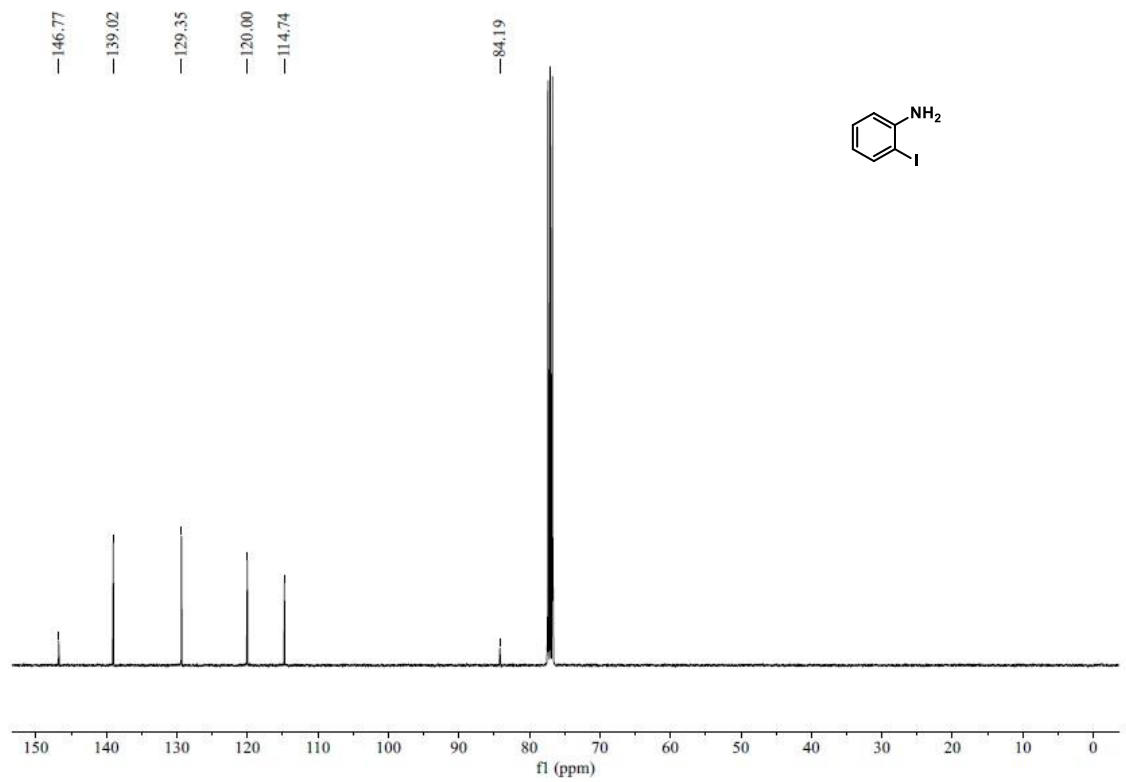
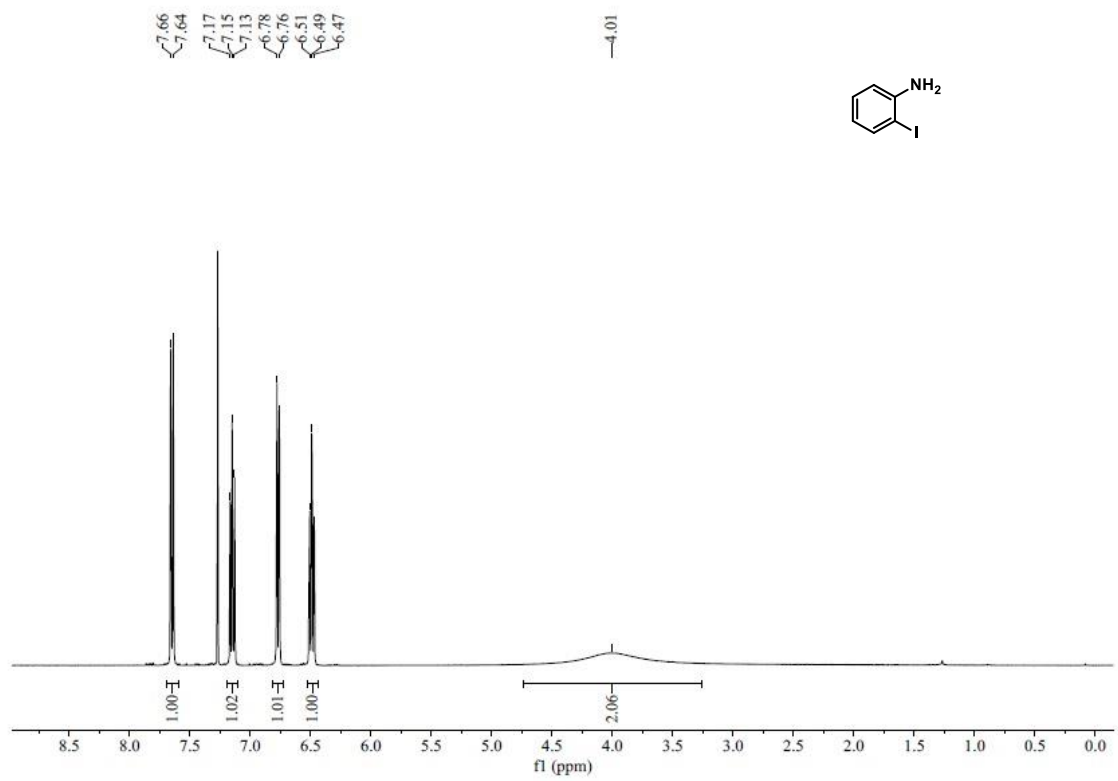
1H), 7.68 (d,  $J = 7.6$  Hz, 1H), 7.57 (t,  $J = 7.6$  Hz, 1H), 5.09 (s, 2H).  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 167.4, 160.7, 158.3, 139.9, 135.5, 132.9, 128.4, 124.1, 122.6, 121.3, 121.2, 115.9, 115.7, 50.9$ . The spectra are in accordance with the literature.<sup>41</sup> GC-MS: calculated for  $\text{C}_{15}\text{H}_{11}\text{NO}_3$  253.3. Found: 253.3.

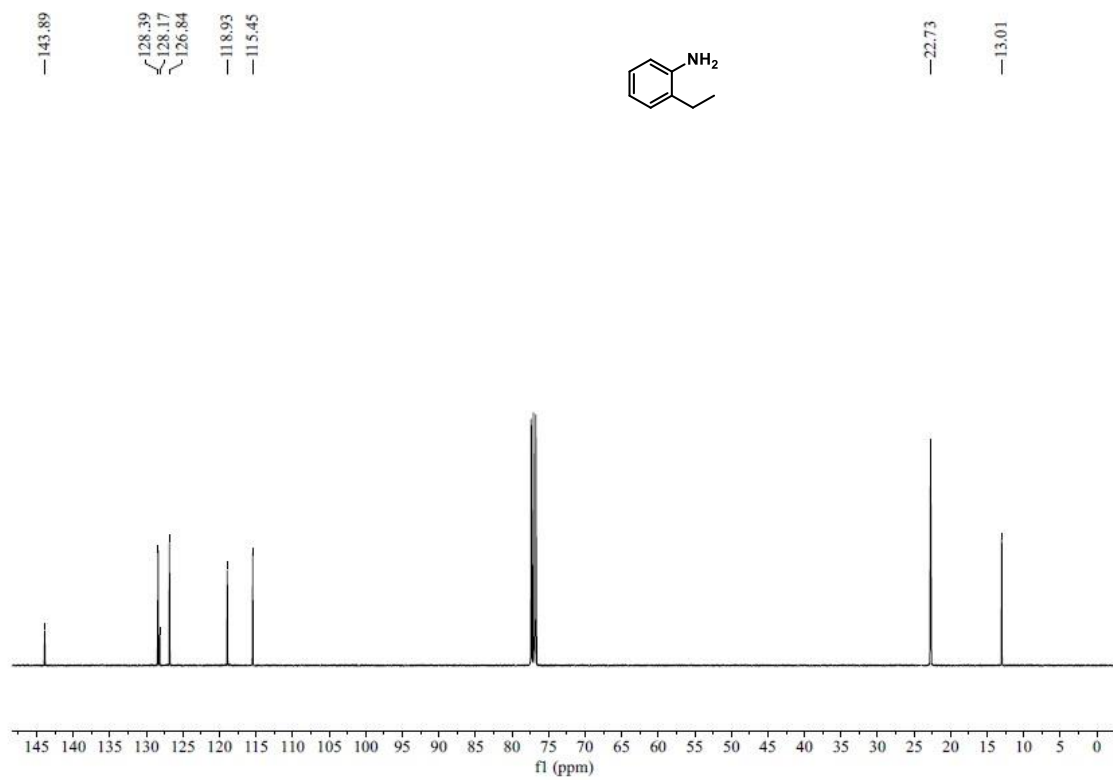
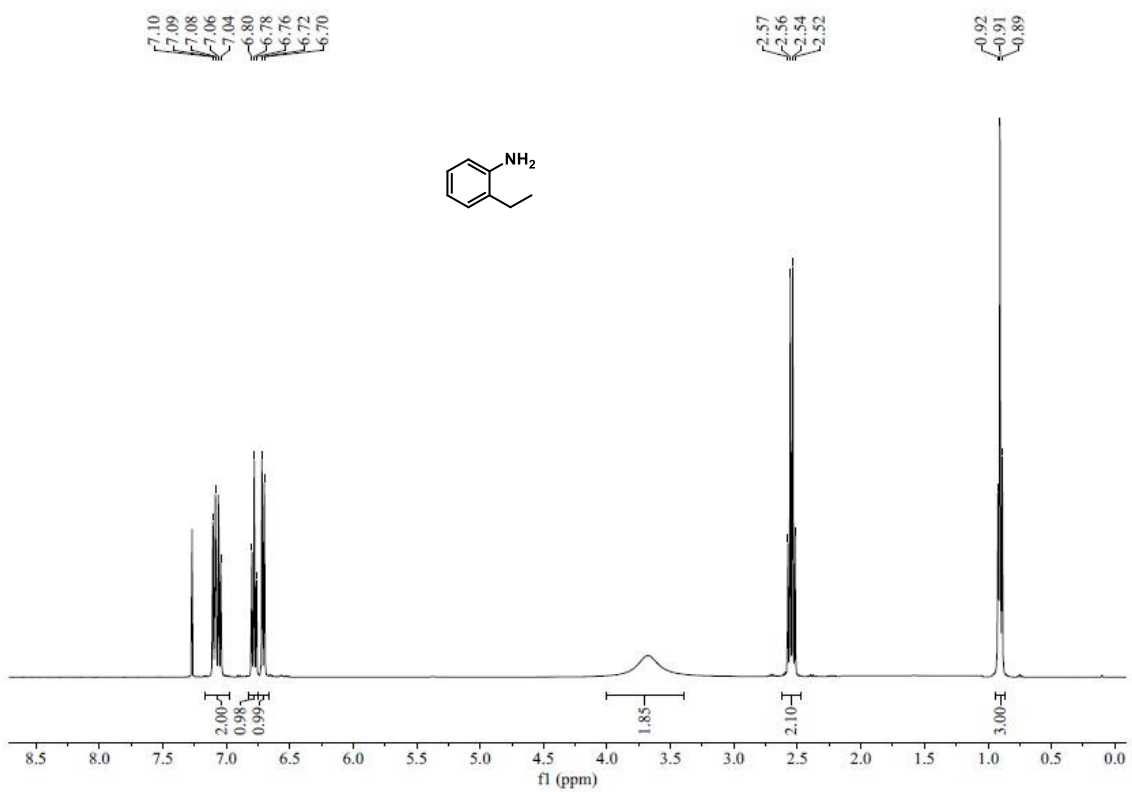


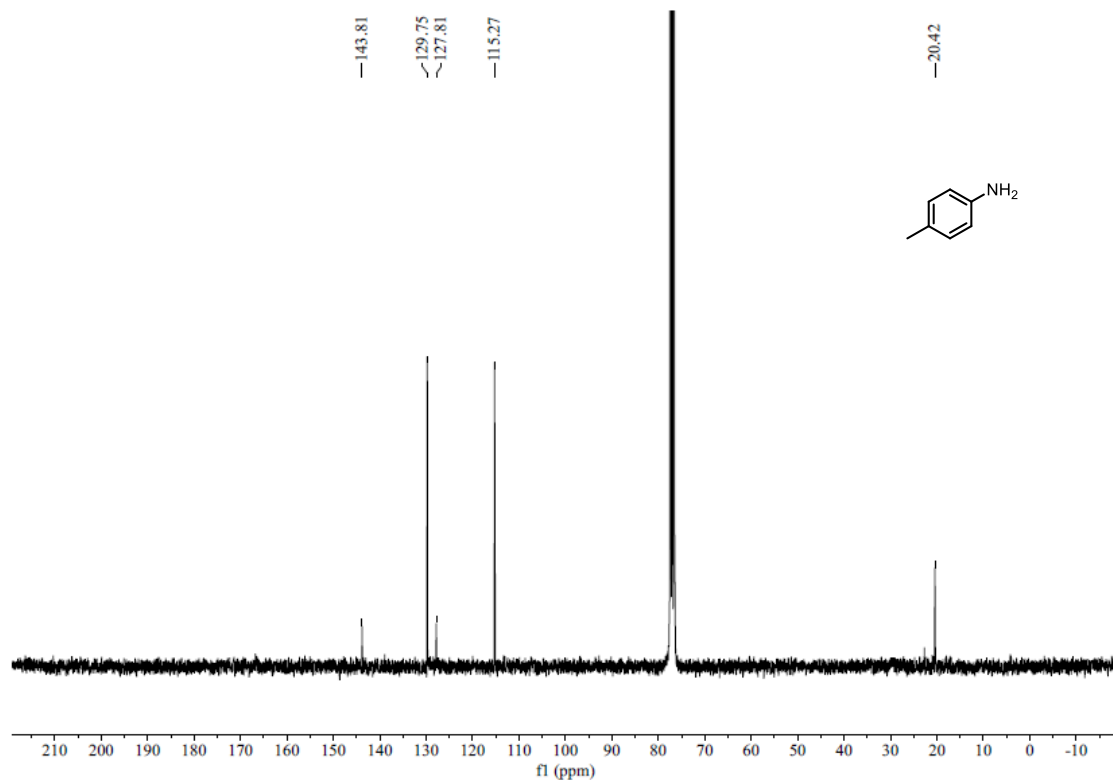
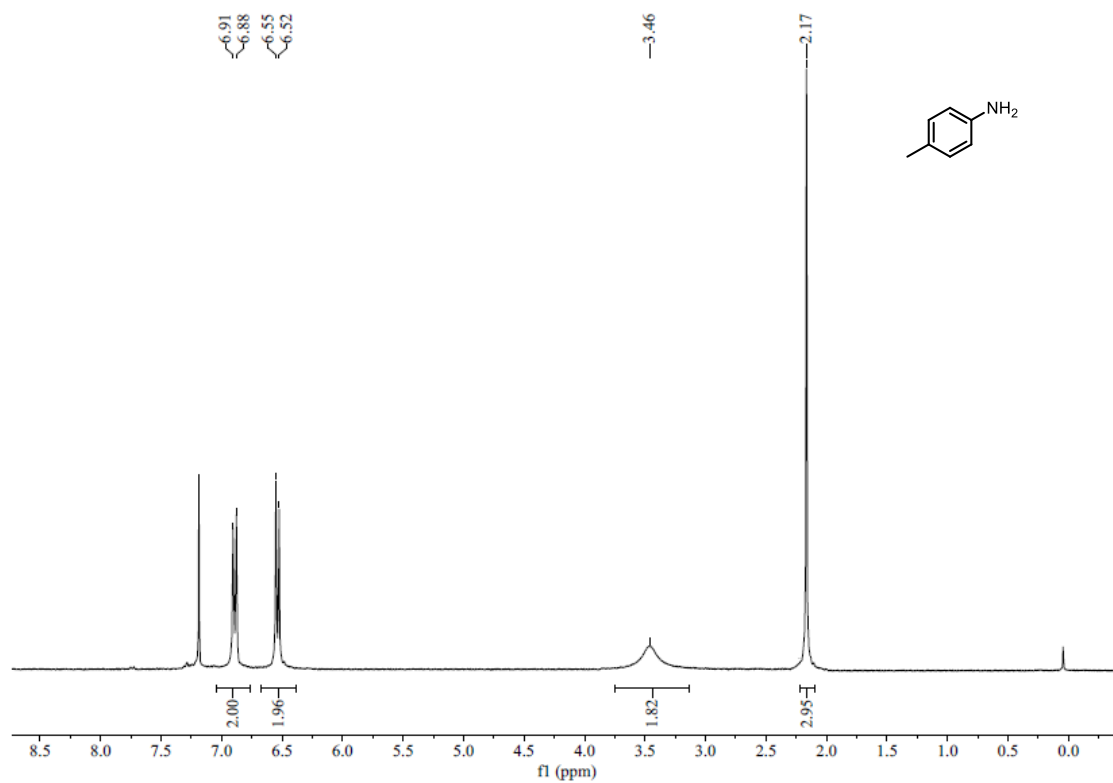




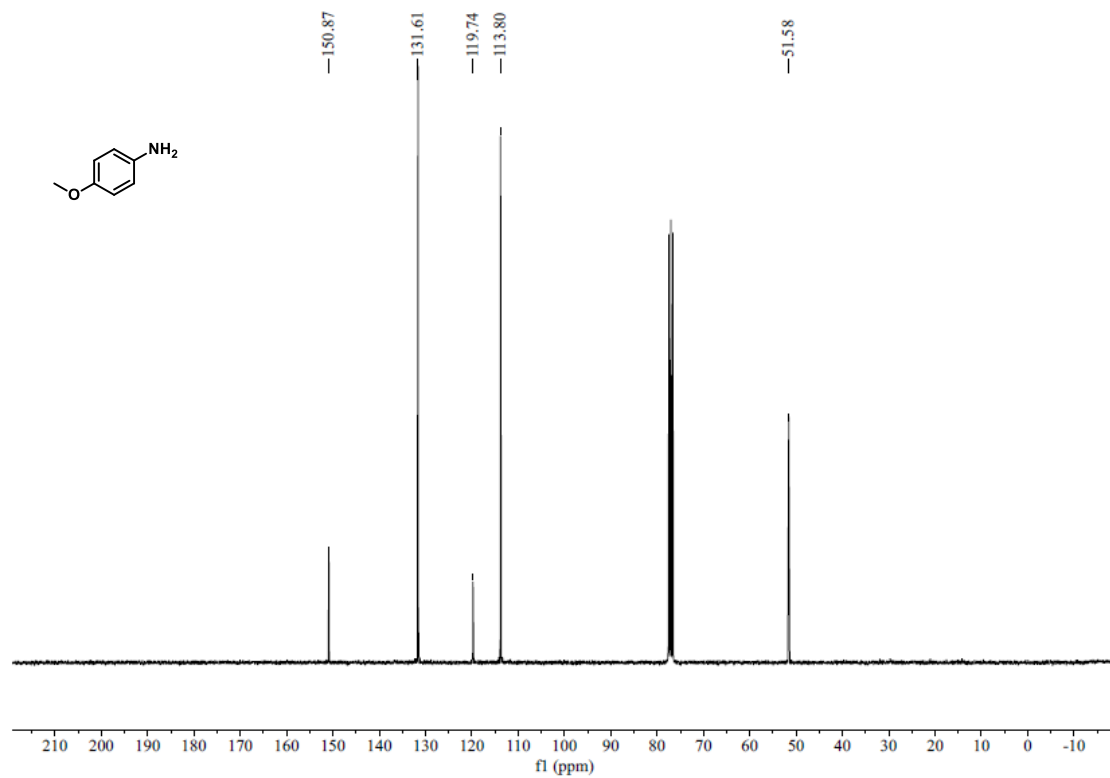
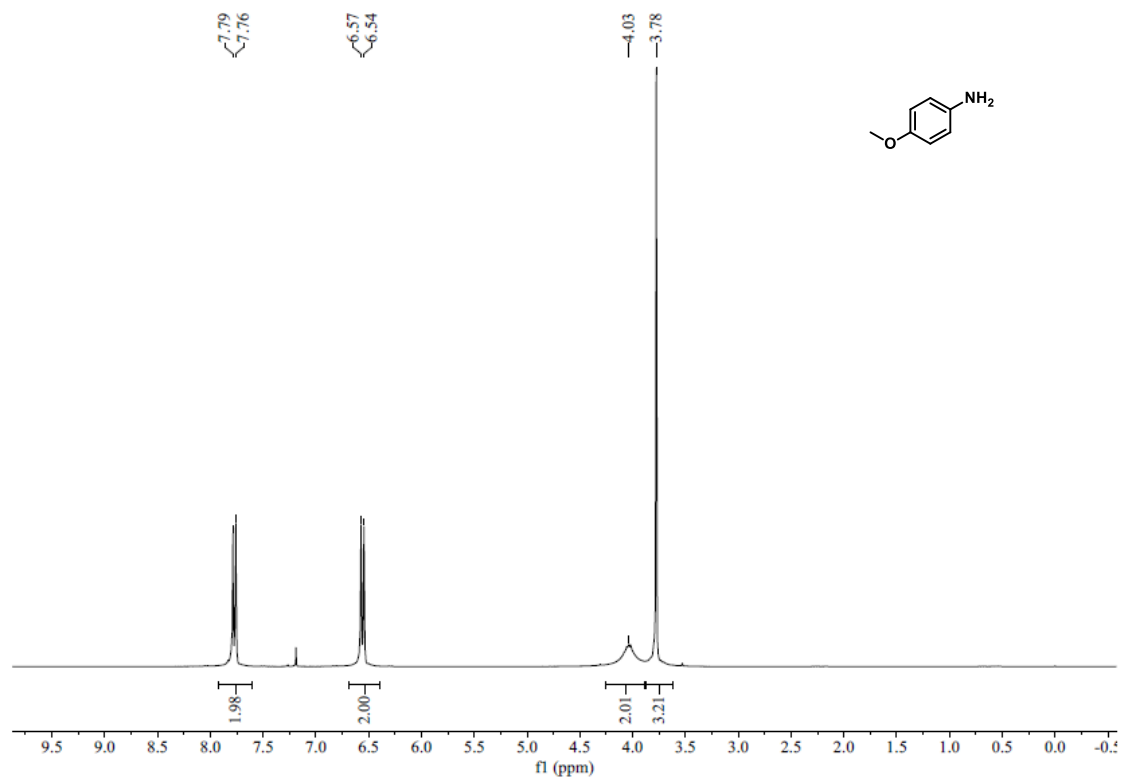


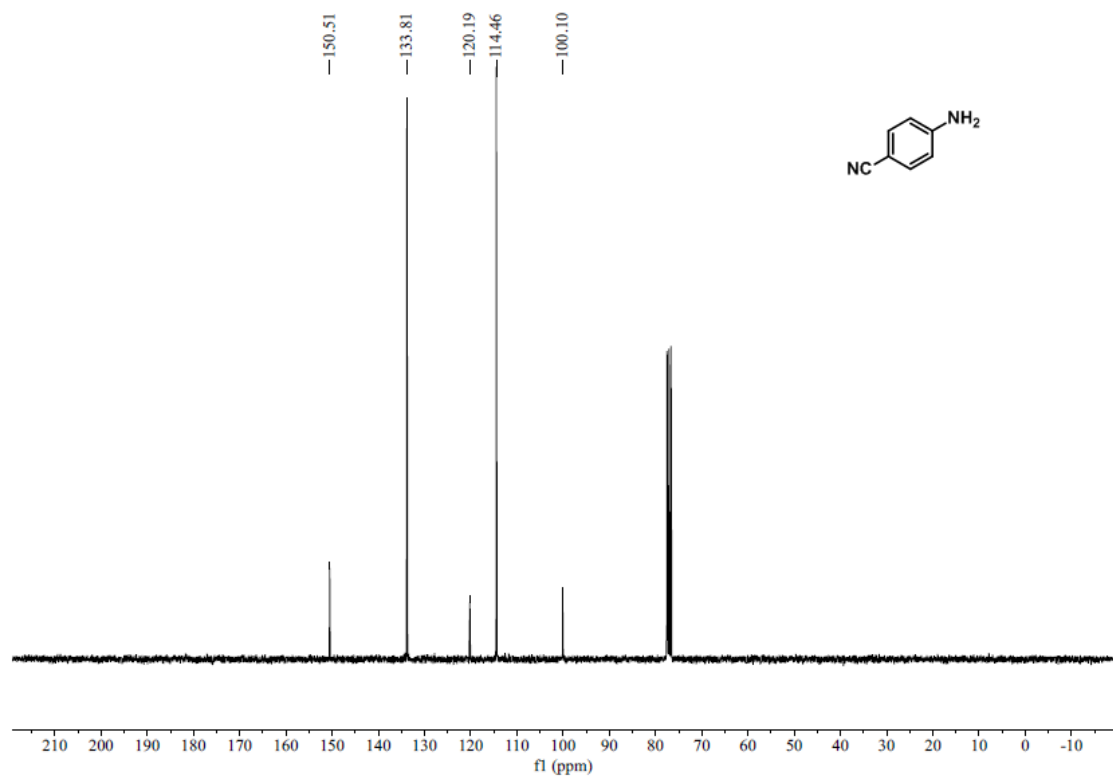
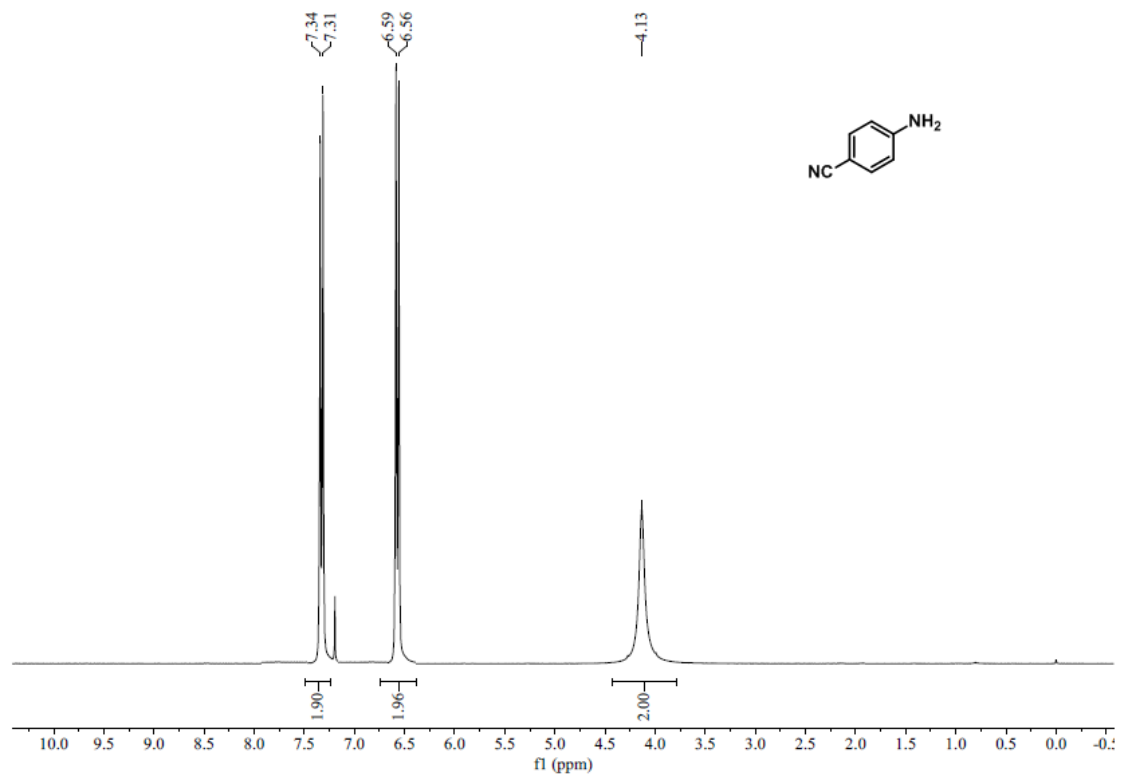


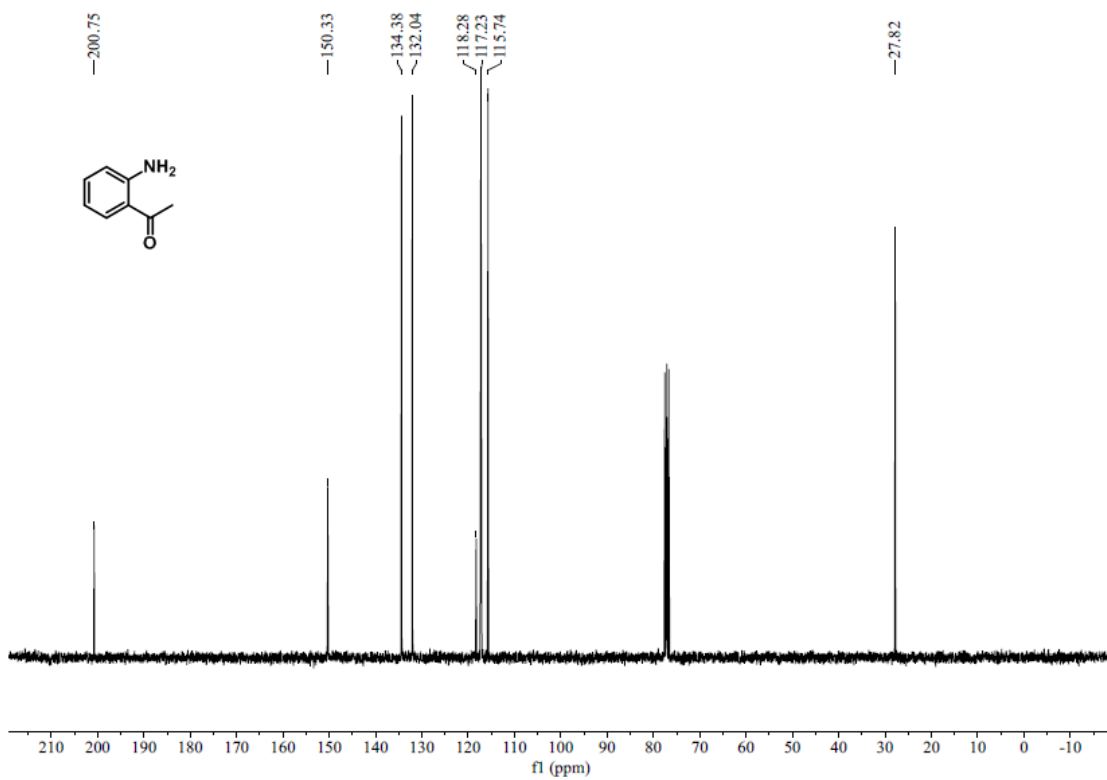
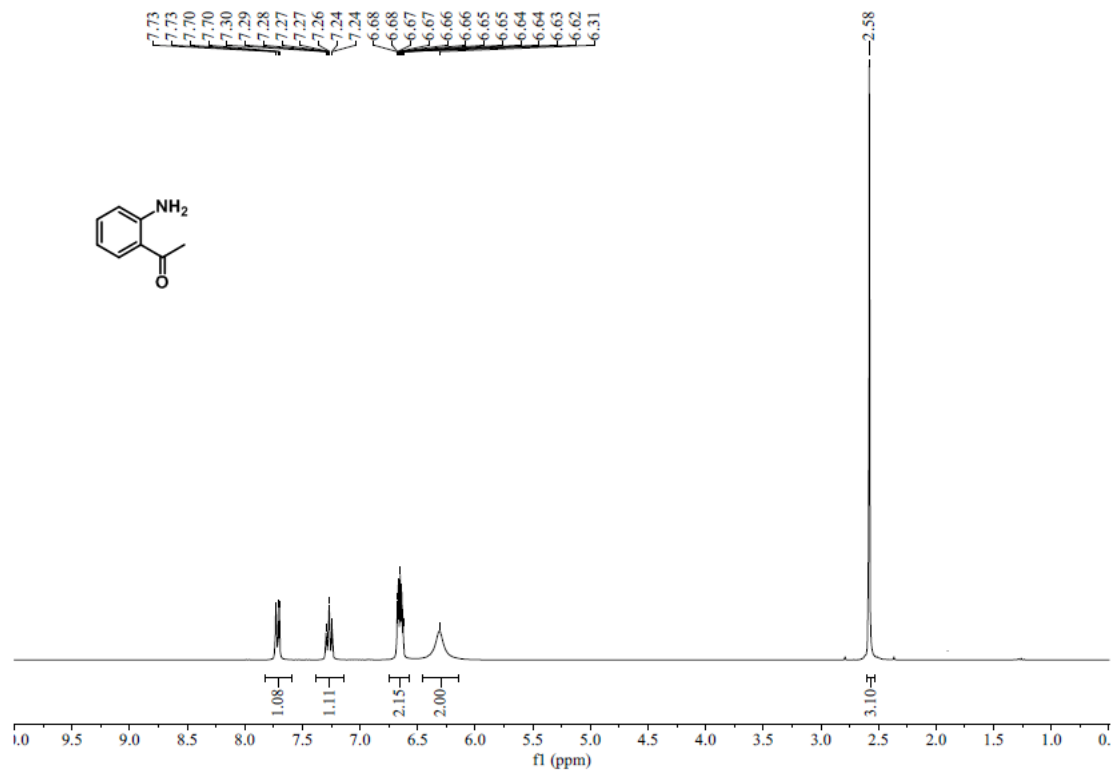


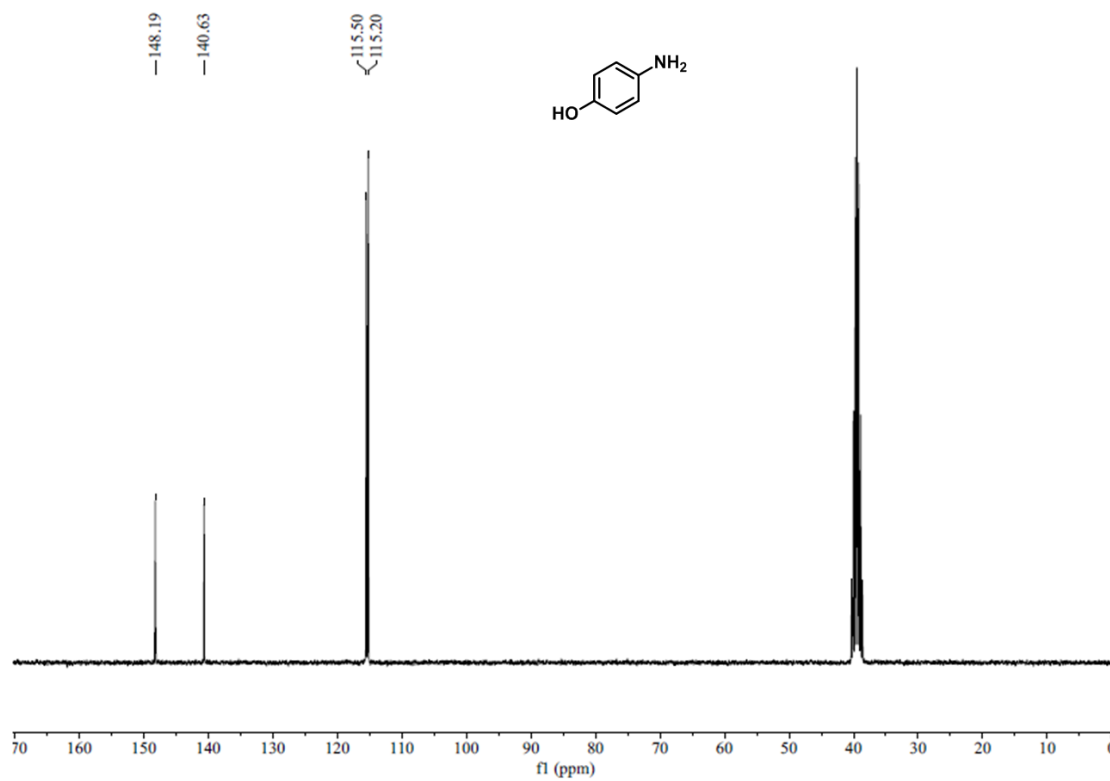
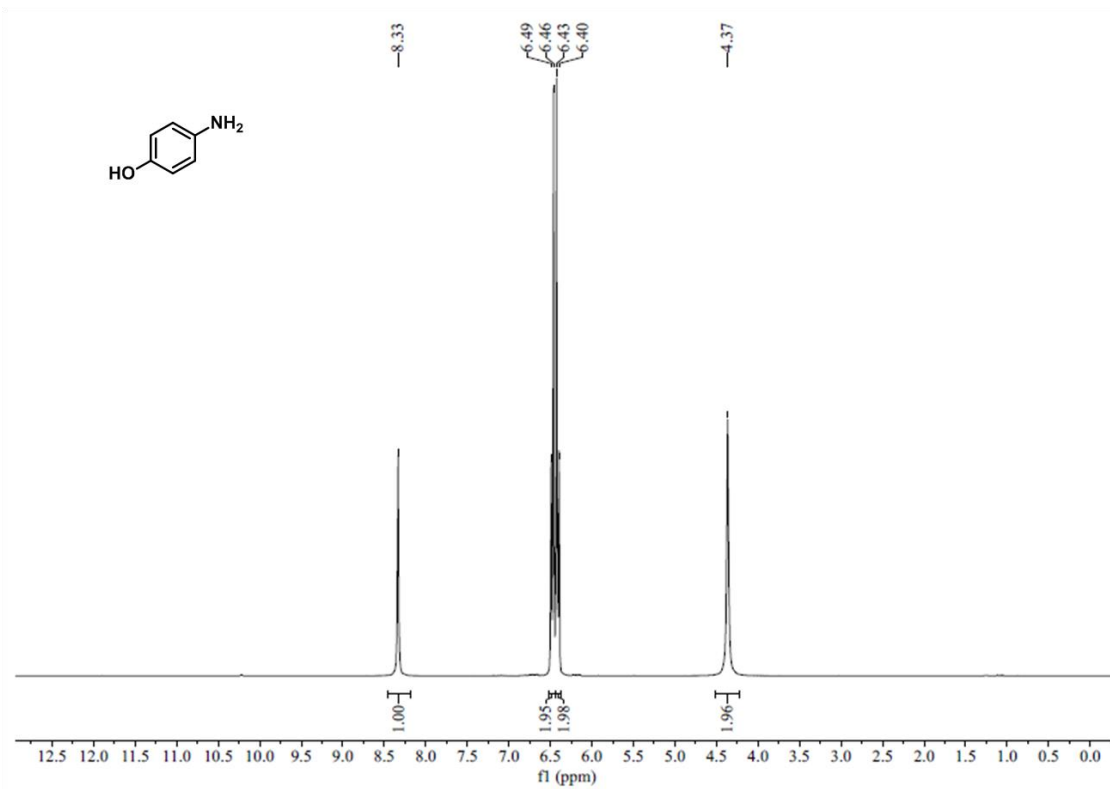


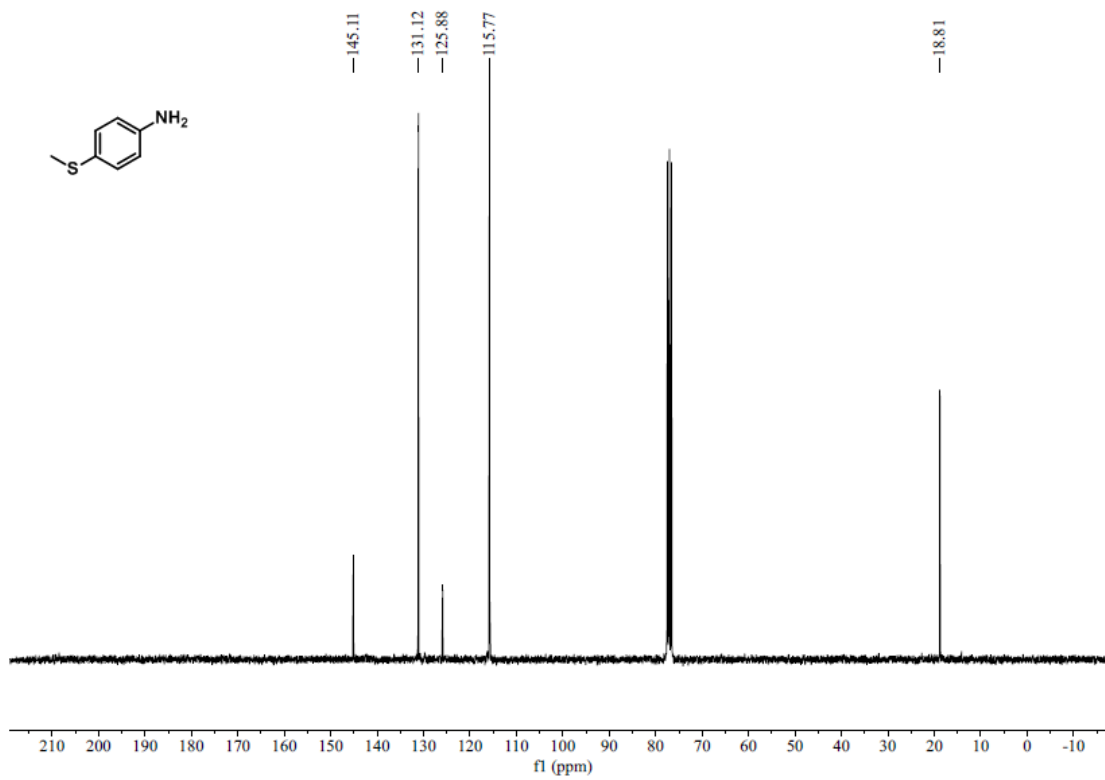
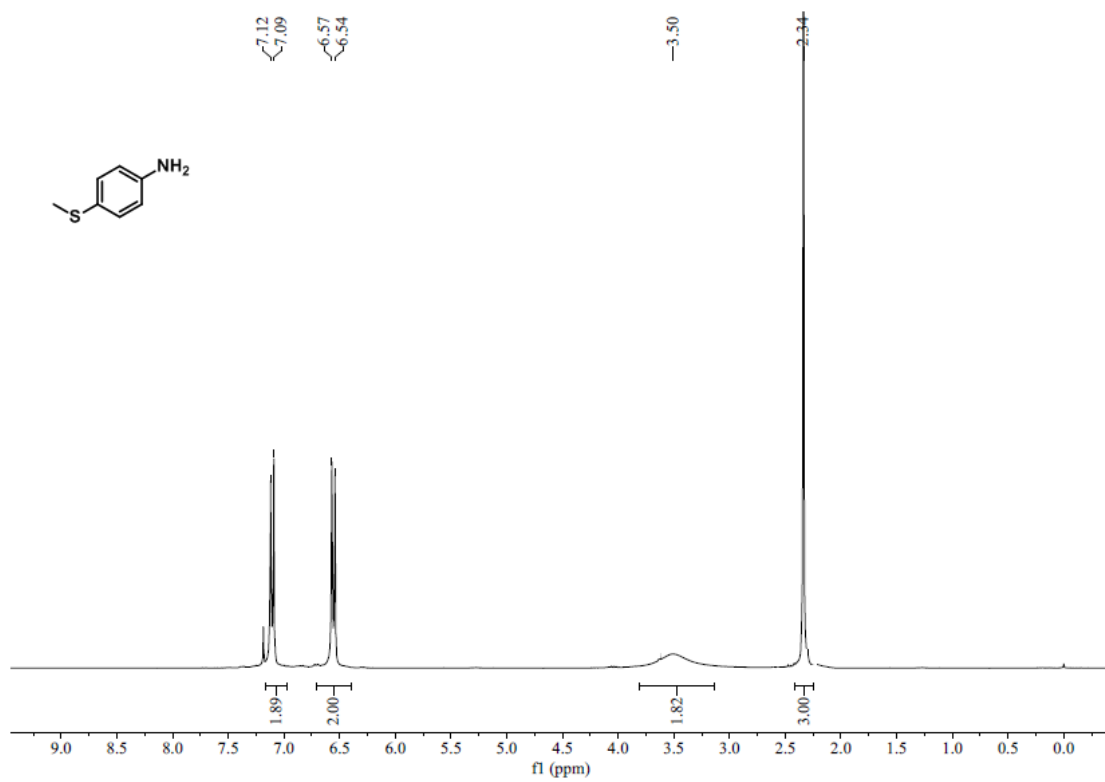


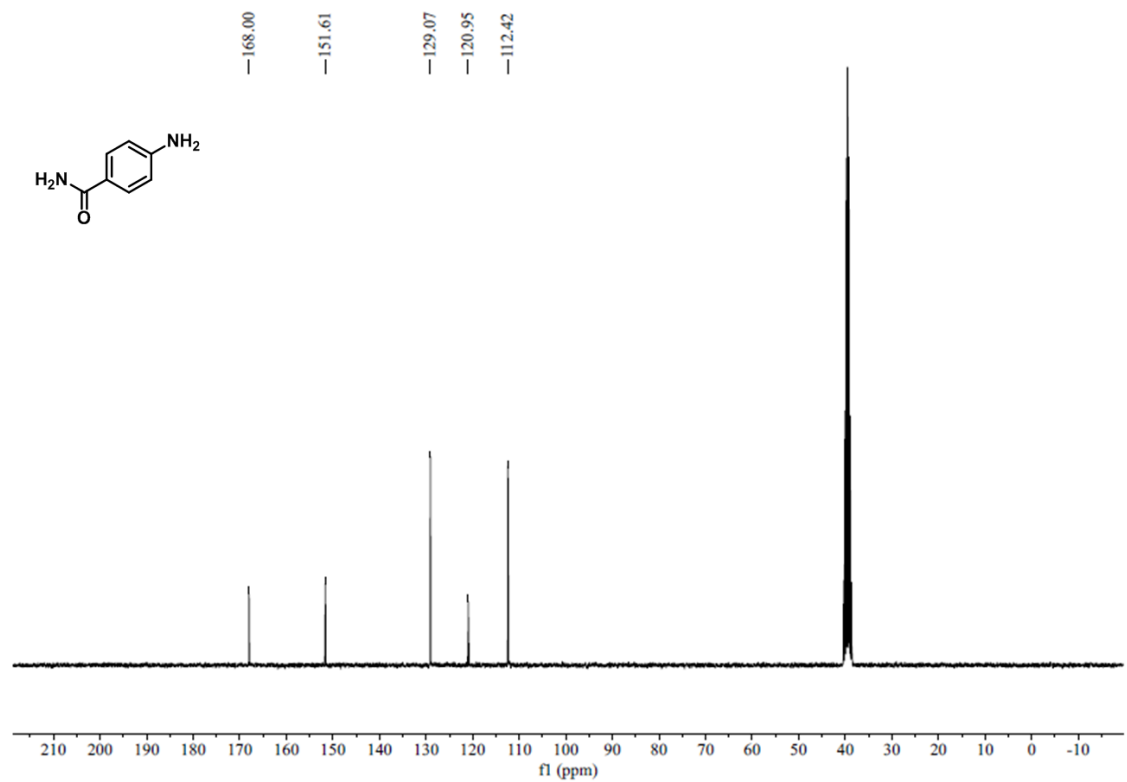
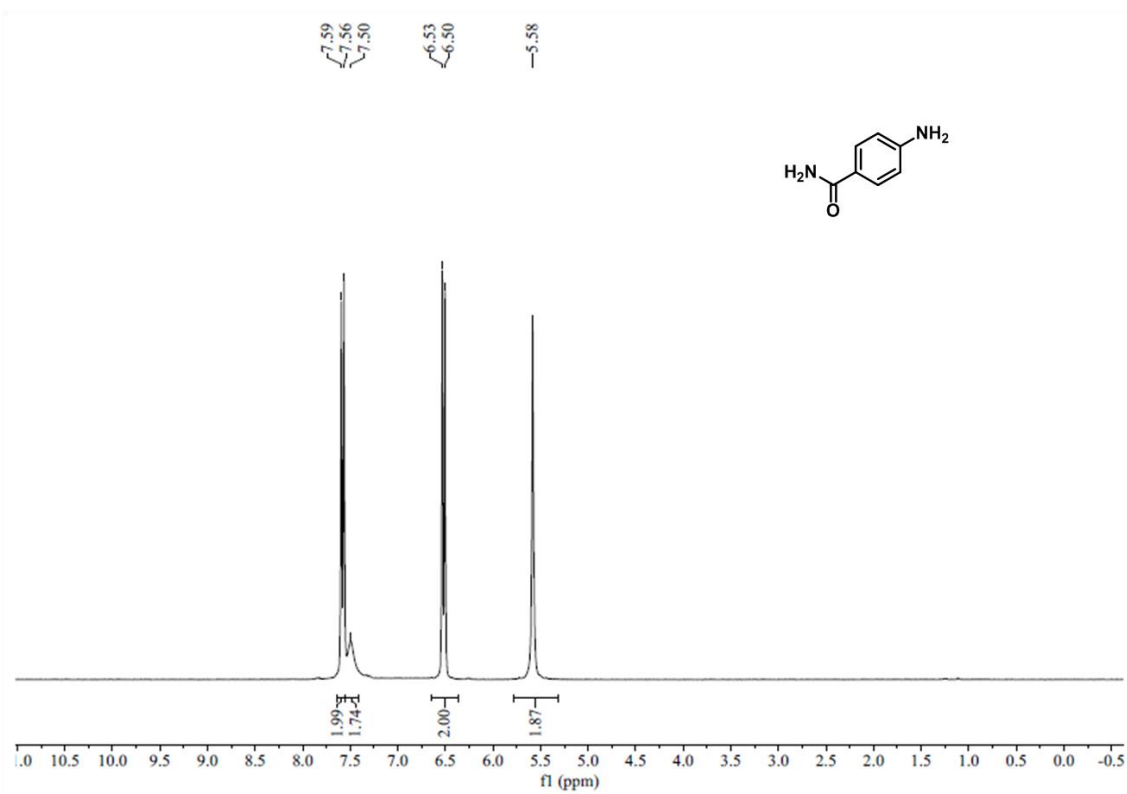


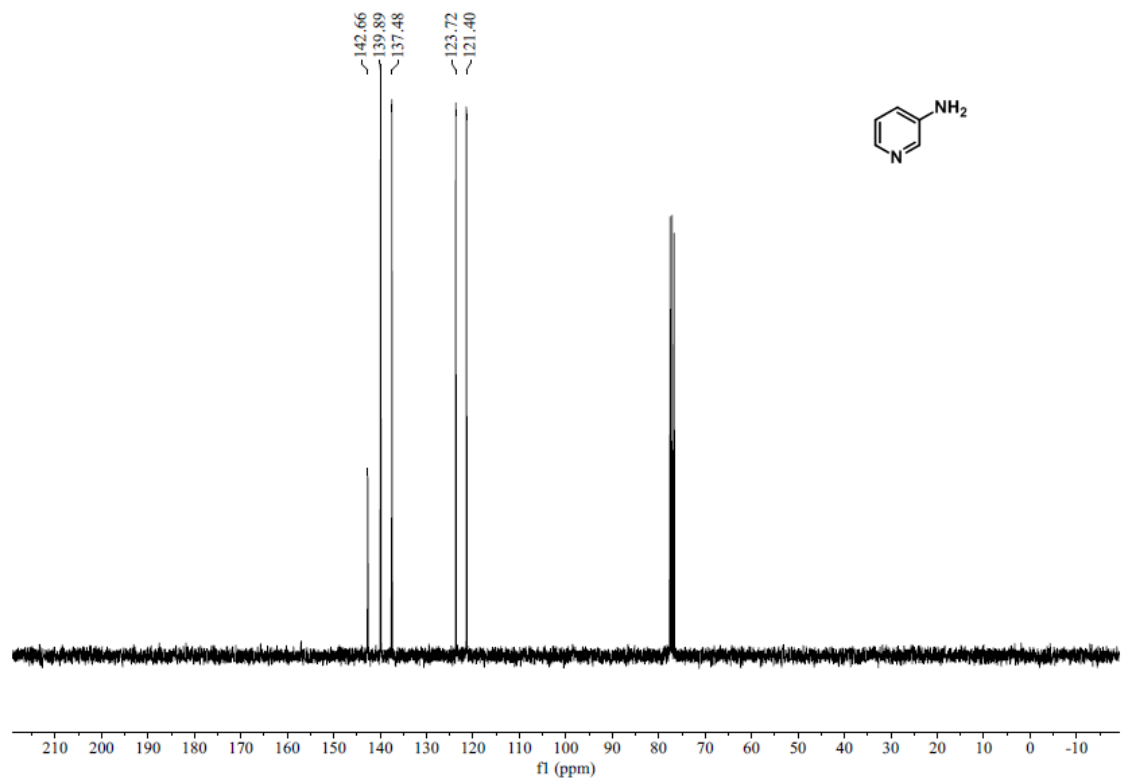
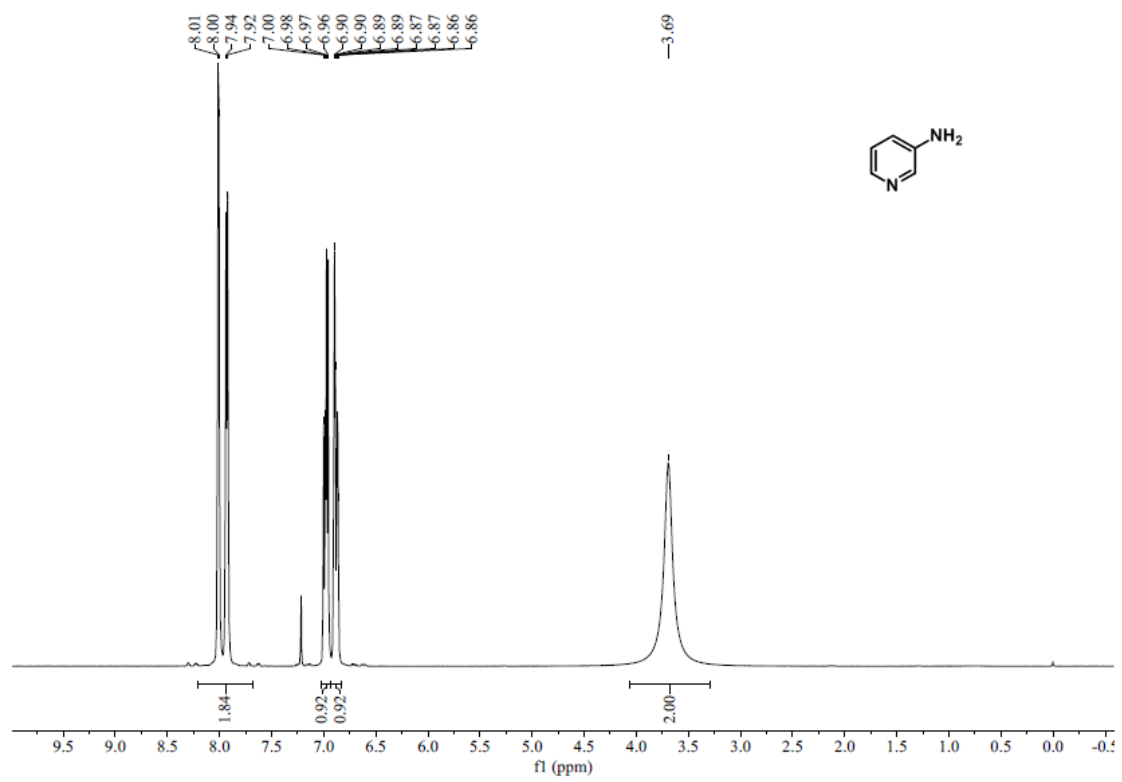


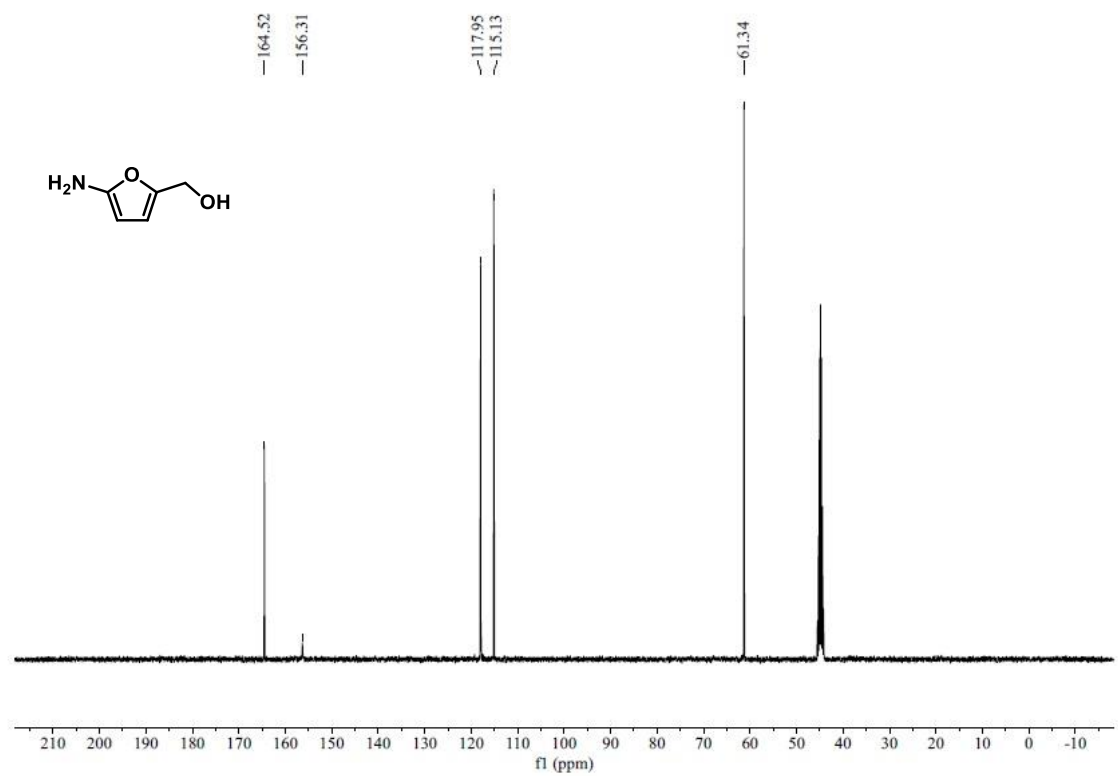
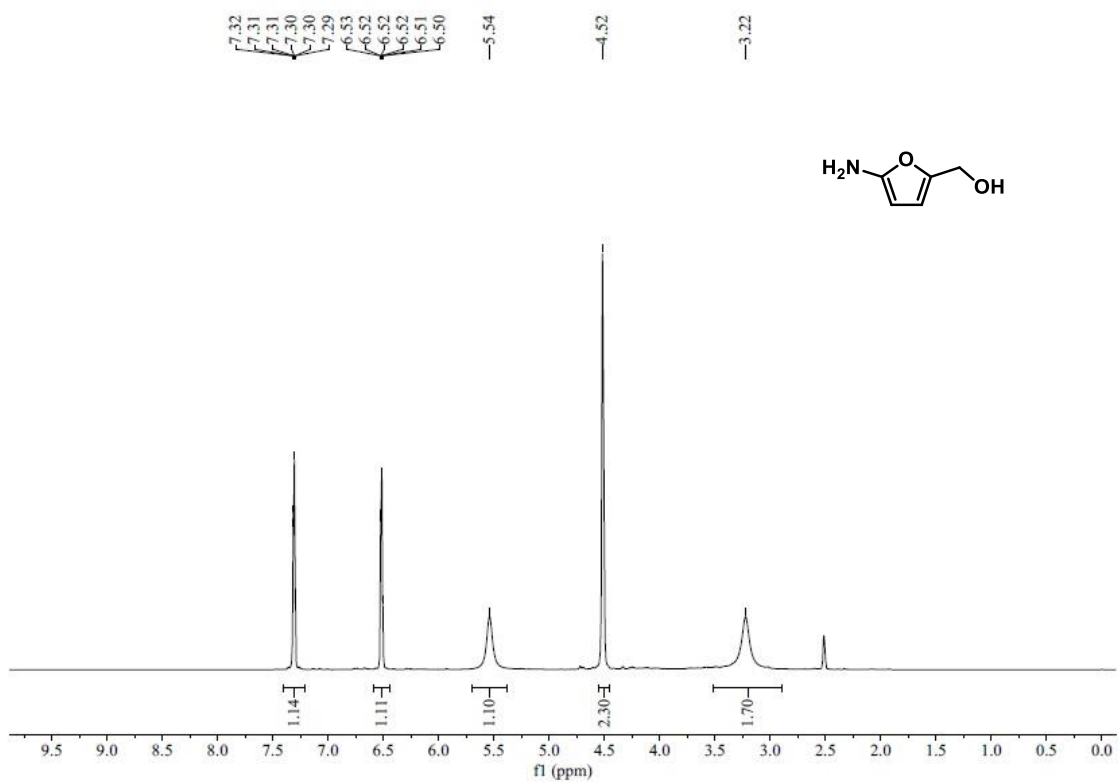




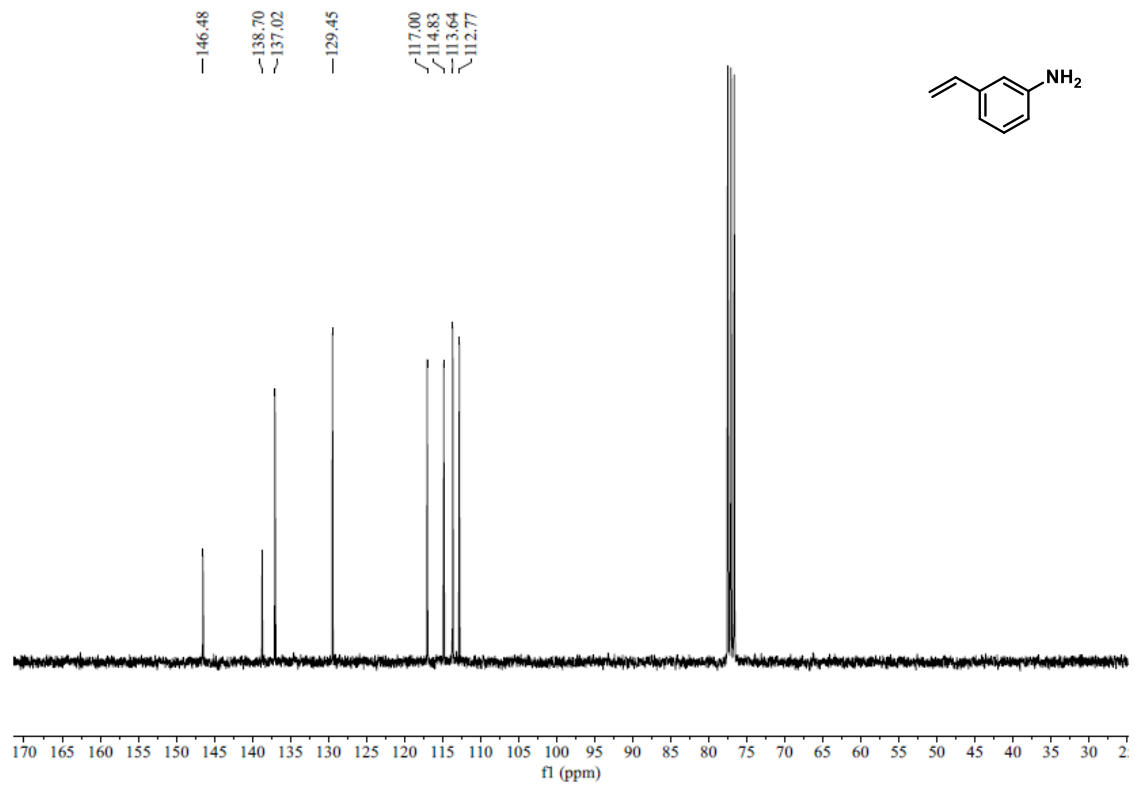
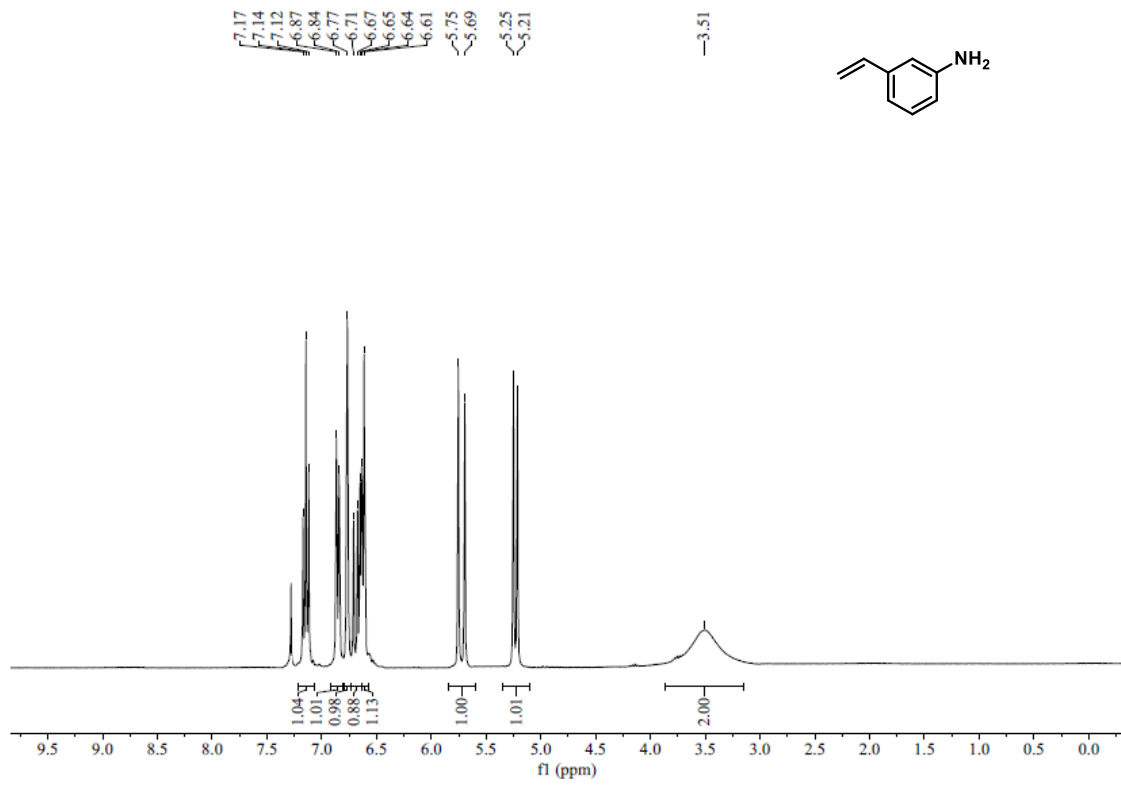


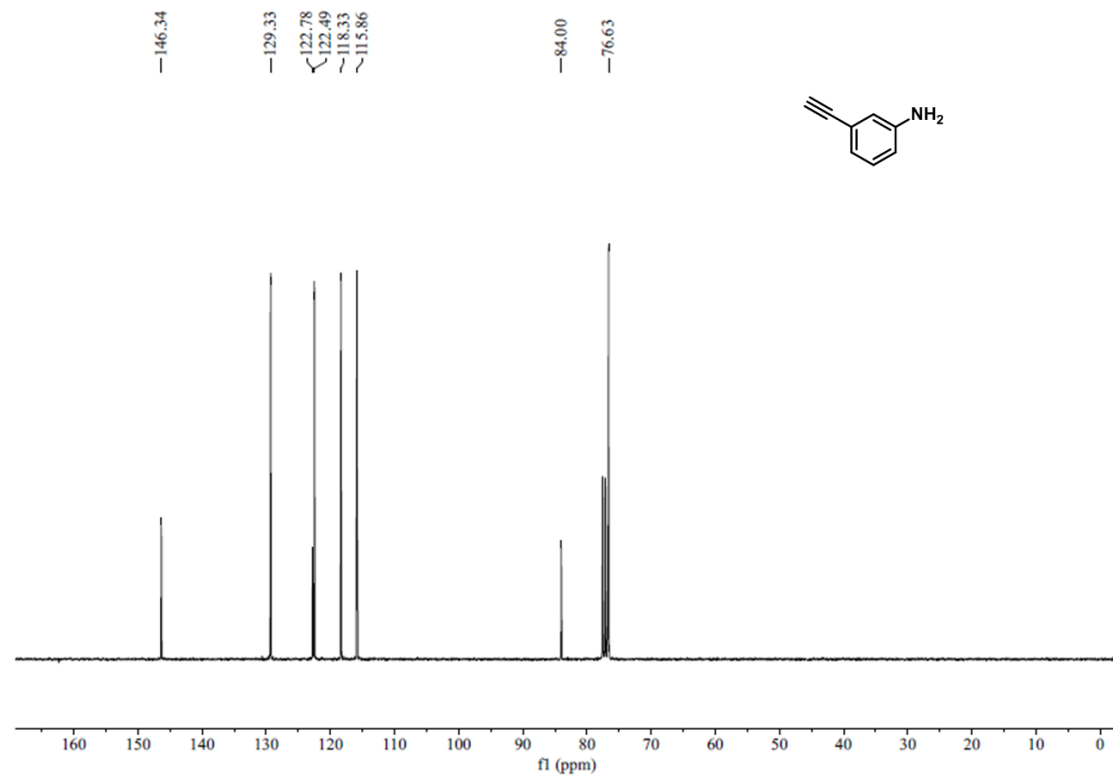
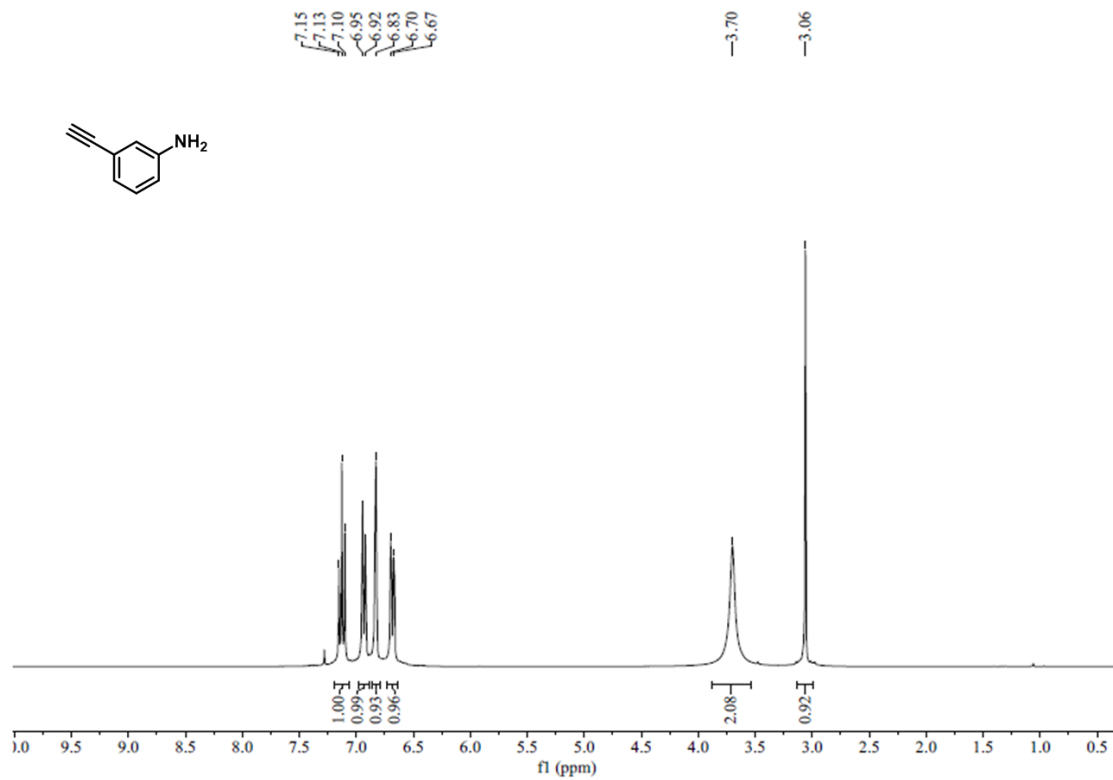


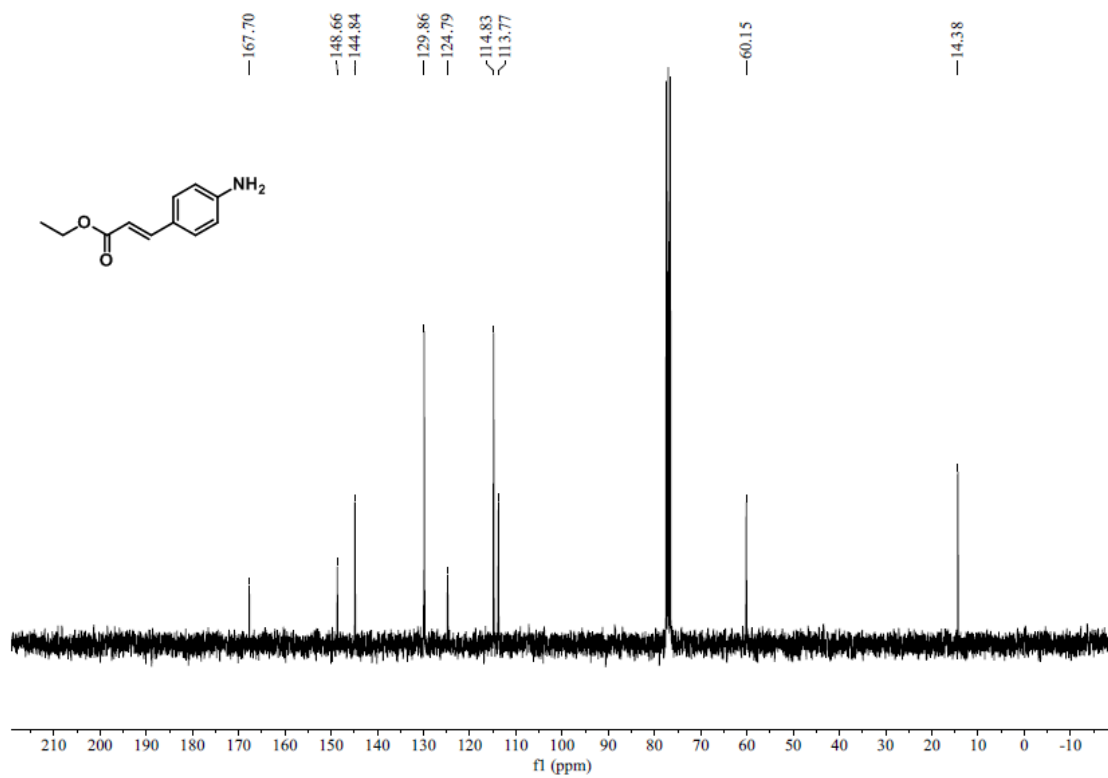
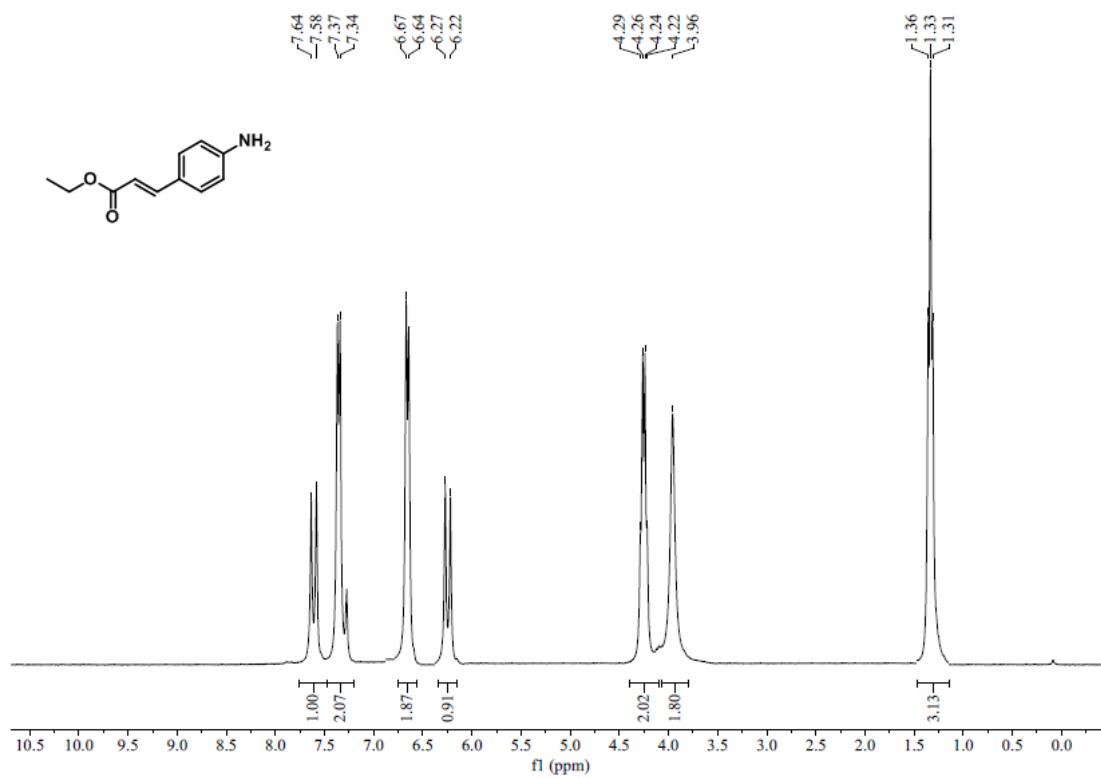


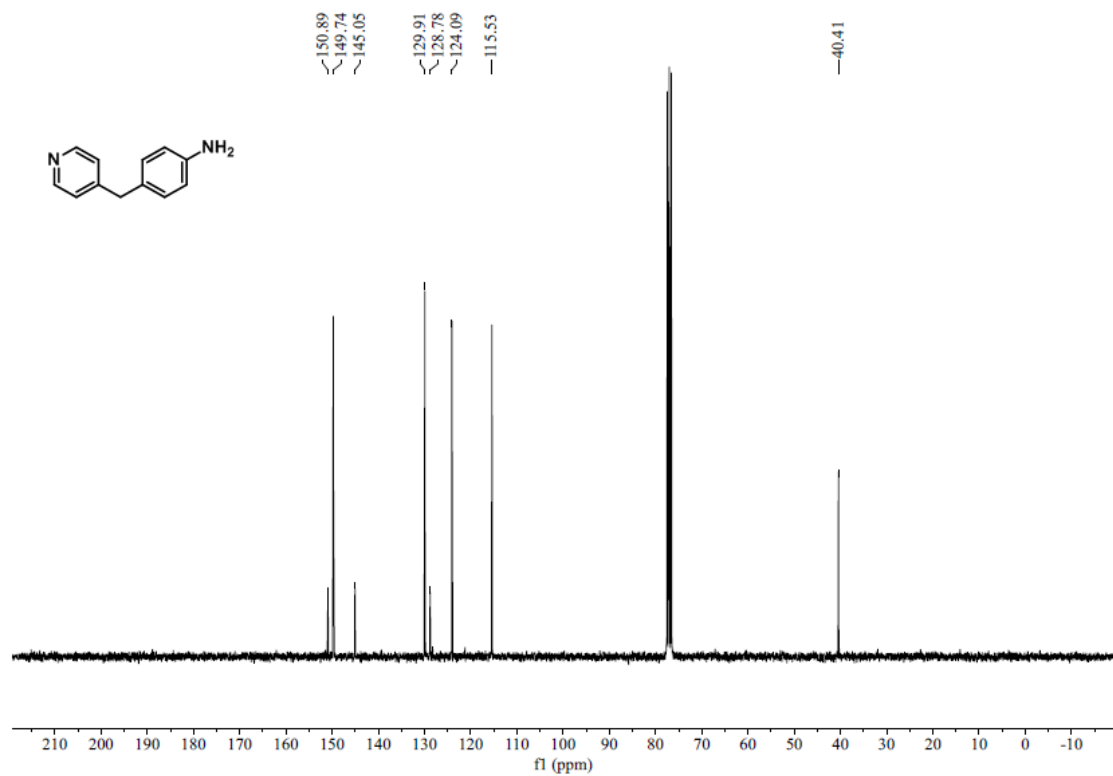
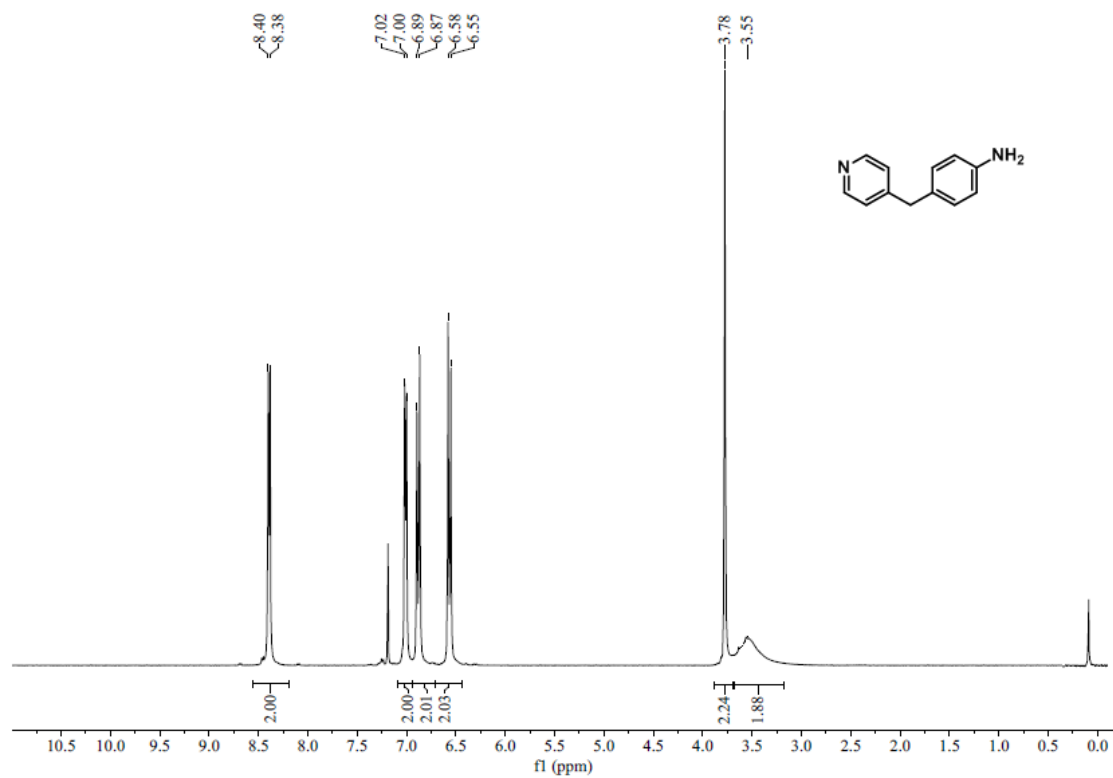


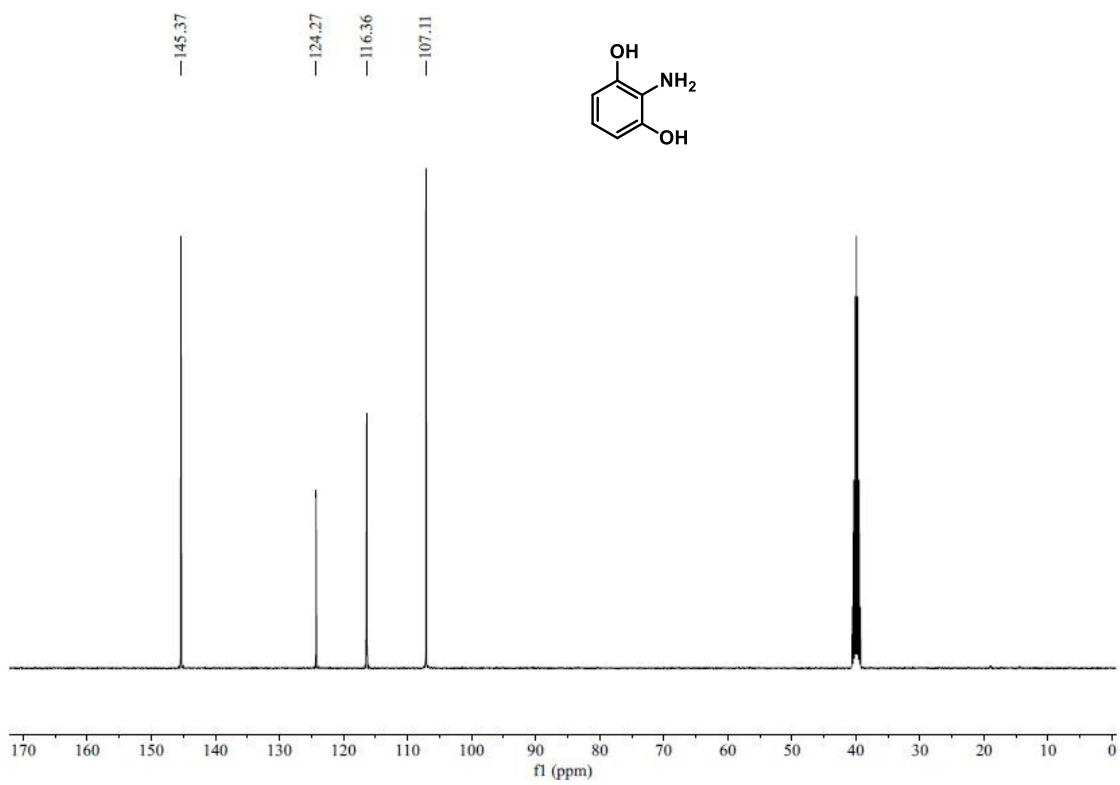
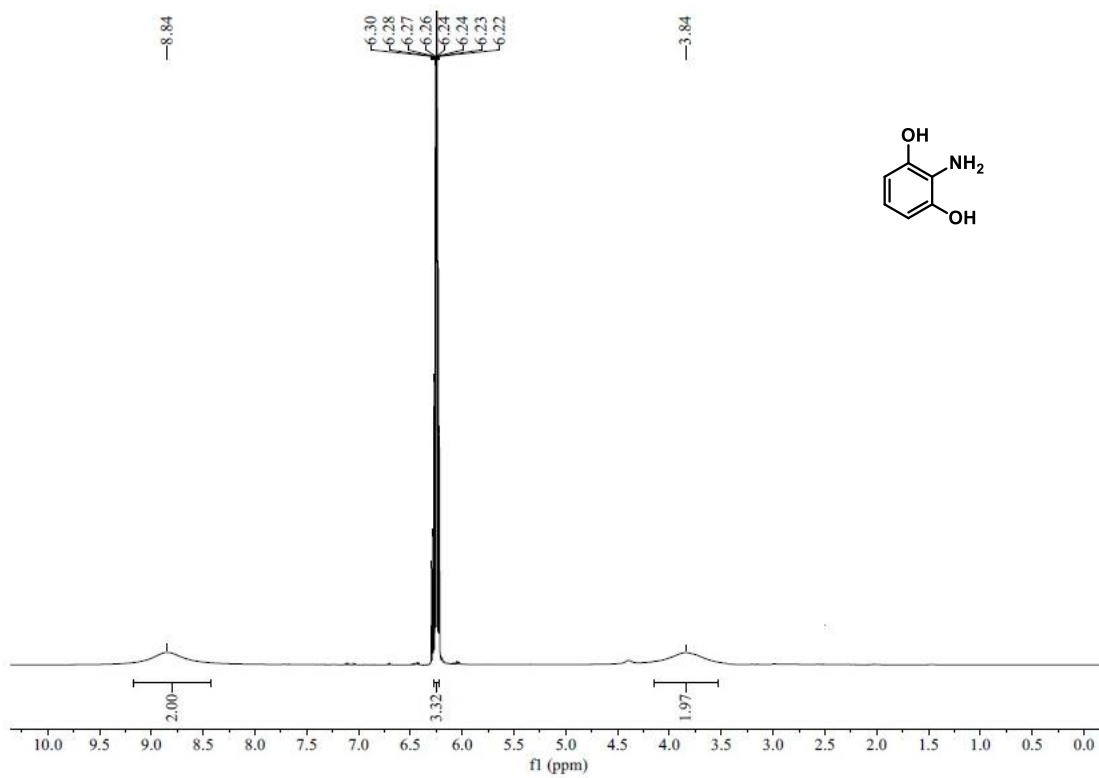


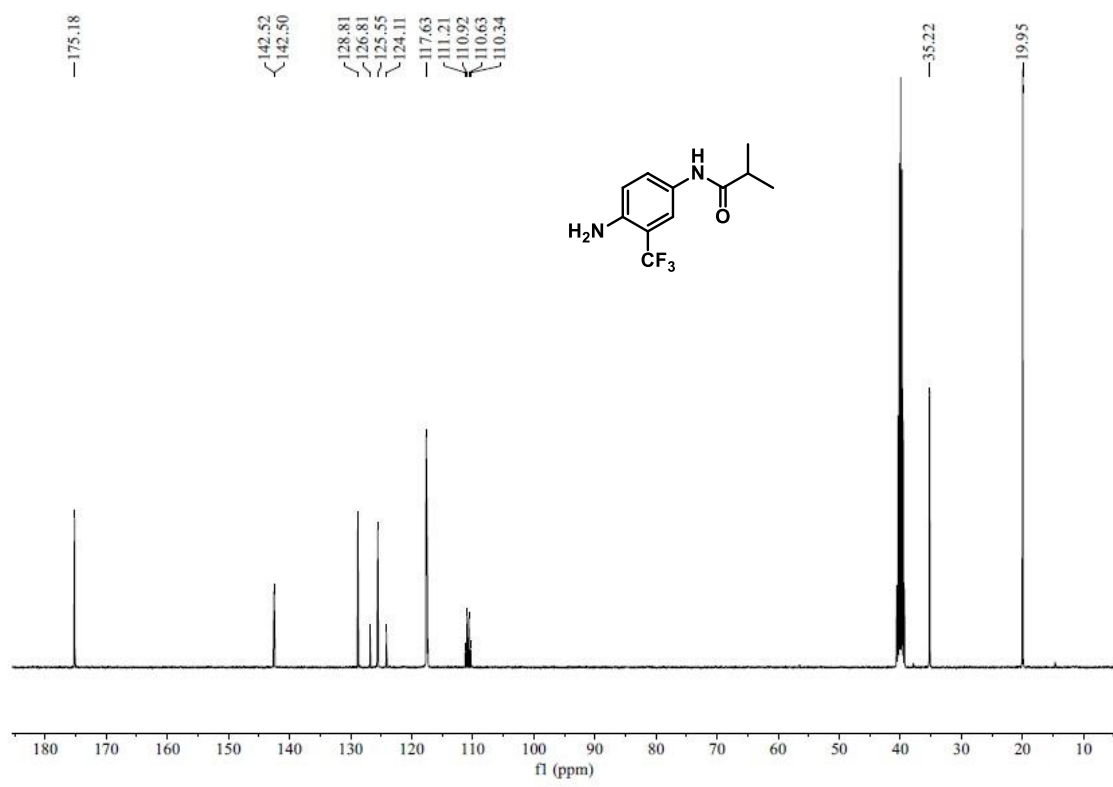
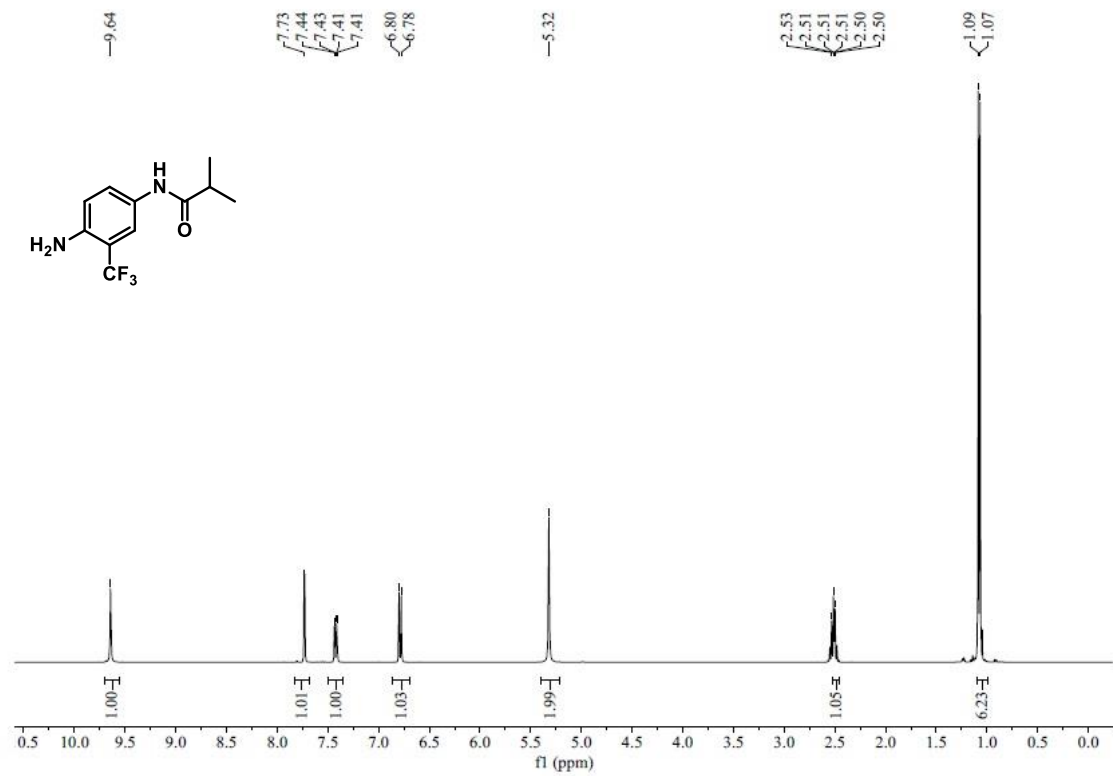


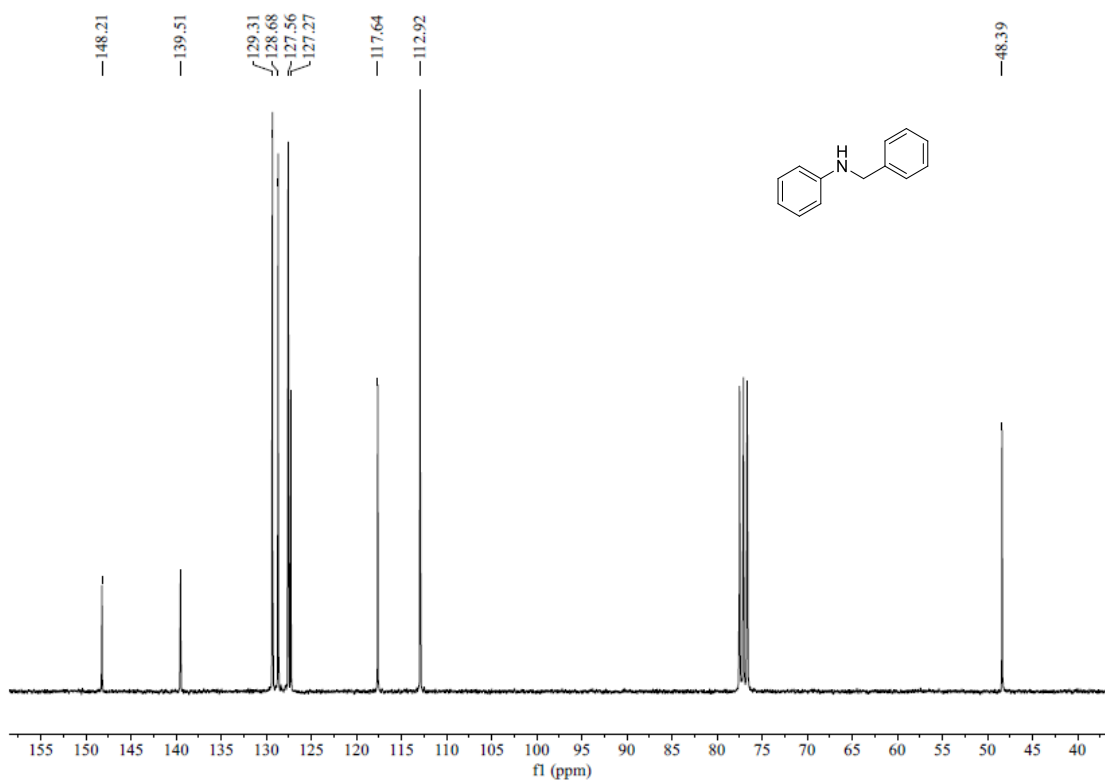
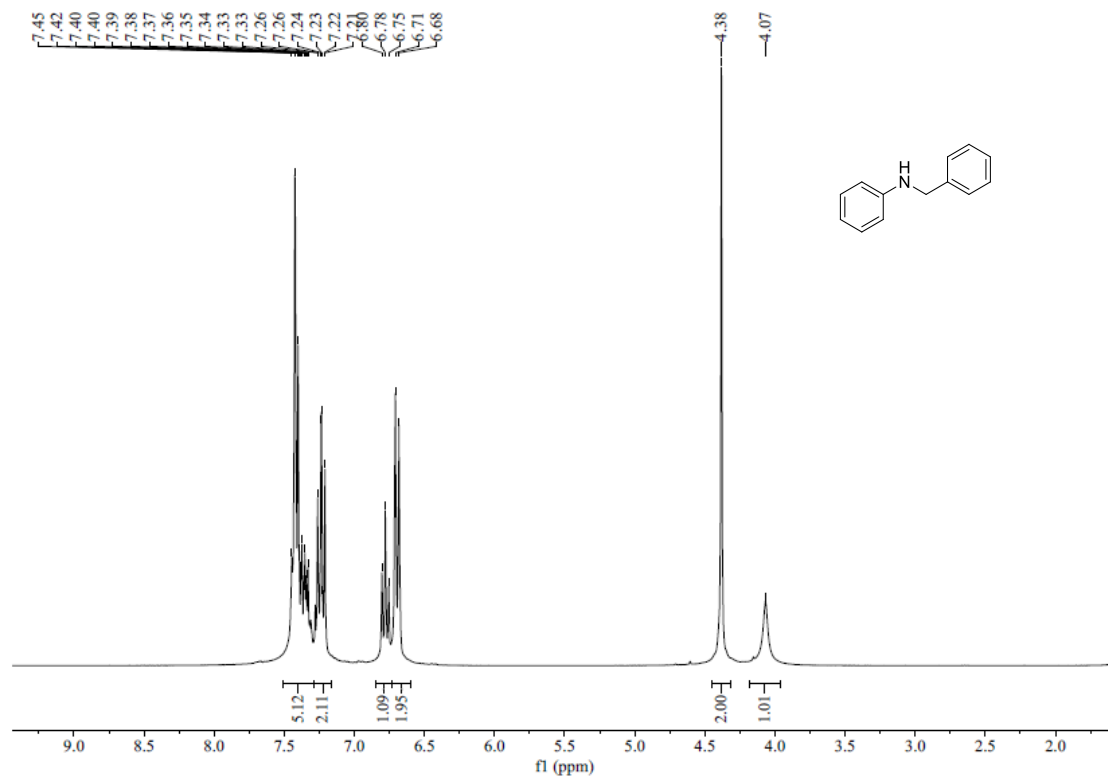


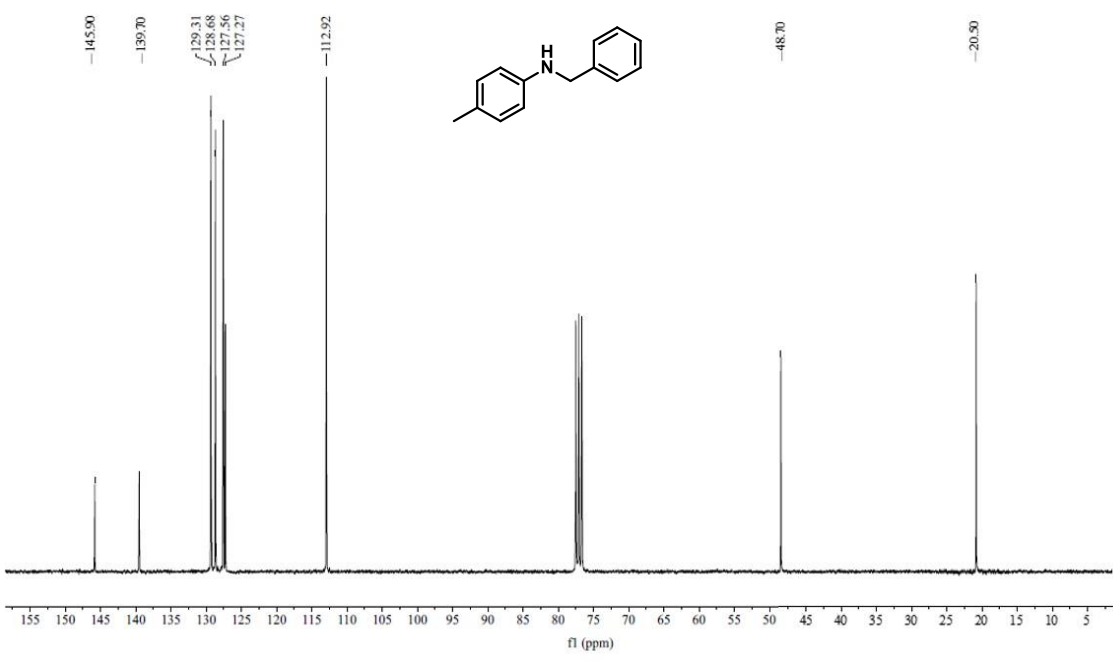
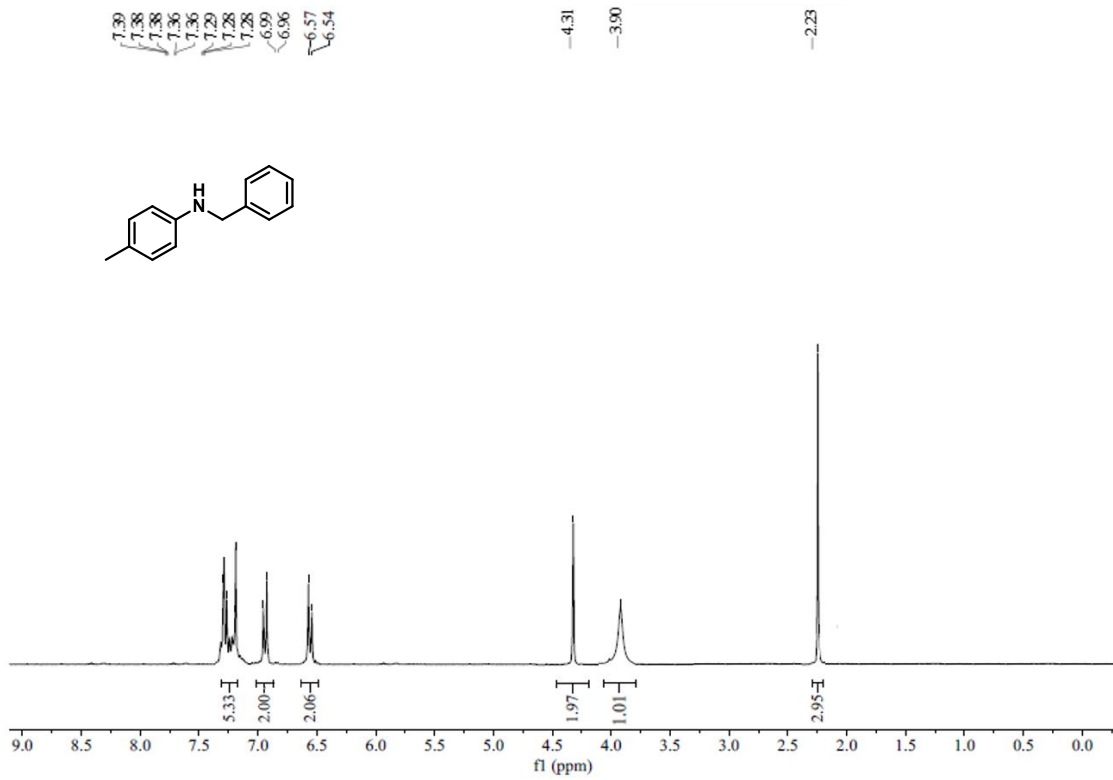




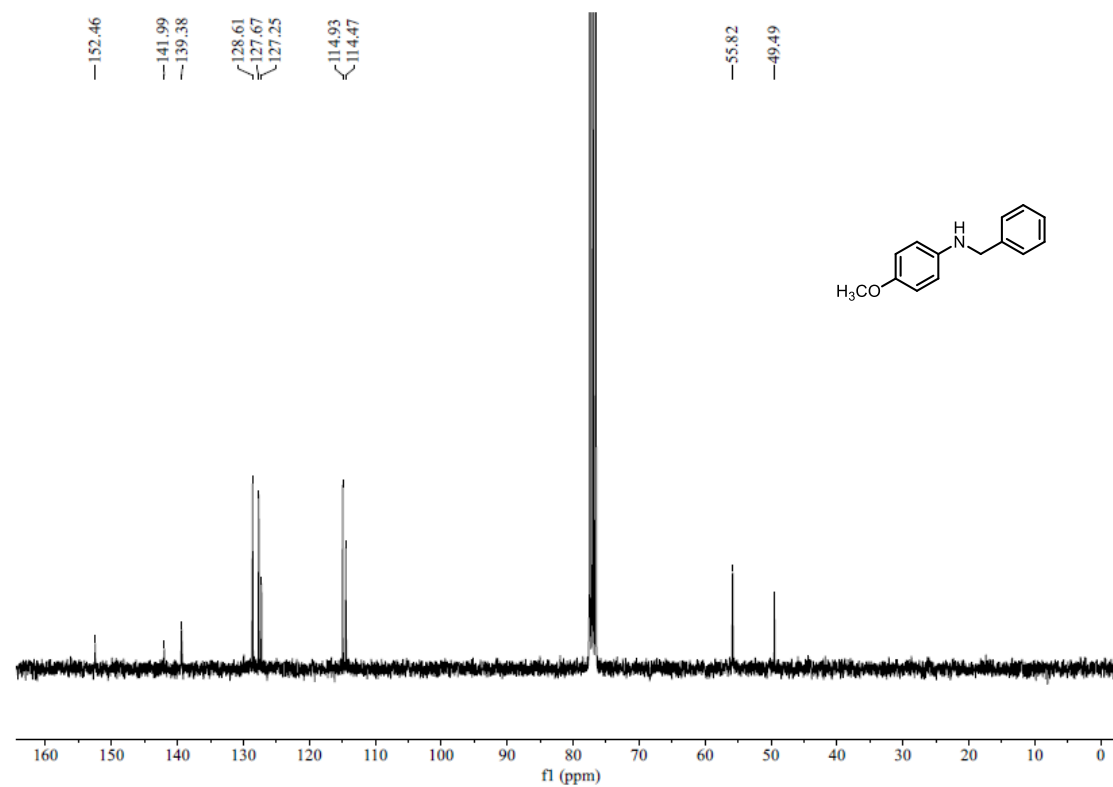
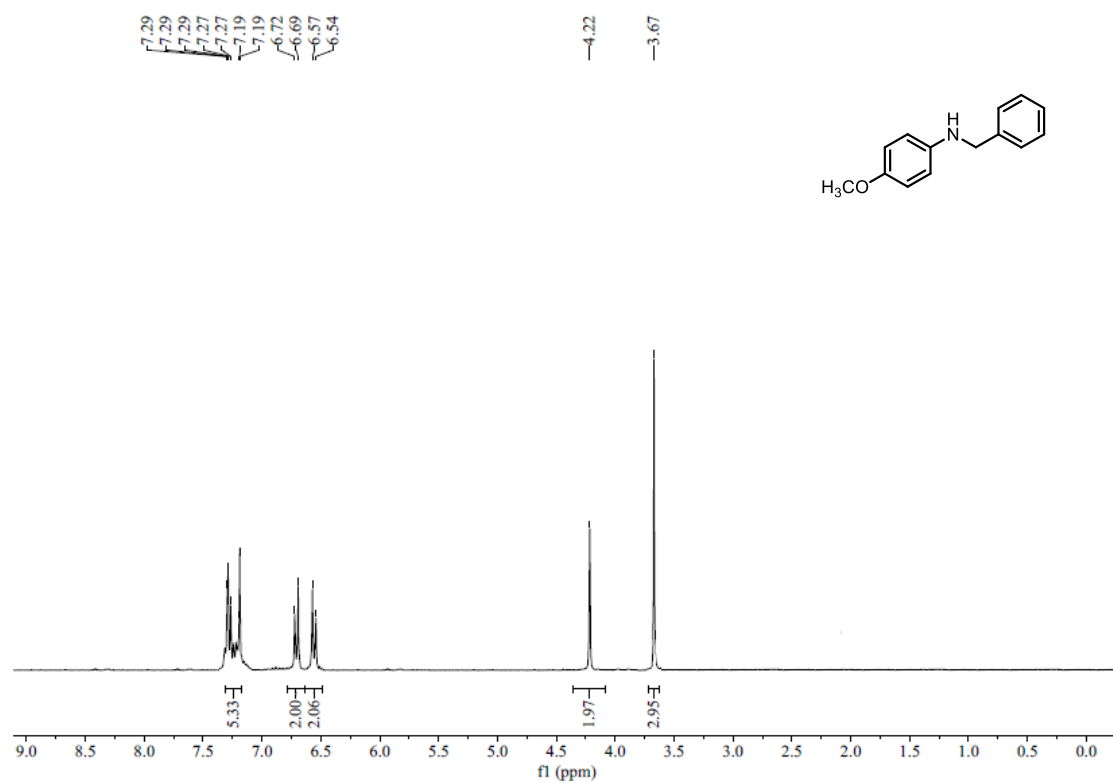


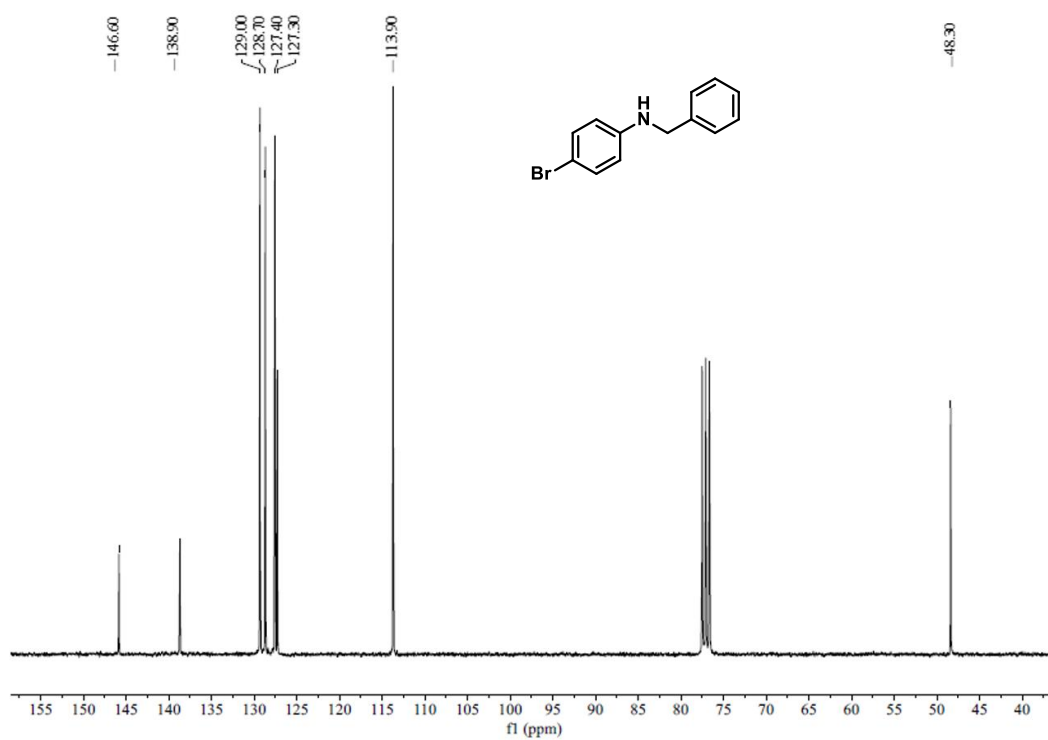
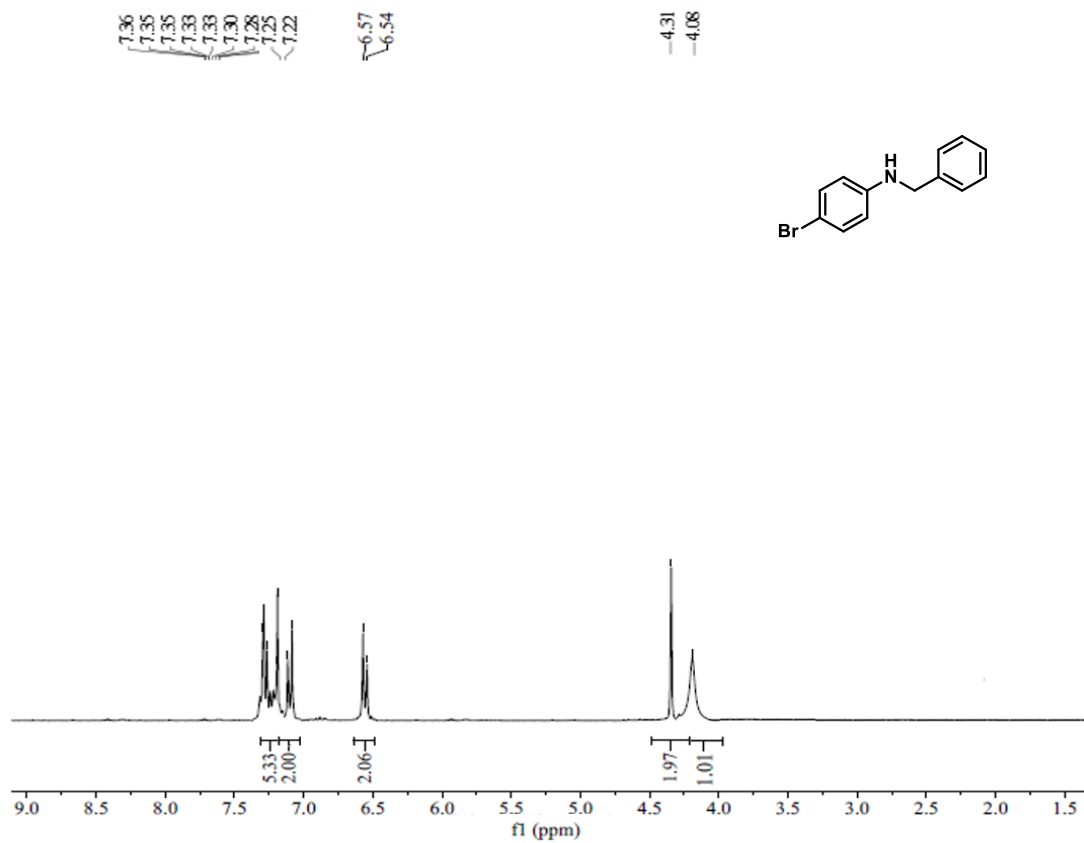


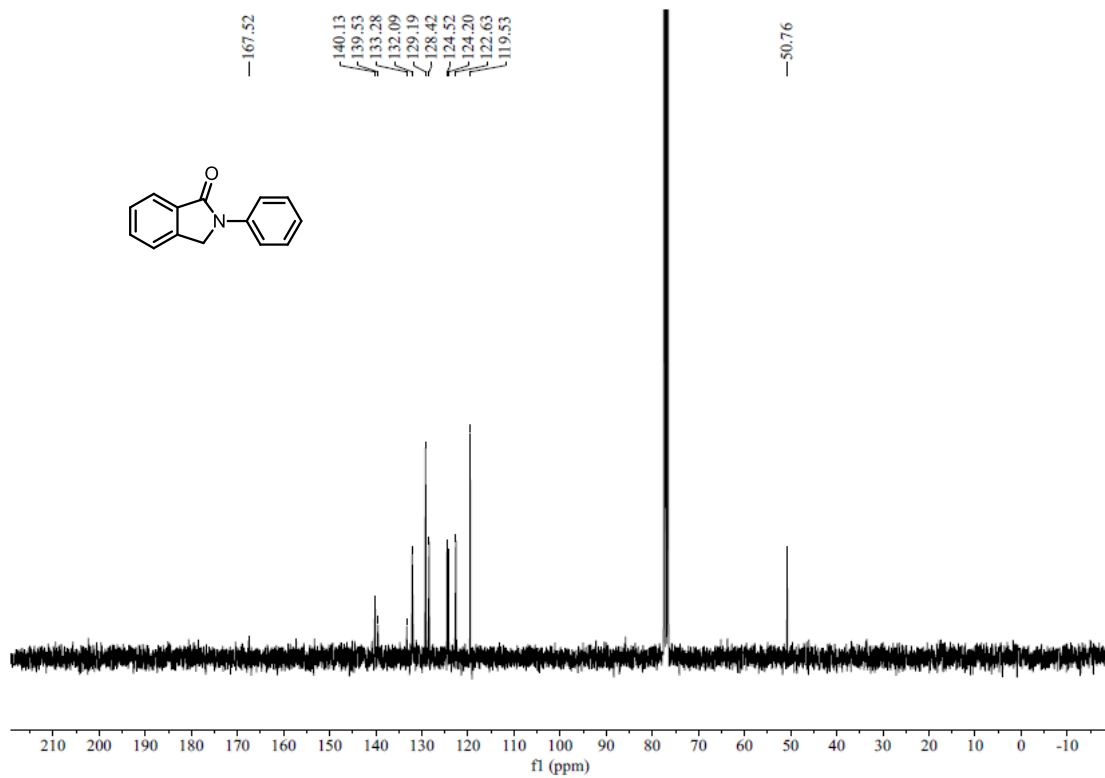
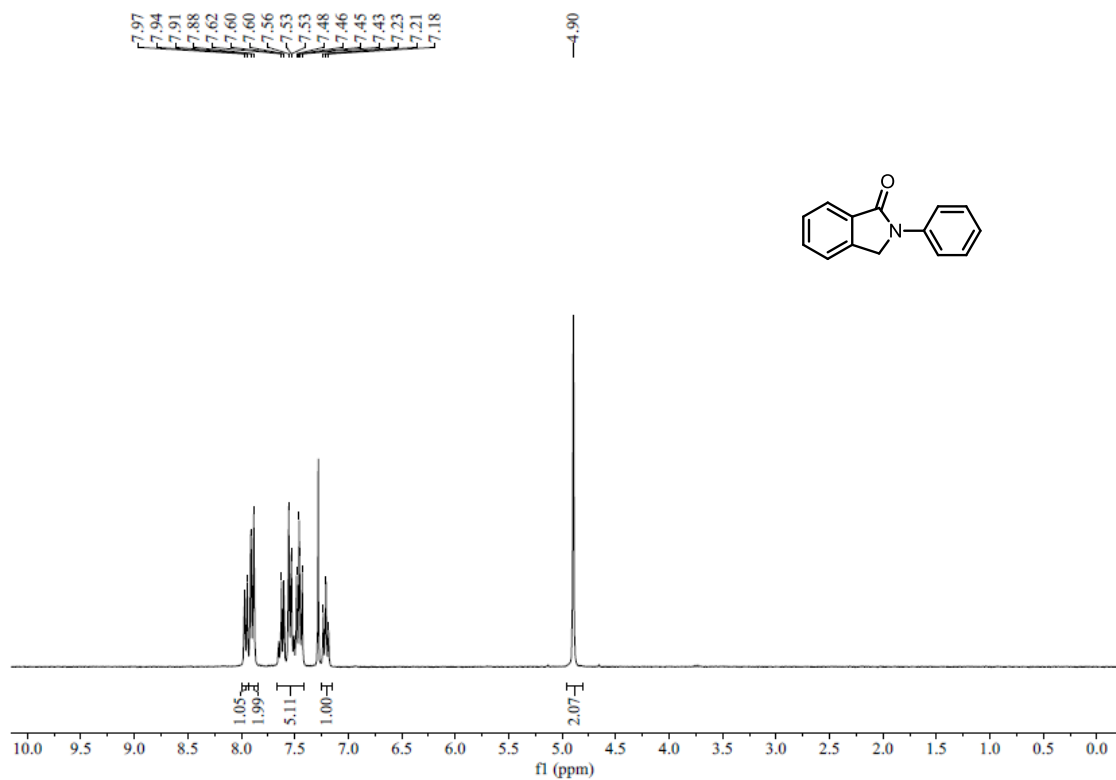


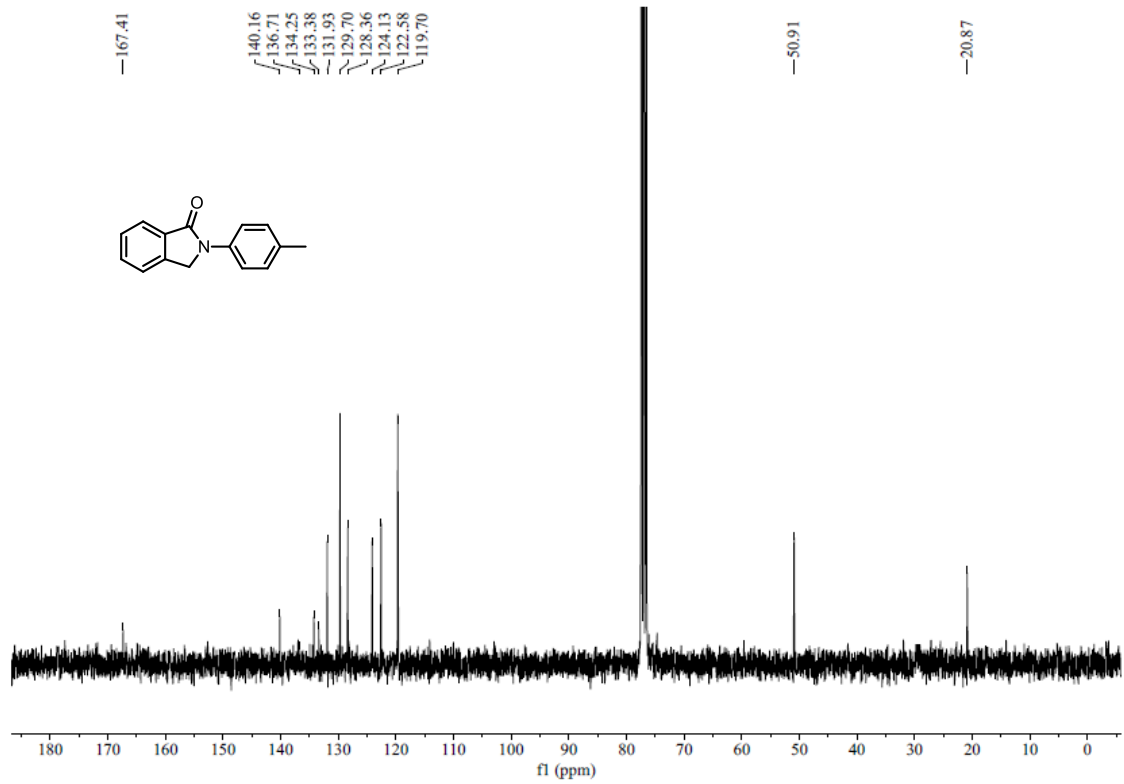
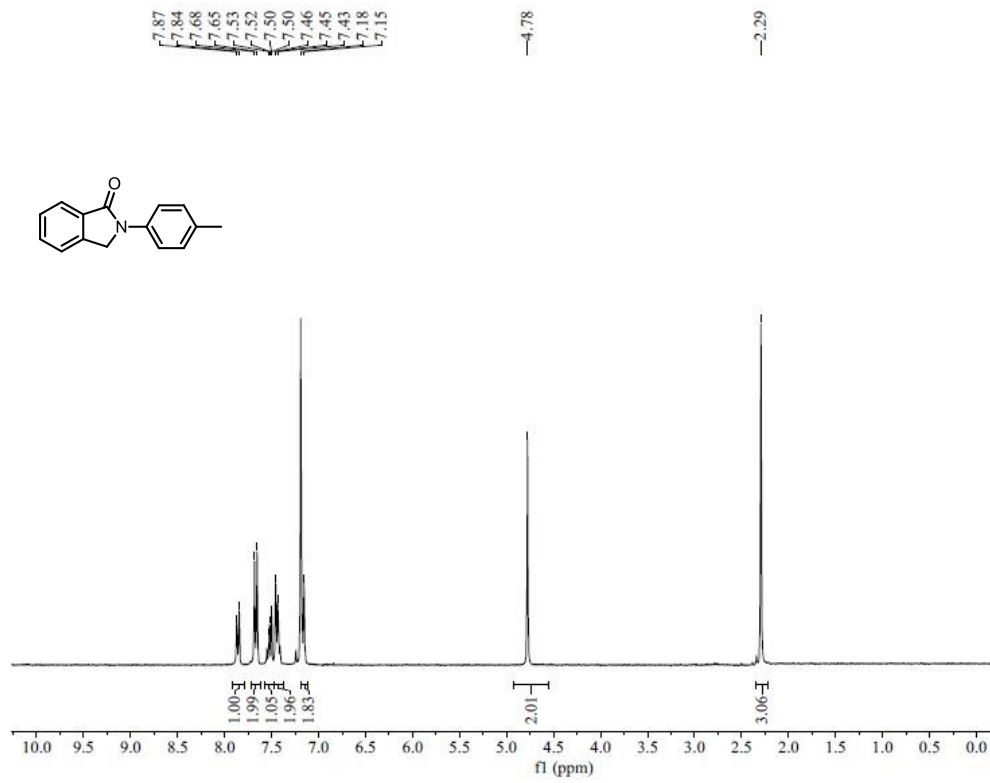


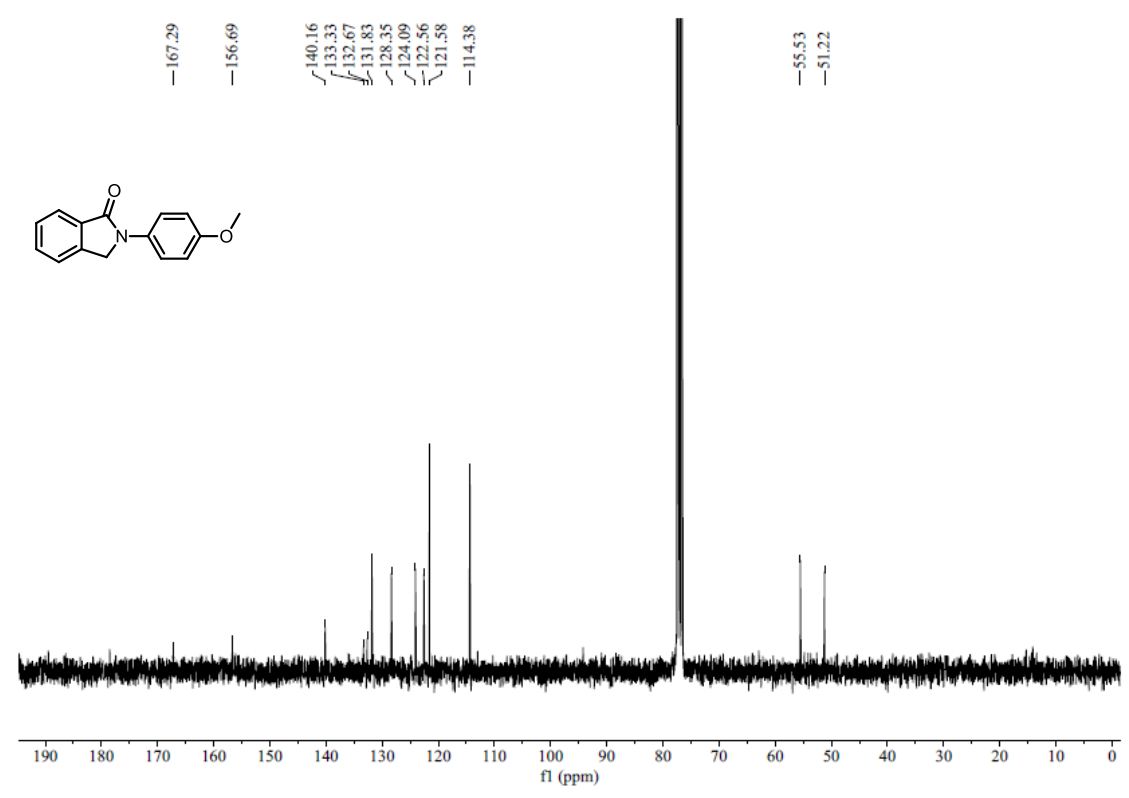
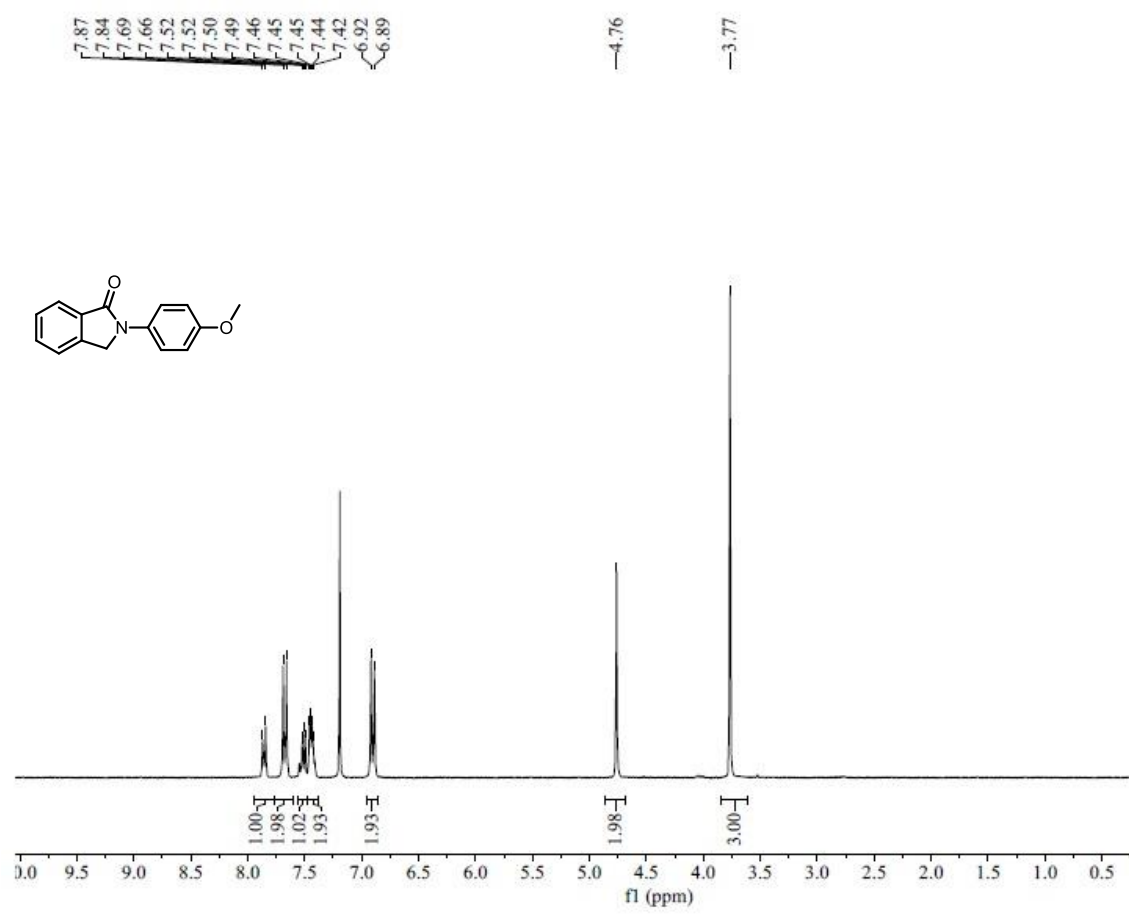


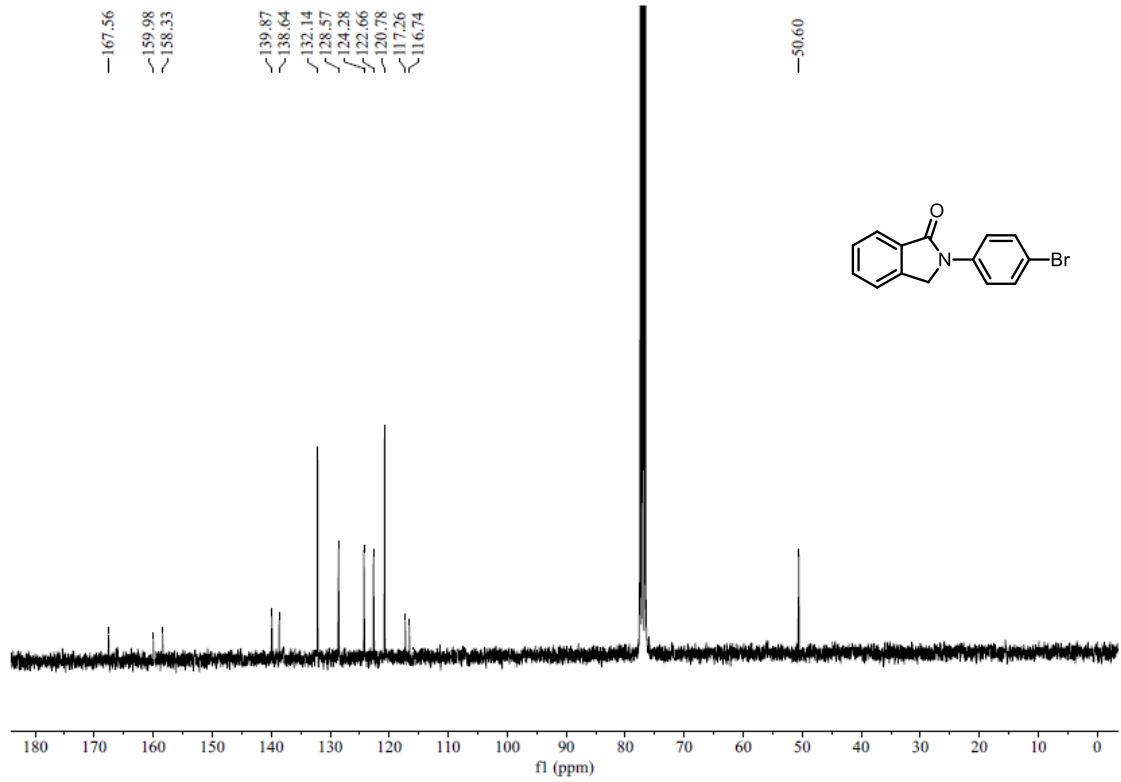
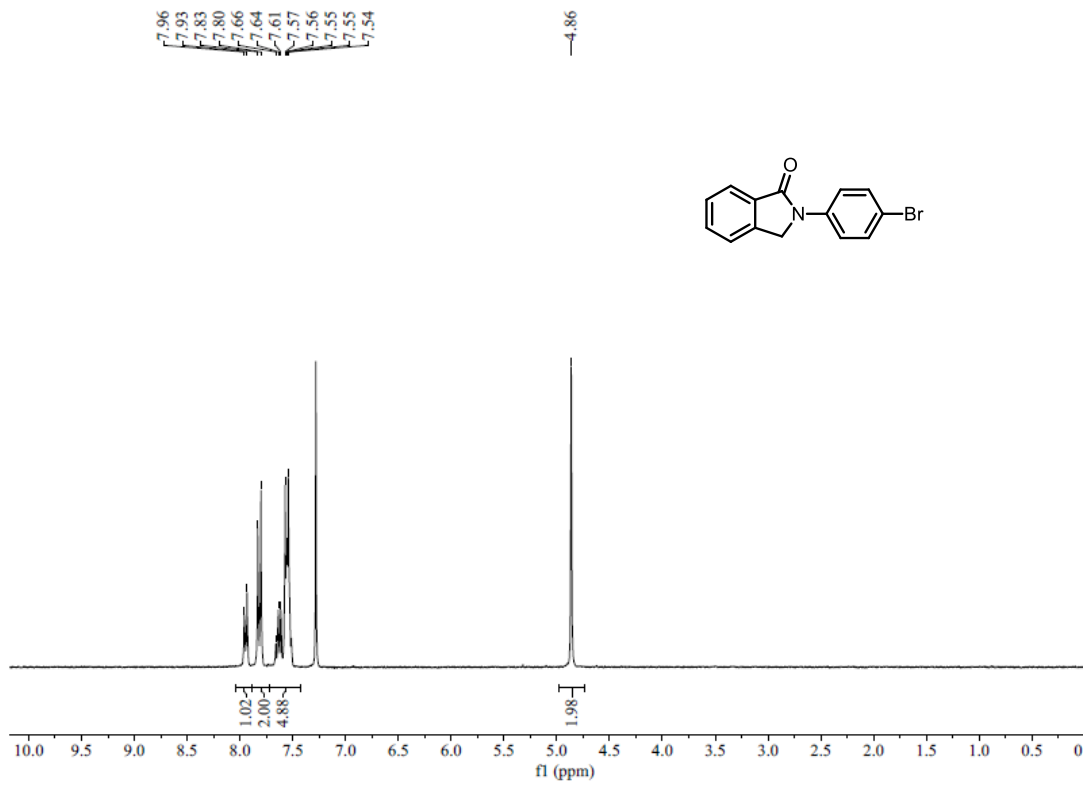












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