

SUPPORTING INFORMATION

Polymethylhydrosiloxane Derived Palladium Nanoparticles for Chemo- and Regioselective Hydrogenation of Aliphatic and Aromatic Nitro Compounds in Water

Dandu Damodara,^a Racha Arundhathi,^a T. Venkata Ramesh Babu,^a Margaret K. Legan,^b Hephzibah Kumpaty^b and Pravin R Likhar^{a*}

^a*Inorganic and Physical Chemistry Division, CSIR- Indian Institute of Chemical Technology, Hyderabad-500007, India.*

^b*Chemistry Department, Wisconsin University, Whitewater- WI-53190-1790 USA.*

*Corresponding author. Tel.: +91-40-27193510; Fax: +91-40-27160921

E-mail address: plikhar@iict.res.in

CONTENTS

1. General Information	S-2
2. Preparation of the catalysts	S-2-S-3
3. Catalyst Characterization	S-3-S-5
4. Typical Experimental Procedure	S-6
5. Stability and Reusability of the catalyst	S-6-S-7
6. Spectroscopic data of representative compounds	S-7-S-13
7. ¹ H NMR spectra of the products	S-13-S-22
8. ¹³ C NMR spectra of the products	S-23-S-32
9. References	S-32

General Information

All reagents were purchased from commercial suppliers and used without further purification. All solvents were dried and distilled by standard methods. Purification of products was carried out by column chromatography using commercial column chromatography grade silica gel (60-120 mesh) purchased from s. d. fine-chemicals Ltd. using mixture of ethyl acetate and hexane as eluting agent and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in CDCl_3 and DMSO. Chemical shifts (δ) were reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz. ^1H NMR and ^{13}C NMR of the compounds were proved either by comparison to the known compounds or the synthesized compounds according to the literature.¹

X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using $\text{Cu K}\alpha$ radiation. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg $\text{K}\alpha$ anode. The pressure in the spectrometer was about 10^{-9} Torr. The particle size and external morphology of the samples were observed on a transmission electron microscope (TEM).

Procedure for the synthesis of palladium catalyst:

The catalysts Pd-HAP, Pd-FAP, Pd/MgO, Pd/ Al_2O_3 , Pd/ TiO_2 , Pd/ SiO_2 and Pd/HT were prepared using literature procedures.² Pd/C was procured commercially and was used as received. The preparation procedure of NAP-MgO-Pd(0)PS catalyst given below.

Procedure for the synthesis of NAP-MgO-Pd(0)PS catalyst:

NAP-Mg-PdCl₄: The brown colored NAP-Mg-PdCl₄ was obtained³ by treating NAP-MgO (BET 600 m²g⁻¹, 1 g) with Na₂PdCl₄ (294 mg, 1 mmol) and dissolved in 100 mL decarbonated water with stirring for 12 h, maintaining a nitrogen atmosphere. The obtained catalyst was filtered, washed with deionized water, acetone and dried at 65 °C in oven.

NAP-Mg-Pd(0)PS: NAP-Mg-PdCl₄ (1 g) catalyst was reduced with PMHS (0.75 mL, 12 mmol) in 30 mL ethylene glycol for 2 h in a round bottom flask under nitrogen atmosphere. After this finally we got the desired black-colored, air-stable NAP-Mg-Pd(0)PS (Pd 0.99 mmolg⁻¹).

As obtained NAP-Mg-Pd(0)PS catalyst was characterized before and after 5th cycle of the hydrogenation reaction. The catalyst was reused five times without significant loss of catalytic activity. The SEM and TEM analysis showed that the particle size and morphology should be almost identical before and after the reaction.

Characterization of synthesized NAP-MgO-Pd(0)PS catalyst:

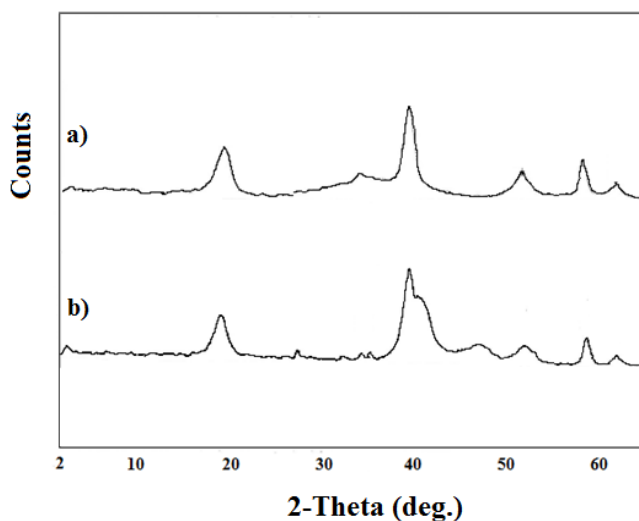
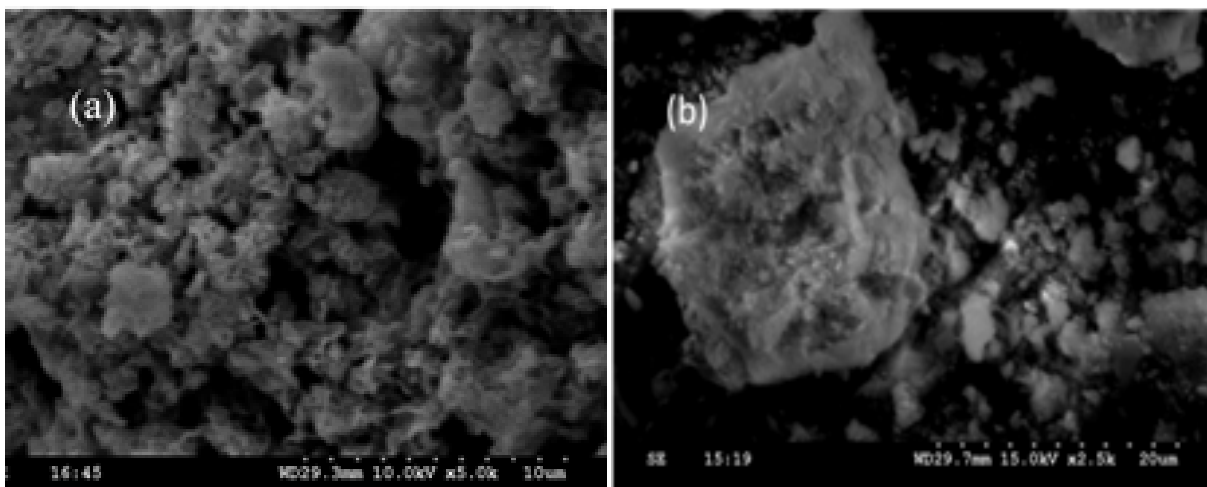


Figure 1. XRD patterns of a) NAP-Mg-PdCl₄; b) NAP-Mg-Pd(0)PS catalyst

The X-ray powder diffraction (XRD) patterns of NAP-Mg-PdCl₄ and fresh NAP-Mg-Pd(0)PS catalyst are shown in Figure . The XRD pattern of the NAP-Mg-Pd(0)PS displayed diffraction lines at $2\theta = 40.0, 46.5^\circ$ indicates the formation of metallic Pd phase.

SEM patterns of [NAP-MgO-Pd(0)PS] catalyst:

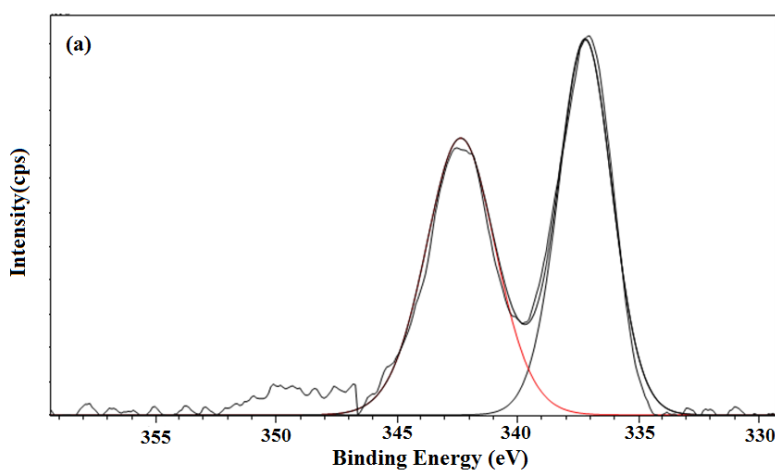


(a) Fresh

(b) Used

Fig. 1 (a) SEM images of freshly prepared NAP-Mg-Pd(0)PS, (b) Recovered NAP-Mg-Pd(0)PS catalyst after 5th cycle.

XPS analysis of synthesized NAP-MgO-Pd(0)PS catalyst:



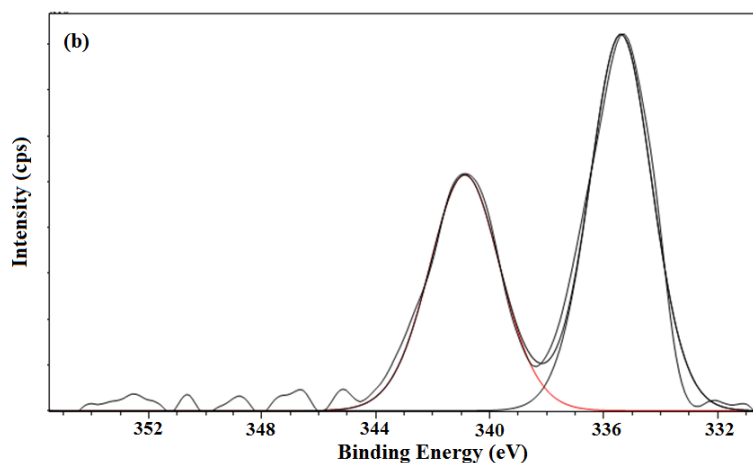
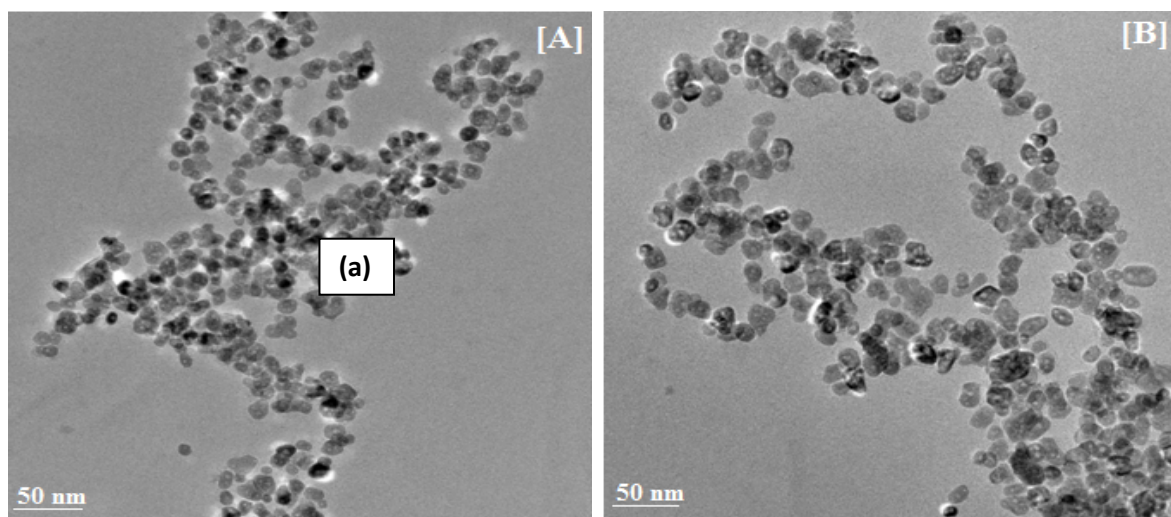


Figure 2. XPS analysis of (a) NAP-Mg-PdCl₄ and (b) NAP-Mg-Pd(0)PS catalyst.

The X-ray photoelectron spectroscopic (XPS) investigation of the prepared NAP-Mg-Pd(0)PS shows a Pd 3d_{5/2} line at 335.4 eV which is an evidence that the Pd metal is in zero oxidation state and stabilized to large extent.

TEM analysis of NAP-Mg-Pd(0)PS catalyst:



(a) Fresh

(b) Used

Fig 2. (A) Transmission electron micrographs of NAP-Mg-Pd(0)PS catalyst freshly prepared and (B) recovered catalyst after 5th cycle.

General procedure for the reduction of nitroarenes to amines:

A 50 mL round bottom flask was charged with nitrocompound (1 mmol), triethylamine (0.72 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), and 3 mL water. PMHS (4 mmol) was slowly added (drop-wise) to avoid violent evolution of gas under nitrogen atmosphere. The reaction was stirred for required period of time at 80 °C. After completion of the reaction as judged by TLC, the reaction flask was opened to the air, diluted with 5–10 mL of diethyl ether, and stirred for 5 minutes. The layers were separated and the aqueous layer was back extracted with diethyl ether. The resulting products were purified by flash column chromatography and characterized by using ¹H NMR and ¹³C NMR (see Supporting Information) spectroscopic methods.

Stability and efficiency of the catalyst, in large scale hydrogenation 2-chloro nitrobenzene.^a

Substrate	Product	Yield(%) ^b	Selectivity(%)
2-chloro nitrobenzene	2-chloro aniline	91	97

^aReaction conditions: 2-chloro nitrobenzene (10 mmol), NAP-Mg-Pd(0)PS (0.20 g, Pd: 1.98 mol%), Et₃N (7.5 mmol), PMHS (40 mmol), H₂O (30 mL), 80 °C for 2h.

Reusability of the catalyst:

Table 1. Recyclability of the catalyst NAP-Mg-Pd(0)PS for the reduction of alicyclic nitro compound.^a

No. of cycles	Run 1	Run 2	Run 3	Run 4	Run 5
Nitrocyclohexane	92	92	91	90	90

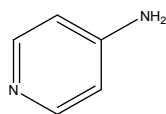
^aReaction conditions: nitrocyclohexane (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), Et₃N (0.75 mmol), PMHS (4 mmol), H₂O (3 mL).

Table 2. Recyclability of the catalyst NAP-Mg-Pd(0)PS for the reduction of aromatic nitro compound.^a

No. of cycles	Run 1	Run 2	Run 3	Run 4	Run 5
4-Nitrobenzaldehyde	91	90	90	89	89

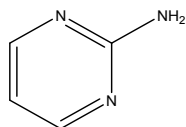
^aReaction conditions: 4-nitrobenzaldehyde (1.0 mmol), NAP-Mg-Pd(0)PS (0.020 g, Pd: 1.98 mol%), Et₃N (0.75 mmol), PMHS (4 mmol), H₂O (3 mL).

Spectroscopic characterization of the products



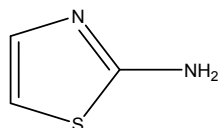
4-Aminopyridine: (Table 2, entry 1)

¹H NMR (300 MHz, CDCl₃, ppm): δ 8.21 (d, *J* = 6.1 Hz, 2H), 6.52 (d, *J* = 6.25 Hz, 2H), 4.18 (bs, 2H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 153.14, 149.10, 108.95.



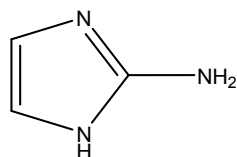
2-Aminopyrimidine: (Table 2, entry 3)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.30 (d, $J = 7.43$ Hz, 2H), 6.62 (t, $J = 4.8$ Hz, 1H) 5.40 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 163.18, 158.27, 111.16.



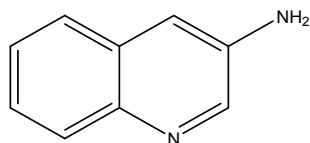
Thiazole-2-amine: (Table 2, entry 7)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.06-7.07 (d, $J = 3.77$ Hz, 1H), 6.51-6.52 (d, $J = 3.58$ Hz, 1H), 5.35 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 168.4, 138.5, 108.2.



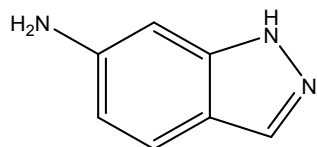
2-Aminoimidazole: (Table 2, entry 9)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 10.35 (s, 1H), 7.12 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 135.17, 121.81.



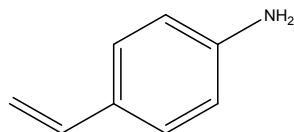
3-Amino quinoline: (Table 2, entry 13)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.50 (s, 1H), 7.96 (d, $J = 9.61$, 1H), 7.58 (d, $J = 9.30$ Hz, 1H), 7.43 (t, $J = 7.17$, 6.86 Hz, 2H), 7.22 (s, 1H), 3.95 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 142.34, 140.96, 130.52, 129.01, 128.61, 126.67, 126.02, 125.98, 113.97.



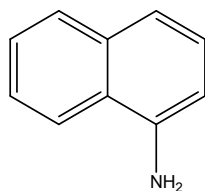
6-Amino indazole: (Table 2, entry 14)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 10.34 (bs, 1H), 8.10 (s, 1H), 7.78 (d, $J = 8.24$ Hz, 1H), 7.51 (d, $J = 9.30$ Hz, 1H), 7.18 (s, 1H), 3.98 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 142.67, 140.04, 134.99, 126.76, 123.22, 120.94, 109.56.



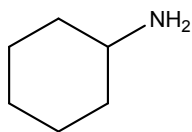
4-Vinylaniline: (Table 3, entry 1)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.18 (d, $J = 6.56$ Hz, 2H), 6.62-6.38 (m, 3H), 5.51 (d, $J = 18.76$ Hz, 1H), 5.01 (d, $J = 13.27$ Hz, 1H), 3.59 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 146.15, 136.69, 127.34, 115.04, 109.96.



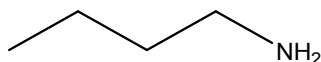
Naphthalene 1-amine: (Table 3, entry 5)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.86-7.72 (m, 2H), 7.48-7.44 (m, 2H), 7.35-7.26 (m, 3H), 6.81 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 141.98, 128.49, 126.30, 125.64, 124.66, 121.99, 120.61, 119.08, 112.62, 109.67.



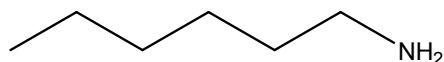
Cyclohexylamine: (Table 3, entry 8)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 2.67-2.58 (m, 1H), 2.01-1.56(m, 6H), 1.32-0.98 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 49.78, 36.01, 25.00, 24.46.



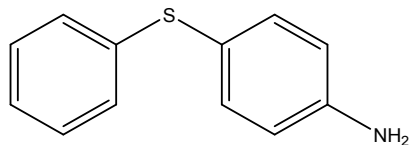
n-Butyl amine: (Table 3, entry 11)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 2.57-2.62 (m, 2H), 1.42-1.50 (m, 2H), 1.28-1.40 (m, 2H), 0.89-0.95 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 49.6, 32.0, 20.3, 13.7.



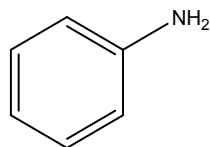
n-Hexyl amine: (Table 3, entry 12)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 2.65-2.70 (t, J = 6.79 Hz, 2H), 1.86 (bs, 2H), 1.39-1.48 (m, 2H), 1.29 (s, 4H), 0.86-0.91 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 42.0, 33.4, 31.5, 26.4, 22.5, 13.9.



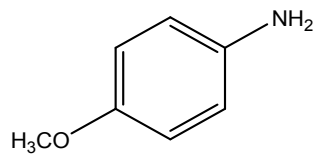
4-(phenylthio)aniline: (Table 3, entry 14)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.31-7.20 (m, 2H), 7.17-7.11 (m, 2H), 7.08-7.03 (m, 3H), 6.61 (d, $J = 8.12$ Hz, 2H), 3.67 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 145.9, 140.02, 135.98, 129.01, 127.64, 125.09, 120.92, 116.07.



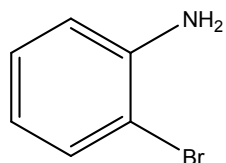
Aniline: (Table 4, entry 1)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.11-7.16 (m, 2H), 6.72-6.77 (t, $J = 7.55$ Hz, 1H), 6.63-6.66 (d, $J = 7.55$ Hz, 2H), 3.59 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 146.2, 129.0, 118.2, 114.9.



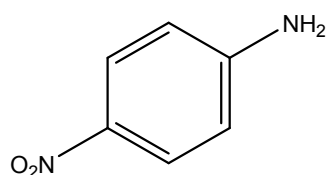
4-Methoxy aniline: (Table 4, entry 2)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.66-6.73 (m, 4H), 3.74 (s, 2H), 3.40 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 152.6, 139.9, 116.3, 114.7, 55.6.



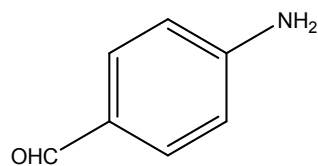
2-Bromo aniline: (Table 4, entry 3)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.37-7.39 (d, $J = 7.99$ Hz, 1H), 7.06-7.09 (t, $J = 6.99$ Hz, 1H), 6.72-6.74 (d, $J = 6.99$ Hz, 1H), 6.58-6.61 (t, $J = 6.99$ Hz, 1H), 4.04 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 143.9, 132.4, 128.2, 119.2, 115.6, 109.1.



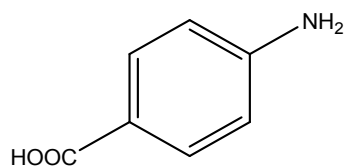
4-Nitroaniline: (Table 4, entry 7)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.03 (d, $J = 9.46$ Hz, 2H) 6.63 (d, $J = 8.67$ Hz, 2H), 5.00 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 153.76, 137.02, 125.72, 112.38.



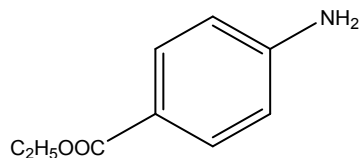
4-Amino benzaldehyde: (Table 4, entry 8)

^1H NMR (300 MHz, CDCl_3 , ppm): δ 10.3 (s, 1H), 8.0 (d, $J = 7.84$ Hz, 2H), 7.56 (d, $J = 7.34$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 170, 149, 139, 128, 124.



4-Amino Benzoic acid: (Table 4, entry 10)

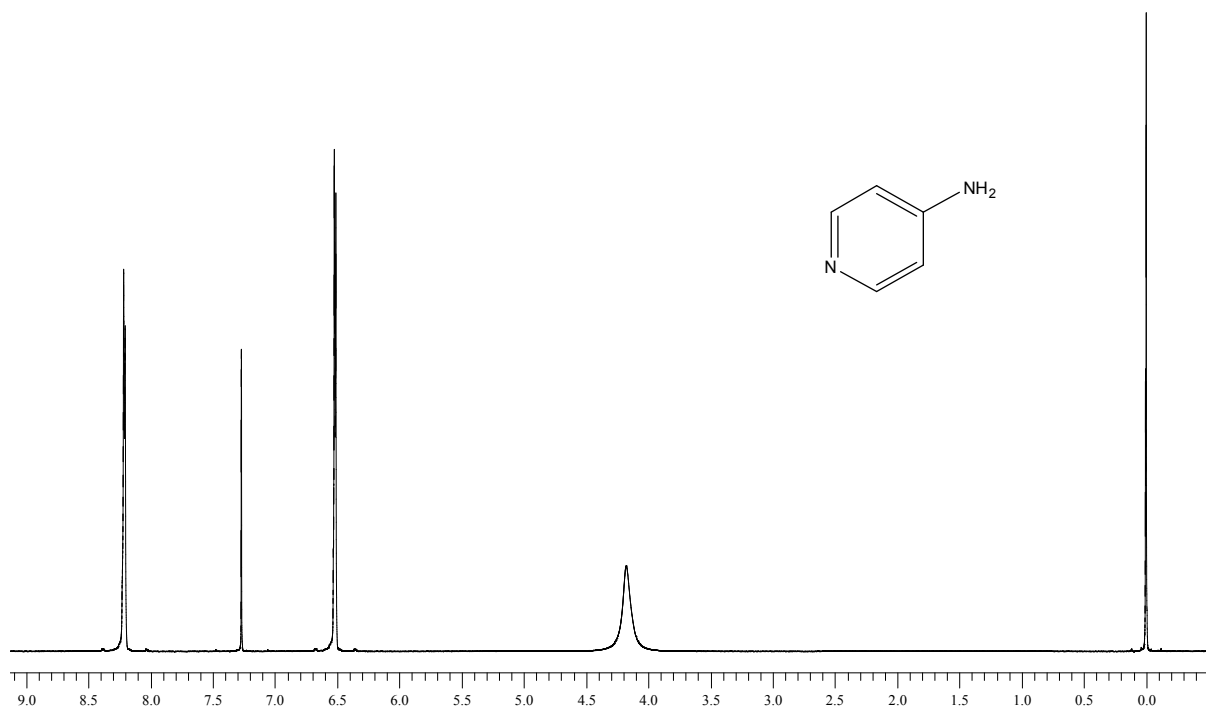
^1H NMR (300 MHz, CDCl_3 +DMSO, ppm): δ 7.78-7.80 (d, J = 8.49 Hz, 2H), 6.61-6.63 (d, J = 9.55 Hz, 2H), 5.40 (bs, 2H); ^{13}C NMR (75 MHz, CDCl_3 +DMSO, ppm): δ 168.3, 151.3, 131.2, 118.5, 113.0.

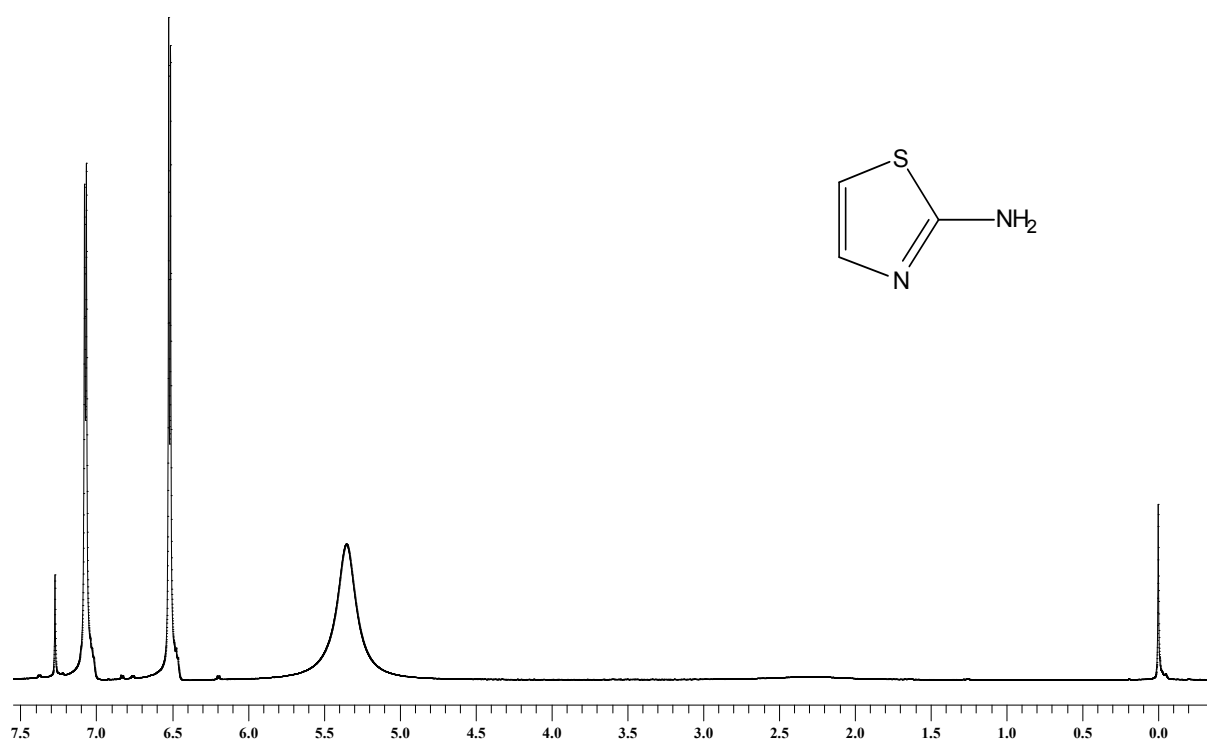
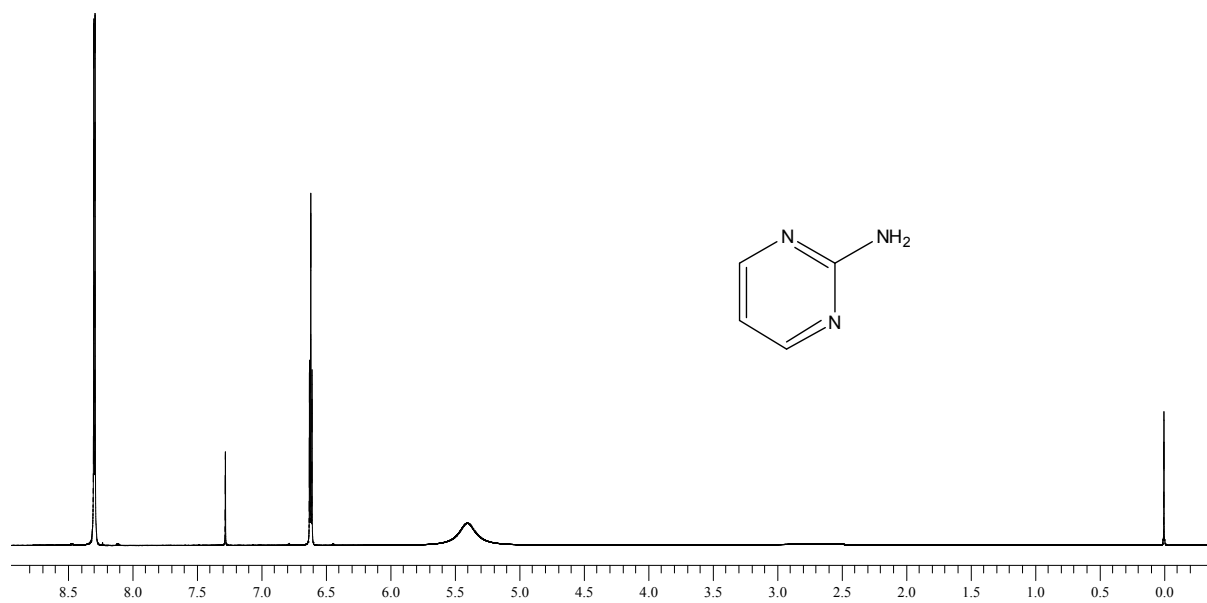


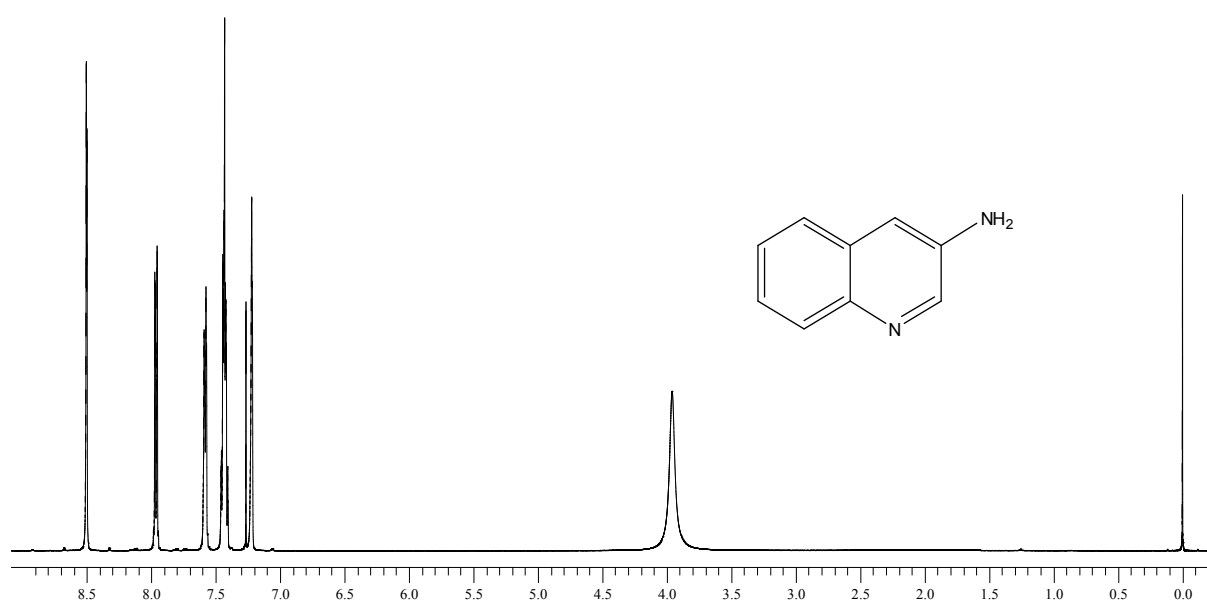
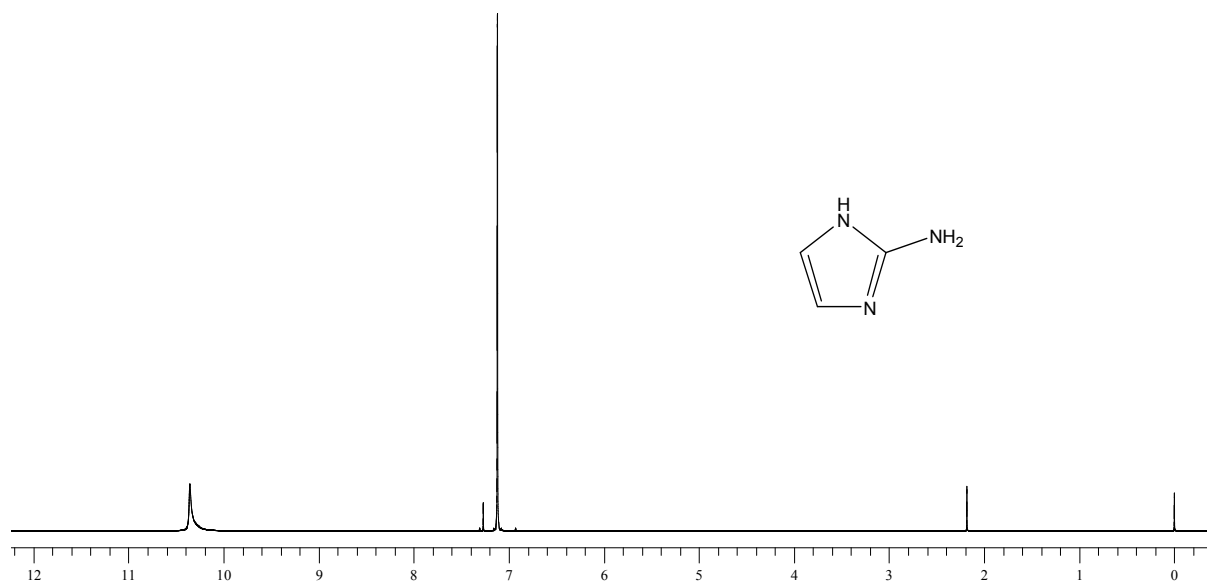
Ethyl 4-aminobenzoate: (Table 4, entry 12)

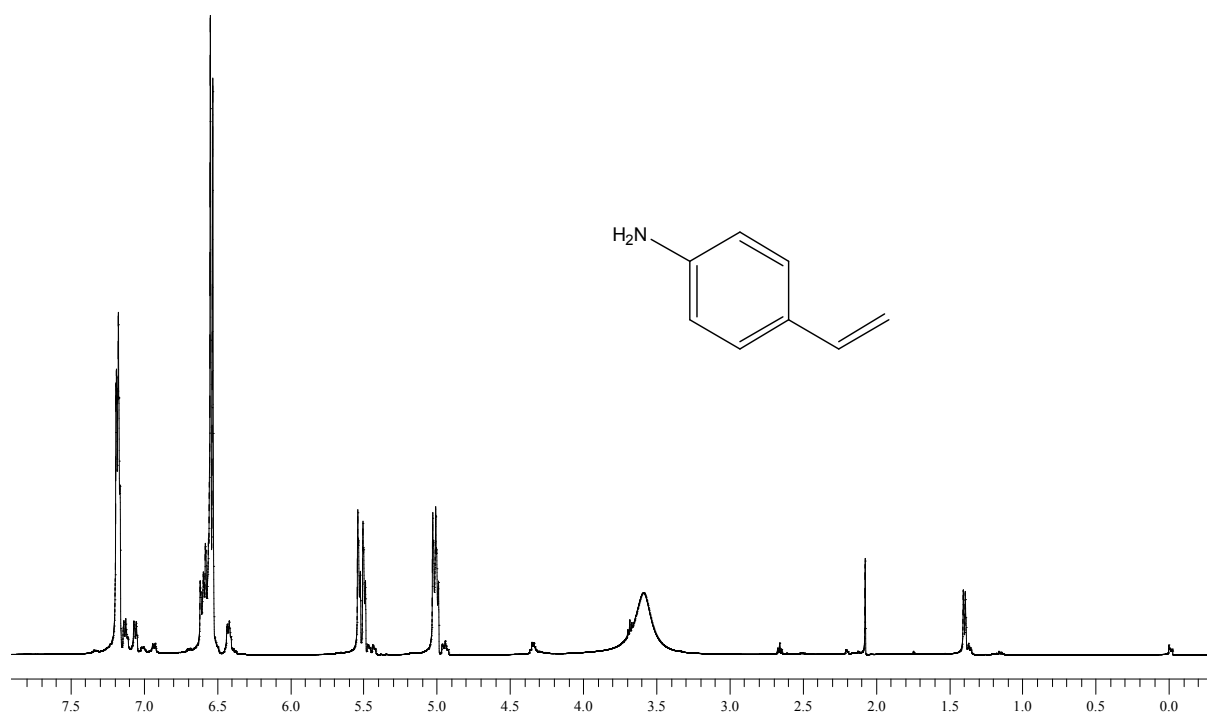
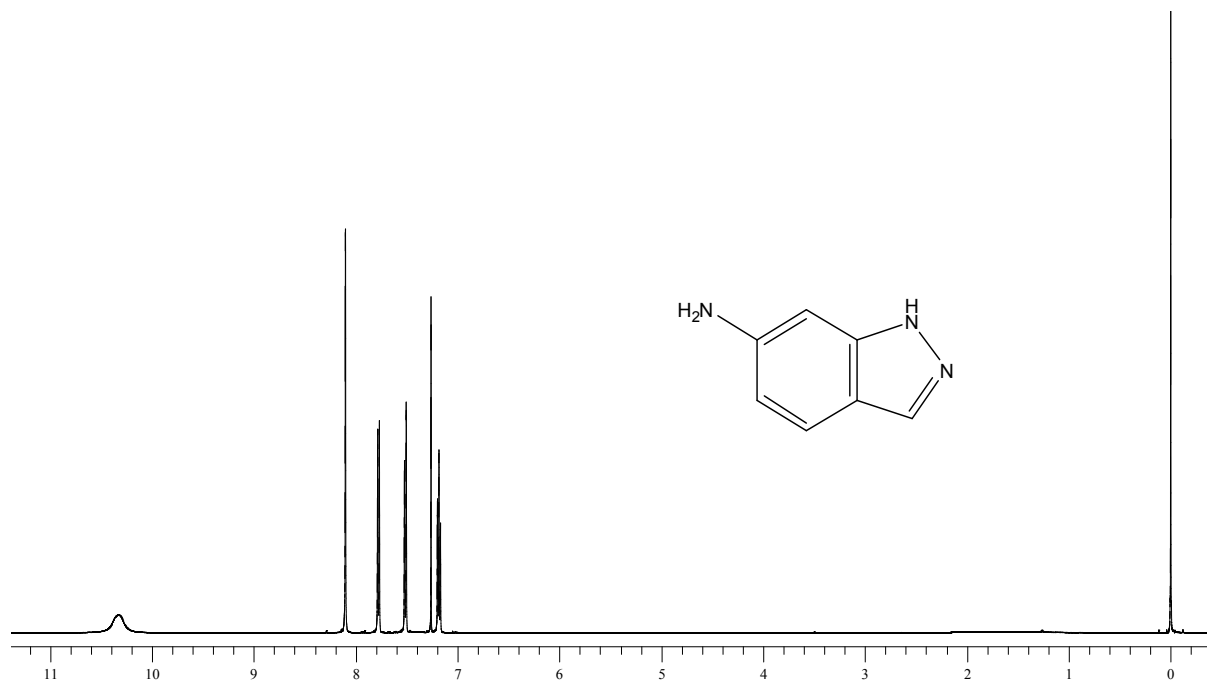
^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.85 (d, J = 9.06 Hz, 2H), 6.63 (d, J = 9.06 Hz, 2H), 4.31 (q, J = 6.7, 7.5 Hz, 2H), 4.01 (bs, 2H), 1.36 (t, J = 6.7, 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 166.69, 150.71, 131.52, 120.05, 113.65, 60.30, 14.30.

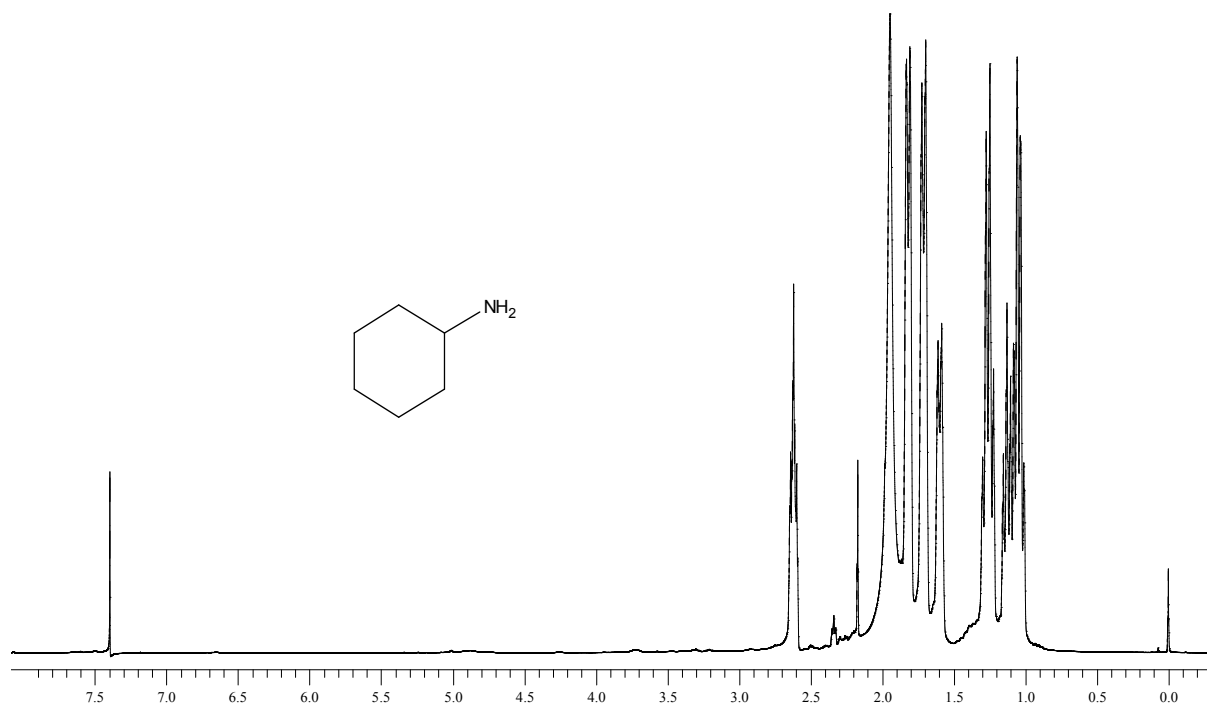
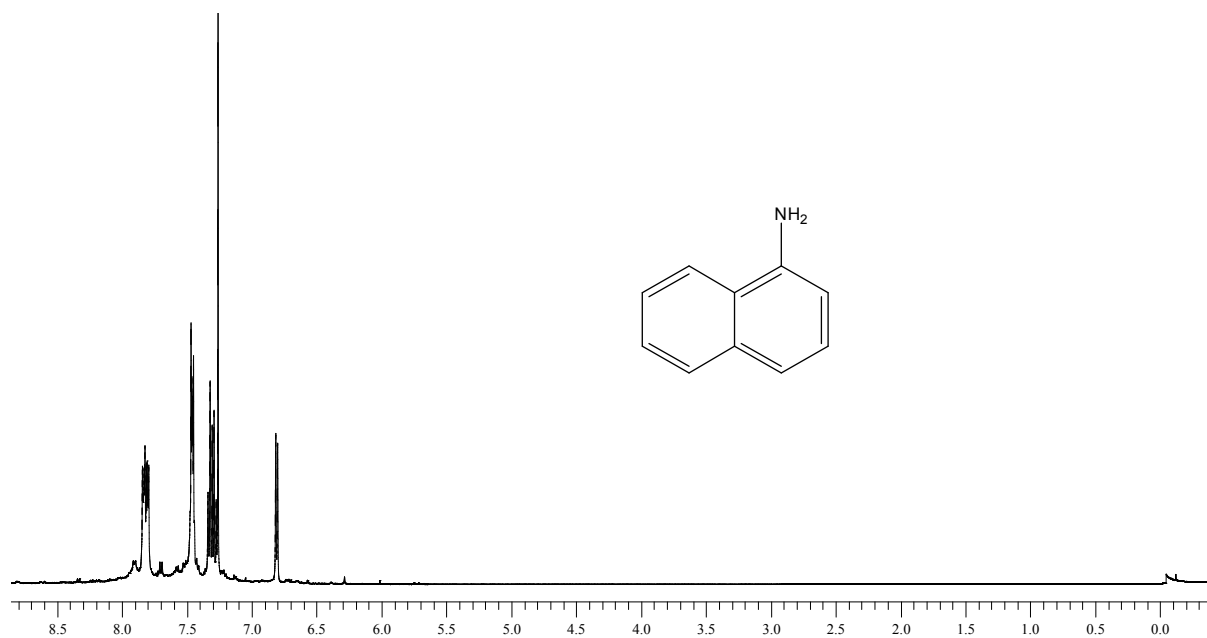
^1H NMR spectra of the products:

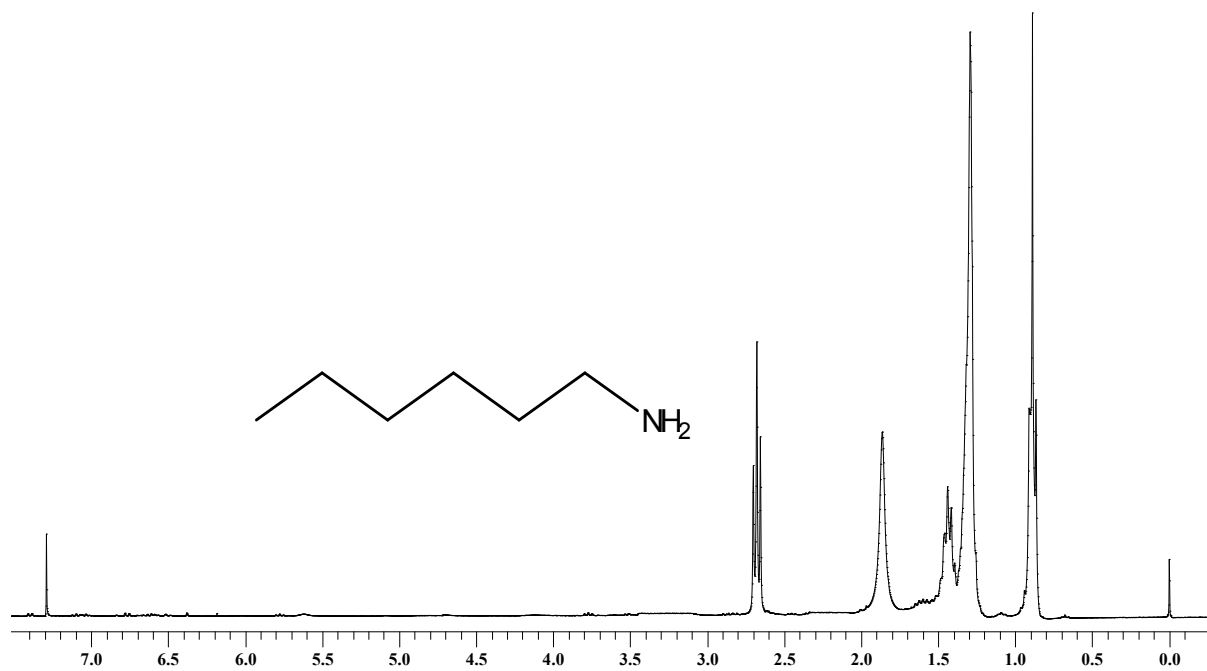
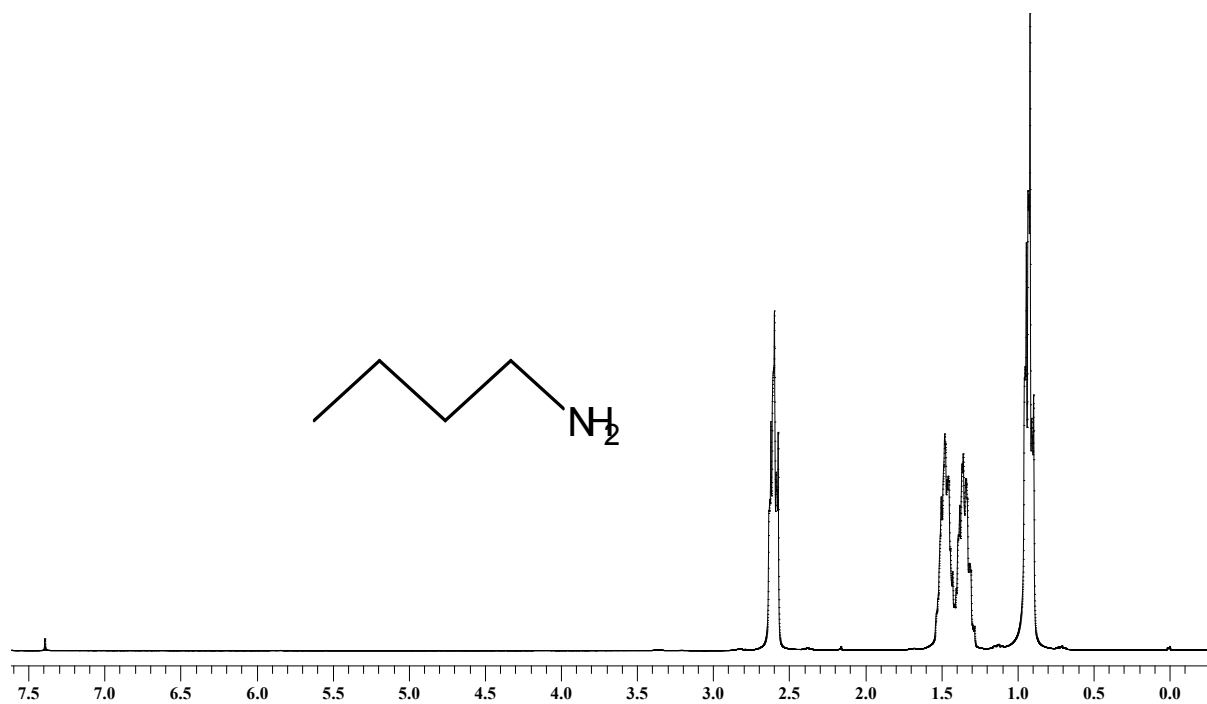


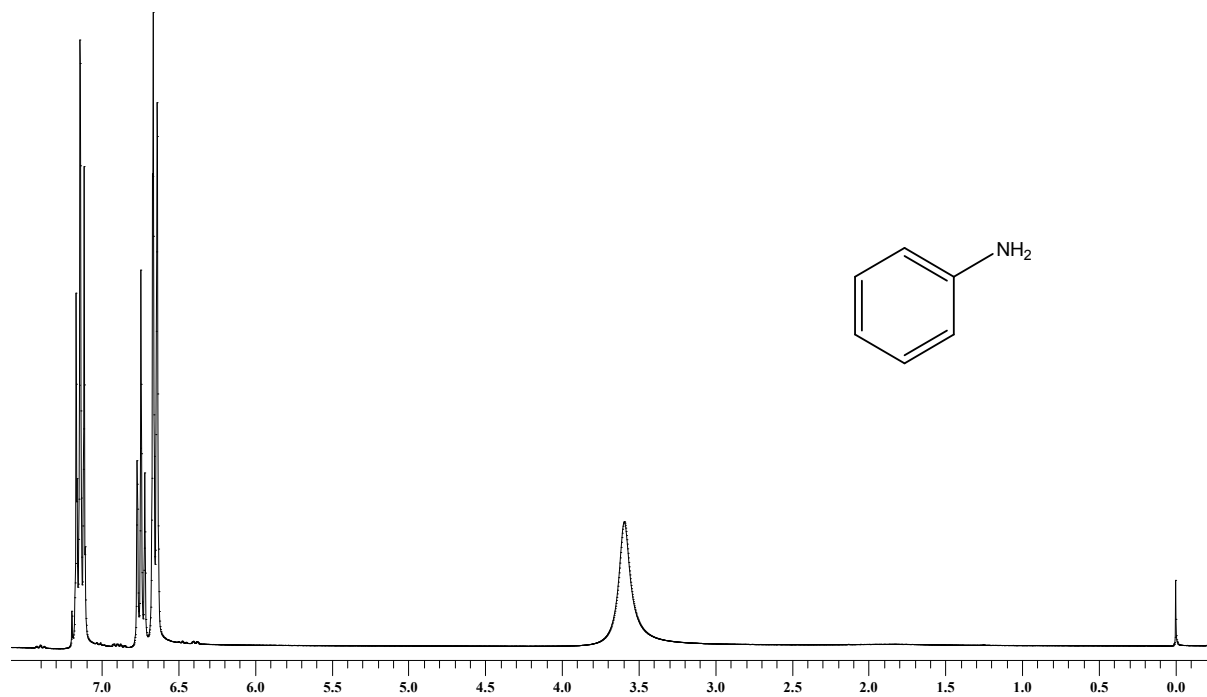
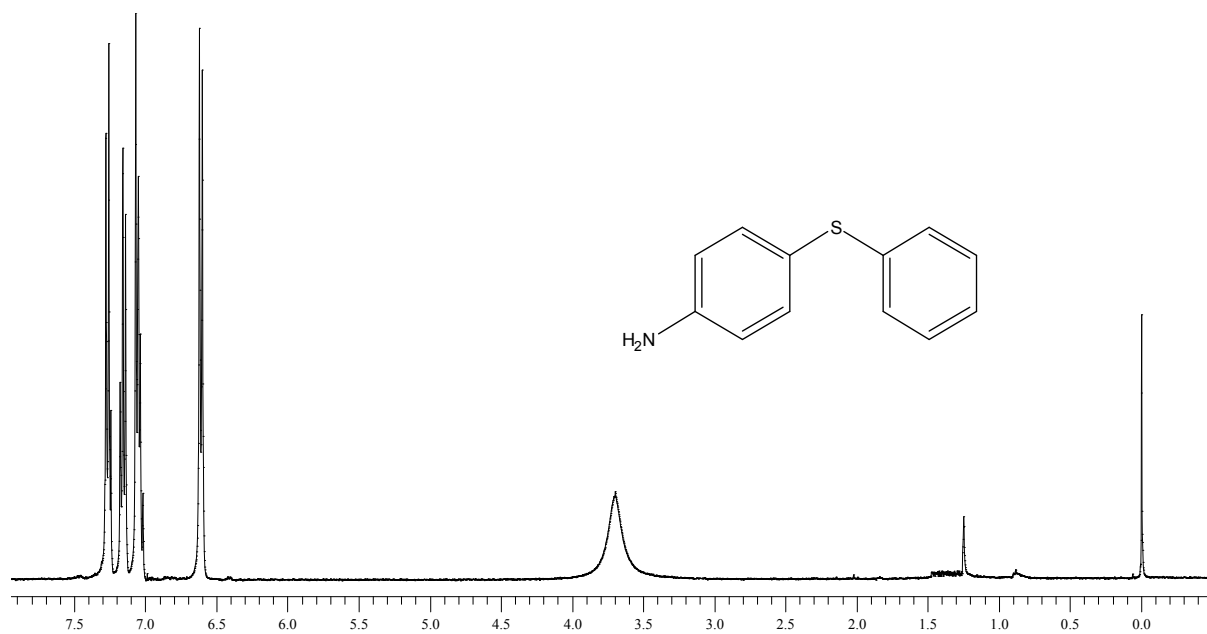


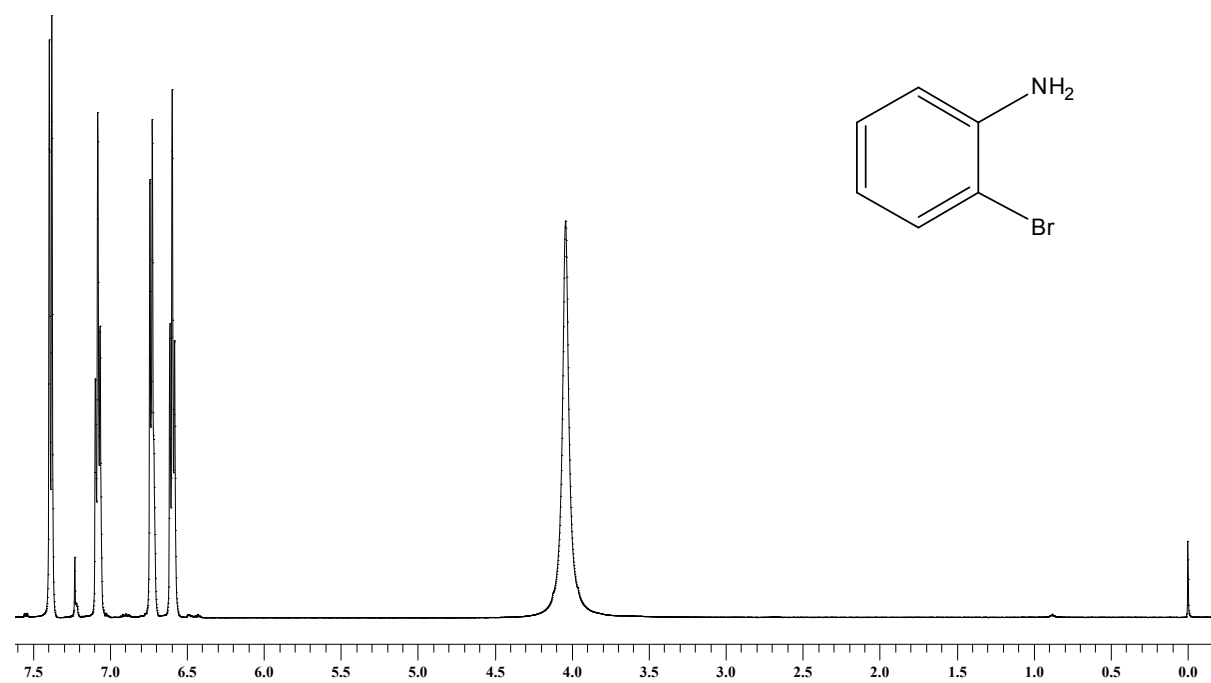
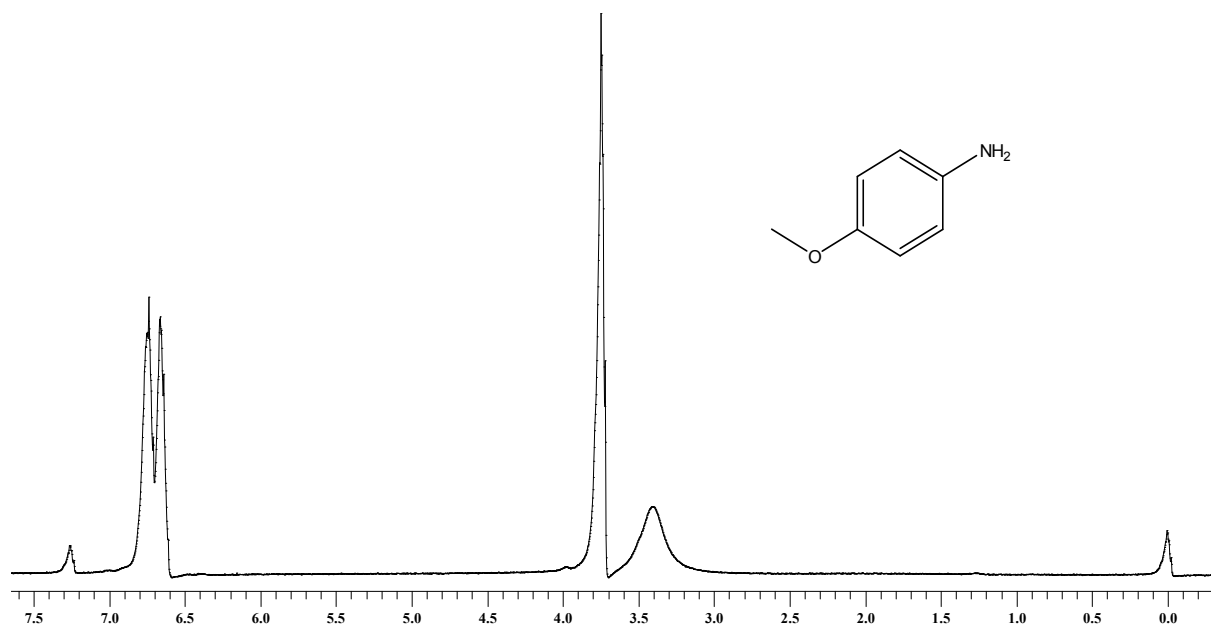


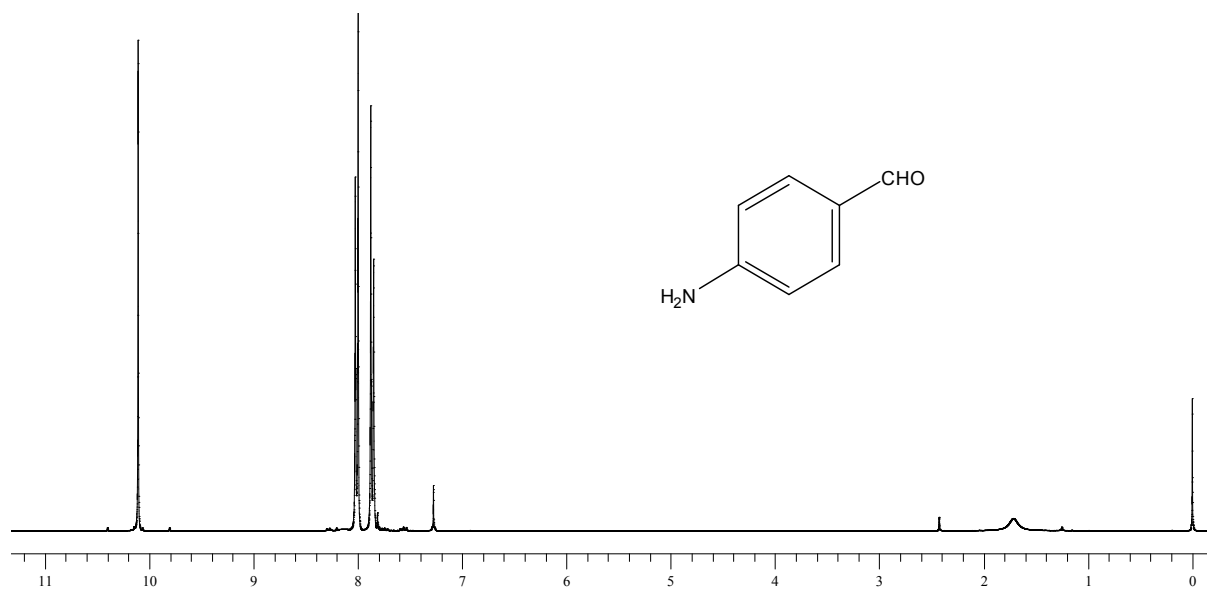
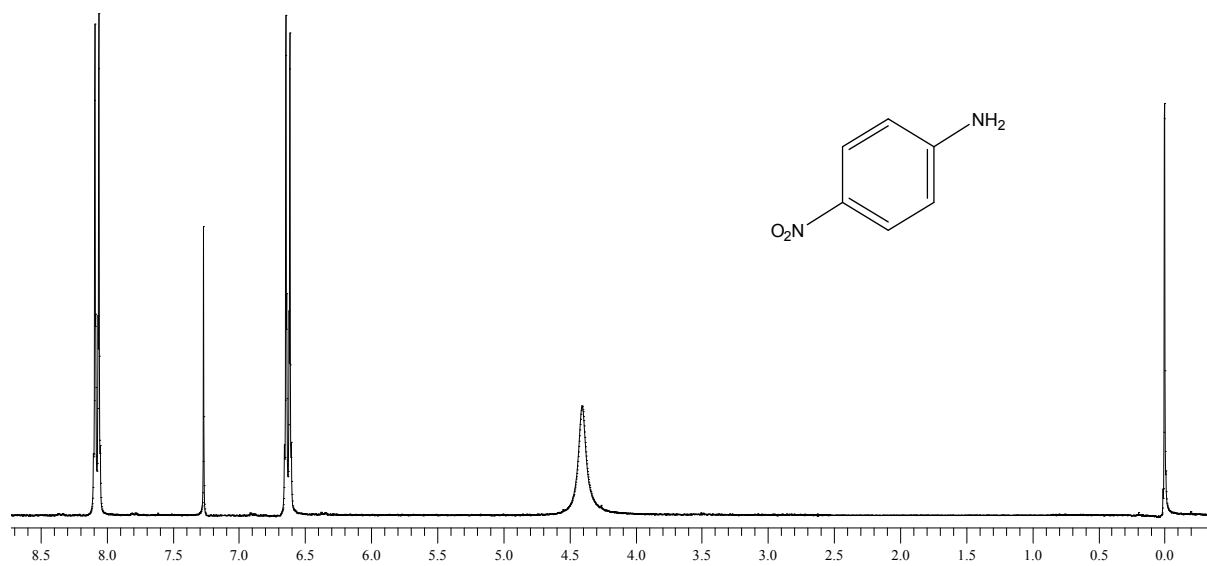


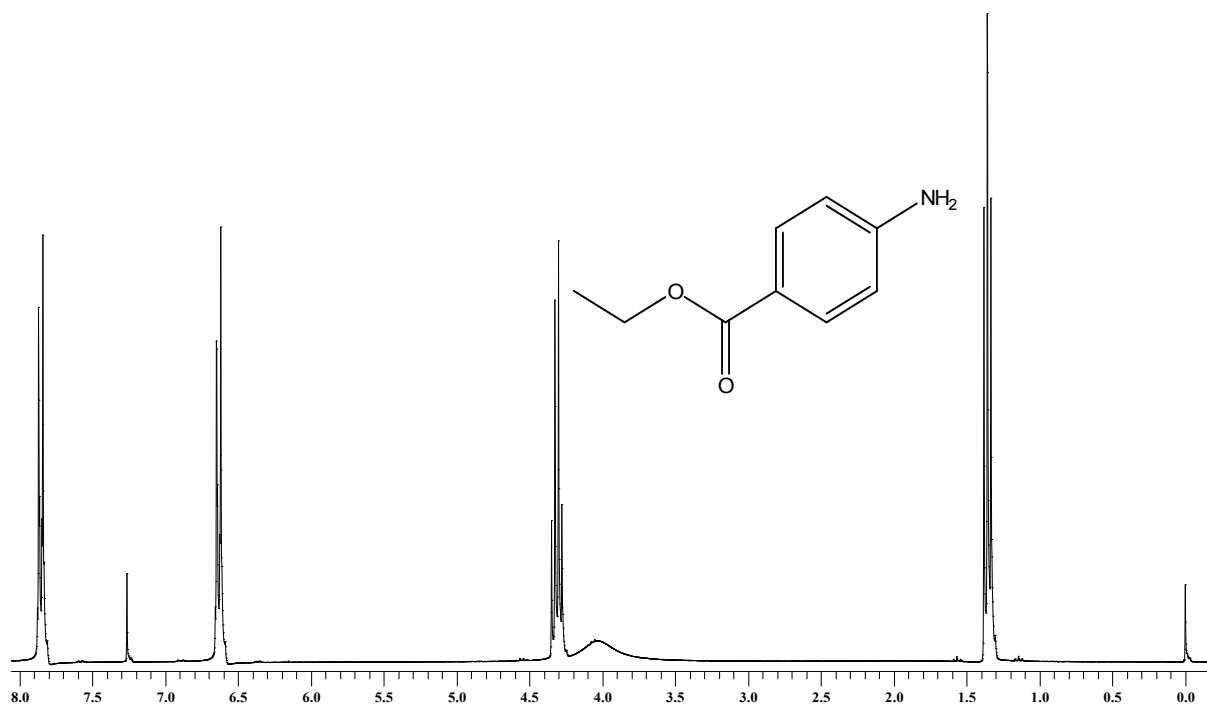
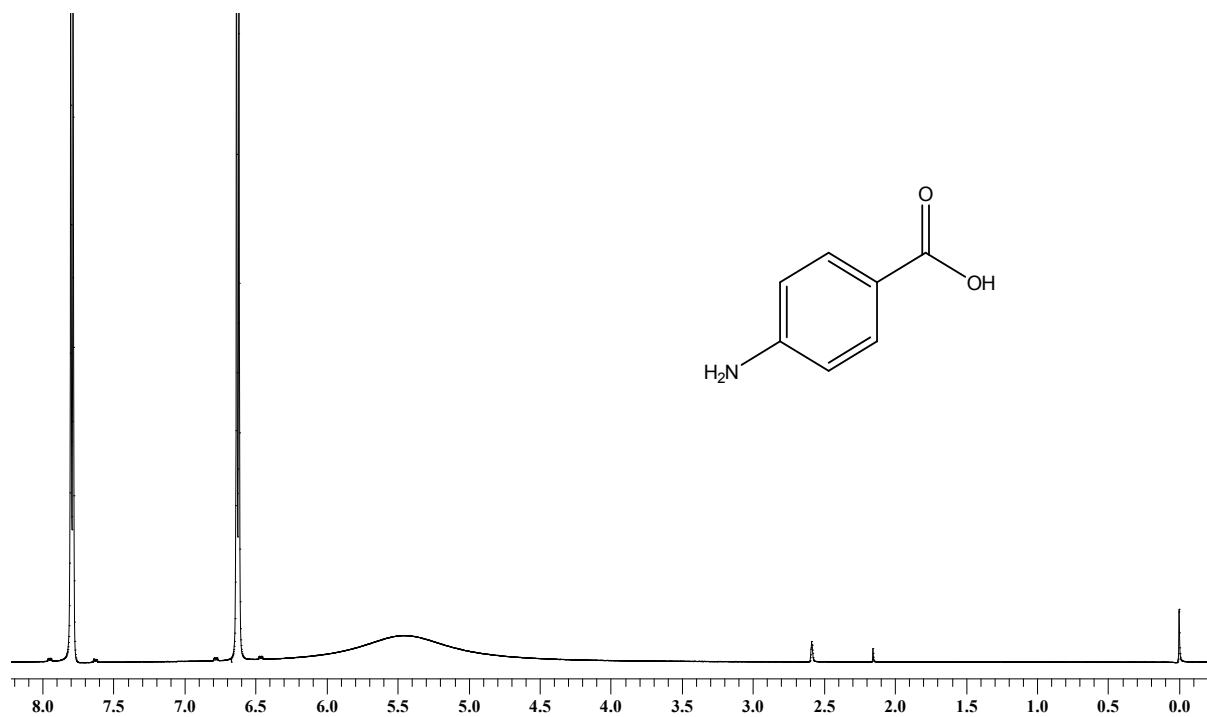




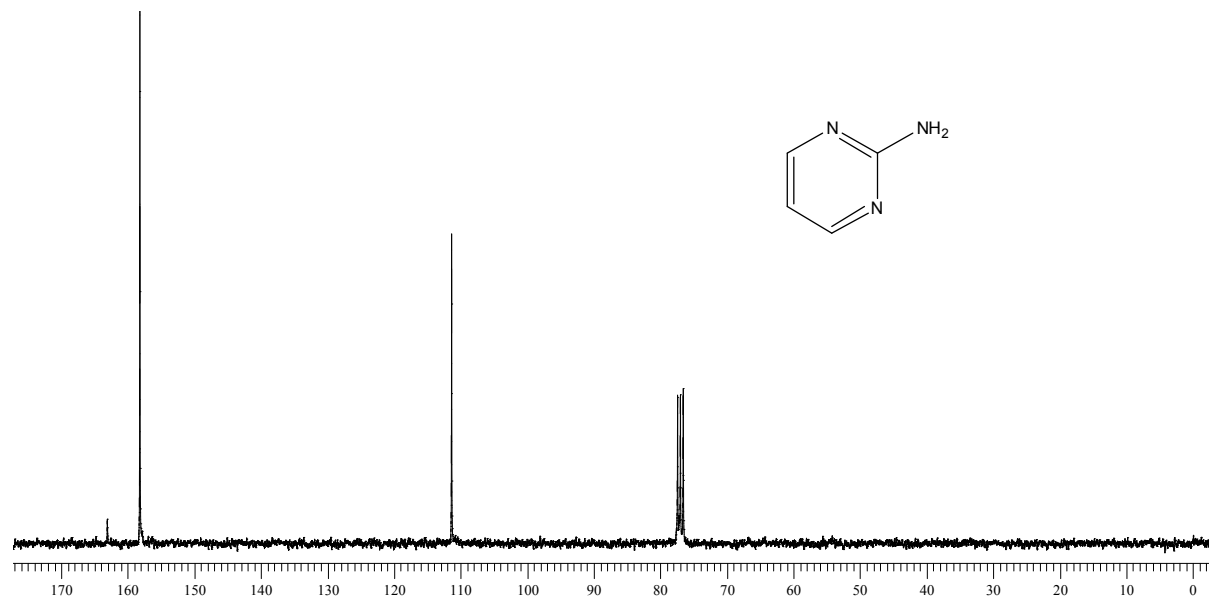
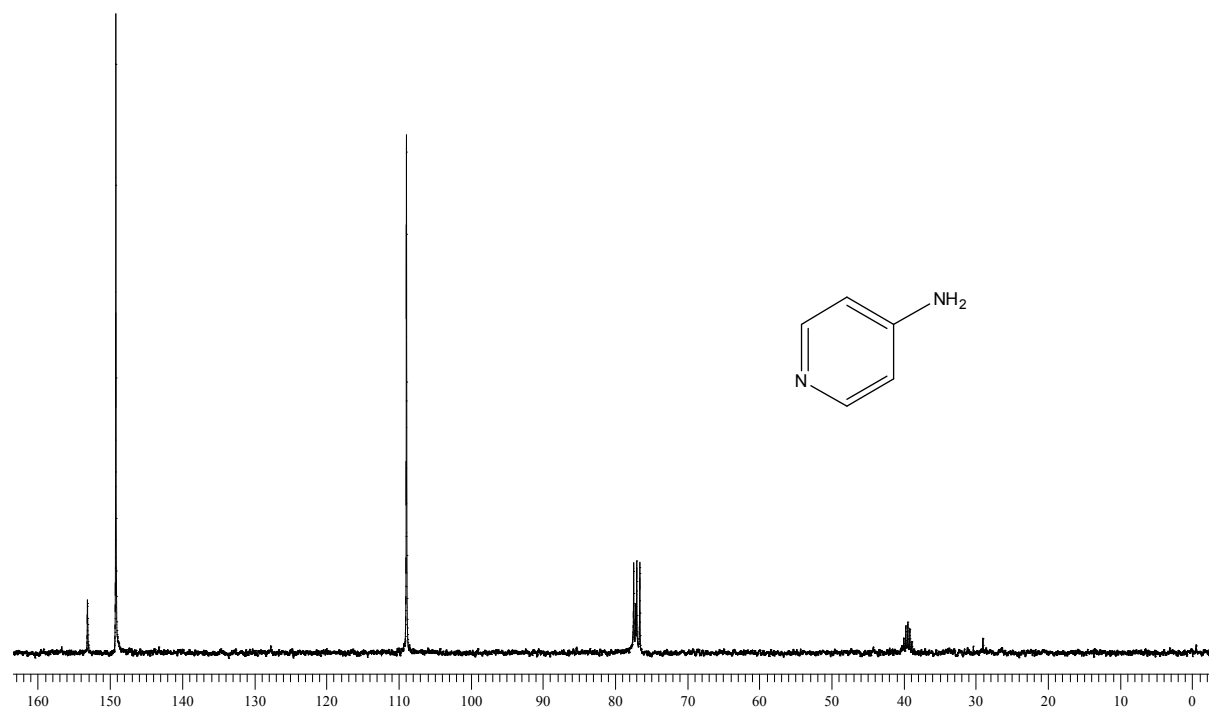


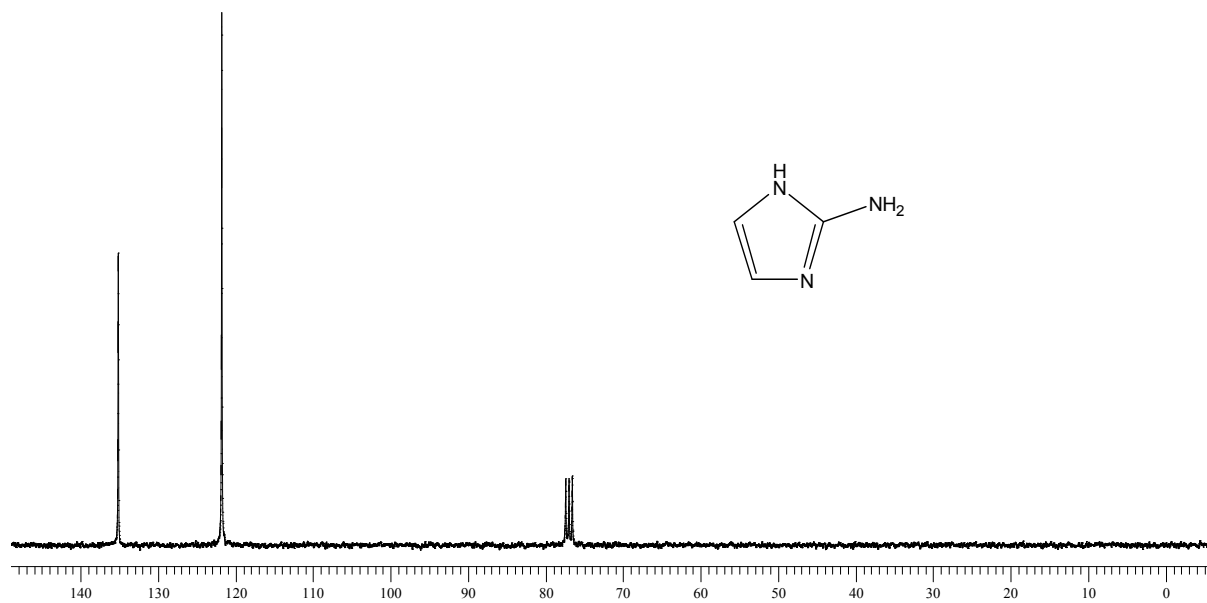
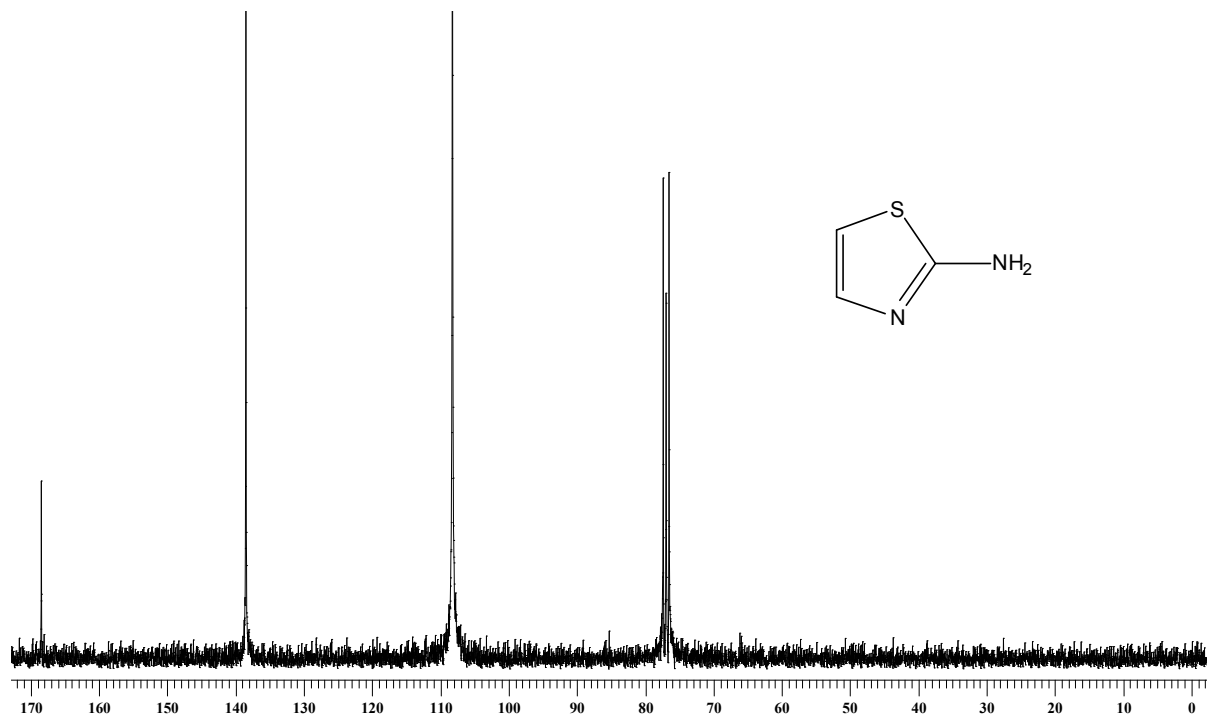


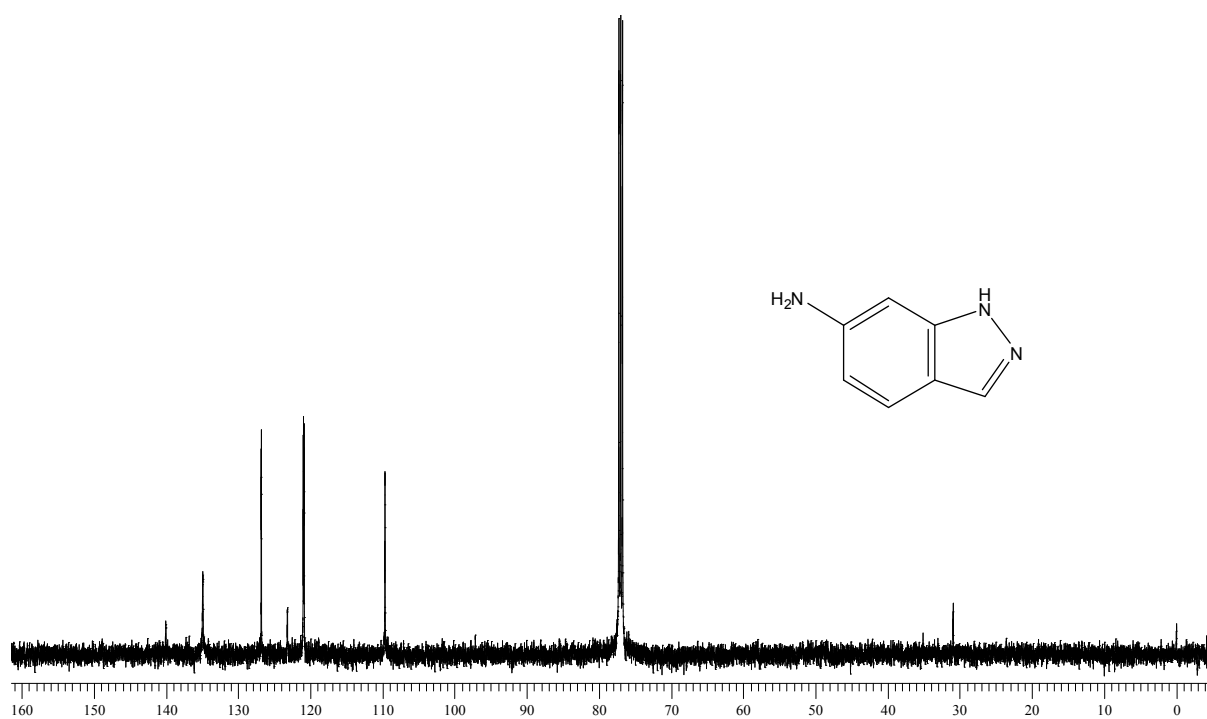
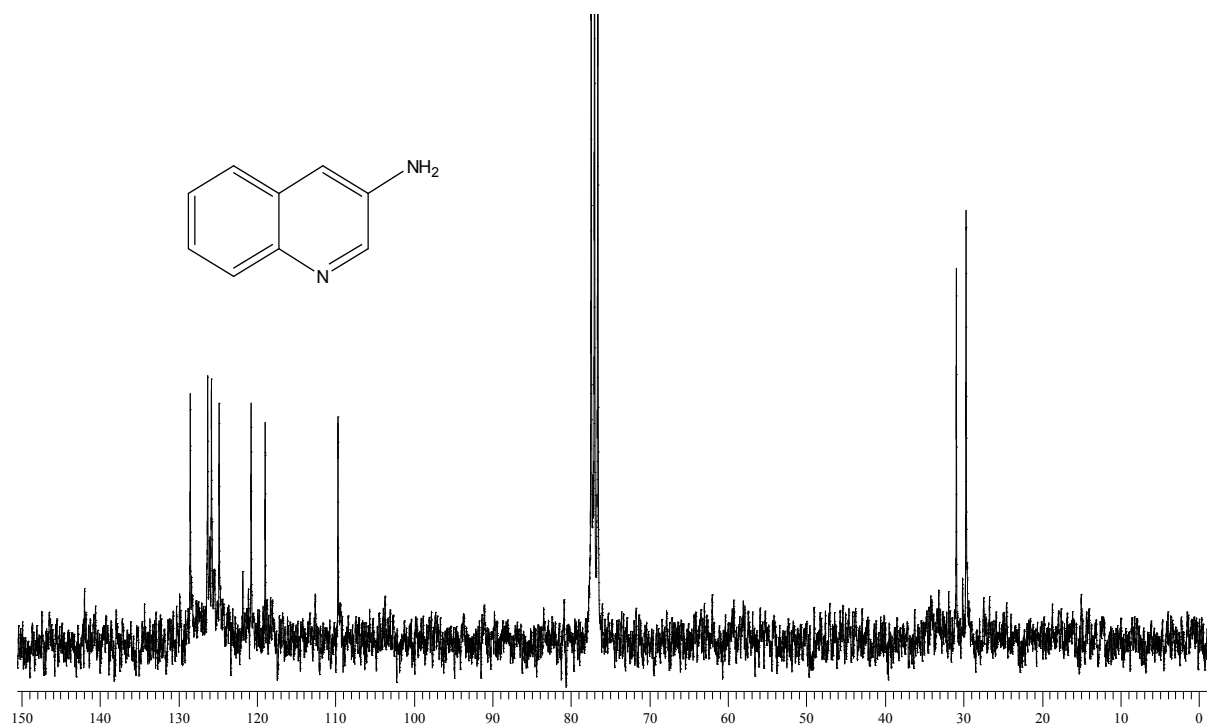


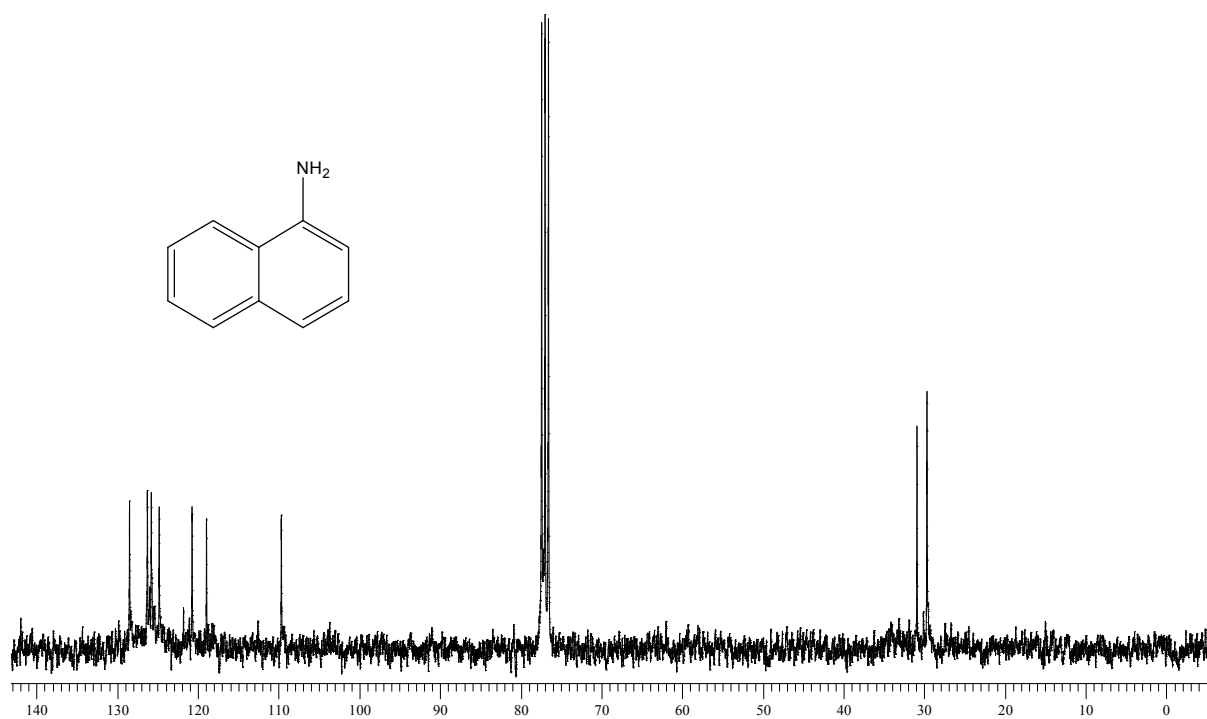
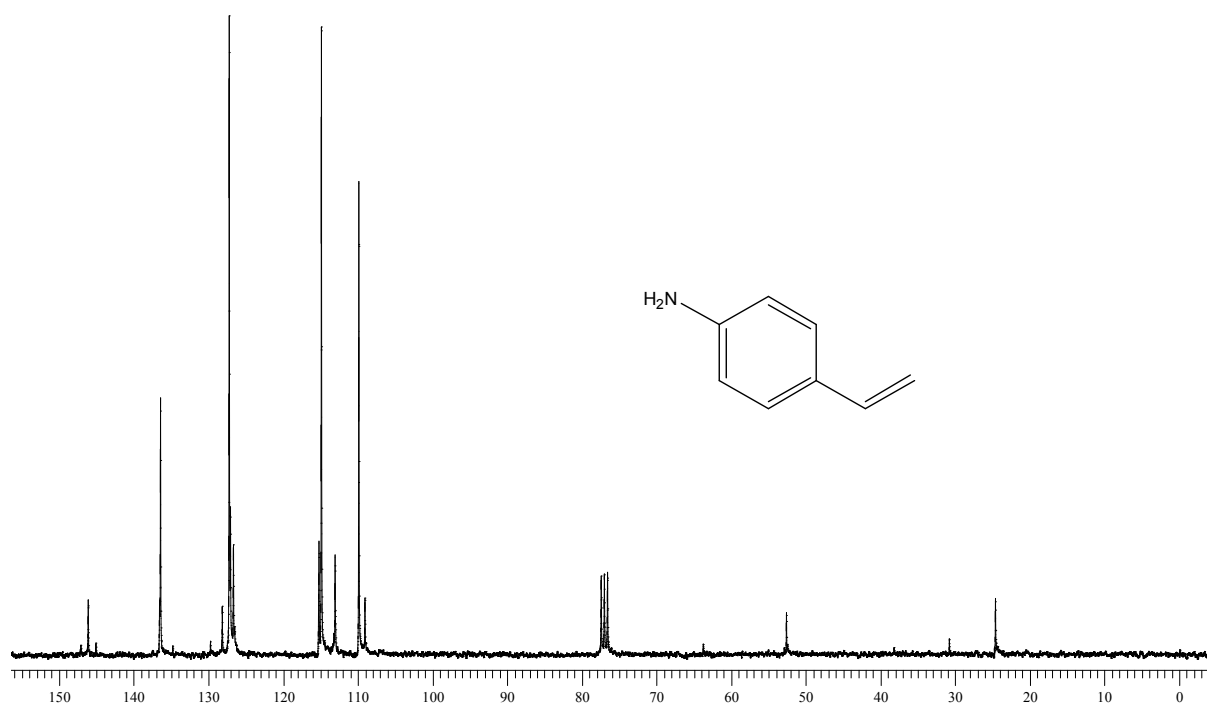


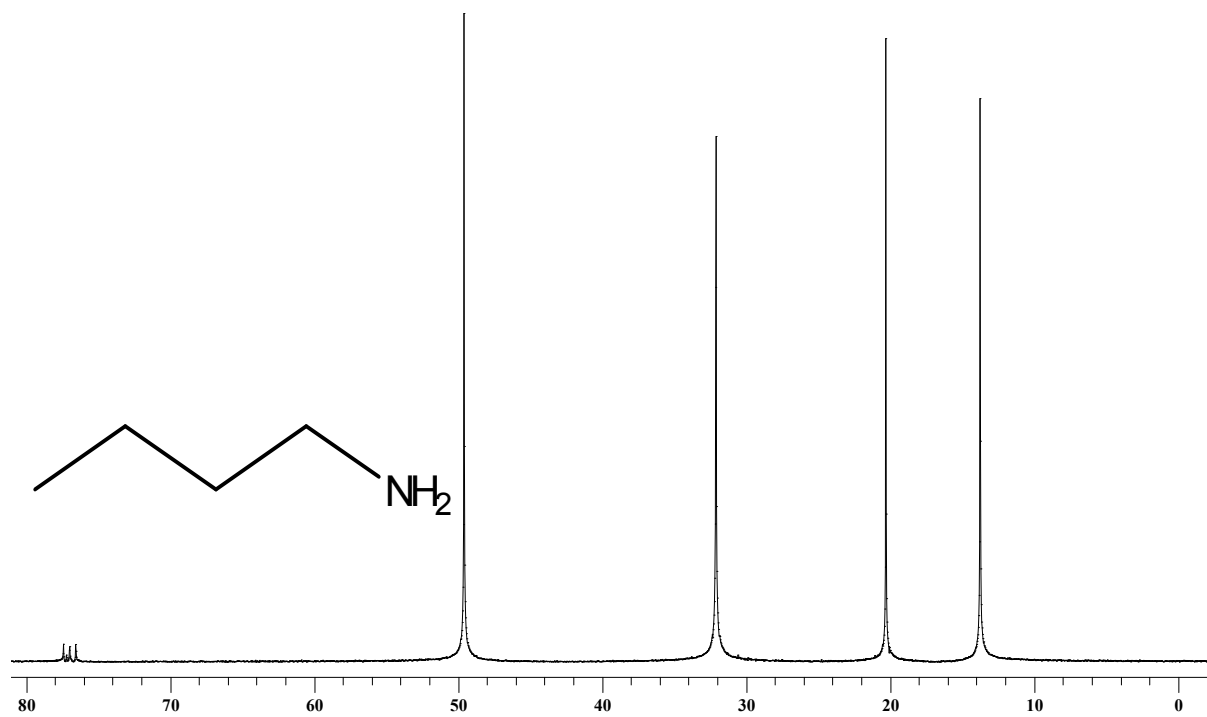
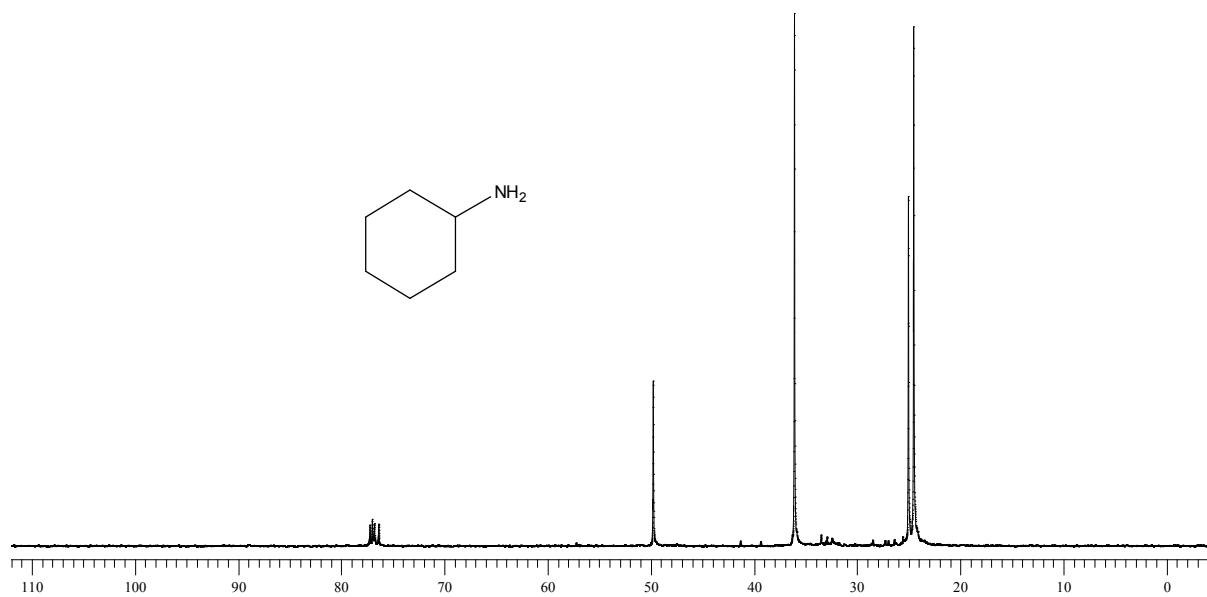
^{13}C NMR spectra of the products:

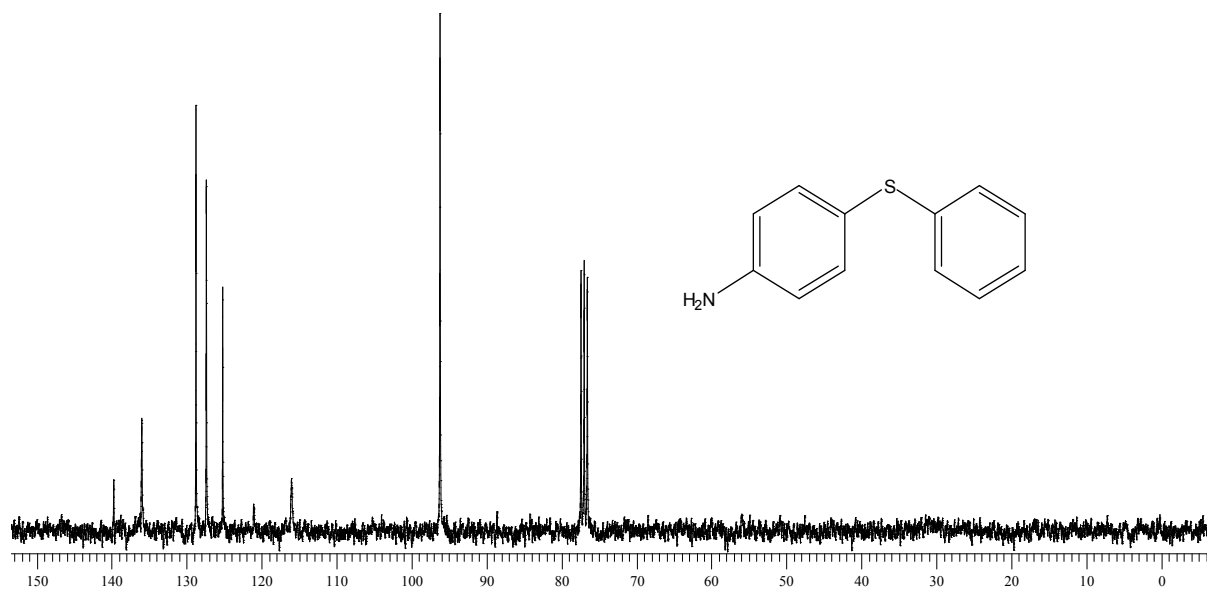
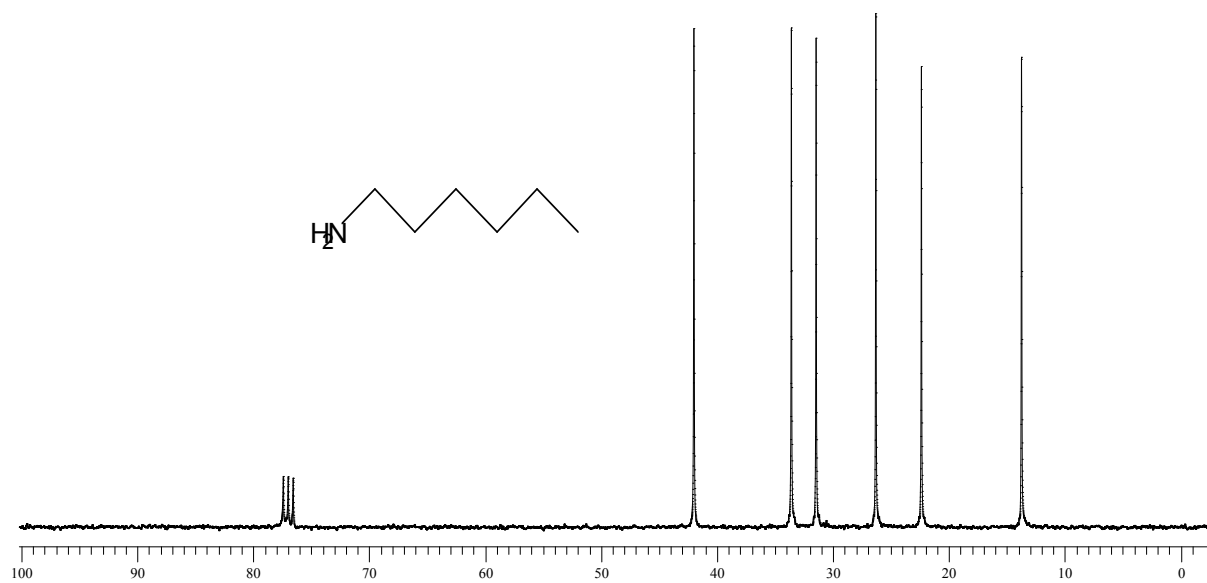


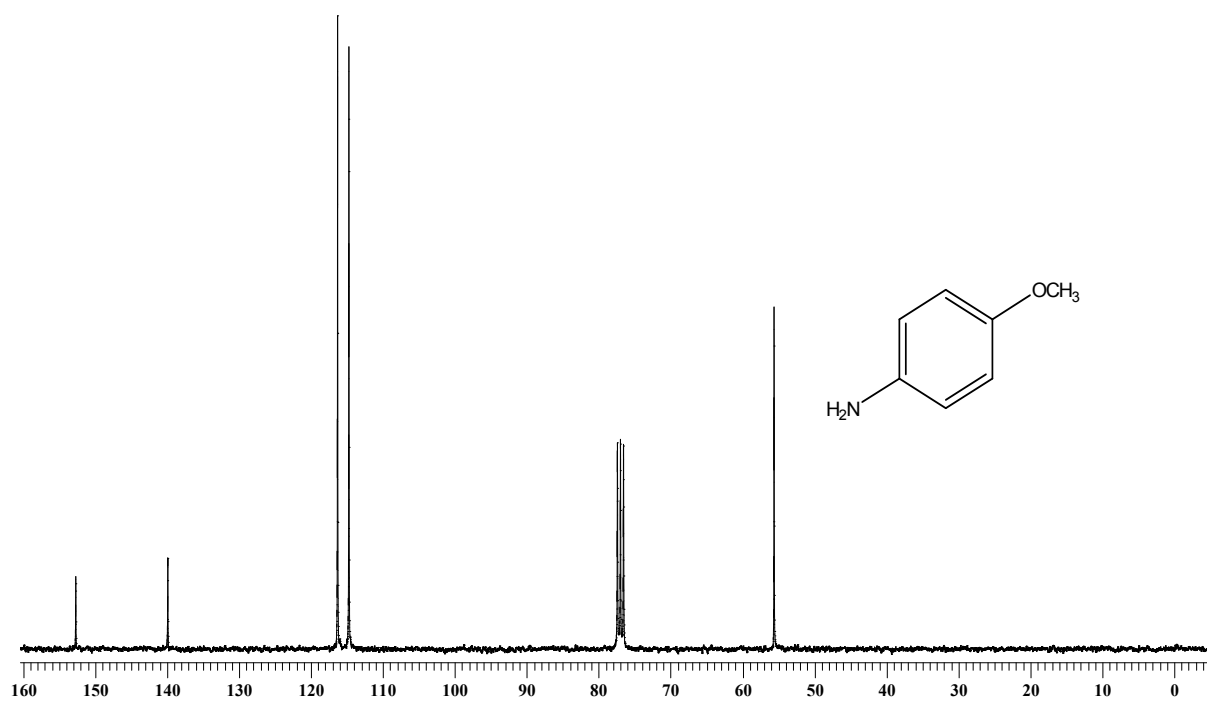
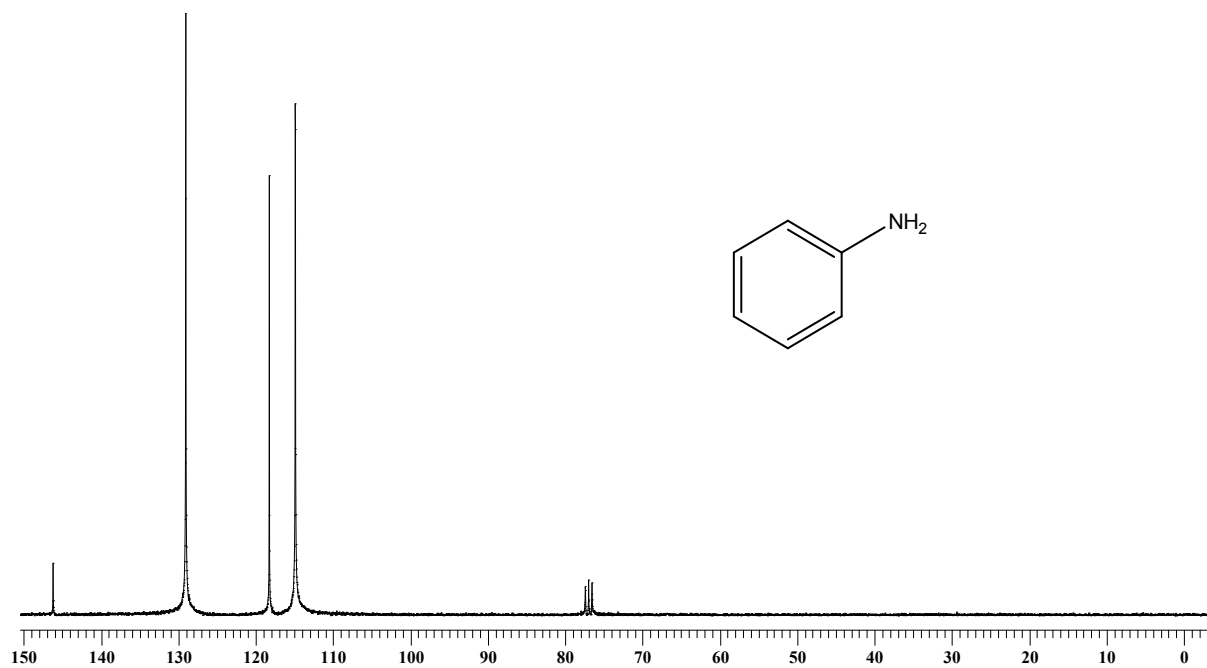


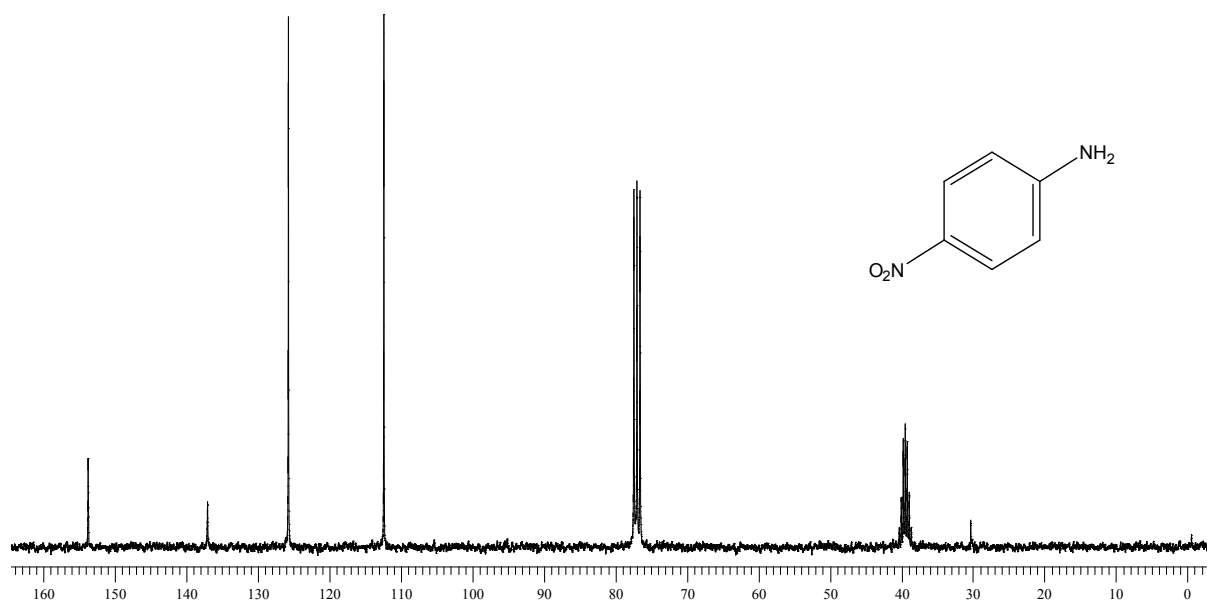
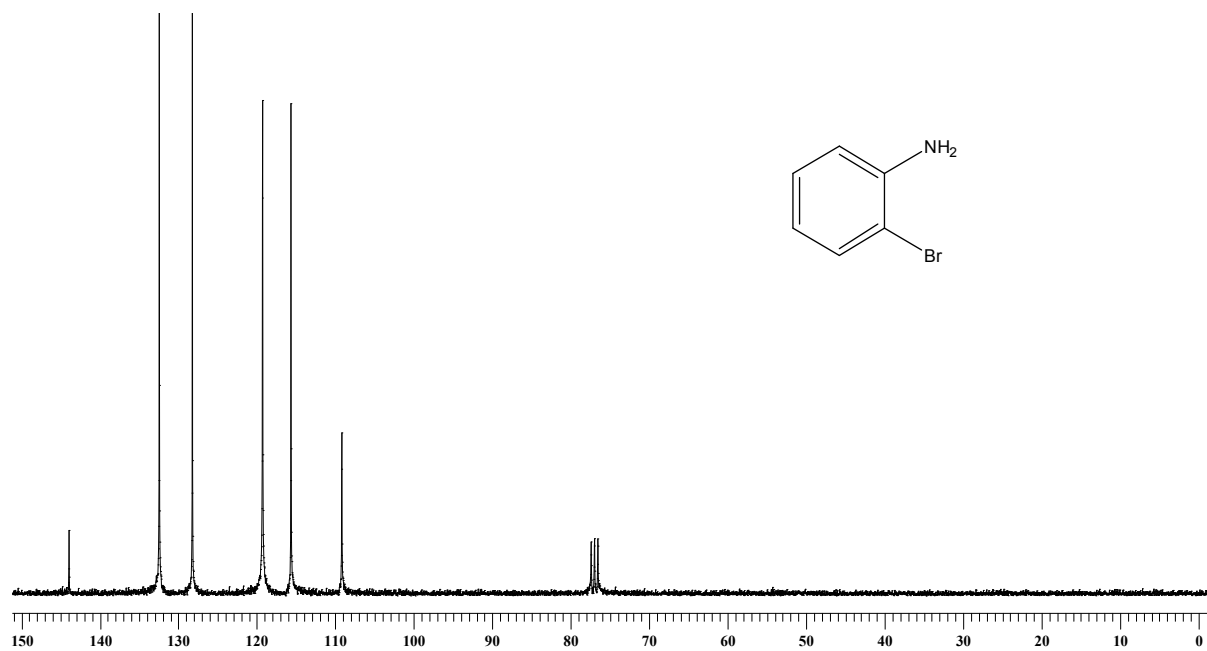


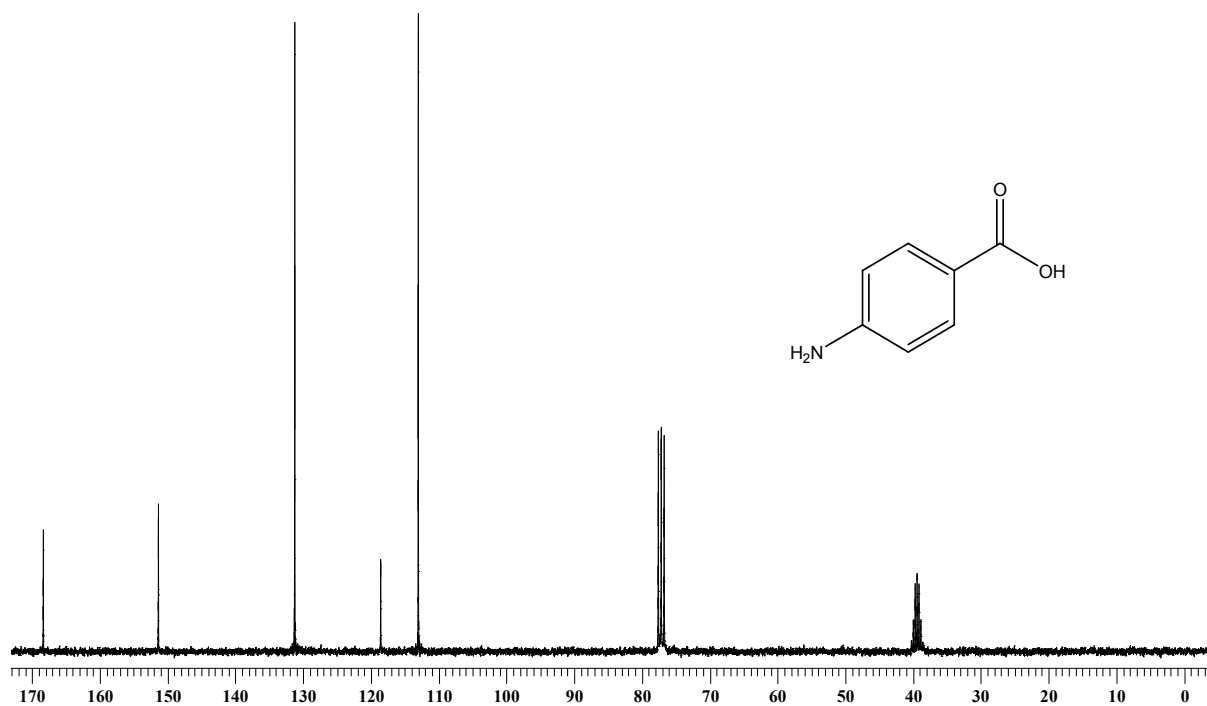
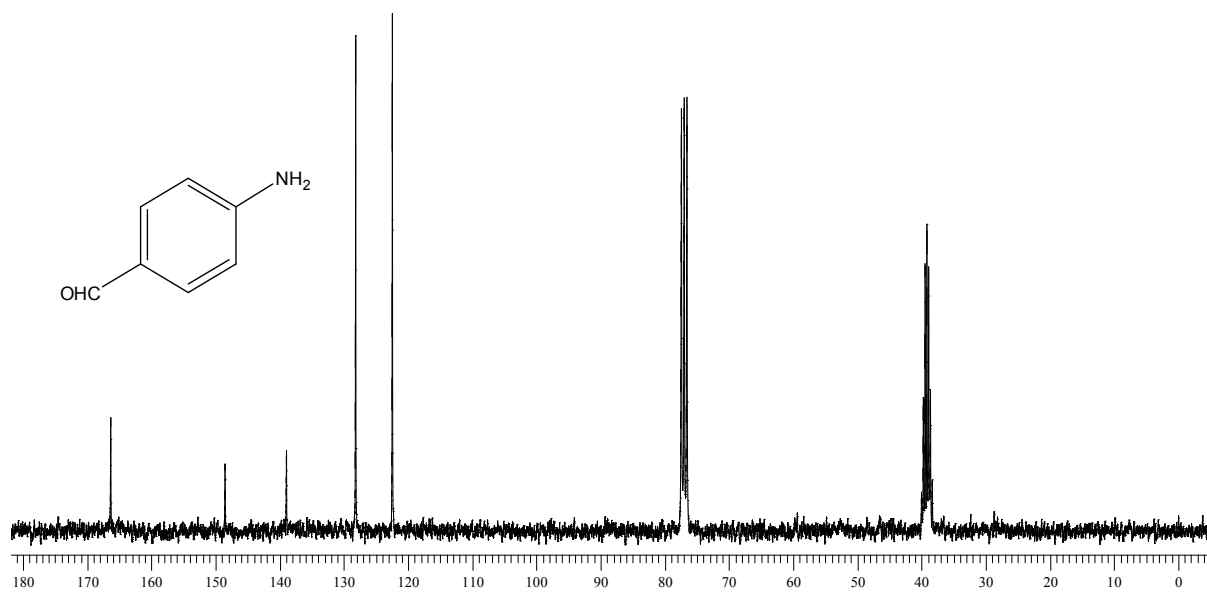


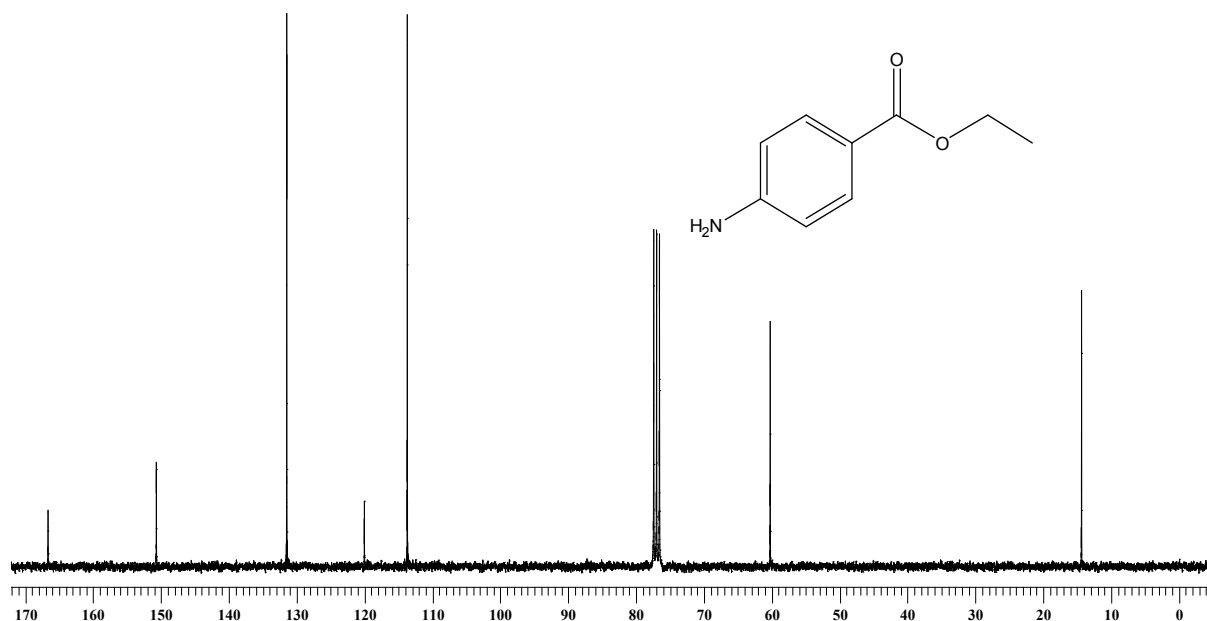












References:

1. (a) R. Dey, N. Mukherjee, S. Ahammed and B. C. Ranu, *Chem. Commun.*, 2012,**48**, 7982–7984; (b) Jr. R. J. Rahaim and Jr. R. E. Maleczka, *Org. Lett.*, 2005, **7**, 5087-5090; (c) K. Junge, B. Wendt, N. Shaikh and M. Beller, *Chem. Commun.*, 2010,**46**, 1769–1771.
2. (a) A. Cwik, Z. Hell, F. Figueras, *Adv. Synth. Catal.* 2006, 348, 523; (b) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.*, 2002, 124, 11572; (c) M. L. Kantam, K. B. S. Kumar, P. Srinivas, B. Sreedhar, *Adv. Synth. Catal.*, 2007, 349, 1141. (d) J. M. D. Consul, C. A. Peralta, E. V. Benvenutti, J. A. C. Ruiz, H. O. Pastore and I. M. Baibich, *J. Mol. Catal. A: Chem.*, 2006, **246**, 33.
3. (a) M. L. Kantam, S. Roy, M. Roy, B. Sreedhar and B. M. Choudary, *Adv. Synth. Catal.*, 2005, **347**, 2002-2008; (b) Keya Layek, H. Maheswaran, R. Arundhathi, M. L. Kantam and S. K. Bhargava, *Adv. Synth. Catal.*, 2011, **353**, 606–616; (c) M. L. Kantam, R. Chakravarti, U. Pal, B. Sreedhar and Suresh Bhargava, *Adv. Synth. Catal.*, 2008, **350**, 822 – 827.