Supporting Information

CuI-Nanoparticles-Catalyzed Selective Synthesis of Phenols, Anilines and Thiophenols from Aryl Halides in Aqueous Solution

Hua-Jian Xu,*[,†,‡] Yu-Feng Liang,[†] Zhen-Ya Cai,[†] Hong-Xia Qi,[†]

Chun-Yan Yang,[†] and Yi-Si Feng*[,†,‡]

[†]*School of Chemical Engineering, Hefei University of Technology, Hefei 230009, P. R. China;* [‡] *Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei 230009, P. R. China.*

E-mail: hjxu@hfut.edu.cn; ysfeng@hfut.edu.cn

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I. General considerations

All reactions were carried out in an oven-dried flask under a pure and dry nitrogen atmosphere. CuI nanoparticles were synthesized in our laboratory. Tetra-*n*-alkylammonium hydroxides water solution was purchased from Sinopharm Chemical Reagent Co. without further purification. These solvents were transferred by syringe to the reaction flask. Generally, aryl iodides and aryl bromides were purchased from commercial sources (Aldrich, Acros, Alfa Aesar, Fluka, Lancaster) and distilled when necessary. 28% ammonia solution and sulfur powder were purchased from commercial sources without further purification. Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Flash column chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded using a Bruker Avance 300 and 400 instruments. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2014 Series GC System. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. The samples were characterized by powder X-ray diffraction (XRD) on a D/Max-rB X-ray diffractometer with monochromatized Cu Kα (λ = 1.5406 Å) incident radiation. XRD patterns were recorded from 20° to 80° (2θ) with a scanning rate of 6°/min. The morphologies of the samples were analyzed by TEM on an H-800 transmission electron microscope operated at 200 kV.

II. Preparation of the catalyst

CuI nanoparticles were prepared by the reaction of $Cu(dmg)_2$ and KI in the autoclave with ethanol as solvent, solvothermal method. Firstly, 0.464 g (4 mmol) of dimethylglyoxime (dmgH) and 0.400 g (2 mmol) of $Cu(OAc)_2 \cdot H_2O$ were added into 50 ml of absolute ethanol in sequence, which was stirred at 0°C for 30 min to get brown precipitates $Cu(dmg)_2$. Then the collected precipitates dispersed in 50 ml of absolute ethanol again. Secondly, 0.664g (4 mmol) KI was added and stirred vigorously for 2 h. After that, the mixture was transferred into 60mL teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 6 h, and then the reactor bomb is allowed to cool to room temperature. Black precipitates were obtained, then centrifugalized and washed with ethanol and deionized water for three times to ensure the removal of the impurities. The final product is then dried in a vacuum oven at room temperature for 12 h.

III. Catalyst characterization

The XRD pattern of the product is shown in *Fig. 1(d-e)*. All diffraction peaks in the XRD pattern can be perfectly indexed to pure CuI (JCPDS, 06-0246). No impurity was detected, indicating that the as-synthesized product was of high purity. The average crystalline size of the product can be estimated by Scherrer equation:

$$D=(K\lambda)/\beta\cos\theta$$

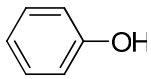
where D is the mean diameter of the nanoparticles, K is a constant (0.94), λ is the X-ray wavelength (0.15406 nm in the present case), β is the corrected X-ray diffraction broadening (β=B-b, B stands for full width at half maximum and b is the instrumental line broadening), and θ is the Bragg angle of the X-ray diffraction peak. Calculation made on the strongest peak of fresh CuI nanoparticals at 2θ=25.40° is 52.3 nm, and 57.5 nm for CuI nanoparticles after the third catalytic cycle.

The morphologies of the as-prepared CuI crystals were studied by TEM. *Fig. 1(a–c)* shows that the CuI crystals are nanoparticals with diameters ranging from 30 to 80 nm, which is coincident with the value measured by XRD.

IV. General experimental procedures for *O*-arylation

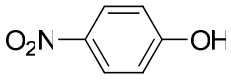
General procedure for hydroxylation of aryl iodides: protocol A (Table 2)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5 mol%, 2.9 mg), the aryl halides if a solid (1 mmol, 1 eq.). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, aryl iodides if a liquid (1 mmol, 1 eq.) and degassed 40% tetra-*n*-butylammonium hydroxides water solution (2.0 mL, 3.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at 60°C for 24h. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethyl acetate and 1 ml of HCl (37%) were added. The mixture were stirred for 2 hours, then filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. Gathered aqueous phases were extracted with ethyl acetate for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5 h.



phenol [1, 2]

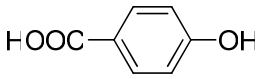
Following general procedure A, iodobenzene (112 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded phenol as a white solid (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (t, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 5.10 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 129.7, 120.9, 115.4 ppm. EI-MS: *m/z* = 94 (M^+).



4-nitrophenol [2]

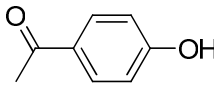
Following general procedure A, 1-iodo-4-nitrobenzene (249 mg, 1 mmol), CuI

nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-nitrophenol as a yellow solid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.11 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 141.8, 126.4, 115.8 ppm. EI-MS: *m/z* = 139 (M^+).



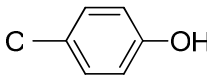
4-hydroxybenzoic acid [3]

Following general procedure A, 4-iodobenzoic acid (248 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-hydroxybenzoic acid as a white solid (99% yield). ^{1}H NMR (300 MHz, CD_3SOCD_3): δ 12.38 (s, 1H), 10.18 (s, 1H), 7.81-7.77 (m, 2H), 6.84-6.70 (m, 2H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 167.7, 162.1, 132.0, 121.9, 115.6 ppm. EI-MS: *m/z* = 138 (M^+).



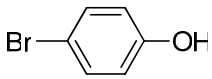
4-hydroxyacetophenone [2]

Following general procedure A, 4-iodoacetophenone (246 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 4-hydroxyacetophenone as a white solid (96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.7 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 2.57 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 161.1, 131.1, 129.8, 115.5, 26.3 ppm. EI-MS: *m/z* = 136 (M^+).



4-chlorophenol [2]

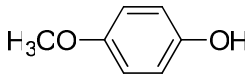
Following general procedure A, 1-chloro-4-iodobenzene (238 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 4-chlorophenol as a white solid (93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.17 (m, 2H), 6.78-6.74 (m, 2H), 4.83 (br-s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.0, 129.6, 125.9, 116.8 ppm. EI-MS: *m/z* = 128 (M^+).



4-bromophenol [4]

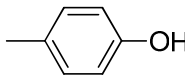
Following general procedure A, 1-bromo-4-iodobenzene (283 mg, 1 mmol), CuI

nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-bromophenol as a yellow solid (93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 5.07 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 132.5, 117.2, 112.8 ppm. EI-MS: m/z = 172 (M^+).



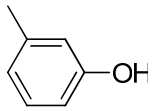
4-methoxyphenol [5]

Following general procedure A, 1-iodo-4-methoxybenzene (234 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-methoxyphenol as a white solid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80-6.75 (m, 4H), 4.56 (br-s, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 149.6, 116.2, 115.0, 55.9 ppm. EI-MS: m/z = 124 (M^+).



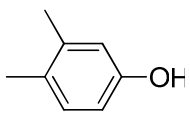
***p*-cresol** [6]

Following general procedure A, *p*-iodotoluene (218 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded *p*-cresol as a white solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 5.16 (br-s, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 130.2, 121.8, 115.3, 20.5 ppm. EI-MS: m/z = 108 (M^+).



***m*-cresol** [7]

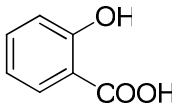
Following general procedure A, *m*-iodotoluene (128 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded *m*-cresol as a yellow oil (89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, J = 8.0 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H), 5.50 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 139.9, 129.5, 121.8, 116.2, 112.5, 21.3 ppm. EI-MS: m/z = 108 (M^+).



3,4-dimethylphenol [8]

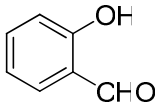
Following general procedure A, 3,4-dimethyliodobenzene (142 μl, 1 mmol), CuI

nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 3,4-dimethylphenol as a white solid (97% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (d, J = 7.8 Hz, 1H), 6.65 (s, 1H), 6.60-6.57 (m, 1H), 4.88 (br-s, 1H), 2.21 (s, 3H) , 2.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 137.9, 130.4, 128.6, 116.6, 112.3, 19.8, 18.7 ppm. EI-MS: m/z = 122 (M^+).



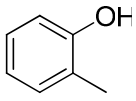
2-hydroxybenzoic acid [9]

Following general procedure A, 2-iodobenzoic acid (248 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 2-hydroxybenzoic acid as a white solid (99% yield). ^{1}H NMR (300 MHz, CD_3SOCD_3): δ 13.87 (br-s, 1H), 11.36 (br-s, 1H), 7.81-7.78 (dd, J = 1.2, 5.7 Hz, 1H), 7.53-7.49 (m, 1H), 6.96-6.90 (m, 2H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 172.4, 161.7, 136.1, 130.8, 119.7, 117.6, 113.5 ppm. EI-MS: m/z = 138 (M^+).



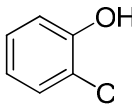
2-hydroxybenzaldehyde [10]

Following general procedure A, 2-iodobenzaldehyde (232 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 2-hydroxybenzaldehyde as a yellow oil (93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.00 (s, 1H), 9.85 (s, 1H), 7.53-7.47 (dd, J = 6.8, 14.8 Hz, 2H), 7.00-6.94 (dd, J = 7.6, 15.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6, 161.5, 136.9, 133.7, 120.6, 119.8, 117.5 ppm. EI-MS: m/z = 122 (M^+).



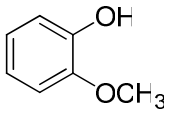
***o*-cresol** [11]

Following general procedure A, *o*-iodotoluene (128 µl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (2.0mL, 3.0 eq.) at 80°C for 36h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded *o*-cresol as a white solid (93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.05 (m, 2H), 6.86-6.82 (m, 1H), 6.76(d, J = 6.0 Hz, 1H), 4.66 (s, 1H), 2.25 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 131.1, 127.2, 123.8, 120.9, 115.0, 15.7 ppm. EI-MS: m/z = 108 (M^+).



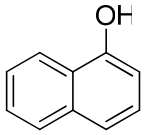
2-chlorophenol [12]

Following general procedure A, 1-chloro-2-iodobenzene (122 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 36h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 2-chlorophenol as a colorless liquid (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (t, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 9.3 Hz, 1H), 6.87 (t, *J* = 5.1 Hz, 1H), 5.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 129.0, 128.4, 121.4, 119.9, 116.3 ppm. EI-MS: *m/z* = 128 (M^+).



2-methoxyphenol [5]

Following general procedure A, 2-iodoanisole (130 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 36h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 2-methoxyphenol as a colorless liquid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 6.0 Hz, 1H), 6.92-6.88 (m, 3H), 5.72 (s, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 145.7, 121.5, 120.2, 114.7, 110.9, 55.9 ppm. EI-MS: *m/z* = 124 (M^+).



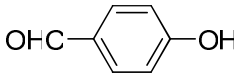
1-naphthalenol [13]

Following general procedure A, 1-iodonaphthalene (146 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 1-naphthalenol as a white solid (88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18-8.15 (dd, *J* = 3.9, 4.8 Hz, 1H), 7.81 (t, *J* = 2.4 Hz, 1H), 7.49-7.42 (m, 3H), 7.29 (t, *J* = 5.7 Hz, 1H), 6.79 (d, *J* = 5.4 Hz, 1H), 5.25 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 134.9, 127.8, 126.5, 125.9, 125.3, 124.5, 121.6, 120.8, 108.7 ppm. EI-MS: *m/z* = 144 (M^+).

General procedure for hydroxylation of aryl bromides: protocol B (Table 3)

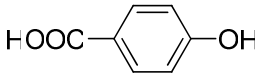
After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5 mol%, 2.9 mg for activated aryl bromides and 110 mol%, 209.5 mg for non-activated aryl bromides), the aryl bromides if a solid (1 mmol, 1 eq.). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three

times). Under a counter flow of nitrogen, aryl bromides if a liquid (1 mmol, 1 eq.) and degassed 40% tetra-*n*-butylammonium hydroxides water solution (2.0 mL, 3.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at 80°C for 48h. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethyl acetate and 1 ml of HCl (37%) were added. The mixture were stirred for 2 hours, then filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. Gathered aqueous phases were extracted with ethyl acetate for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5 h.



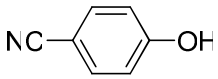
4-hydroxybenzaldehyde [2]

Following general procedure B, 4-bromobenzaldehyde (185 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 4-hydroxybenzaldehyde as a white solid (96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.25 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 161.8, 133.0, 130.2, 116.1 ppm. EI-MS: *m/z* = 122 (M^+).



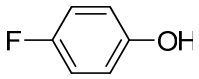
4-hydroxybenzoic acid [3]

Following general procedure B, 4-bromobenzoic acid (201 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-hydroxybenzoic acid as a white solid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.38 (s, 1H), 10.18 (s, 1H), 7.81-7.77 (m, 2H), 6.84-6.70 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7, 162.1, 132.0, 121.9, 115.6 ppm. EI-MS: *m/z* = 138 (M^+).



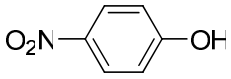
4-hydroxybenzonitrile [14]

Following general procedure B, 4-bromobenzonitrile (182 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 4-hydroxybenzonitrile as a white solid (95% yield). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 11.27 (br-s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.1, 132.6, 132.3, 130.6, 128.1 ppm. EI-MS: *m/z* = 119 (M^+).



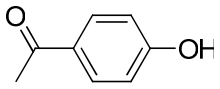
4-fluorophenol [10]

Following general procedure B, 1-fluoro-4-bromobenzene (115 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 4-fluorophenol as a white solid (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.84 (br-s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 156.1, 151.4, 116.2 ppm. EI-MS: *m/z* = 112 (M^+).



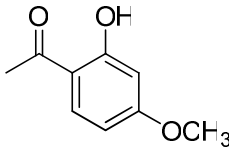
4-nitrophenol [2]

Following general procedure B, 1-bromo-4-nitrobenzene (202 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-nitrophenol as a yellow solid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.11 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 141.8, 126.4, 115.8 ppm. EI-MS: *m/z* = 139 (M^+).



4-hydroxyacetophenone [2]

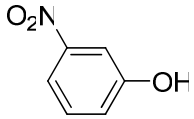
Following general procedure B, 4-bromoacetophenone (199 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 4-hydroxyacetophenone as a white solid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.7 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 2.57 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 161.1, 131.1, 129.8, 115.5, 26.3 ppm. EI-MS: *m/z* = 136 (M^+).



1-(2-hydroxy-4-methoxyphenyl)ethanone [15]

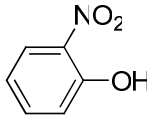
Following general procedure B, 1-(2-bromo-4-methoxyphenyl)ethanone (229 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 1-(2-hydroxy-4-methoxyphenyl)ethanone as a white

solid (89% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.73 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 6.44-6.40 (dd, *J* = 2.4, 11.1 Hz, 2H), 3.82 (s, 3H), 2.54 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.6, 166.1, 165.2, 132.3, 113.9, 107.5, 100.8, 55.5, 26.2 ppm. EI-MS: *m/z* = 166 (M^+).



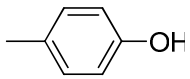
3-nitrophenol [16]

Following general procedure B, 1-bromo-3-nitrobenzene (119 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 3-nitrophenol as a yellow solid (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.73 (s, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.01 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 130.3, 122.3, 122.1, 115.9, 110.6 ppm. EI-MS: *m/z* = 139 (M^+).



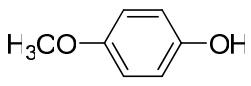
2-nitrophenol [17]

Following general procedure B, 1-bromo-2-nitrobenzene (202 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (2.0mL, 3.0 eq.) at 60°C for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 2-nitrophenol as a yellow solid (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.58 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 137.5, 125.0, 120.2, 119.9 ppm. EI-MS: *m/z* = 139 (M^+).



***p*-cresol** [6]

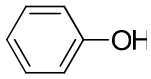
Following general procedure B, *p*-bromotoluene (123 μl, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% *n*Bu_4NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded *p*-cresol as a white solid (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.16 (br-s, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 130.2, 121.8, 115.3, 20.5 ppm. EI-MS: *m/z* = 108 (M^+).



4-methoxyphenol [5]

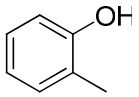
Following general procedure B, 1-bromo-4-methoxybenzene (129 μl, 1 mmol), CuI

nanoparticles (209.5 mg, 110 mol%), 40% *n*Bu_4NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=3/1) afforded 4-methoxyphenol as a white solid (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80-6.75 (m, 4H), 4.56 (br-s, 1H), 3.76 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 149.6, 116.2, 115.0, 55.9 ppm. EI-MS: *m/z* = 124 (M^+).



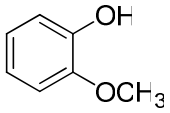
phenol [1, 2]

Following general procedure B, bromobenzene (105 µl, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% *n*Bu_4NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded phenol as a white solid (76% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (t, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 5.10 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 129.7, 120.9, 115.4 ppm. EI-MS: *m/z* = 94 (M^+).



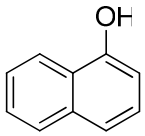
***o*-cresol** [10]

Following general procedure B, *o*-bromotoluene (121 µl, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% *n*Bu_4NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded *o*-cresol as a white solid (78% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.05 (m, 2H), 6.86-6.82 (m, 1H), 6.76(d, *J* = 6.0 Hz, 1H), 4.66 (s, 1H), 2.25 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 131.1, 127.2, 123.8, 120.9, 115.0, 15.7 ppm. EI-MS: *m/z* = 108 (M^+).



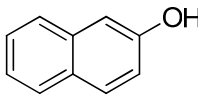
2-methoxyphenol [5]

Following general procedure B, 2-bromoanisole (125 µl, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% *n*Bu_4NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 2-methoxyphenol as a colorless liquid (68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 6.0 Hz, 1H), 6.92-6.88 (m, 3H), 5.72 (s, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 145.7, 121.5, 120.2, 114.7, 110.9, 55.9 ppm. EI-MS: *m/z* = 124 (M^+).



1-naphthalenol [13]

Following general procedure B, 1-bromonaphthalene (140 μl, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% nBu$_4$NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=4/1) afforded 1-naphthalenol as a white solid (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18-8.15 (dd, J = 3.9, 4.8 Hz, 1H), 7.81 (t, J = 2.4 Hz, 1H), 7.49-7.42 (m, 3H), 7.29 (t, J = 5.7 Hz, 1H), 6.79 (d, J = 5.4 Hz, 1H), 5.25 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.4, 134.9, 127.8, 126.5, 125.9, 125.3, 124.5, 121.6, 120.8, 108.7 ppm. EI-MS: m/z = 144 (M^+).



2-naphthalenol [11]

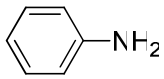
Following general procedure B, 2-bromonaphthalene (207 mg, 1 mmol), CuI nanoparticles (209.5 mg, 110 mol%), 40% nBu$_4$NOH water solution (3.3mL, 5.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 2-naphthalenol as a white solid (81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (t, J = 6.6 Hz, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 6.9 Hz, 1H), 7.35 (t, J = 6.9 Hz, 1H), 7.15-7.10 (m, 2H), 5.08 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 136.6, 129.9, 129.0, 127.8, 126.5, 126.4, 123.7, 117.7, 109.5 ppm. EI-MS: m/z = 144 (M^+).

V. General experimental procedures for *N*-arylation

General procedure for amination of aryl iodides: protocol C (Table 4)

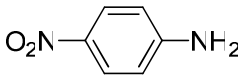
After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5 mol%, 2.9 mg), the aryl halides if a solid (1 mmol, 1 eq.). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, aryl iodides if a liquid(1 mmol, 1 eq.), degassed 40% tetra-*n*-butylammonium hydroxides water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at room temperature (25±3°C) for 24h. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethyl acetate was added, then filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. Gathered aqueous phases were extracted with ethyl acetate for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5

h.



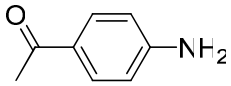
aniline [18]

Following general procedure C, iodobenzene (112 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded aniline as a yellow oil (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (t, *J* = 10.0 Hz, 2H), 6.73 (t, *J* = 10.0 Hz, 1H), 6.63 (d, *J* = 11.2 Hz, 2H), 3.53 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 129.0, 118.0, 114.8 ppm. EI-MS: *m/z* = 93 (M^+).



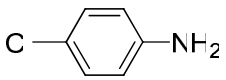
4-nitroaniline [19]

Following general procedure C, 1-iodo-4-nitrobenzene (202 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=6/1) afforded 4-nitroaniline as a yellow solid (97% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 4.37 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 139.3, 126.5, 113.5 ppm. EI-MS: *m/z* = 138 (M^+).



4-aminoacetophenone [20]

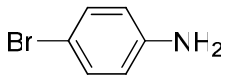
Following general procedure C, 4-iodoacetophenone (246 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 4-aminoacetophenone as a white solid (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 2.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 151.2, 130.9, 128.0, 113.8, 26.2 ppm. EI-MS: *m/z* = 135 (M^+).



4-chloroaniline [19]

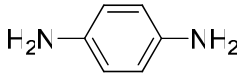
Following general procedure C, 1-chloro-4-iodobenzene (238 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1)

afforded 4-chloroaniline as a white solid (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.65 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 129.1, 123.1, 116.3 ppm. EI-MS: *m/z* = 127 (M^+).



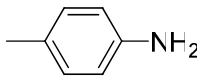
4-bromoaniline [20]

Following general procedure C, 1-bromo-4-iodobenzene (283 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 4-bromoaniline as a yellow solid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, *J* = 6.6 Hz, 2H), 6.56 (d, *J* = 6.6 Hz, 2H), 3.65 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 132.1, 116.8, 110.3 ppm. EI-MS: *m/z* = 171 (M^+).



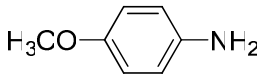
***p*-phenylenediamine** [22]

Following general procedure C, 4-iodoaniline (219 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded *p*-phenylenediamine as a brown solid (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 4H), 3.32 (s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 116.8 ppm. EI-MS: *m/z* = 108 (M^+).



***p*-toluidine** [20]

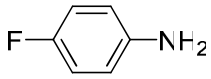
Following general procedure C, *p*-iodotoluene (218 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded *p*-toluidine as a white solid (93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 3.41 (s, 2H), 2.26 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 129.8, 127.7, 115.3, 20.4 ppm. EI-MS: *m/z* = 107 (M^+).



4-methoxyaniline [20]

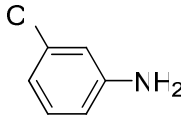
Following general procedure C, 1-iodo-4-methoxybenzene (234 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1)

afforded 4-methoxyaniline as a white solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.41 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.0, 116.5, 114.9, 55.9 ppm. EI-MS: *m/z* = 123 (M^+).



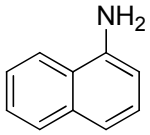
4-fluoroaniline [23]

Following general procedure C, 1-fluoro-4-iodobenzene (116 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 4-fluoroaniline as a yellow oil (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86 (t, *J* = 8.7 Hz, 2H), 6.64-6.60 (m, 2H), 3.51 (br-s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.1, 155.0, 142.2, 116.3 ppm. EI-MS: *m/z* = 111 (M^+).



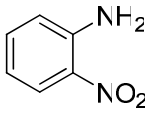
3-chloroaniline [24]

Following general procedure C, *m*-chloroiodobenzene (124 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 3-chloroaniline as a yellow oil (89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 2.4 Hz, 1H), 6.55-6.53 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.71 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 134.8, 130.3, 118.4, 114.9, 113.1 ppm. EI-MS: *m/z* = 127 (M^+).



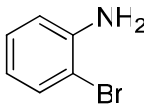
1-naphthalenamine[20]

Following general procedure C, 1-iodonaphthalene (146 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 1-naphthalenamine as a white solid (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, *J* = 2.4 Hz, 2H), 7.49-7.46 (m, 2H), 7.37-7.30 (m, 2H), 6.80 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.5, 128.6, 126.4, 125.9, 124.9, 123.7, 120.9, 119.0, 109.7 ppm. EI-MS: *m/z* = 143 (M^+).



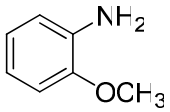
2-nitroaniline [25]

Following general procedure C, 2-nitroiodobenzene (249 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 2-nitroaniline as a pale yellow solid (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, J = 5.4 Hz, 1H), 7.35 (t, J = 8.7 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 6.70 (t, J = 7.2 Hz, 1H), 6.05 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 135.7, 132.4, 126.3, 118.8, 117.1 ppm. EI-MS: m/z = 138 (M^+).



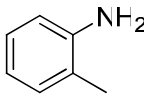
2-bromoaniline [26]

Following general procedure C, 1-bromo-2-iodobenzene (129 µl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at 45°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 2-bromoaniline as a yellow oil (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, J = 6.6 Hz, 1H), 7.12 (t, J = 8.1 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 6.61 (t, J = 7.8 Hz, 1H), 4.05 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 132.5, 128.3, 119.3, 115.7, 109.3 ppm. EI-MS: m/z = 171 (M^+).



2-methoxyaniline [27]

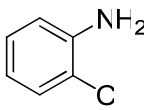
Following general procedure C, 2-iodoanisole (130 µl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 2-methoxyaniline as a yellow oil (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78-6.73 (dd, J = 2.0, 6.8 Hz, 2H), 6.73-6.68 (m, 2H), 3.82 (s, 3H), 3.76 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 136.2, 121.1, 118.5, 115.0, 110.5, 55.4 ppm. EI-MS: m/z = 123 (M^+).



***o*-toluidine** [28]

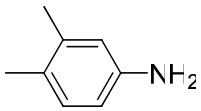
Following general procedure C, *o*-iodotoluene (128 µl, 1 mmol), CuI nanoparticles

(2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded *o*-toluidine as a yellow oil (86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, *J* = 7.6 Hz, 2H), 6.76-6.69 (m, 2H), 3.60 (s, 2H), 2.20 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 130.4, 126.9, 122.3, 118.6, 114.9, 17.3 ppm. EI-MS: *m/z* = 107 (M^+).



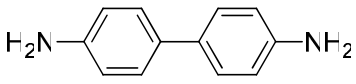
2-chloroaniline [29]

Following general procedure C, 1-chloro-2-iodobenzene (122 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at 45°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 2-chloroaniline as a yellow oil (73% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-6.68 (m, 4H), 4.02 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 129.4, 127.9, 127.6, 119.0, 115.9 ppm. EI-MS: *m/z* = 127 (M^+).



3,4-dimethylaniline [30]

Following general procedure C, 3,4-dimethyliodobenzene (142 μl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 3,4-dimethylaniline as a white solid (97% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.1 Hz, 1H), 6.53-6.45 (m, 2H), 3.45 (s, 2H), 2.19 (s, 3H),2.16 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 137.4, 130.4, 130.3, 117.0, 112.7, 19.8, 18.7 ppm. EI-MS: *m/z* = 121 (M^+).

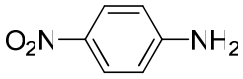


benzidine [31]

Following general procedure C, 4,4'-diiodobiphenyl (406 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at room temperature for 24h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded benzidine as a gray solid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.7 Hz, 4H), 6.45-6.41 (m, 8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.0, 131.8, 127.3, 115.5 ppm. EI-MS: *m/z* = 184 (M^+).

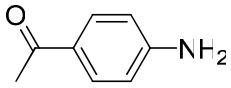
General procedure for amination of aryl bromides: protocol D (Table 5)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (3 mol%, 5.7 mg), the aryl bromides if a solid (1 mmol, 1 eq.). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, aryl bromides if a liquid (1 mmol, 1 eq.), degassed 40% tetra-*n*-butylammonium hydroxides water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at 80°C for 48h. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethyl acetate was added, then filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. Gathered aqueous phases were extracted with ethyl acetate for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5 h.



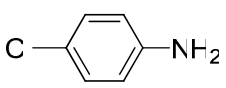
4-nitroaniline [19]

Following general procedure D, 1-bromo-4-nitrobenzene (202 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=6/1) afforded 4-nitroaniline as a yellow solid (87% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 4.37 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 139.3, 126.5, 113.5 ppm. EI-MS: *m/z* = 138 (M^+).



4-aminoacetophenone [20]

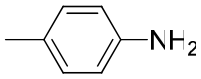
Following general procedure D, 4-bromoacetophenone (199 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 4-aminoacetophenone as a white solid (91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.11 (s, 2H), 2.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 151.2, 130.9, 128.0, 113.8, 26.2 ppm. EI-MS: *m/z* = 135 (M^+).



4-chloroaniline [21]

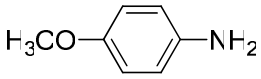
Following general procedure D, 1-bromo-4-chlorobenzene (192 mg, 1 mmol), CuI

nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 4-chloroaniline as a white solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.8 Hz, 2H), 3.65 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 129.1, 123.1, 116.3 ppm. EI-MS: m/z = 127 (M^+).



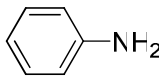
p-toluidine [20]

Following general procedure D, p-bromotoluene (123 μl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded p-toluidine as a white solid (53% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (d, J = 8.1 Hz, 2H), 6.63 (d, J = 8.1 Hz, 2H), 3.41 (s, 2H), 2.26 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 129.8, 127.7, 115.3, 20.4 ppm. EI-MS: m/z = 107 (M^+).



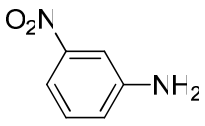
4-methoxyaniline [20]

Following general procedure D, 1-bromo-4-methoxybenzene (129 μl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 4-methoxyaniline as a white solid (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 3.41 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 140.0, 116.5, 114.9, 55.9 ppm. EI-MS: m/z = 123 (M^+).



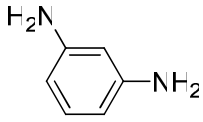
aniline [18]

Following general procedure D, bromobenzene (105 μl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded aniline as a yellow oil (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (t, J = 10.0 Hz, 2H), 6.73 (t, J = 10.0 Hz, 1H), 6.63 (d, J = 11.2 Hz, 2H), 3.53 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 129.0, 118.0, 114.8 ppm. EI-MS: m/z = 93 (M^+).



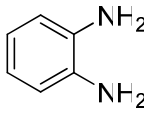
3-nitroaniline [25]

Following general procedure D, 1-bromo-3-nitrobenzene (202 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 3-nitroaniline as a yellow solid (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 8.1 Hz,1H), 7.49 (s, 1H), 7.27 (t, J = 8.1 Hz, 1H), 6.97-6.94 (dd, J = 1.8, 8.1 Hz,1H), 4.04 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5, 129.9, 120.6, 113.1, 109.0 ppm. EI-MS: m/z = 138 (M^+).



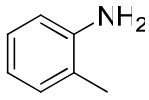
***m*-phenylenediamine** [32]

Following general procedure D, 3-bromoaniline (172 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded *m*-phenylenediamine as a gray solid (75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (d, J = 8.1 Hz, 4H), 6.13-6.10 (dd, J = 1.8, 7.8 Hz, 2H), 6.01 (s, 1H), 3.56 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6, 130.2, 105.9, 102.0 ppm. EI-MS: m/z = 108 (M^+).



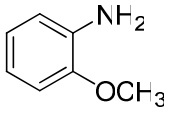
1,2-diaminobenzene [33]

Following general procedure D, 2-bromoaniline (172 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 1,2-diaminobenzene as a gray solid (72% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75-6.69 (m, 4H), 3.36 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.8, 120.3, 116.7 ppm. EI-MS: m/z = 108 (M^+).



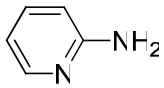
***o*-toluidine** [27]

Following general procedure D, *o*-bromotoluene (121 μl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded *o*-toluidine as a yellow oil (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (t, J = 7.6 Hz, 2H), 6.76-6.69 (m, 2H), 3.60 (s, 2H), 2.20 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 130.4, 126.9, 122.3, 118.6, 114.9, 17.3 ppm. EI-MS: m/z = 107 (M^+).



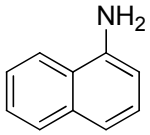
2-methoxyaniline [28]

Following general procedure D, 2-bromoanisole (125 µl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded 2-methoxyaniline as a yellow oil (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78-6.73 (dd, J = 2.0, 6.8 Hz, 2H), 6.73-6.68 (m, 2H), 3.82 (s, 3H), 3.76 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 136.2, 121.1, 118.5, 115.0, 110.5, 55.4 ppm. EI-MS: m/z = 123 (M^+).



pyridin-2-amine [20]

Following general procedure D, 2-bromopyridine (158 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=10/1) afforded pyridin-2-amine as a white solid (81% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 4.2 Hz, 1H), 7.43-7.31 (m, 1H), 6.64-6.60 (dd, J = 5.1, 6.3 Hz, 1H), 6.48 (d, J = 8.1 Hz, 1H), 4.39 (br-s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 148.0, 137.7, 113.8, 108.6 ppm. EI-MS: m/z = 94 (M^+).



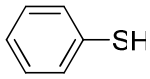
1-naphthalenamine [20]

Following general procedure D, 1-bromonaphthalene (140 µl, 1 mmol), CuI nanoparticles (5.7 mg, 3 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.6 mL, 10.0 eq.) at 80°C for 48h. Column chromatography using a solvent mixture (petroleum ether/ethyl acetate=5/1) afforded 1-naphthalenamine as a white solid (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, J = 2.4 Hz, 2H), 7.49-7.46 (m, 2H), 7.37-7.30 (m, 2H), 6.80 (d, J = 6.8 Hz, 1H),3.71 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 134.5, 128.6, 126.4, 125.9, 124.9, 123.7, 120.9, 119.0, 109.7 ppm. EI-MS: m/z = 143 (M^+).

VI. General experimental procedures for *S*-arylation: protocol E (Table 6)

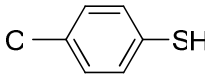
After standard cycles of evacuation and back-filling with dry and pure nitrogen, an

oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5 mol%, 2.9 mg for aryl iodides and 3.0 mol%, 5.7 mg for aryl bromides), the aryl halides if a solid (1 mmol, 1 eq.), sulfur powder (3 mmol, 96 mg). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, aryl halides if a liquid (1 mmol, 1 eq.), degassed 40% tetra-*n*-butylammonium hydroxides water solution (1.3 mL, 2.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at 40°C for 24h for aryl iodides and 80°C for 48h for aryl bromides. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethylether was added, then filtered through a plug of silica gel, and washed with 10-20 mL ethylether. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide aryl disulfides. To the aryl disulfide ethylether (10 mL) and Zn dust (0.65g, 10.0 mmol) were added, and then 5% HCl (20 mL) was added dropwise with cooling by ice-water. After the resultant reaction solution was stirred for 5 h, 37% HCl (1 mL) was added to quench the reaction. The mixture was extracted with ethylether, gathered aqueous phases were extracted with ethylether for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the thiophenols with satisfactory purity (>95%).



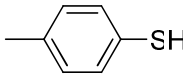
benzenethiol [34]

Following general procedure E, iodobenzene (112 µl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 1,2-diphenyldisulfane, followed by reductive cleavage to yield benzenethiol as a colorless liquid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.31 (m, 4H), 7.20 (t, J = 6.9 Hz, 1H), 3.50 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.9, 129.5, 129.2, 115.7 ppm. EI-MS: m/z = 110 (M^+).



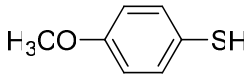
4-chlorobenzenethiol [34]

Following general procedure E, 1-chloro-4-iodobenzene (238 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 1,2-bis(4-chlorophenyl)disulfane, followed by reductive cleavage to yield 4-chlorobenzenethiol as a white solid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (s, 4H), 3.45 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 130.8, 129.3, 129.2 ppm. EI-MS: m/z = 144 (M^+).



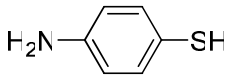
4-methylbenzenethiol [35]

Following general procedure E, *p*-iodotoluene (218 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 1,2-dip-tolyldisulfane, followed by reductive cleavage to yield 4-methylbenzenethiol as a colorless liquid (92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 3.40 (s, 1H), 2.31 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6, 129.9, 129.9, 126.6, 20.9 ppm. EI-MS: m/z = 124 (M^+).



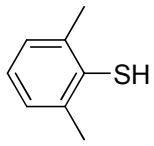
4-methoxybenzenethiol [35]

Following general procedure E, 1-iodo-4-methoxybenzene (234 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 1,2-bis(4-methoxyphenyl)disulfane, followed by reductive cleavage to yield 4-methoxybenzenethiol as a colorless liquid (91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H), 3.32 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 132.4, 116.3, 114.7, 55.3 ppm. EI-MS: m/z = 140 (M^+).



4-aminobenzenethiol [36]

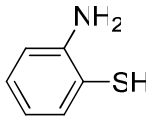
Following general procedure E, 4-iodoaniline (219 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 4,4'-disulfanediyldianiline, followed by reductive cleavage to yield 4-aminobenzenethiol as a black solid (91% yield). ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.15 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 5.00 (s, 1H), 2.99 (s, 2H) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3): δ 206.1, 135.2, 123.8, 115.4 ppm. EI-MS: m/z = 125 (M^+).



2,6-dimethylbenzenethiol [37]

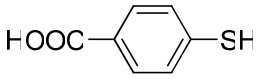
Following general procedure E, 2-iodo-1,3-dimethylbenzene (145 µl, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% nBu$_4$NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 1,2-bis(2,6-dimethylphenyl)disulfane, followed by reductive cleavage to yield 2,6-dimethylbenzenethiol as a colorless liquid (86% yield). ^{1}H NMR

(300 MHz, $CDCl_3$): δ 7.11-7.01 (m, 1H), 3.29 (s, 1H), 2.41 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.0, 131.1, 128.0, 125.0, 22.1 ppm. EI-MS: *m/z* = 138 (M^+).



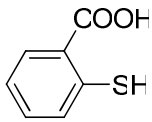
2-aminobenzenethiol [36]

Following general procedure E, 2-iodoaniline (219 mg, 1 mmol), CuI nanoparticles (2.9 mg, 1.5 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 40°C for 24 h. Column chromatography using petroleum ether afforded 2,2'-disulfanediyldianiline, followed by reductive cleavage to yield 2-aminobenzenethiol as a colorless liquid (89% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 9.3 Hz, 2H), 6.77-6.70 (m, 2H), 4.08 (br-s, 2H), 3.10 (s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9, 135.0, 131.7, 129.2, 118.9, 115.2 ppm. EI-MS: *m/z* = 125 (M^+).



4-mercaptobenzoic acid [35]

Following general procedure E, 4-iodobenzoic acid (248 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3.0 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 80°C for 48 h. Column chromatography using petroleum ether afforded 4,4'-disulfanediyldibenzoic acid, followed by reductive cleavage to yield 4-mercaptobenzoic acid as a white solid (87% yield). ^1H NMR (300 MHz, CD_3SOCD_3): δ 13.12 (br-s, 1H),7.93 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 3.39 (s, 1H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 167.0, 141.2, 130.7, 130.1, 126.5 ppm. EI-MS: *m/z* = 154 (M^+).



2-mercaptobenzoic acid [35]

Following general procedure E, 2-iodobenzoic acid (248 mg, 1 mmol), CuI nanoparticles (5.7 mg, 3.0 mol%), 40% *n*Bu_4NOH water solution (1.3 mL, 2.0 eq.) and sulfur power (96mg, 3.0 eq.) at 80°C for 48 h. Column chromatography using petroleum ether afforded 2,2'-disulfanediyldibenzoic acid, followed by reductive cleavage to yield 2-mercaptobenzoic acid as a white solid (84% yield). ^1H NMR (300 MHz, CD_3SOCD_3): δ 11.2 (br-s, 1H),8.01-7.90 (m, 1H), 7.53-7.19 (m, 3H), 3.46 (s, 1H) ppm. ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 168.0, 139.4, 133.6, 132.0, 128.5, 126.4, 125.4 ppm. EI-MS: *m/z* = 154 (M^+).

VII. Procedure for intermolecular competition experiment (Scheme 1)

After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (1.5 mol%, 2.9 mg), sulfur powder (3 mmol, 96 mg). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, iodobenzene (1 mmol, 114 μl), degassed 40% tetra-*n*-butylammonium hydroxides water solution (1.3 mL, 2.0 eq.) and 28% ammonia solution (0.3 mL, 5.0 eq.) were added by syringe. The tube was sealed and the mixture was allowed to stir at 40°C for 24h. The reaction mixture was then allowed to cool to ambient temperature, 10 ml of ethylether was added, then filtered through a plug of silica gel, and washed with 10-20 mL ethylether. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide phenyl disulfide. To the phenyl disulfide ethylether (10 mL) and Zn dust (0.65g, 10.0 mmol) were added, and then 5% HCl (20 mL) was added dropwise with cooling by ice-water. After the resultant reaction solution was stirred for 5 h, 37% HCl (1 mL) was added to quench the reaction. The mixture was extracted with ethylether, gathered aqueous phases were extracted with ethylether for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the thiophenol as colorless liquid (99.6 mg, 91% yield).

VIII. Procedure for one-pot synthesis of 4-aminophenol (Scheme 2)

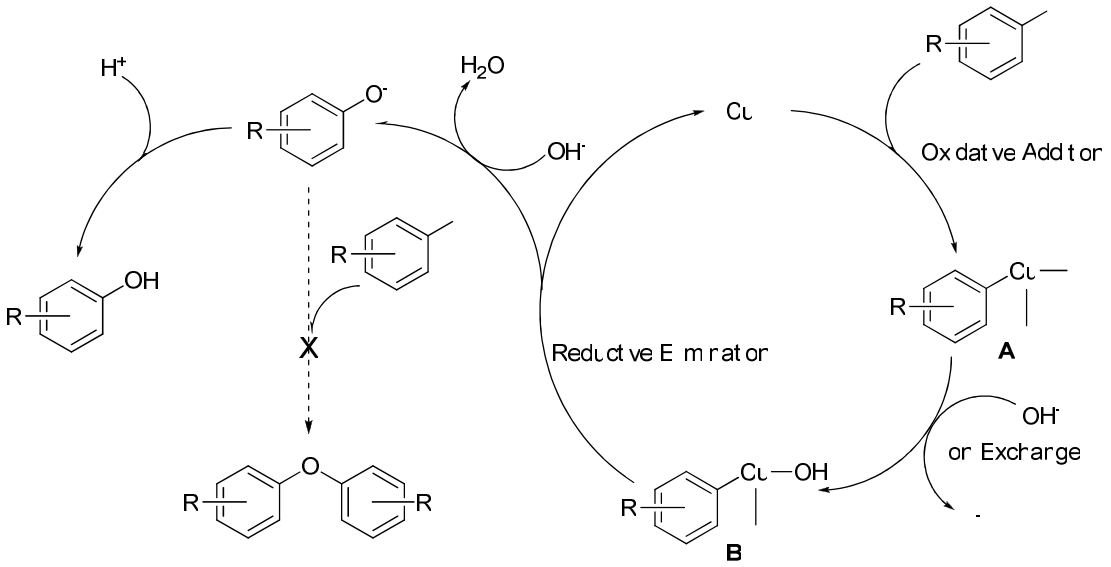
After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with CuI nanoparticles (3 mol%, 5.7 mg), 1-bromo-4-iodobenzene (1 mmol, 283 mg). The tube was evacuated and backfilled with nitrogen (this procedure was repeated three times). Under a counter flow of nitrogen, degassed 40% tetra-*n*-butylammonium hydroxides water solution (2.5 mL, 4.0 eq.) was added by syringe. The tube was sealed and the mixture was allowed to stir at 60°C for 24h. The reaction mixture was then allowed to cool to ambient temperature, 28% ammonia solution (0.6 mL, 10.0 eq.) was added by syringe under a counter flow of nitrogen. The tube was sealed again and the new mixture was allowed to stir at 80°C for 48h. After cooling to room temperature, 10 ml of ethyl acetate was added, and then 10% formic acid water solution (5 mL, 11 mmol) was added dropwise. The mixture were stirred for 2 hours, then filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. Gathered aqueous phases were extracted with ethyl acetate for three times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product. The obtained crude was purified by column chromatography on silica gel and the product was dried under vacuum for at least 0.5 h, affording 4-aminophenol as a brown solid (57% yield). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.48 (br-s, 1H), 6.59-6.57 (m, 2H), 6.56-6.51 (m, 2H), 4.02 (br-s, 1H) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3): δ 205.4, 120.6, 115.6, 115.3 ppm. EI-MS: m/z = 109 (M^+).

IX. Leaching study of CuI nanoparticles

To verify whether the observed catalysis is derived from CuI nanoparticles or leached copper species, the hydroxylation of iodobenzene was carried out under the conditions described in Table 2 and the catalyst was removed from the reaction mixture by filtration after 14 hours (at this time, approximately 50% yield of phenol was producted). After removal of the catalyst, iodobenzene (0.5 mmol) was newly added to the filtrate and the reaction was carried out again with the resulting filtrate under the conditions described in Table 2. In this case, no further production of phenol was observed. For the amination of iodobenzene, the reaction was also completely stopped with the removal of the catalyst by filtration, and so did the thiolation of iodobenzene. In addition, it was confirmed by inductively coupled plasma (ICP) analysis that no copper was detected in the filtrate (below the detection limit). All these results can rule out any contribution to the observed catalysis from copper species that leached into the reaction solution; therefore, the observed catalysis is intrinsically heterogeneous. We thus consider that loss of catalyst during the separation process, rather than the leaching of copper species from CuI nanoparticles, was the main factor responsible for the slight decrease of catalytic activity during the recycling tests.

X. Suggested mechanism of hydroxylation of aryl halides

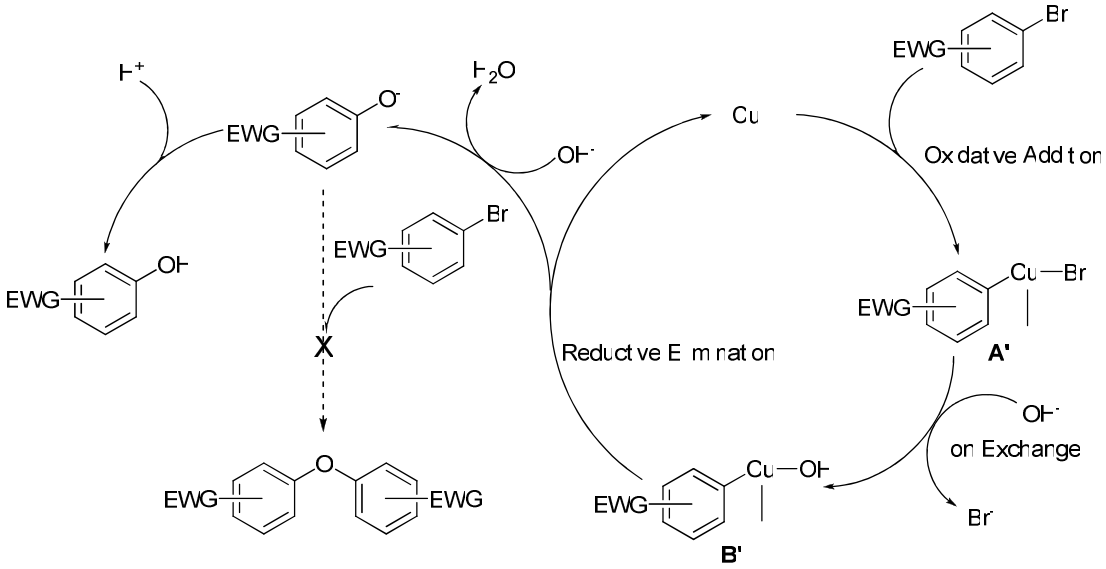
Scheme S1: Suggested mechanism of hydroxylation of aryl iodides (the stabilising tetra-*n*-butylammonium ions are omitted and CuI nanoparticles are instead by CuI molecular formula for clarity)



A possible mechanism of hydroxylation of aryl iodides catalyzed by CuI nanoparticles is depicted. Initial oxidative addition of aryl iodides to CuI affords complex A. Subsequent ion exchange between the complex A and hydroxide ion

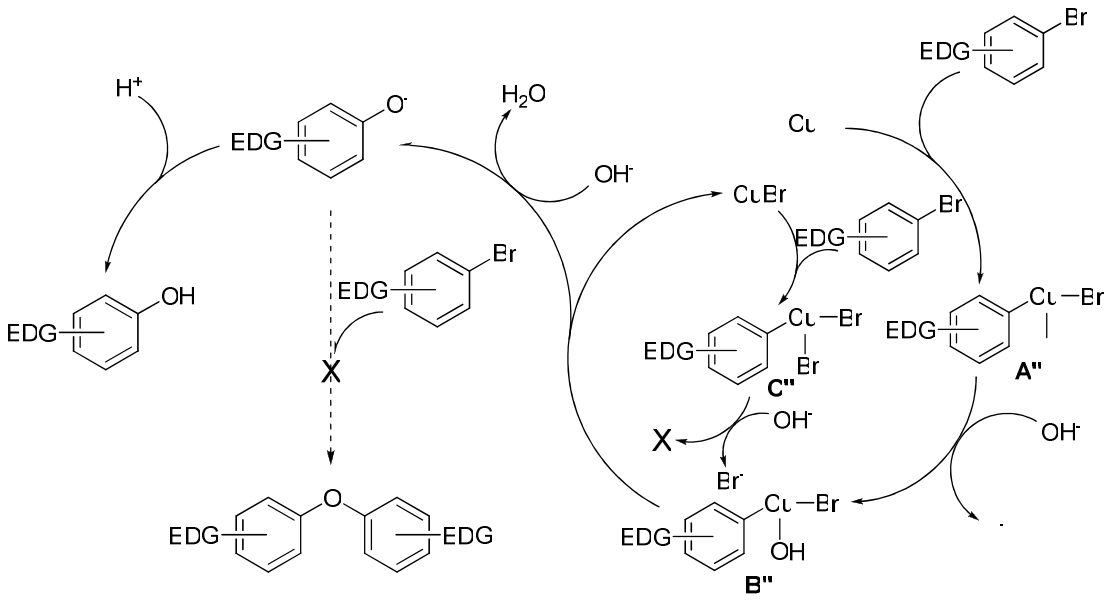
provides complex B, which can undergo reductive elimination to give aryl oxide anion and regenerate CuI. Finally, phenols are produced when aryl oxide anion is treated with HCl. Meanwhile, aryl oxide anion can react with aryl iodides afford symmetric ethers, which are the major by-products in other protocols that synthesis of phenols from aryl halides. However, the corresponding symmetric ethers are found in very small amount (<1%) in our reaction system, proving this protocol has better selectivity.

Scheme S2: Suggested mechanism of hydroxylation of activated aryl bromides (the stabilising tetra-*n*-butylammonium ions are omitted and CuI nanoparticles are instead by CuI molecular formula for clarity)



For activated aryl bromides, whose activity is similar with aryl iodides, the hydroxylation processes are very close to that of aryl iodides. Oxidative addition of activated aryl bromides to CuI affords the intermediate A', then one of the two halogen atoms connected to copper atom center is bromine, the other is iodine. Ion exchange will take place between the bromine and hydroxide ion to form complex B' affected by electron withdrawing group (EWG), which can undergo reductive elimination to give aryl oxide anion and regenerate CuI. And finally, phenols are obtained when aryl oxide anion is treated with HCl.

Scheme S3: Suggested mechanism of hydroxylation of inactivated aryl bromides (the stabilising tetra-*n*-butylammonium ions are omitted and CuI nanoparticles are instead by CuI molecular formula for clarity)



The experimental results shed some light on the mechanism of hydroxylation of inactivated aryl bromides with CuI nanoparticles. We suggest that aryl bromide co-ordinates to CuI, forming complex A". The electron-donating group (EDG) makes the Cu-Br bond hard to cleavage, then ion exchange can only take place between the iodide of complex A" and hydroxide ion to form complex B", which could undergo reductive elimination to give CuBr and the final produt after acidification. If oxidative addition of aryl bromide to CuBr affords complex C", the two halogen atoms connected to copper atom center both are bromine, making ion exchange difficult because Cu-Br bond is stronger than Cu-I bond. As such, the catalyst can be used only once time. One important difference between nanoparticles and monoatomic complexes is that the positive charge created in the oxidative addition can be shared among the copper atoms in the nanoparticles, this may facilitate the reductive elimination step to form the product. Unfortunately, chlorobenzene can't be reacted (Table 2, entry 21), it may because the Cu-Cl bond of complex B'" make the reductive elimination step hard.

XI. Experimental References

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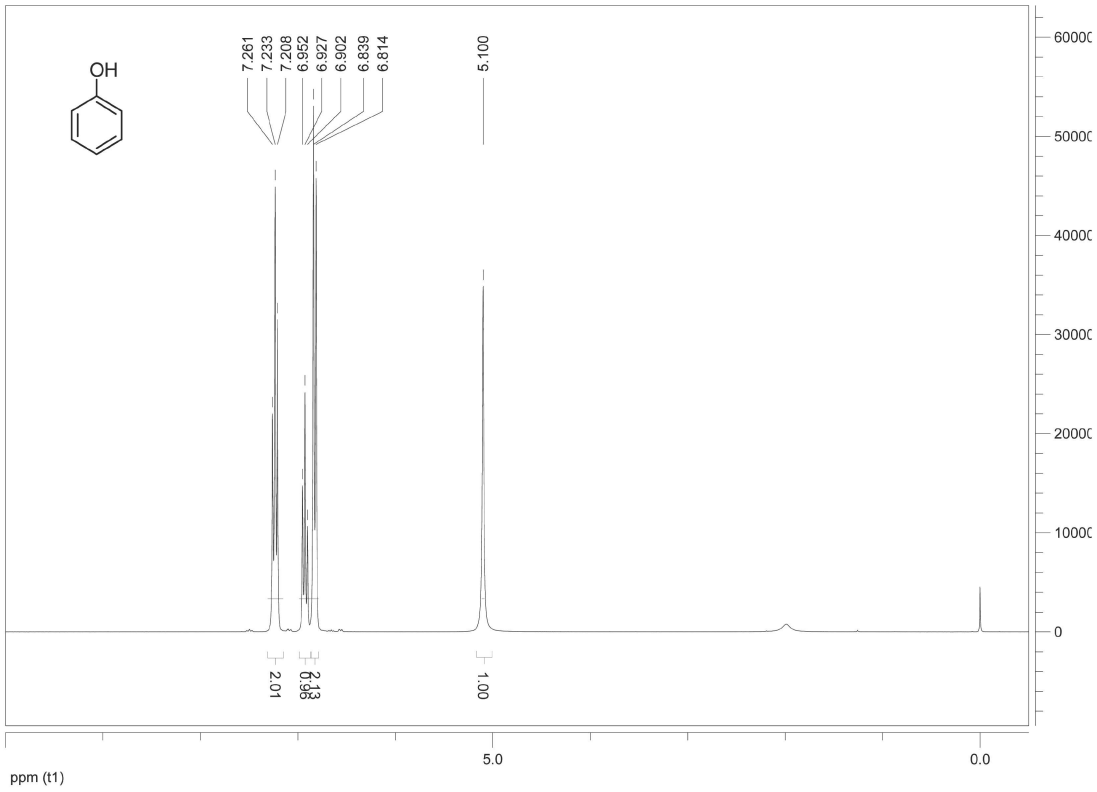
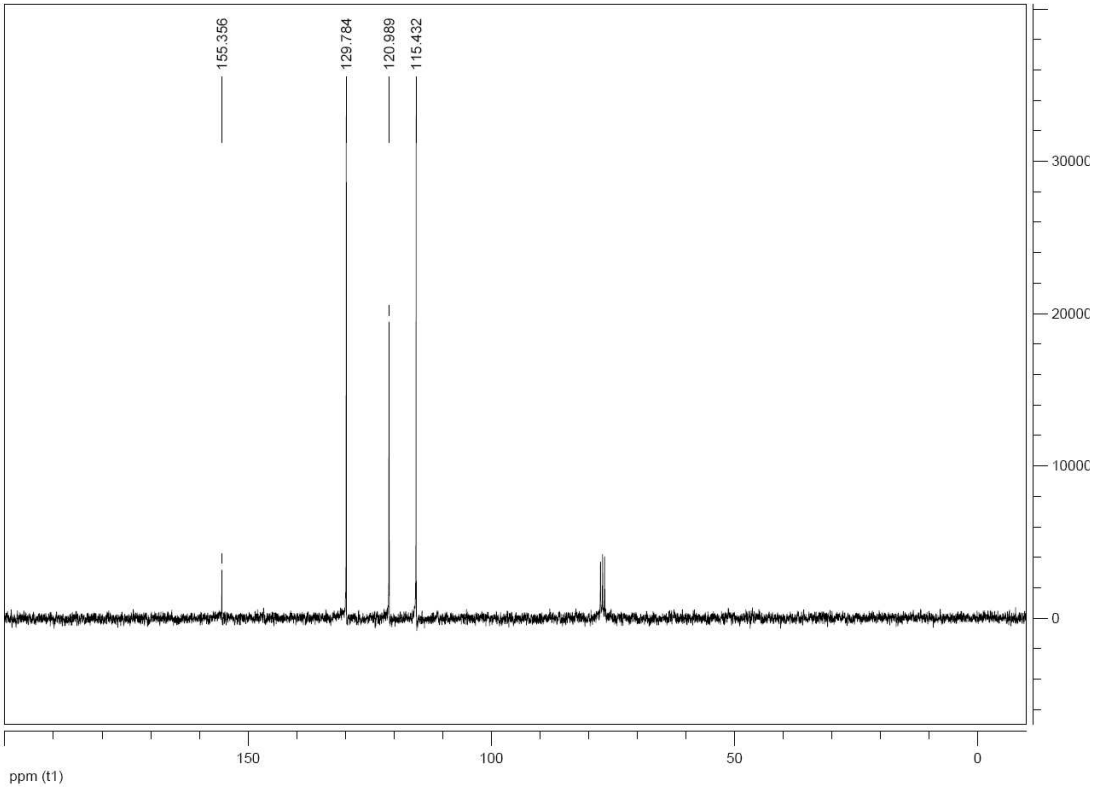
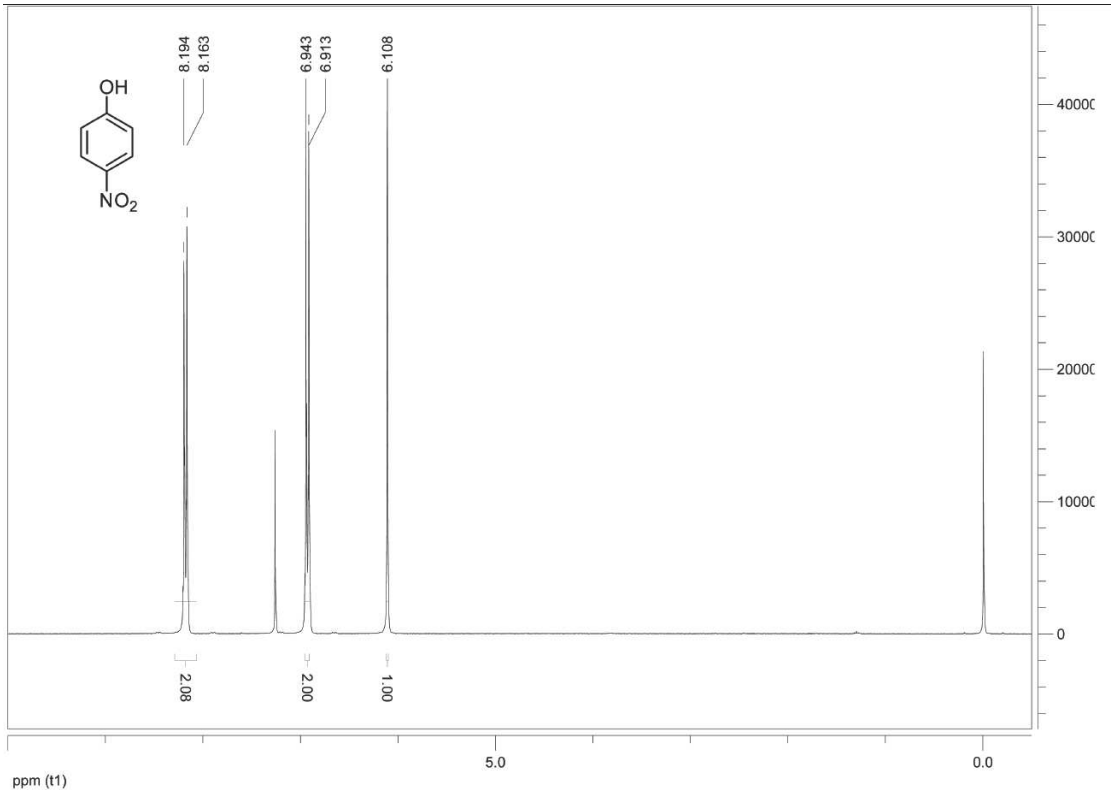
XII. Copies of ^{1}H NMR and ^{13}C NMR spectra

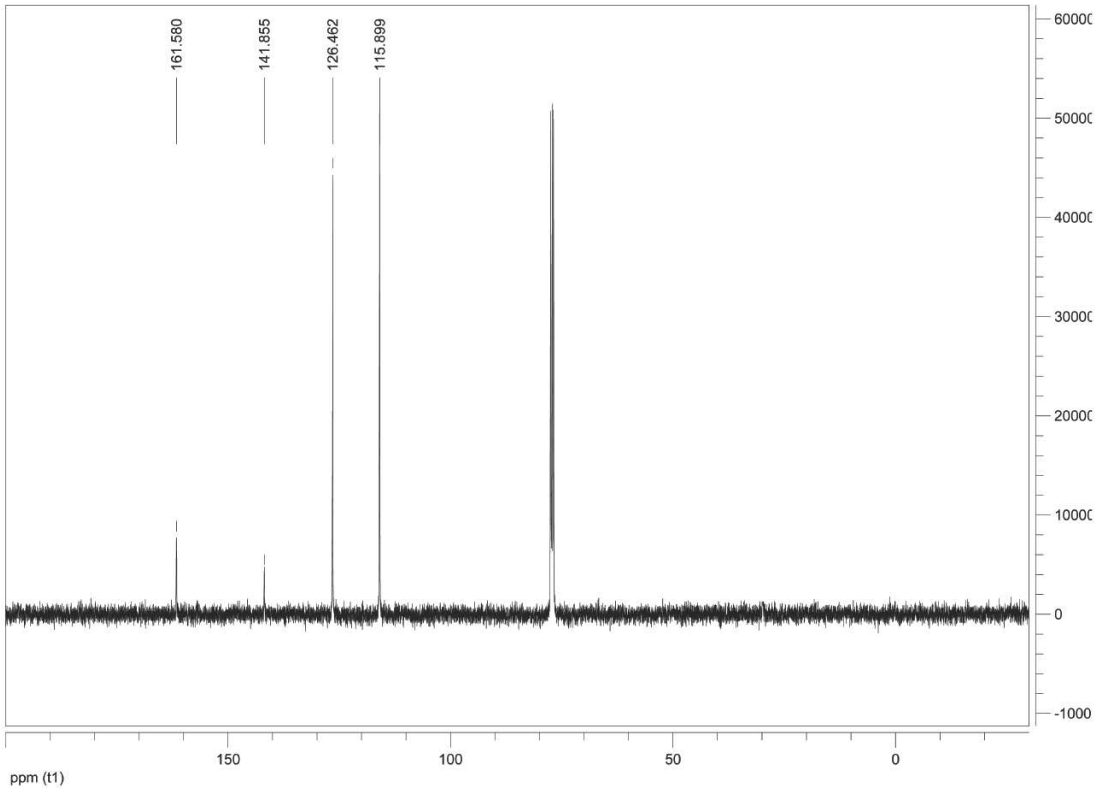
phenol



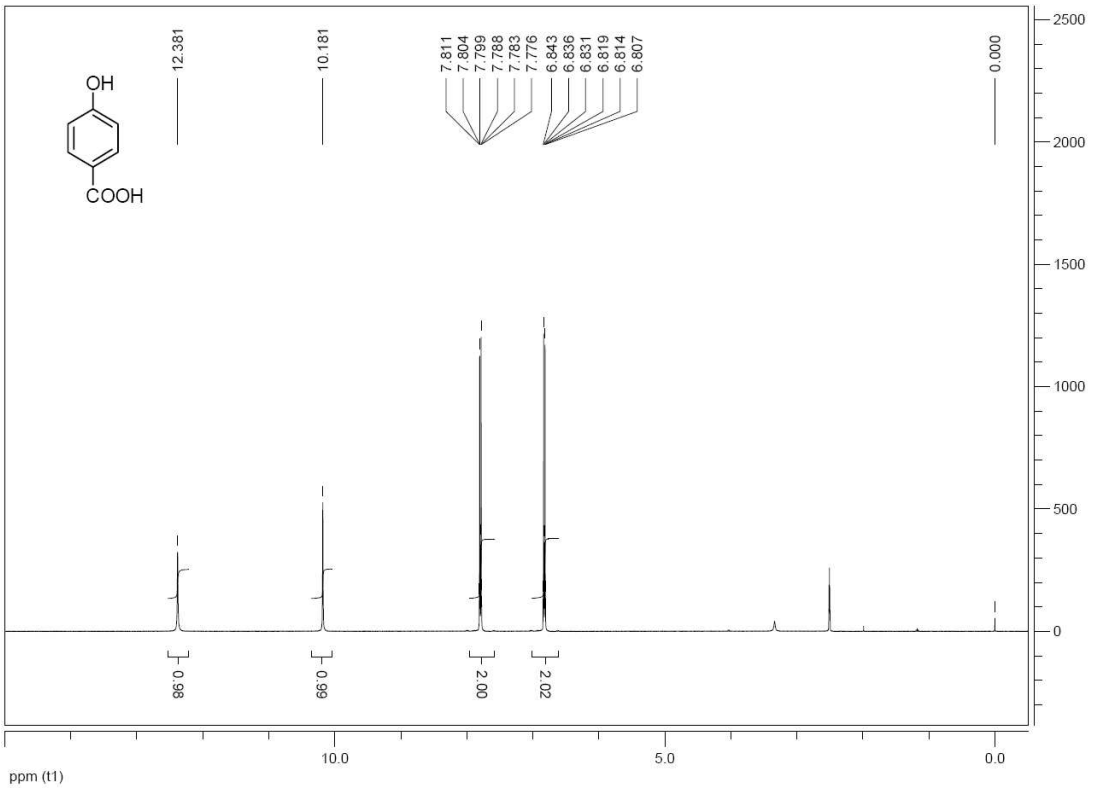


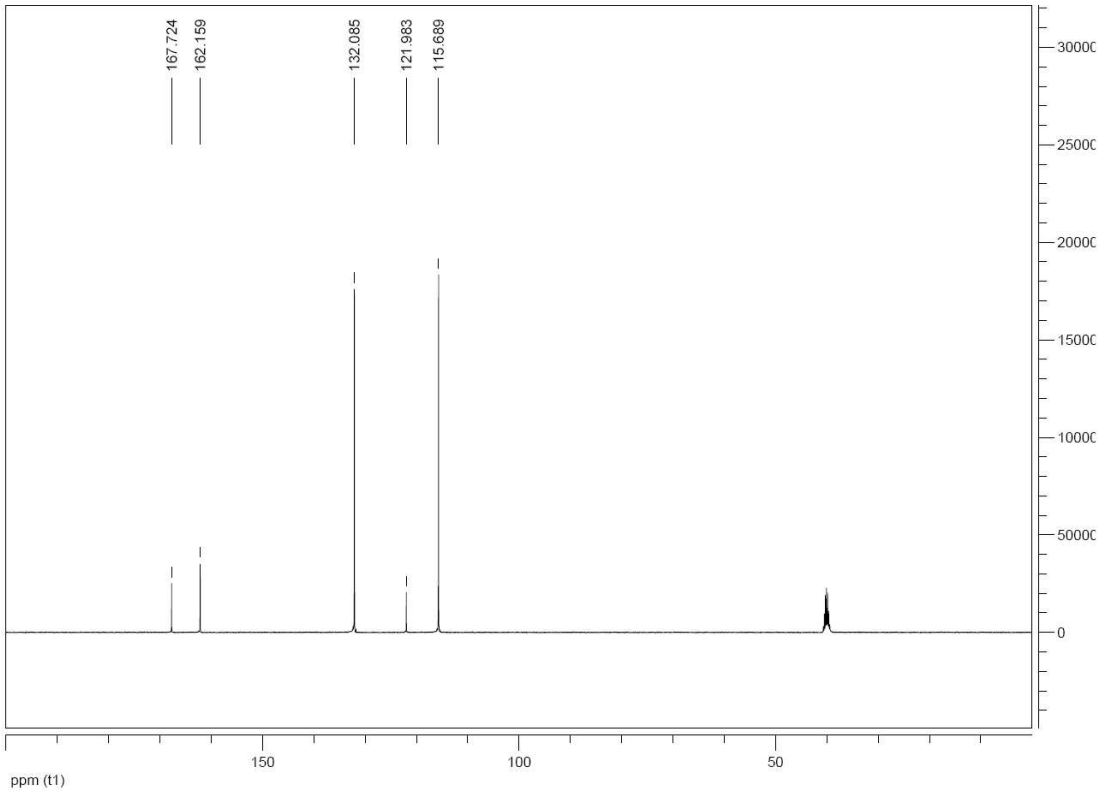
4-nitrophenol



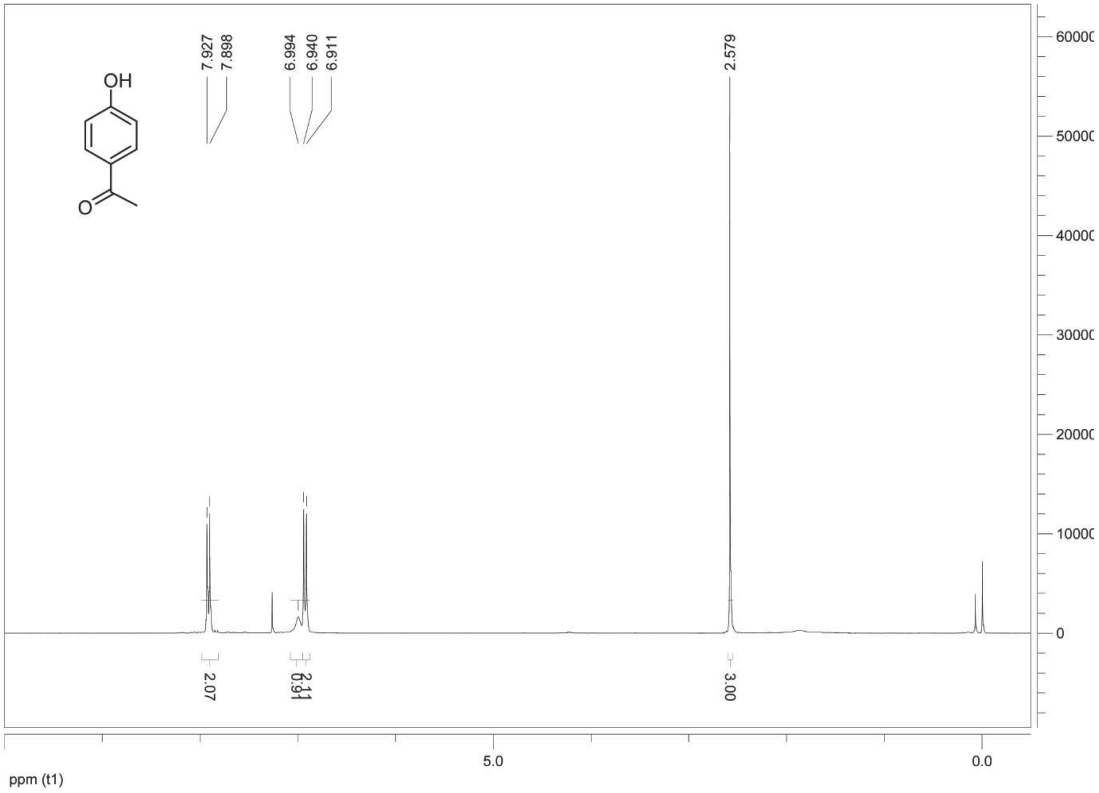


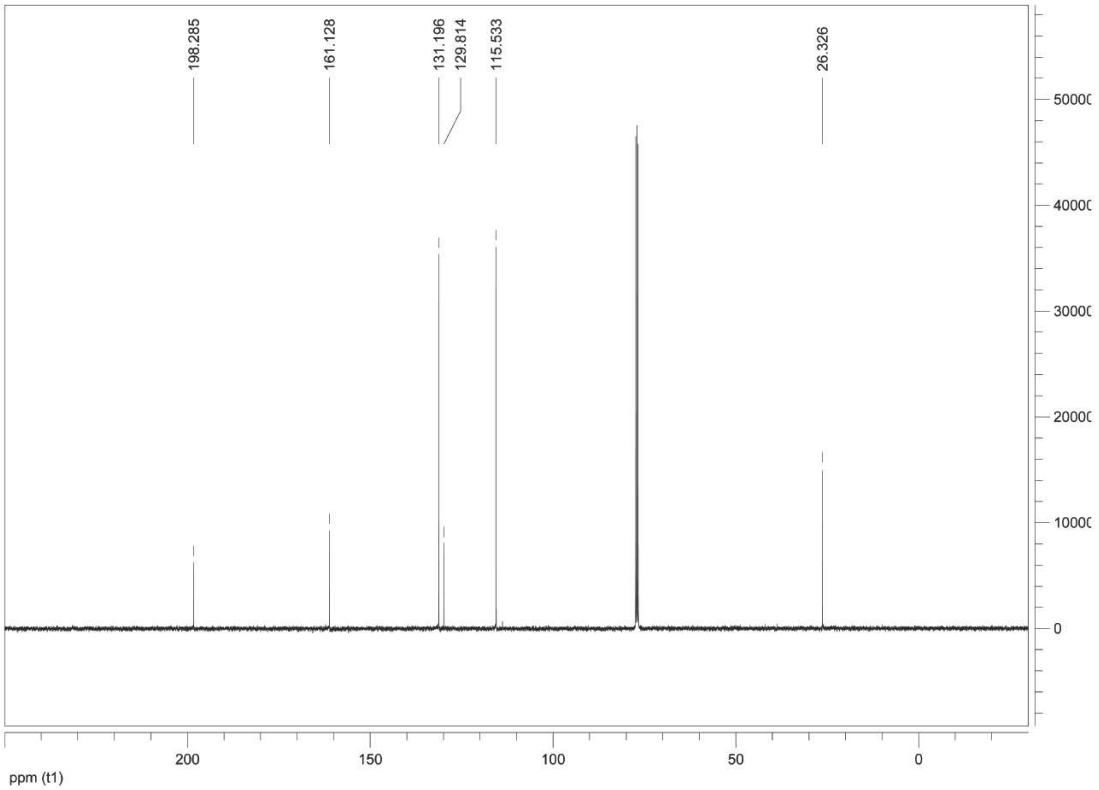
4-hydroxybenzoic acid



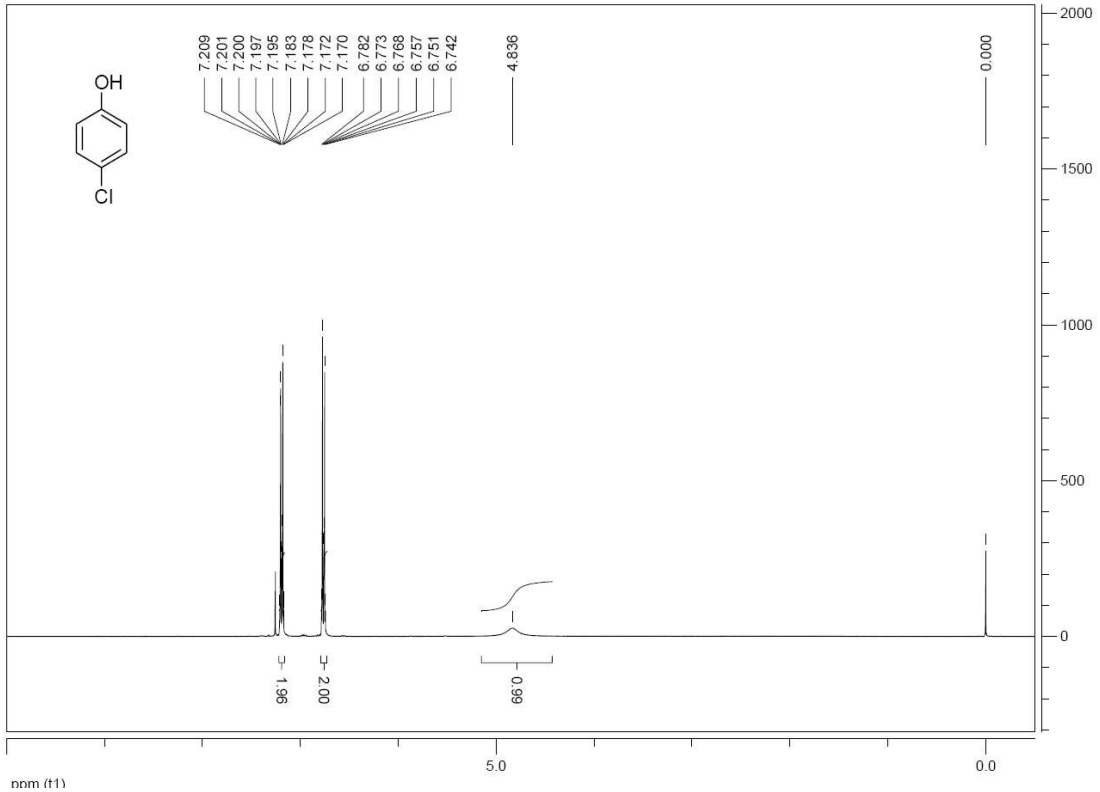


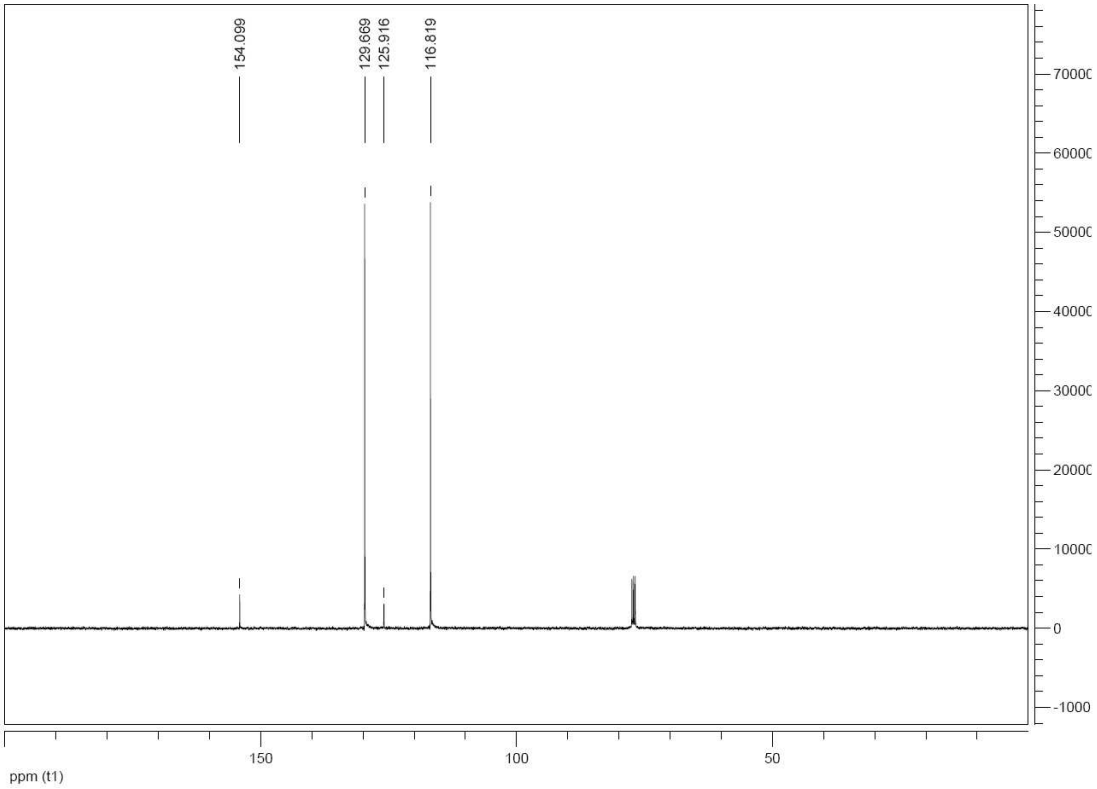
4-hydroxyacetophenone



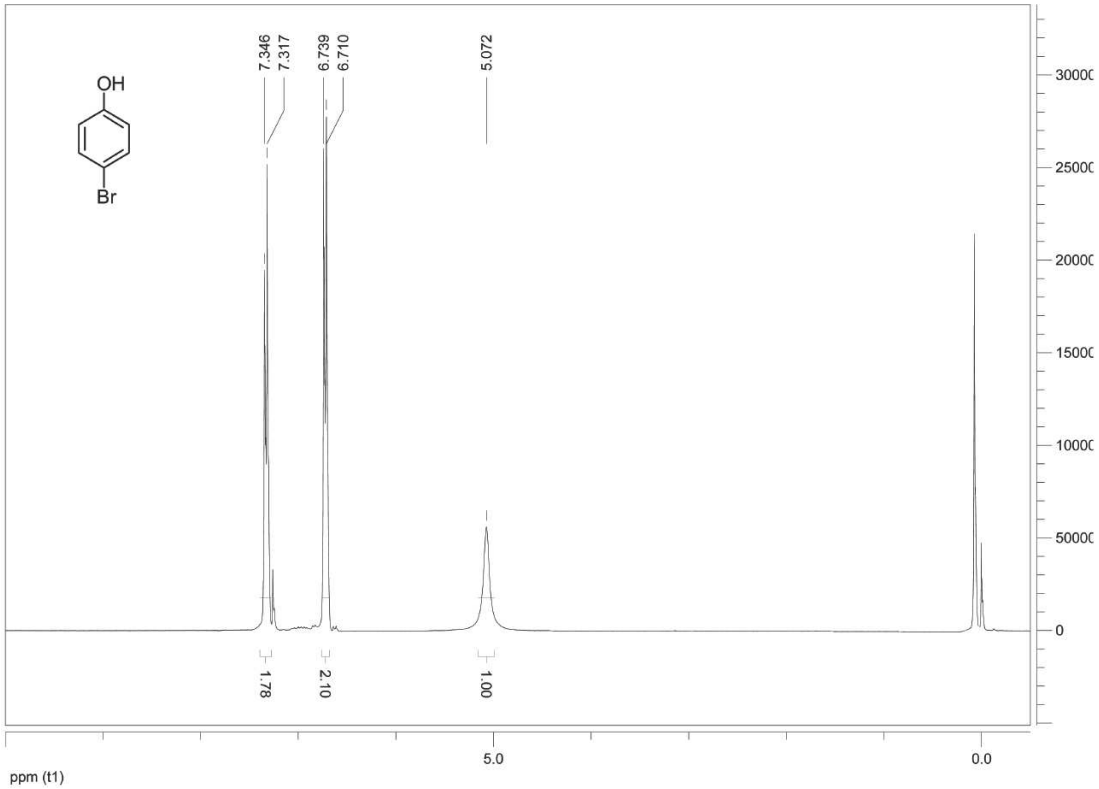


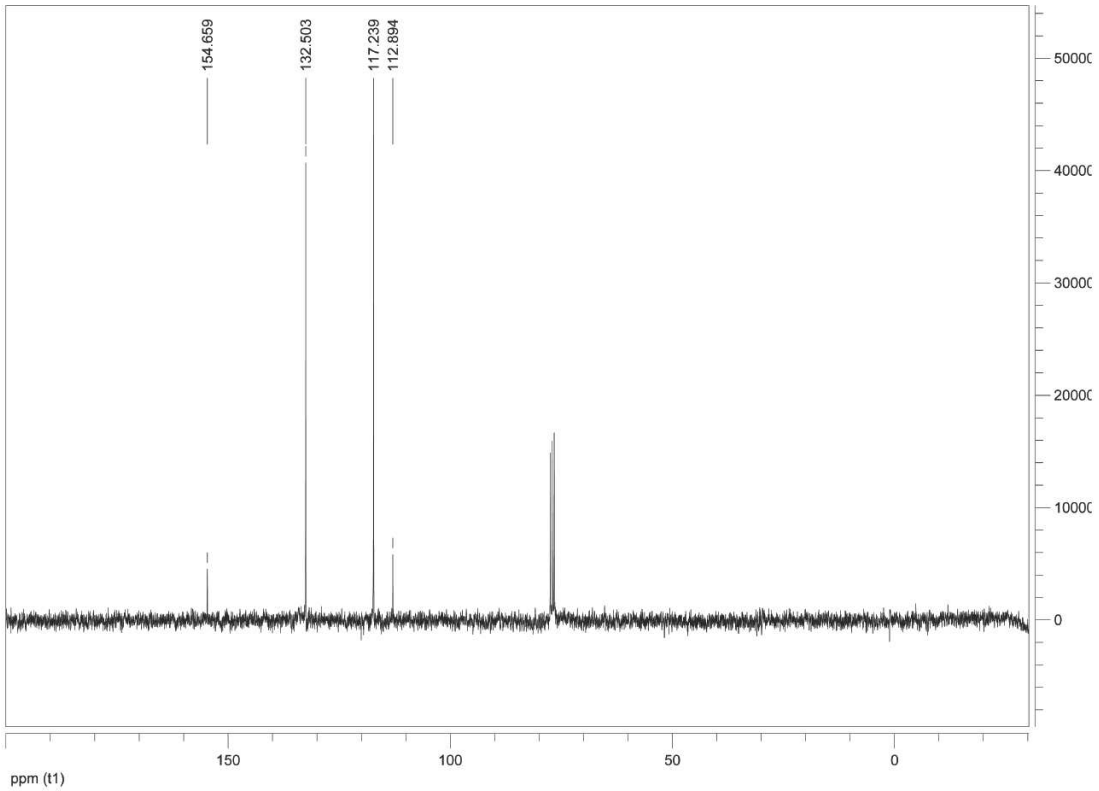
4-chlorophenol



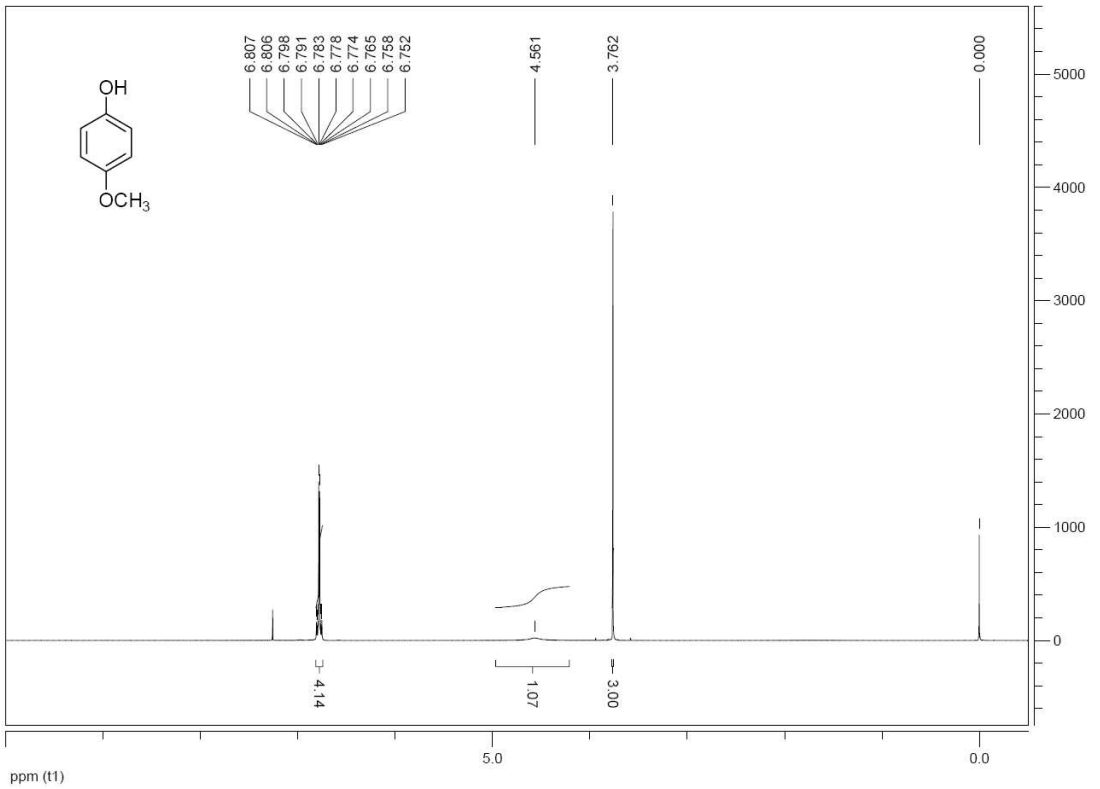


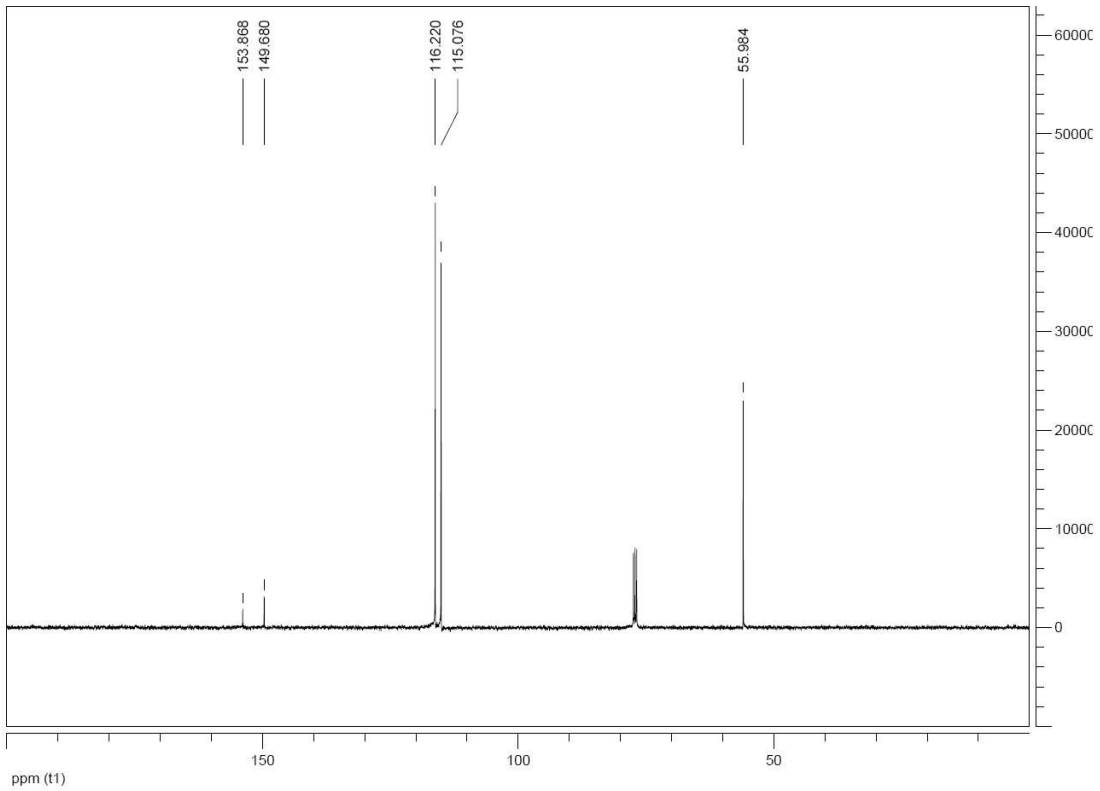
4-bromophenol



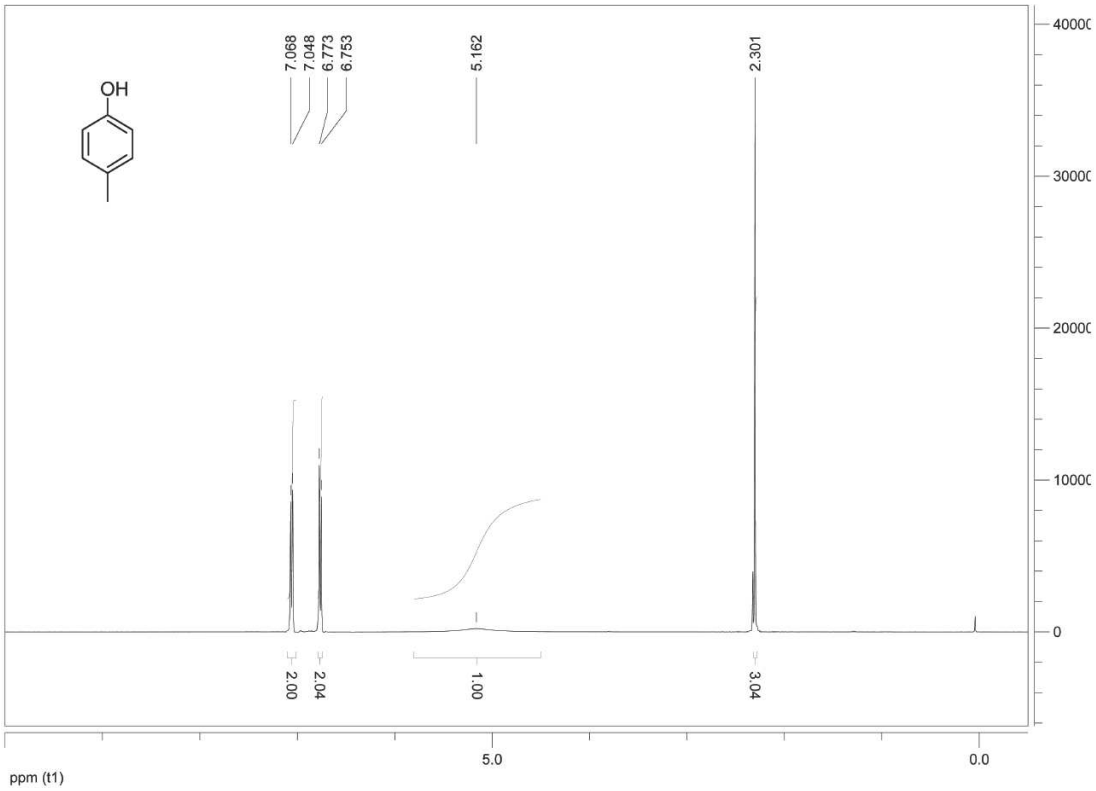


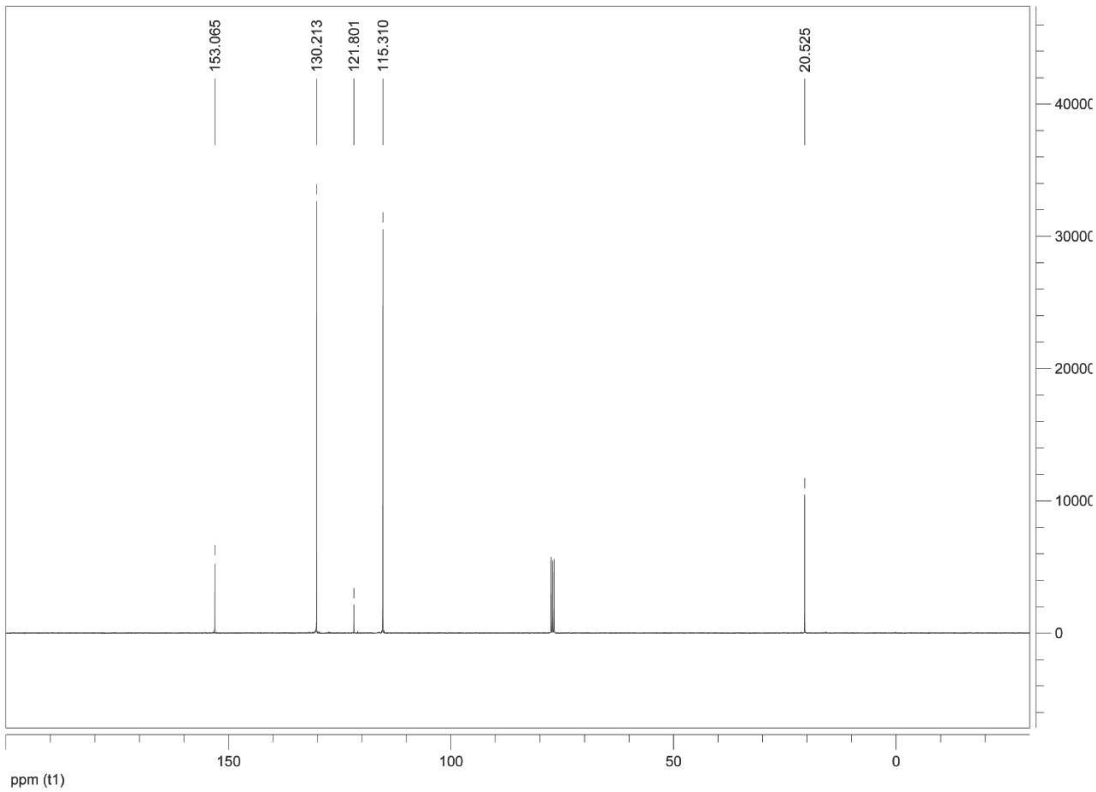
4-methoxyphenol





***p*-cresol**


OH
7.068
7.048
6.773
6.753
5.162
2.301
2.00
2.04
1.00
3.04
5.0
0.0
ppm (t1)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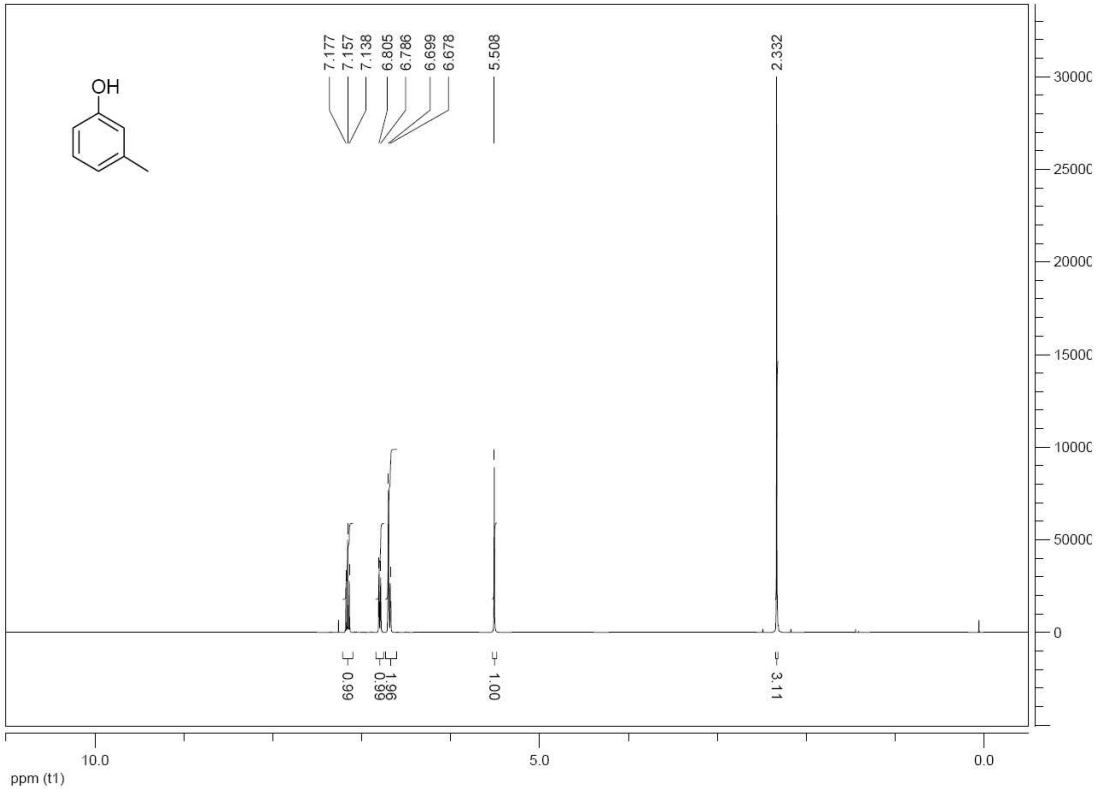
130.213
121.801
115.310
20.525
150
100
50
0
ppm (t1)

***m*-cresol**


OH
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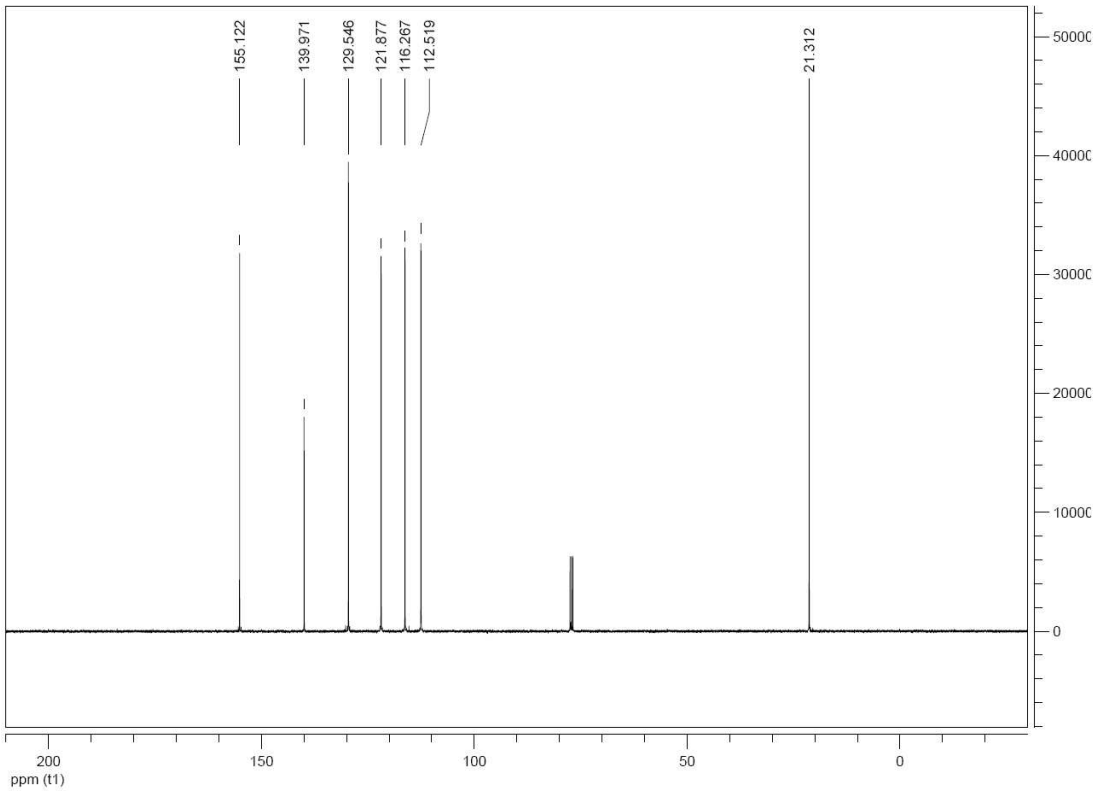
7.157
7.138
6.805
6.786
6.699
6.678
5.508
2.332
0.99
0.99
0.98
1.00
3.11
10.0
5.0
0.0
ppm (t1)


155.122
139.971
129.546
121.877
116.267
112.519
21.312
200
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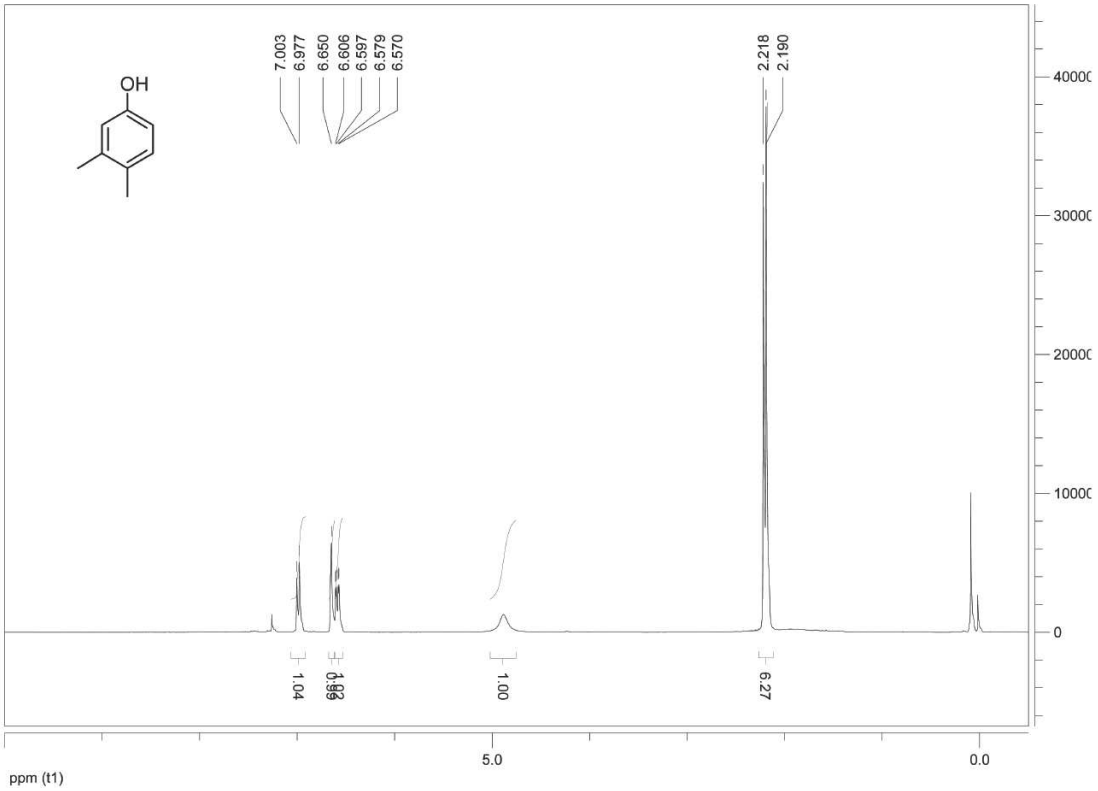
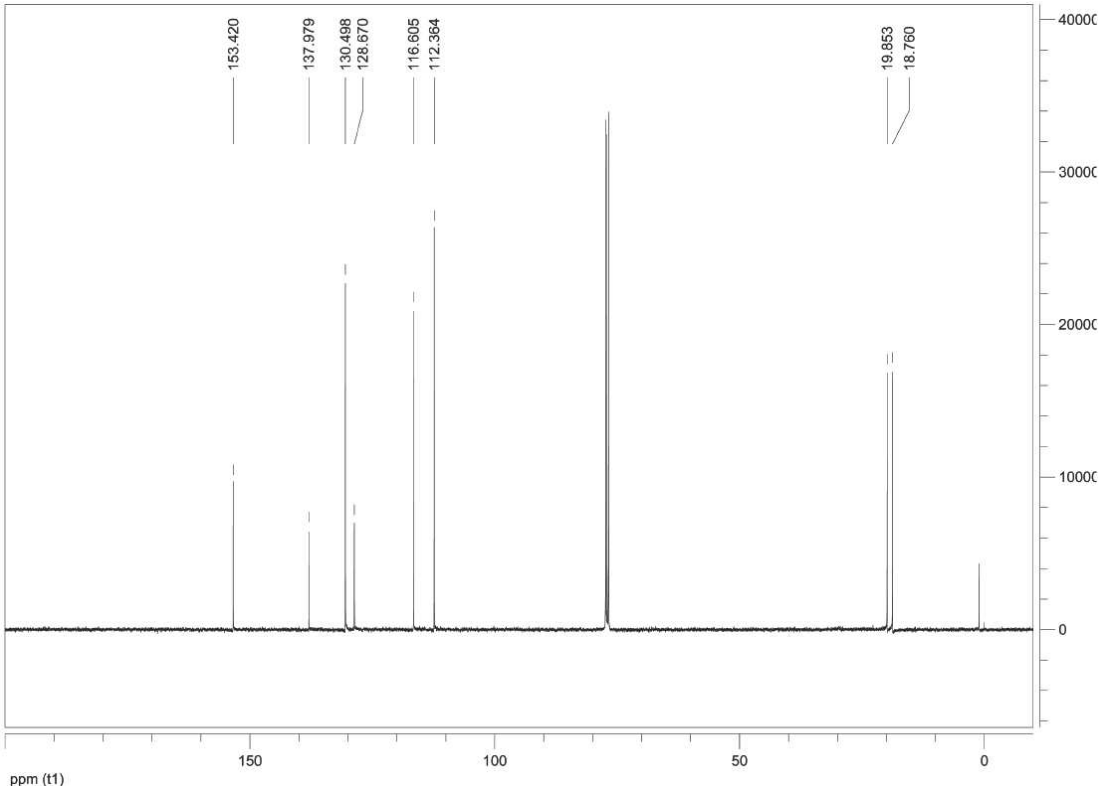
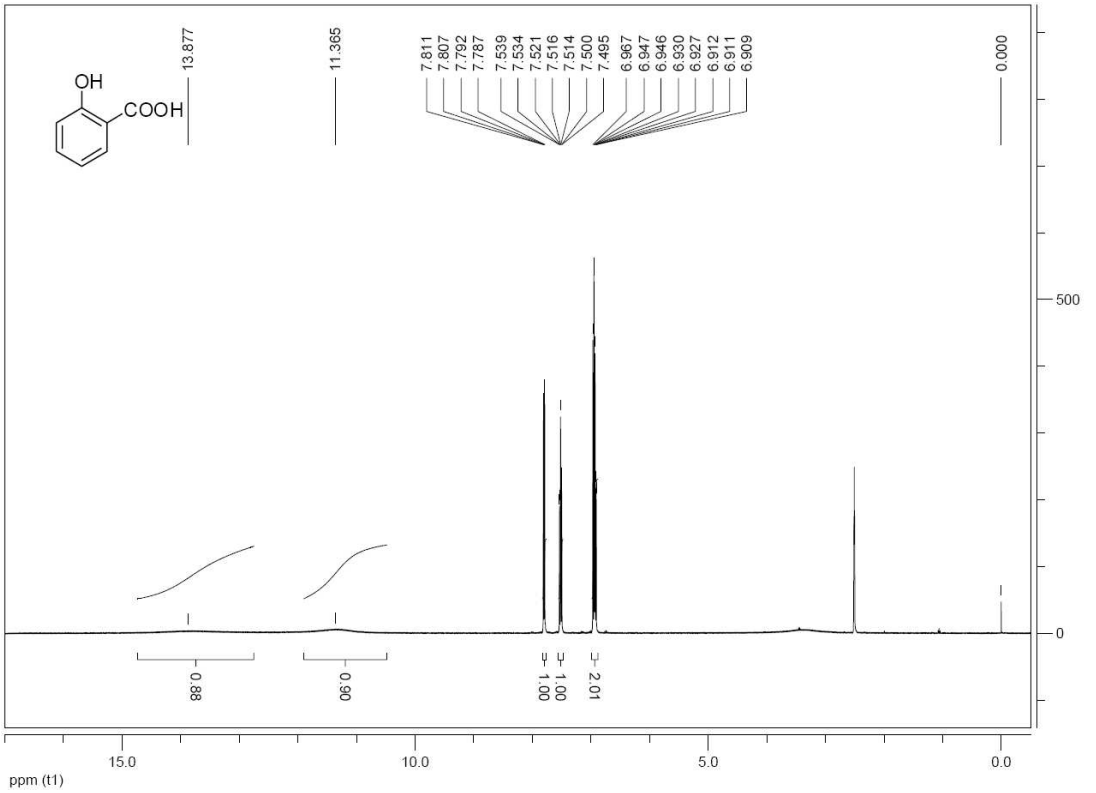
100
50
0
ppm (t1)

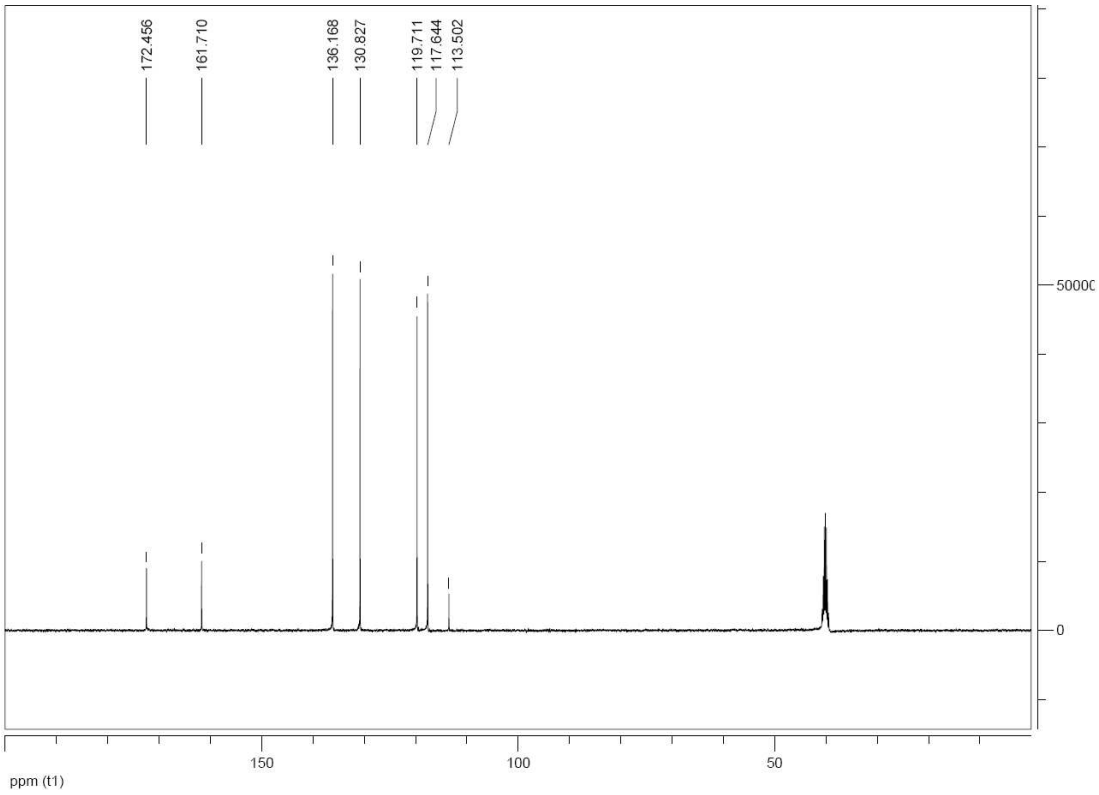
3,4-dimethylphenol



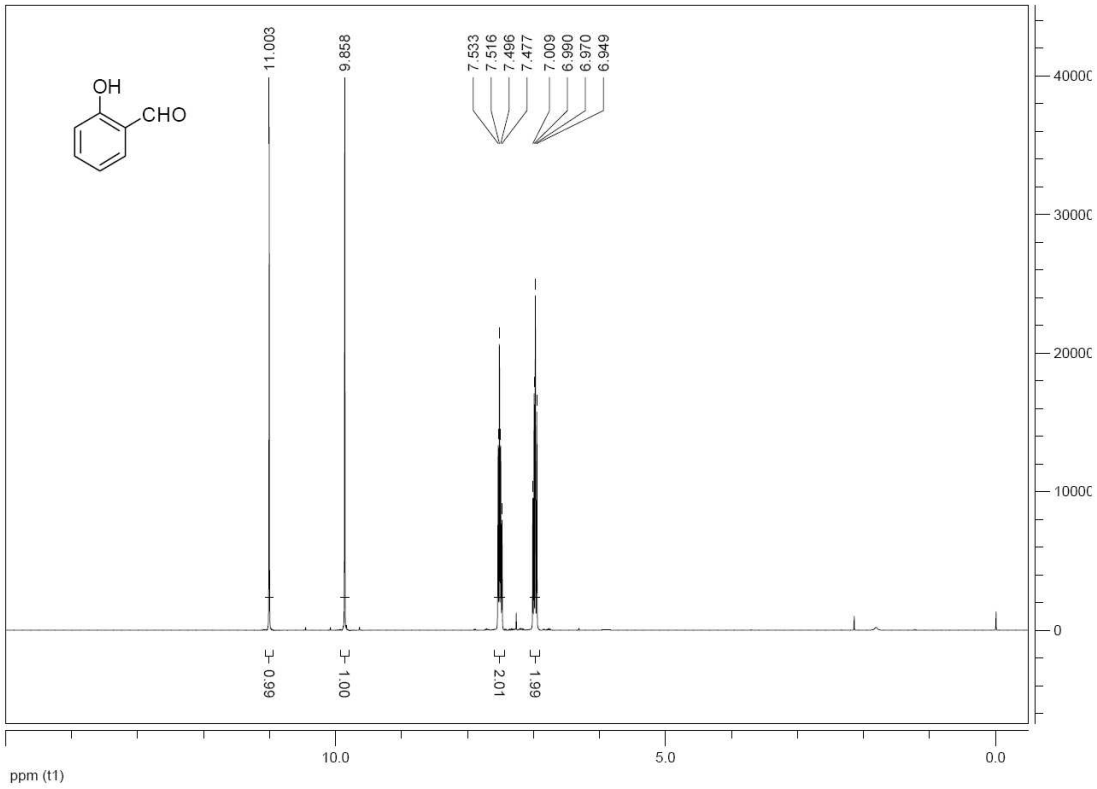


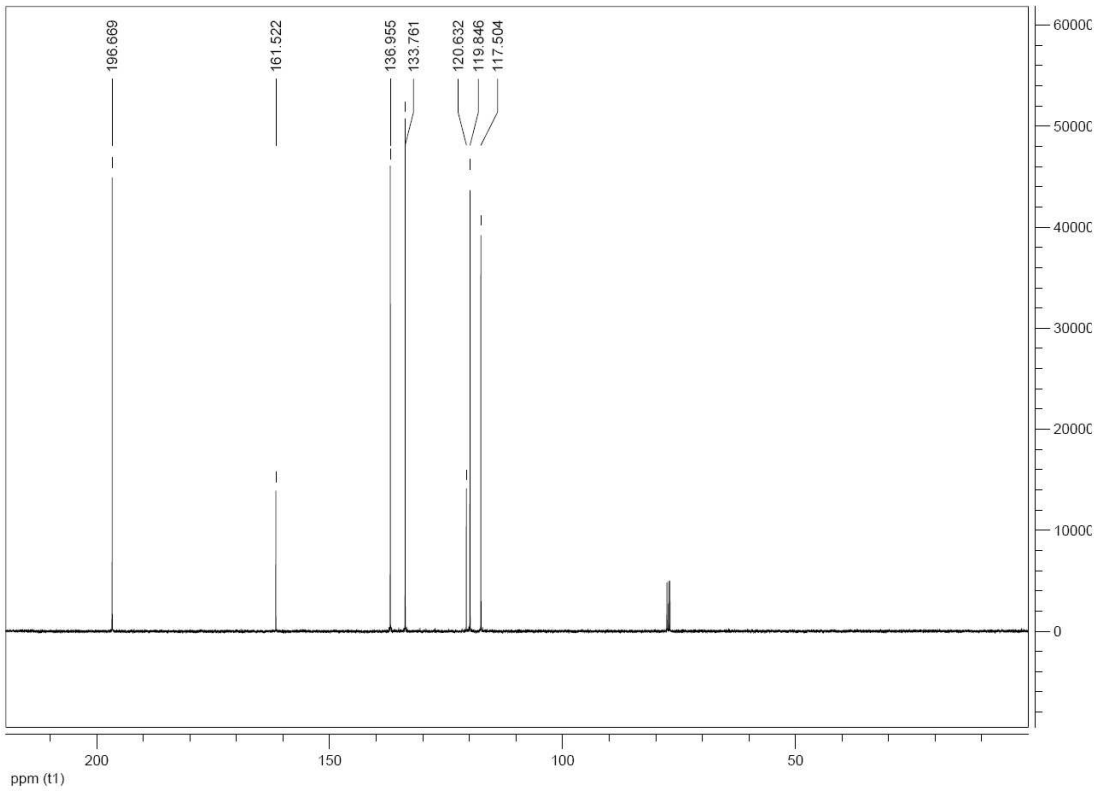
2-hydroxybenzoic acid



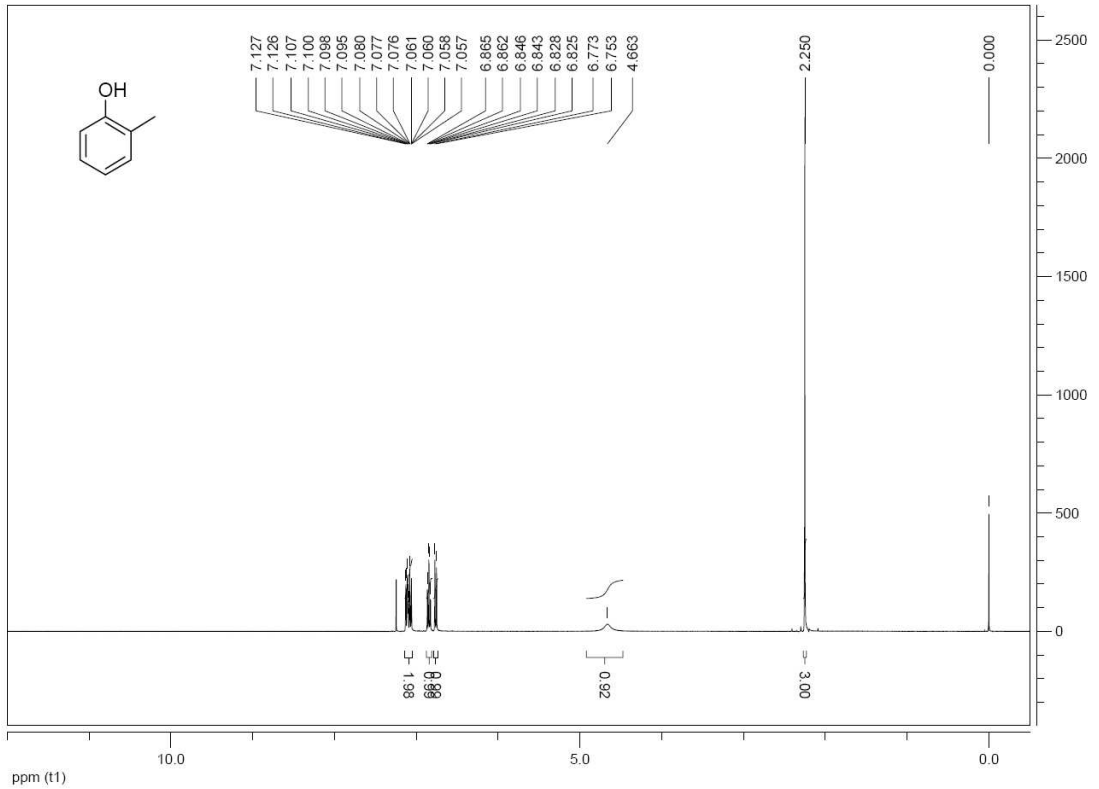


2-hydroxybenzaldehyde





***o*-cresol**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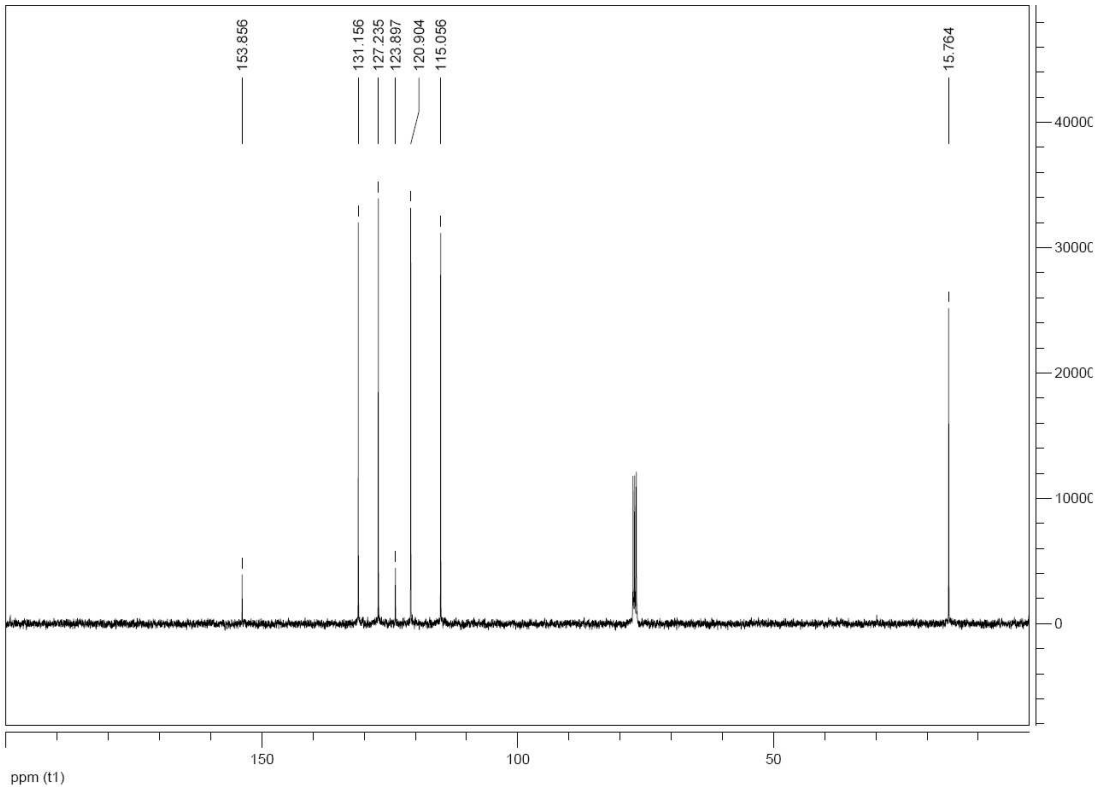
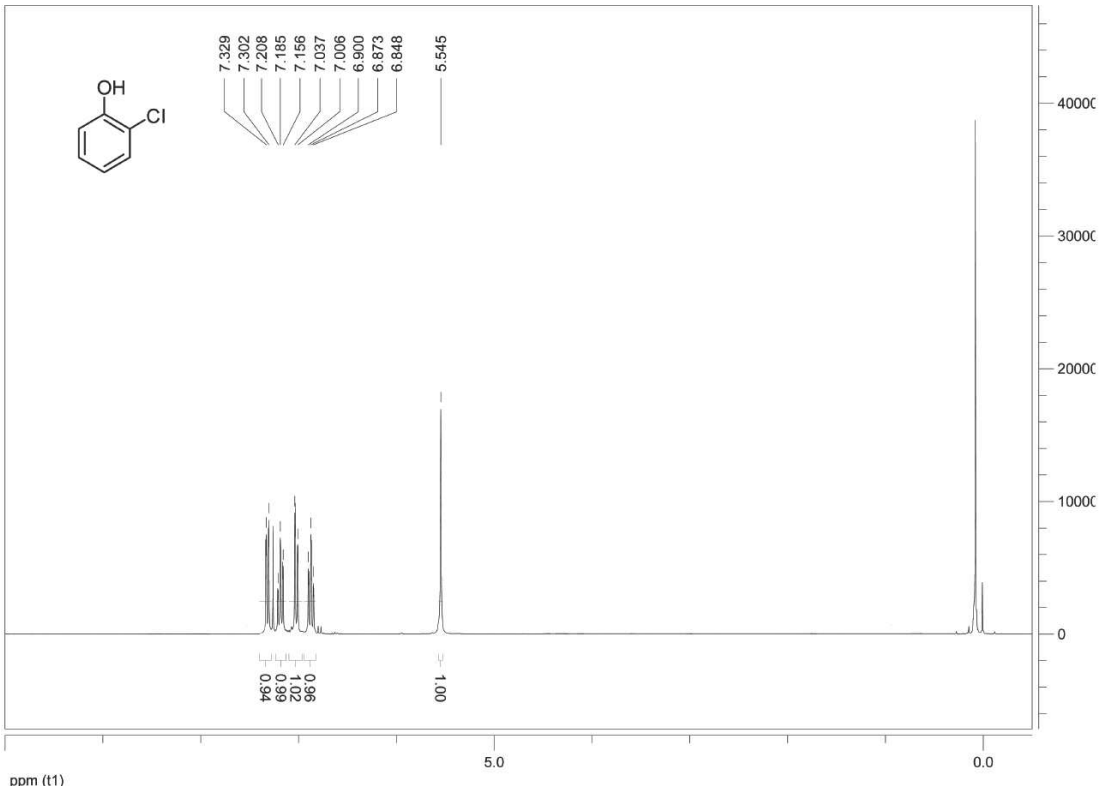
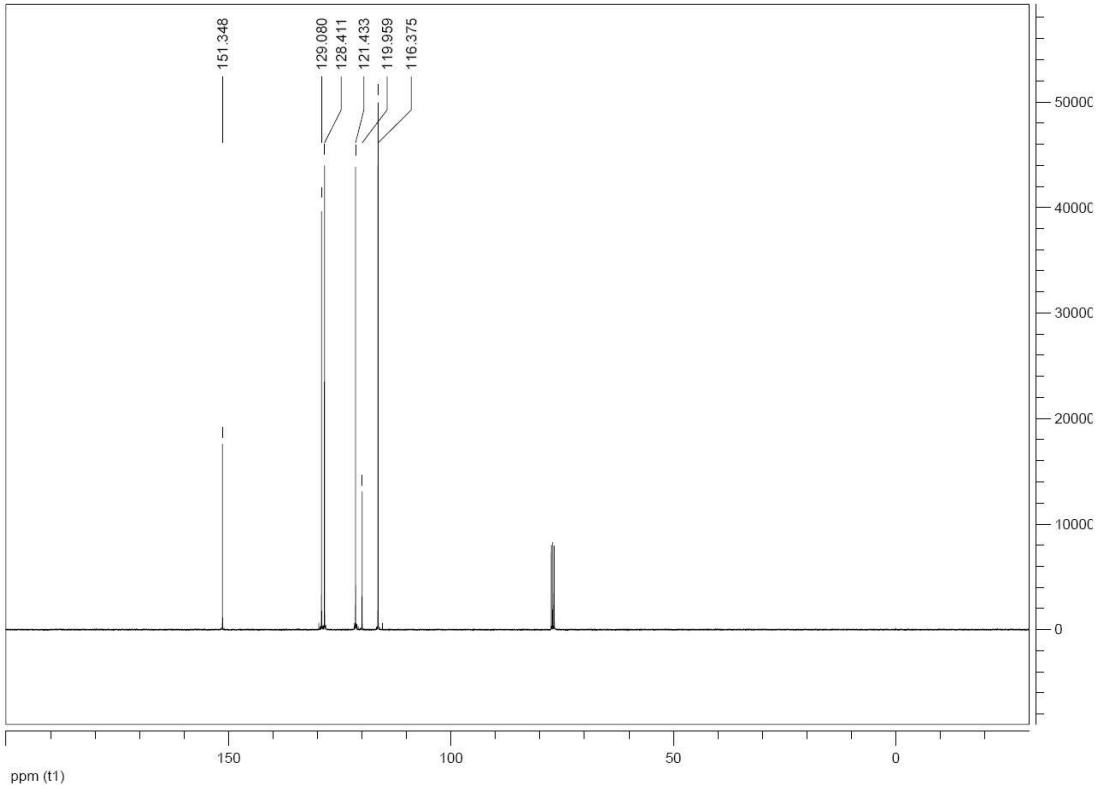
7.126
7.107
7.100
7.098
7.095
7.080
7.077
7.076
7.061
7.060
7.058
7.057
6.865
6.862
6.846
6.843
6.828
6.825
6.773
6.753
4.663
2.250
0.000
1.98
0.92
3.00
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

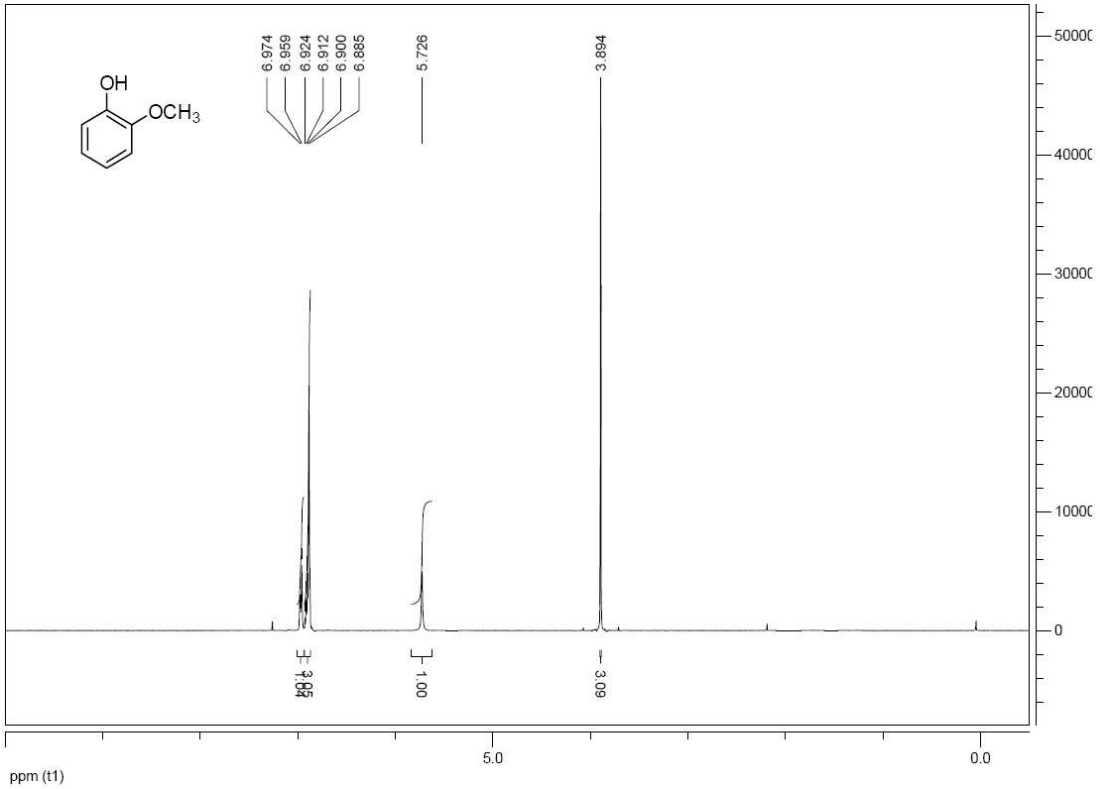

153.856
131.156
127.235
123.897
120.904
115.056
15.764
40000
30000
20000
10000
0
150
100
50
ppm (t1)

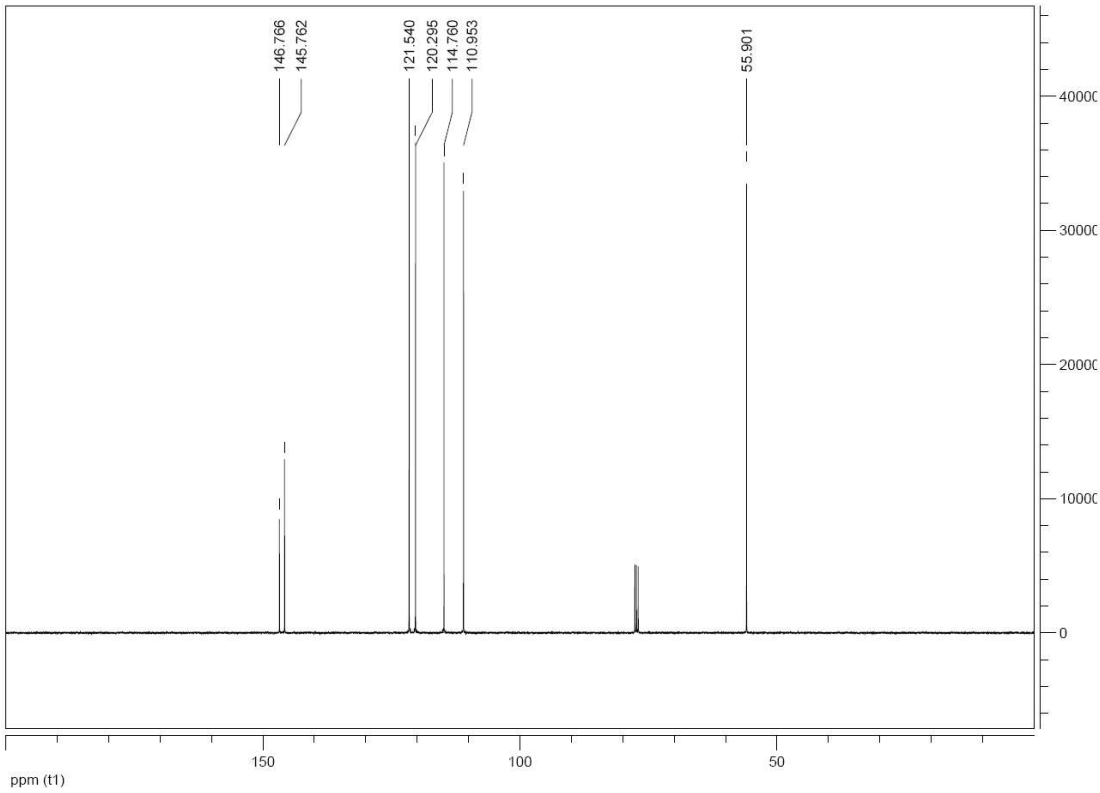
2-chlorophenol



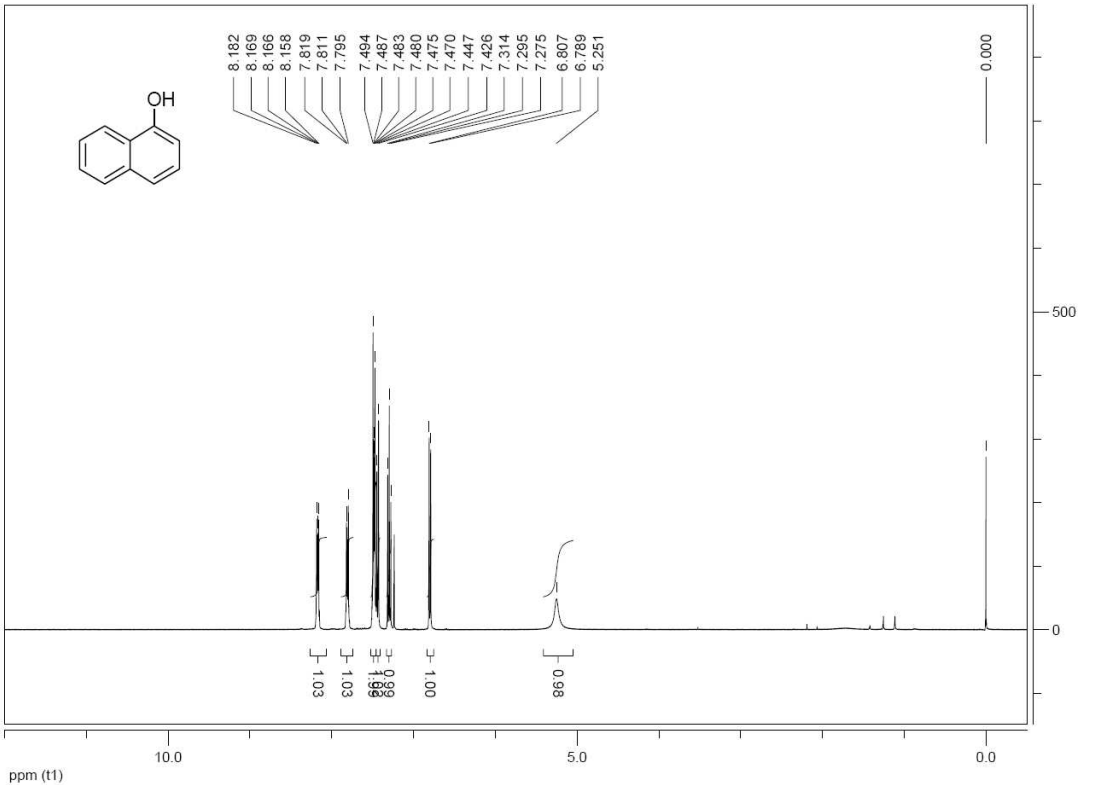


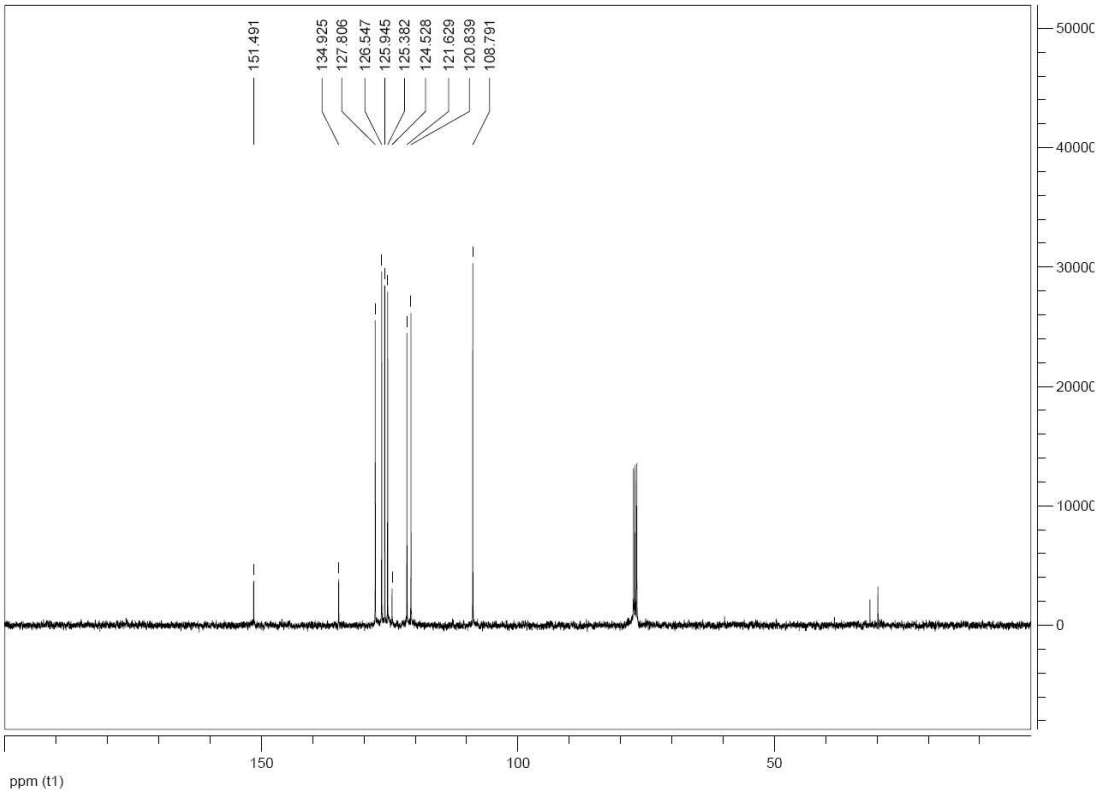
2-methoxyphenol



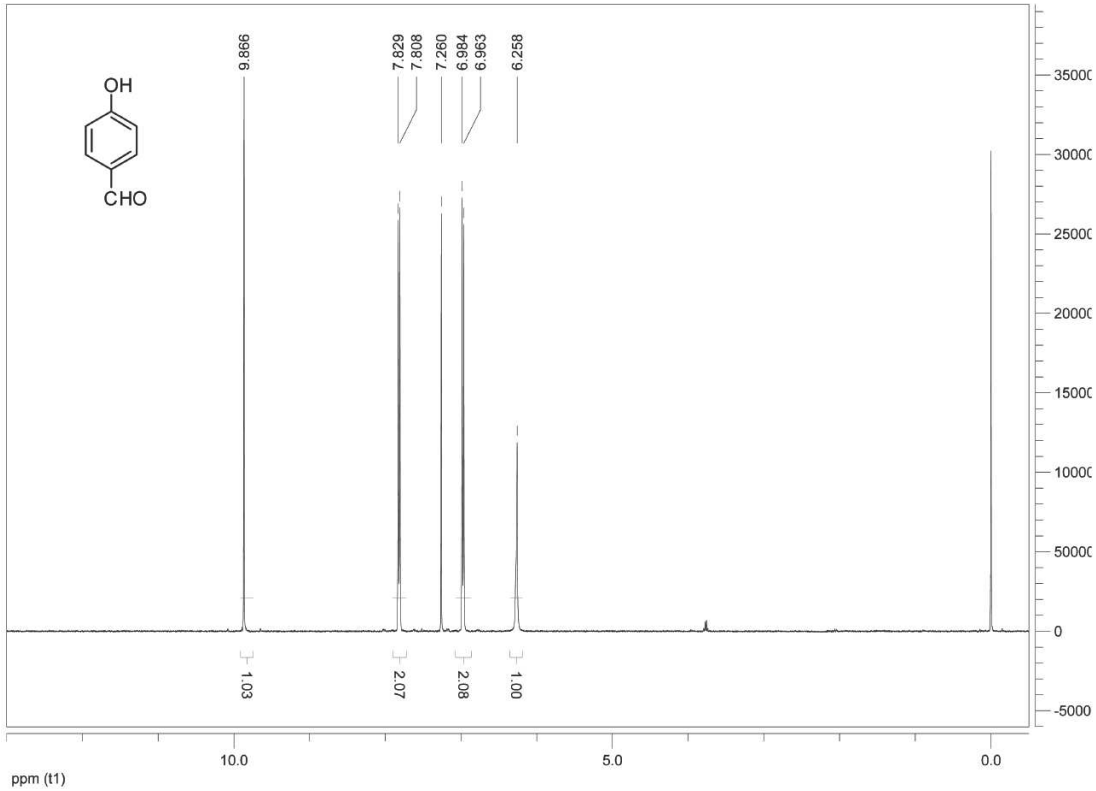


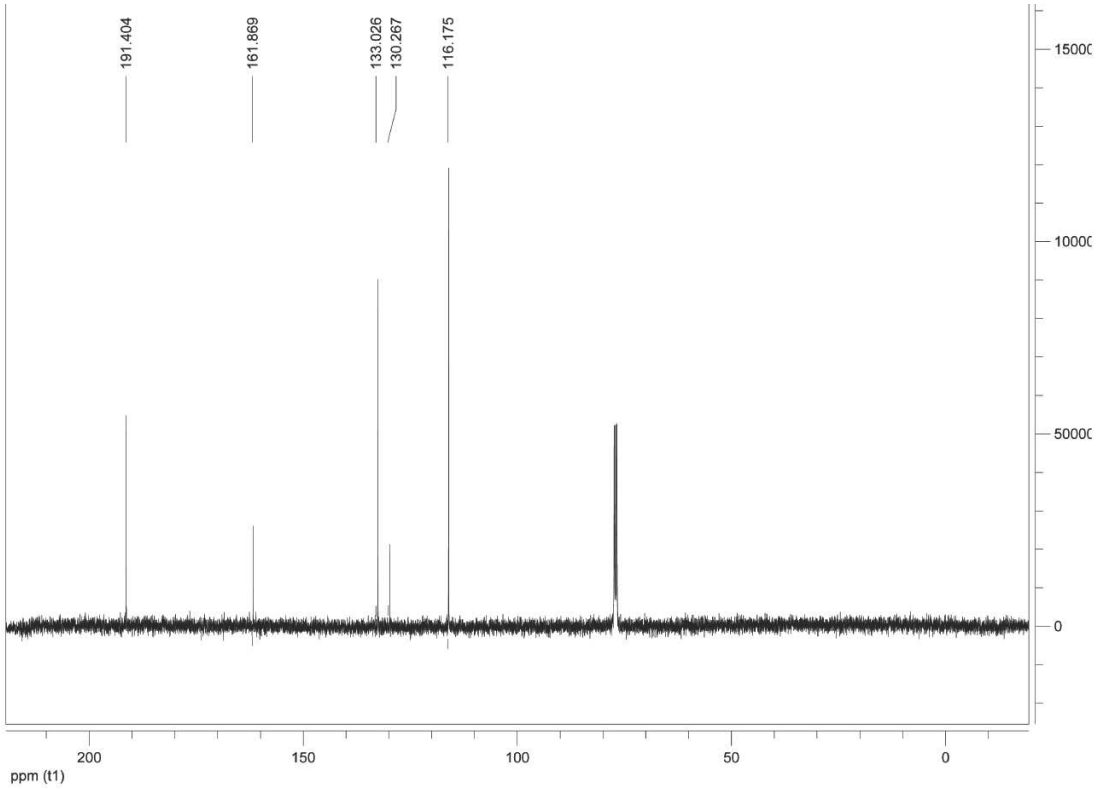
1-naphthalenol



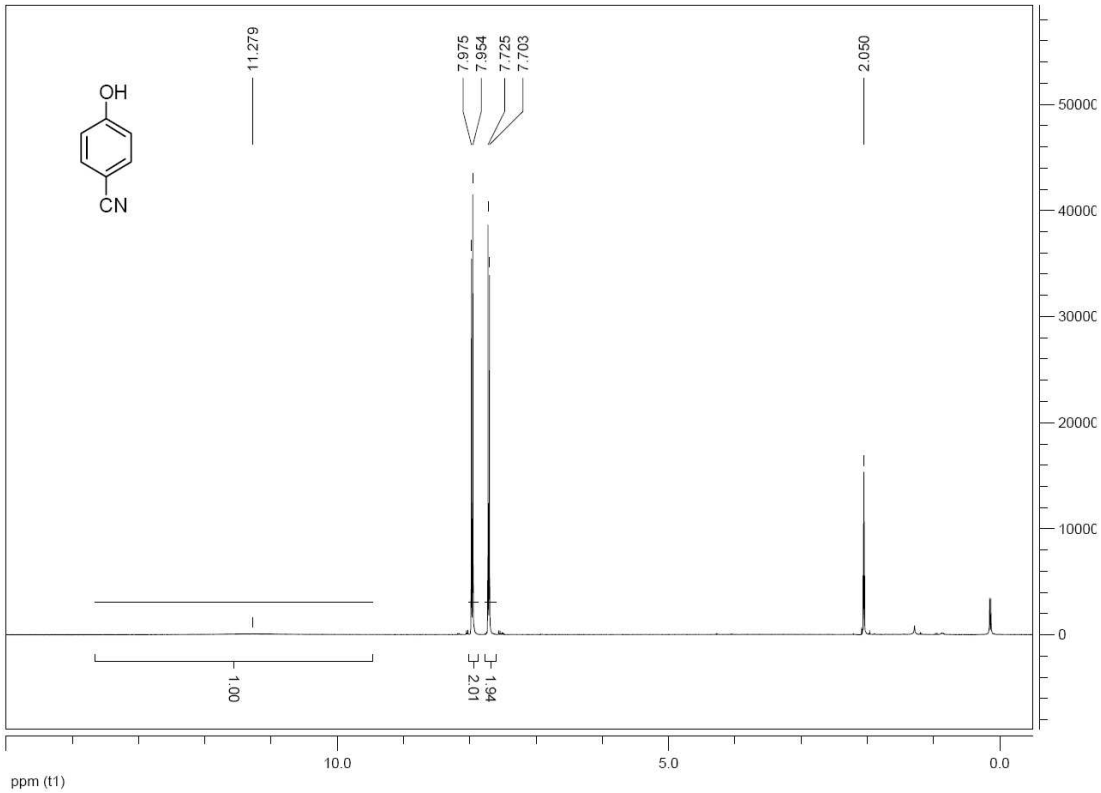


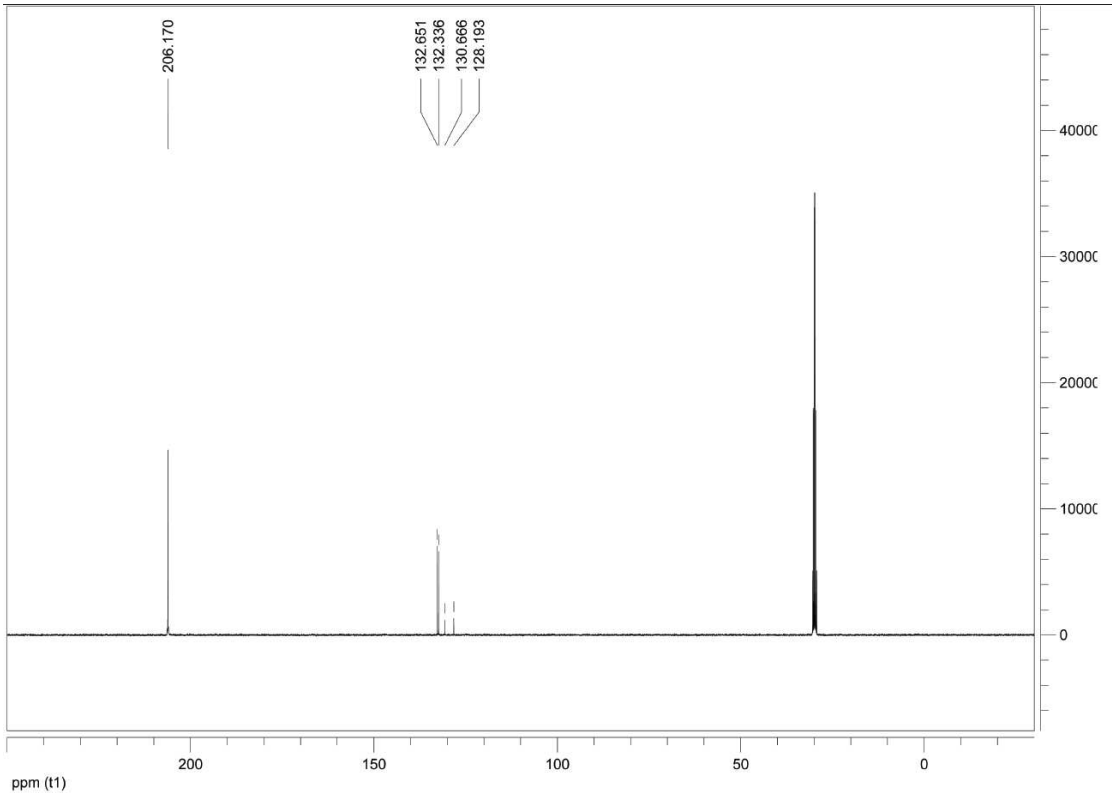
4-hydroxybenzaldehyde



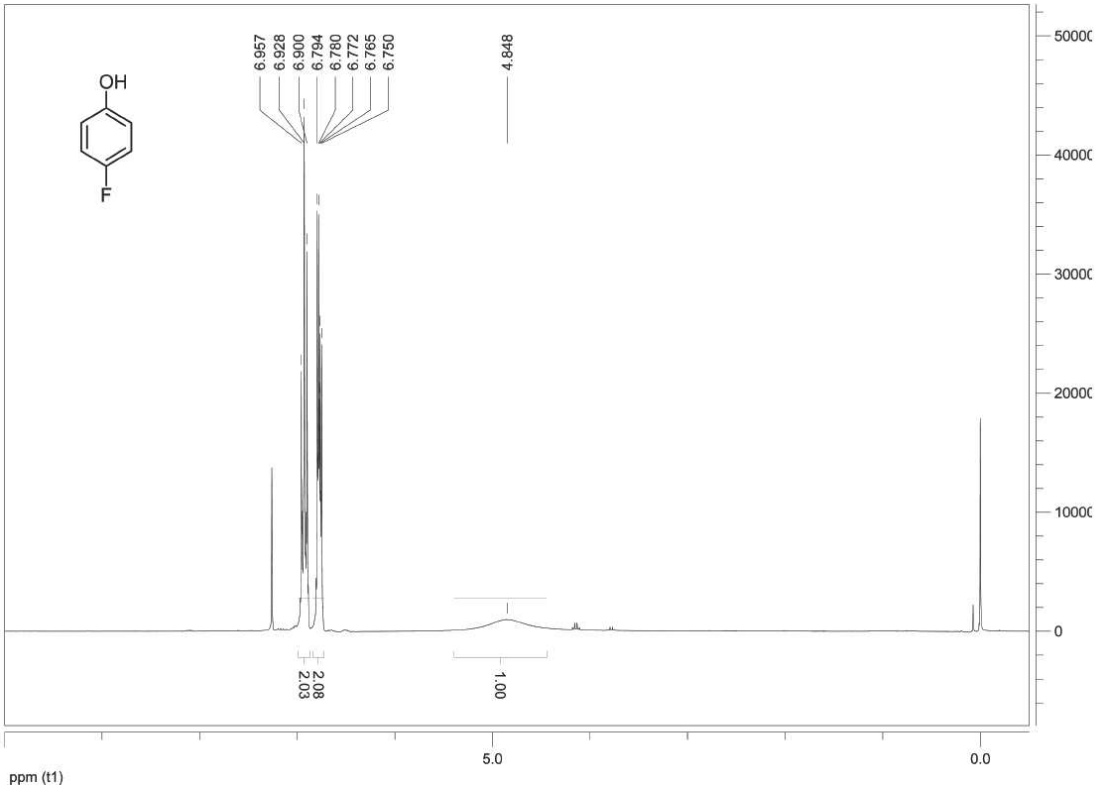


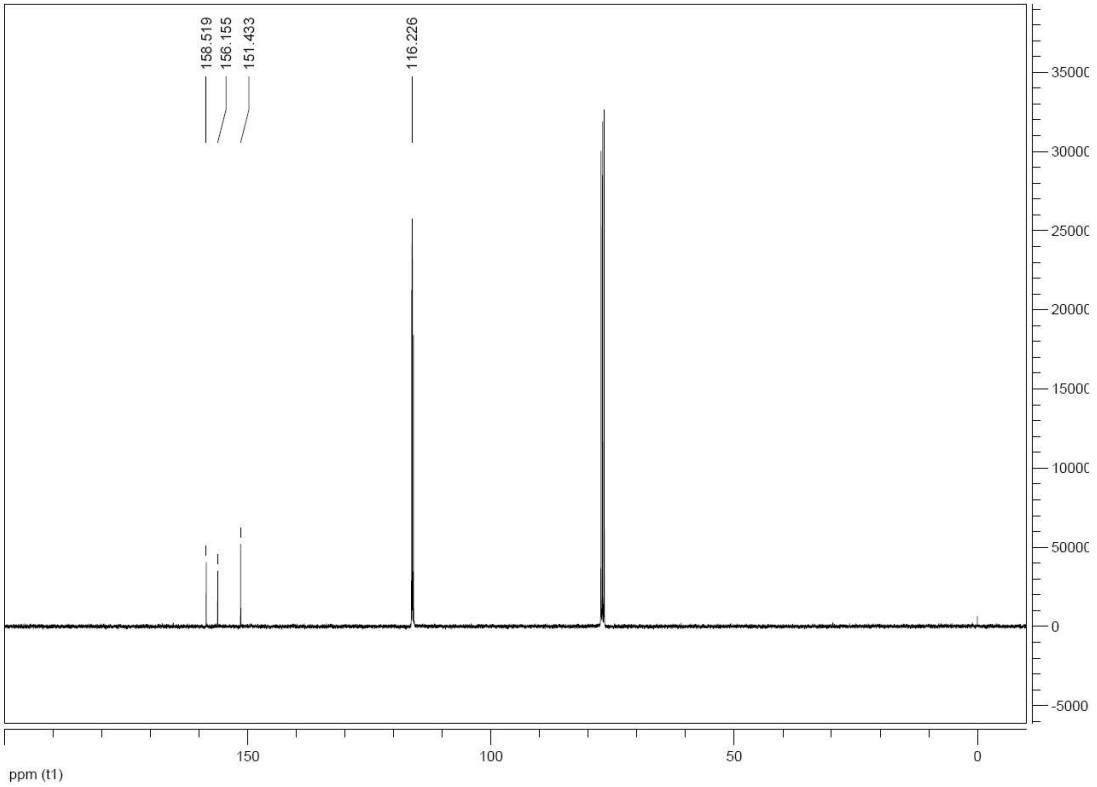
4-hydroxybenzonitrile



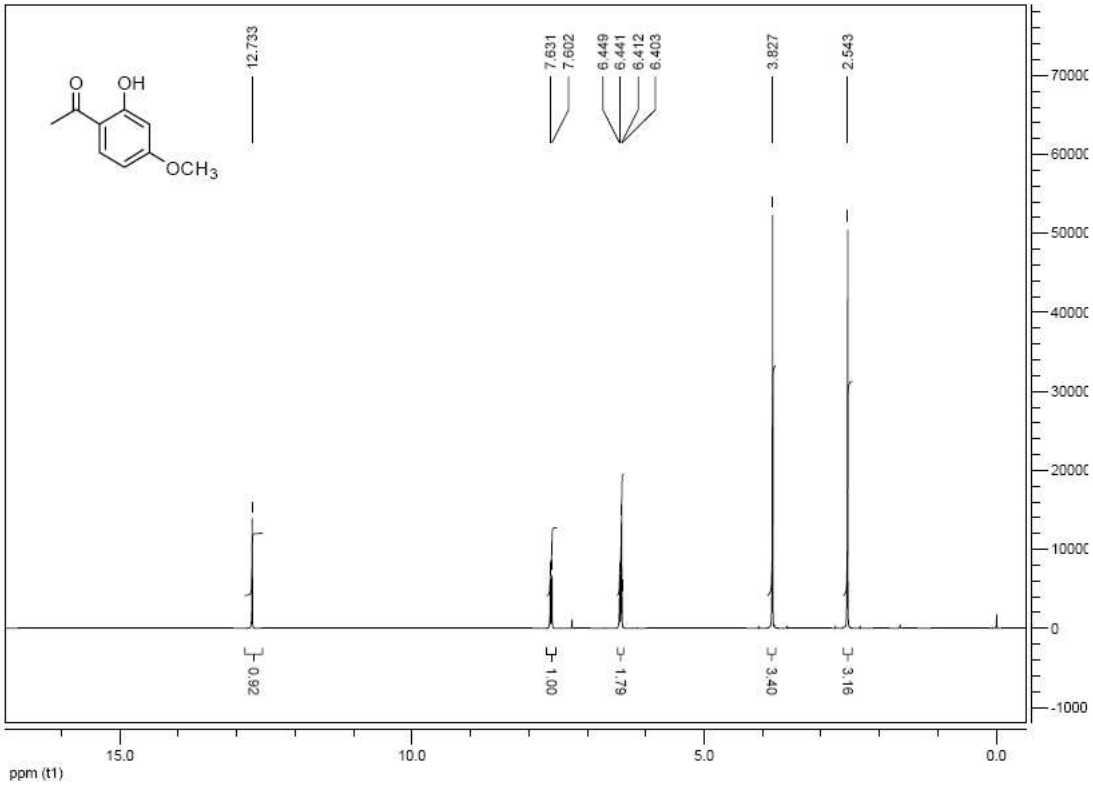


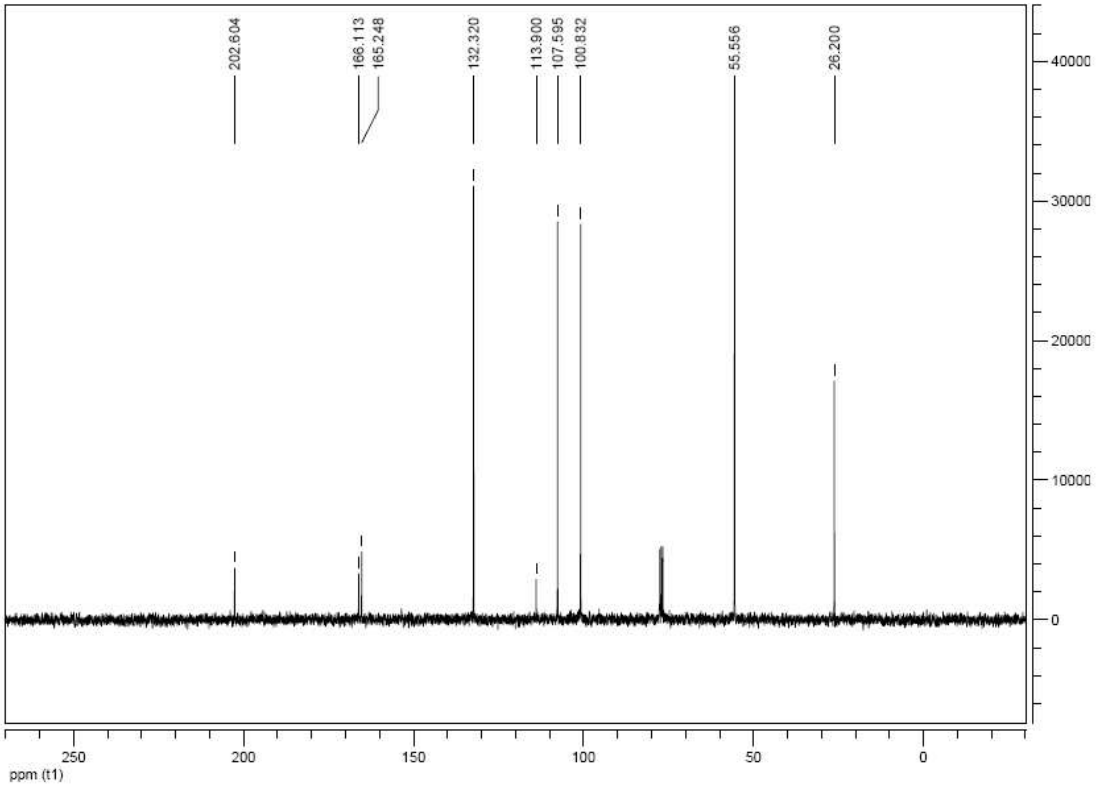
4-fluorophenol



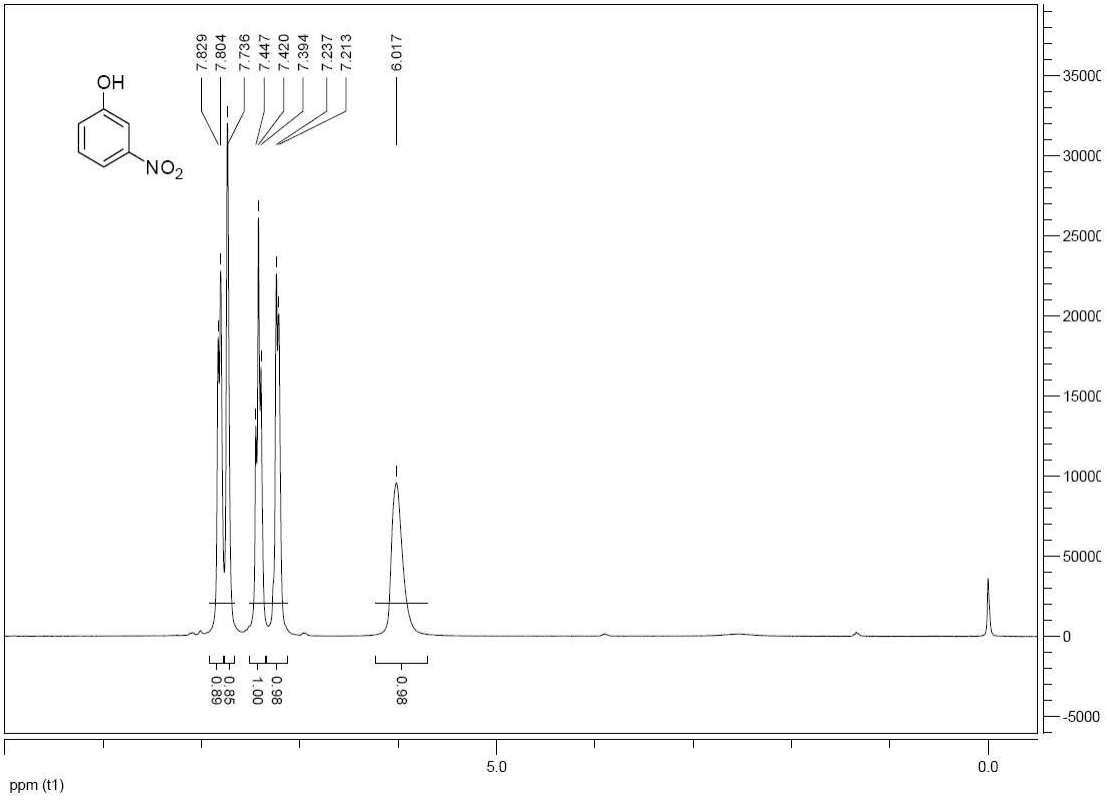


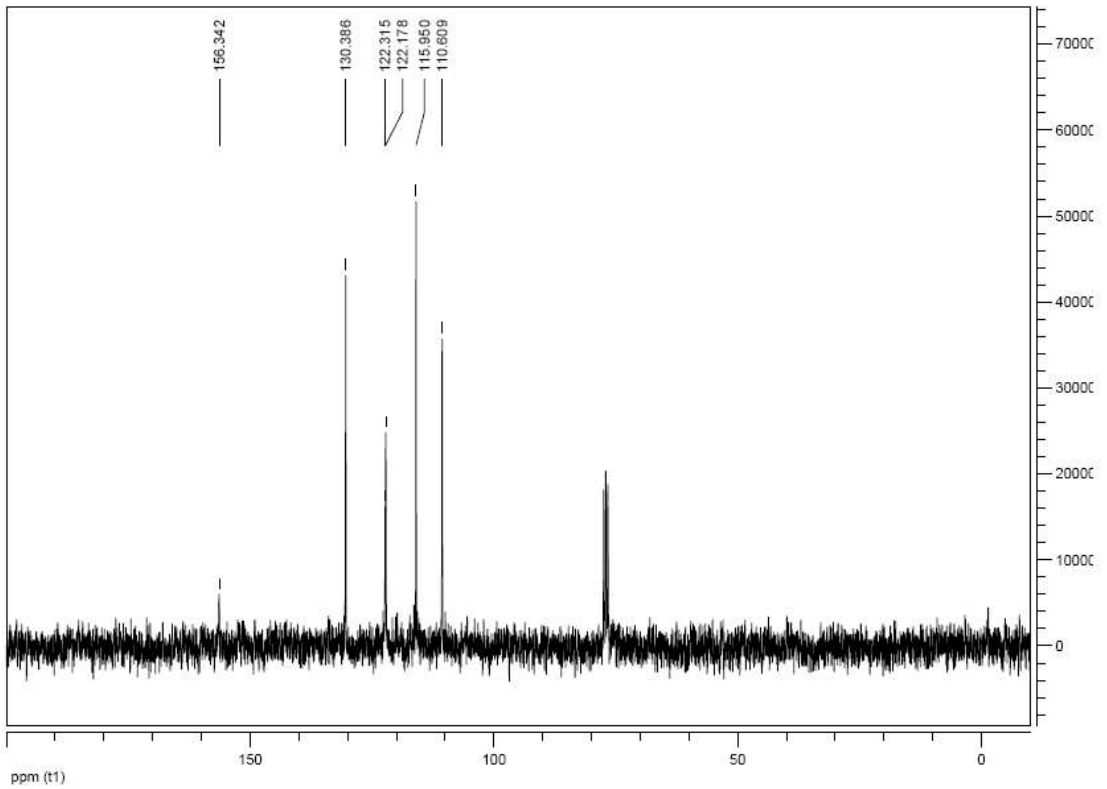
1-(2-hydroxy-4-methoxyphenyl)ethanone



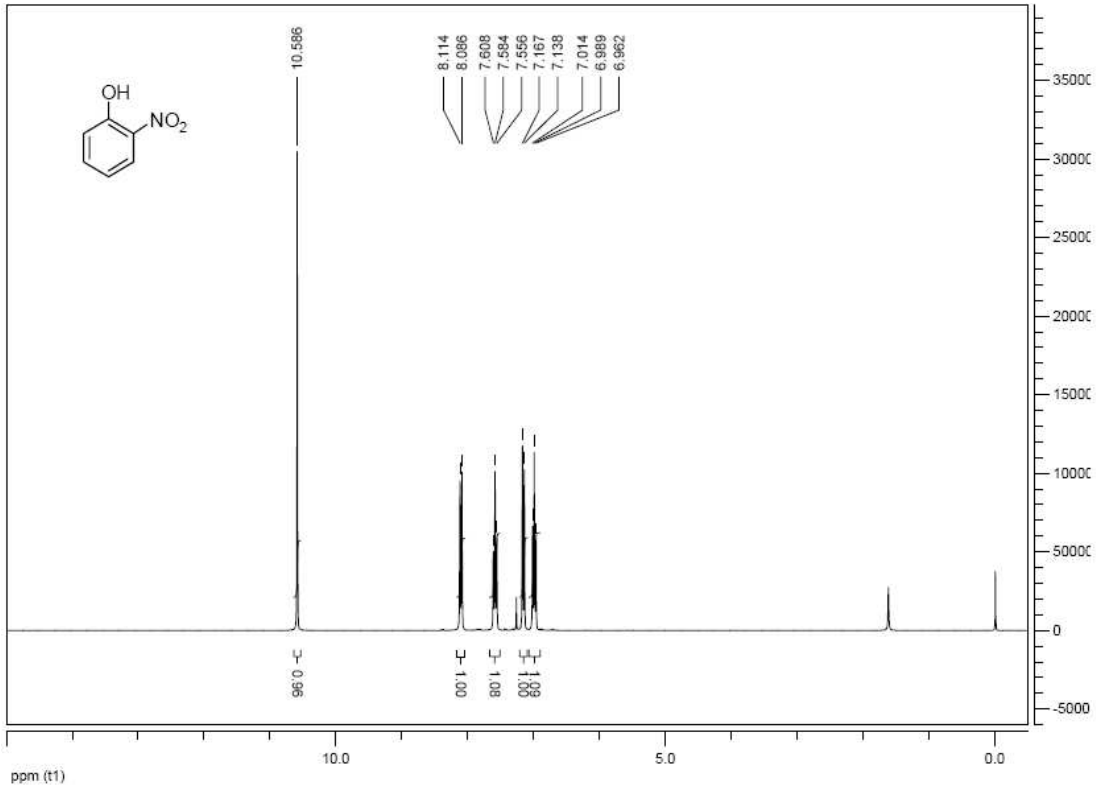


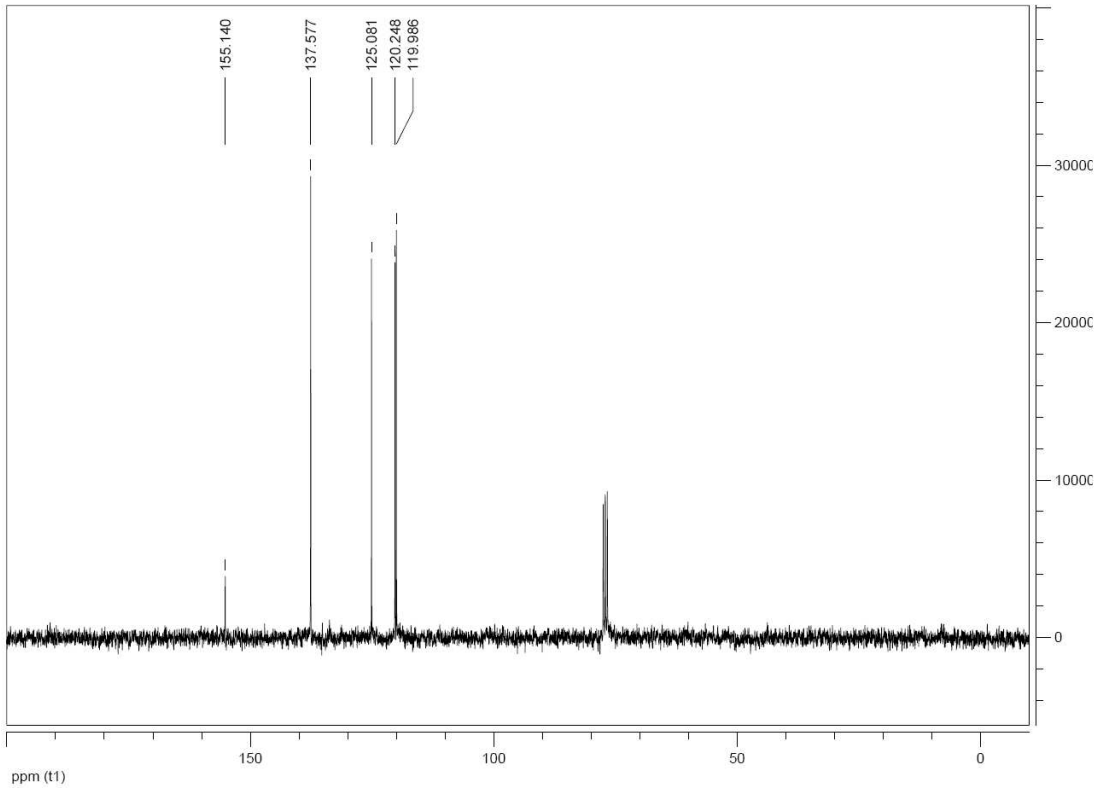
3-nitrophenol



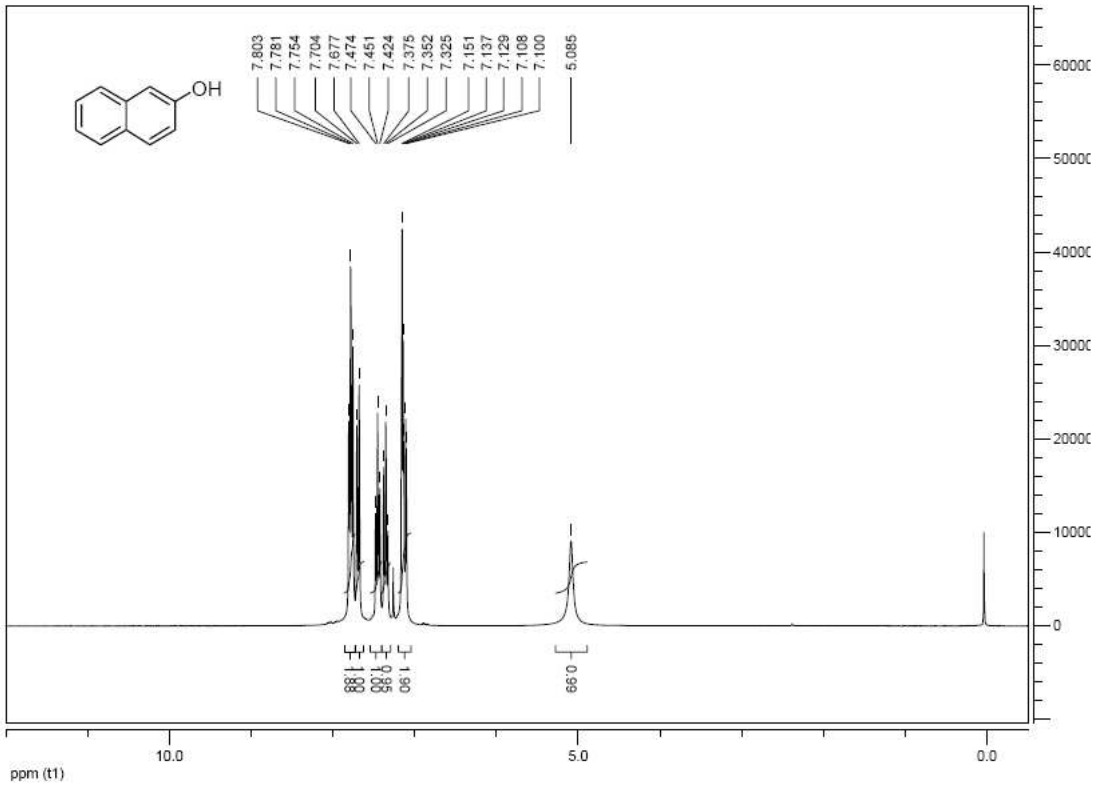


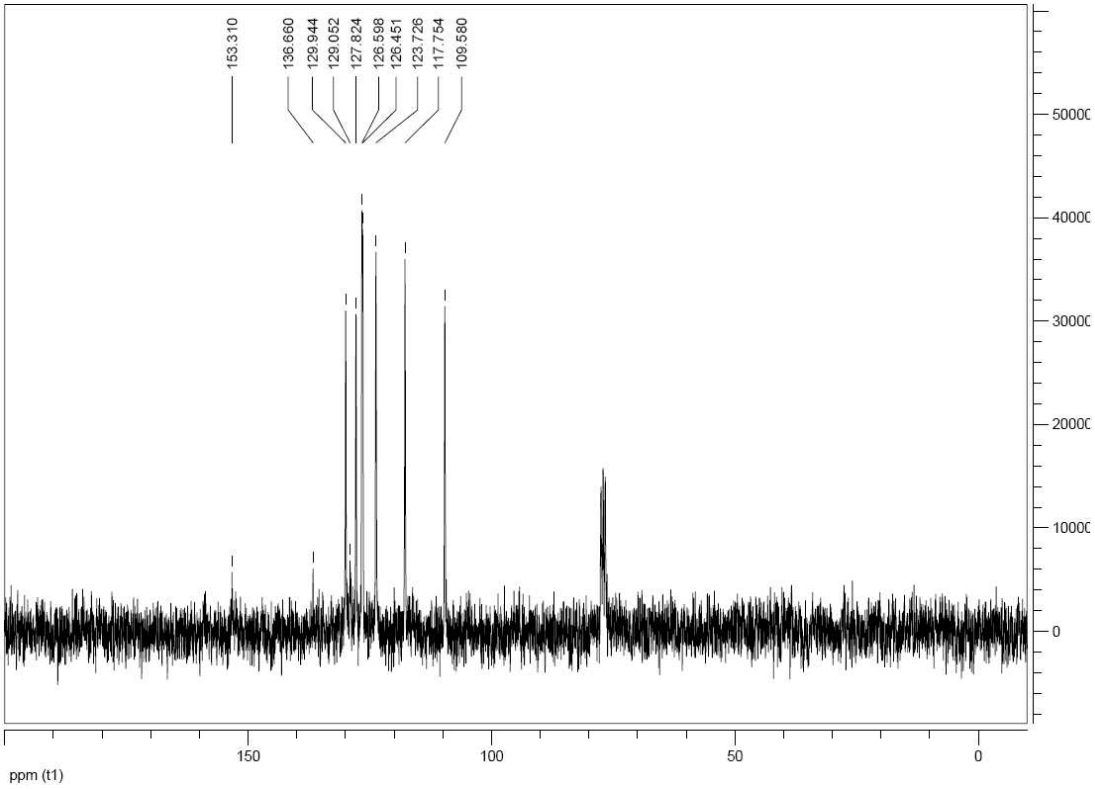
2-nitrophenol



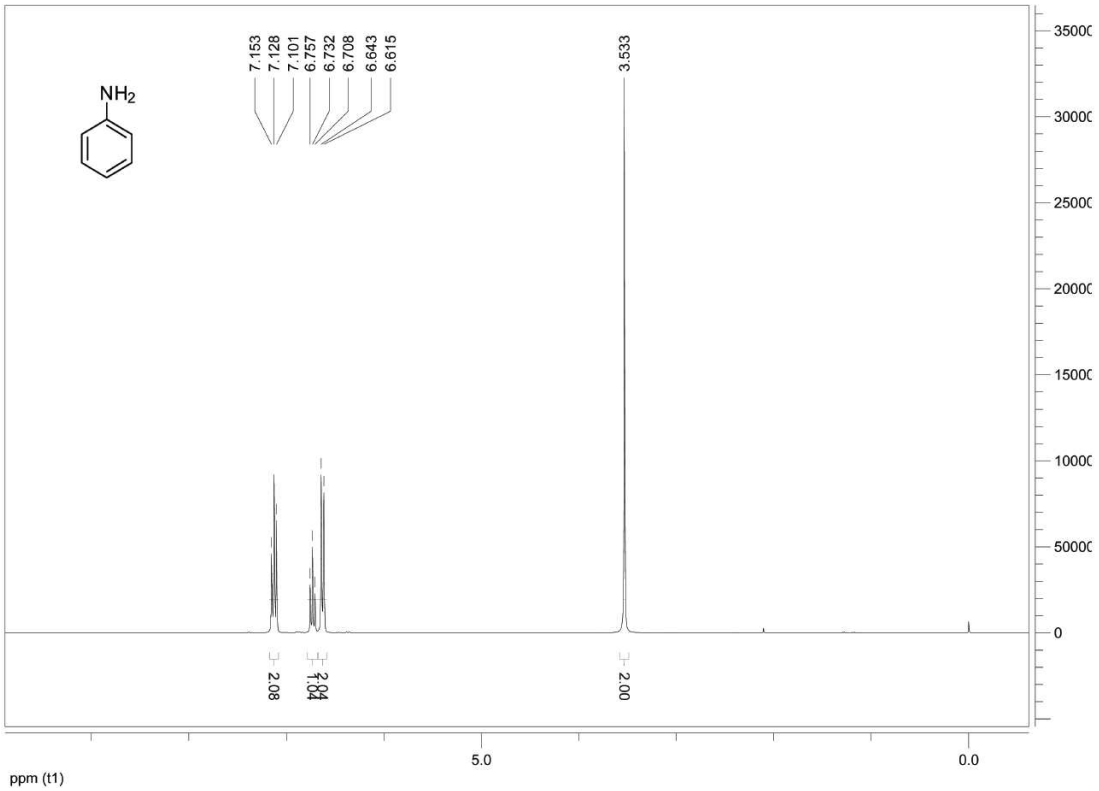


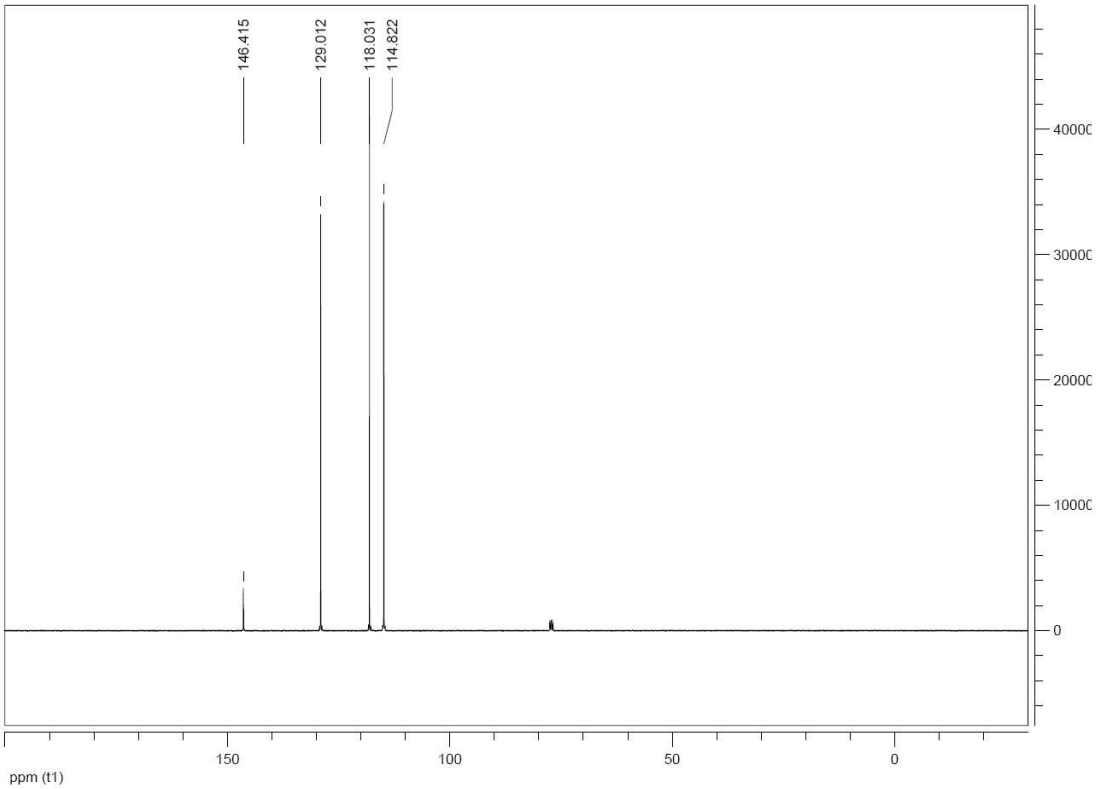
2-naphthalenol



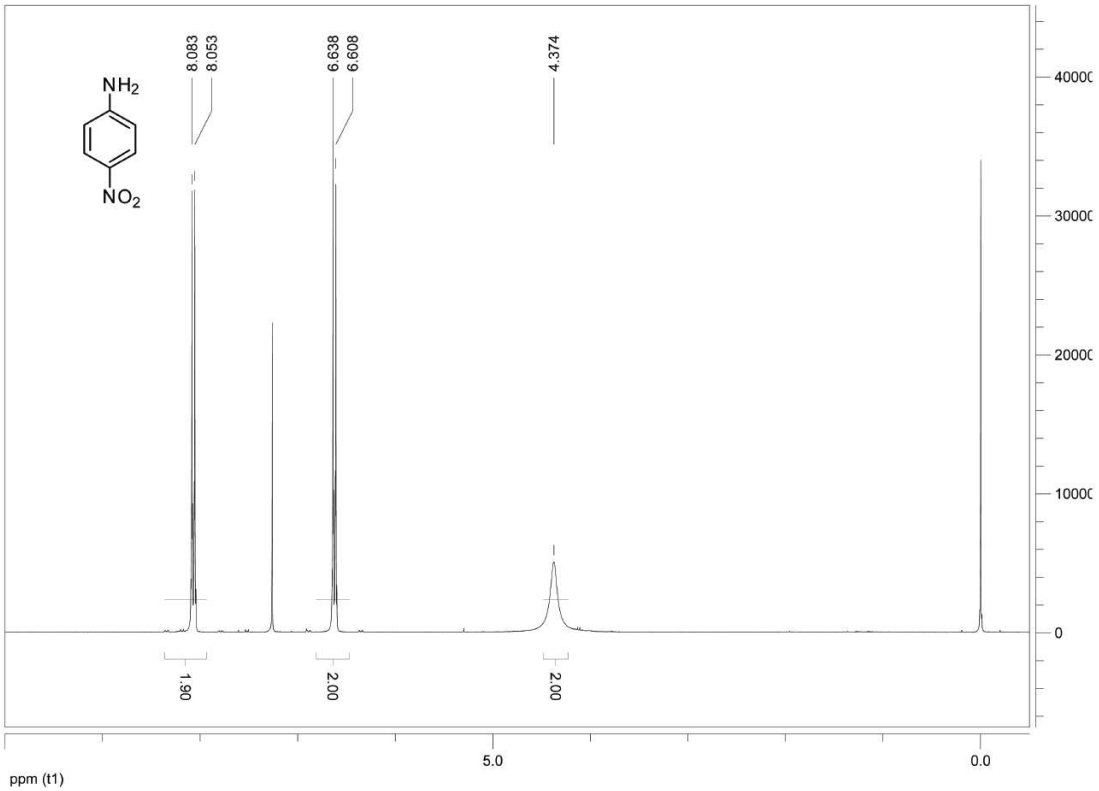


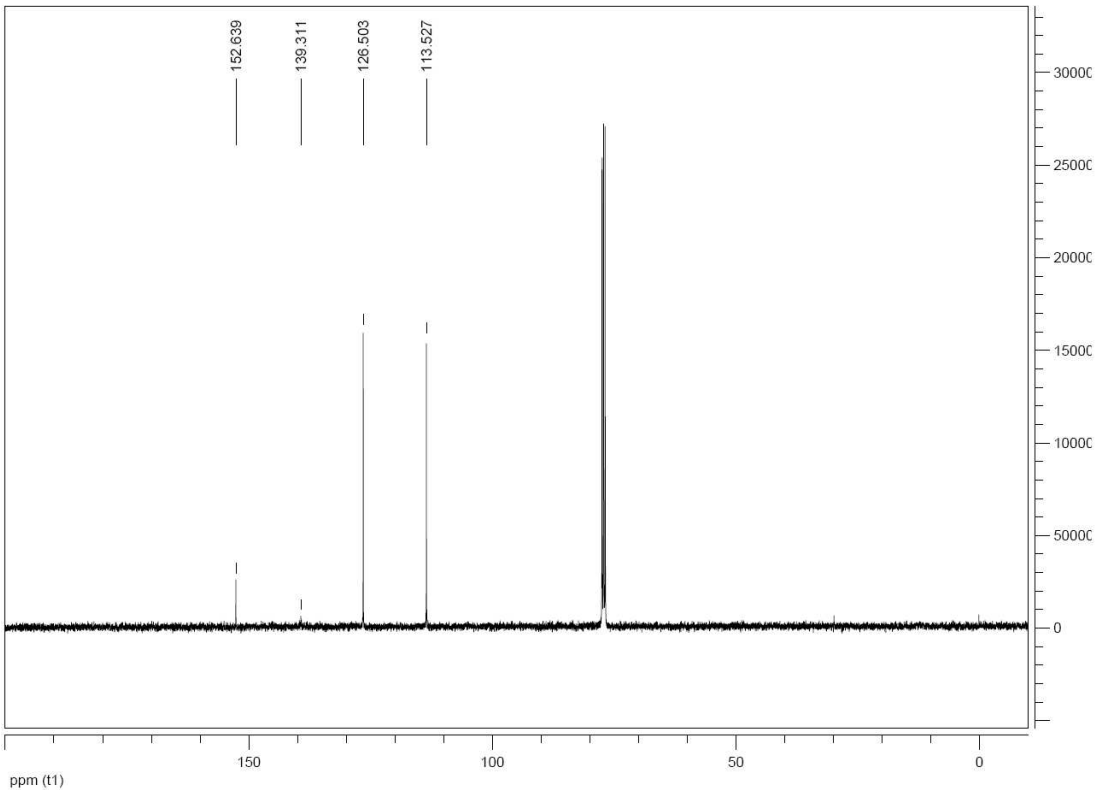
aniline


NH2
7.153
7.128
7.101
6.757
6.732
6.708
6.643
6.615
3.533
2.08
2.04
2.04
2.00
5.0
0.0
ppm (t1)

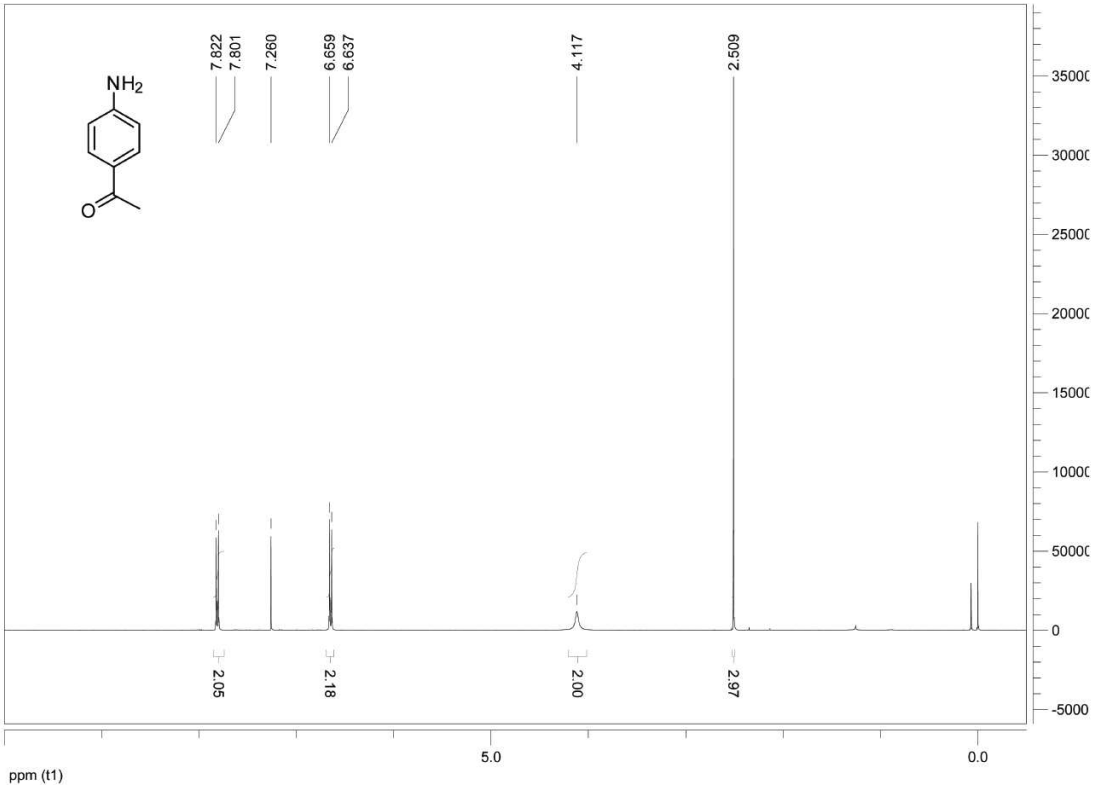

146.415
129.012
118.031
114.822
150
100
50
0
ppm (t1)

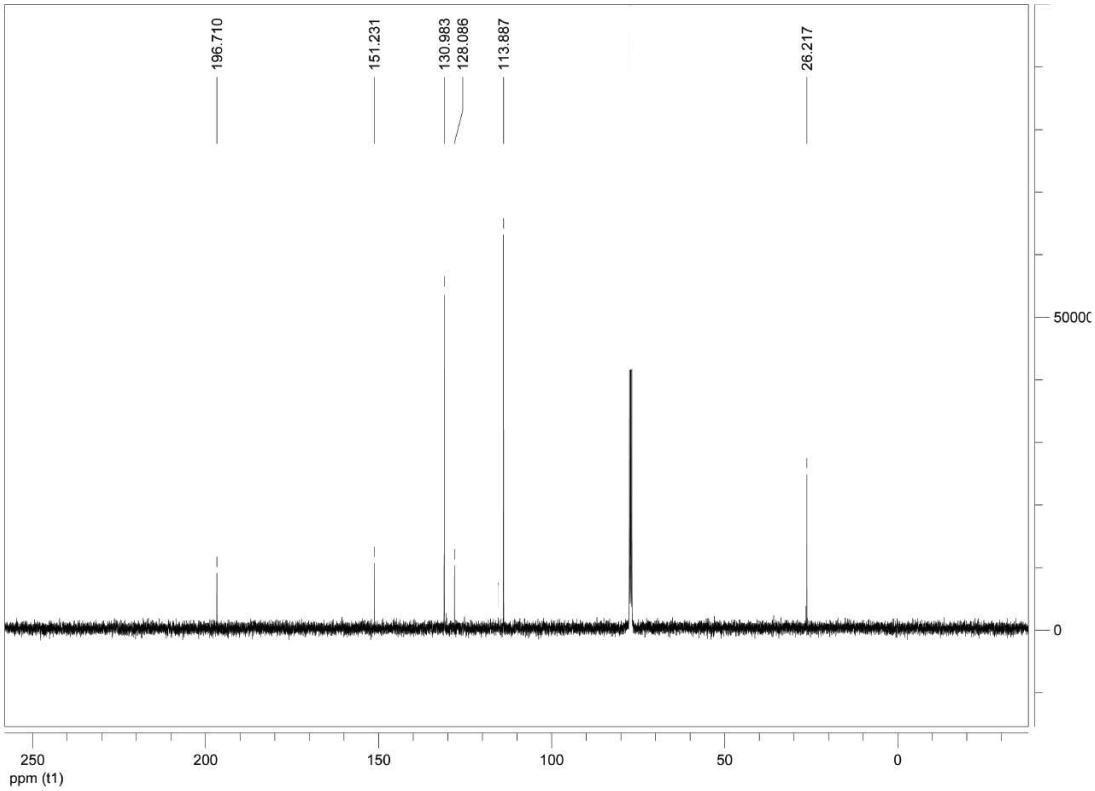
4-nitroaniline



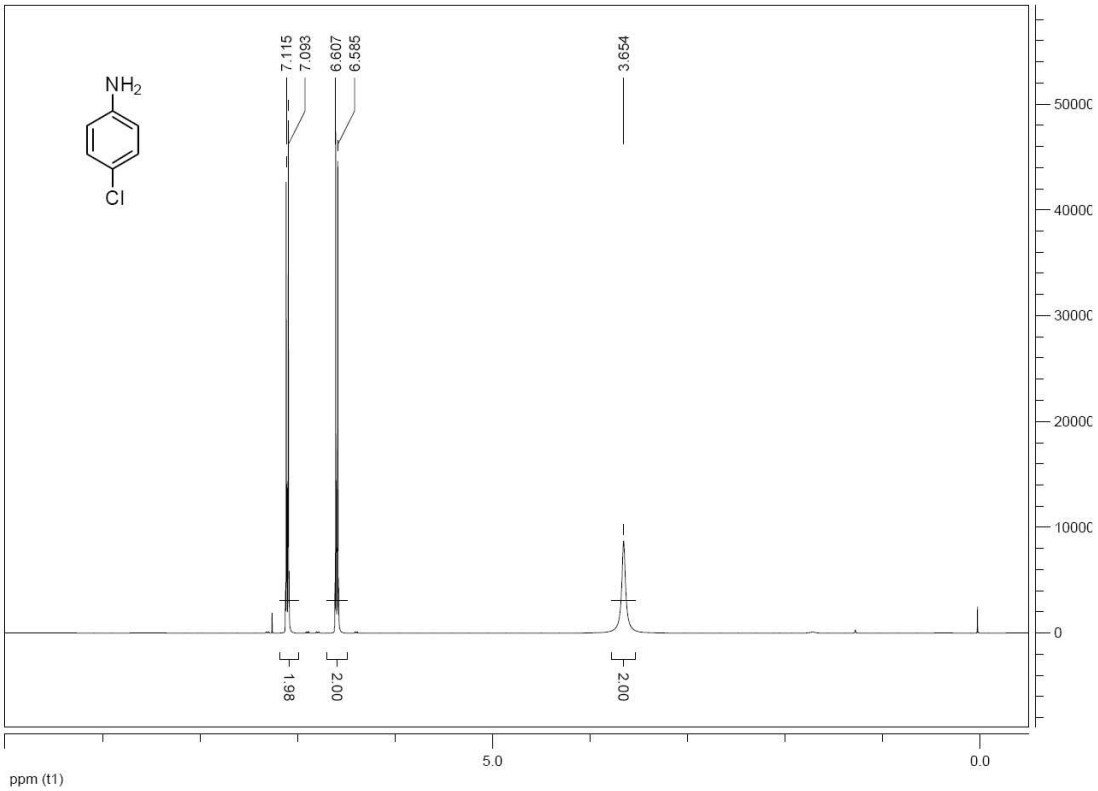


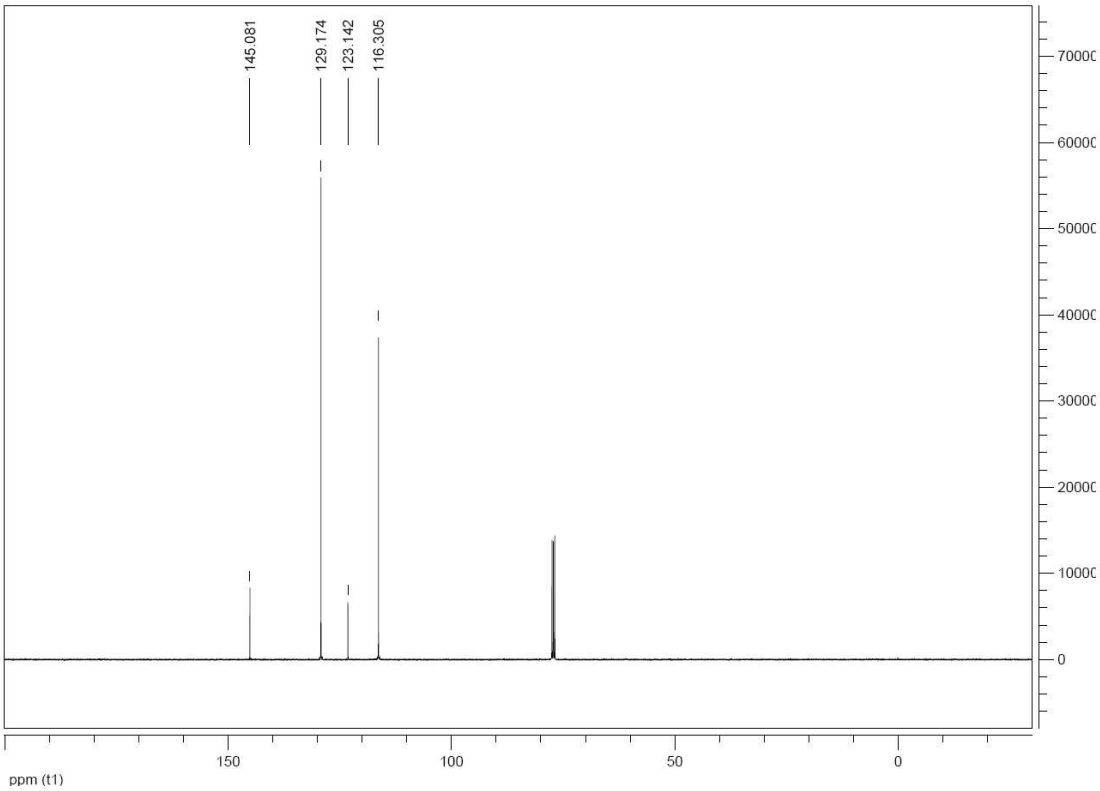
4-aminoacetophenone



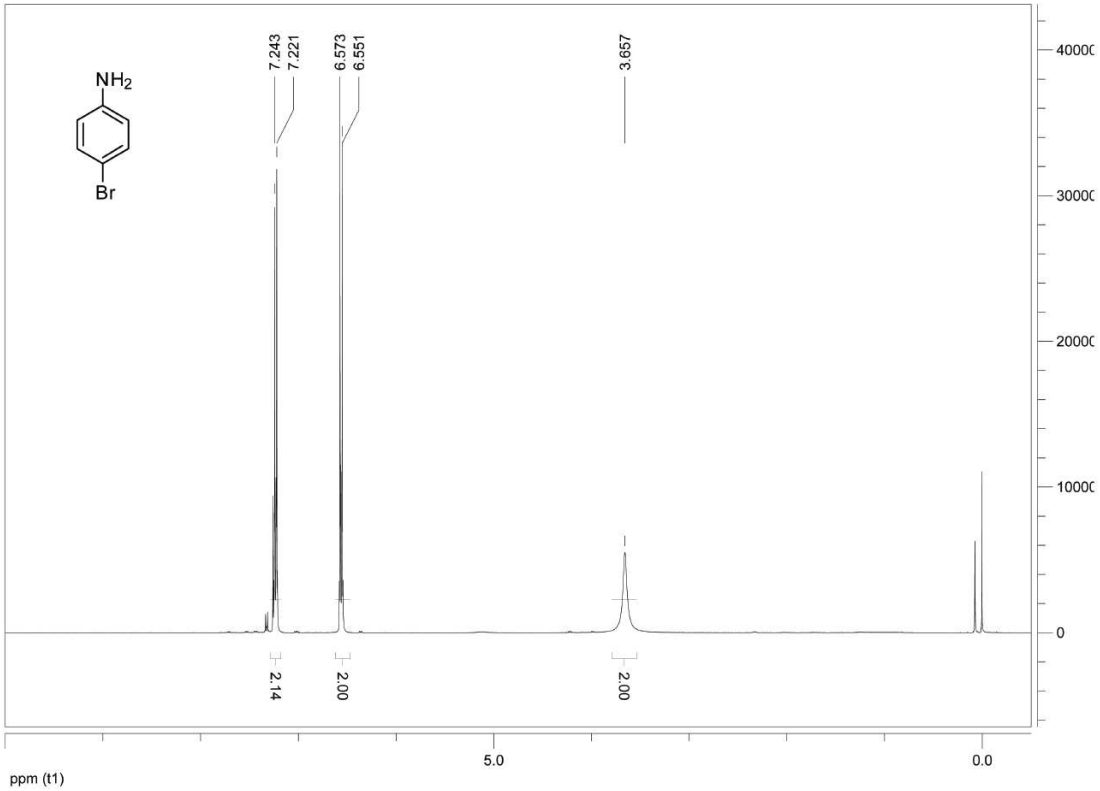


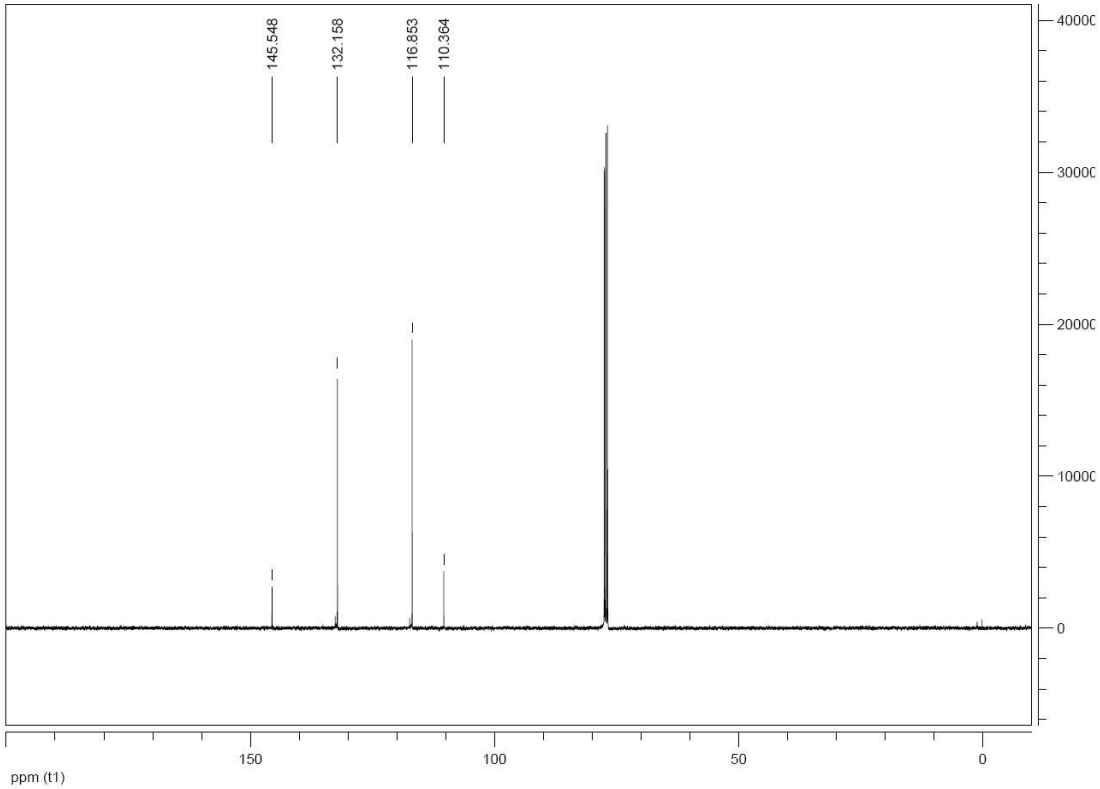
4-chloroaniline



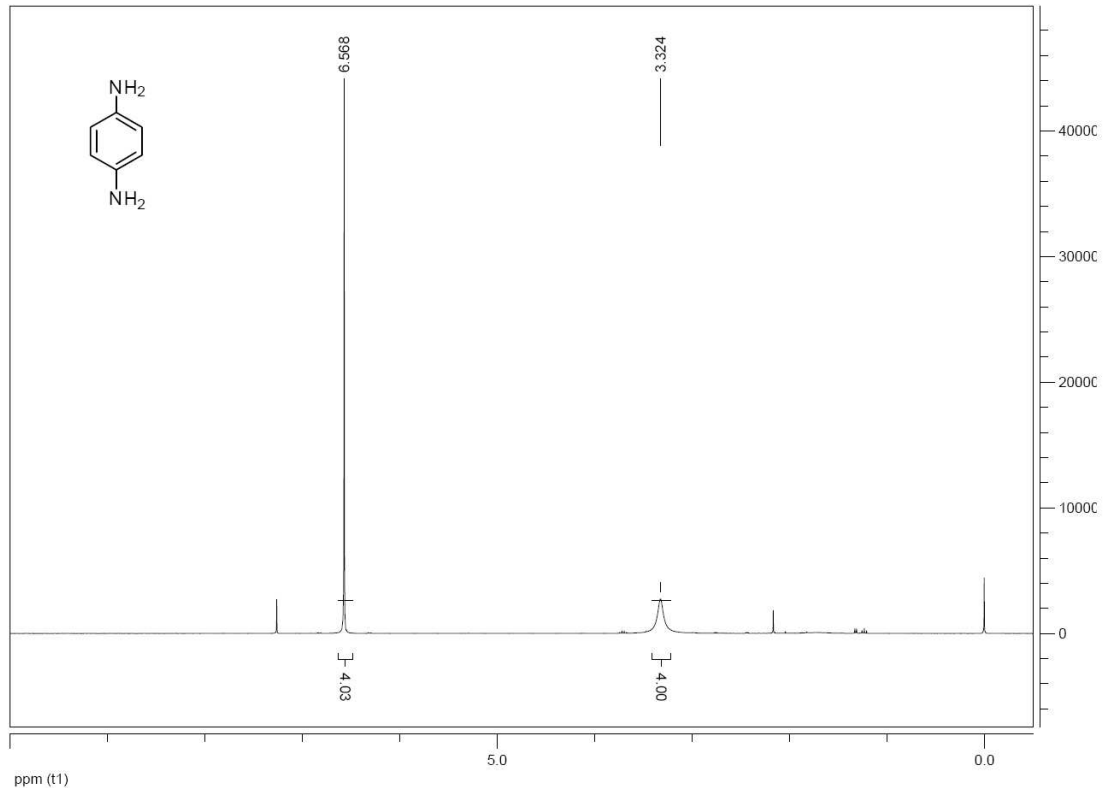


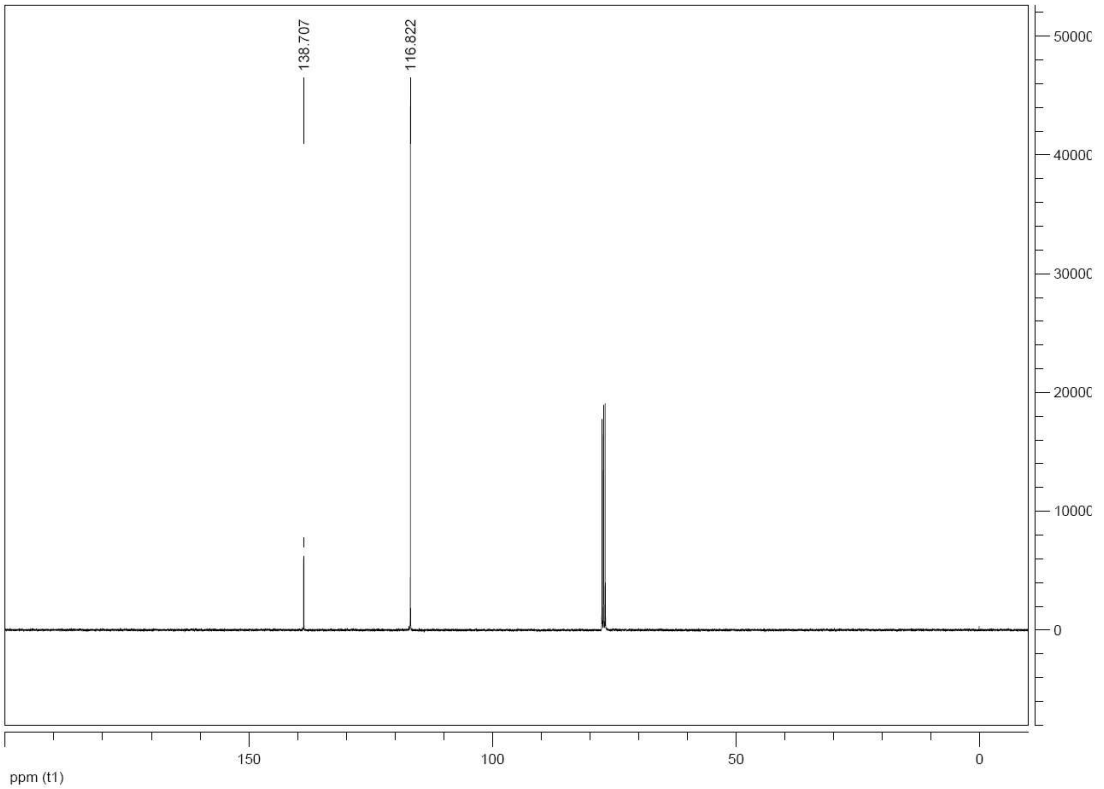
4-bromoaniline



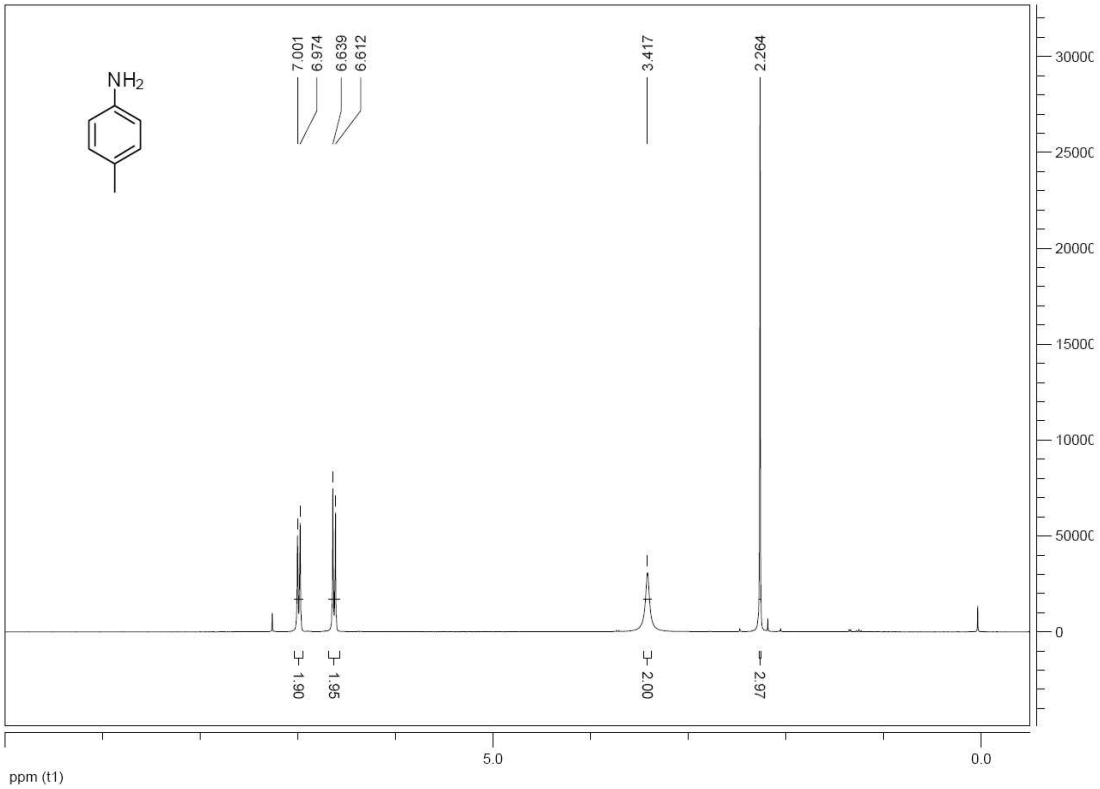


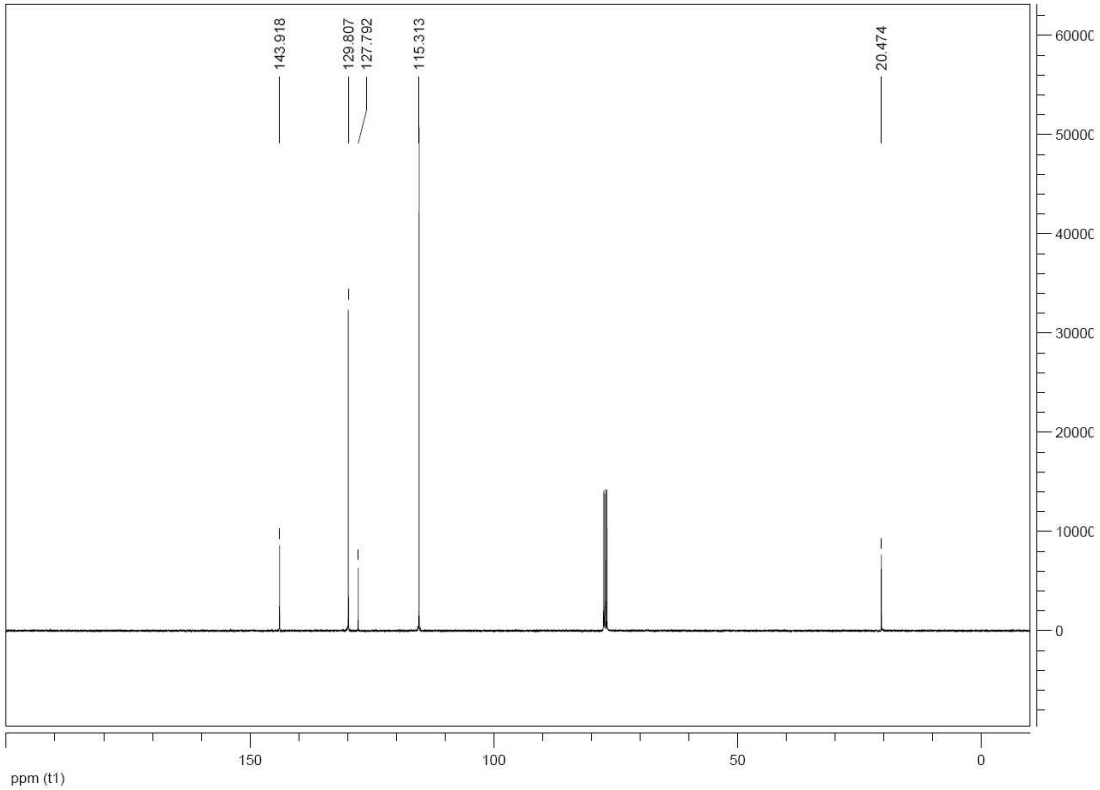
***p*-phenylenediamine**



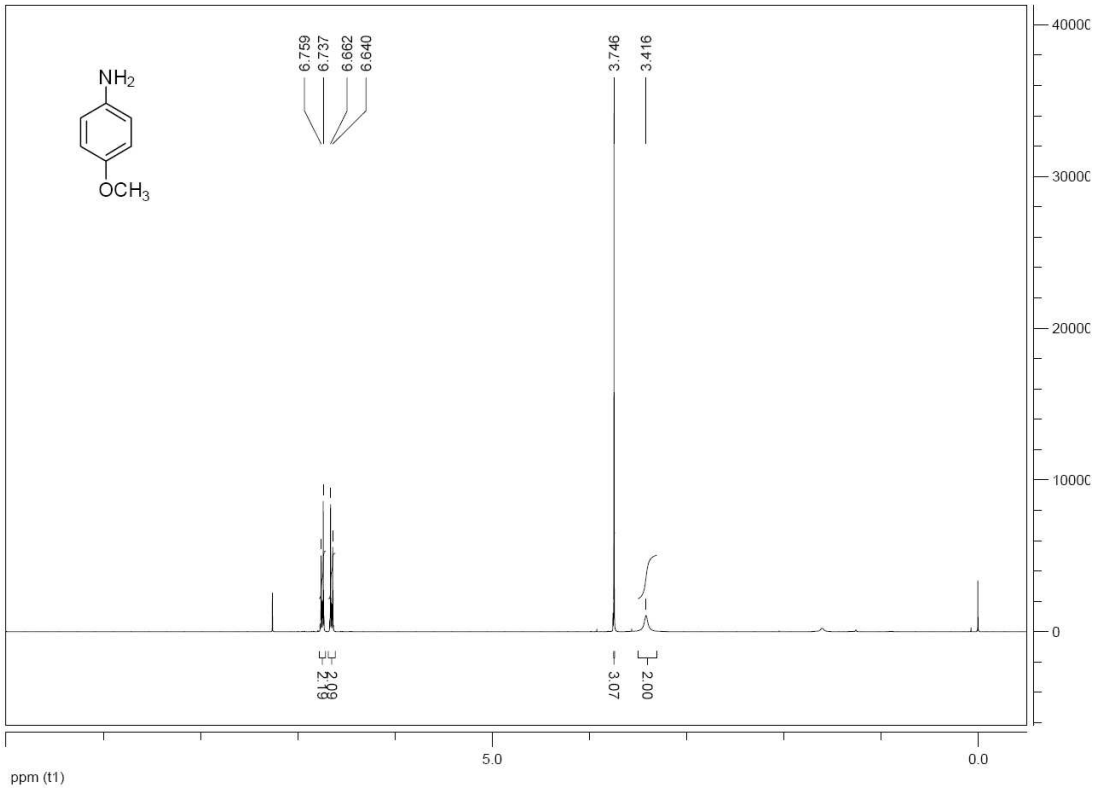


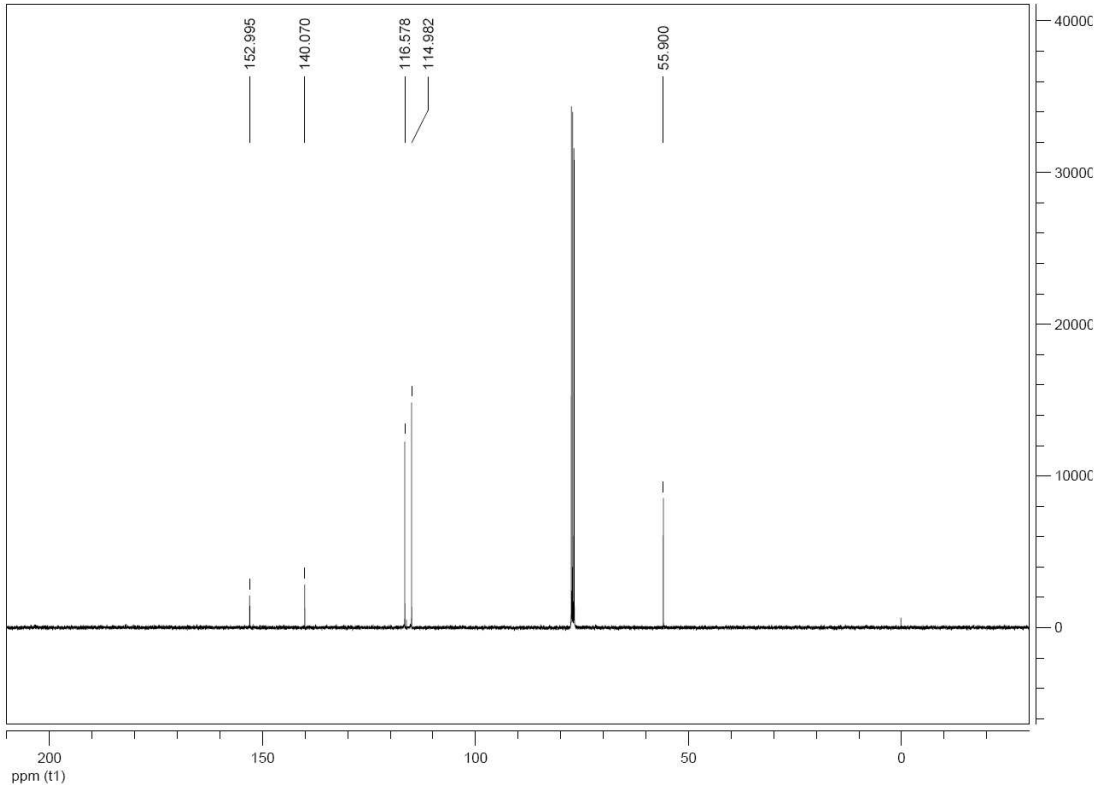
***p*-toluidine**


NH2
7.001
6.974
6.639
6.612
3.417
2.264
1.90
1.96
2.00
2.97
ppm (t1)

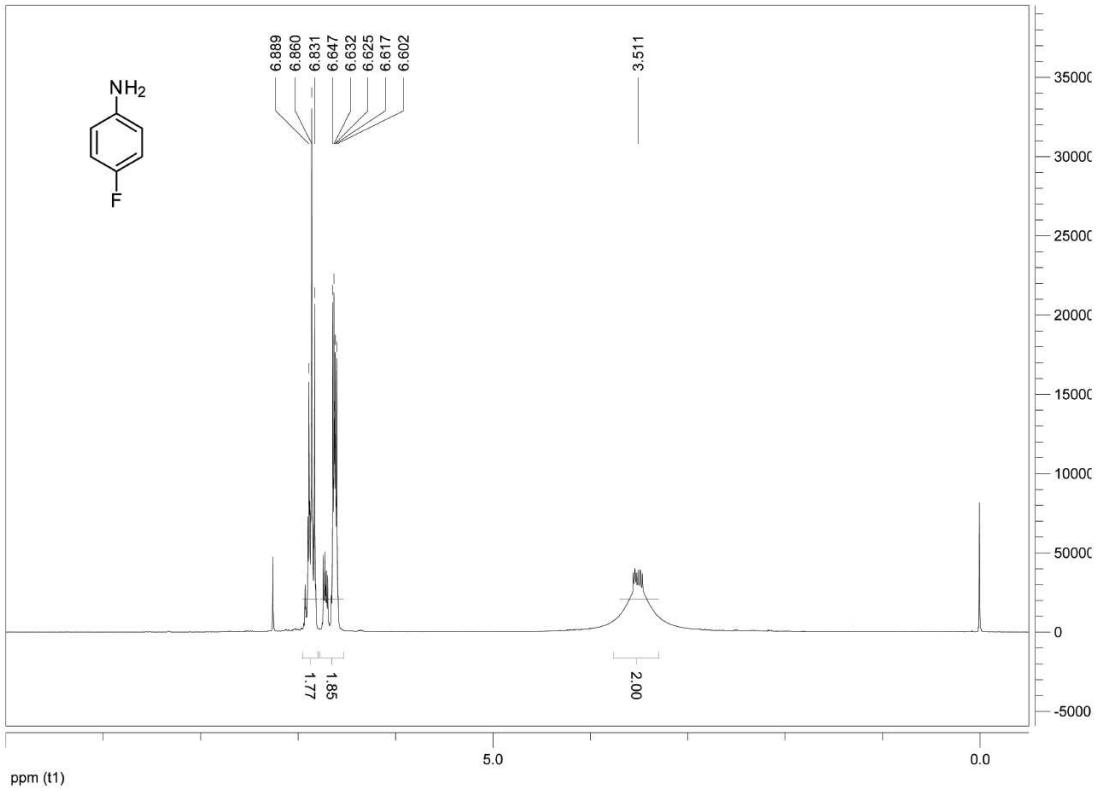

143.918
129.807
127.792
115.313
20.474
ppm (t1)

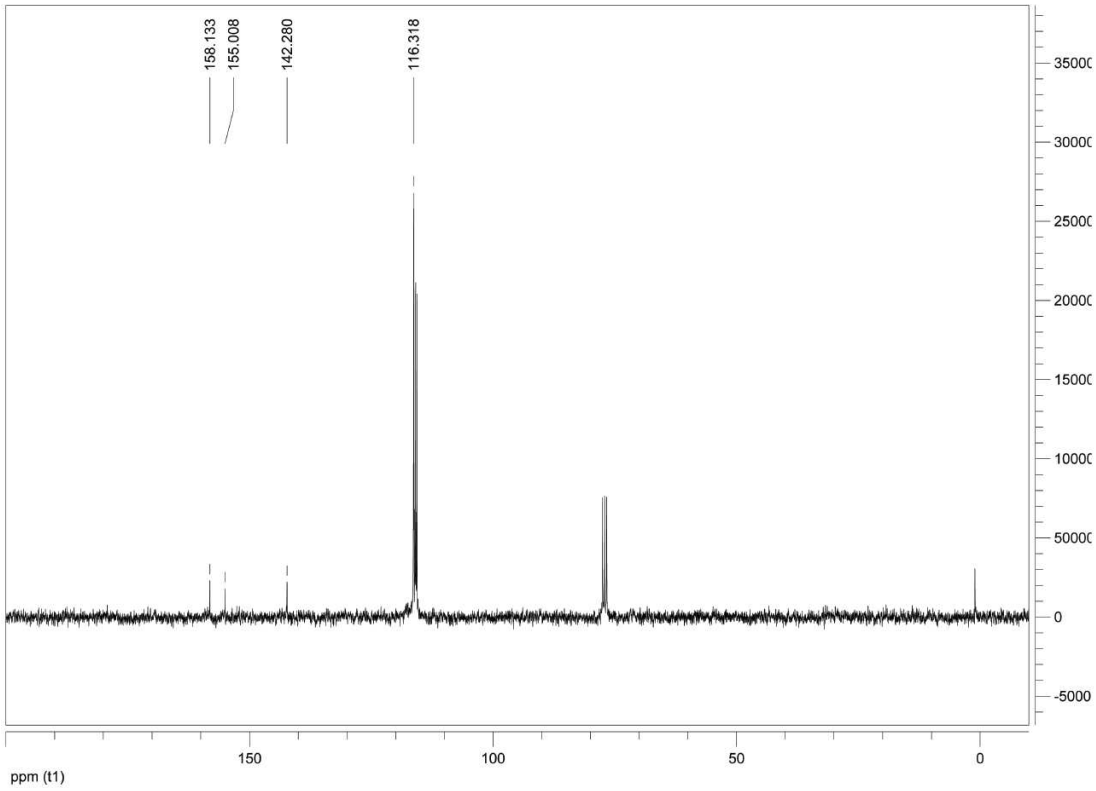
4-methoxyaniline



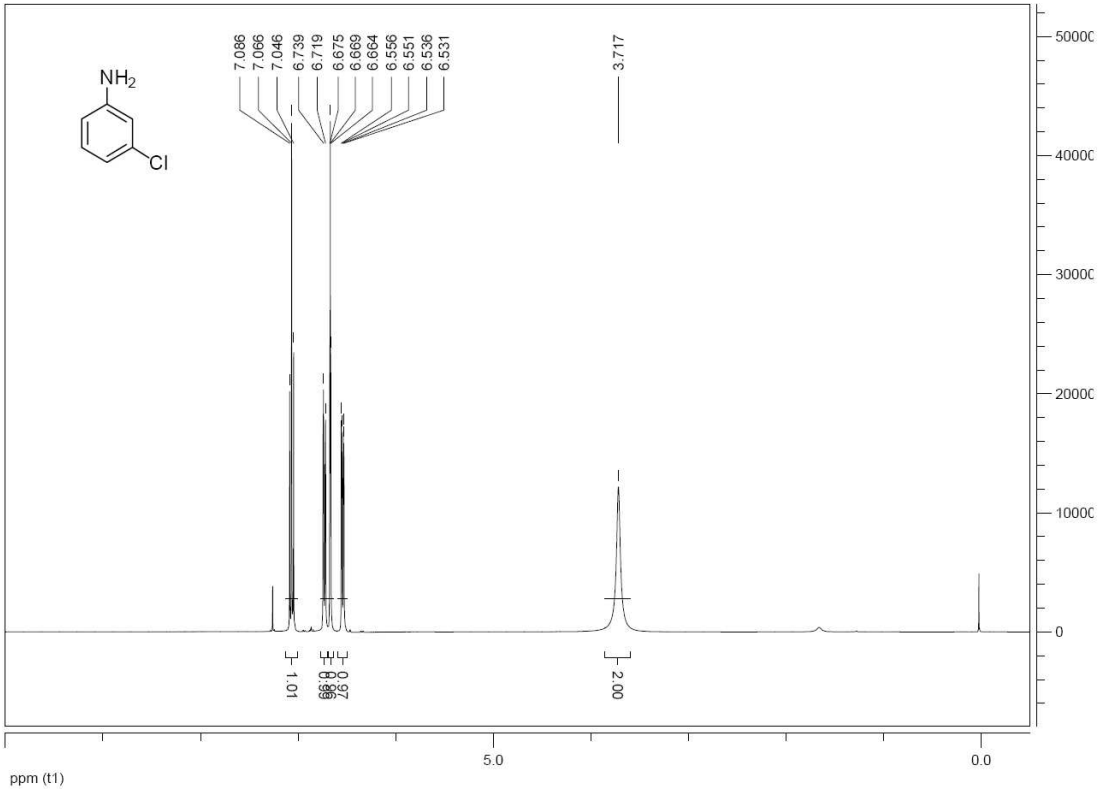


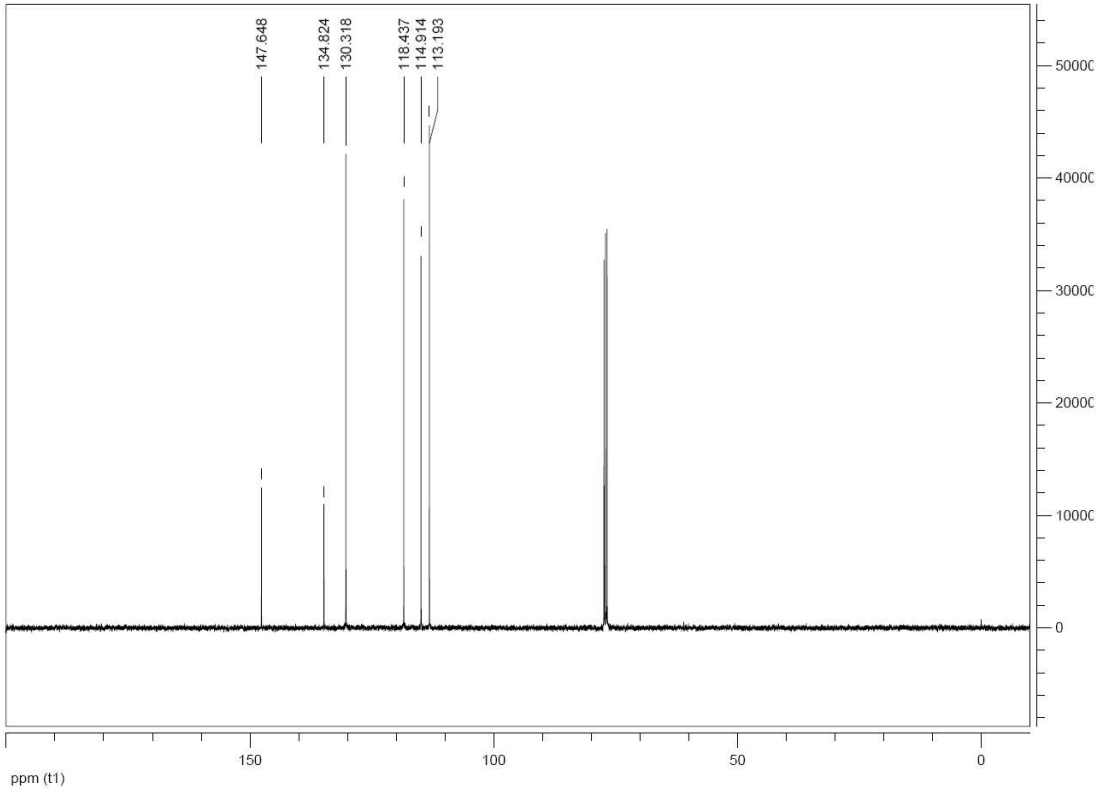
4-fluoroaniline



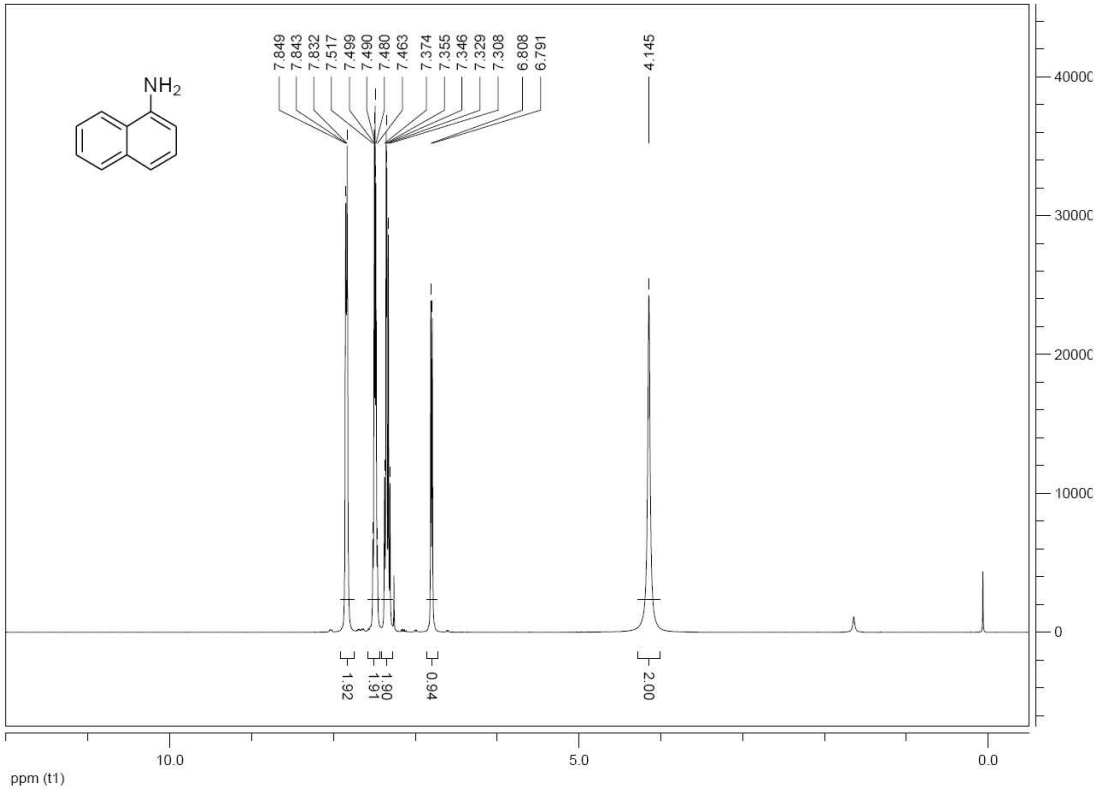


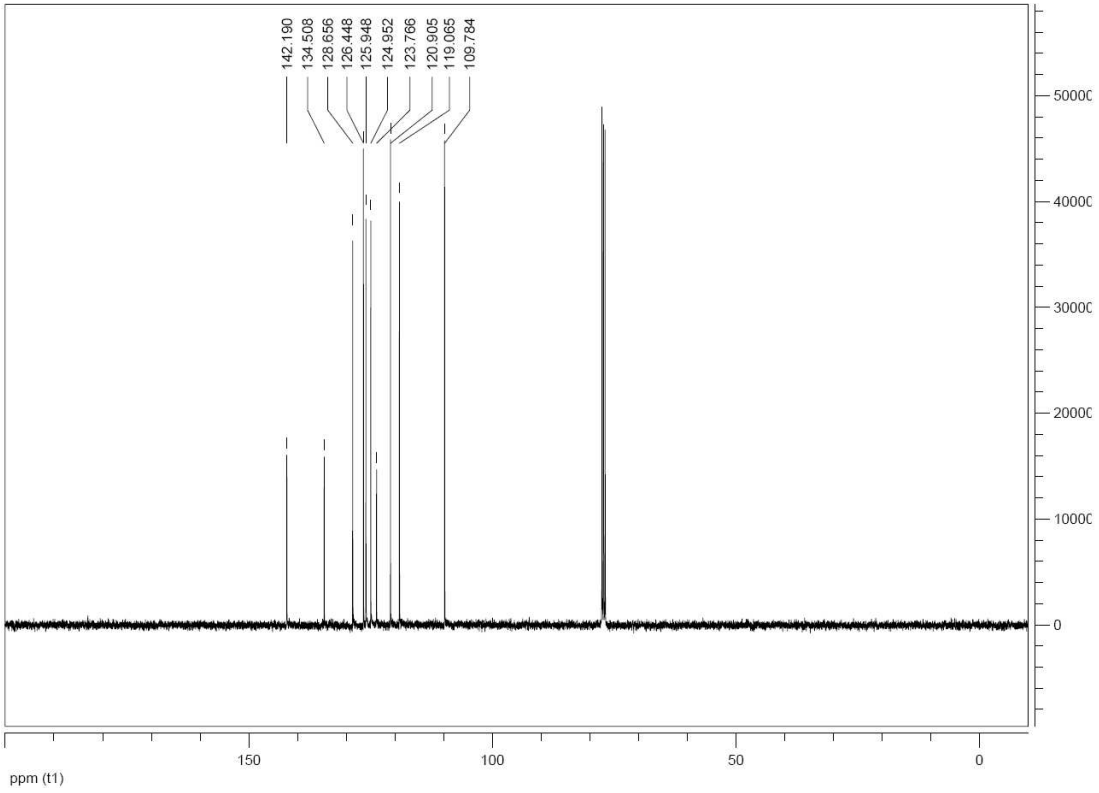
3-chloroaniline



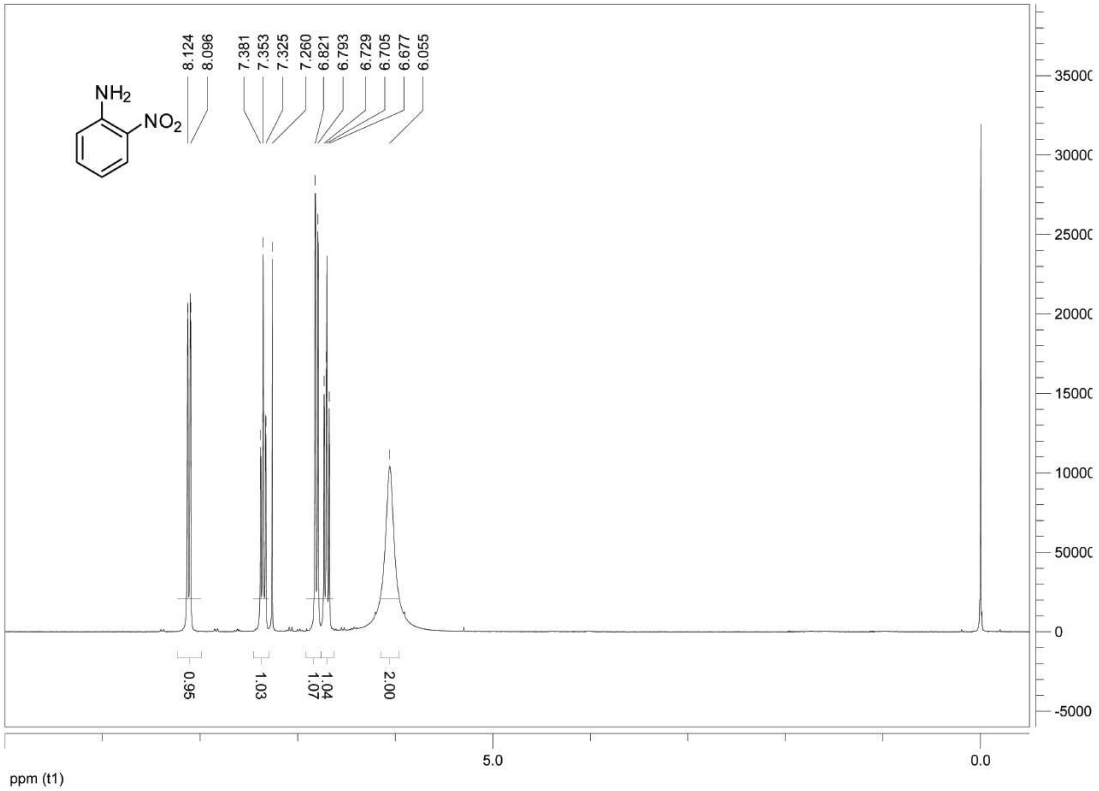


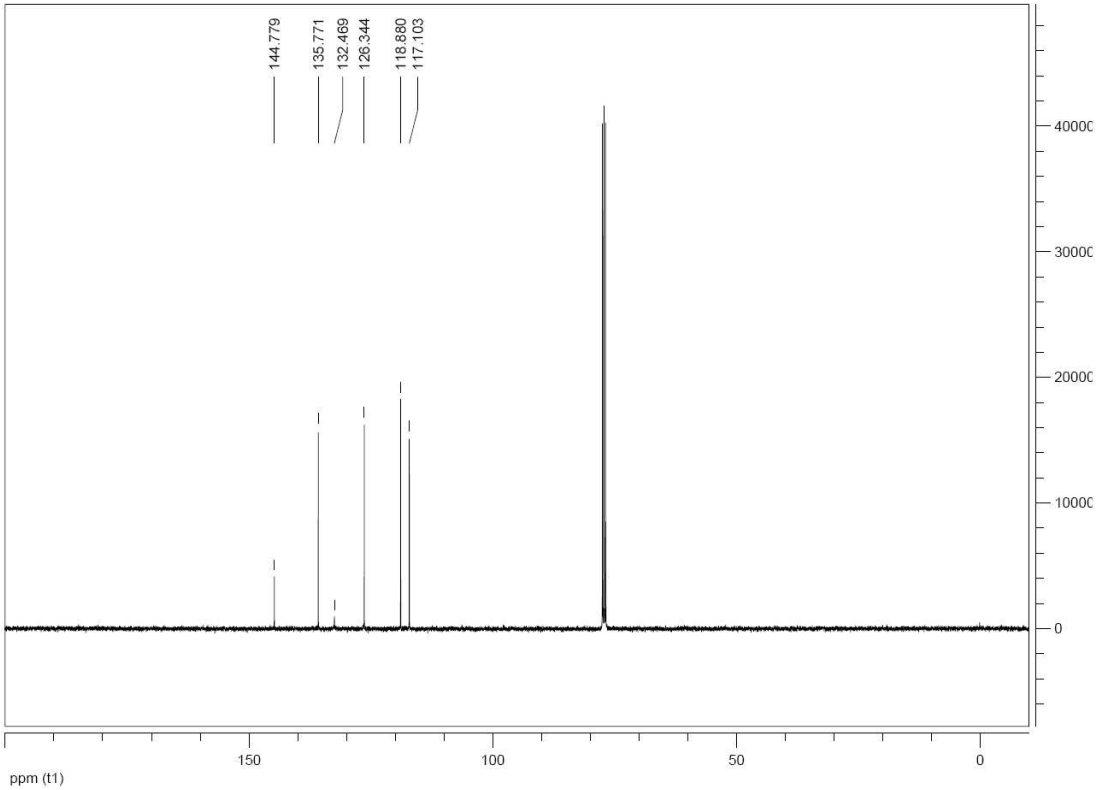
1-naphthalenamine



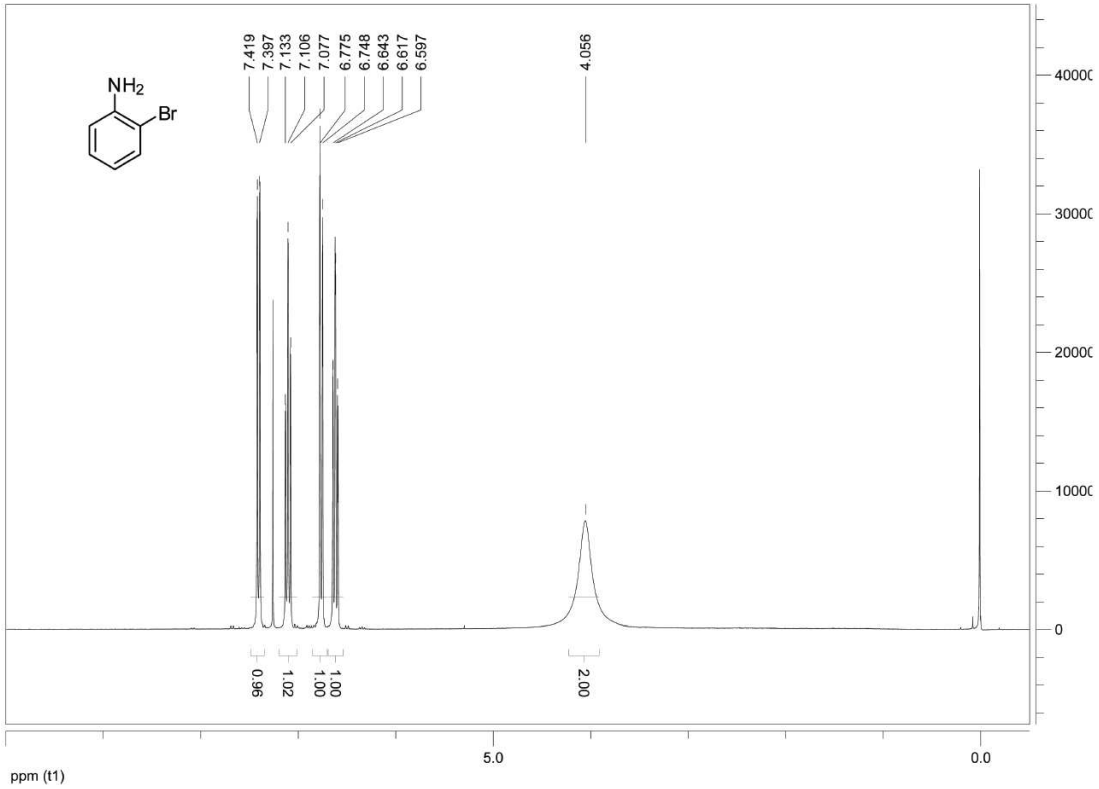


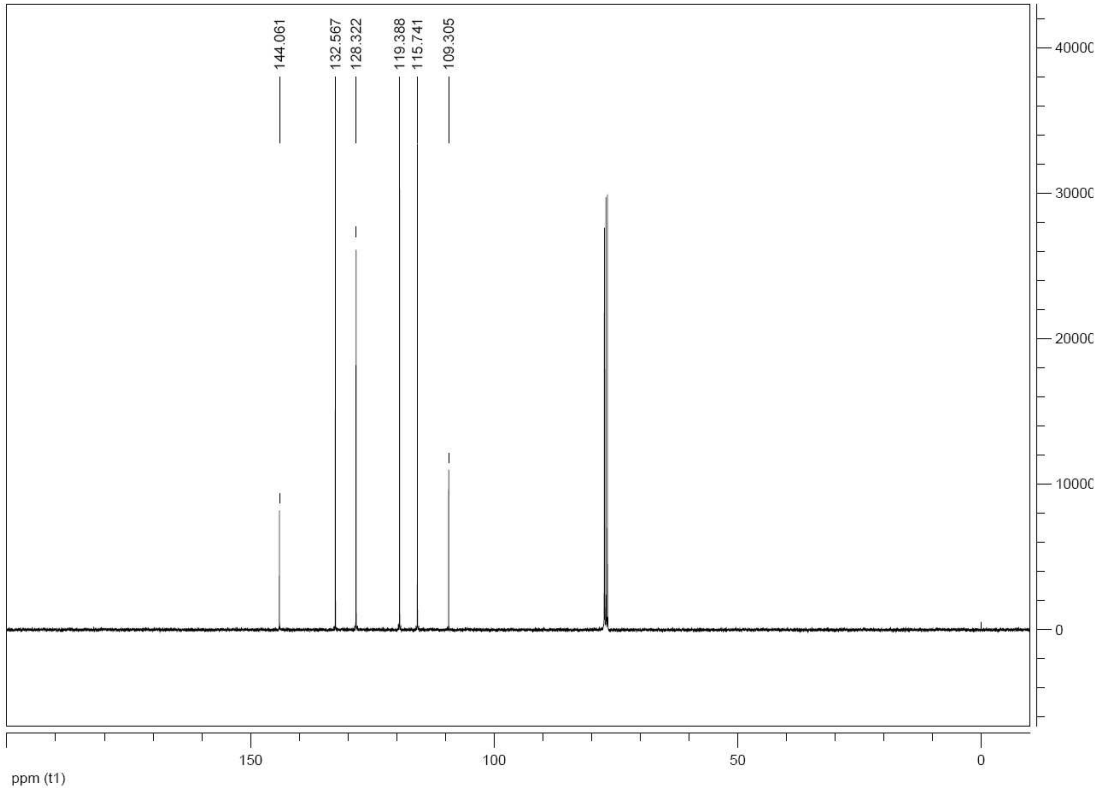
2-nitroaniline



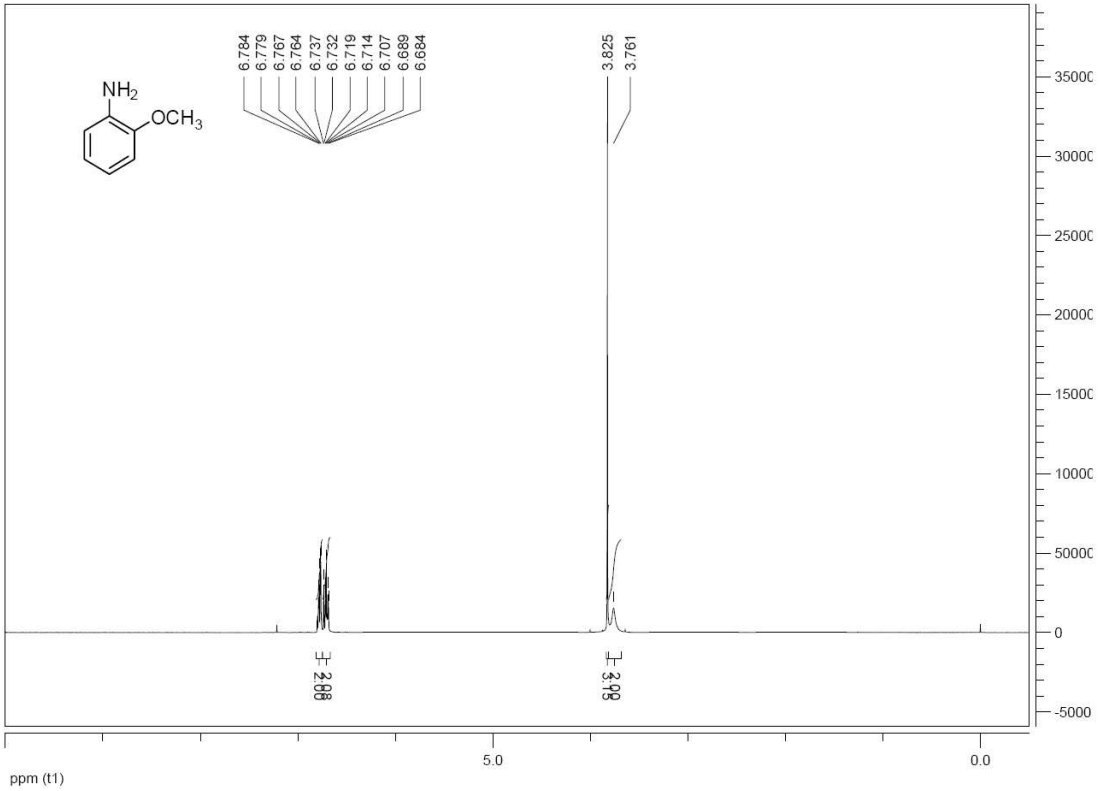


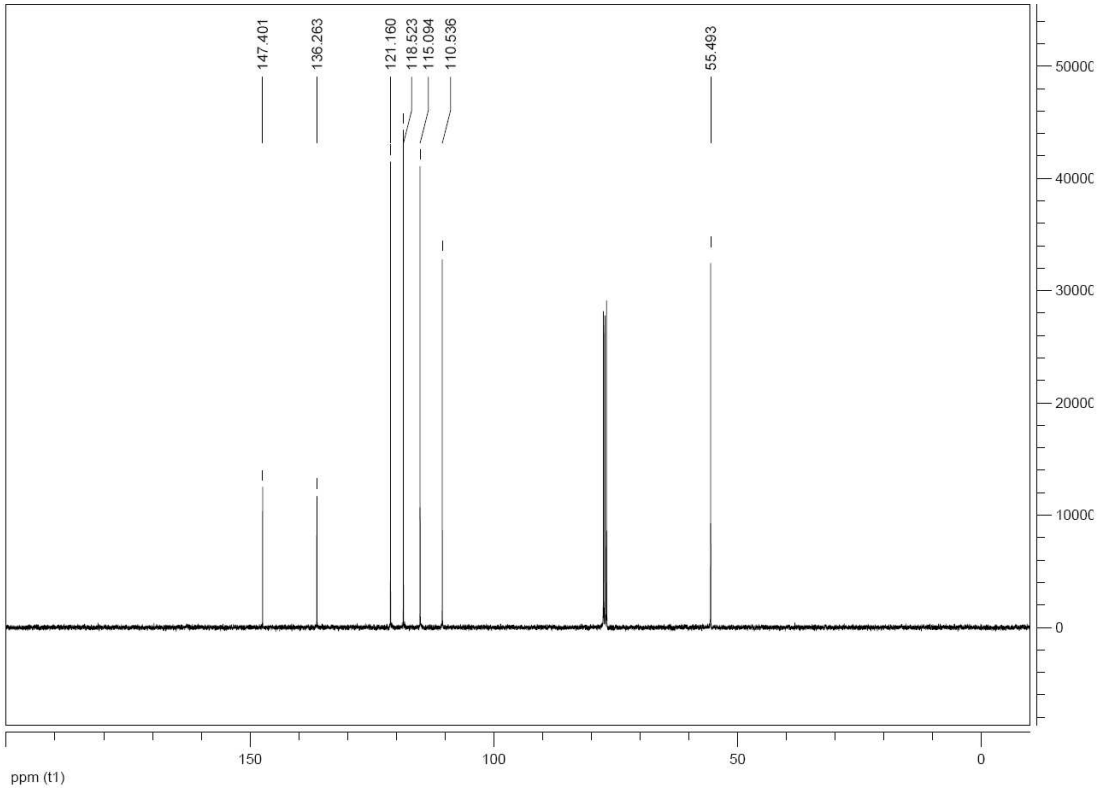
2-bromoaniline



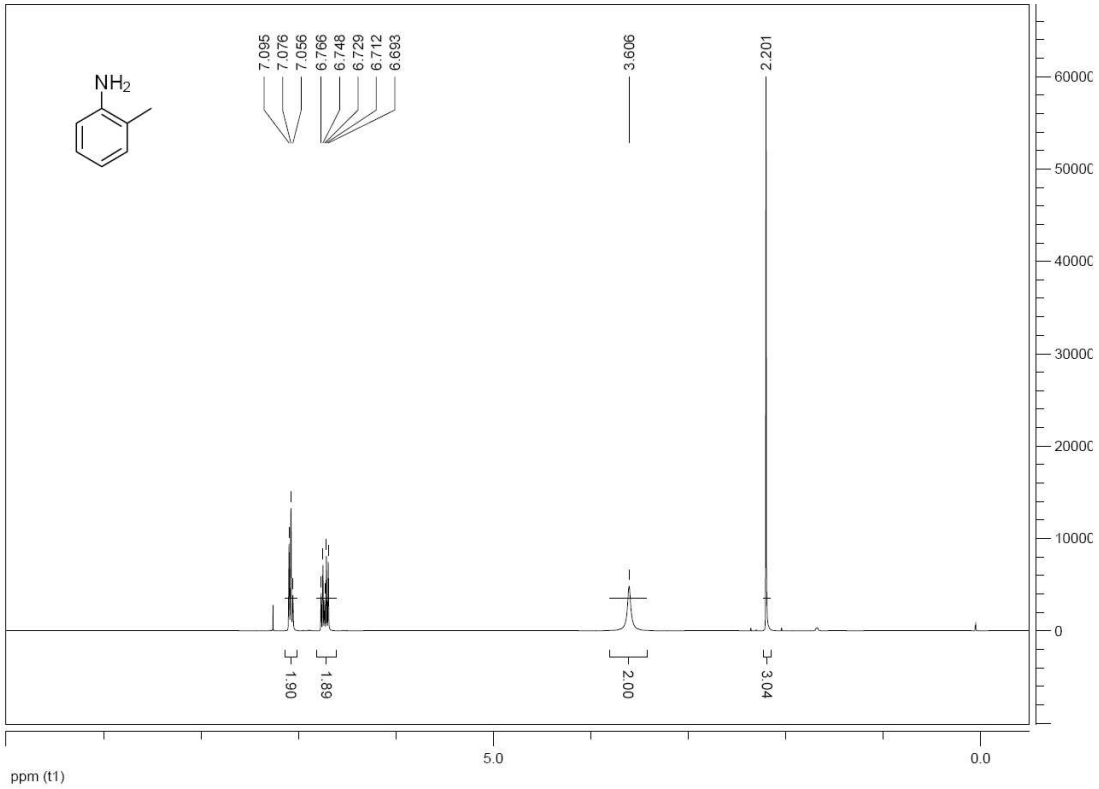


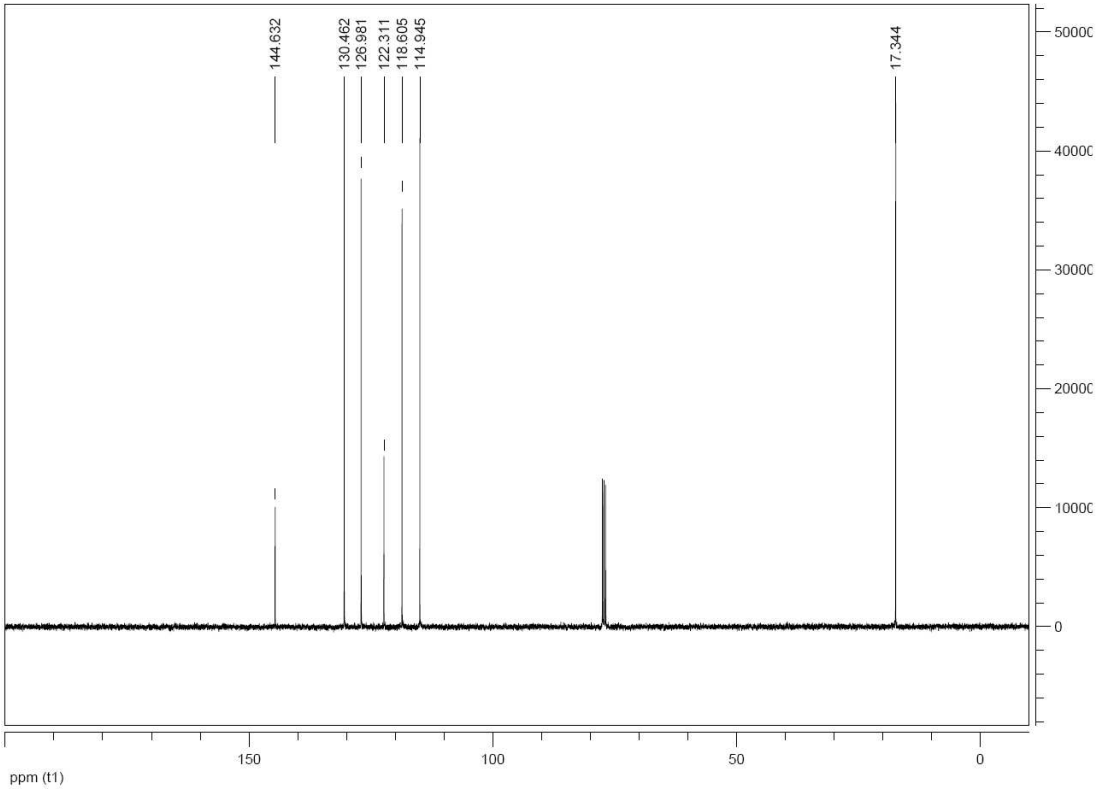
2-methoxyaniline



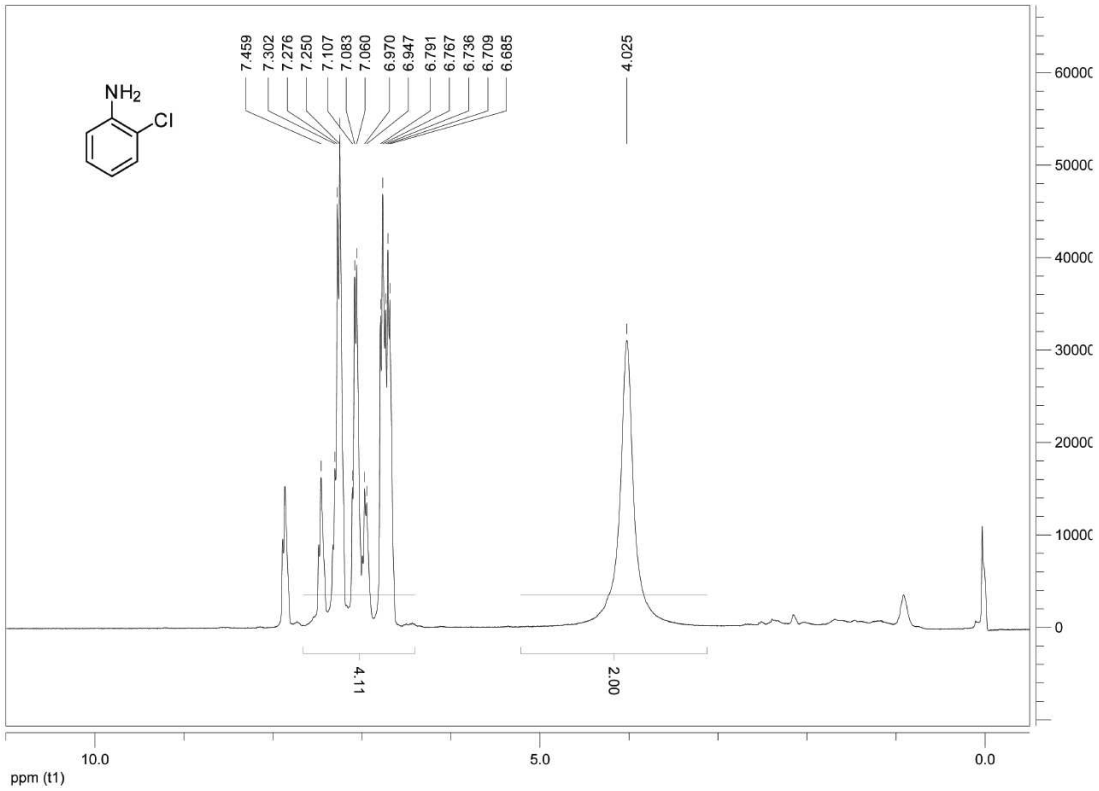


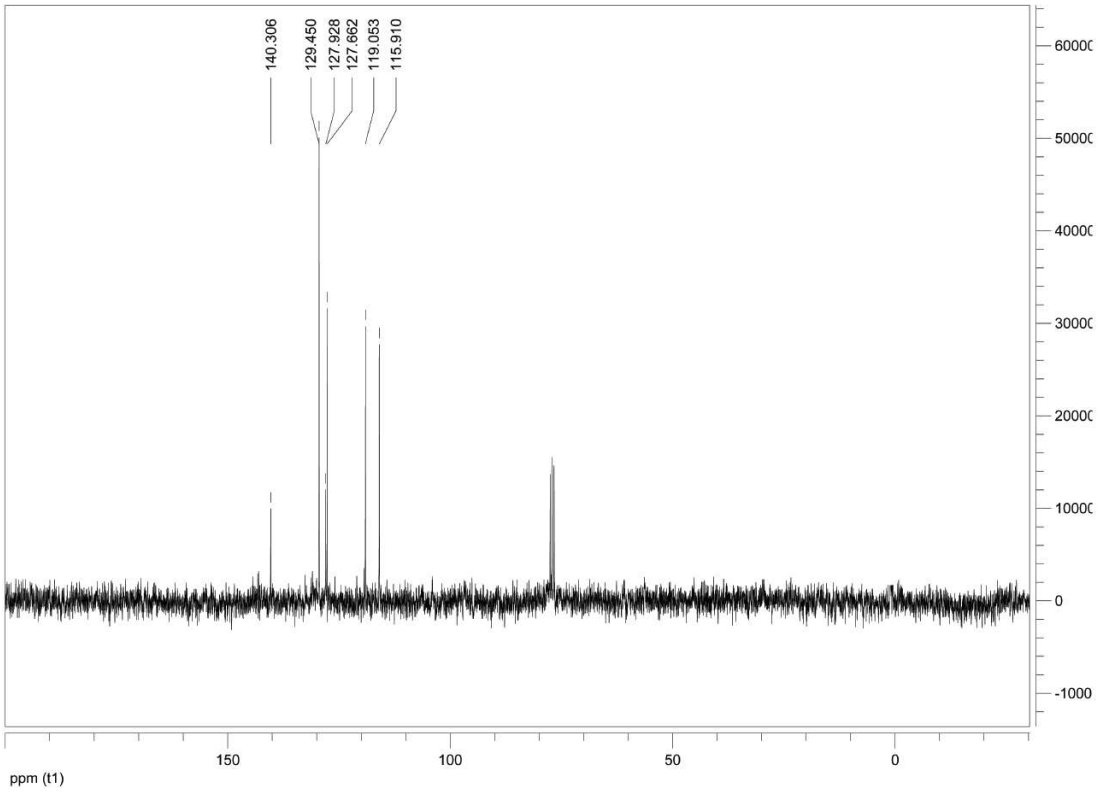
***o*-toluidine**


NH2
7.095
7.076
7.056
6.766
6.748
6.729
6.712
6.693
3.606
2.201
1.90
1.89
2.00
3.04
5.0
0.0
ppm (t1)

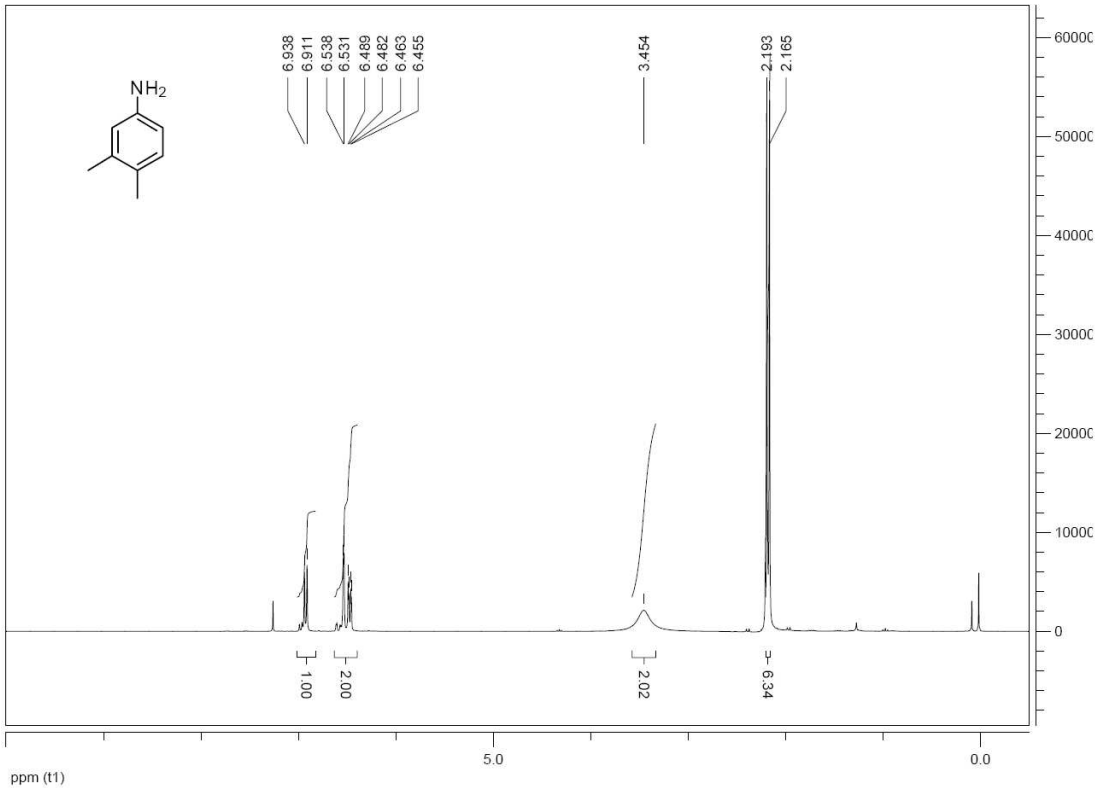

144.632
130.462
126.981
122.311
118.605
114.945
17.344
150
100
50
0
ppm (t1)

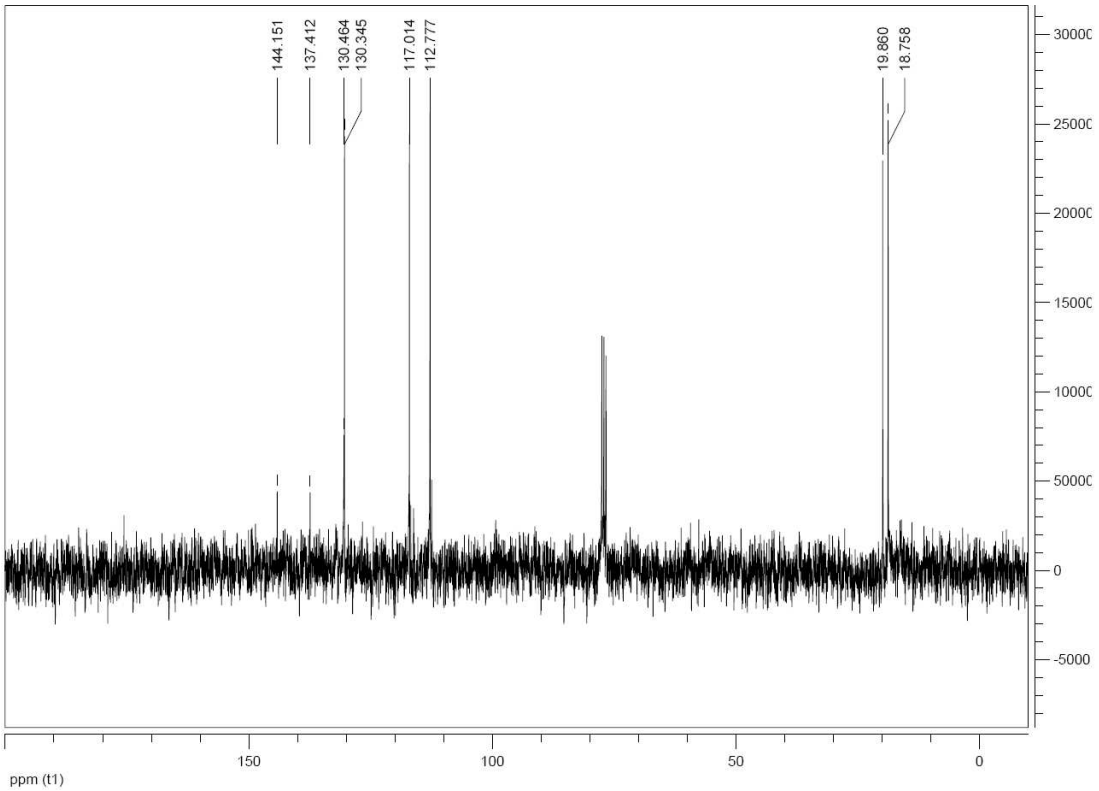
2-chloroaniline



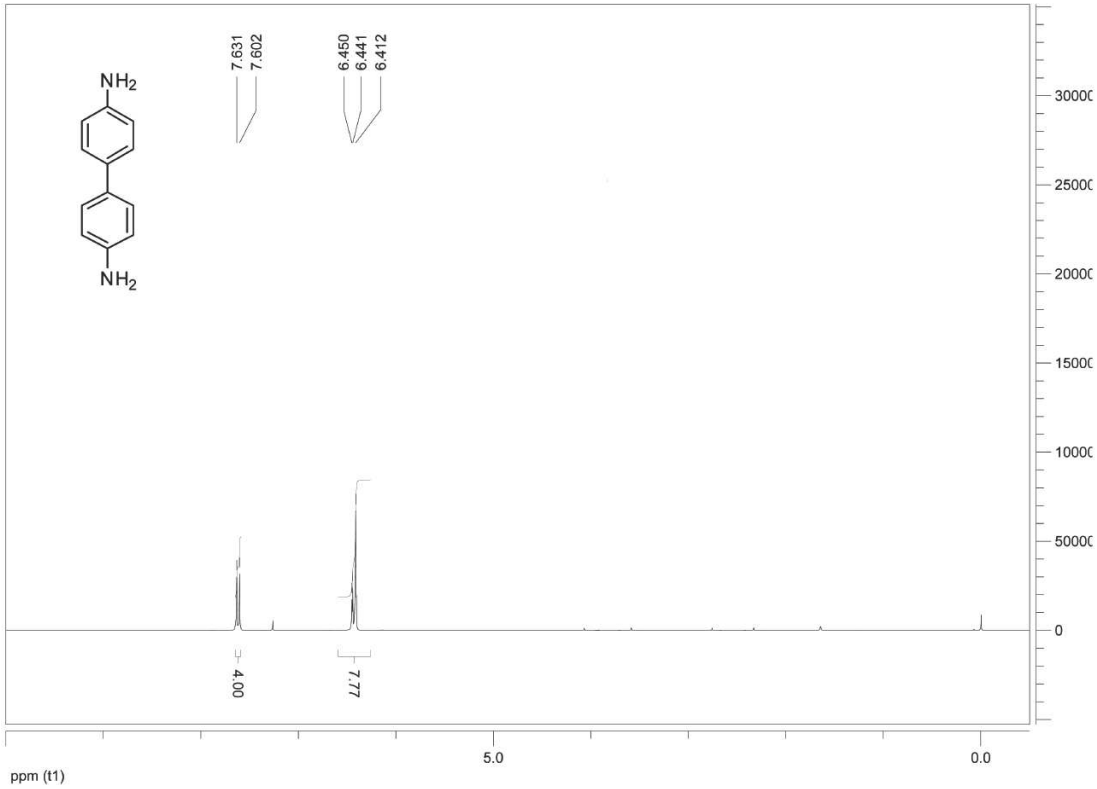


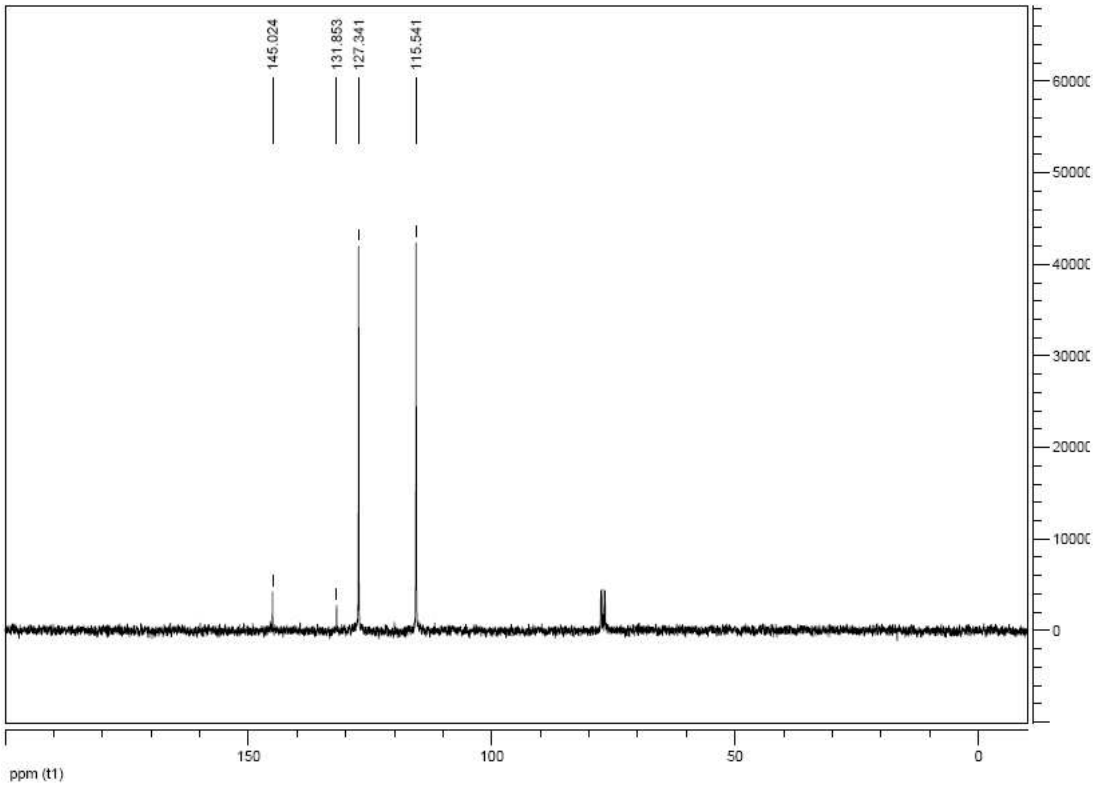
3,4-dimethylaniline



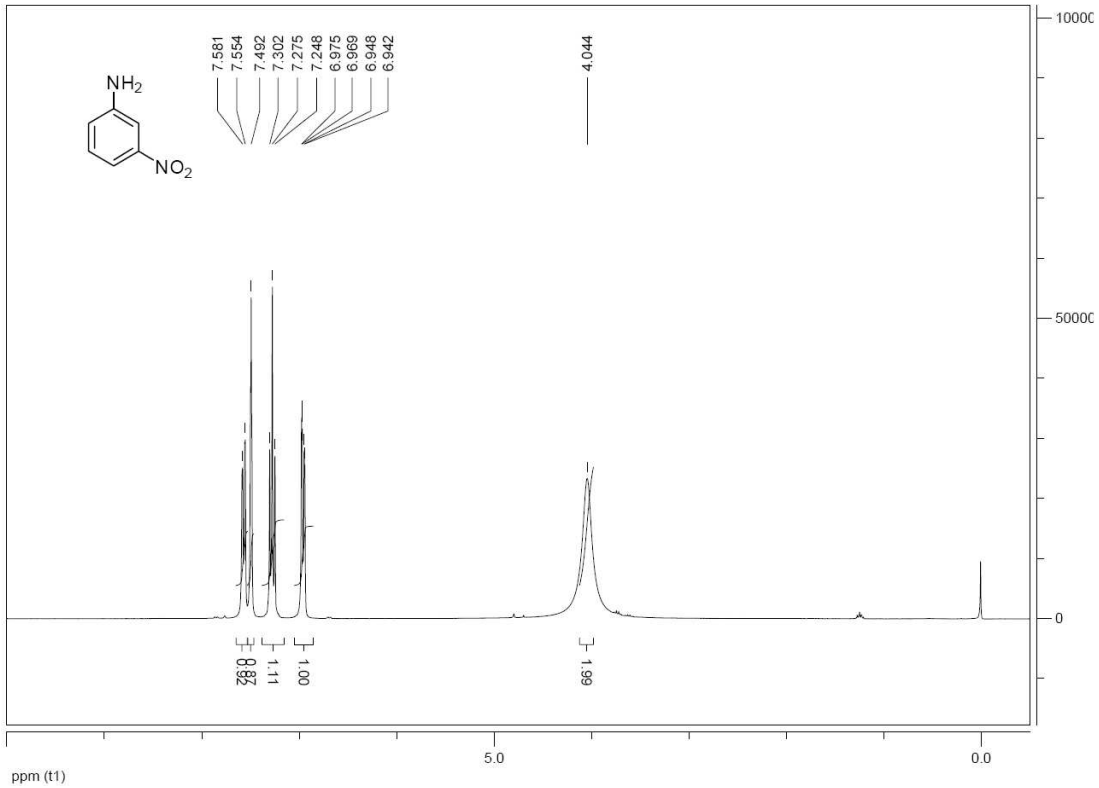


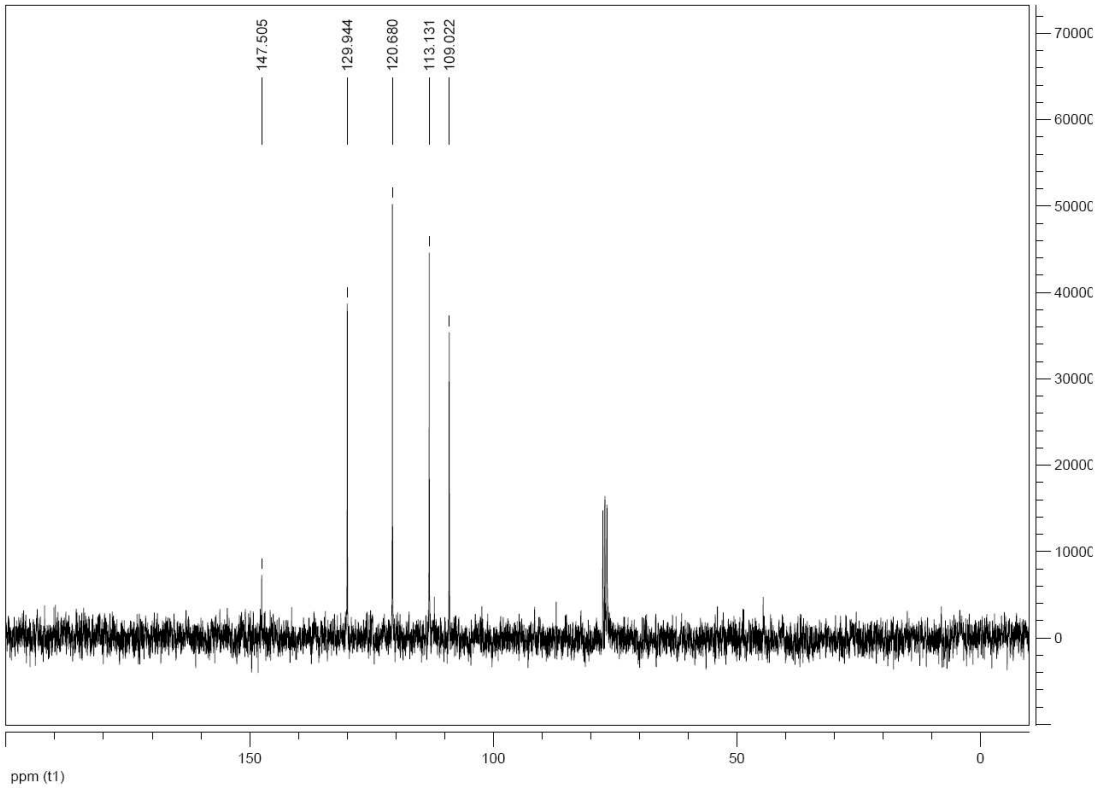
benzidine


NH2
NH2
7.631
7.602
6.450
6.441
6.412
4.00
7.77
5.0
0.0
ppm (t1)

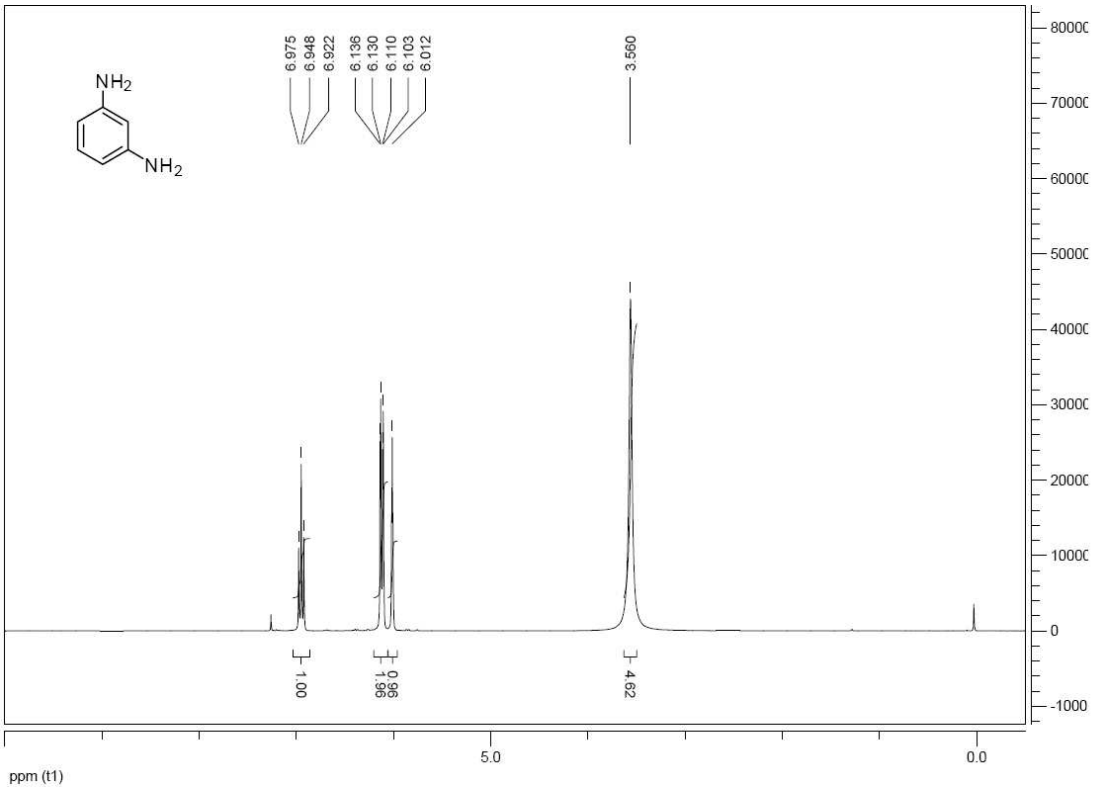

145.024
131.853
127.341
115.541
150
100
50
0
ppm (t1)

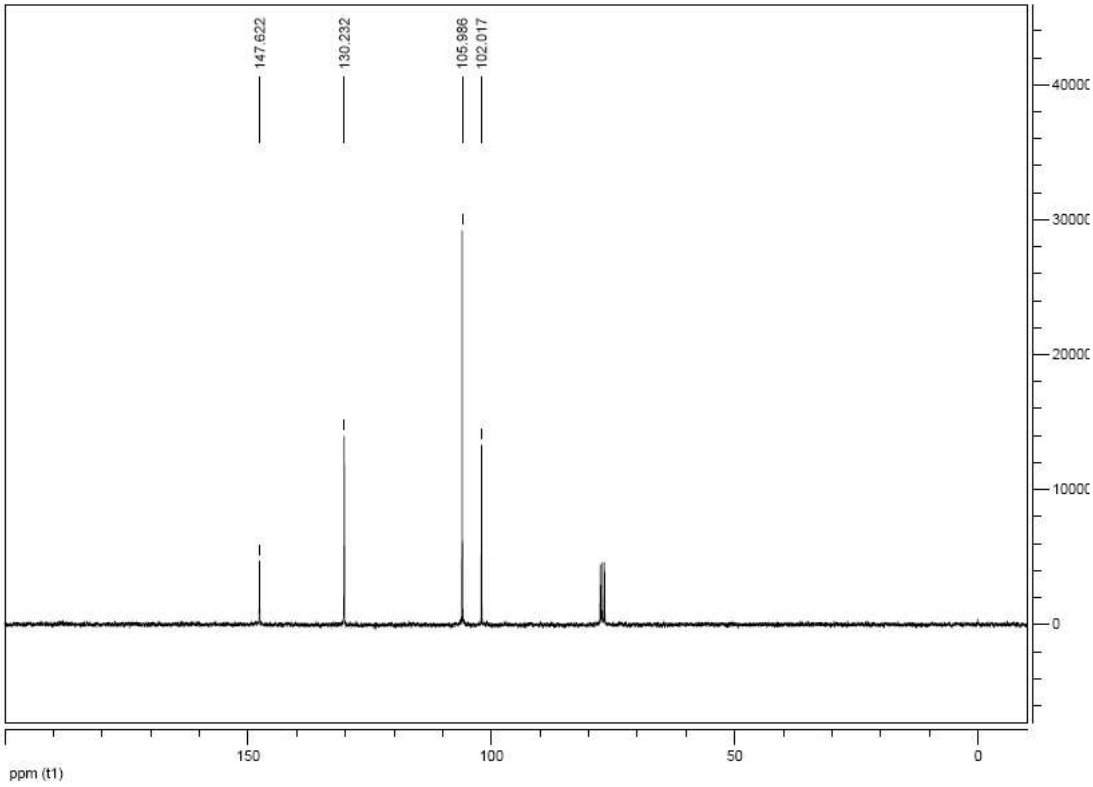
3-nitroaniline



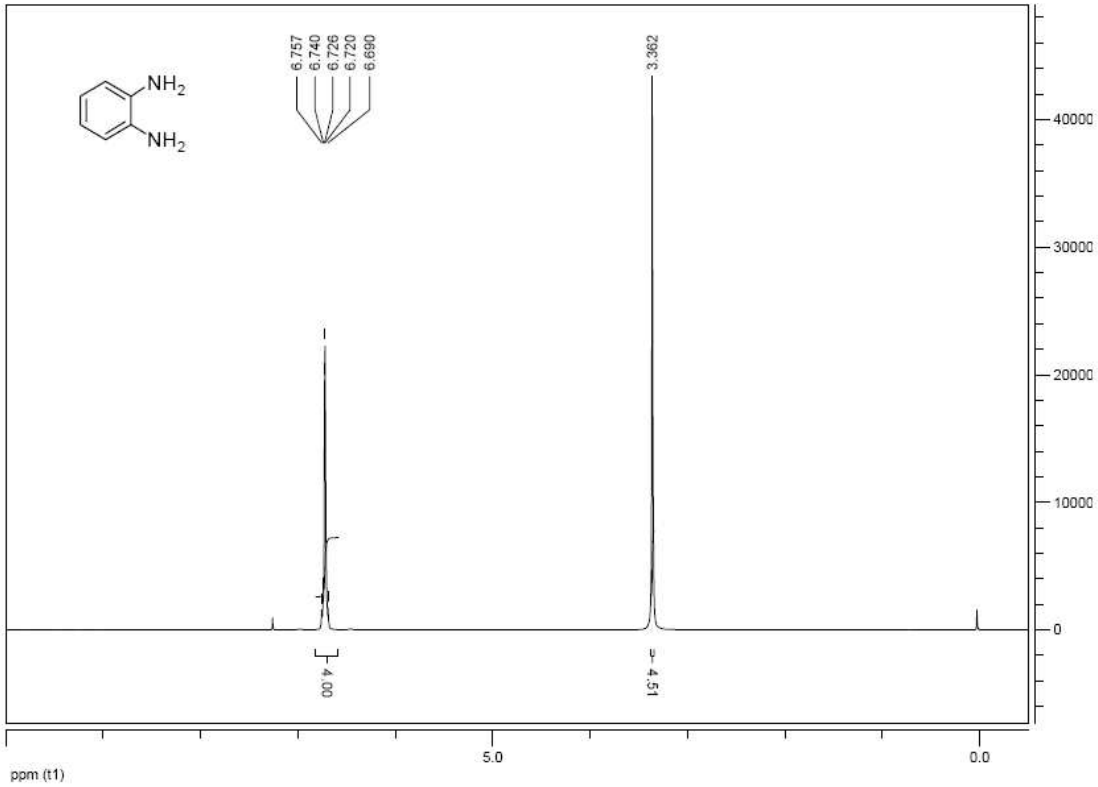


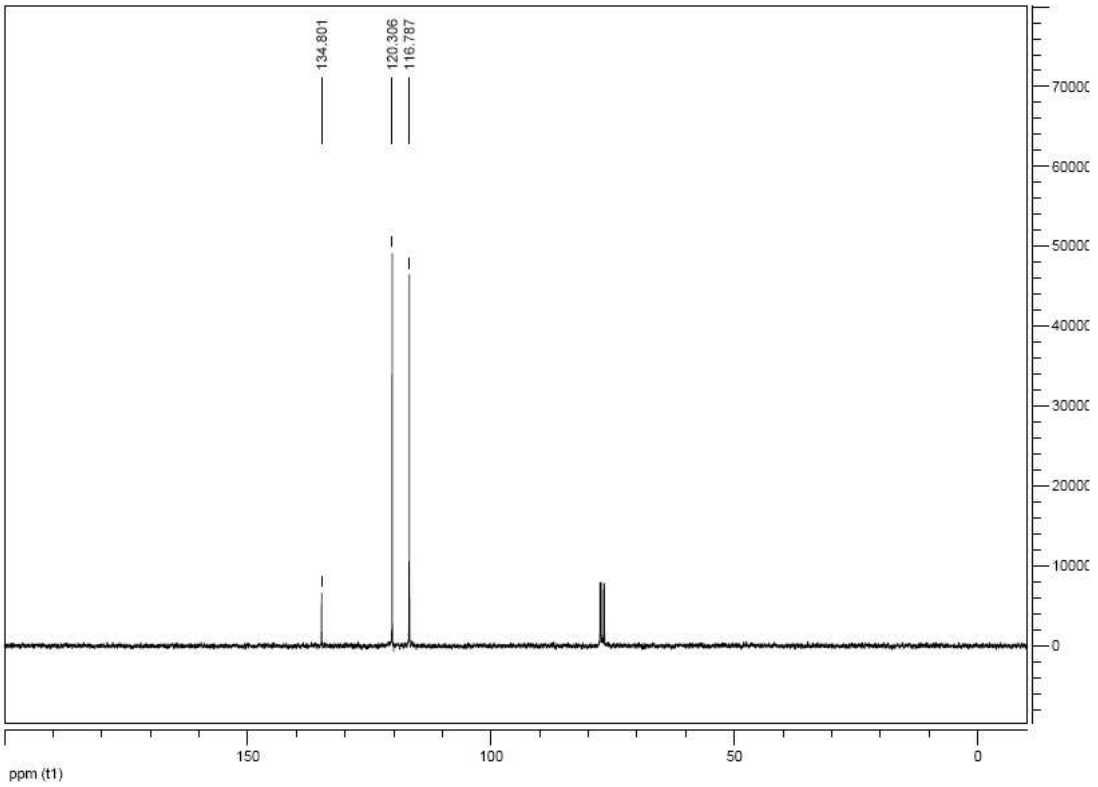
***m*-phenylenediamine**



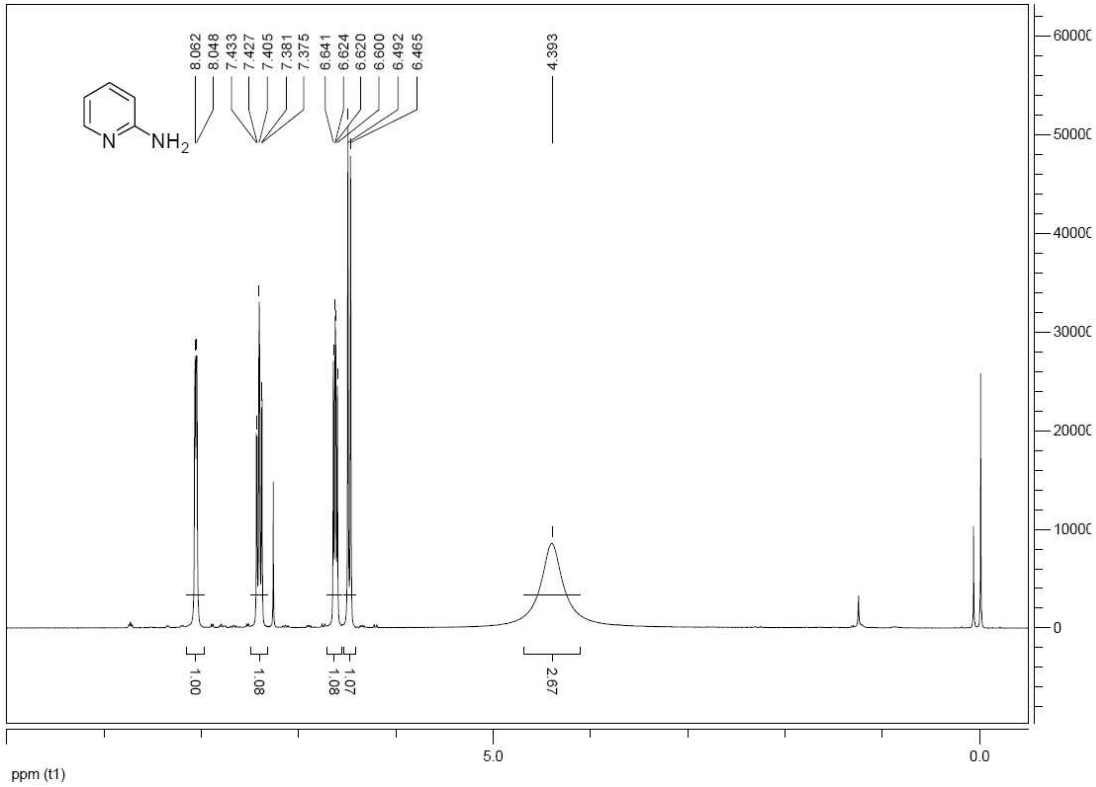


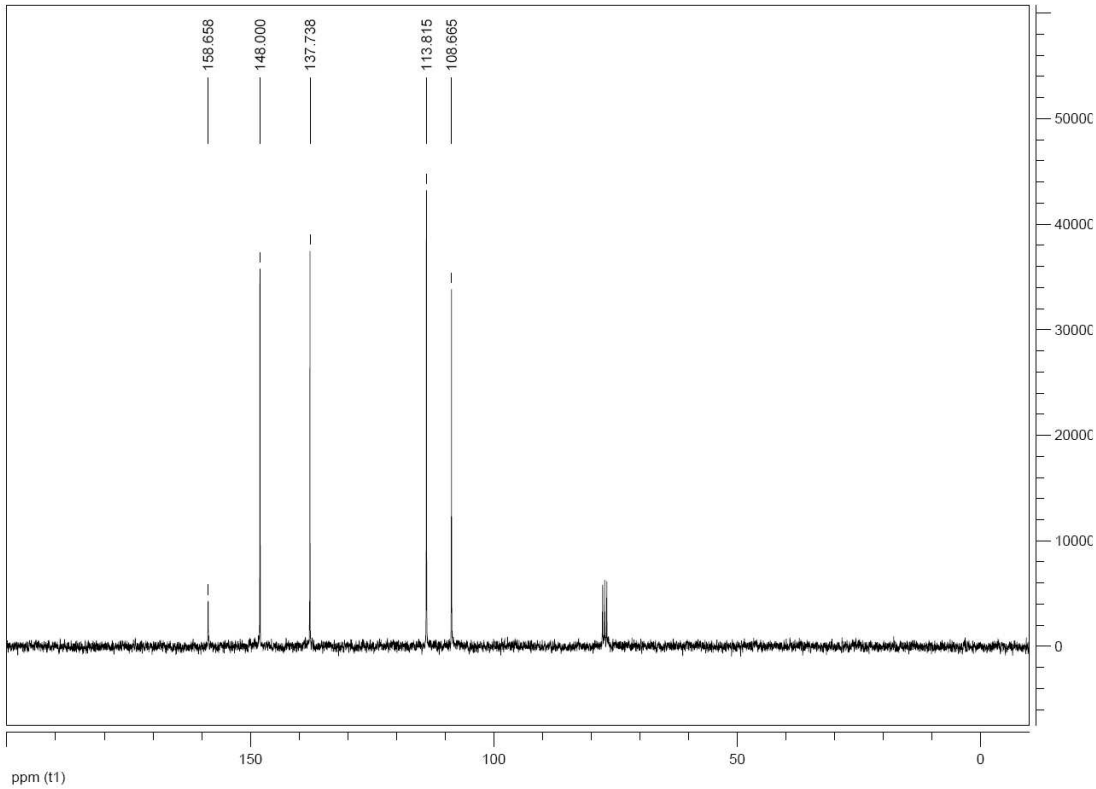
1,2-diaminobenzene



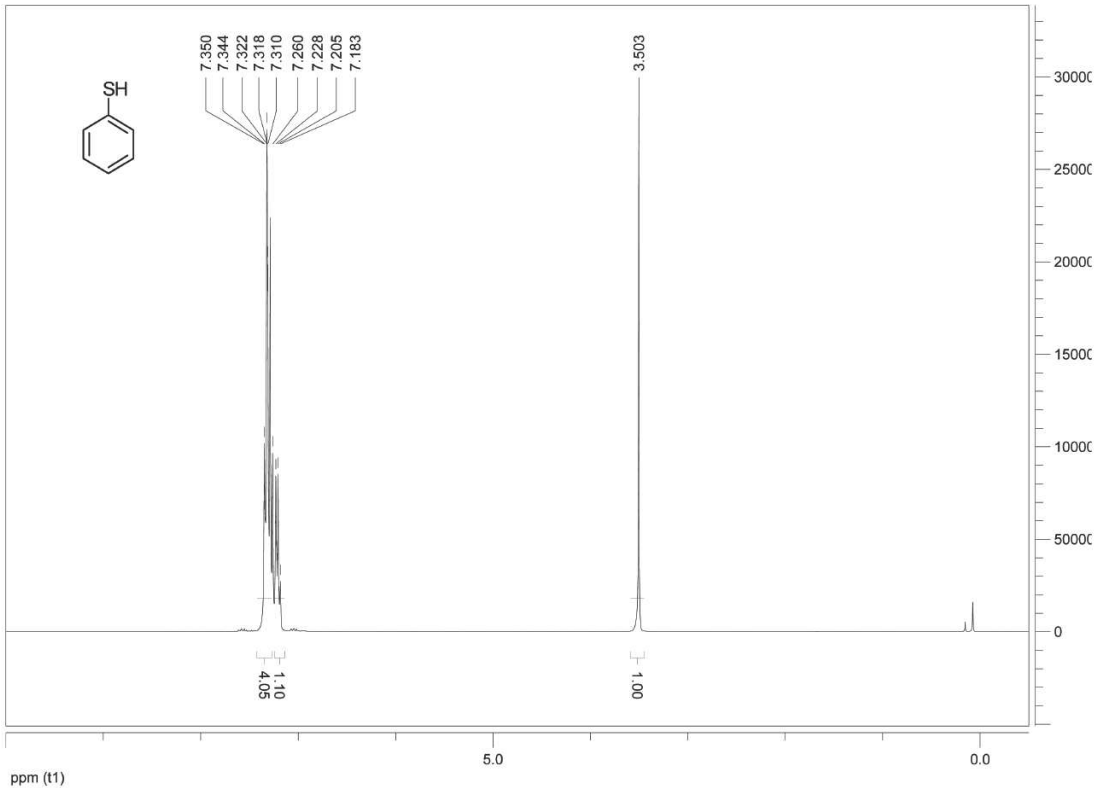


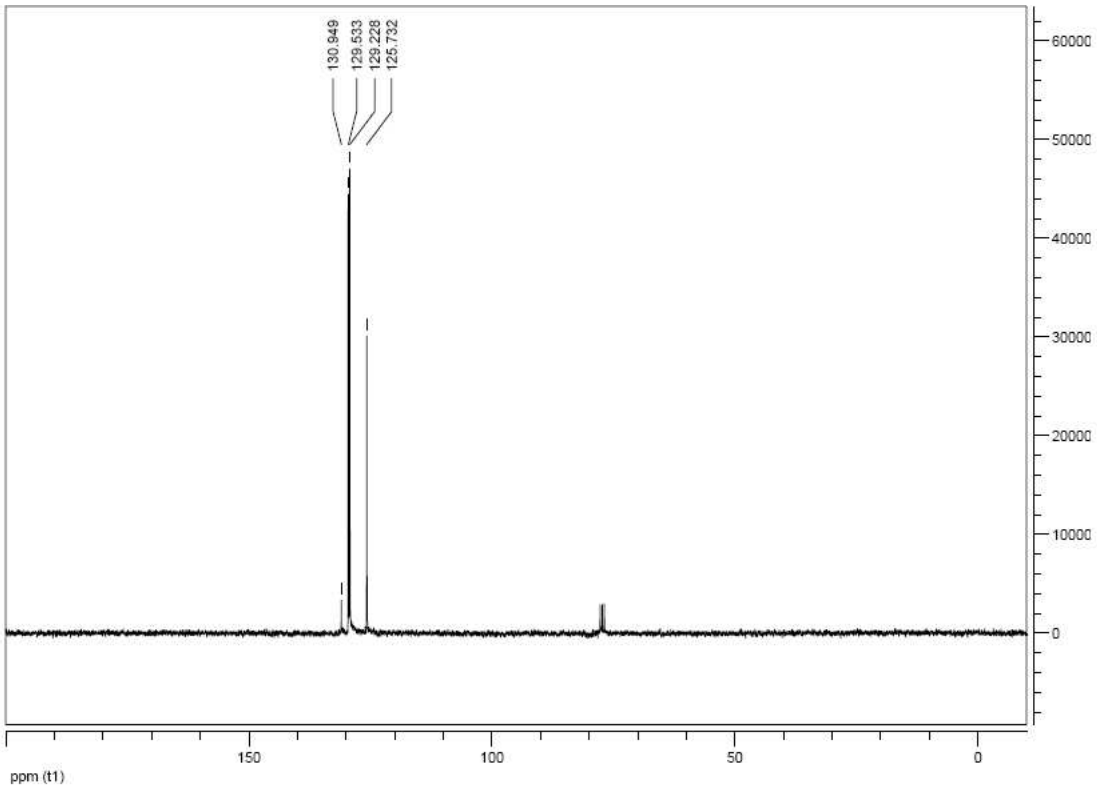
pyridin-2-amine



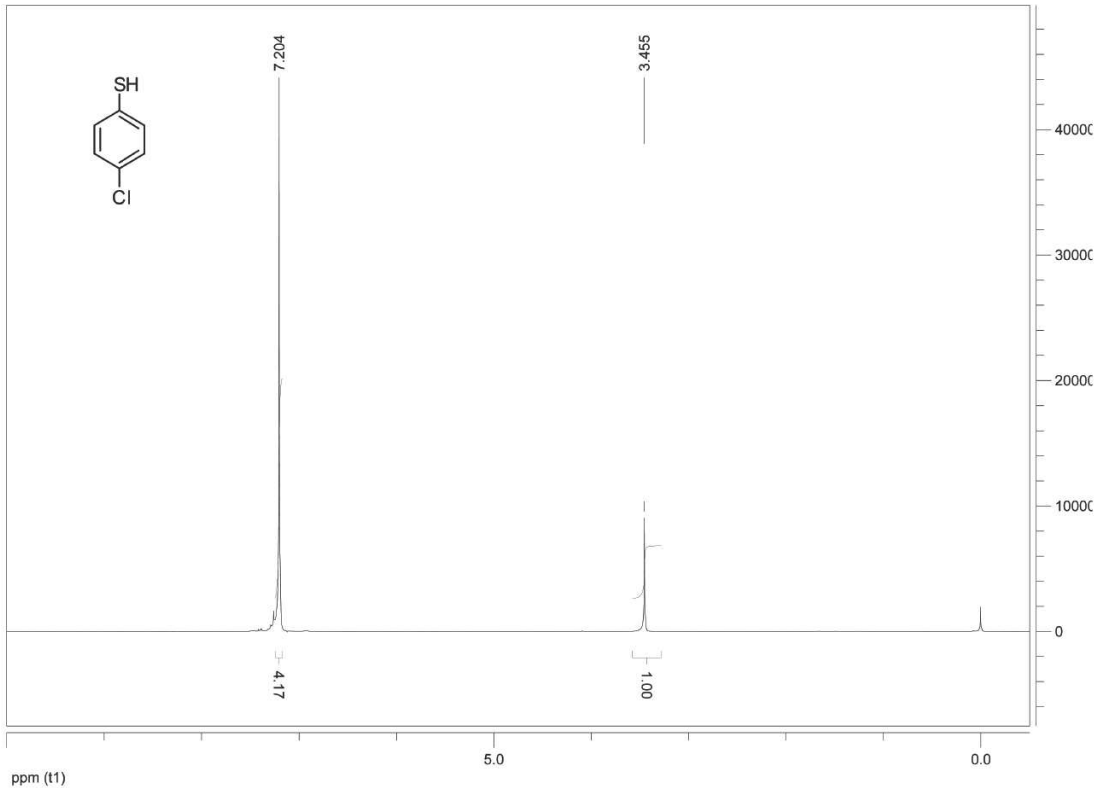


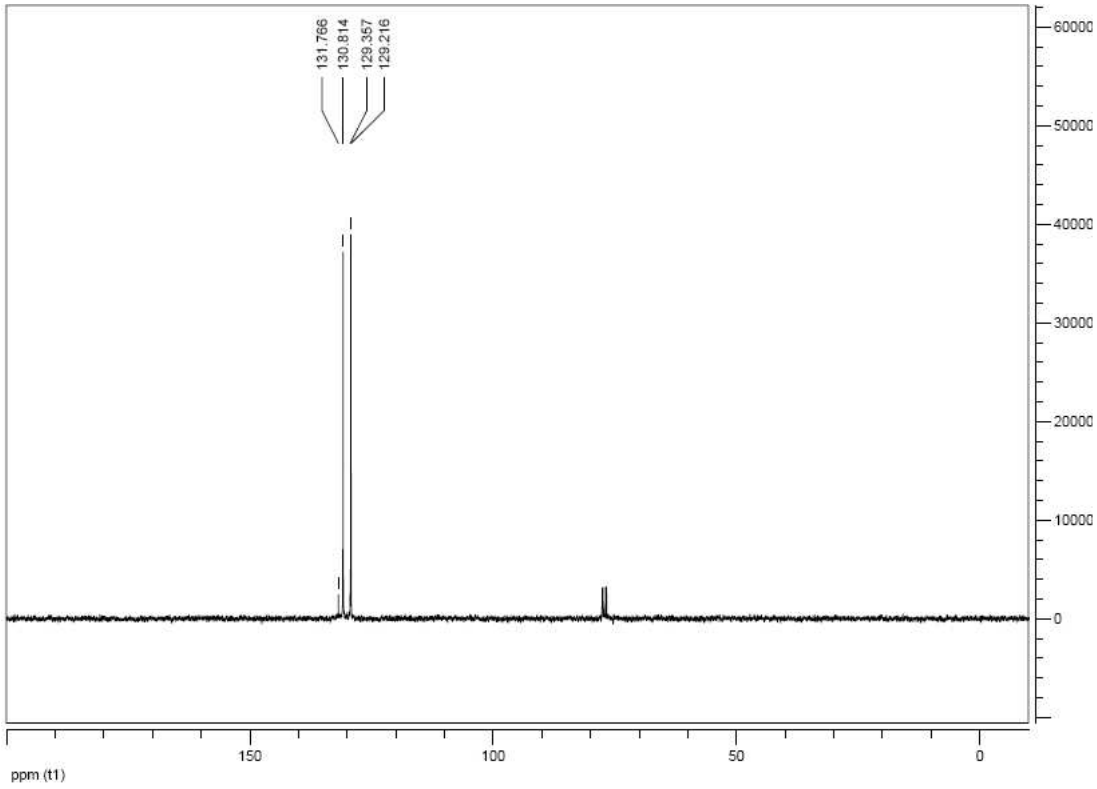
benzenethiol



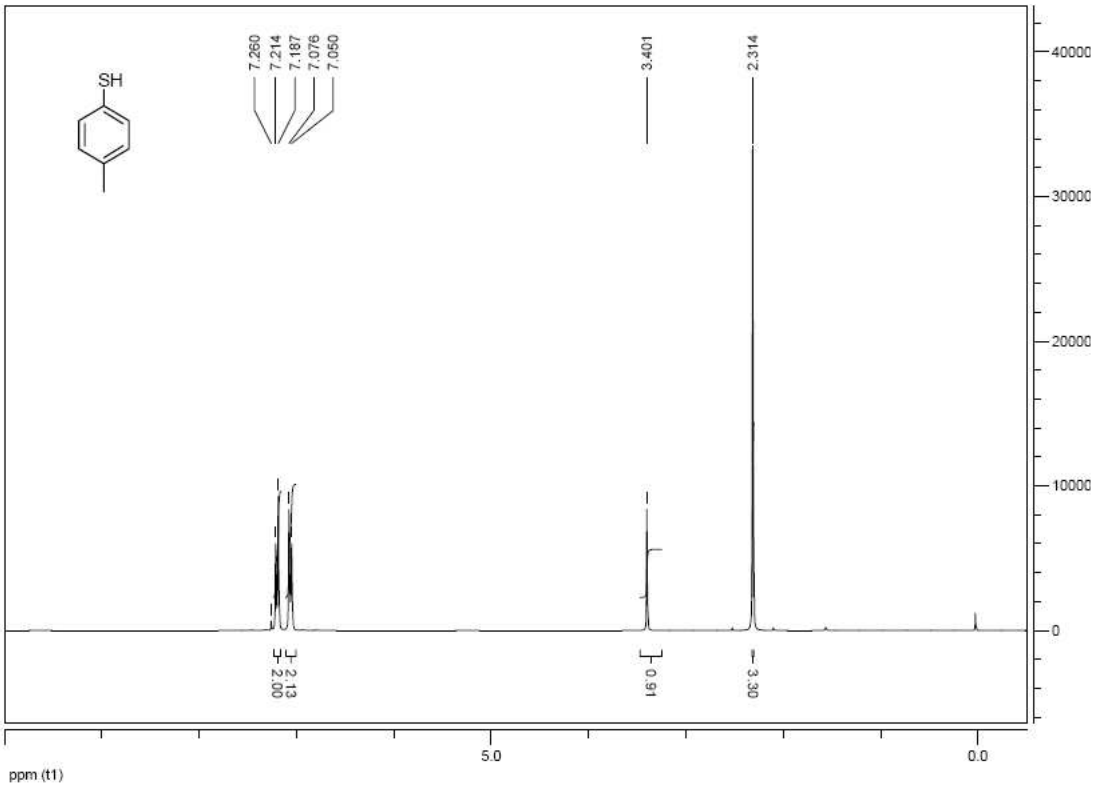


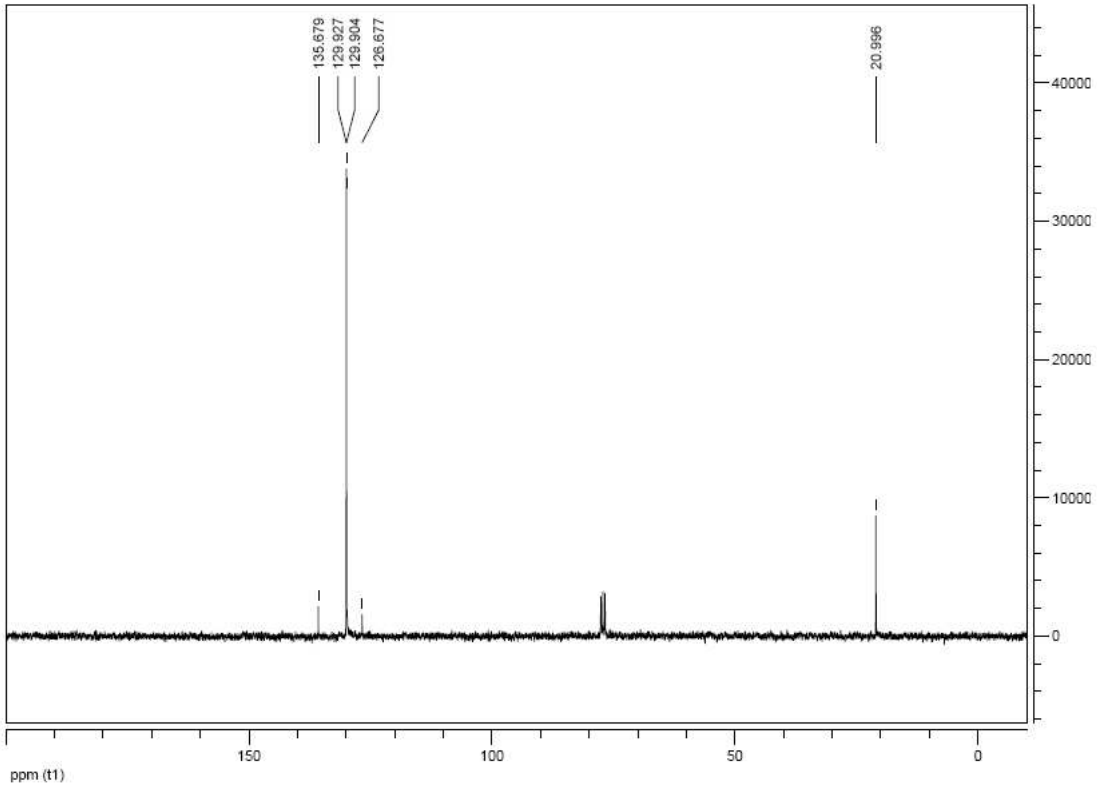
4-chlorobenzenethiol



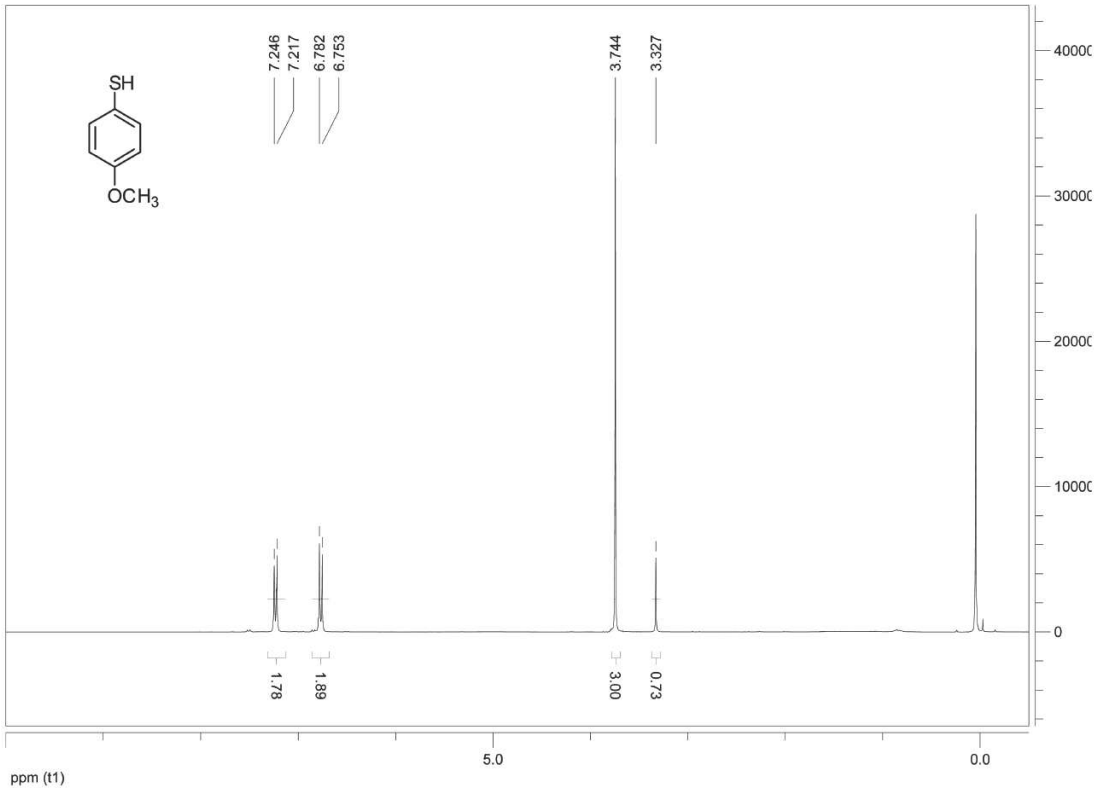


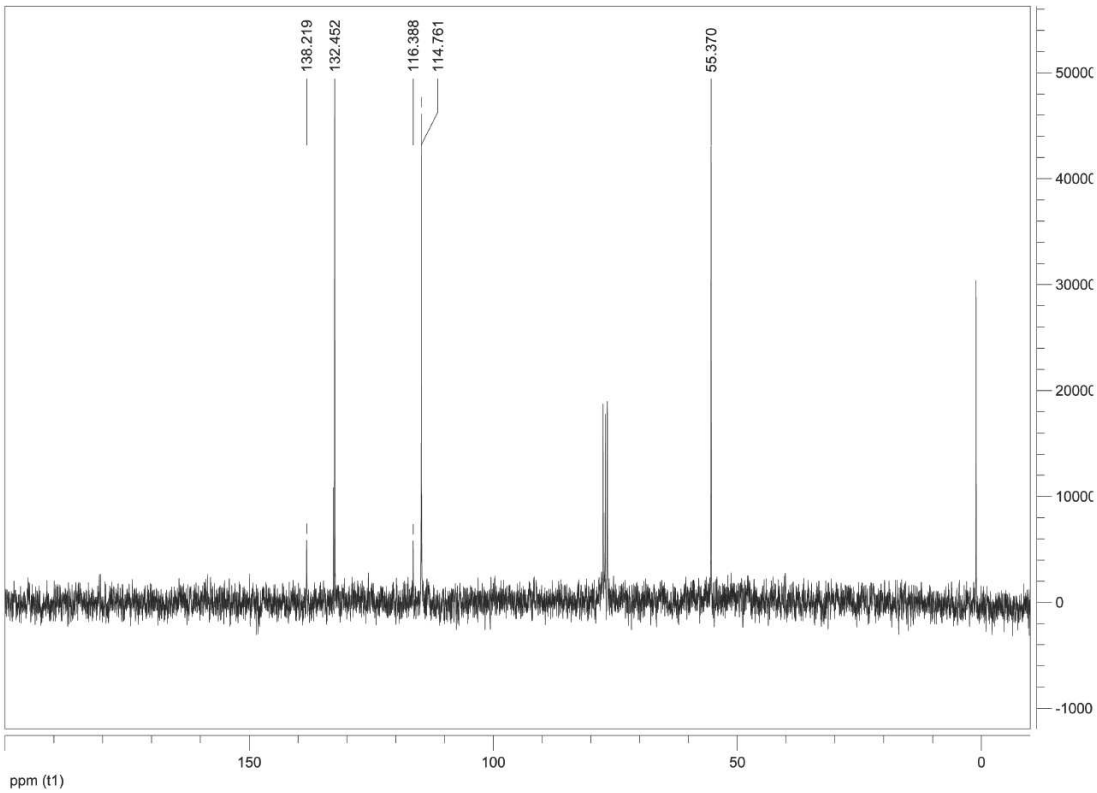
4-methylbenzenethiol



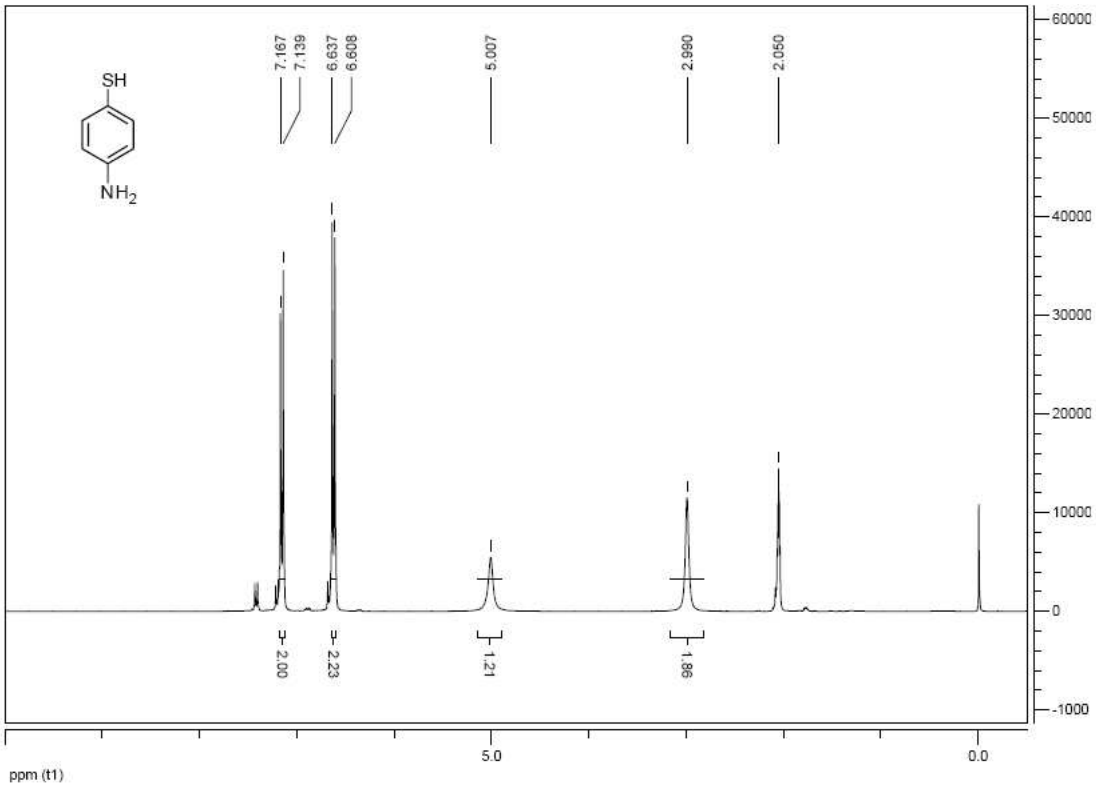


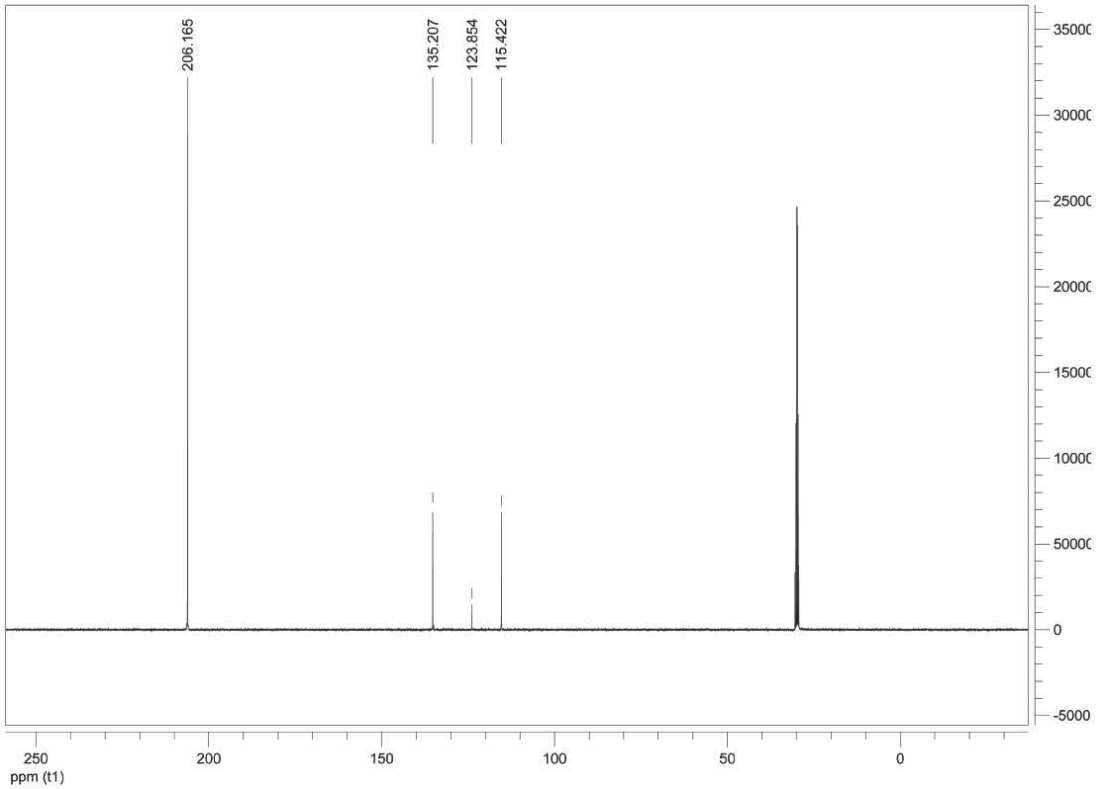
4-methoxybenzenethiol



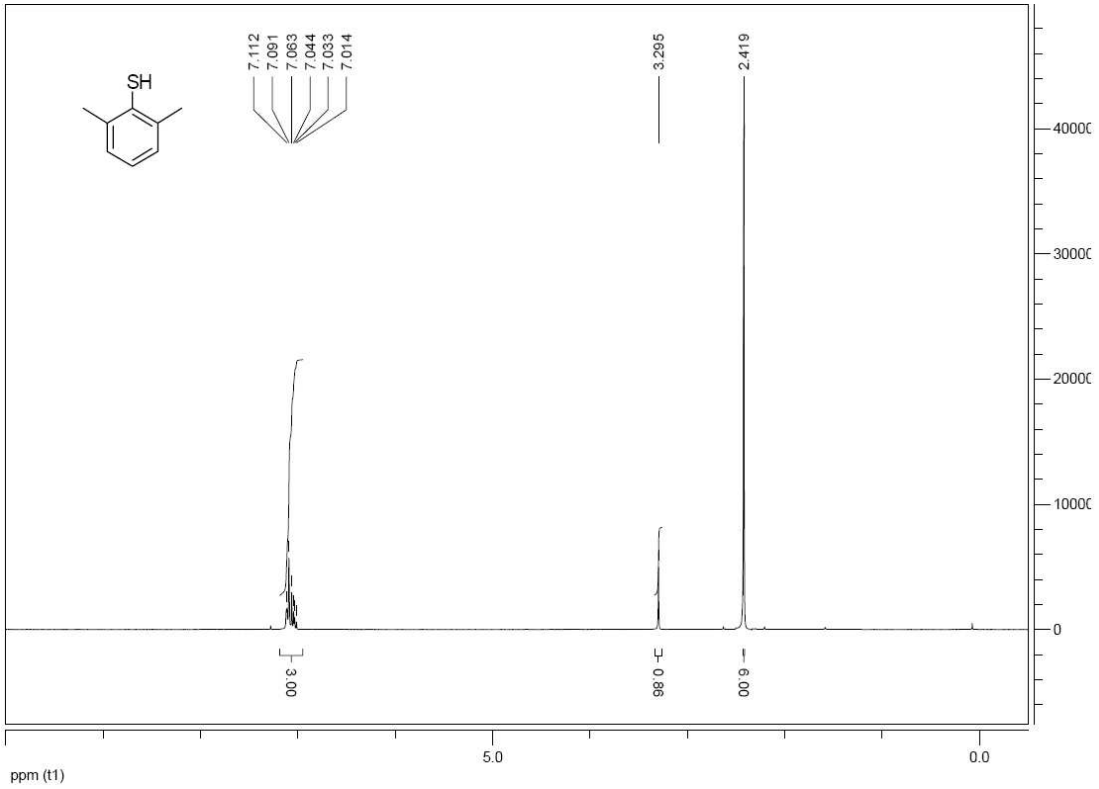


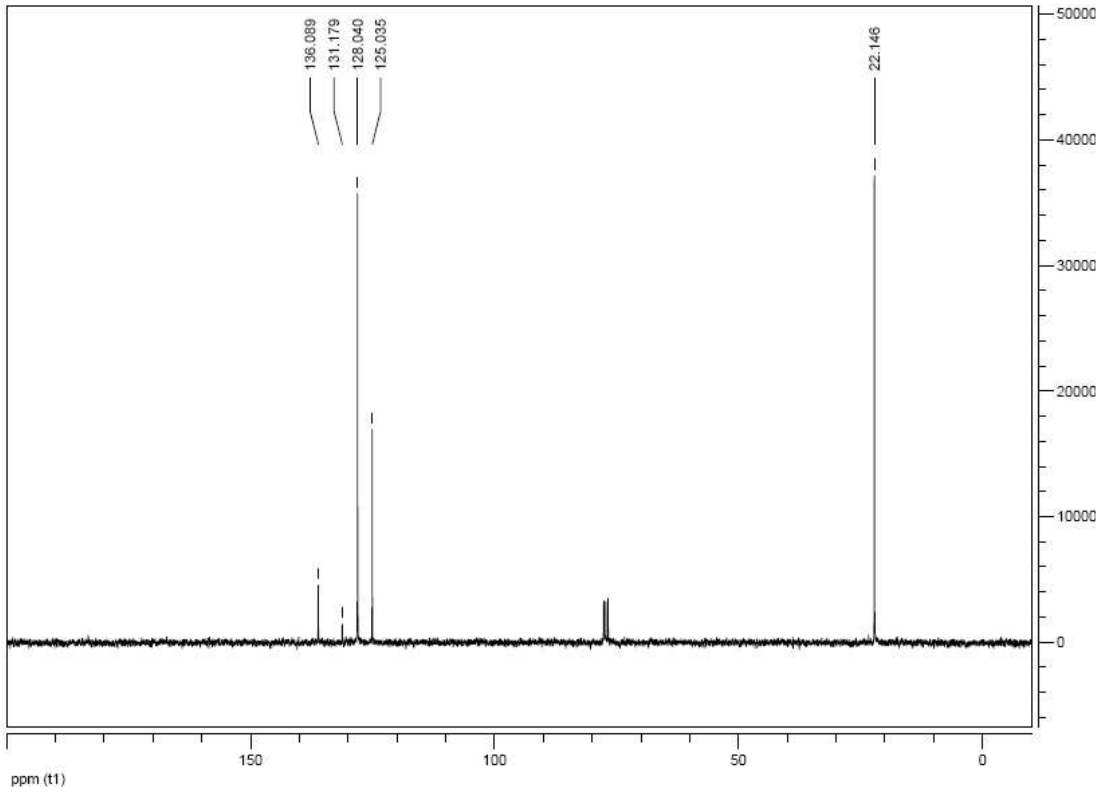
4-aminobenzenethiol



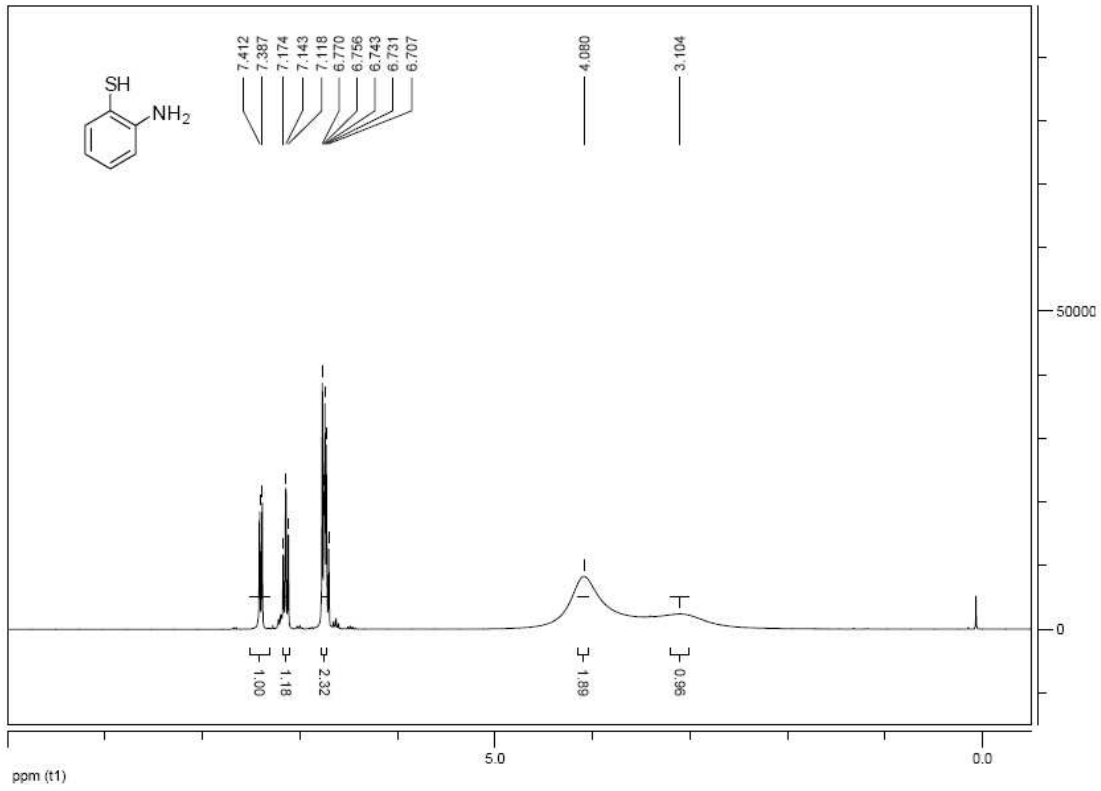


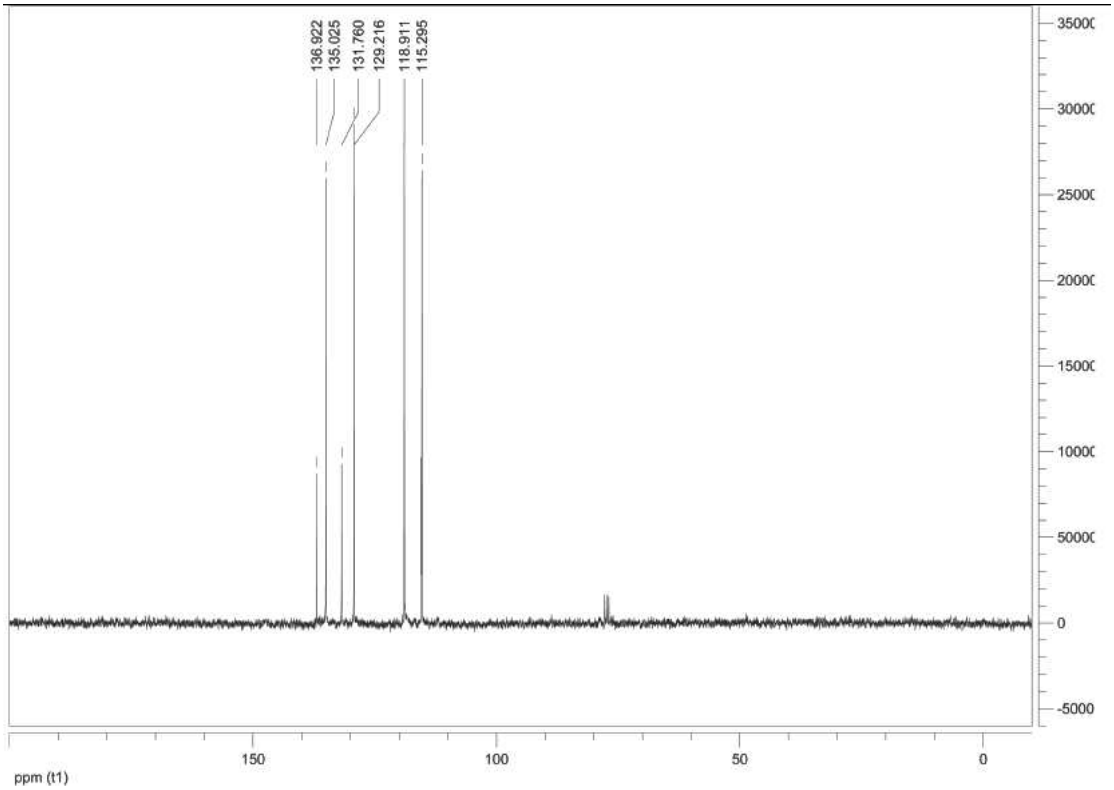
2,6-dimethylbenzenethiol



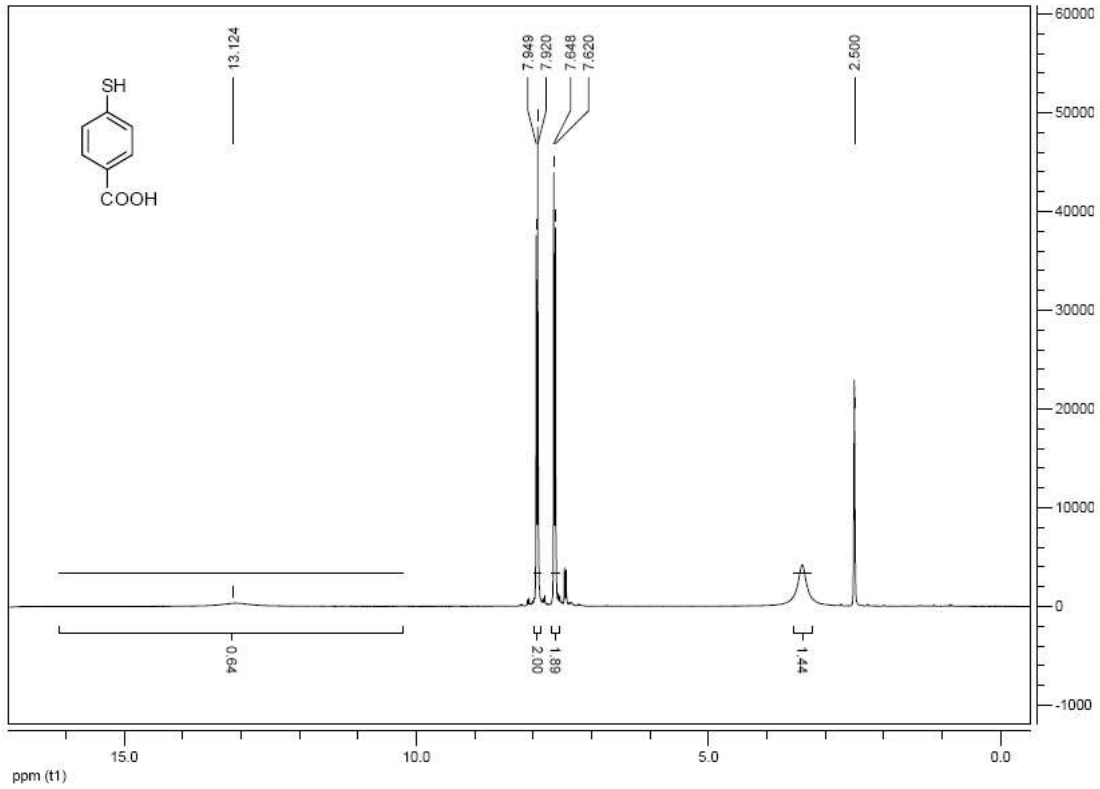


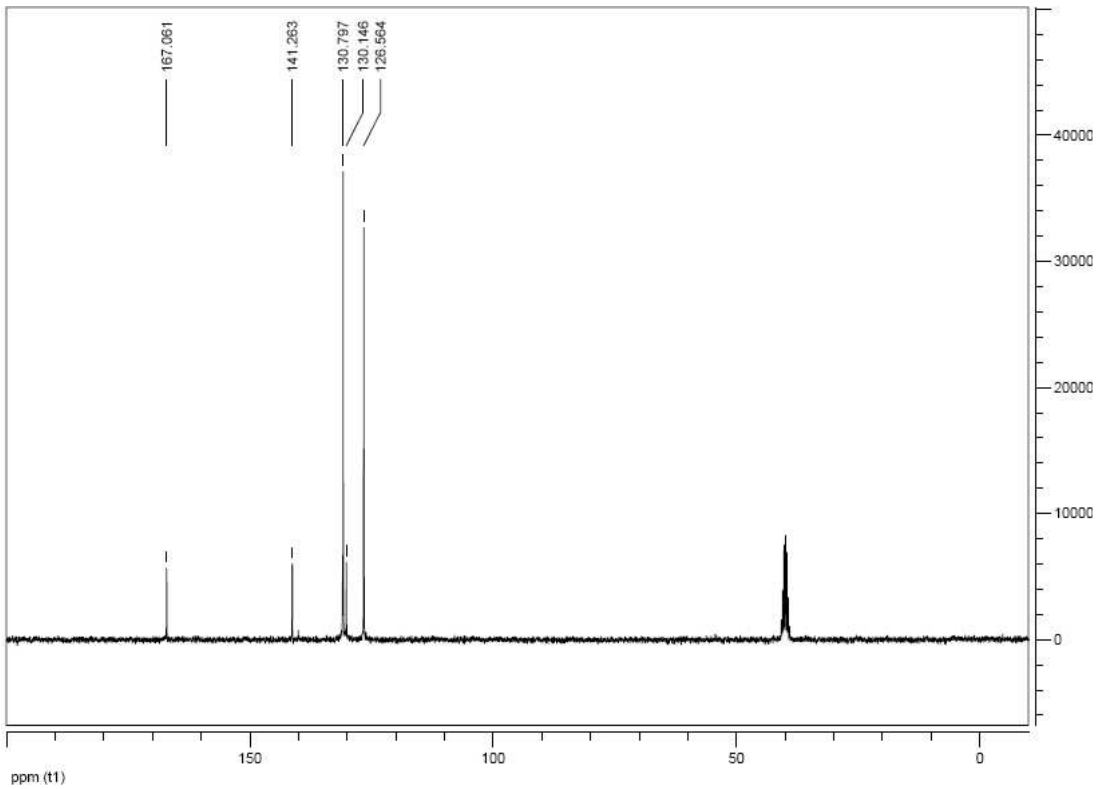
2-aminobenzenethiol





4-mercaptobenzoic acid





2-mercaptobenzoic acid