Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Nitrogen rich graphitic-carbon stabilized cobalt nanoparticles for chemoselective hydrogenation of nitroarenes at milder conditions

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(A) General Information

All the chemicals were purchased from commercial grade and used without further any treatment. The hydrogen gas used was from Hydro Gas India Pvt. Ltd., India.

All the hydrogenation reactions were performed in a 100 mL stainless steel autoclave high-pressure reactor (Autoclave Engineers, EZE-Seal Reactor, USA). ^{1}H and ^{13}C NMR spectra of compounds were measured in $CDCl_3$ and CD_3OD as a solvent by using TMS as an internal standard, on a Bruker Avance 500 MHz FT-NMR. Infrared Spectra were recorded using KBr pellet on a Perkin-Elmer, G-FTIR. The catalyst was activated overnight at 120 ^{o}C prior to use. Transmission Electron Microscopy images of glycoluril, Co catalyst was carried out on a JEOL JEM-2100 microscope with an acceleration voltage of 200 kV using carbon coated 200 mesh copper grids. The samples were ultrasonically dispersed in acetone for 10 min and deposited on the copper grid using capillary and left to dry overnight in air. Thermogravimetric analysis (TGA) was carried out by using a Mettler TGA/SDTA 851e equipment in flowing N_2 (flow rate = 50 ml/min), at a heating rate of 10 ^{o}C/min and data were processed by Stare software. XRD pattern of the samples were analyzed on a Philips X'pert X-ray powder diffractometer by using Cu Kα (λ= 1.54178Å) radiation. Samples were grounded to make fine powder before XRD analysis. XPS analysis of the catalyst was done on Omicron Nanotechnology. Inductive Coupled Plasma (ICP) of the cobalt catalyst was carried out on Perkin Elmer, Optima 2000. Gas Chromatography of the samples was carried out on a Shimadzu GC-2010 with a capillary column, column oven temperature of 110 ^{o}C, FID of 200 ^{o}C, Pressure was 110 kPa. Samples were prepared by using DCM as a solvent.

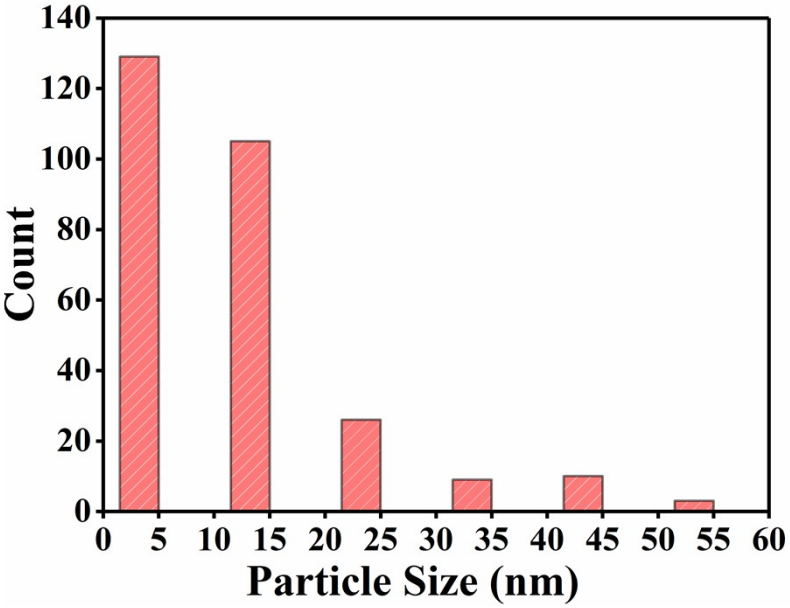
(B) Synthesis of glycoluril[1]

In a single necked 500 mL RB flask, 40% glyoxal (40 mL; 0.35 mol) and urea (53.4 g, 0.89 mol, 2 eqv.) were taken, and the resulting solution was stirred for 15-20 min. Subsequently, water (80 mL) was added to the reaction mixture and further stirred for 15 min followed by the addition of 8.5 mL conc. HCl in 20 mL of water very slowly. After complete addition of acid (pH= 1.5-2), the reaction mixture was refluxed on a steam bath that triggered precipitation of white solid. The heating and stirring were continued for about 45 min, cooled to room temperature, poured into ice water, filtered, and the solid was washed with cold water (2 x 50 mL) and finally with acetone (2 x 50 mL). The resulting white solid was allowed to dry overnight at 80-85 ^{o}C. (Yield: 32.69 g, 65%).

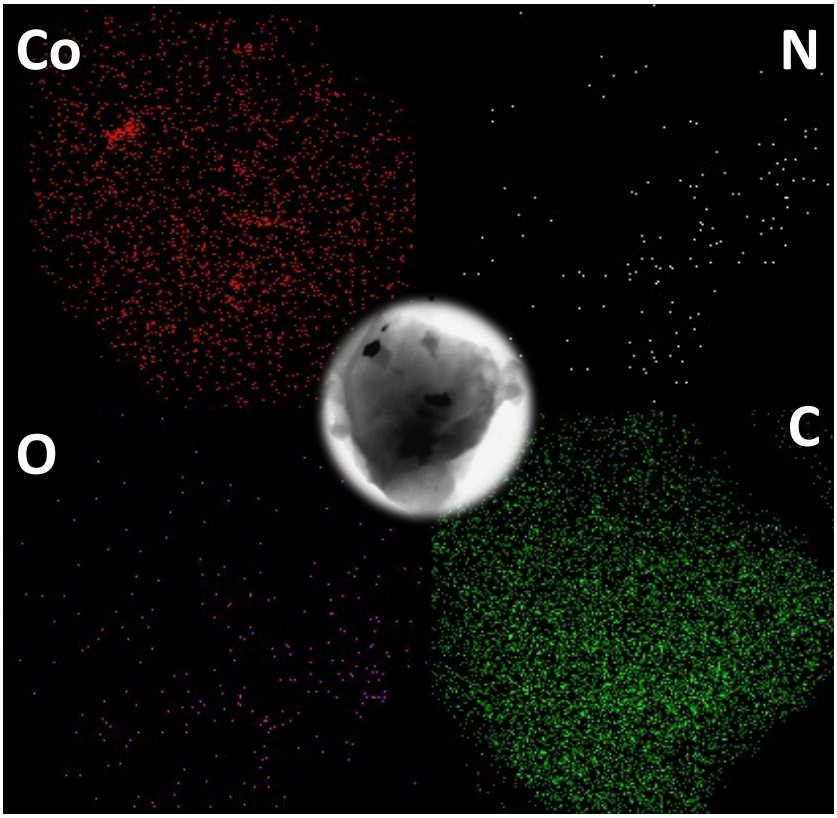
(C) Synthesis of CB[6][2]

In a single necked 250 mL RB flask which is equipped with dean-stark apparatus and a condenser, glycoluril (15 g, 106 mmol) and 37% aqueous formaldehyde were taken to which conc. H_2SO_4 (14.3 mL) and water (100 mL) were added, and the resulting mass was heated for 12 h. During that time water was removed completely from the reaction mixture, after that the reaction mixture was stirred at 160 ^{o}C for 24 h. Then the reaction mixture was cooled down to RT and poured into water (250 mL). A yellowish precipitate was formed, which was filtered off, and the solid mass was dissolved in Conc. HCl. The clear brown solution was diluted with water to get a white precipitate that was washed thoroughly with water and dried at 130-140^{o}C (Yield: 80.9%).

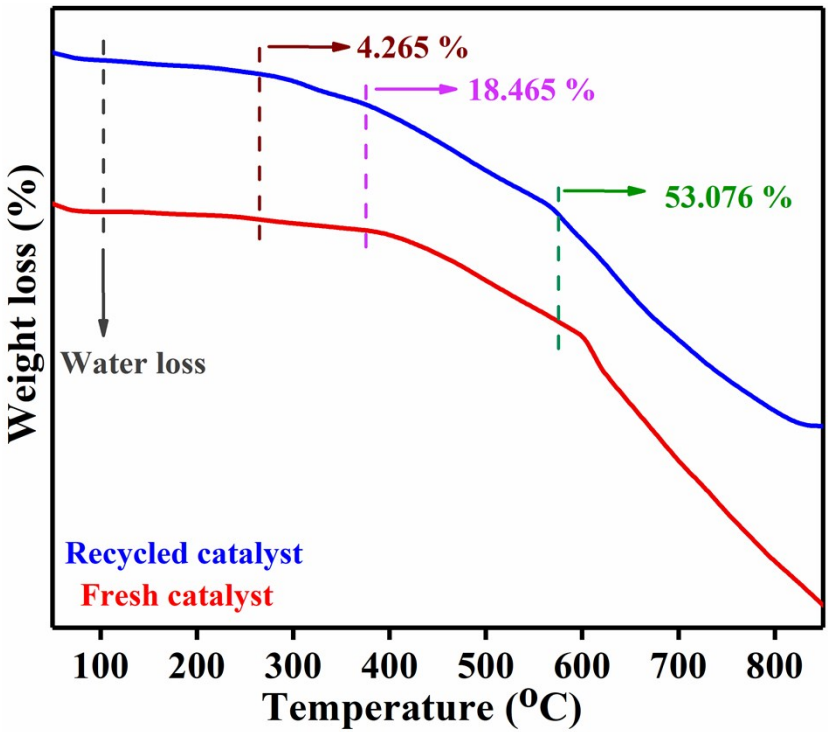
(D) Particle distribution of the catalyst



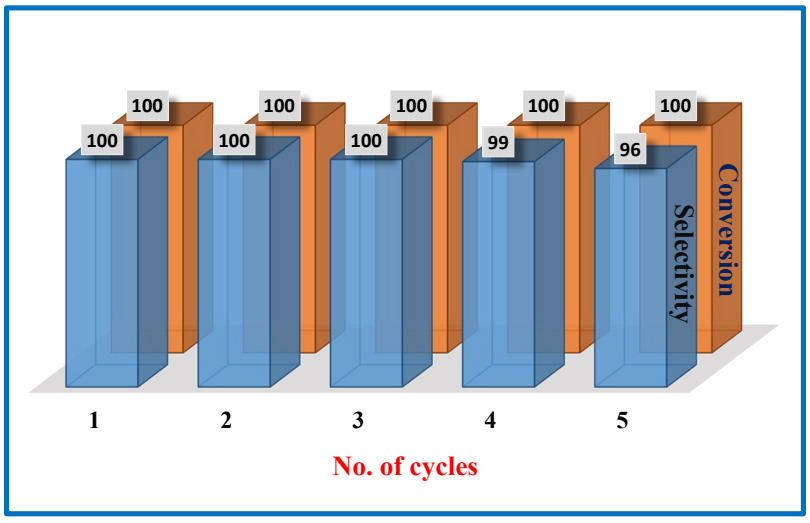
(E) TEM elemental mapping of catalyst



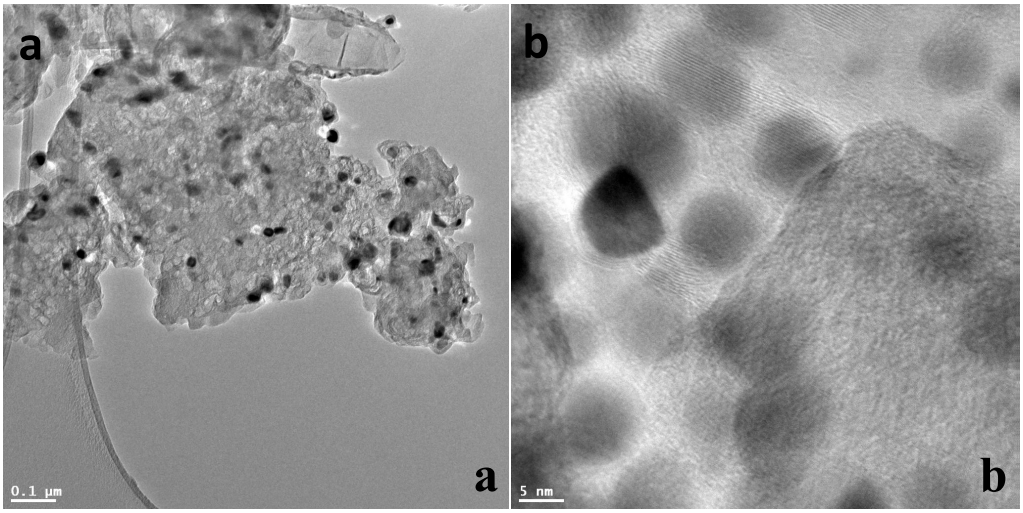
(F) Thermogravimetric analysis of the catalyst



(G) Recyclability of the catalyst



(H) TEM images of the recycled catalyst



(I) Filtration method procedure and its results

To verify the cobalt leaching in the reaction mixture, the filtration test was carried out at room temperature. A 100 mg of catalyst was stirred with 5 mL of nitrobenzene in 20 mL of water-THF mixture under typical reaction conditions, i.e. bubbling hydrogen gas at 50 ^{o}C. After 1.5 h, the reaction showed 56% of conversion of nitrobenzene without affecting selectivity of aniline. At this point the catalyst was removed from the liquid phase by filtration through Whatman filter paper and the reaction mixture was allowed to further react under reaction conditions. It was observed that in the absence of a catalyst, no further change in nitrobenzene conversion was observed even after 3 h which confirms zero Co leaching.

(J) Procedure for preparation of ICP samples

Catalyst sample was mixed with pure conc. HNO_3 acid solution (20% v/v) in 50 mL PFA beaker. The sample was heated in a Parr bomb at 100 ^{o}C in an oven for 3 h. After cooling the sample, the solution was taken out in a volumetric flask. The solution was then diluted to 100 mL using milli

Q water by using calibrated volumetric flask which was further subjected to ICP analysis. Metal leaching was studied by ICP-AES analysis of the catalyst before, after first and third reaction cycles. The Co concentration was found to be negligible before and after the reaction, which confirmed negligible Co leaching; this is due to strong metal support interaction.

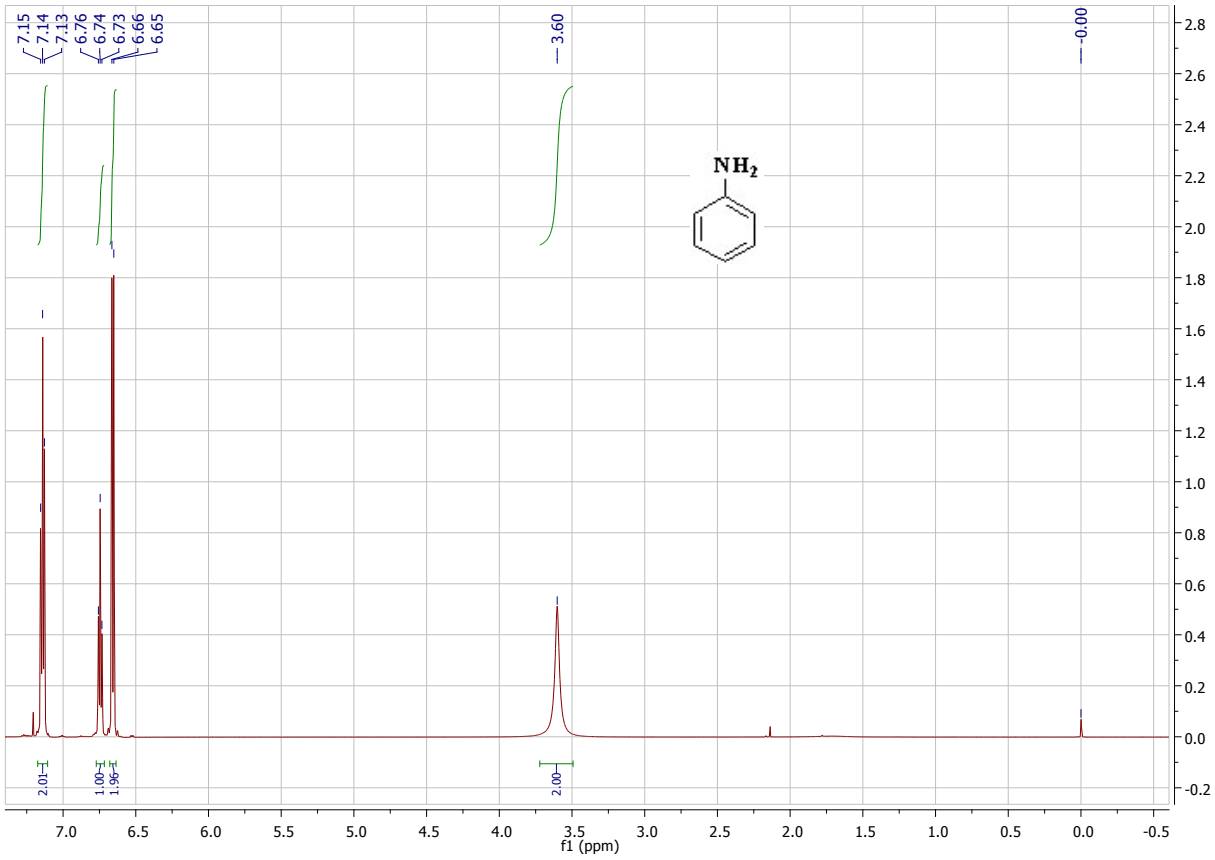
(K) Table 1. Comparison chart

No.	Catalyst	Reaction Conditions	Hydrogen Source	Reaction Scale	Time	Yield	Ref.
1	$Co(Phen)_2(OAc)_2$ adsorbed on Vulcan XC72R	110 °C, 50 bar, THF:H_2O		0.5mmol	4h	98	3
2	Co_3O_4/NGr@C						4
3	CoOx@NCNTs	110 °C, EtOH, 30 bar		1mmol	2.5h	98	5
4	Co nanocomposite	110 °C, EtOH: H_2O, 50 bar		1.5mmol	15h	>99	6
5	Co/CoO@Carbon	120 °C, THF/H_2O, 30 bar		1mmol	4-24h	>80	7
6	Co-Co_3O_4/NGr@C or Fe_2O_3/NGr@C	70-120 °C, EtOH: H_2O, 20 bar, Et_3N	H_2	0.5mmol	20-28h	>99	8
7	Nanolayered Co-Mo-S	150 °C, 11 bar, Toluene		0.25	7h	>99	9
8	Zr_{12}-TPDC-Co	110 °C, 40 bar, Toluene		0.4	42h	100	10
9	Co@NMC	80 °C, 10 bar, EtOH		1	1.5h	99	11
10	CoPd@CNT	RT, H_2O:MeOH	$NaBH_4$	1	3-5 min	>99	12
11	Co-Co_3O_4@carbon-700	110 °C, 40 bar, EtOH/H_2O		0.5	6	>99	13
12	**Co@g-C/N-800**	**50 °C, H_2O:THF, 10 bar**	**H_2**	**48mmol**	**12h**	**>99**	**This Work**

(L) Analytical data and NMR spectra of the products

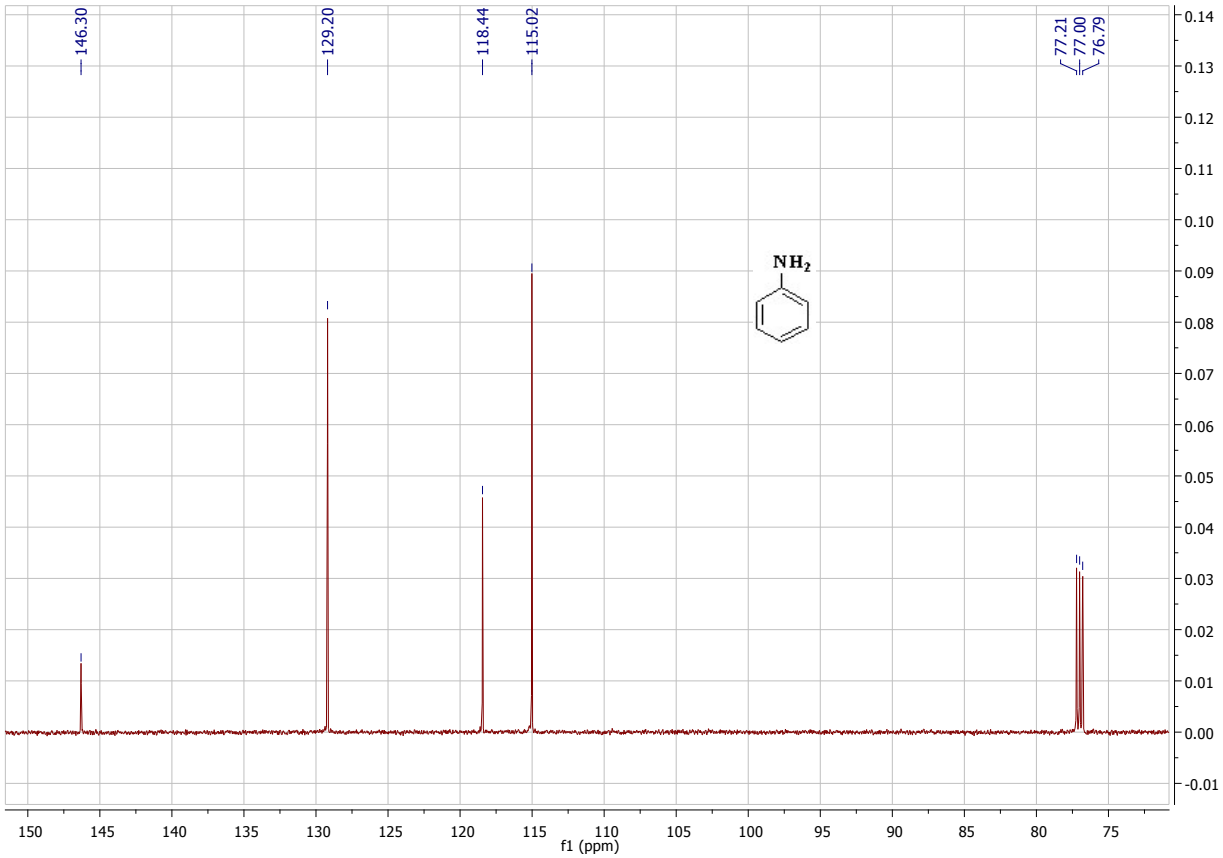
^{1}H NMR of aniline[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.15-7.13(m, 2H), 6.76-6.73(m, 1H), 6.66-6.65(d, 2H, J= 7.5Hz), 3.60 (s, 2H).



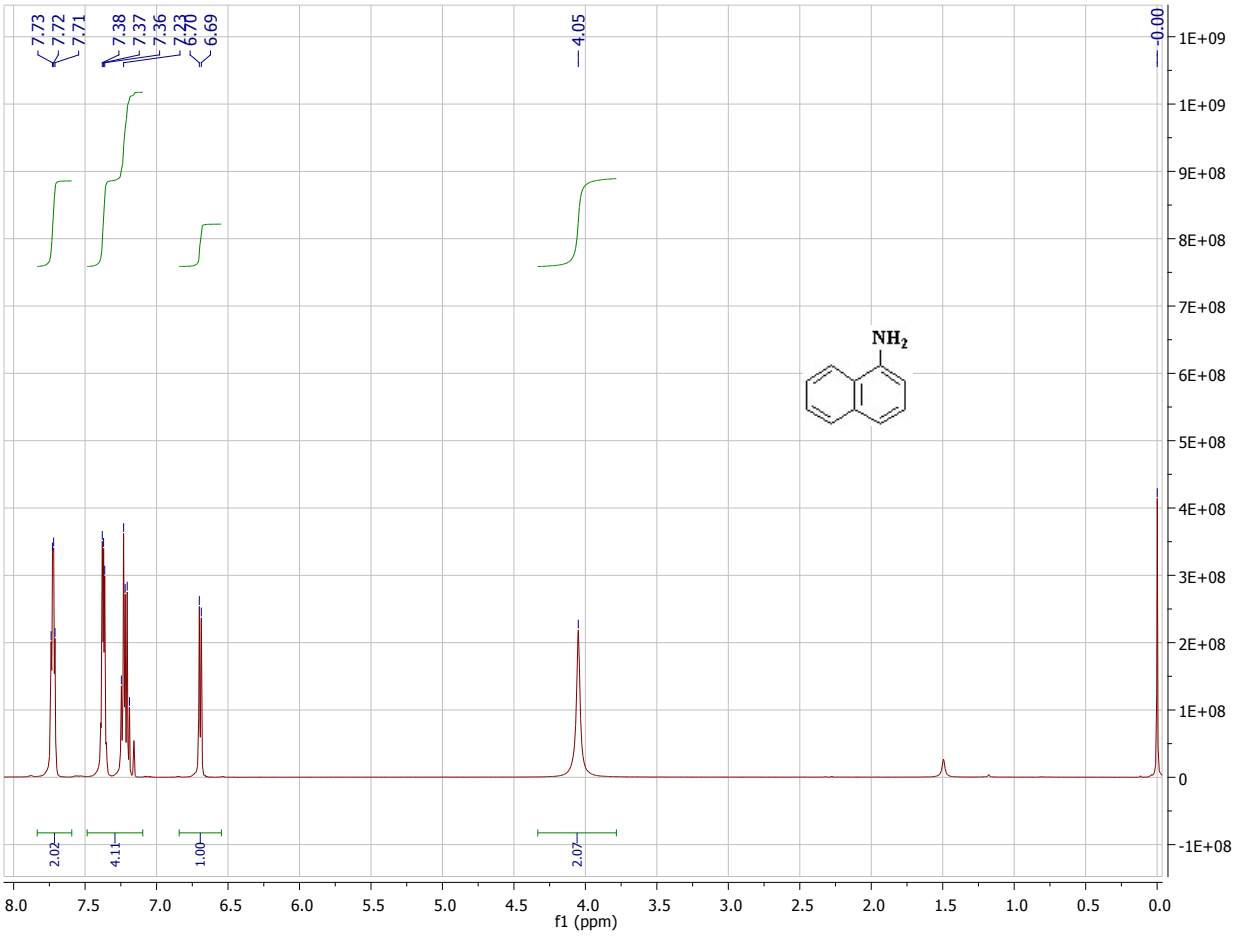
^{13}C NMR of aniline

^{13}C NMR ($CDCl_3$, 125MHz) δ = 115.02, 118.44, 129.20, 146.30.



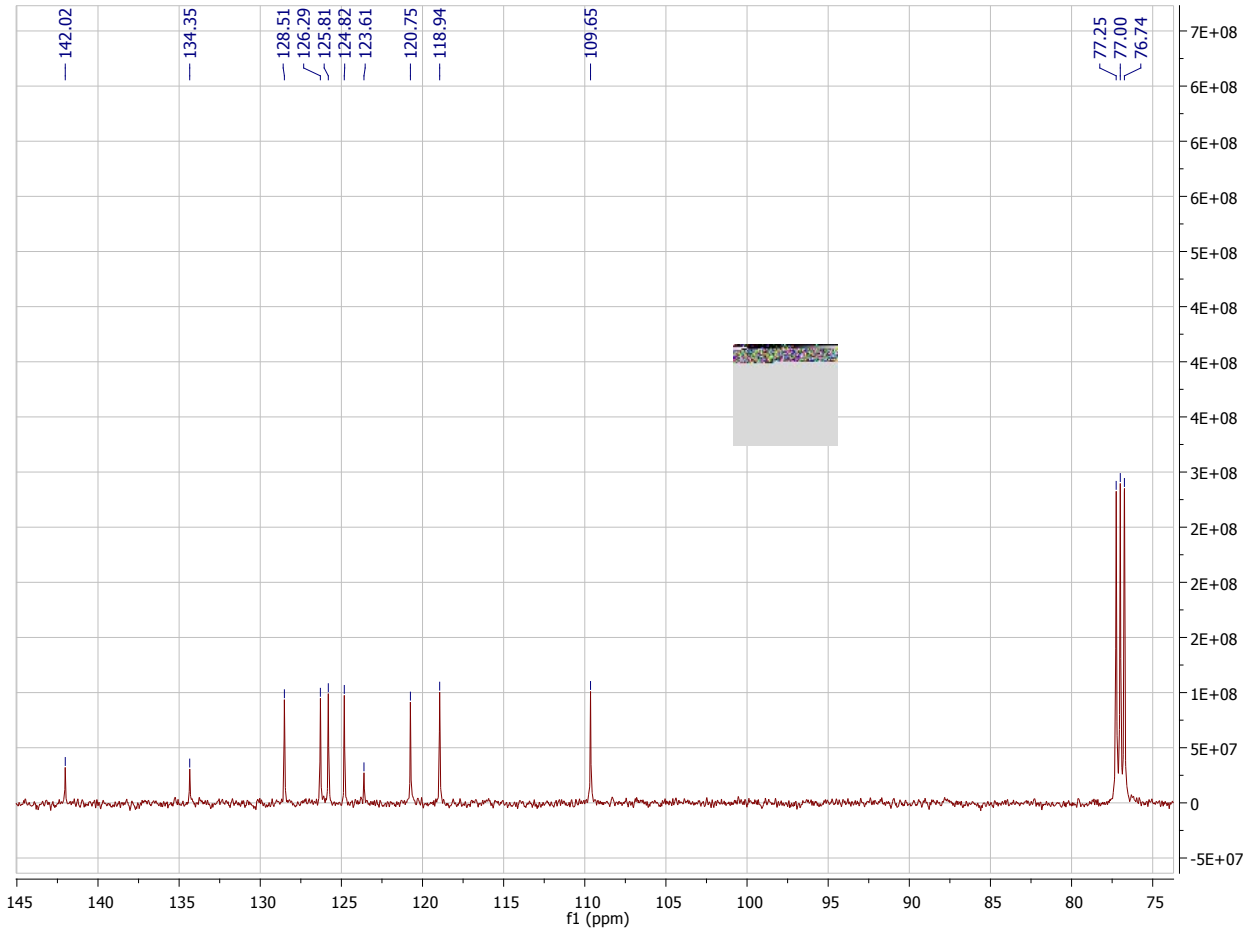
^{1}H NMR of 1-naphthylamine[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.73-7.71(m, 2H), 7.38-7.23 (m, 4H), 6.70-6.69 (d, 1H, J= 7), 4.05 (s, 2H).



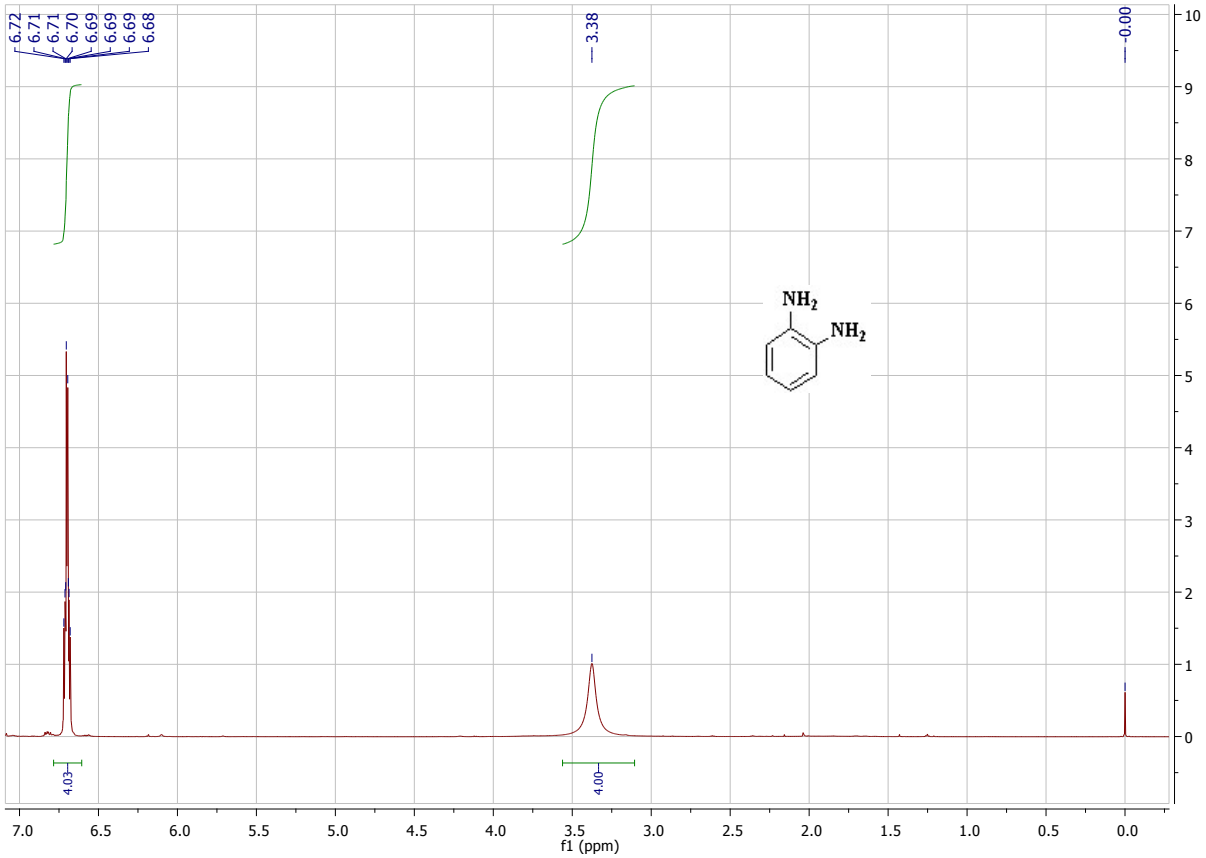
^{13}C NMR of 1-naphthylamine

^{13}C NMR ($CDCl_3$, 125MHz) δ = 142.02, 134.35, 128.51, 126.29, 125.81, 124.82, 123.61, 120.75, 118.94, 109.65.



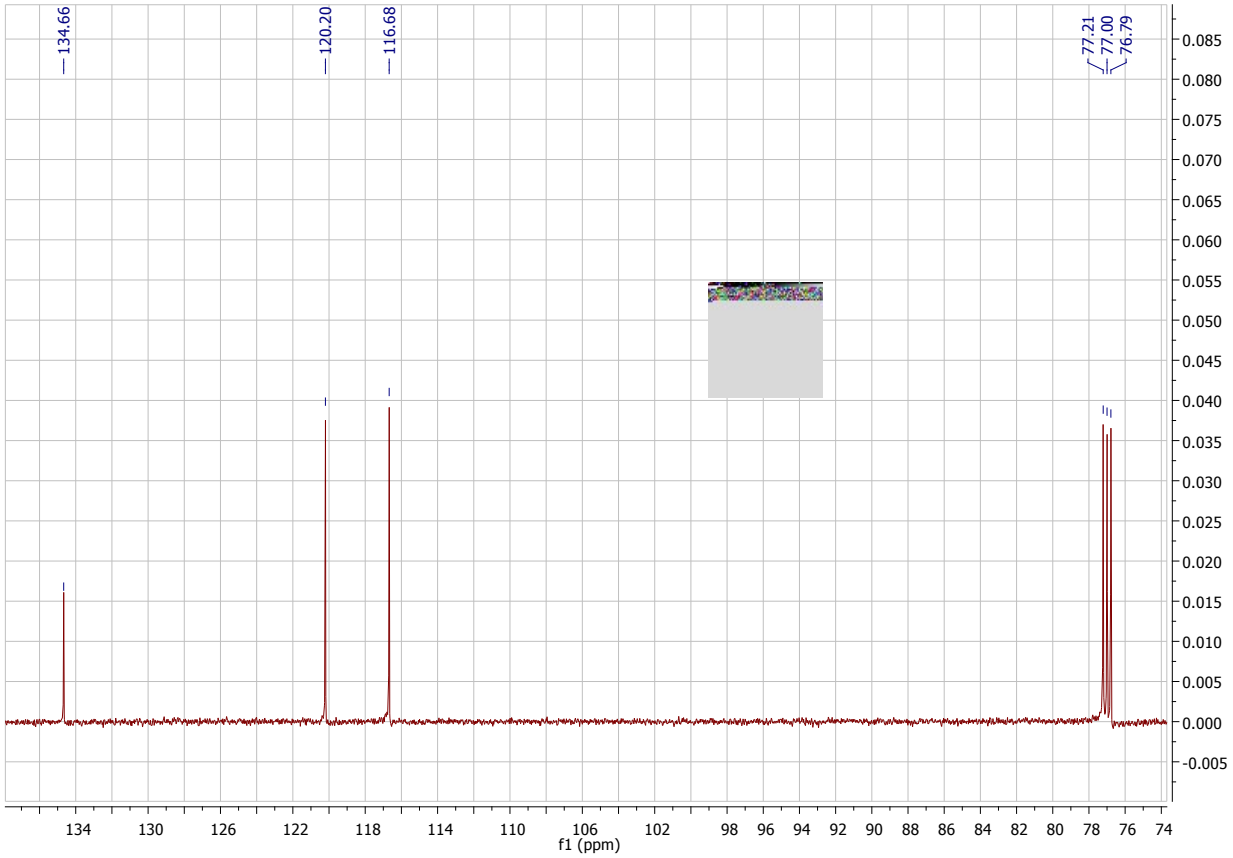
^{1}H NMR of 1,2-diaminobenzene[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 6.72-6.68 (m, 4H), 3.38 (s, 4H).



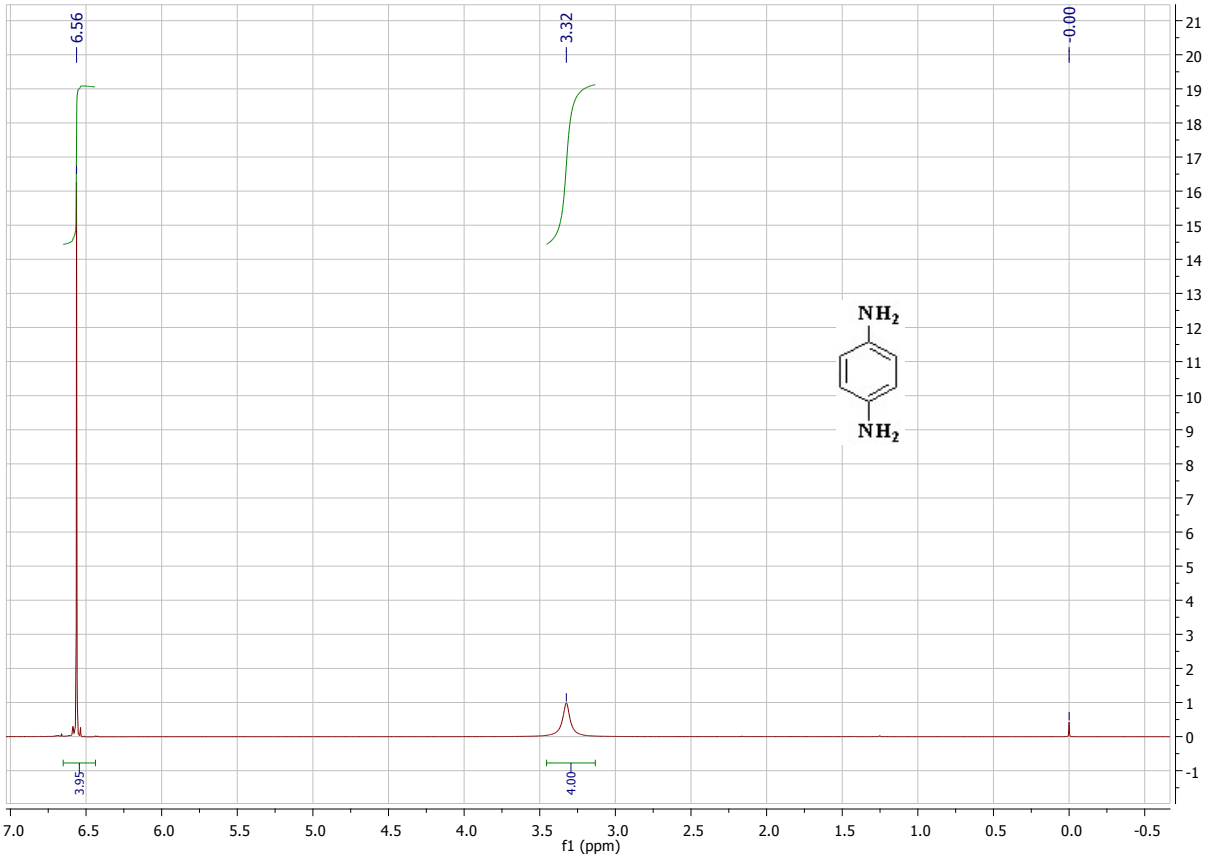
^{13}C NMR of 1,2-diaminobenzene

^{13}C NMR ($CDCl_3$, 125MHz) δ = 134.66, 120.20, 116.68.



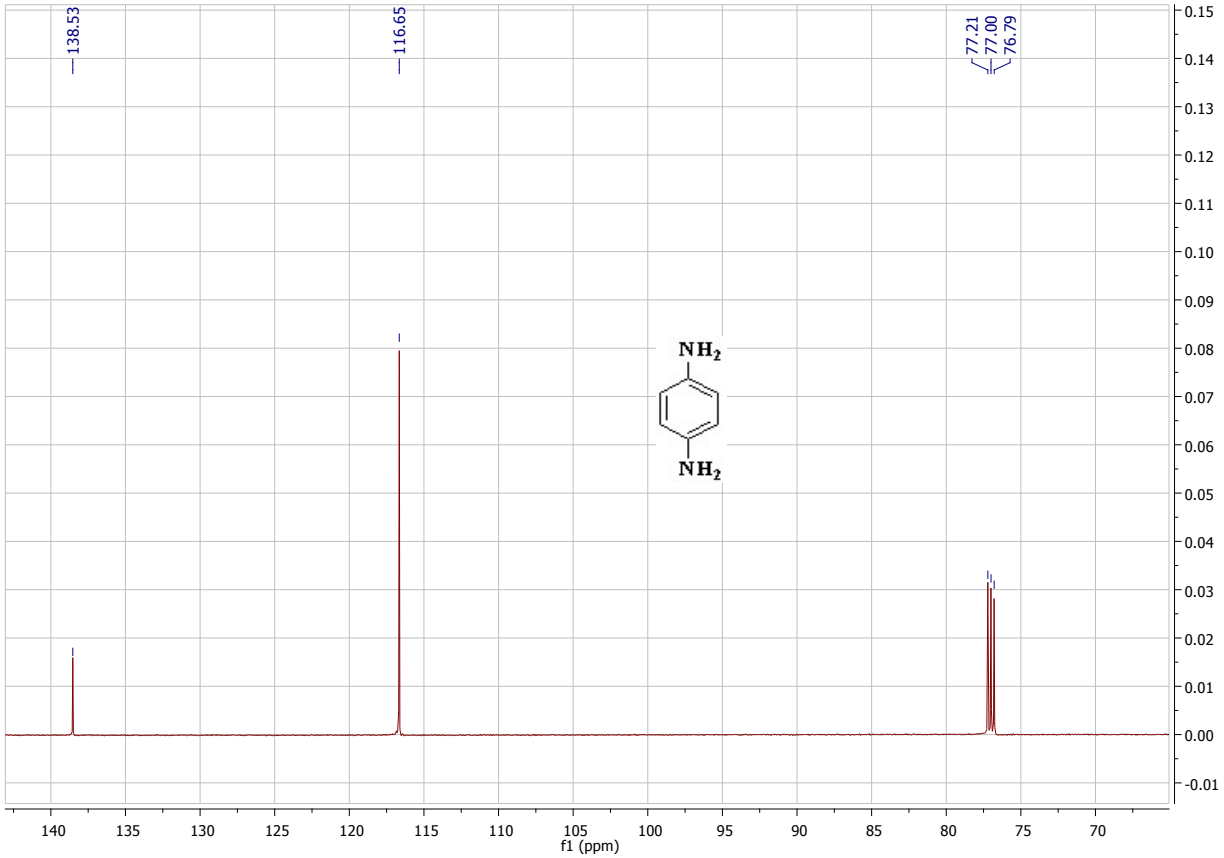
^{1}H NMR of 1,4-diaminobenzene[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 6.56 (s, 4H), 3.32 (bs, 4H).



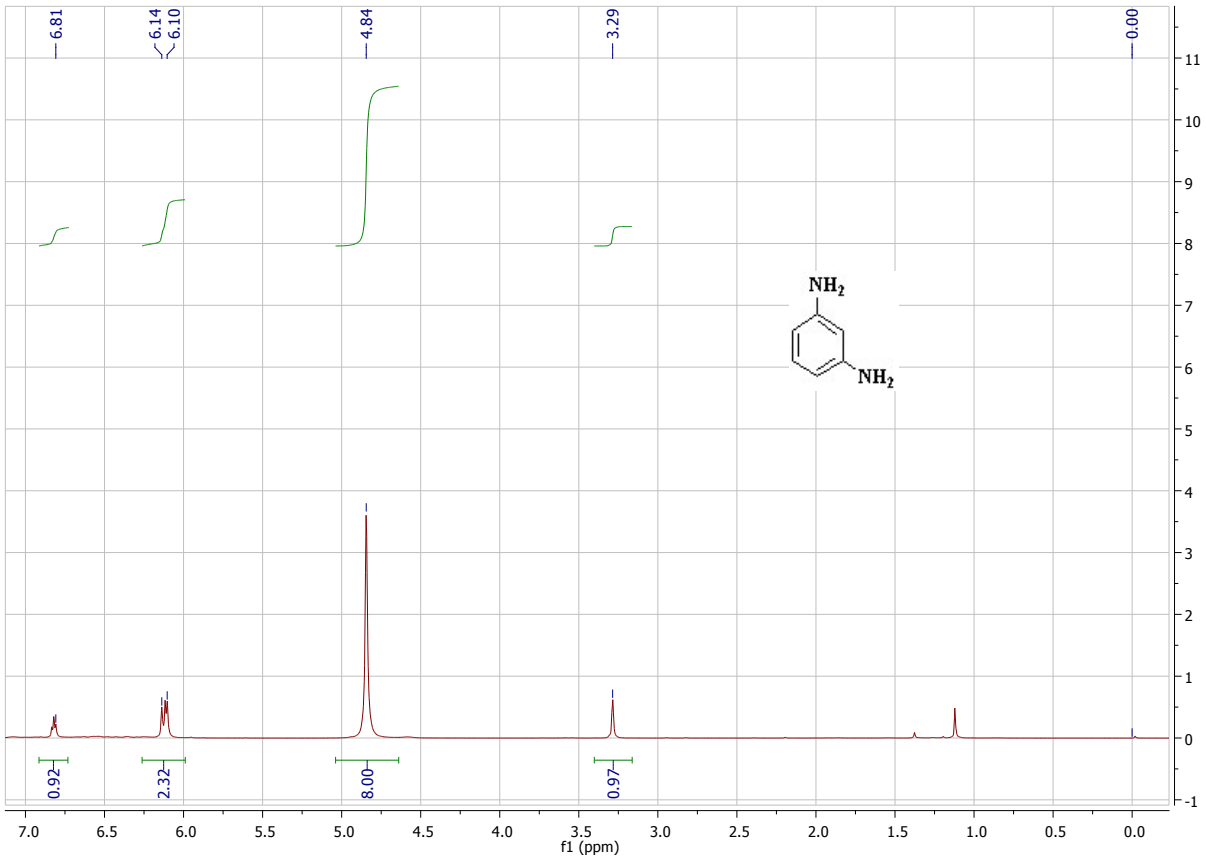
^{13}C NMR of 1,4-diaminobenzene

^{13}C NMR ($CDCl_3$, 125MHz) δ = 116.65, 138.53.



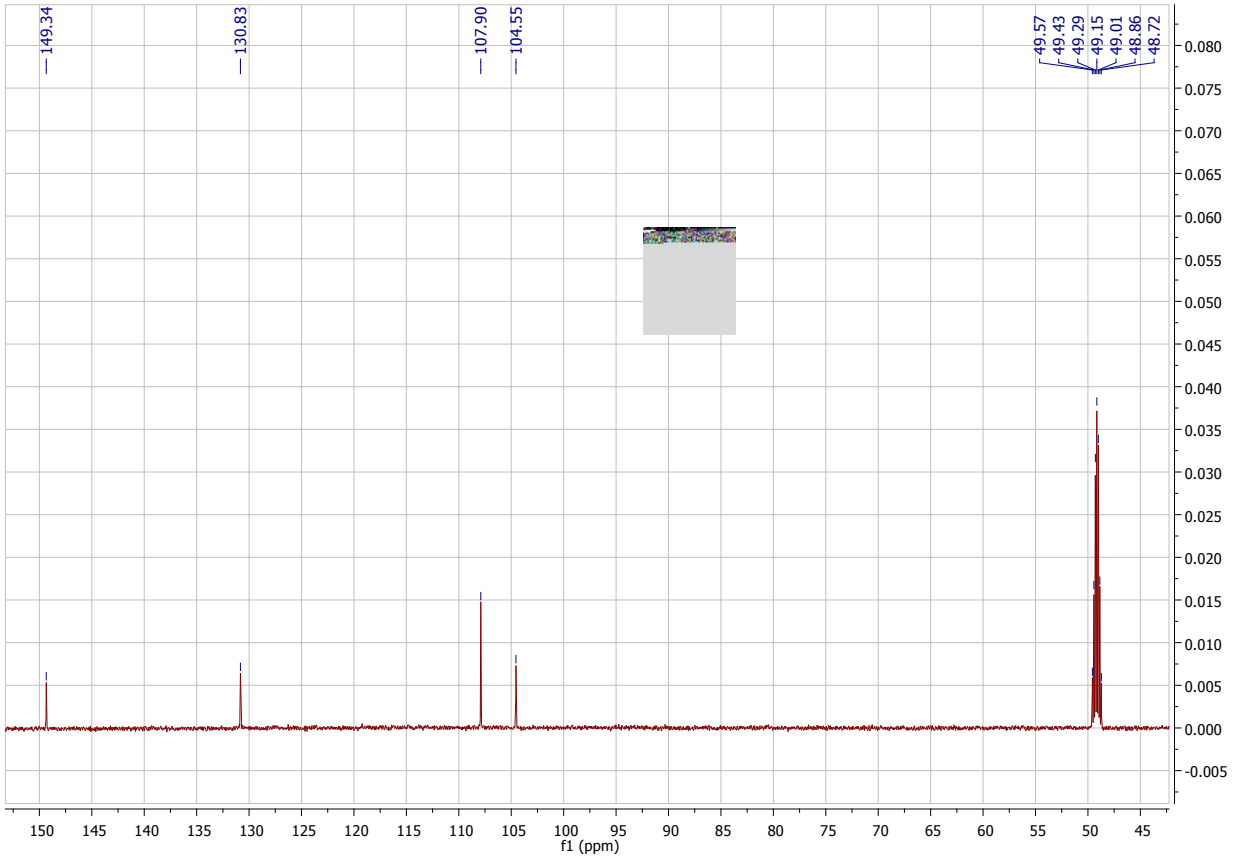
^{1}H NMR of 1,3-diaminobenzene[14]

^{1}H NMR (MeOD, 500MHz, TMS) δ = 6.81(m, 1H), 6.14-6.10 (m, 2H), 4.84 (s, 8H), 3.29 (s, 1H).



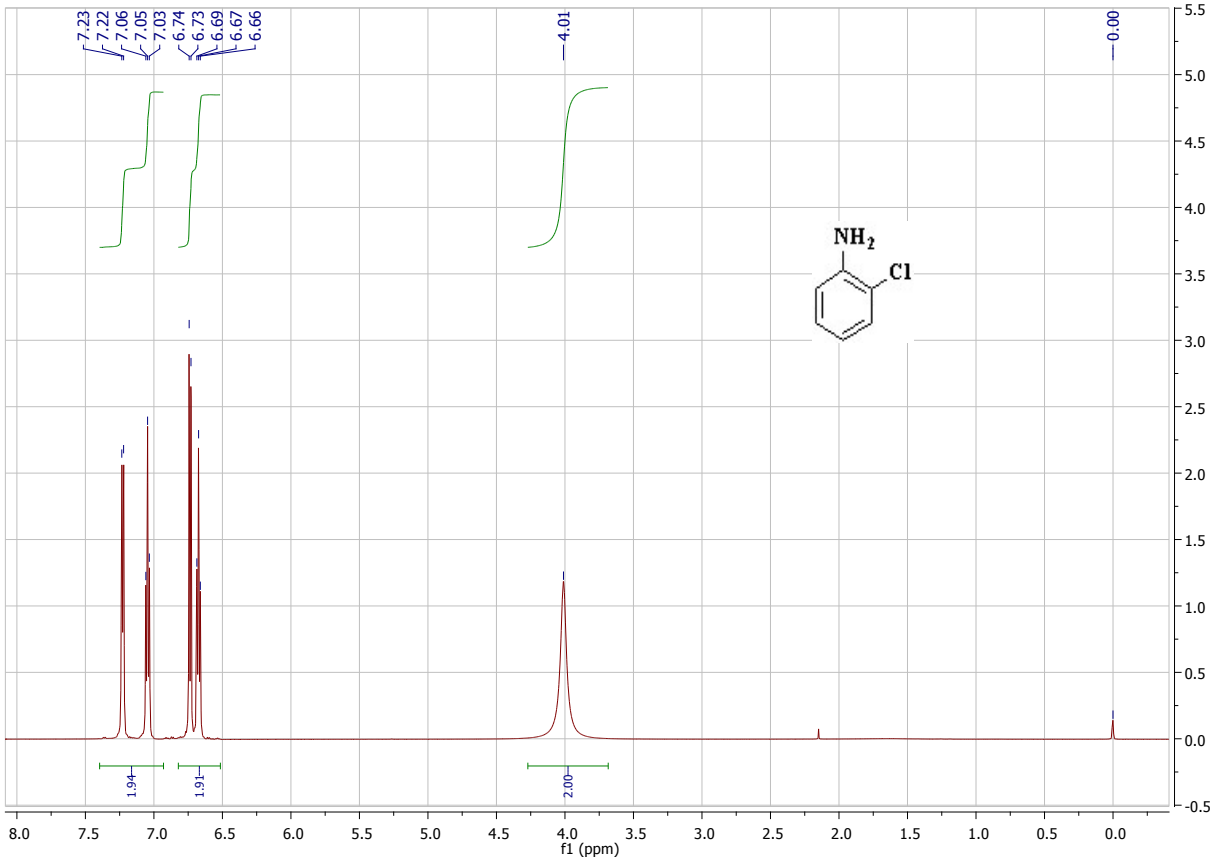
^{13}C NMR of 1,3-diaminobenzene

^{13}C NMR (MeOD, 125MHz) δ = 149.34, 130.83, 107.90, 104.55.



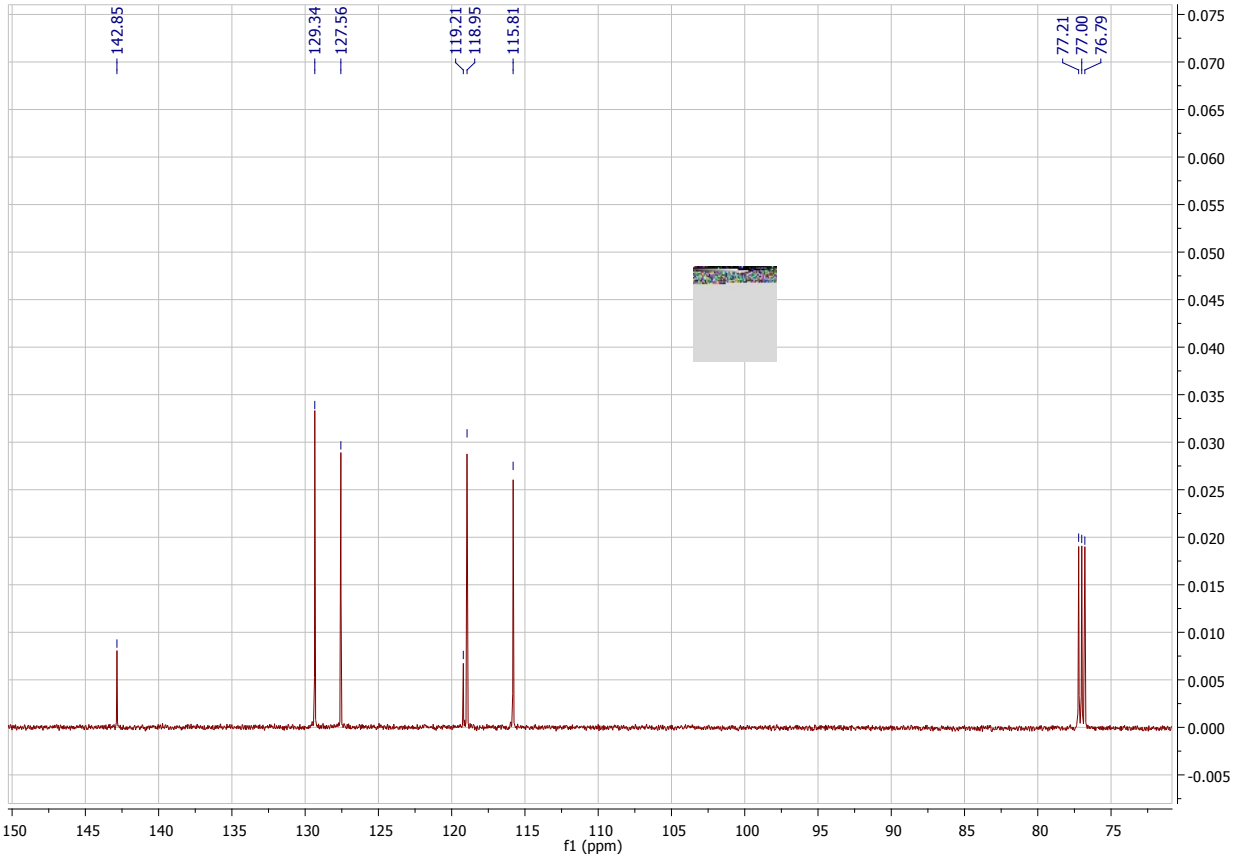
^{1}H NMR of 2-chloroaniline[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.23-7.03 (m, 2H), 6.74-6.66 (m, 2H), 4.01 (s, 2H).



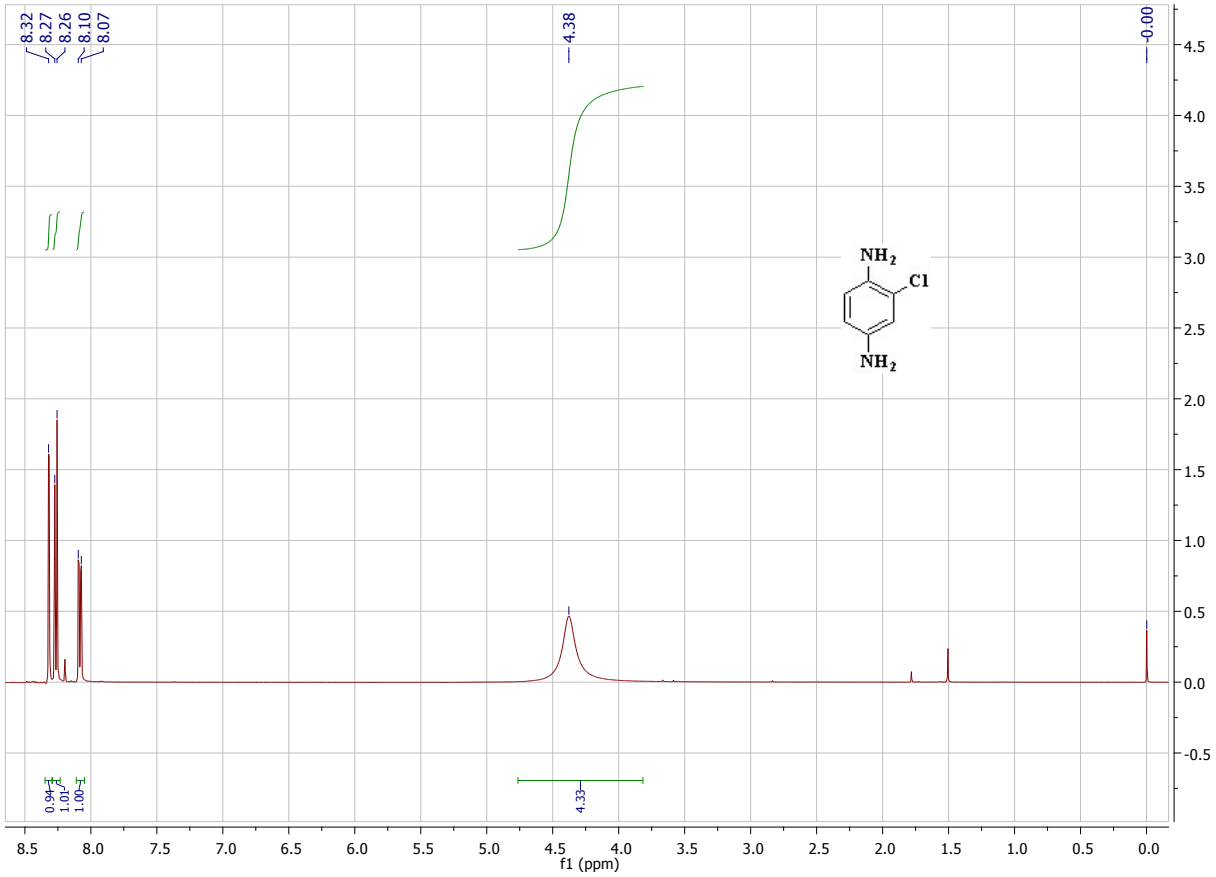
^{13}C NMR of 2-chloroaniline

^{13}C NMR ($CDCl_3$, 125MHz) δ = 142.85, 129.34, 127.56, 119.21, 118.95, 115.81.



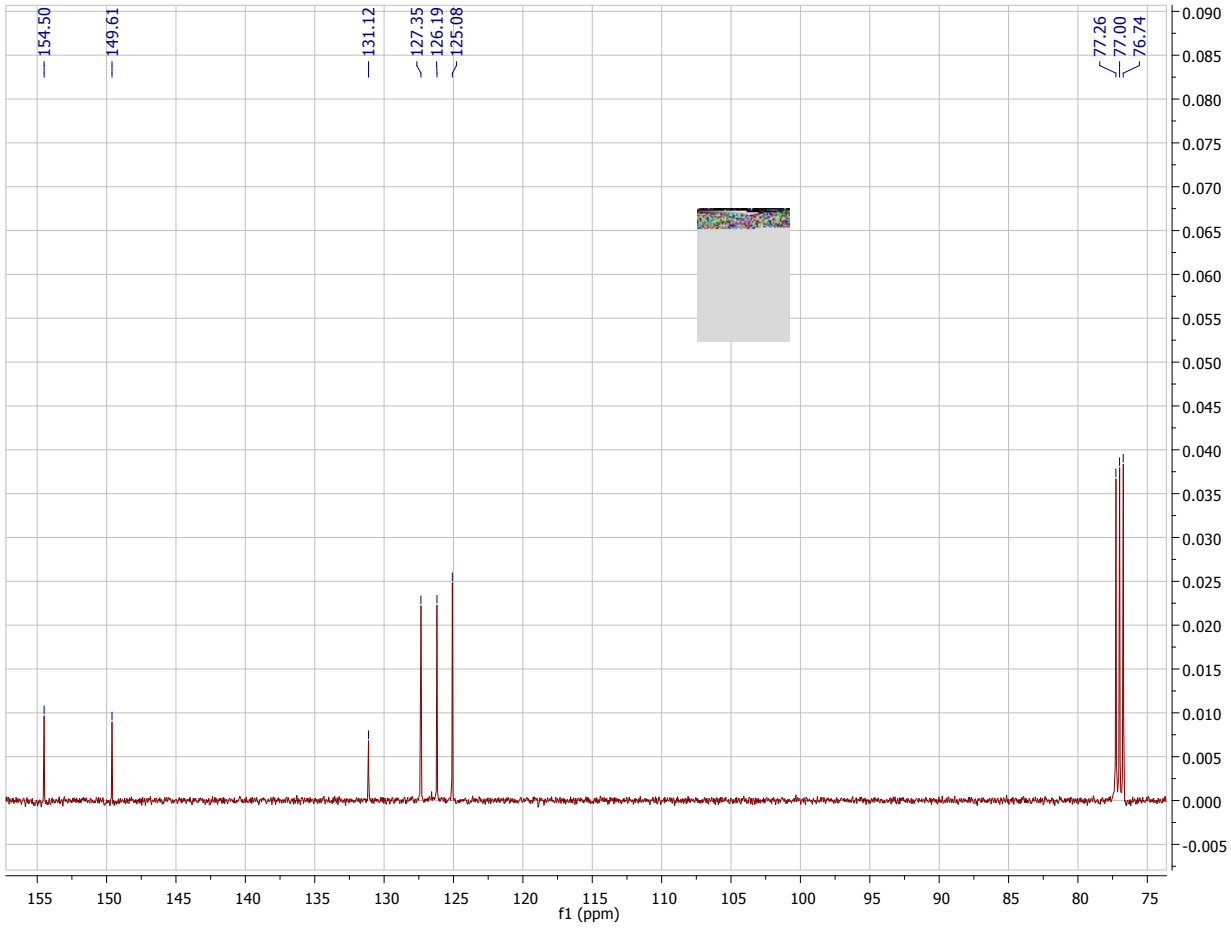
^{1}H NMR of 2-chloro-1,4-diaminobenzene[16]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 8.32-8.26 (m, 2H), 8.10-8.07 (m, 1H), 4.38 (s, 4H).



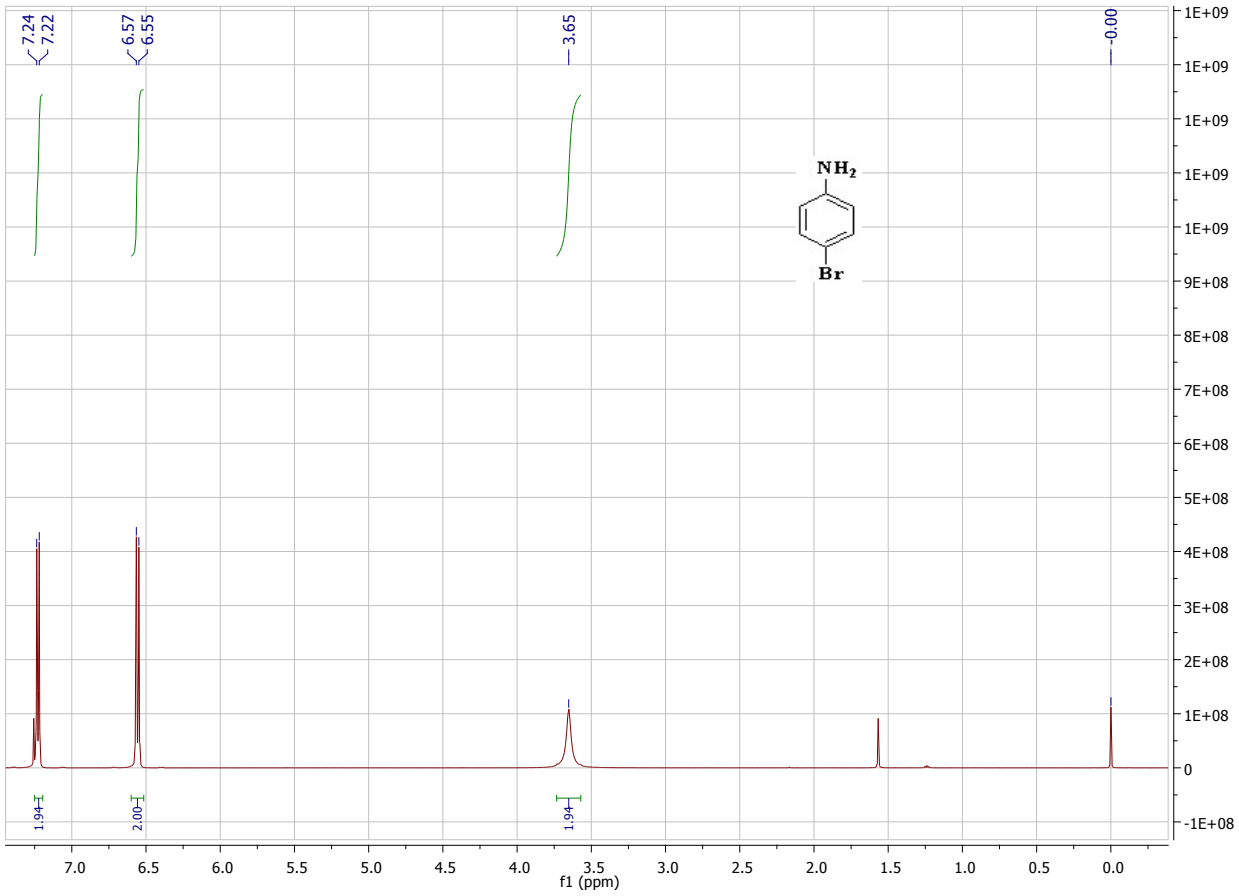
^{13}C NMR of 2-chloro-1,4-diaminobenzene

^{13}C NMR ($CDCl_3$, 125MHz) δ = 154.50, 149.61, 131.12, 127.35, 126.19, 125.08.



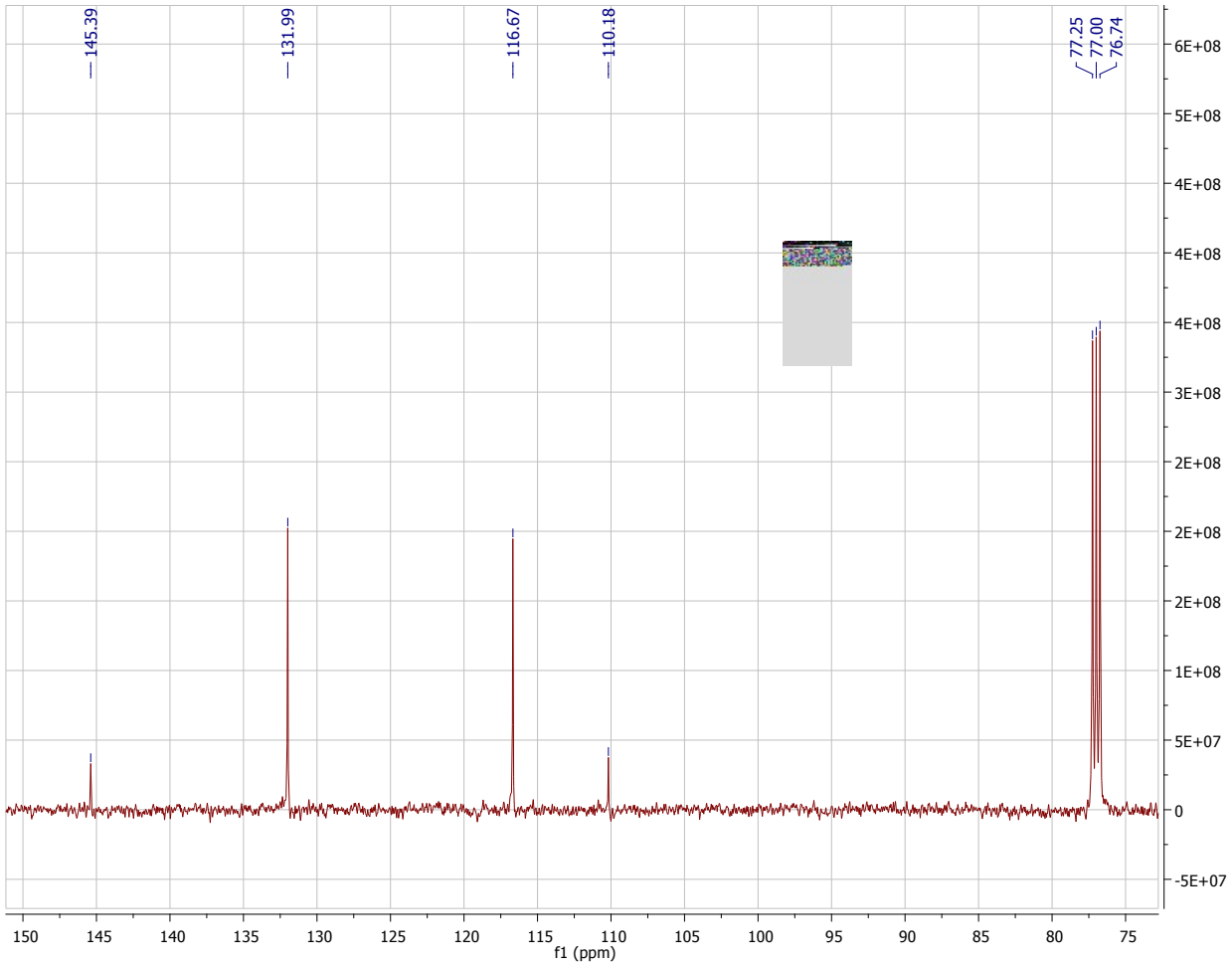
^{1}H NMR of 4-bromoaniline[5]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.24-7.22 (d, 2H, J= 9), 6.57-6.55 (d, 2H, J= 9), 3.65 (s, 2H).



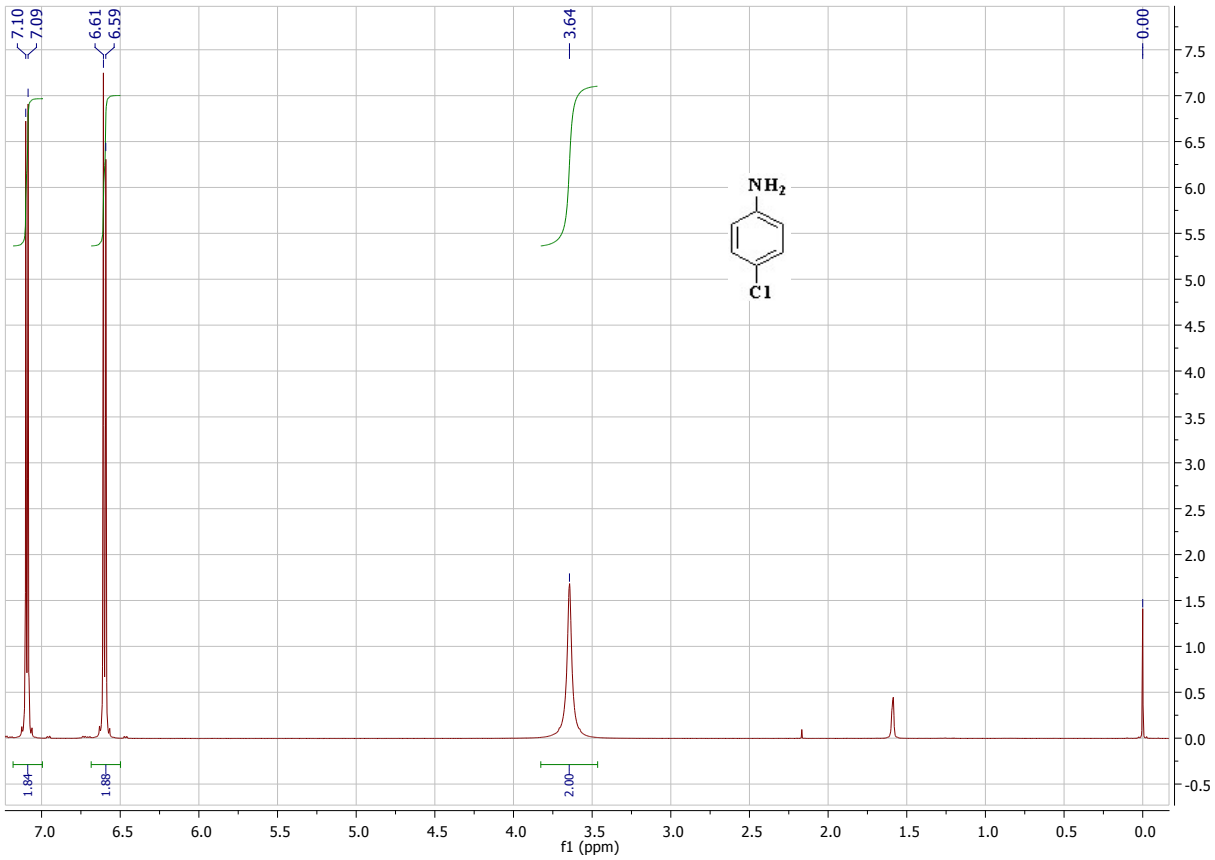
^{13}C NMR of 4-bromoaniline

^{13}C NMR ($CDCl_3$, 125MHz) δ = 145.39, 131.99, 116.67, 110.18.



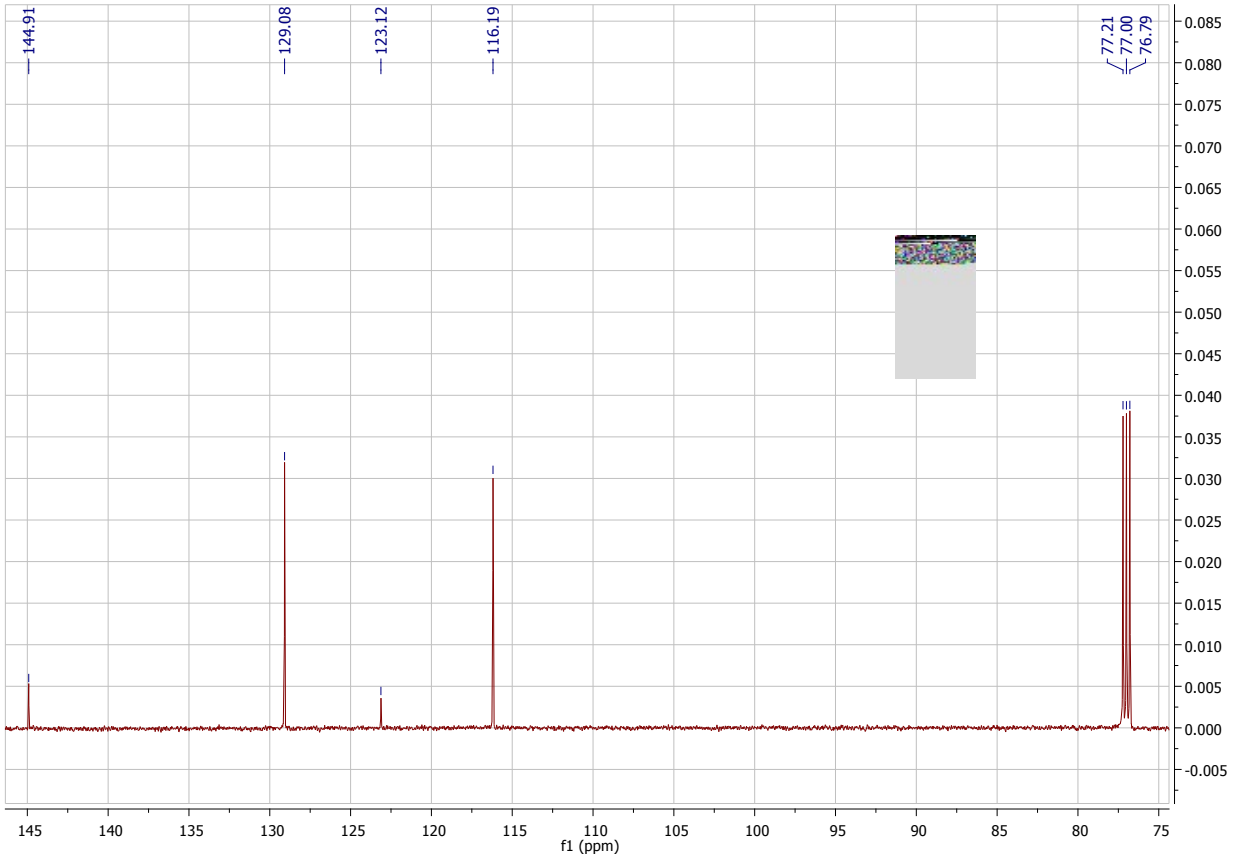
^{1}H NMR of 4-chloroaniline[5]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.10-7.09 (d, 2H, J= 8.5), 6.61-6.59 (d, 2H, J= 8.5), 3.64 (s, 2H).



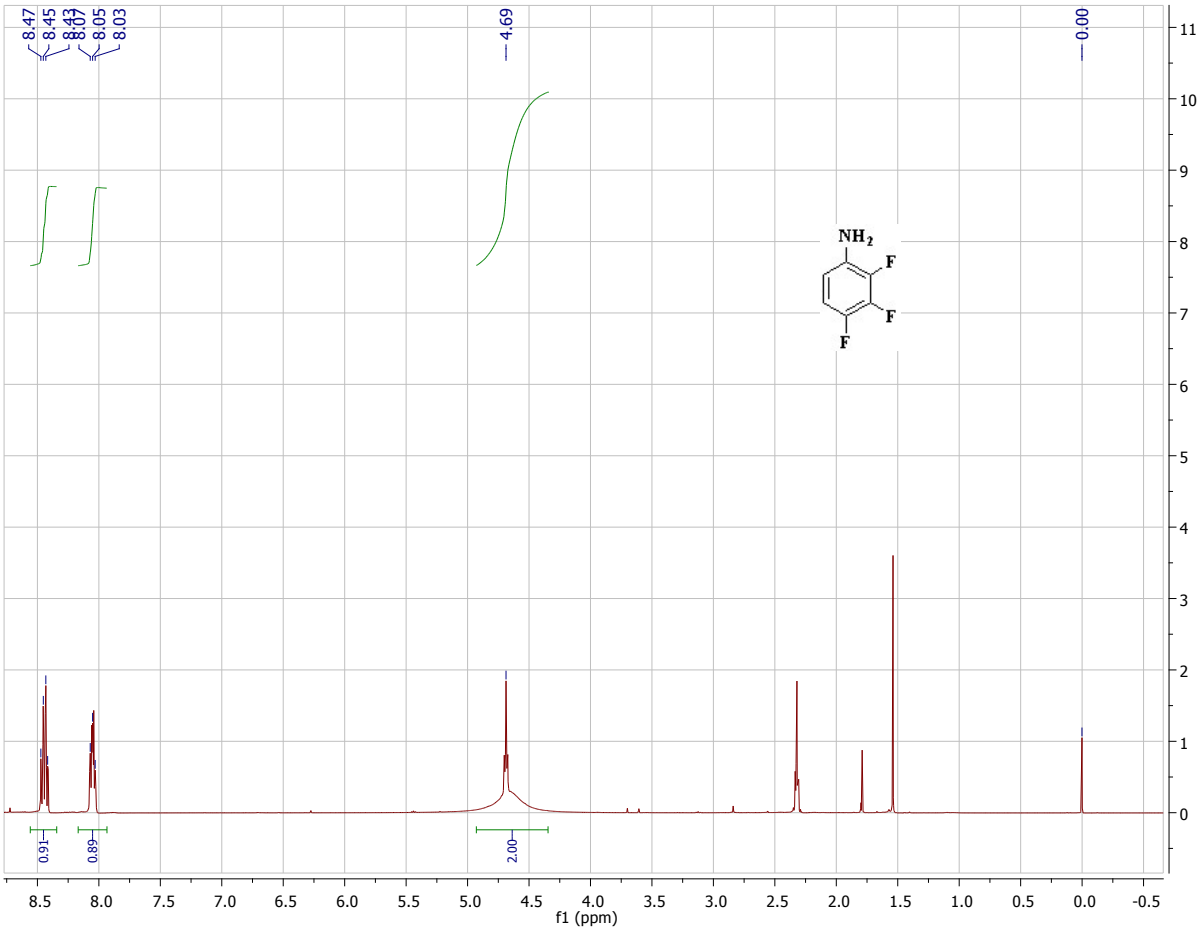
^{13}C NMR of 4-chloroaniline

^{13}C NMR ($CDCl_3$, 125MHz) δ = 144.91, 129.08, 123.12, 116.19.



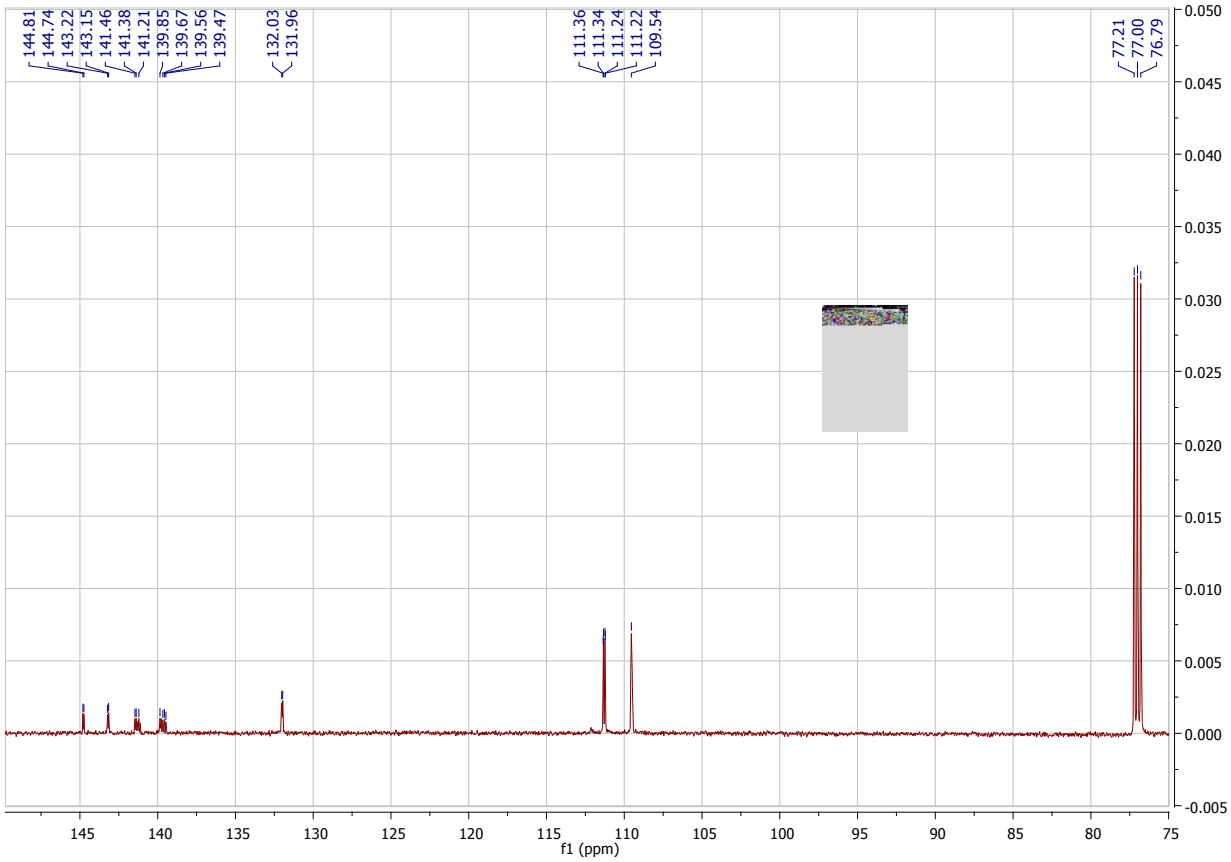
^{1}H NMR of 2,3,4-fluoroaniline[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 8.47-8.43 (m, 1H), 8.07-8.03 (m, 1H), 4.69 (s, 2H).



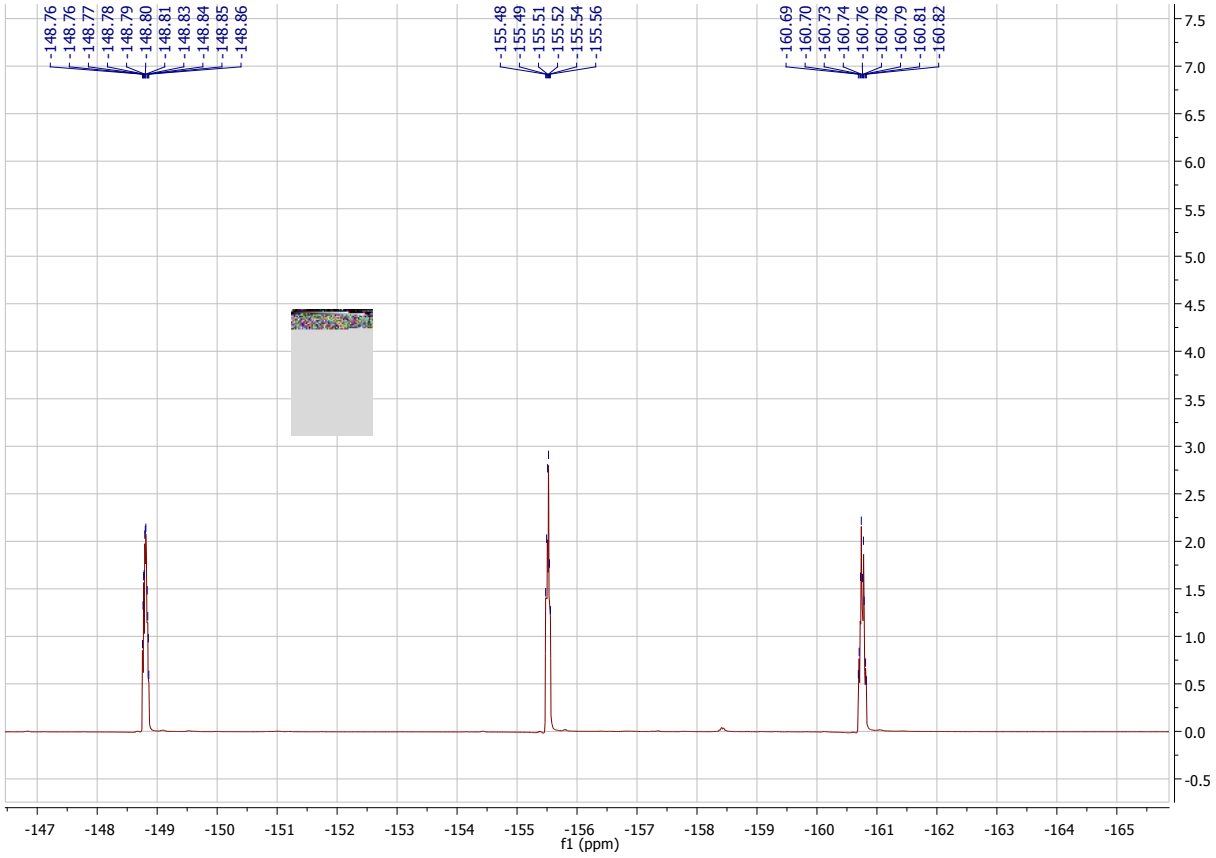
^{13}C NMR of 2,3,4-fluoroaniline

^{13}C NMR ($CDCl_3$, 150MHz) δ = 144.81-144.74 (d, 0.5C), 143.22-143.15 (d, 0.5, C), 141.46-141.21 (m, 1C), 139.85-139.47 (m, 1C), 132.03-131.96 (m, 1C), 111.36-111.22 (m, 1C), 109.54 (s, 1C)



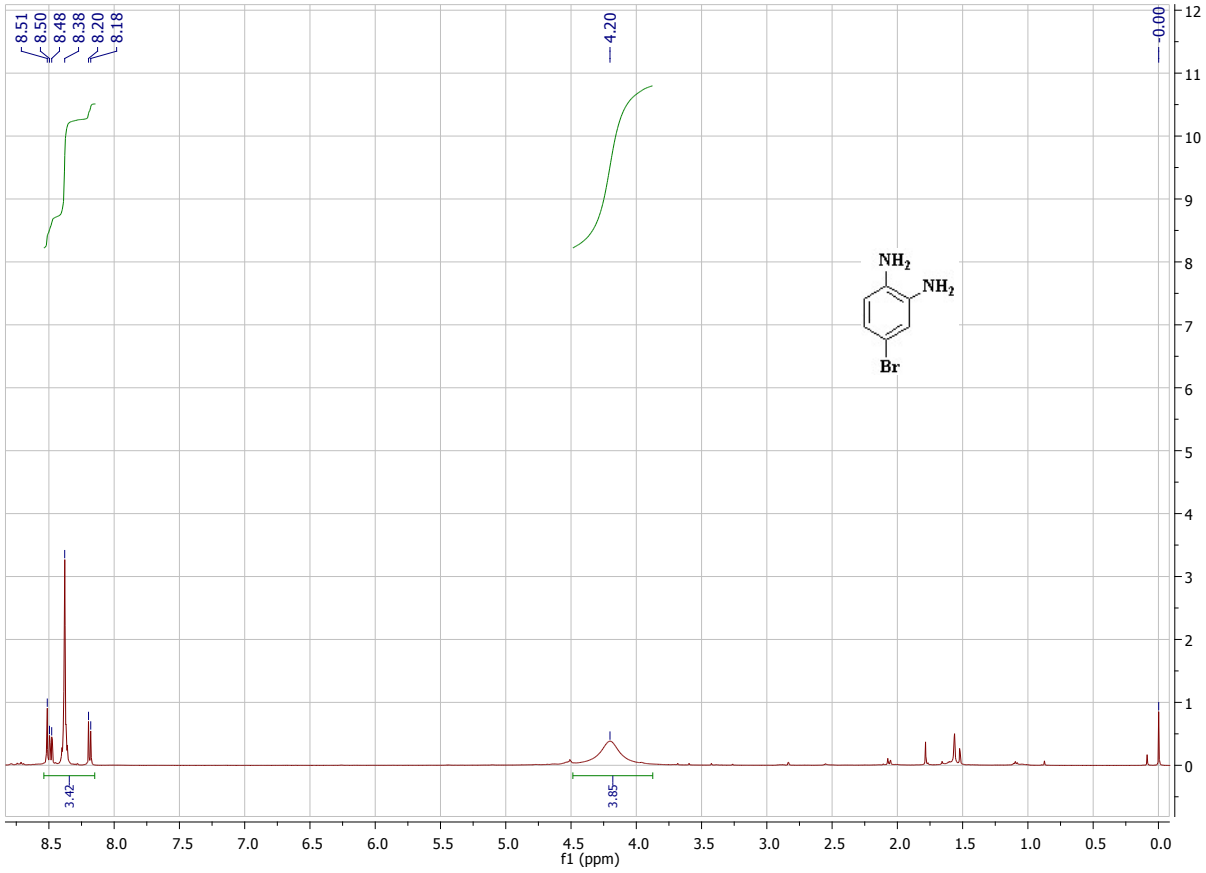
^{19}F NMR of 2,3,4-fluoroaniline

^{19}F NMR ($CDCl_3$, 564.72MHz) δ = (-)148.76- (-)148.86 (m, 1F), (-)155.48- (-)155.56 (m, 1F), (-)160.69- (-)160.82 (m, 1F).



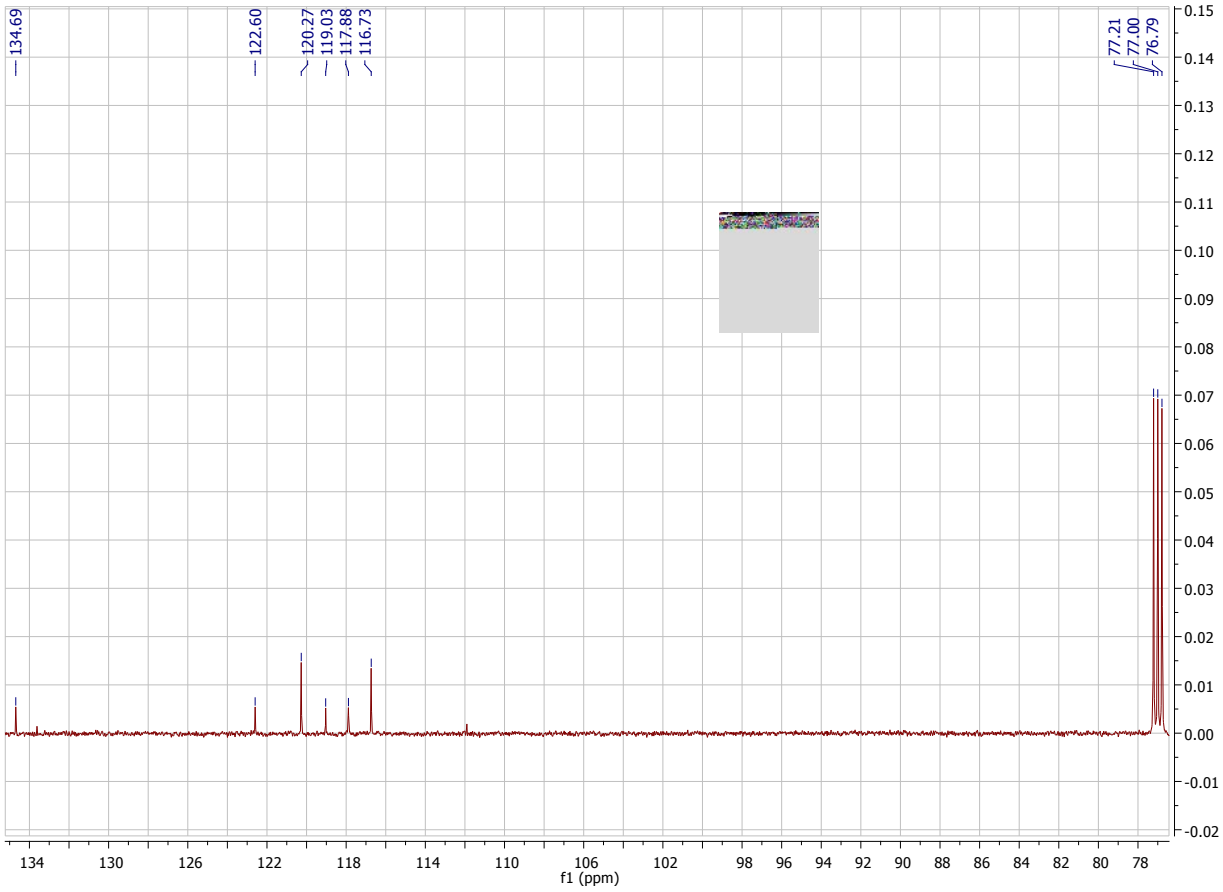
^{1}H NMR of 4-bromo-1,2-diaminobenzene[16]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 8.51-8.18 (m, 3H), 4.20 (bs, 4H).



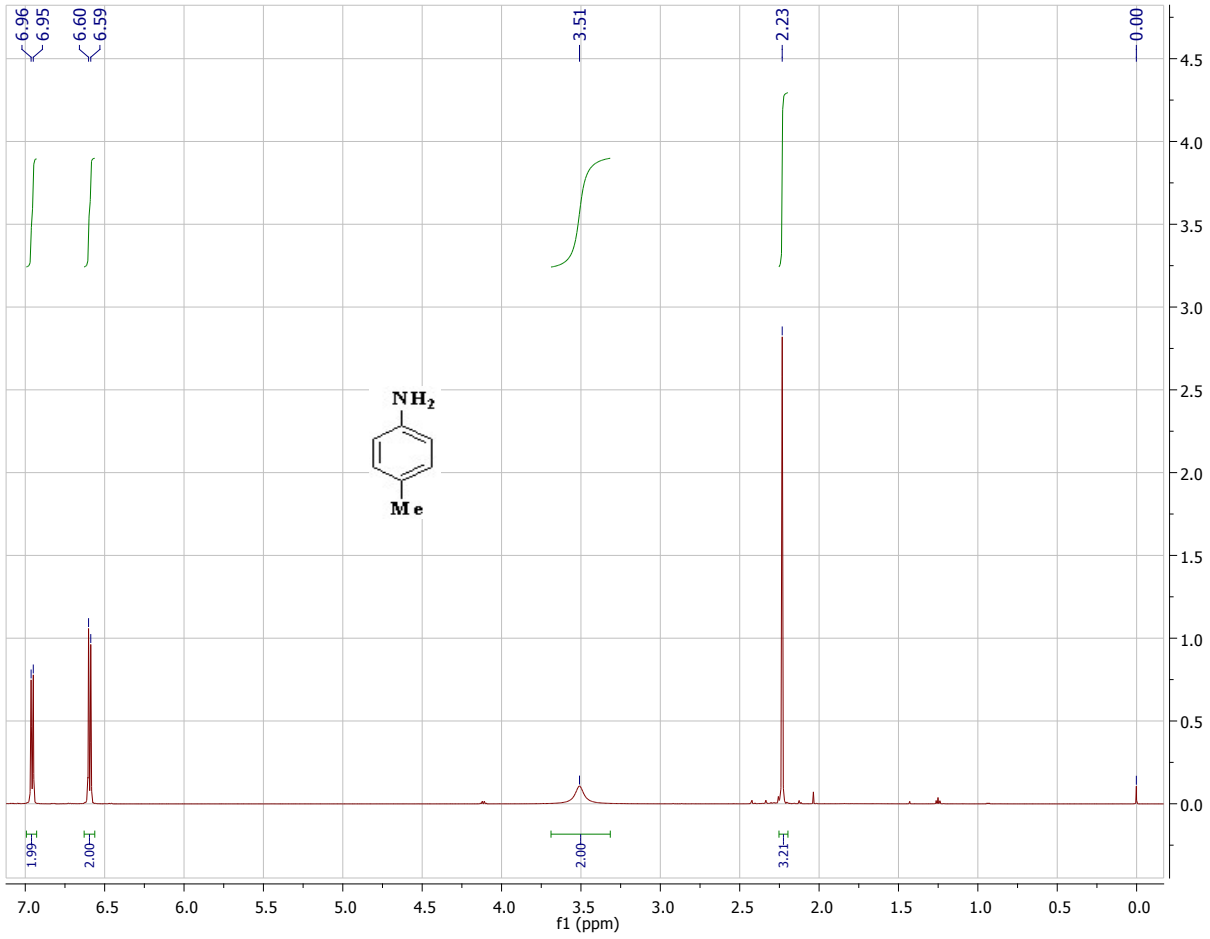
^{13}C NMR of 4-bromo-1,2-diaminobenzene

^{13}C NMR ($CDCl_3$, 125MHz) δ = 134.69, 122.60, 120.27, 119.03, 117.88, 116.73.



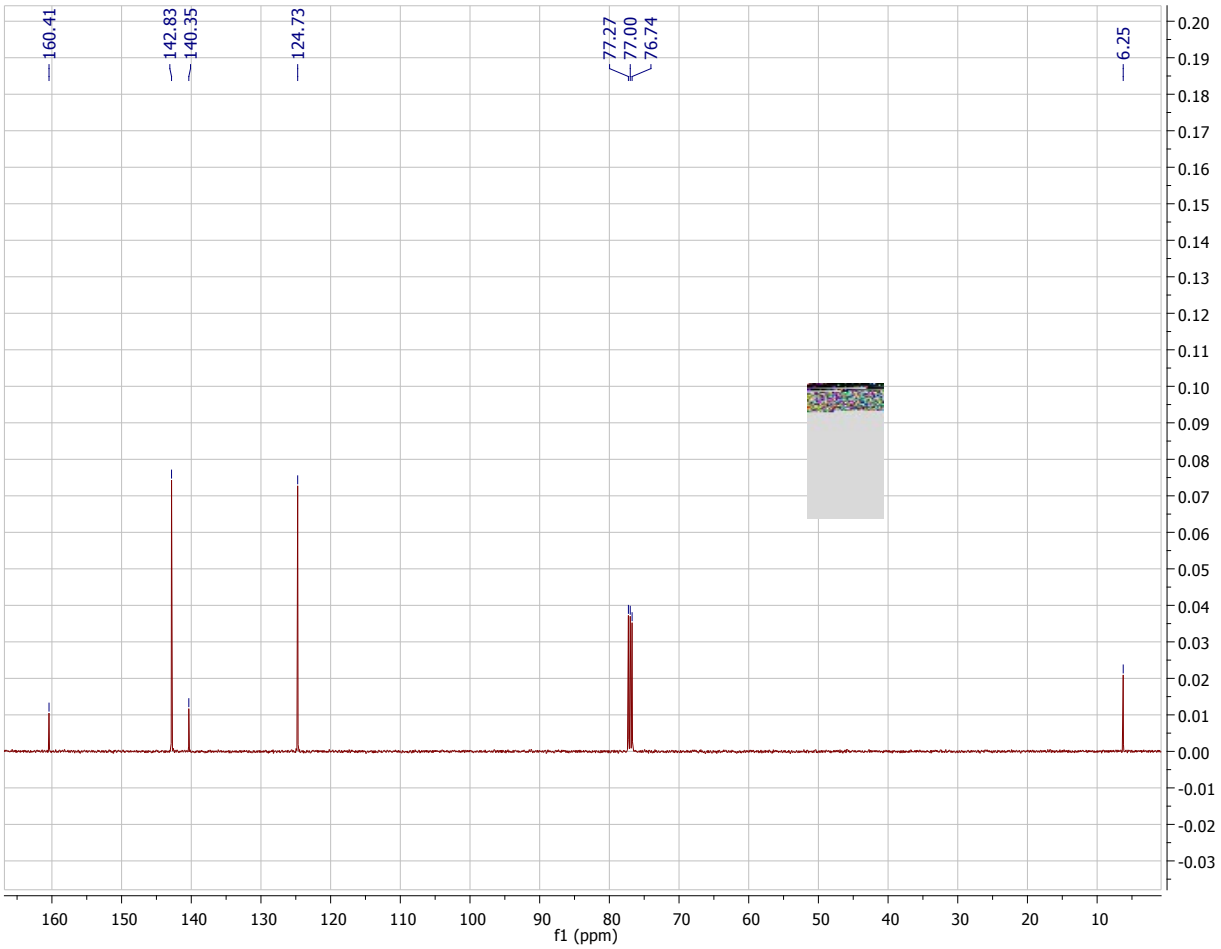
^{1}H NMR of 4-methylaniline[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 6.96-6.95 (d, 2H, J= 6.5), 6.60-6.59 (d, 2H, J= 7), 3.51 (bs, 2H), 2.23 (s, 3H).



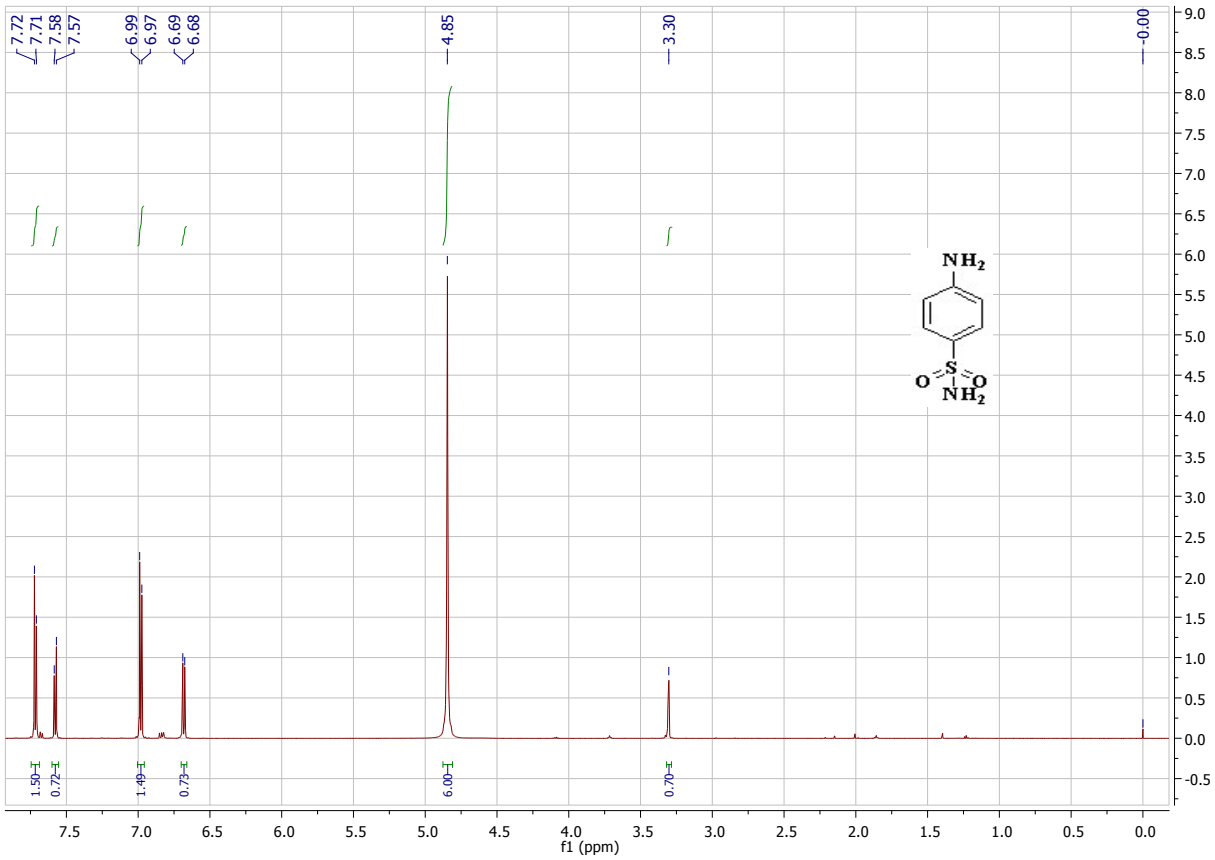
^{13}C NMR of 4-methylaniline

^{13}C NMR ($CDCl_3$, 125MHz) δ = 160.41, 142.83, 140.35, 124.73, 6.25.



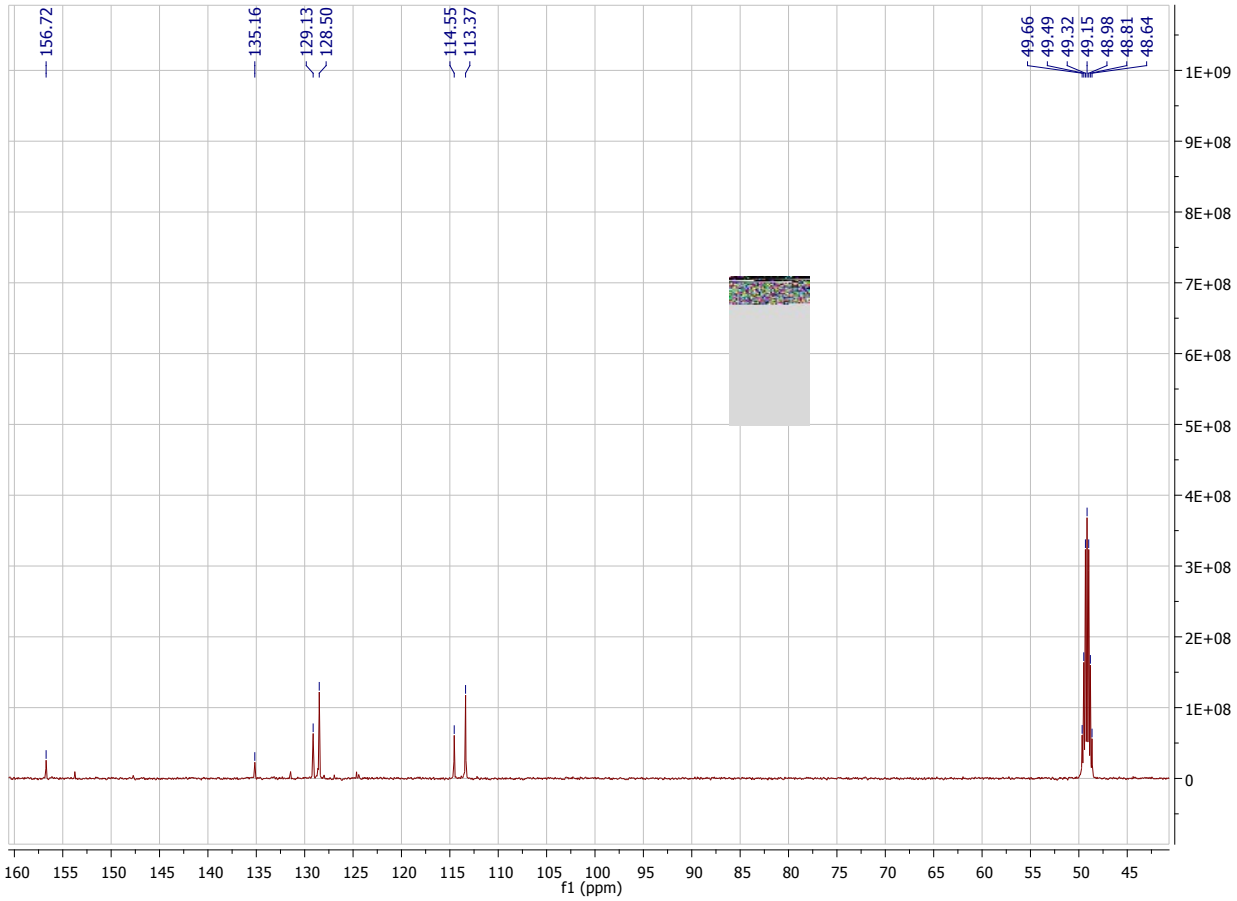
^{1}H NMR of 4-aminobenzenesulfonamide[14]

^{1}H NMR (MeOD, 500MHz, TMS) δ = 7.72-7.57 (m, 2H), 6.99-6.97 (d, 2H, J= 9), 6.69-6.68 (d, 1H, J= 8.5), 4.85 (s, 6H), 3.30 (s, 1H).



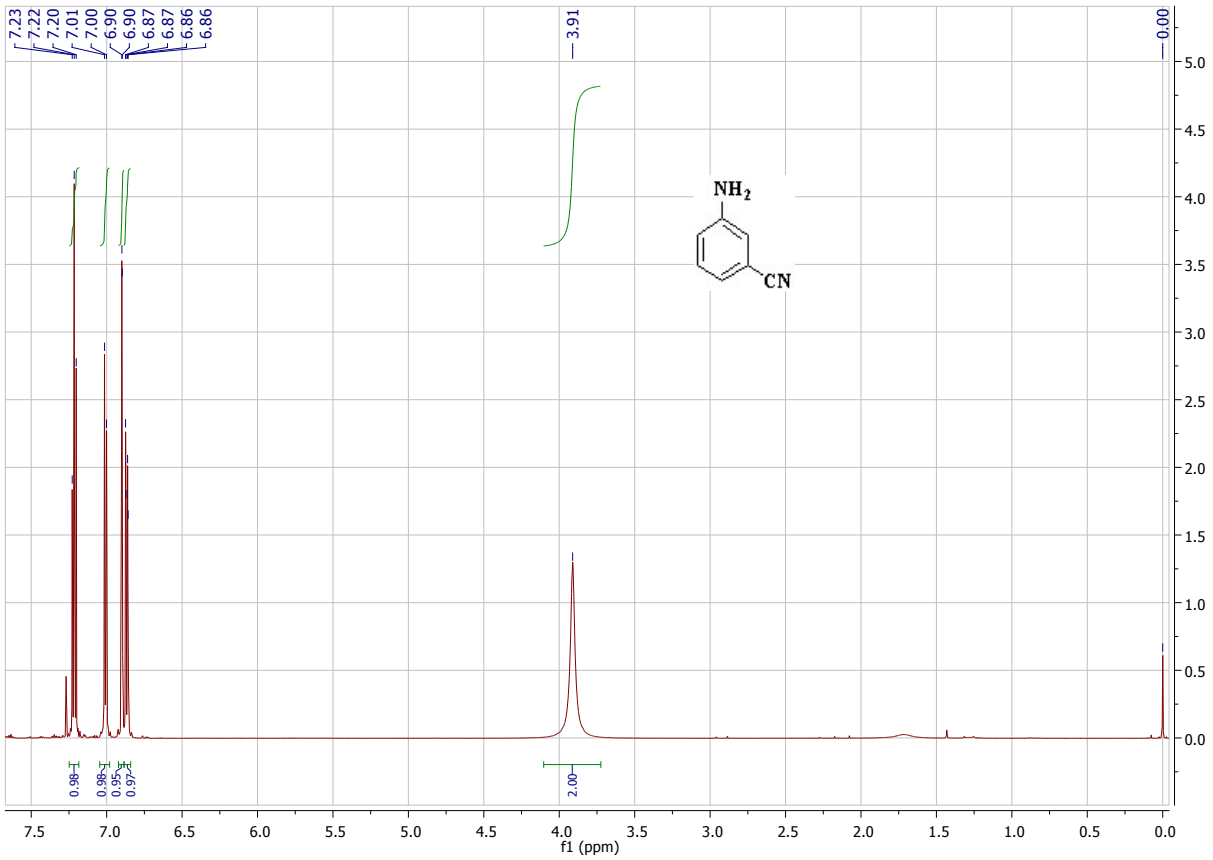
^{13}C NMR of 4-aminobenzenesulfonamide

^{13}C NMR (MeOD, 125MHz) δ = 156.72, 135.16, 129.13, 128.50, 114.55, 113.37.



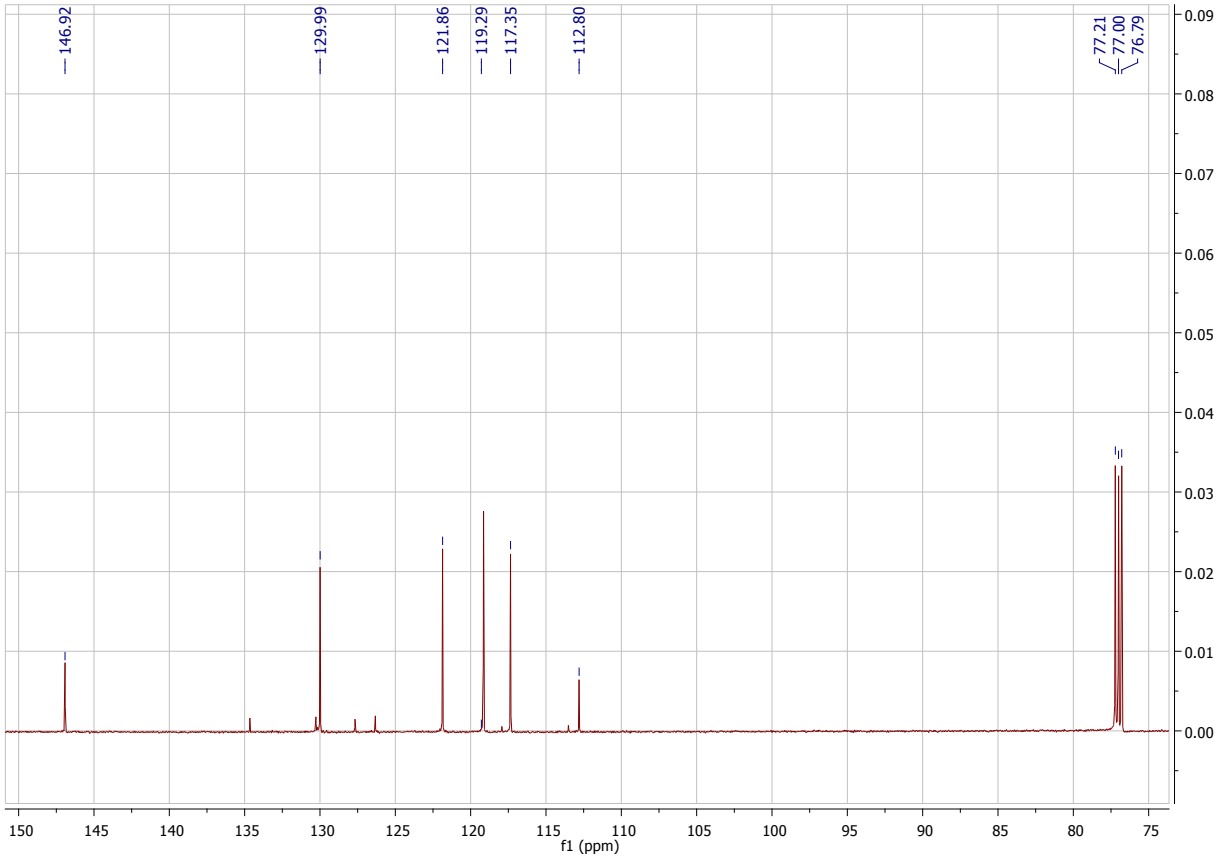
^{1}H NMR of 3-aminobenzonitrile[14]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 7.23-7.20 (m, 1H), 7.01-7.00 (m, 1H), 6.90-6.86 (m, 2H), 3.91 (bs, 2H).



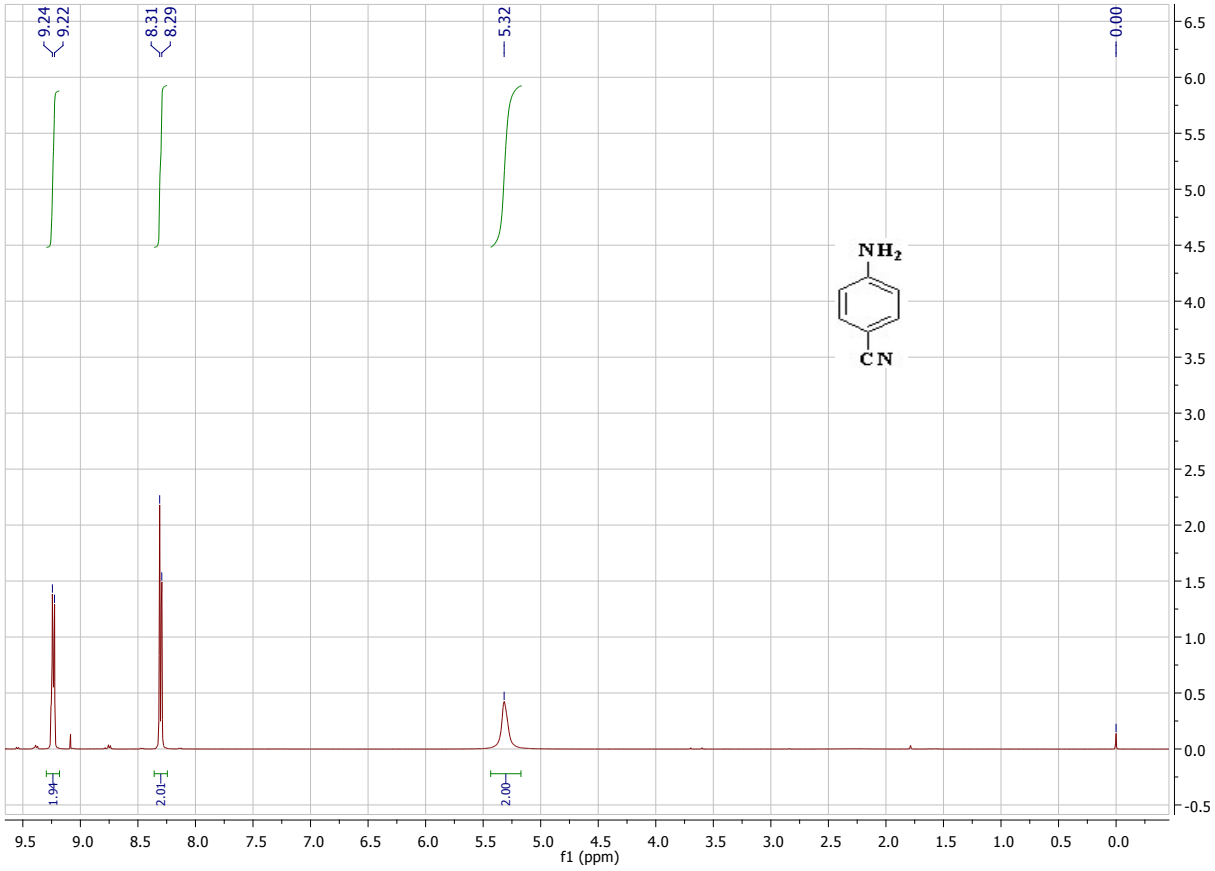
^{13}C NMR of 3-aminobenzonitrile

^{13}C NMR ($CDCl_3$, 125MHz) δ = 146.92, 129.99, 121.86, 119.29, 117.35, 112.80.



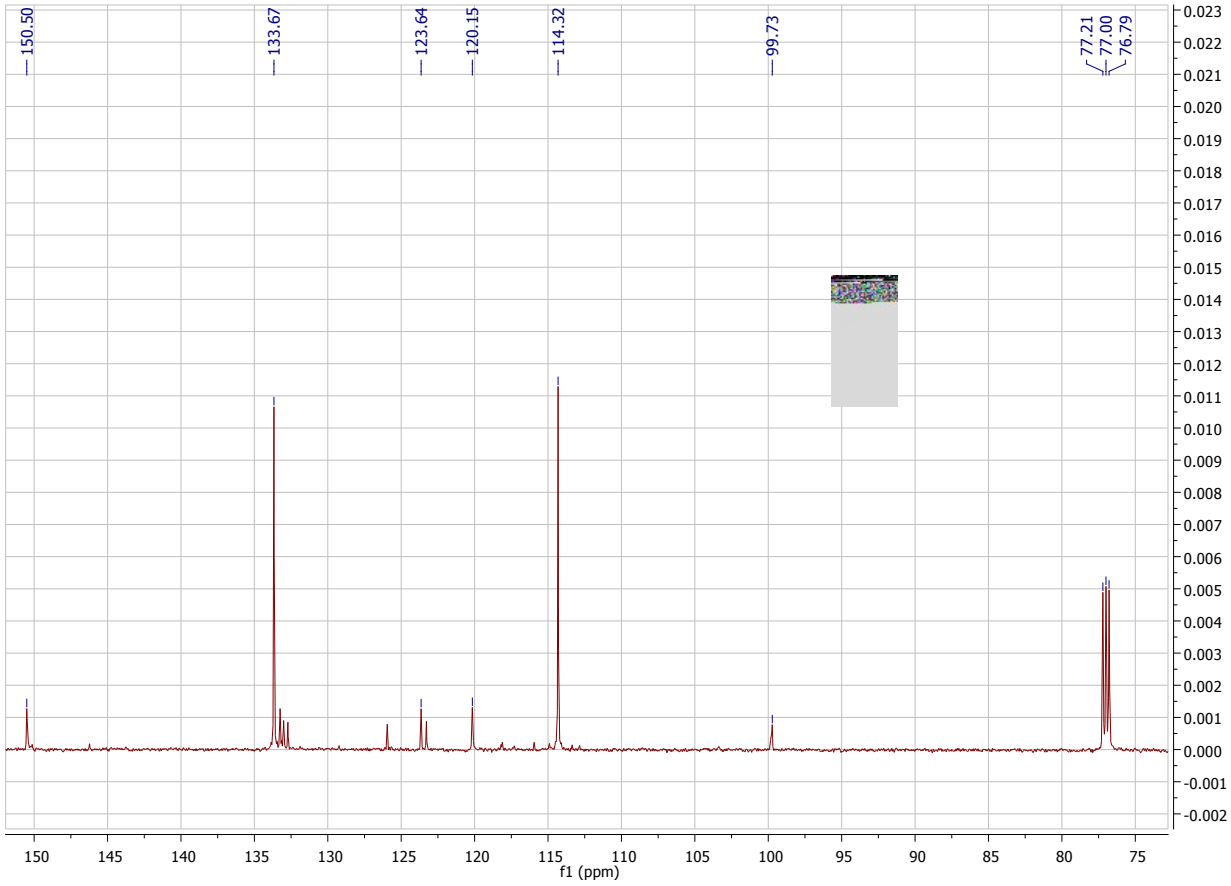
^{1}H NMR of 4-aminobenzonitrile[5]

^{1}H NMR ($CDCl_3$, 500MHz, TMS) δ = 9.24-9.22 (d, 2H, J= 9), 8.31-8.29 (d, 2H, J=9), 5.32 (bs, 2H).



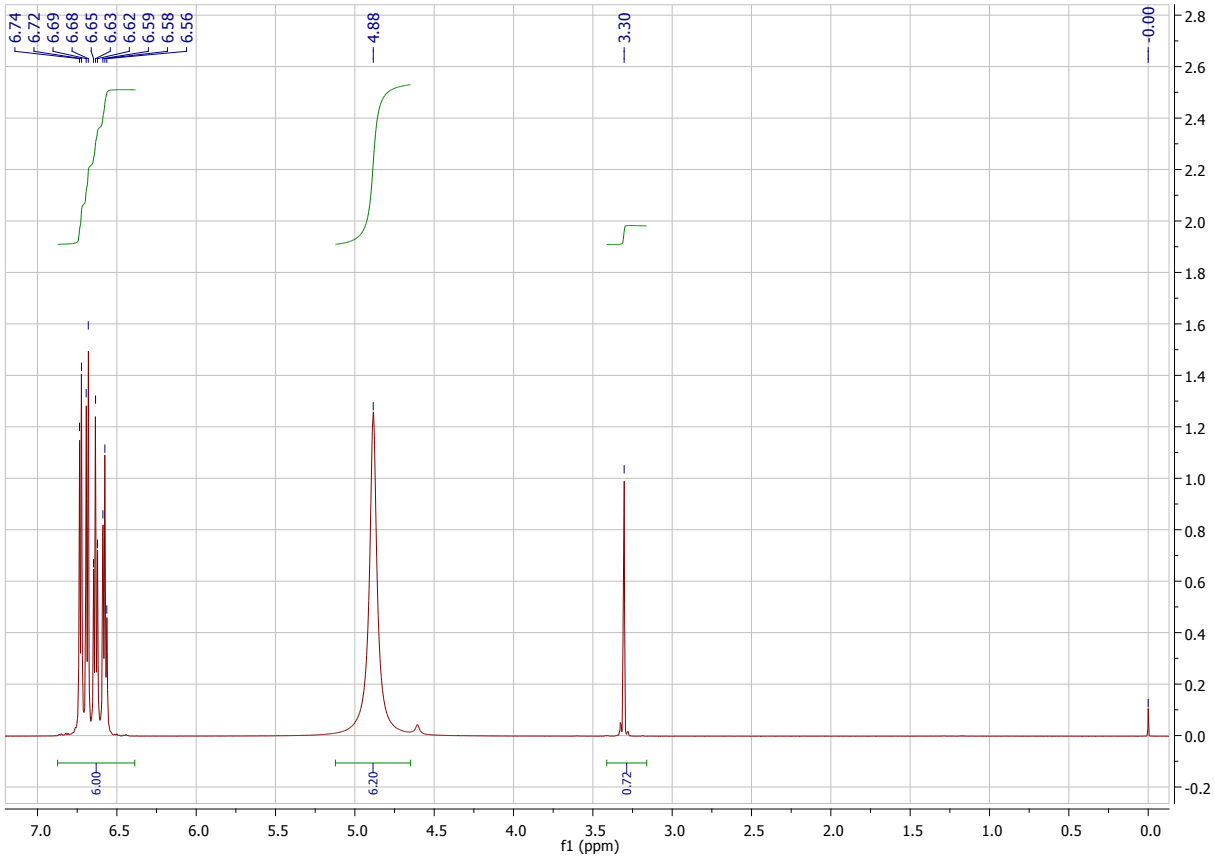
^{13}C NMR of 4-aminobenzonitrile

^{13}C NMR ($CDCl_3$, 125MHz) δ = 150.50, 133.67, 123.64, 120.15, 114.32, 99.73.



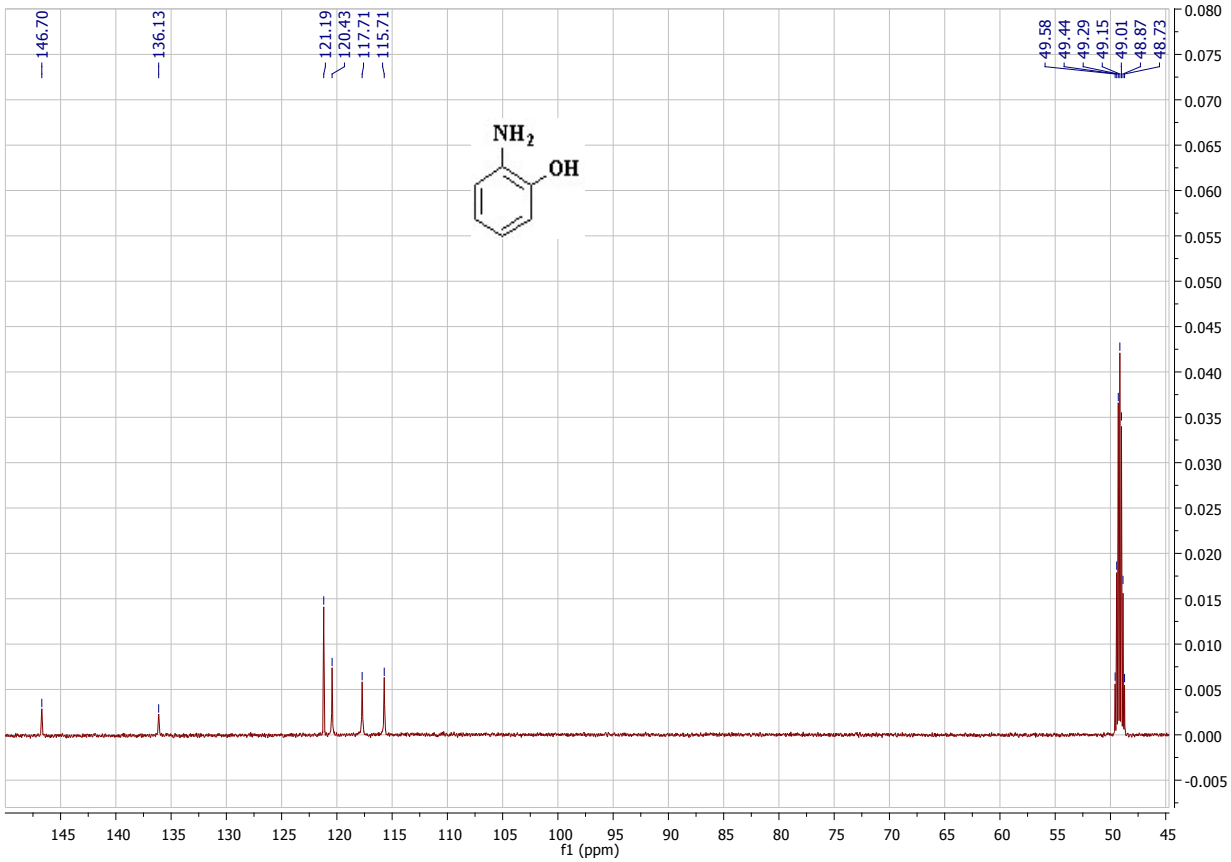
^{1}H NMR of 2-aminophenol[14]

^{1}H NMR (MeOD, 500MHz, TMS) δ = 6.74-6.56 (m, 6H), 4.88 (s, 6H), 3.30 (s, 1H).



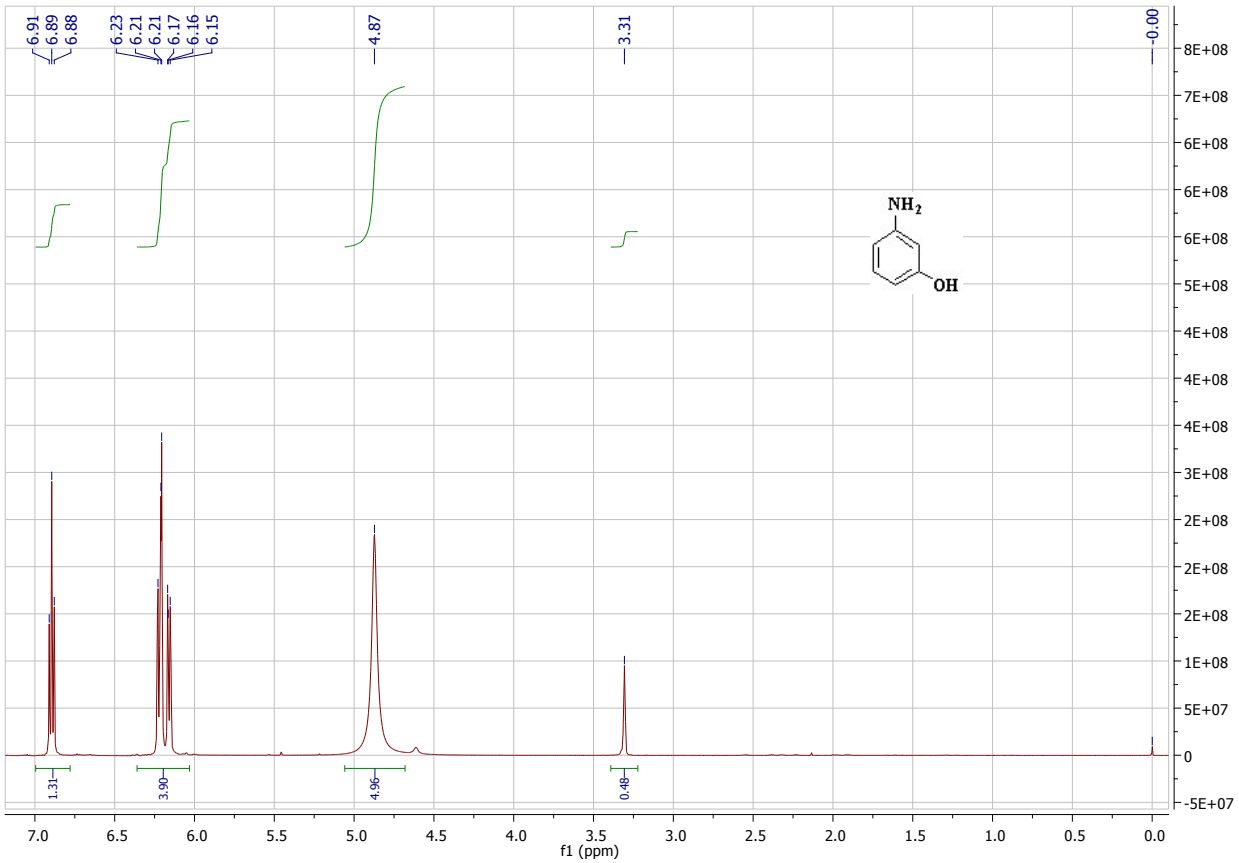
^{13}C NMR of 2-aminophenol

^{1}H NMR (MeOD, 125MHz) δ = 146.70, 136.13, 121.19, 120.43, 117.71, 115.71.



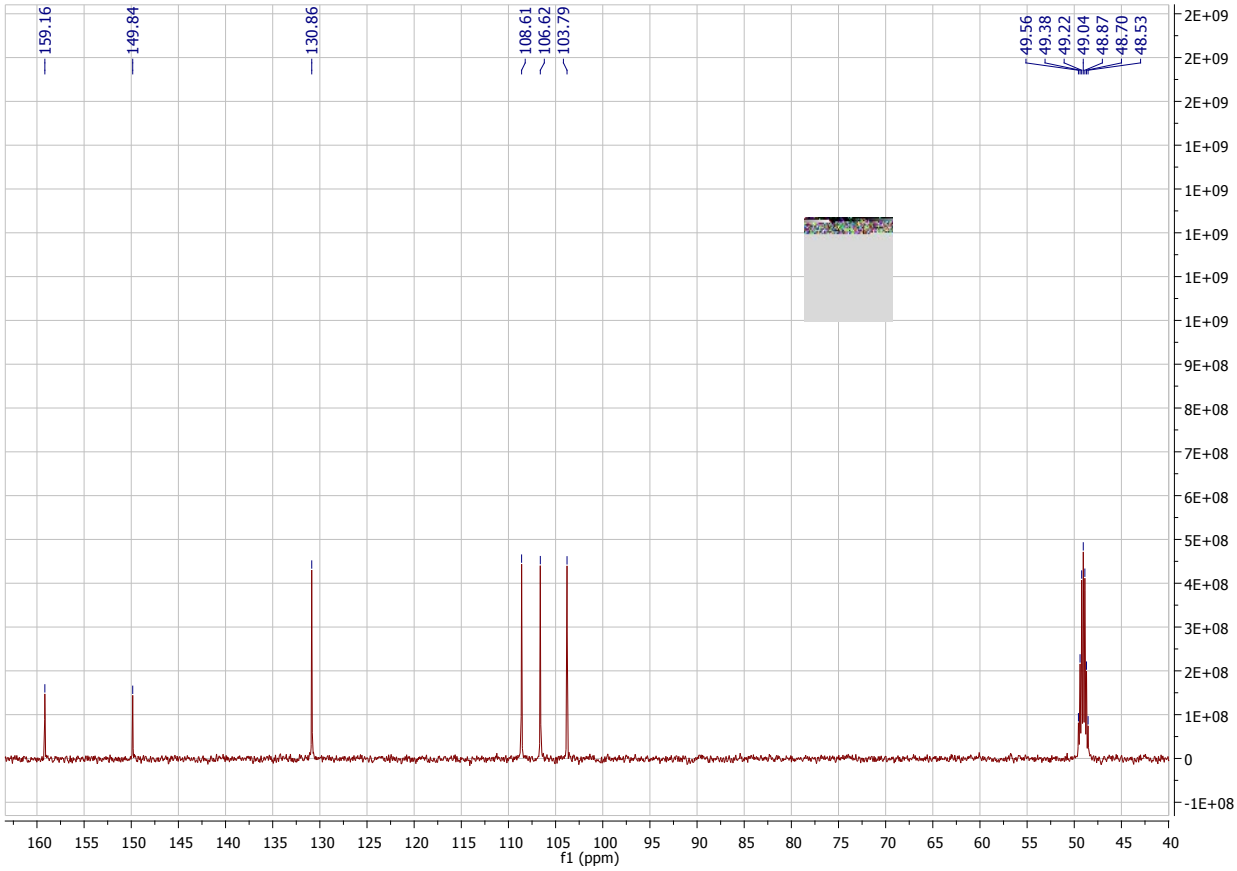
^{1}H NMR of 3-aminophenol[17]

^{1}H NMR (MeOD, 500MHz, TMS) δ = 6.91-6.88 (t, 1H, J=8), 6.23-6.15 (m, 4H), 4.87 (s, 5H), 3.31 (s, 1H).



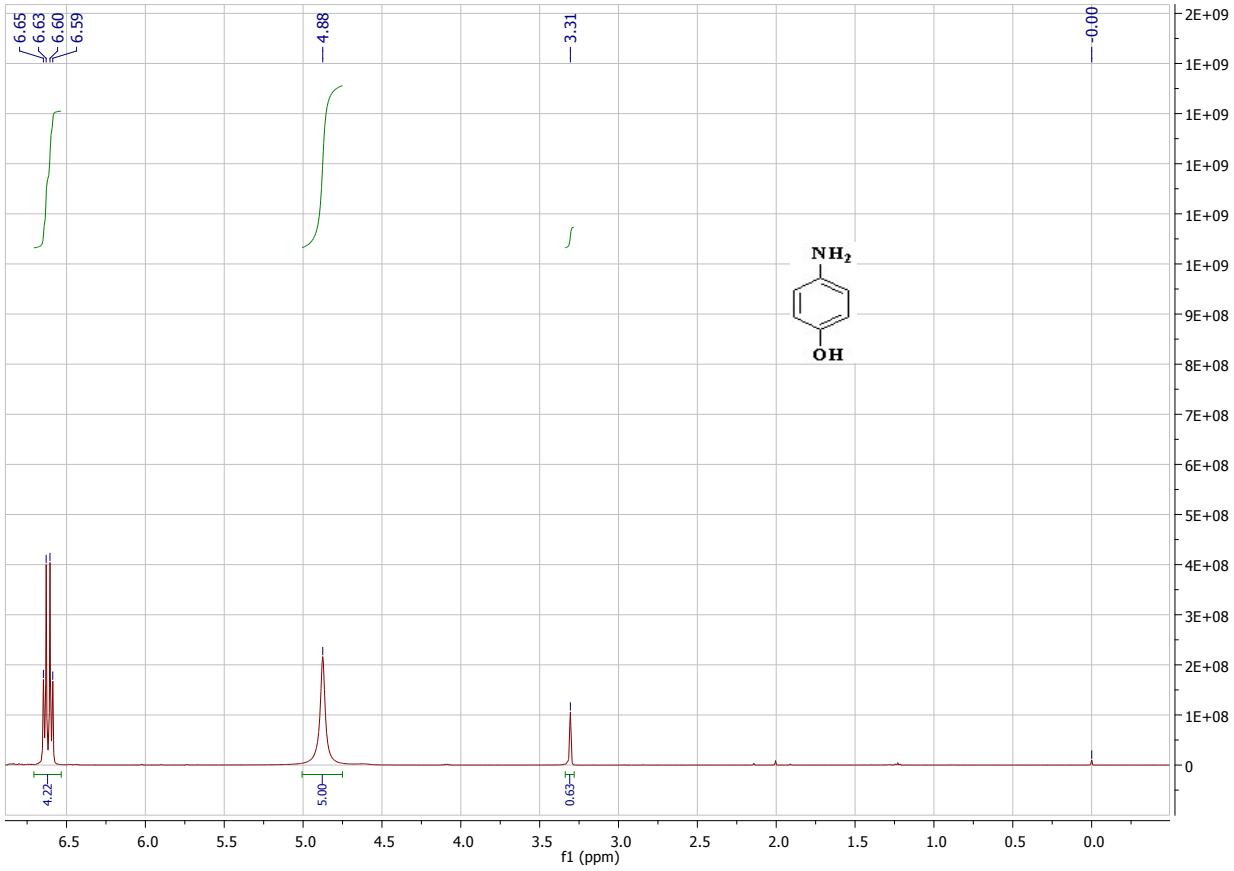
^{13}C NMR of 3-aminophenol

^{1}H NMR (MeOD, 125MHz) δ = 159.16, 149.84, 130.86, 108.61, 106.62, 103.79.



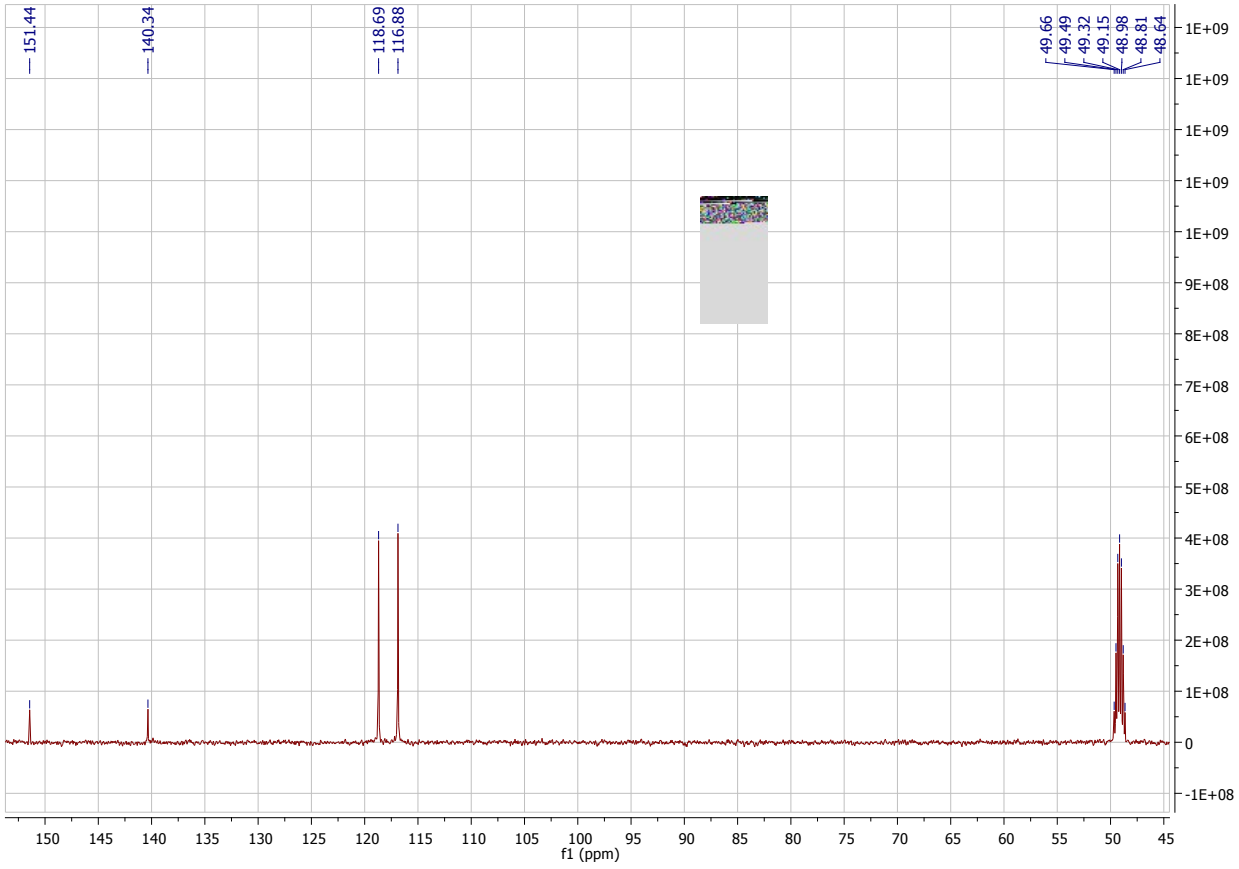
^{1}H NMR of 4-aminophenol[5]

^{1}H NMR (MeOD, 500MHz, TMS) δ = 6.65-6.59 (m, 4H), 4.88 (s, 6H), 3.31 (s, 1H).



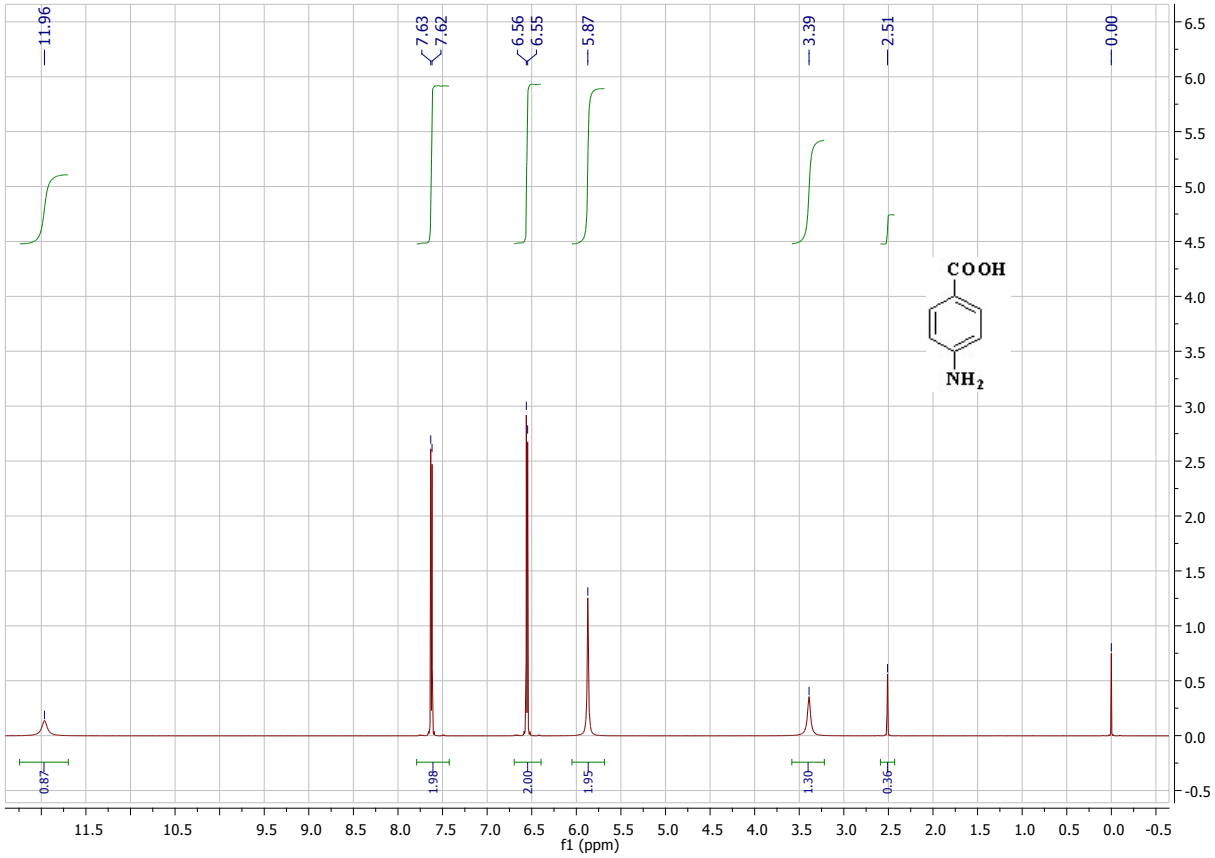
^{13}C NMR of 4-aminophenol

^{13}C NMR (MeOD, 125MHz) δ = 151.44, 140.34, 118.69, 116.88.



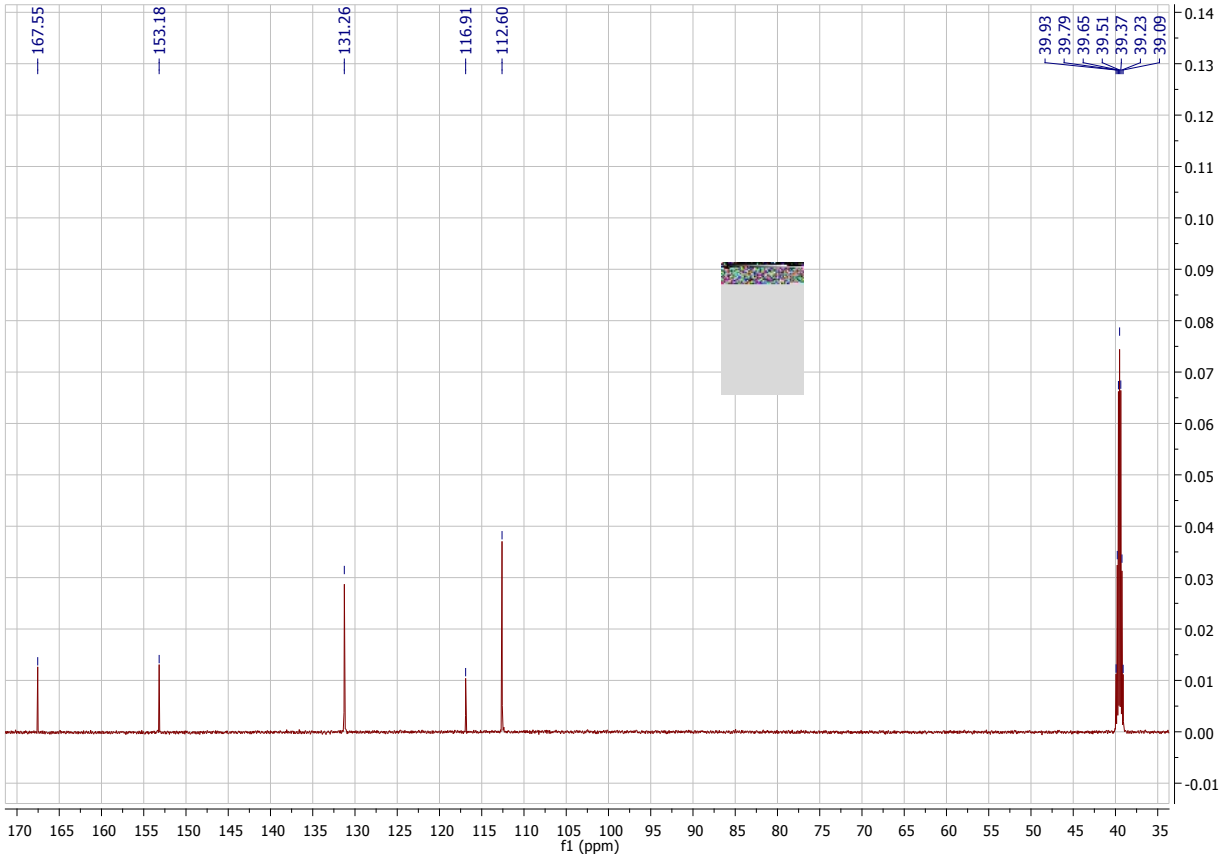
^{1}H NMR of 4-aminobenzoic acid[14]

^{1}H NMR (DMSO, 500MHz, TMS) δ = 11.96 (bs, 1H), 7.63-7.62 (d, 2H, J= 8.5), 6.56-6.55 (d, 2H, J= 8.5), 5.87 (s, 2H), 3.39 (s, 3H), 2.51 (s, 1H).



^{13}C NMR of 4-aminobenzoic acid

^{1}H NMR (DMSO-D_6, 125MHz) δ = 167.55, 153.18, 131.26, 116.91, 112.60.



(M) References

(1) F. B. Slezak, A. Hirsch, I. Rosen, J. Org. Chem. 25 (4) (1960) 660-661.

(2) K. Jansen, H-J. Buschmann, A. Wego, D. Döpp, C. Mayer, H.-J. Drexler, H.-J. Holdt, E. Schollmeyer, J. Incl. Phenom. Macrocycl. Chem., 39 (3-4) (2001) 357-363.

(3) F. A. Westerhaus, R. V. Jagadeesh, G. Wienhöfer, M-M. Pohl, J. Radnik, A-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner, M. Beller, Nat. Chem. 5 (2013), 537–543.

(4) R. V. Jagadeesh, T. Stemmler, A-E. Surkus, M. Bauer, M-M. Pohl, J. Radnik, K. Junge, H. Junge, A. Brückner, M. Beller, Nat. Protoc. 10 (2015), 916–926.

(5) Z. Wei, J. Wang, S. Mao, D. Su, H. Jin, Y. Wang, F. Xu, H. Li, Y. Wang, ACS Catal. 5 (8) (2015) 4783–4789.

(6) T. Schwob, R. Kempe, Angew. Chem. Int. Ed. 55 (48) (2016) 15175–15179.

(7) B. Chen, F. Li, Z. Huang, G. Yuan, *ChemCatChem* 8 (2016), 1132–1138.

(8) D. Formenti, C. Topf, K. Junge, F. Ragainia, M. Beller, *Catal. Sci. Technol.* 6 (2016), 4473-4477.

(9) I. Sorribes, L. Liu, A. Corma, *ACS Catal.* 7 (2017), 2698–2708.

(10) P. Ji, K. Manna, Z. Lin, X. Feng, A. Urban, Y. Song, W. Lin, *J. Am. Chem. Soc.* 139 (2017), 7004–7011.

(11) F. Zhang, C. Zhao, S. Chen, H. Li, H. Yang, X-M. Zhang, *J. Catal.* 348 (2017), 212–222.

(12) H. Göksu, B. Celik, Y. Yıldız, F. Şen, B. KılbaŞ, *Chemistryselect*, 1 (2016), 2366-2372.

(13) B. Sahoo, D. Formenti, C. Topf, S. Bachmann, M. Scalone, K. Junge, M. Beller, ChemSusChem 10 (15) (2017) 3035-3039.

(14) S. Nandi, P. Patel, A. Jakhar, N. H. Khan, A. V. Biradar, R. I. Kureshy, H. C. Bajaj, Chemistryselect, 2 (31) (2017) 9911-9919.

(15) Z. Zhao, H. Yang, Y. Li, X. Guo, *Green Chem.*, 16 (2014), 1274.

(16) S. Urban, N. Ortega, F. Glorius, *Angew. Chem. Int. Ed.* 50 (2011), 3803–3806.

(17) Ö. Metin, A. Mendoza-Garcia, D. Dalmızrak, M. S. Gültekin, S. Sun, *Catal. Sci. Technol.*, 6 (2016), 6137-6143.