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A RAPID, SIMPLE, NOVEL AND GREEN APPROACH FOR THE REDUCTION OF NITROARENES TO ANILINES BY Fe/$NH_2NH_2 \cdot H_2SO_4$

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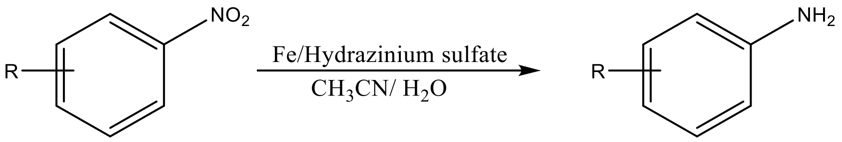
ABSTRACT

Hydrazine and its derivatives have long been used as reducing agents in organic synthesis. Use of hydrazine in organic synthesis has attracted considerable attention in recent years as it finds application in the reduction of a number of functional groups in the presence or absence of catalysts.

The present project report reveals the selective and rapid reduction of nitroarenes into the corresponding anilines using hydrazinium sulfate in the presence of iron metal powder in aq. CH_3CN in very good to excellent yields (70–98%). The products obtained are of high purity and the reactions proceed at 70–80 ºC without any adverse effect on other substituents such as: chloro, ester, nitro, -COCl, acid and acetyl groups. This method serves as direct and easy method for the synthesis of substituted anilines from nitroarenes, which are intermediates in the industries of agro, polymer, liquid crystals and photographic chemicals. The reaction is cheap, simple and superior when compared with the existing methods of preparation of anilines from nitroarenes as it involves use of abundant and inexpensive Fe metal.



R = H, Cl, $COOCH_3$, COOEt, $COCH_3$, NO_2, COCl, COOH

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Project Report entitled

A RAPID, SIMPLE, NOVEL AND GREEN APPROACH FOR THE REDUCTION OF NITROARENES TO ANILINES BY $Fe/NH_2NH_2.H_2SO_4$

submitted to

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SIR SYED COLLEGE (AIDED),
TALIPARAMBA, KERALA
(Affiliated to Kannur University)

In partial fulfilment required for the award of
Master of Science Degree in Chemistry
By

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[C1PSCH1410]

Under the guidance of

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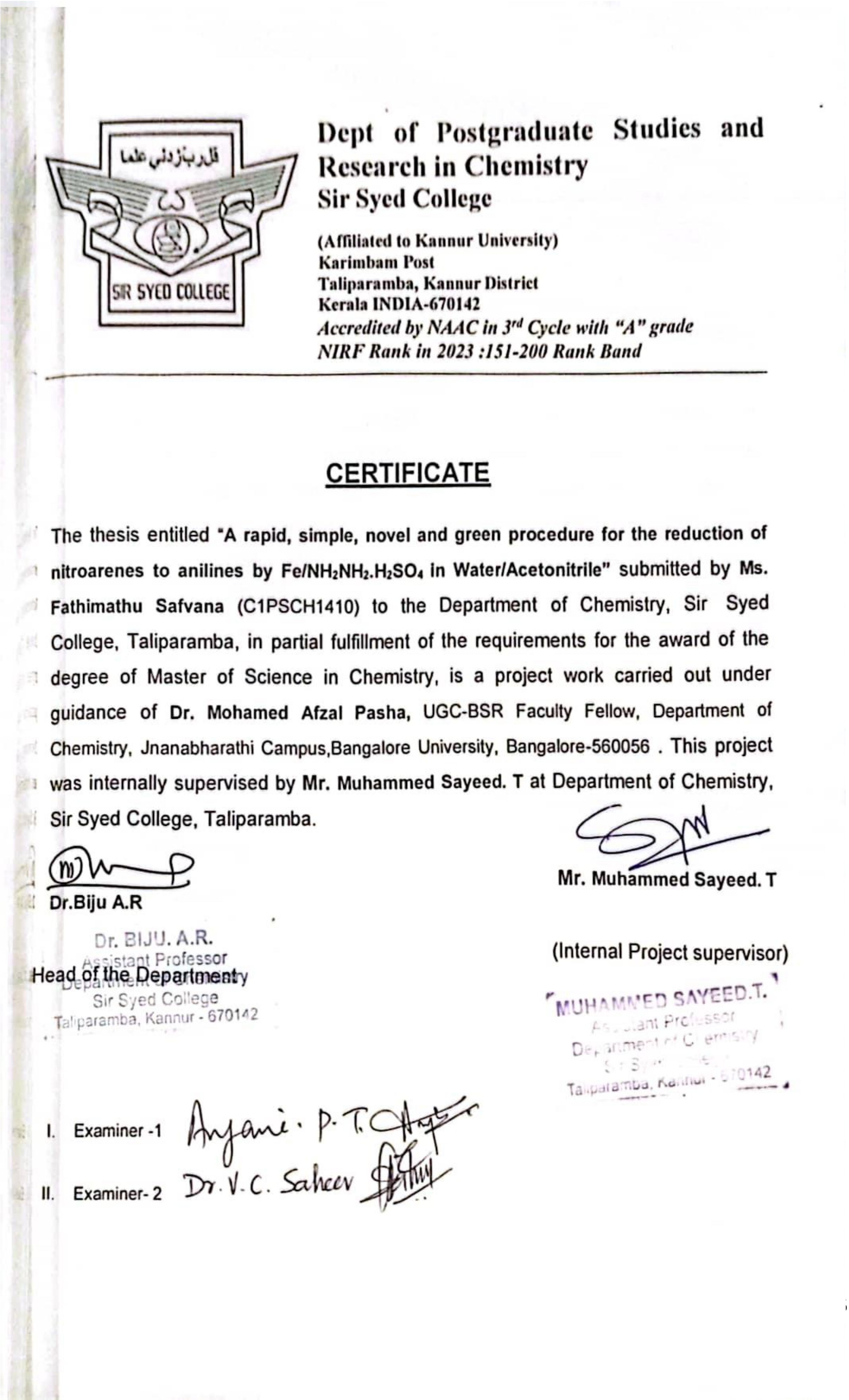
March 2023



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CERTIFICATE

The thesis entitled **"A rapid, simple, novel and green procedure for the reduction of nitroarenes to anilines by Fe/$NH_2NH_2.H_2SO_4$ in Water/Acetonitrile"** submitted by **Ms. Fathimathu Safvana** (C1PSCH1410) to the Department of Chemistry, Sir Syed College, Taliparamba, in partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry, is a project work carried out under guidance of **Dr. Mohamed Afzal Pasha,** UGC-BSR Faculty Fellow, Department of Chemistry, Jnanabharathi Campus,Bangalore University, Bangalore-560056 . This project was internally supervised by **Mr. Muhammed Sayeed. T** at Department of Chemistry, Sir Syed College, Taliparamba.

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DECLARATION

I hereby declare that, the Project Report entitled: **“A rapid, simple, novel and green approach for the reduction of nitroarenes to anilines by $Fe/NH_2NH_2\cdot H_2SO_4$”** is the result of the work carried out under the guidance of **Dr. Mohamed Afzal Pasha**, UGC-BSR Faculty Fellow, Department of Chemistry, Jnanabharathi Campus, Bangalore University, Bangalore-560056, and **Mr. Muhammed Sayeed. T**, Internal Guide, during 1st January- 4th March, 2023. Further, I have not submitted this Project Report to any other Institute or University for the award of any Degree or Diploma.

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I am extremely indebted to my Parents whose unfailing courage and counselling nurtured and motivated me to pursue my academics and their unrestrained affection and support made me stand at this juncture and this project work would have been just impossible without them.

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Fathimathu Safvana

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CHAPTER-I

Direct metal and metal/catalyst reduction of nitroarenes into anilines: An overview

1. Introduction

Anilines are important intermediates in the synthesis of several nitrogen-containing biologically active compounds and agrochemicals; anilines form substructures of many pharmaceutical compounds aswell. Anilines are also widely used as important substrates or intermediates in the synthesis of chemicals such as dyes, pigments, conducting polymers, antioxidants and photographic chemicals. They serve as the precursors for many synthetically important intermediates like amides, imines, azobenzenes, hydrazoarenes, Nitrosoarenes, N-hydroxyanilines, isocyanates and diazonium salts which could be converted into various other functional groups. Therefore, the synthesis of Anilines has gained acceptance and popularity among the synthetic chemist community.

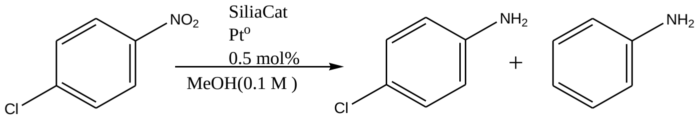
Although quite a good number of methods are available in the literature for the conversion of nitroarenes to aromatic amines (anilines), the discovery of newer, simpler, fast and efficient method is still the goal of organic chemists; and the following reagents have been successfully used to synthesize anilines from nitroarenes.

(1). Hydrogen gas/catalyst;
(2). $NaBH_4$;
(3). silyl hydrides;
(4). hydrazine hydrate;
(5). *in situ* H_2 generation;
(6). Direct metal;
(7). MPV type redox processes using organic reducing agents (transfer hydrogenation);
(8). light-induced photocatalysis;
(9). biotic reduction.

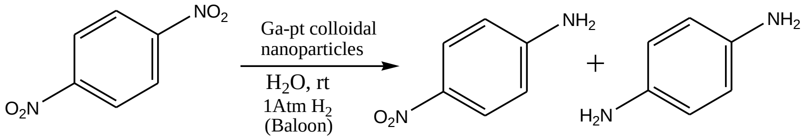
One of the most important reactions for this conversion involve the use of metals directly in the presence of additional reagents andthe other one is Hydrogenation in the presence of different metals or metal catalysts. Out of many reactions that are available in the literature on t40he use of direct metals in the presence of additional reagents and Hydrogenation in the presence of different metals or metal catalysts, a few of them have been discussed below:

1.1 Use of H_2/Platinum

1. Panduras, V *et al*., have reduced 4-chloronitrobenzene into 4-choloroaniline and a very small amount of aniline by Pt^0catalysed hydrogenation in the presence of Silia catalyst in methanol as shown below.[1]

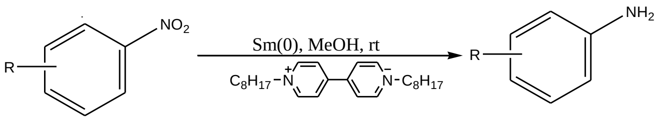


2. Colloidal Pt NPs-GA has been used as catalyst for the reduction of 1,4-dinitrobenzene into 4-nitroaniline and *p*-phenylenediamine under 1 Atm. H_2 in water as a solvent as shown in the following equation.[2]

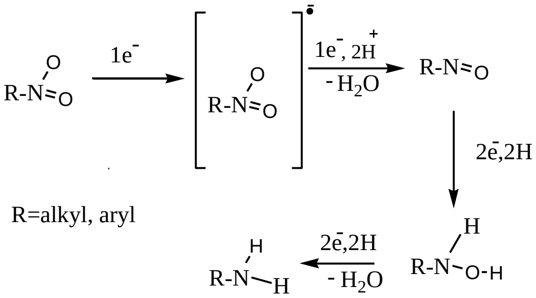


1.2 Use of Samarium (0)

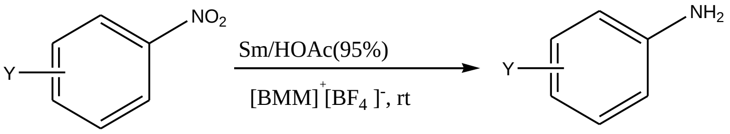
1. A mild and efficient electron-transfer method has been developed for the chemoselective reduction of aromatic nitro groups using samarium(0) metal in the presence of catalytic amount of 1,1′-dioctyl-4,4′-bipyridinium dibromide.[3] This method is found to give the aromatic amines in 79–99% yield with selectivity over a number of other functional and protecting groups such as alkene, azide, benzyl ether, nitrile, amide, halide, *p*-toluenesulfonamide, *t*-Boc, *tert*-butyldiphenylsilyl ether and aliphatic nitro groups.



The results also indicated that, samarium (0) plays an important role in the reduction and that 1,1′-dioctyl-4,4′-bipyridinium dibromide acts as an electron-transfer catalyst. The major active reducing agent responsible for the reduction is believed to be the radical cation species formed from 1,1′-dioctyl-4,4′-bipyridinium dibromide as shown below.



2. Sm metal and acetic acid in ionic liquid $[BMIM]^+ [BF_4]^-$were used at room temperature for the nitro group reduction in inert atmosphere by Zheng and Zhang. In this system halogen, CHO, COOH, CN, and NHTs groups were unaffected and corresponding anilines were obtained in 83 to 98% yields.[4]

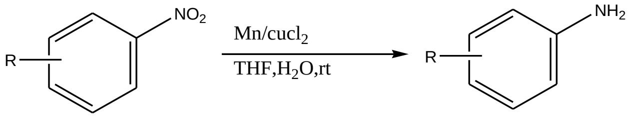


1.3 Use of Tellurium metal

Te metal was used as a reducing agent for the preparation of anilines from nitroarenes in near critical water at 275 °C by Wang *et al*.[5] Electron-donating (Me) and electron-withdrawing (MeCO, Cl) substituents were well tolerated. However, in the case of Br and I derivatives, competitive dehalogenation takes place. Carboxylic acid group also undergoes decarboxylation. This process does not reduce aliphatic nitro and nitrostyrenes.

1.4 Use of Manganese metal

Reduction of aromatic nitro compounds to anilines in THF–water mixture at room tempertaure using Mn metal as a reducing agent and $CuCl_2$as a catalyst has been reported by Sarmah and Dutta.[6] Nitro group was selectively reduced to NH_2 in the presence of OH, NH_2, Cl, COOH, ester and CN groups with 75–88% yield.



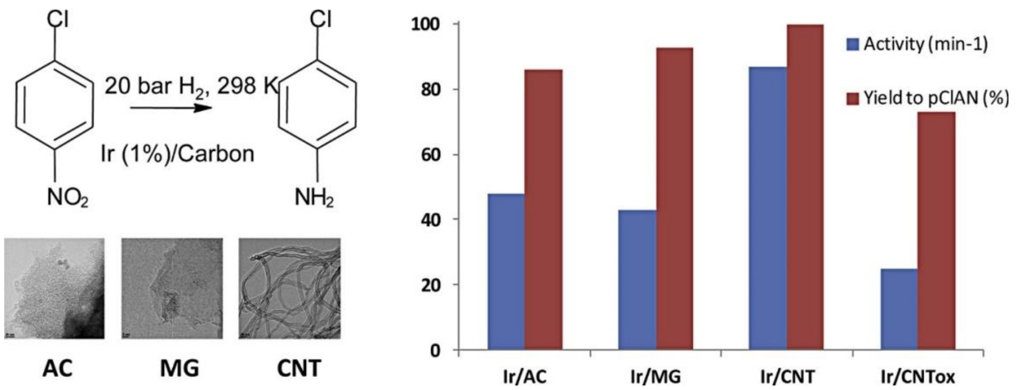
1.5 Use of H_2/Ruthenium

A novel microwave assisted synthesis of ruthenium nanoparticles supported on carbon nanotubes is developed and the catalyst was found to be active in the selective hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline in low boiling alcohol or a mixture of ethanol/water as a solvent at 60 °C and 4 MPa of H_2, with total selectivity.[7]

1.6 Use of H_2/Iridium

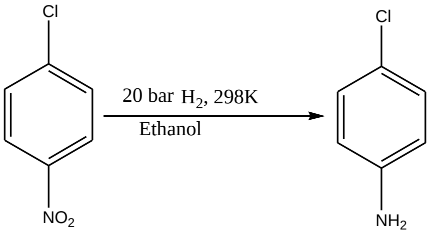
1. The selective hydrogenation of halogenated nitrobenzene over noble metal catalyst Ir has attracted much attention owing to its high efficiency and environmental friendliness. sub-nano (< 3 nm) Ir particles were prepared, and their catalytic properties for hydrogenation of halogenated nitrobenzene was evaluated. Results showed that, high selectivity (> 99%) was achieved over small Ir nanoparticles.[8]

2. A. B. Dongil *et al*., have studied the effect of carbon supports with different graphitic character [carbon nanotubes (CNT), mesoporous graphite (MG) and activated carbon (AC)] on the catalytic performance of iridium nanoparticles on the liquid phase chemoselective hydrogenation of *p*-chloronitrobenzene at room temperature.[9]



1.7 Use of H_2/Palladium

A. B. Dongil *et al.*, have studied the synthesis of palladium nanoparticles over carbon nanotubes (Pd/CNT) and graphene (Pd/G) and these catalysts have been tested for their catalytic performance in the liquid phase chemoselective hydrogenation of *p*-chloronitrobenzene at room temperature.[10] Pd/CNT was more active which can be ascribed to the different surface area and electronic properties of the Pd nanoparticles over CNT, and the selectivity was 100%.



1.8 Use of H_2/Nickel

Ma, C *et al*., developed novel structure of a porous carbon–metal composite and constructed from nitrogen-doped carbon quantum dots (NCQDs) and Ni. NCQDs (3–5 nm) with rich surface groups adsorbed with Ni ions can assemble into a carbon flake structure (50–60 nm) *via* atomic bonding, in which Ni is effectively dispersed and separated by NCQDs. As a robust catalyst, Ni@NCQDs was found to promote the nitroreduction of *p*-chloronitrobenzene to *p*-chloroaniline with high activity (100%) and selectivity (99.8%) at 4.28 times the reaction rate of commercial Raney Ni.[11]

1.9 Use of Indium

Yoo *et al*., have shown that, the In/$NbCl_5$ system mediates an efficient and mild reduction of aromatic nitro compounds to the corresponding anilines.[12] The Br, Cl, $COOCH_3$ and $COCH_3$functionalities remain unaffected.

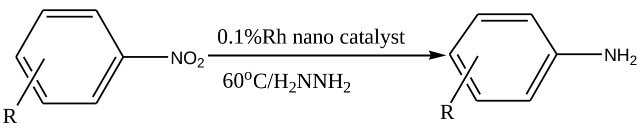
$$ArNO_2 \xrightarrow[\text{THF, rt}]{\text{Nbcl}_5\text{/In}} Ar\text{-}NH_2$$

1.10 Use of H_2/Gold

Fernando C,-L *et al*., have reported, for the first time, the exclusive (and time invariant) gas phase hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline over Au/Al_2O_3 at 393 K.[13] Exclusive formation of the corresponding haloaniline is also demonstrated over Au/Al_2O_3 for a series of mono- and di-substituted halonitroarenes.

1.11 Use of H_2/Rhodium

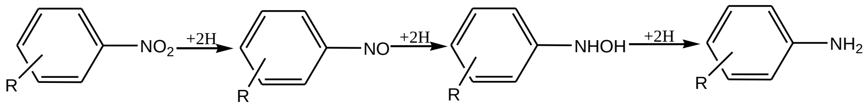
A highly efficient and selective Rh nanocatalyst was demonstrated for the reduction of nitroarenes with hydrazine monohydrate. Functional groups such as halides (F, Cl, Br and I), CN, NH_2, OH, alkene, ester and amide were untouched during the hydrogenation of the nitroarenes, and the corresponding anilines were obtained quantitatively.[14]



R=F, Cl, Br, I, CH_2=CH_2, CN, NH_2, OH, etc

1.12 Use of Silver

Nanoporous silver was used as the catalyst for the reduction of aromatic nitro compounds even in the presence of sensitive functional groups under mild conditions with excellent yields.[15] A reduced amount of $NaBH_4$ was used in this reaction.



1.13 Use of H_2/Cobalt

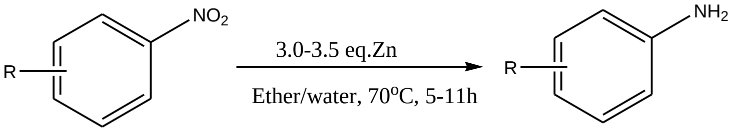
Cobalt nanoparticles supported on N-doped activated carbons have been prepared and studied as catalysts for the hydrogenation of 1-chloro-4-nitrobenzene to the corresponding chloro-aniline.[16] It is demonstrated that the catalytic activity is enhanced by the presence of nitrogen species in the support.

1.14 Use of Zinc

1. Chemoselective reduction of nitroarenes to anilines was reported using Zn and NH_4Cl in water at 80 °C by Tsukinoki andTsuzuki.[17] Functionalities like ester, amide and halogen were unaffected, and sterically hindered 2,6-dimethylnitrobenzenewas also reduced to corresponding aniline in 95% yield.

$$\text{Ph-NO}_2 \xrightarrow[\text{Solvent, } 80^{o}\text{C}]{\text{Zn,additives}} \text{Ph-NH}_2$$

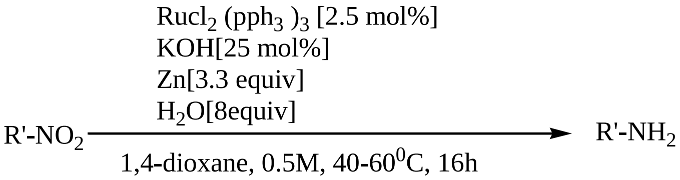
2. Zinc powder in aqueous solution of chelating ethers was used by Kumar and Lokanatha Rai for the reduction of nitroarenes to anilines.[18] Other reducible groups such as: ester, chloro, amide, ketone and styryl remained unaffected. Interestingly, the aliphatic nitro functionality present in 2-nitrodihydroindole could also be reduced by this method. The donor ether acts as a ligand and also serves as a co-solvent with water being the proton source.



3. Using the commercially available designer surfactant TPGS-750-M along with Zn dust and NH_4Cl reduction of nitroarenes to anilines was achieved. This reaction took place under mild condition at room temperature andtolerated a wide range of functionalities as shown below.[19]

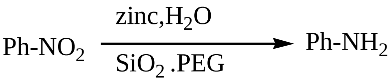
R = alkane, alkene, alkyne, halide, amide,
ester, ketone, aldehyde, amine, ether,

4. Nitro groups were chemoselectively reduced using $RuCl_2(Ph_3P)_3$ as catalyst and Zn/water as stoichiometric reductant by Plietker and coworkers.[20]



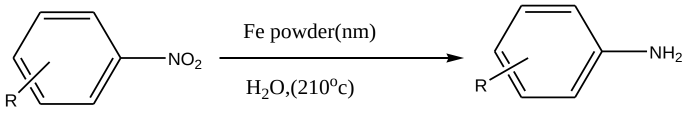
$$R'\text{-}NO_2 \xrightarrow[\text{1,4-dioxane, 0.5M, 40-60}^0\text{C, 16h}]{\text{Rucl}_2\text{ (pph}_3\text{)}_3\text{ [2.5 mol\%], KOH[25 mol\%], Zn[3.3 equiv], H}_2\text{O[8equiv]}} R'\text{-}NH_2$$

5. Reduction of nitro compounds to anilines was achieved in water using zinc powder and silica gel supported PEG by Reza *et al*. The products were isolated in 68–92% yield by simple acid–base purification with retention of other substituents like NH_2 and COOH, and also sensitive functionalities like CHO, Cl and CH_2Br.[21]

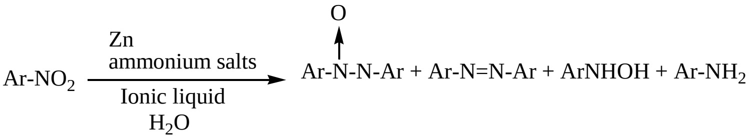


$$Ph\text{-}NO_2 \xrightarrow[\text{SiO}_2\text{ .PEG}]{\text{zinc,H}_2\text{O}} Ph\text{-}NH_2$$

6. A practical reduction of nitroarenes with nano size activated metallic iron powder in water at 210 °C (near-critical water) has been developed. The reduction generates the corresponding aromatic amines in excellent yields.[22]



7. Nitroarenes were chemoselectively reduced to the corresponding anilines using zinc and aqueous ammonium salts in ionic liquids as safe and recyclable reaction media. The results specify the effect of ammonium salts in the process; the combination of Zn/NH_4Cl in $[bmim][PF_6]$ or Zn/HCO_2NH_4 in $[bmim][BF_4]$ were the suitable for the reduction of nitroarenes. Azobenzenes were also smoothly reduced to hydrazobenzenes with Zn/HCO_2NH_4 (aq.) in recyclable $[bmim][BF_4]$ without any over reduction to the corresponding anilines.[23]



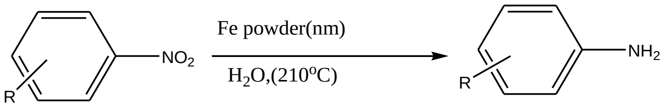
$$Ar\text{-}NO_2 \xrightarrow[\text{Ionic liquid, H}_2\text{O}]{\text{Zn, ammonium salts}} Ar\text{-}\overset{\overset{\displaystyle O}{\uparrow}}{N}\text{-}N\text{-}Ar + Ar\text{-}N{=}N\text{-}Ar + ArNHOH + Ar\text{-}NH_2$$

2. Use of Fe (0) and Fe based catalysts in the synthesis of anilines

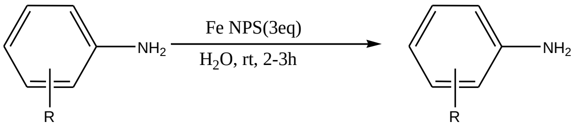
Iron metal catalyzed organic synthesis has emerged as a sustainable chemistry due to the highly competitive cost, high natural abundance and ecologically acceptable properties of metallic iron. Moreover, its extensive range of oxidation states (–II to +VI) provides numerous opportunities to perform multiple organic reactions. Recently, iron catalysts have started competing the established precious metals. Among organic scaffolds, amines are important building blocks which are useful in the various fields starting from drugs, crop protection chemicals to dyes and pigments. Typically, catalytic hydrogenation or reduction of functional groups such as imines, amides, nitroarenes and nitriles results into anilines. This part of the chapter is focused on the synthesis of aniline and its derivatives *via* nitroarenes using iron metal and iron based catalysts. The phenomenal progress in this focused area is summarized to witness this transformation towards sustainable development in the field of synthesis of anilines.

2.1.1 Use of Iron metal

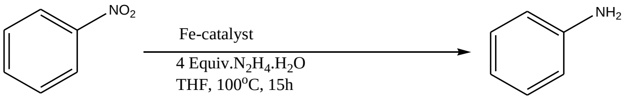
1. Active metals can react with water to liberate hydrogen. This liberated hydrogen in the presence of metal can bring aboutreduction of a nitro group. Also, metal could directlyreduce a nitro group by electron-transfer reaction with water acting as proton source. Nano size activated metallic iron powder was used as reducing agent by Wang *et al*. for reduction of nitroarenes to anilines in water at 210 ℃ (near critical water).[24] This method, avoids the use of strong acidic conditions and could sustain substituents like OMe, COMe, COOEt, F, Cl, Br and I.



2. Ranu and coworkers have achieved similarly highly selective reduction of nitroarenes using iron metal NPs in water at room temperature. During the reaction a change in shape of the Fe NPs was observed.[25] The easily reducible functional groups CHO, COMe, CO_2Me, COOH, $CONH_2$, CN, N_3, I, Br, Cl, F, SCN, *O*-benzyl, *O*-allyl, *O*-TBDMS, *N*-benzyl and *N*-allyl and styrenoid double and triple bonds were found to be unaffected.

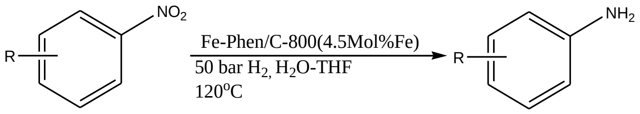


3. Pyrolysis of Fe–phenanthroline complexes supported on carbon leads to highly selective catalysts for the reduction of structurally diverse nitroarenes to anilines in 90–99% yields. Excellent chemoselectivity for the nitro group reduction is demonstrated.[26]

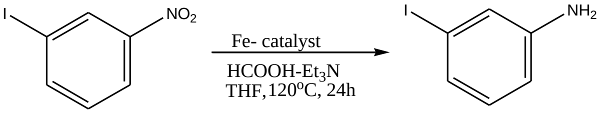


2.1.2 Use of Iron based catalysts

1. Hydrogenation using iron oxide–based nanocatalysts for the synthesis of anilines has been described. Pyrolysis of a $Fe(OAc)_2$-phenanthroline complex on carbon at 800 °C under argon atmosphere results in the formation of nanoscale Fe_2O_3 particles surrounded by nitrogen-doped graphene layers. By applying these catalysts, the hydrogenation of structurally diverse and functionalized nitroarenes to anilines proceeds with excellent selectivity. The overall time required for the catalyst preparation and for the hydrogenation reactions are 35 h and 20–35 h, respectively.[27]



2. Nanoscaled iron oxide catalysts on carbon were modified with nitrogen-doped graphene (NGr) and found to be excellent catalysts for the chemoselective transfer hydrogenation of nitroarenes to anilines.[28]

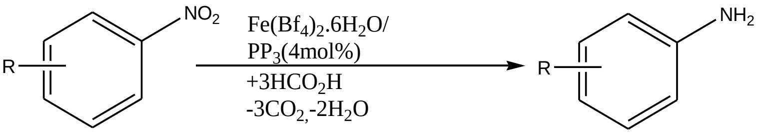


3. Supported single-metal atom catalysts (SACs) are constituted of isolated active metal centers, which are heterogenized on inert supports such as graphene, porous carbon, and metal oxides. Fe-SACs with a focus on anchoring single atoms (SA) on carbon/graphene supports and used for hydrogenation of nitroarenes into anilines.[29]

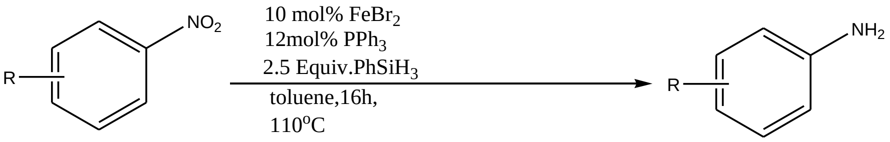
4. Zerovalent iron (Fe0) has been successfully employed to reduce nitrobenzene to aniline in synthetic wastewater in both batch and continuous flow reactors in the presence of $CoCl_2·6H_2O$, which acted as a catalyst.[30]

$$C_6H6_5NO_2 + 3Fe^o + 6H^+ \longrightarrow C_6H_5NH_2 + 3Fe^{2+} + 2H_2O$$

5. The first well-defined iron-based catalyst system for the reduction of nitroarenes to anilines has been developed applying formic acid as reducing agent. A broad range of substrates including other reducible functional groups were converted to the corresponding anilines in good to excellent yields at mild conditions. Notably, the process constitutes a rare example of transfer hydrogenations.[31]

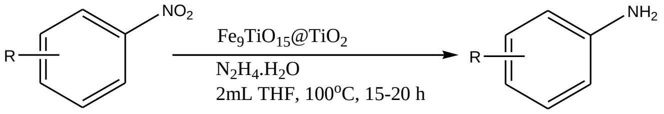


6. The iron-catalyzed reduction of aromatic nitro compounds to the corresponding anilines applying organosilanes is reported. In the presence of FeX2–R3P catalysts a series of nitroarenes is selectively reduced tolerating a wide range of functional groups.[32]



7. Iron-based nanomaterials are of central importance due to the ‘noble’ features of iron such as its high abundance, low cost and non-toxicity. A simple sol–gel method for the synthesis of novel iron–titanium

nanocomposite-based material ($Fe_9TiO_{15}@TiO_2$) was prepared. And found to be a sustainable catalyst for selective synthesis of anilines*via* reduction of structurally diverse and functionalized nitroarenes.[33]



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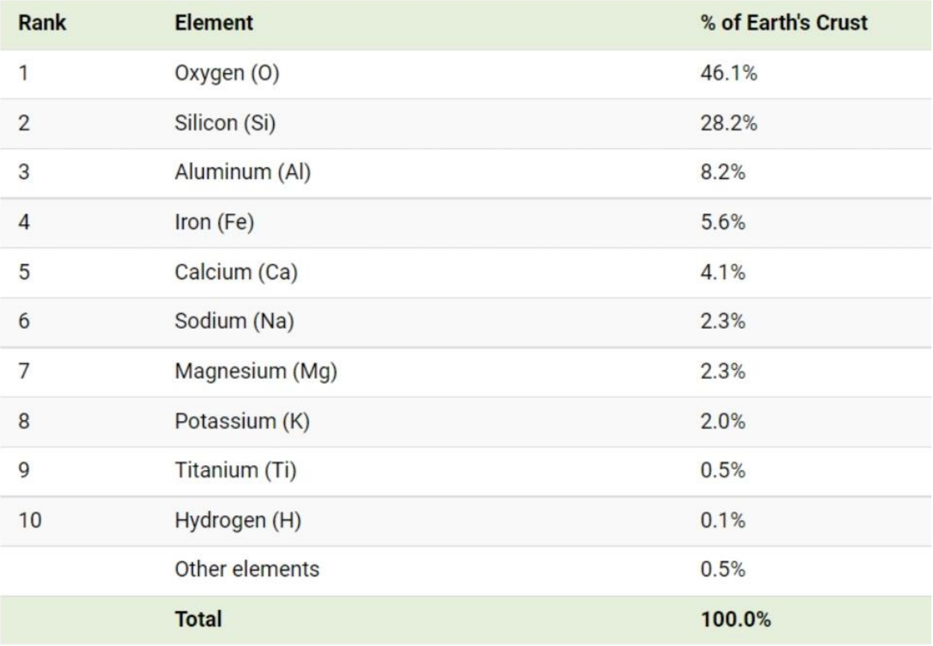
CHAPTER-II

A rapid, simple, novel and green approach for the reduction of nitroarenes to anilines by Fe metal/$NH_2NH_2.H_2SO_4$

1. Introduction

Hydrazine and its derivatives have long been used as reducing agents in organic synthesis. Use of hydrazine in organic synthesis has attracted considerable attention in recent years as it finds applications in the reduction of a number of functional groups in the presence or absence of catalysts.

The present chapter reveals the selective and rapid reduction of nitroarenes into the corresponding anilines using hydrazinium sulfate in the presence of iron powder in aq. CH_3CN in very good to excellent yields (70–98%). The products obtained are of high purity and the reactions proceed at 70–80 ºC without any adverse effect on other substituents such as: chloro, ester, nitro, -COCl, acid and acetyl groups. This method serves as direct and easy method for the synthesis of substituted anilines from nitroarenes, which are intermediates in the industries of agro, polymer, liquid crystals and photographic chemicals. The reaction is cheap, simple and superior when compared with the existing methods of preparation of anilines from nitroarenes as it involves use of abundant and inexpensive Fe metal (see below Table).



Rank	Element	% of Earth's Crust
1	Oxygen (O)	46.1%
2	Silicon (Si)	28.2%
3	Aluminum (Al)	8.2%
4	Iron (Fe)	5.6%
5	Calcium (Ca)	4.1%
6	Sodium (Na)	2.3%
7	Magnesium (Mg)	2.3%
8	Potassium (K)	2.0%
9	Titanium (Ti)	0.5%
10	Hydrogen (H)	0.1%
	Other elements	0.5%
	Total	**100.0%**

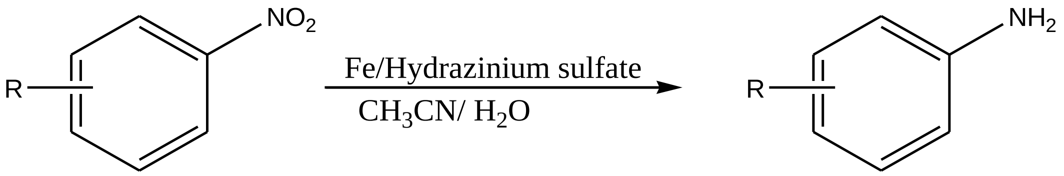
2. Present Work

In continuation of our research group's successful program on the reduction of nitroarenes to the corresponding anilines[1] and organic transformations employing hydrazine hydrate and its derivatives,[2-3] we have now directed our effort towards the synthesis of anilines utilizing readily available reagents, producing high yield and high purity of the products in shorter reaction duration.

As mentioned in the Chapter I, anilines are widely used as important intermediates in the synthesis of chemicals such as dyes, polymers, antioxidants, photographic, pharmaceutical, as liquid crystals and agricultural chemicals.[4] Many anilines exhibit biological activity[5], therefore, the synthesis of anilines has gained acceptance and popularity among the synthetic chemist community.

Though anilines have been synthesized by the reduction of corresponding nitroarenes using catalytic hydrogenation,[6] catalytic hydrogenations using molecular hydrogen are less chemoselective than the stoichiometric methods. As a result, a variety of other reduction conditions have been developed for this class of transformation as mentioned in the Chapter-I.

Organic reactions carried out in water have received considerable attention in recent years.[7] In this Chapter, we report a rapid, simple, novel and efficient method for the reduction of different substituted nitroarenes just by stirring with hydrazinium sulfate in presence of Fe metal powder in aqueous acetonitrile medium in very good to excellent yields. The reduction of nitroarenes using hydrazinium sulfate in presence of Iron metal was complete within 3–9 h. The course of reaction was monitored by thin layer chromatography. The work-up and isolation were easy. Thus all the products obtained by this system were isolated in high yields (70-98%). All the products were characterized by comparison of their TLC, IR spectra, and melting/boiling points with authentic samples.



R= H, Cl, $COOCH_3$, COOEt, $COCH_3$, NO_2, COCl, COOH

The reaction can be considered as a simple from the practical point of view use of an abundant Fe metal and has great potential for future applications. The obvious advantages of the proposed method over previous methods are: high selectivity, convenience and high purity of the products and a number of functional groups including –Cl can be tolerated in this reaction.

3. Experimental Section

All nitro compounds were of commercial grade. Commercially available reagents and solvents were used throughout and purified before use. *m*-Nitro methyl benzoate and *m*-nitro ethyl benzoate were prepared in the lab and purified before use. Yields refer to the isolated yields of the products after purification by column chromatography using 60-120 mesh silica gel with a suitable eluent or by the recrystallization using aqueous alcohol. Analytical TLC performed on pre-coated aluminum plates with

Merck silica gel 60 F-254 as the adsorbent. The developed plates were air dried and observed under a UV lamp. Melting points/boiling points were taken in open capillaries using silicone oil bath. The ^1H NMR spectra were recorded on Bruker 400 MHz spectrometer as $CDCl_3$ solutions with TMS as internal standard. FT-IR was recorded in ATR technique using Bruker instrument.

3.1 Preparation of *m*-nitromethyl benzoate and *m*-nitroethyl benzoate

Experimental procedure:

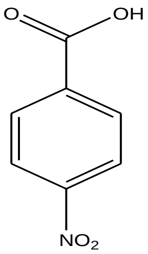
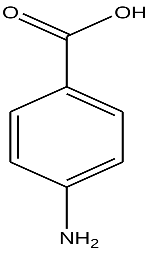
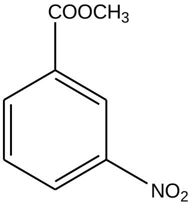
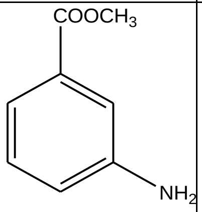
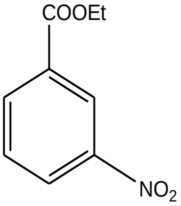
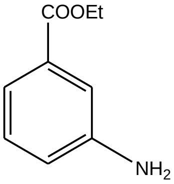
1. 6 mL of concentrated H_2SO_4 was added in to a 100 mL beaker.
2. The beaker was cooled in an ice bath for about 10 min.
3. 2.8 mL of methyl benzoate was added into a cold H_2SO_4 in a 100 mL beaker.
4. The mixture solution (con. H_2SO_4/ethyl or methyl benzoate) was well mixed and cooled again to 0 ^oC for 5 min.
5. 2 mL con. H_2SO_4 and 2 mL con. HNO_3 was mixed together to get nitration mixture (in order to produce the electrophile: NO_2^+).
6. The nitration mixture (con. H_2SO_4/con. HNO_3) was cooled in the ice bath.
7. The nitrating mixture was then dropped slowly into the mixture of con. H_2SO_4/ethyl or methyl benzoate (while swirling the flask after each addition).
8. The reaction mixture was kept aside.
9. After the complete addition, the mixture was allowed to attain the room temperature.
10. After 15 min the mixture was poured in about 10 g crushed ice taken in a beaker.
11. Solid product had formed and the product was collected by vacuum filtration.
12. The filtered solid product was rinsed with a little amount of ice cold 50 % methanol to get the crude product, which was then recrystallized by using methanol as recrystallization solvent.

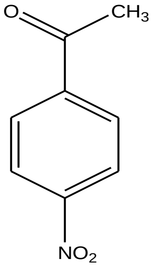
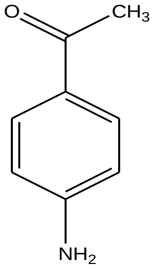
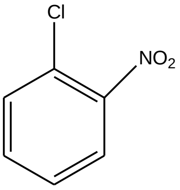
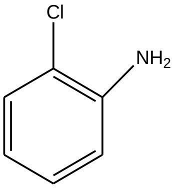
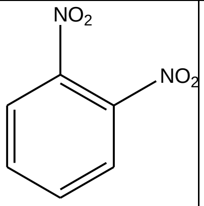
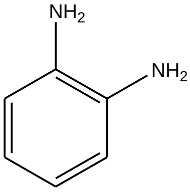
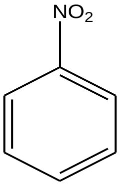
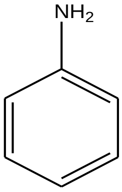
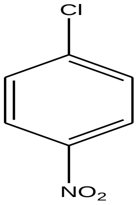
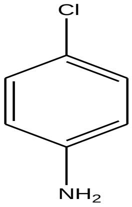
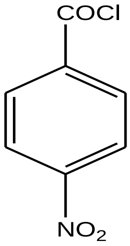
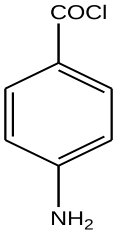
4. General Procedure

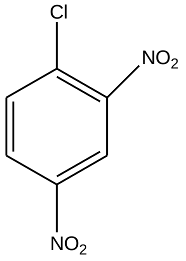
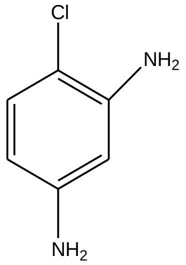
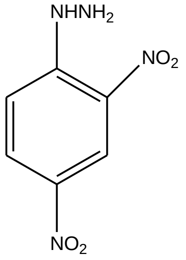
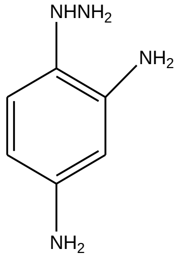
4.1 Rapid and selective reduction of nitroarenes

Nitroarene (10 mmol) in 1 mL of acetonitrile and hydrazinium sulfate (20 mmol) was taken in a round bottomed flask. Iron powder (1 g) and 5 mL distilled water were added and the contents stirred till the disappearance of the starting material on the TLC (30% Ethyl acetate and *n*-Hexane) as an eluent and the product is formed (see **Table 1**). The reaction mixture was filtered through a celite pad, and the crude product was extracted with ethyl acetate, washed with 10% HCl, then 10% NaOH was added and extracted with diethyl ether, dried over anhydrous Na_2SO_4 and the solvent was evaporated to get the pure substituted anilines.

Table 1: Reduction of nitroarenes to corresponding anilines by Fe/hydrazinium sulfate in CH_3CN/water.

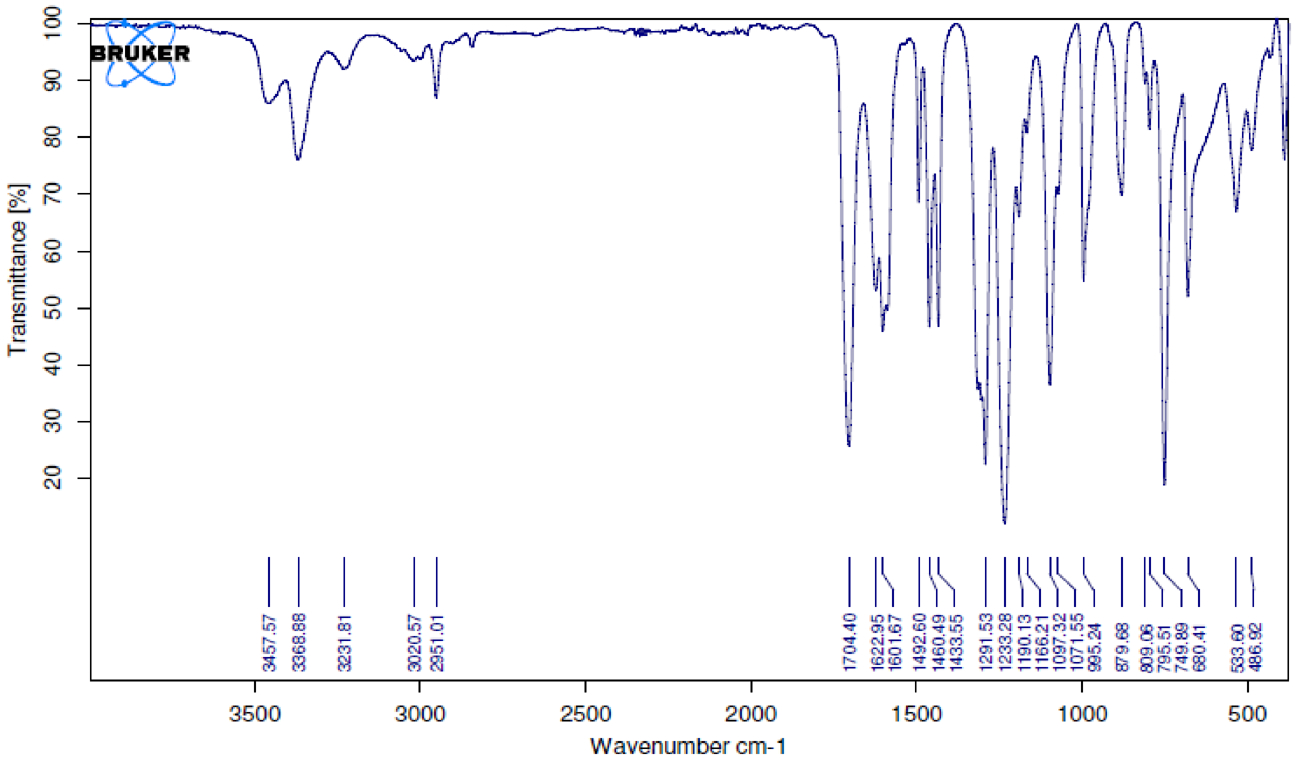
Sl. No	**Substrate**	**Product**	**Reaction time**	**M. P (^{o}C)**		**B.P (^{o}C)**		**Yield %**
				Obs.	Rept.	Obs.	Rept.	
01			9 h	188	187-189	-	-	90
02			7 h	-	-	300	300	95
03			8 h, 30 min	-	-	173	172-175	98

04			7 h	105	103-107	-	-	70
05			9 h	63	64	-	-	95
06			7 h	216-218	216-219	-	-	85
07			3h, 53 min	-	-	179	178	85
08			5 h	67	68	-	-	70
09			4 h	-	-	283	285	70

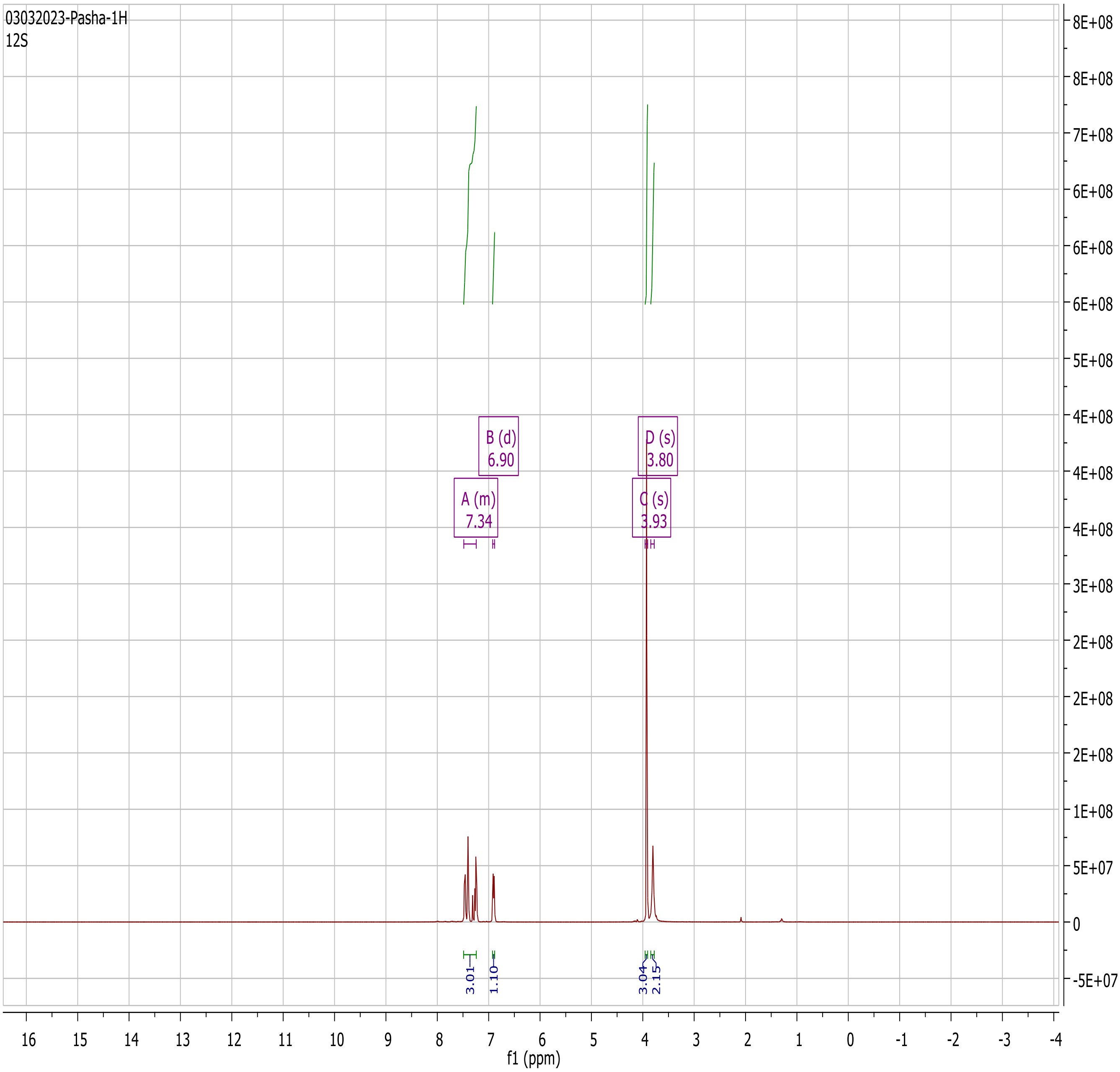
10			4 h, 45 min	90	91	-	-	80
11			10 h	374	378.6	-	-	80

5. Characterization of Anilines

IR Spectrum of *m*-aminomethyl benzoate (2)

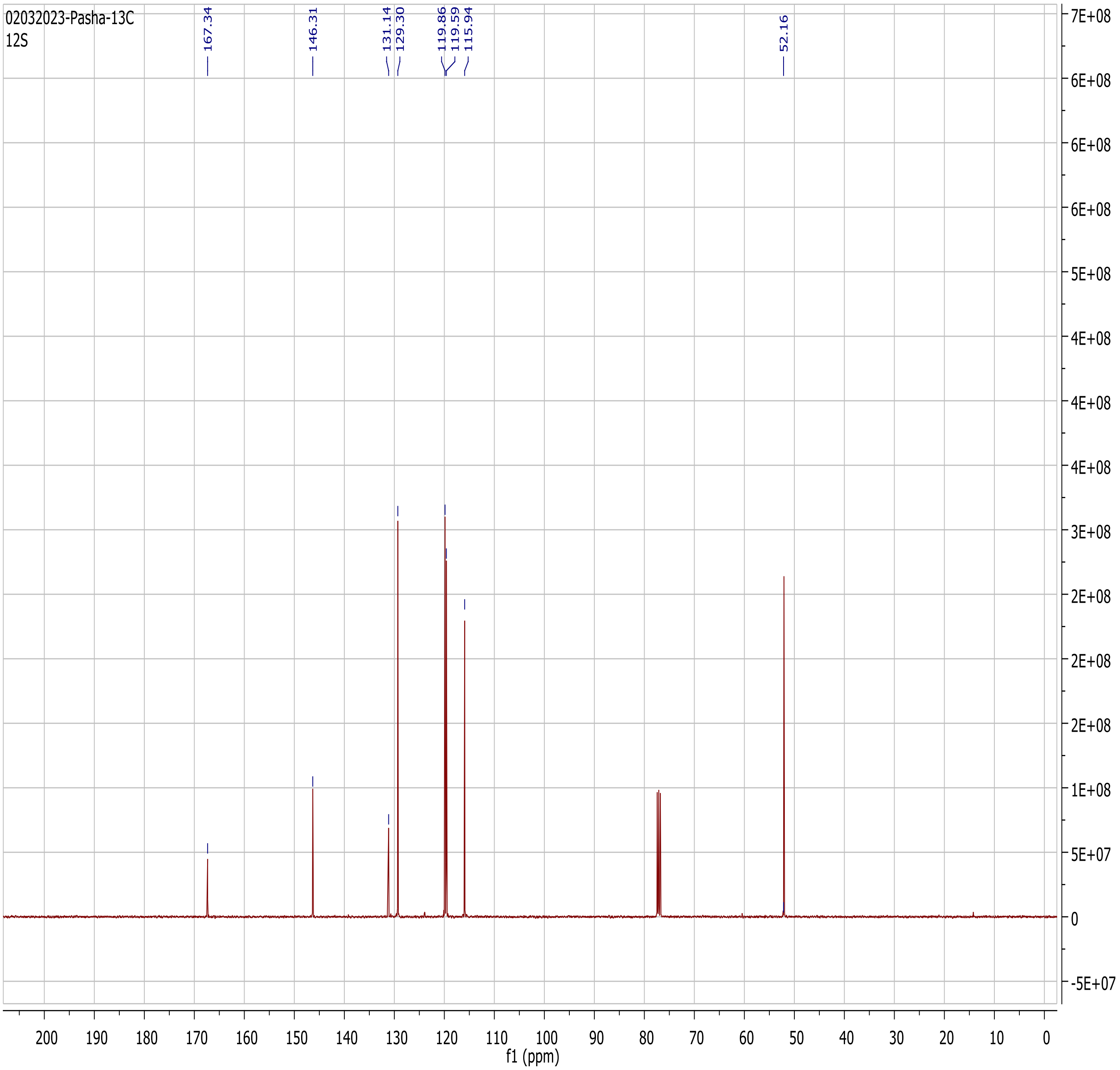


PMR Spectrum of *m*-aminomethyl benzoate (2)



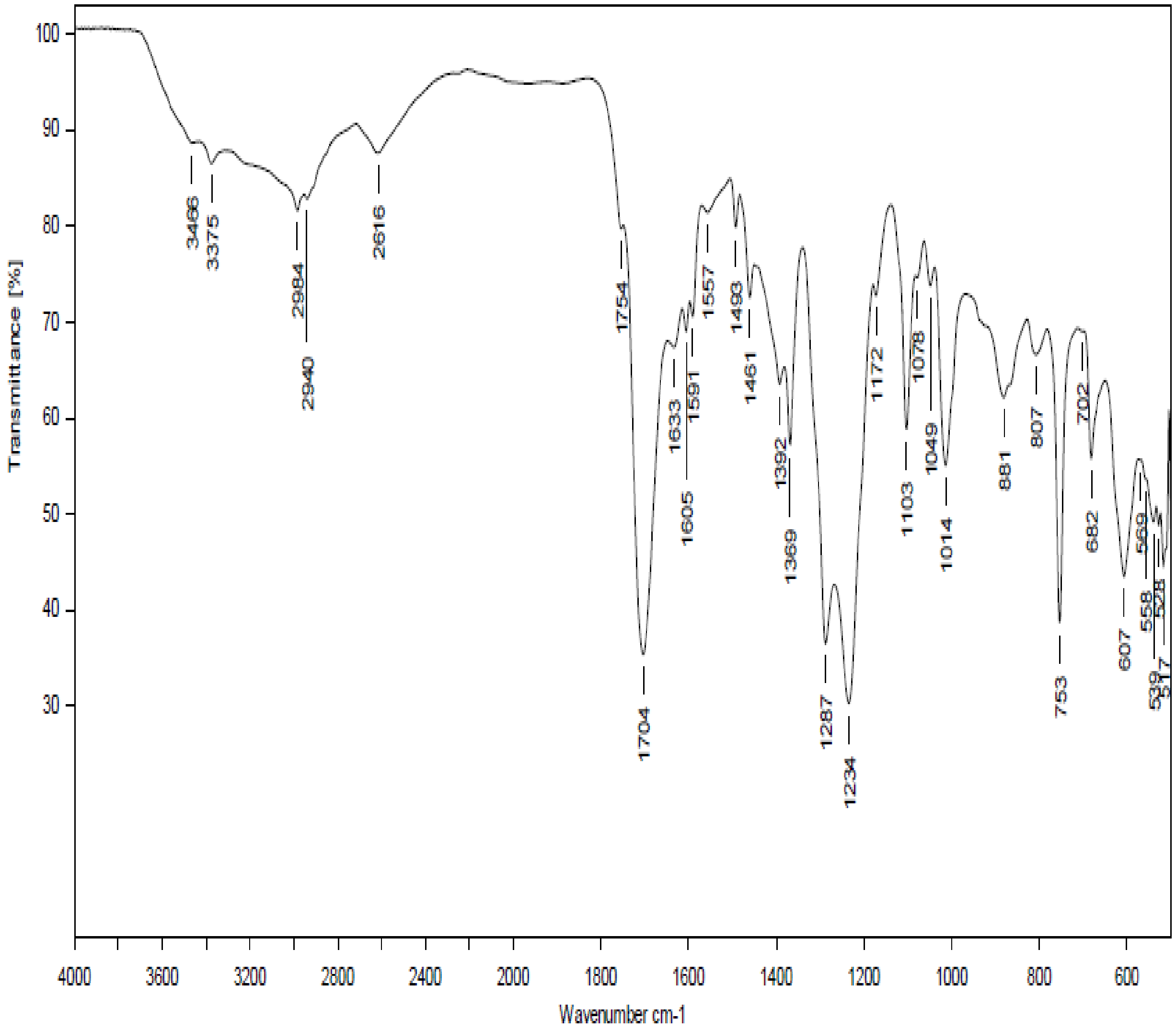
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.24 (m, 3H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.93 (s, 2H), 3.80 (s, 3H) ppm.

^{13}C NMR Spectrum of *m*-amino methyl benzoate (2)

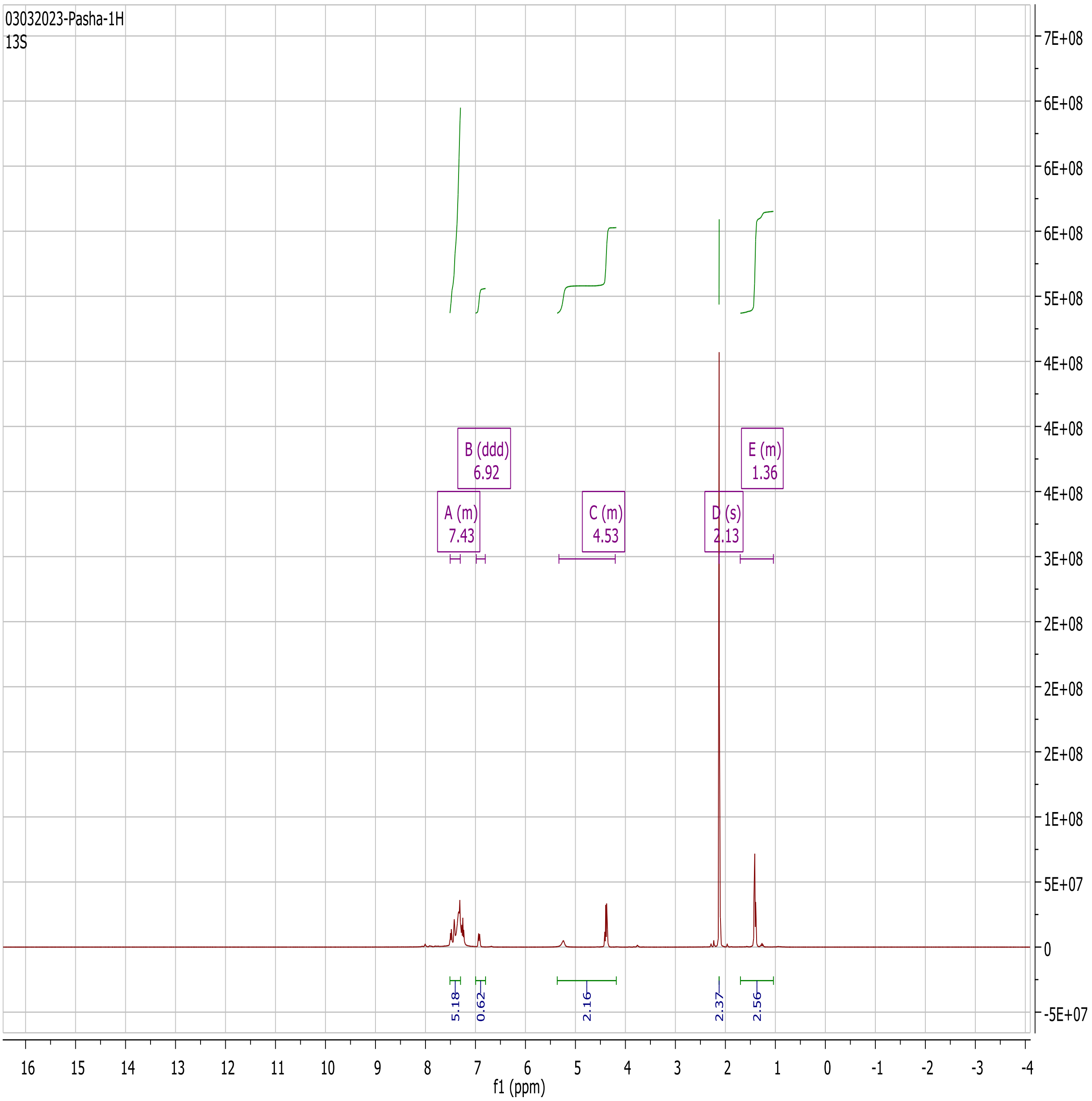


^{13}C NMR (101 MHz, $CDCl_3$): δ 167.34, 146.31, 131.14, 129.30, 119.86, 119.59, 115.94, 52.08 ppm

IR spectrum of *m*-amino ethyl benzoate (3)

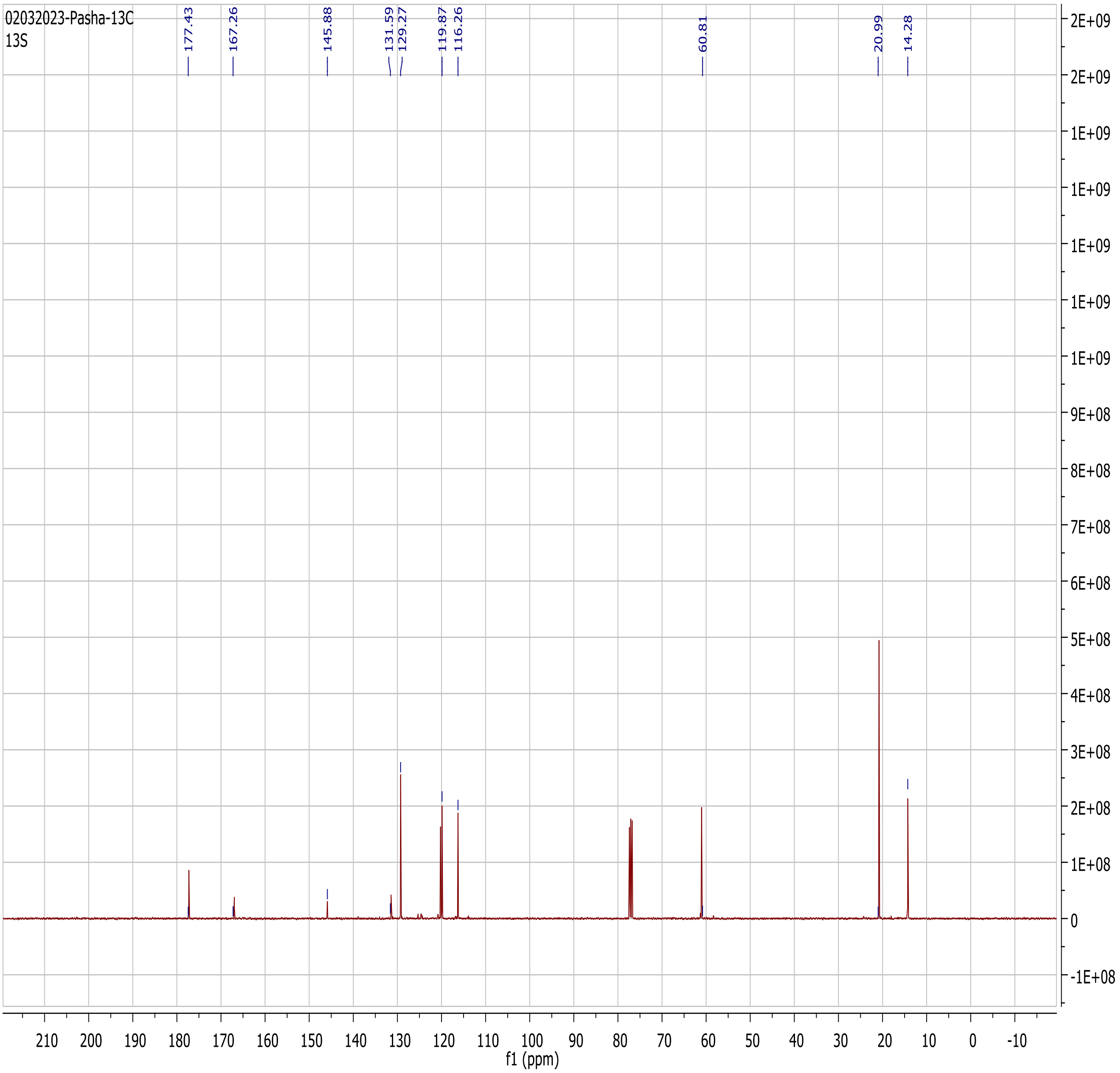


PMR spectrum of *m*-amino ethyl benzoate (3)



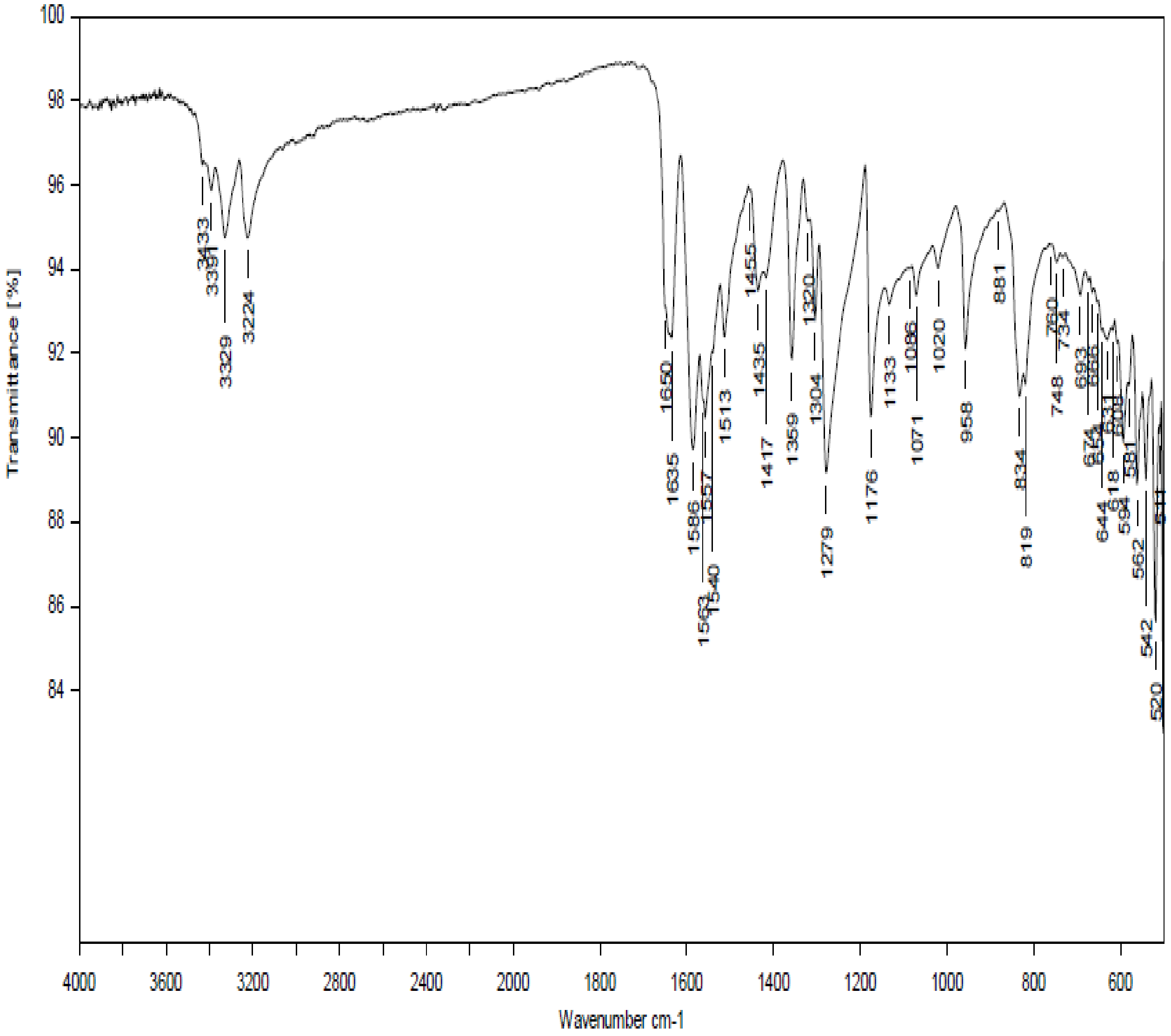
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.30 (m, 5H), 6.92 (ddd, *J* = 20.5, 9.4, 8.6 Hz, 1H), 5.33–4.20 (m, 2H), 2.13 (s, 2H), 1.70–1.04 (m, 3H) ppm.

^{13}C NMR Spectrum of *m*-amino ethyl benzoate (3)

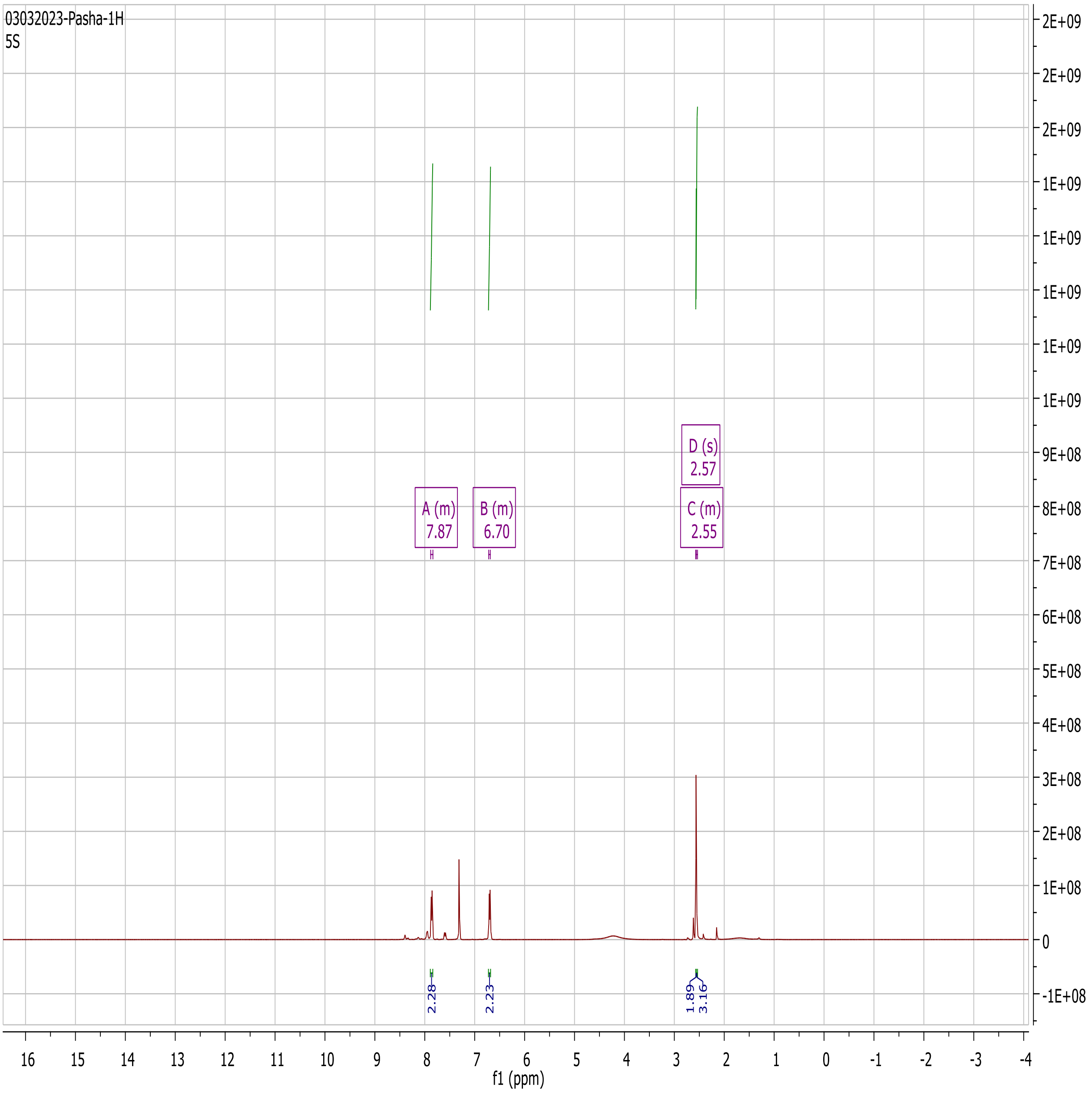


^{13}C NMR (101 MHz, $CDCl_3$): δ 177.43, 167.26, 145.88, 131.59, 129.27, 119.87, 116.26, 60.81, 20.99, 14.28 ppm.

IR Spectrum of *p*-amino acetophenone (4)

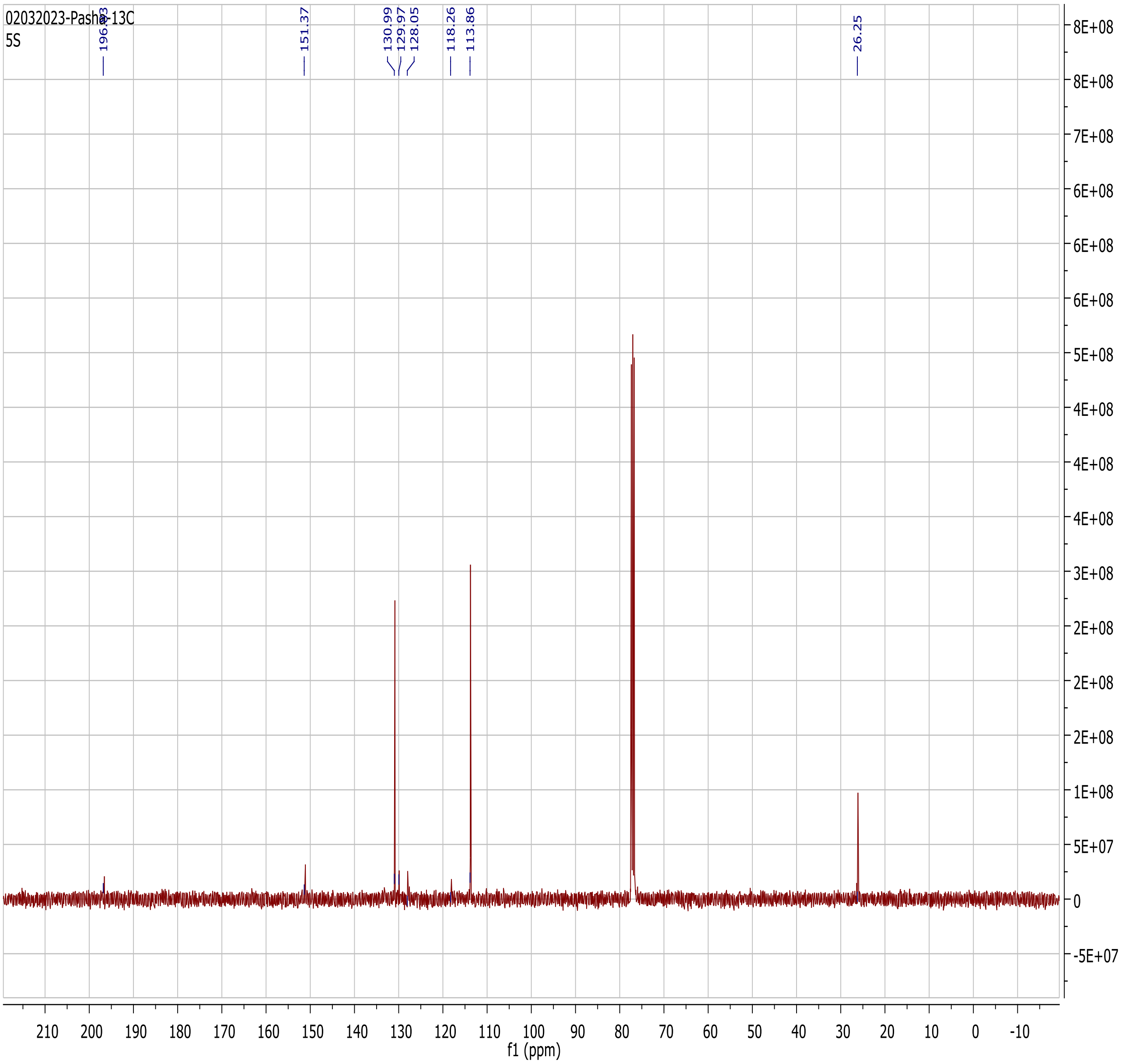


<u>PMR Spectrum of *p*-amino acetophenone (4)</u>



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.84 (m, 2H), 6.72–6.69 (m, 2H), 2.57 (s, 2H), 2.56–2.54 (m, 3H) ppm

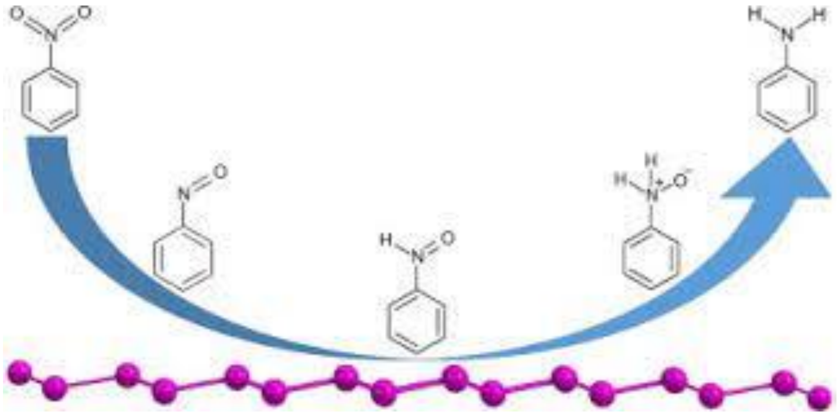
^{13}C NMR Spectrum of *p*-amino acetophenone (4)



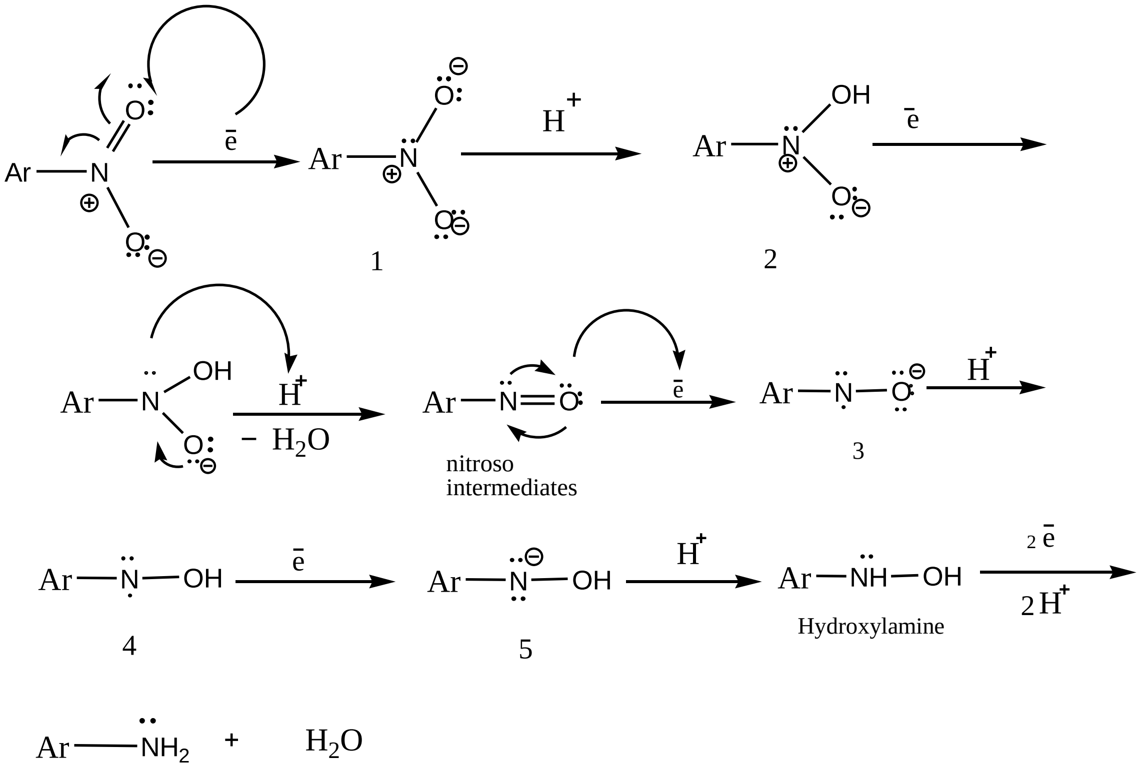
^{13}C NMR (101 MHz, $CDCl_3$): δ 196.83, 151.37, 130.99, 129.97, 128.05, 118.26, 113.86, 26.25 ppm.

6. Mechanism

The present reaction of reduction of nitrobenzes into anilines by Fe metal in the presence of hydrazinium sulphate is expected to proceed through the formation of nitrosoarene and hydroxyaniline intermediates on the surface of the Fe metal as shown below. Formation and disappearance of these intermediates was observed while following the reactions on TLC.



Further, the Fe metal may be expected to participate in the reaction by donating the electrons in the presence of hydrazinium sulphate which may serve as a proton source through the nirosoarene and hydroxyl aniline intermediates as shown below.



7. Supporting Information

4-Aminobenzoic acid (1)[8]

^{1}H NMR (300MHz, CD_3OD): δ 7.75(d, J=7.5Hz, 2H), 6.63(d, J=7.5Hz, 2H) ppm;
^{13}C NMR (7.5MHz, CD_3OD): δ 170.7, 152.3, 131.1, 119.9, 113.0 ppm.

2-Chloroaniline (5)[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J = 7.9Hz, 1H), 7.09 (t, J = 7.09 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.72 (t, J = 7.9 Hz, 1H), 4.03 (s, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9, 129.4, 127.6, 119.2, 119.0, 115.8 ppm;
MS-EI: m/z: 129 (30%), 127 (100%), 100 (10%), 92 (16%), 65 (18%).

Aniline (7)[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20 (t, J = 9.0 Hz, 2H), 6.80 (t, J = 9.0 Hz, 1H), 6.72 (d, J = 9.0 Hz, 2H), 3.64 (s, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3, 129.3, 118.5, 115.1 ppm;
MS-EI: m/z: 93 (100%), 66 (40%).

4-Chloroaniline (8)[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 3.58 (s, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 129.1, 123.1, 116.2 ppm;
MS-EI: m/z: 129 (30%), 127 (100%), 100 (12%), 92 (16%), 65 (24%).

8. Conclusions

In summary, we report a simple, novel and green protocol for the reduction of nitroarenes to anilines by Fe/Hydrazinium sulphate in water/acetonitrile as a medium, in very high to excellent yield. The reaction is a highly selective reduction which can be achieved just by controlling the molar ratio of nitroarene to hydrazinium sulphate (1:2); the products can be obtained without effecting other substituents including –Cl present in the nitroarenes. The use of water as a green solvent, broad substrate scope, functional compatibility and the absence of copious waste products in this direct hydrogenation makes our work more admirable.

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