Chapter 5. Extensional activities on Tollens' Reaction

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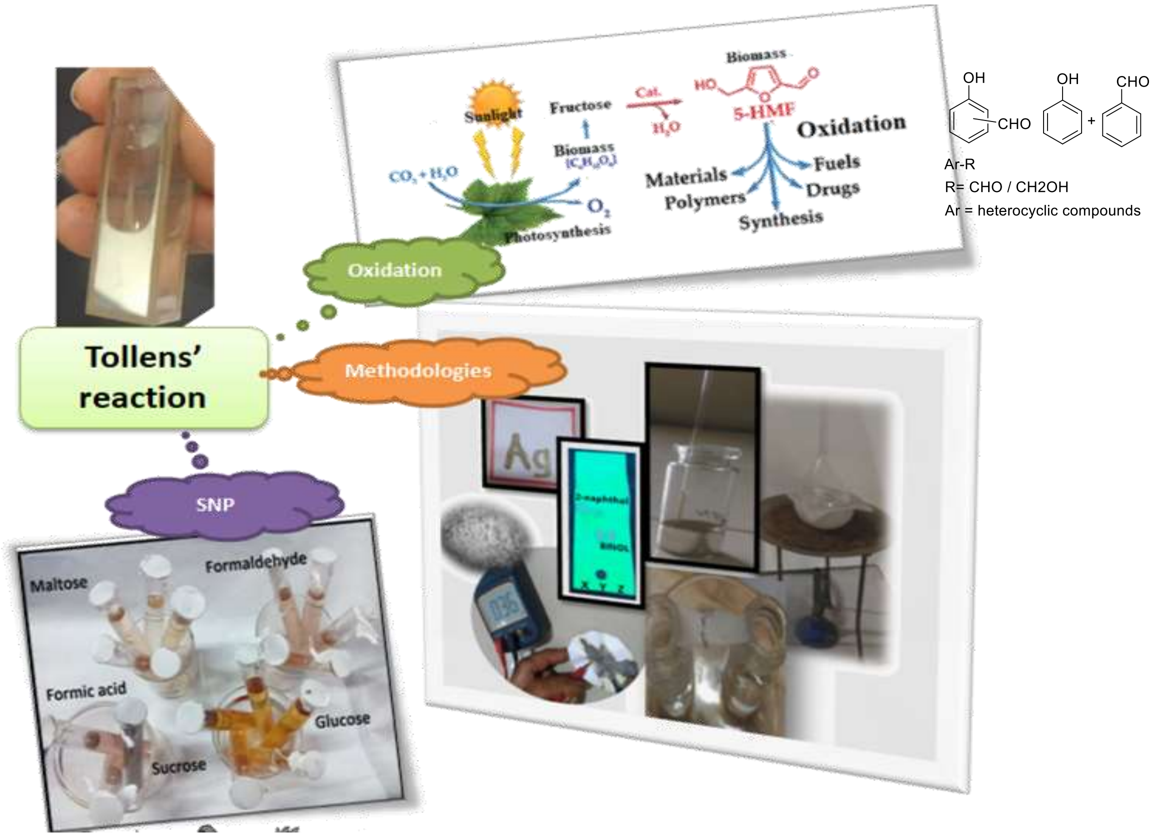


Abstract

Three different studies were developed and presented in this chapter using Tollens' reaction as an extensional activity. This chapter is divided into 3 sections.

Section 5.1 discusses the chemo-selectivity of Tollens' reagent, in two parts. In the first part 5.1.1, chemo-selective oxidations reaction of two functional groups, aldehyde and phenol will be tested, where aldehyde oxidizes to acid while phenol to C-C oxidative coupling. Attempts are made to understand Tollens' reaction of aldehyde and phenol functional groups (I) on different molecules and (II) in the same molecule. In absence of NaOH, the chemo-selective oxidative coupling of phenol remained favored over the oxidation of aldehyde. In the second part 5.1.2, the oxidation of aldehyde and alcohol derivatives of hetero-aromatic have been studied. For this study, an important bio-mass 5-hydroxymethylfuran-2-carboxaldehyde (HMF) was chosen. Tollens' reaction of HMF resulted in the chemo-selective formation of 5-formylfuran-2-carboxylic acid (FFCA), with possible two ways of mechanism. To understand the correct mechanism, the oxidation of aldehyde and methanol derivatives of other heterocyclic compounds was studied. The products were isolated and analyzed using spectroscopic analysis.

Section-5.2 deals with four interesting methods/ways of mixing Tollens' reagent with reducing agents. These methods' can find applications in modern-day technologies and are not limited to educational activity, such as (I) carrying oxidative C-C coupling reaction directly on TLC plate, (II) carrying C-C oxidative coupling during sublimation, (III) silver film formation on capillary, and (IV) silver film formation on tissue paper: by connecting vial containing Tollens' reagent and reducing agent solution using a paper strip.

In section-5.3, the silver nanoparticles have been synthesized using modified Tollens' reagent by using different reducing agents.

All these experiments were repeated many times. The products were quantified and characterized wherever possible, and results and the scope of reaction methods are presented.

5.1 Study of the selective oxidation reaction

In this part, the chemo-selectivity of Tollens' reagent has been demonstrated by two methods. The competition reactions between aldehyde and phenol (5.1.1) and methanol derivatives of heteroaromatic compounds (5.1.2) were planned.

5.1.1 Aldehyde versus phenol oxidation

In the first part 5.1.1, the competitive reaction of aldehyde to acid and phenol to C-C coupling of phenols has been studied, by attempting Tollens' reactions. We posed a simple question: What happens if Tollens' reaction of a mixture of two molecules, one with an aldehyde functional group and the other with phenol is carried out? Will it give selective C-C oxidative coupling reaction of phenol, or will give selective oxidation of aldehyde, or both? To understand this chemo-selectivity, the following two sets of the experiment will be discussed.

Experimental

Material

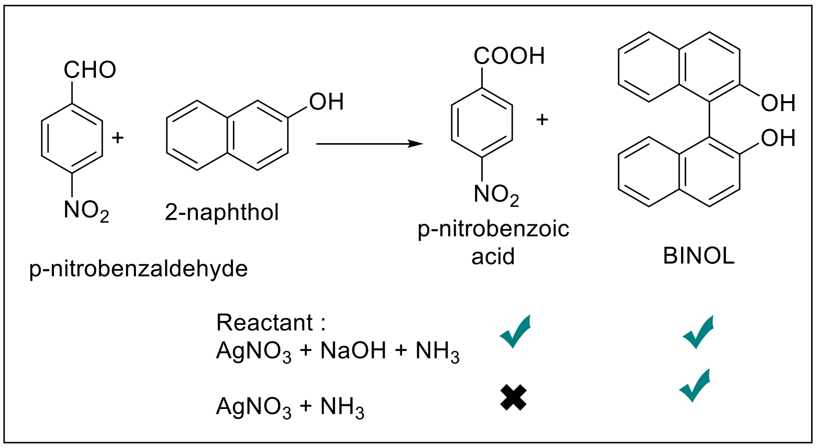
All chemicals were of chemical grade quality, purchased commercially from Avra chemicals, and used without further purification.

5.1.1.1 Procedure for competitive oxidation reaction between aldehyde and phenol functionality on two different molecules

0.3 ml 0.1 N Sodium hydroxide solution was added to the silver nitrate (0.051 g, 0.3 mmol), followed by liquor ammonia (0.3 ml) solution to prepare the silver ammine complex. 4-nitrobenzaldehyde (0.015 g, 0.1 mmol) and 2-Naphthol (0.014 g, 0.1 mmol) were mixed and dissolved in absolute ethanol (2.0 ml). This solution was added to the silver ammine complex solution and stirred using a magnetic stirrer. The reaction was monitored using TLC, and products were not isolated.

Result and discussion

Scheme S5.1: Competitive reaction of 4-nitro benzaldehyde derivative and 2-naphthol



Tollens' reaction of 2-naphthol and 4-nitro-benzaldehyde mixture was carried out, as shown in scheme S5.1 at room temperature for two days. The BINOL and 4-nitro benzoic acid were both formed in this reaction. This Tollens' reaction of 2-naphthol and 4-nitro-benzaldehyde mixture was repeated by excluding NaOH. This reaction resulted in selectively BINOL formation, and no acid formation was observed. Detailed characterization of acid products is not carried out. But, these experimental results revealed that the addition of hydroxyl salt is necessary for the oxidation of aromatic aldehyde using the silver ammine complex. In contrast, phenol coupling was selectively obtained by avoiding basic conditions that benefit clean and easy work-up.

Experimental

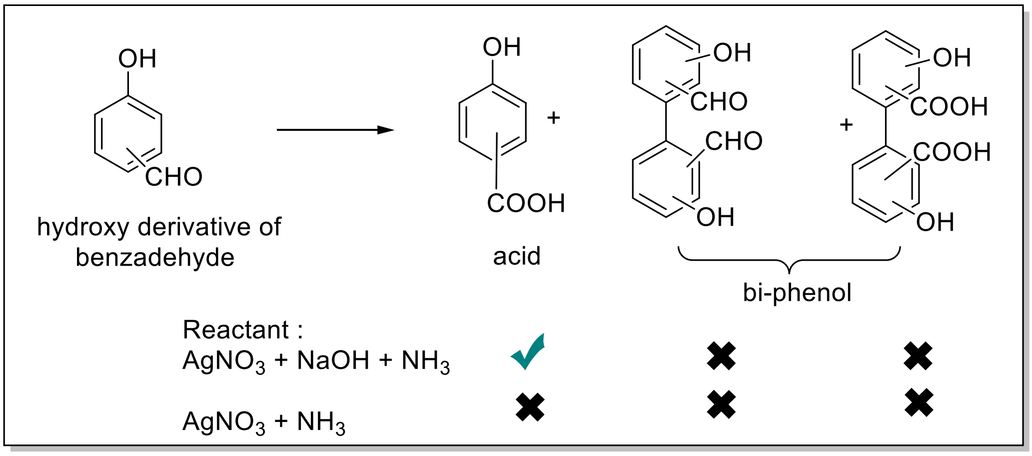
Material

Hydroxybenzaldehyde derivatives (2-Hydroxybenzaldehyde, 3-Hydroxybenzaldehyde, and 4-Hydroxybenzaldehyde) were of analytical grade quality, purchased commercially from Avra chemicals, and used without further purification. All other chemicals were of chemical grade quality, purchased commercially from Avra chemicals, and used without further purification.

5.1.1.2 Procedure for Tollens' reagent of aldehyde and phenol functionalized on one molecule

0.3 ml 0.1 N Sodium hydroxide solution was added to the Silver nitrate (0.051 g, 0.3 mmol), followed by liquor ammonia (0.3 ml) solution to prepare the silver ammine complex. The solution of hydroxybenzaldehyde (0.1 mmol in 2.0 ml absolute ethanol) was added to the silver ammine complex solution and stirred using a magnetic stirrer. The reaction was monitored by TLC, and products were not isolated.

Result and discussion



Scheme S5.2: General scheme for Tollens' reaction of Hydroxybenzaldehyde derivatives

The Tollens' reaction of 2-hydroxybenzaldehyde was carried out, as shown in scheme S5.2. Silver mirror formation was observed due to selective formation of 2-hydroxybenzoic acid, with no C-C oxidative coupled product. The Tollens' reaction of 2-hydroxybenzaldehyde was carried out again by avoiding the addition of NaOH, where a silver mirror was not obtained indicating no redox reaction even after heating the reaction mixture. The Tollens' reaction of 3-hydroxybenzaldehyde and 4-hydroxybenzaldehydes were also carried out as shown in scheme 5.2, which resulted only in corresponding acid product formation and no oxidative C-C coupled product. Characterization of products was carried out using TLC only.

These experimental results demonstrate selective oxidation of hydroxybenzaldehyde to the corresponding acid using the silver ammine complex.

5.1.2 Oxidation of Hetero-aromatic alcohol derivatives and aldehyde derivatives

The oxidation of alcohol and aldehyde derivatives is significant from a synthetic perspective due to its applicability in pharmaceutical, agrochemical, and fine chemical synthesis.[1] The 5-hydroxymethylfuran-2-carboxaldehyde (HMF) has attracted industries, which is considered one of the vital biomass synthesized from bio-waste of fructose.[2,3] The HMF has been reported as an important bio-mass, which forms multiple oxidation products, depending on the selective oxidation of aldehyde and alcohol functional groups. The oxidized products of HMF serve as a key component for many industries, not limited to, resin and polymers of amides esters and ethanes, drugs, and crown ethers.[2,3] In this part, Tollens' reagent has been explored for the selective oxidation of methanol derivatives and aldehydes derivatives of hetero-cyclic/hetero-aromatics. To understand the mechanism of oxidation of HMF, the oxidation of hetero-aromatic alcohol derivatives and aldehyde derivatives was also carried out with Tollens' reaction.

Experimental

Material

The methanol derivatives studied were 2-pyridine methanol (B), 3-pyridine methanol (C), 4-pyridine methanol (E), and 2-furfuryl alcohol (F). The Aldehydes studied were 2-pyridine aldehyde (1B), 3-pyridine aldehyde (1C), 4-pyridine aldehyde (1D), and 2-furfural (1E). All chemicals were of analytical grade quality, purchased commercially from Sigma-Aldrich, and used without further purification.

(I) Procedure for oxidation of HMF (A) using Tollens' reagent

0.3 ml 2 N Sodium hydroxide solution was added to the silver nitrate (2 N, 0.6 ml) solution, followed by liquor ammonia (~0.6 ml) solution to prepare the silver ammine complex. HMF (0.2 mmol) in ethanol (0.2 ml) was added to the silver ammine complex solution. The mixture was stirred for 1 hr at room temperature using a magnetic stirrer. After completing the reagent consumption, organics were extracted with dichloromethane (MDC) and dried using a rotary evaporator.

(II) General procedure for oxidation of hetero-cyclic alcohol using Tollens' reagent

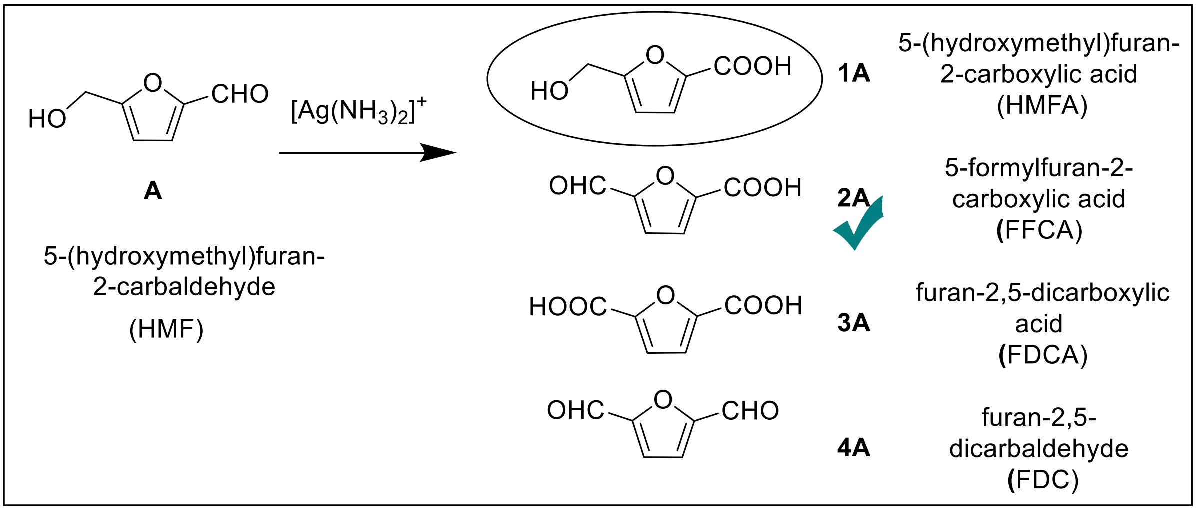
0.4 ml 2.0 N Sodium hydroxide solution was added to the silver nitrate (2.0 N 0.2 ml) solution, followed by liquor ammonia (0.2 ml) solution to prepare the silver ammine complex. The solution of the methanol derivative of pyridine/furfuryl (0.2 mmol) in ethanol (0.2 ml) was added into the silver ammine complex solution. The mixture was stirred at room temperature using a magnetic stirrer. After completing the reagent consumption, organics were extracted with dichloromethane (MDC) and dried using a rotary evaporator.

(III) General procedure for oxidation of heterocyclic aldehyde using Tollens' reagent

0.4 ml 2 N Sodium hydroxide solution was added to the silver nitrate (2 N, 0.2 ml) solution, followed by liquor ammonia (0.2 ml) solution to prepare the silver ammine complex. The solution of aldehyde derivative of pyridine/furfuryl (0.2 mmol) in ethanol (0.2 ml) was added into the silver ammine complex solution. The mixture was stirred at room temperature using a magnetic stirrer. After completing the reagent consumption, organics were extracted with dichloromethane (MDC) and dried using a rotary evaporator.

Result and discussion

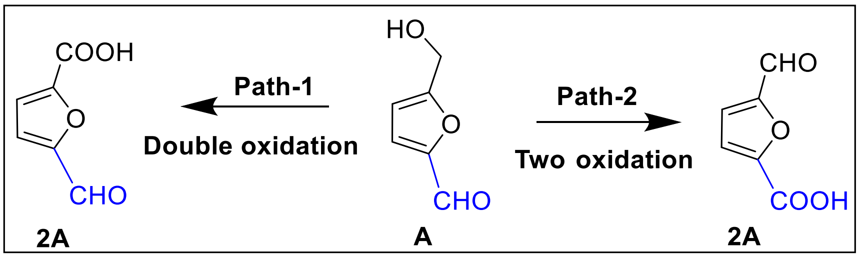
Scheme S5.3: Oxidation of HMF using Tollens' reaction and probable oxidation products formation



The Tollens' reaction of HMF was carried out for possible selective aldehyde to acid conversion, as shown in scheme S5.3, (Refer to above section (I) for detailed experimental procedure). Interestingly Tollens' reaction of HMF resulted in chemo-selectively 5-formylfuran-2-carboxylic acid (FFCA / 2A), and not 5-hydroxymethylfuran-2-carboxylic acid (HMFA / 1A). Product 2A was characterized by FT-NMR (^{1}H and ^{13}C) spectroscopy, and mass spectrometry analysis. These spectra are shown in section 5.5. Every time reaction showed un-reacted HMF, therefore reaction was performed by using an excess of Tollens' reagent, say 2, 4, and 6 equivalent of silver ammine complex as noted in table 5.1. Reactions were also repeated at high temperatures, or by changing the addition method, but the yields were not improved.

Proposed mechanism

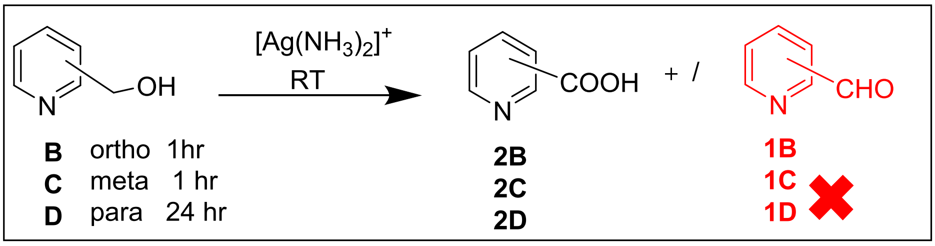
Scheme S5.4: Proposed pathways for oxidation of HMF



Two mechanistic paths were proposed for this chemo-selective conversion of A to 2A. Path-1 selective double oxidation of methanol functional group to carboxylic acid and path-2 aldehyde oxidation to acid along with alcohol oxidation to aldehyde, as shown in scheme

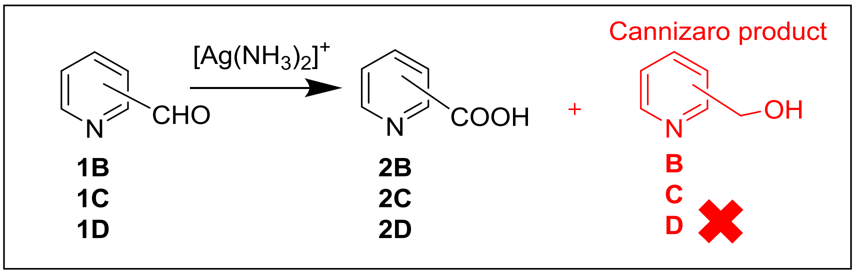
S5.4. This transformation can be confirmed by Tollens' reaction of HMF containing radio-labeled aldehydic carbon. In this case, if the product FFCA has radio-labeled carbon in aldehydic carbon can confirm path-1, otherwise path-2. However, instead of this a chemical pathway was designed to understand this conversion, as shown in schemes S5.5 to S5.7.

Scheme S5.5: Tollens' reaction of methanol derivatives of pyridine



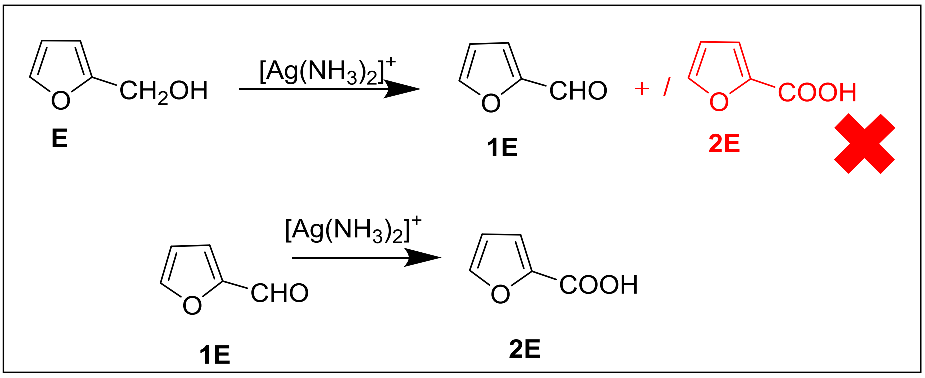
The oxidation of methanol derivatives of pyridine (at *ortho*, *meta*, or *para* position) was carried out using Tollens' reagent, as shown in scheme S5.5. The 2-pyridylalcohol (B) and 3-pyridylalcohol (C) converted to acid (2B and 2C) by double oxidation within 1 hr, whereas 4-pyridylalcohol (D) needed around 24 hr to convert to acid (2D) (Refer to above section (II) for detailed experimental procedure). The presence of unreacted methanol derivative of pyridine along with the acid product (even after performing reactions at high temperature for a longer time) dictated the probability of cannizzaro reaction of intermediate aldehyde forming in the reaction. (Aldehyde's disproportion reaction conversion to alcohol and acid in the presence of a base has been known as a cannizzaro reaction.[4])

Scheme S5.6: Tollens' reaction of aldehyde derivatives of pyridine



The Tollens' reactions of 1B, 1C, and 1D were carried out, as shown in scheme S5.6 (Refer to above section (III) for detailed experimental procedure). These reactions resulted in corresponding acid products (2B, 2C, and 2D) and no formation of ethanol derivatives (B, C, D). Yields (not very high) of the formation of acid products are shown in table T5.1.

Scheme S5.7: Tollens' reaction of E and 1E



The oxidation of furan-2-methanol (E) was also carried out, as shown in scheme S5.7. Here selectively formation of 2-furaldehyde (1E) and not in 2-furic acid (2E) was observed. Therefore, the Tollens' reaction of 1E was carried out separately, which resulted in 2E formation only, as shown in table T5.1. Thus, this study reveals the need for isolation of intermediate in these consecutive oxidation reactions for conversion of E to acid 2E using Tollens' reaction. All the products were characterized by FT-NMR (^{1}H and ^{13}C) spectroscopy, and mass spectrometry analysis, as shown below section 5.5.

Table T5.1: Oxidation of alcohol and acid derivatives of heteroaromatic compounds using $[Ag(NH_3)_2]^+$ *

Reactant	$[Ag(NH_3)_2]^+$ Equv.	Temperature	Time	Major Product	Aldehyde product	Acid product	Reactant	$[Ag(NH_3)_2]^+$ Equiv.	Temperature	Time	Major Product	Acid yield
B	2	30 °C	1 hr	2B	-	24 %	**1B**	2	30 °C	1 hr	2B	55 %
B	4	30 °C	1 hr	2B	-	60 %	**1C**	2	30 °C	1 hr	2B	37 %
B	6	30 °C	1 hr	2B	-	58 %	**1D**	2	30 °C	6 hr	2D	42 %
B	4	70 °C	1 hr	2B	-	55 %	**1E**	2	30 °C	1 hr	2E	60 %
C	4	30 °C	1 hr	2C	-	36 %	**A**	2	30 °C	1 hr	2A	5 %
D	4	30 °C	1 hr	2D	-	38 %	**A**	4	30 °C	1 hr	2A	12 %
D	4	30 °C	24 hr	2D	-	40 %	**A**	6	30 °C	1 hr	2A	18 %
D	4	70 °C	3 hr	2D	-	38 %	**A**	8	30 °C	1 hr	2A	17 %
E	4	30 °C	1 hr	1E	55 %	-	**A**	6	70 °C	8 hr	2A	13 %
E	4	30 °C	24 hr	1E	58 %	-						
E	6	30 °C	1 hr	1E	56 %	-						
E	4	70 °C	1 hr	1E	55 %	-						

*Where, products obtained and isolated yields were shown in %

This investigation shows Tollens' reaction on A is chemo-selective and forms 2A by selective-oxidation of both aldehyde and alcohol functionality to acid and aldehyde, as proposed in path-2.

Characterization of products

All the organic products were known and identified by matching their melting point, FT-NMR (^{1}H and ^{13}C) spectroscopic data, and mass spectrometric data with literature.[5] The spectral data are shown in section 5.5.

5-Formylfuran-2-carboxylic acid (2A): m.p. 209 °C (rep: 207-210 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) δ ppm: 7.39 (1H, d, *J* = 7.6 Hz), 7.52 (1H, d, *J* = 7.6 Hz), 10.162-10.496 (2H, b); ^{13}C NMR (400 MHz, $CDCl_3$, 291 K) δ ppm: 125.07, 130.03, 132.04, 132.85; ESI-MS m/z: $[M+1]^{+1}$: 141.1 (molecular weight: 140.09 g/mol). Explore different methodologies to carry out the reaction

Picolinic acid/Pyridine-2-carboxylic acid (2B): m.p. 136-137 °C (rep: 137-138 °C); ^{1}H NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 7.52 (1H, dd, *J* = 7.6, 4.8 Hz), 7.86 (1H, m), 8.01 (1H, m), 8.46 (1H, d, *J* = 4.8 Hz), 10.41 (1H, b). ^{13}C NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 125.8, 128.3, 136.7, 148.7, 151.8, 165.0; ESI-MS m/z: $[M]^{+1}$: 123.9 (molecular weight: 123.11 g/mol).

Nicotinic acid (2C): m.p. > 190 °C (rep: m.p. 235-238 °C f.p. 193c); ^{1}H NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 7.49 (1H, ddd, *J* = 8, 4.8, 0.4), 8.23 (1H, td, *J*= 8, 2), 8.81 (1H, dd, *J* = 4.8, 2), 9.04 (1H, d, *J* = 2.0) 10.80 (1H, b, -COOH) ; ^{13}C NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 123.33, 126.67, 138.84, 150.01, 151.33, 165.84; ESI-MS m/z: $[M-1]^{+1}$: 122.1 (molecular weight: 123.11 g/mol).

Isonicotinic acid (2D): m.p. > 200 °C (rep: 311 °C); ^{1}H NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 7.47 (2H, dd, *J* = 3.2), 8.66 (2H, dd, *J* = 3.2), 9.95 (1H, b, -OH); ^{13}C NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 127.1, 131.7, 134.3, 168.3; ESI-MS m/z: $[M]^{+1}$: 123.9 (molecular weight: 123.11 g/mol).

Furan-2-carboxylic acid (2E): m.p. 130-132 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 7.77 (1H, d, *J* = 1.7), 7.48 (1H, d, *J* = 3.2), 6.74 (1H, dd, *J* = 3.2,1.7); ^{13}C NMR (400 MHz, DMSO-d_6, 291 K) δ ppm: 125.12, 127.56, 134.25, 136.62, 164.2; ESI-MS m/z: $[M-1]^{+1}$: 111.0 (molecular weight: 112.0 g/mol).

Furan-2-carbaldehyde (1E): b.p. 161.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 291 K) δ ppm: .58 (1H, dd, *J* = 3.6, 1.6 Hz), 7.24 (1H, d, *J* = 3.6 Hz), 7.67 (1H, dd, *J* = 0.8, 1.6 Hz), 9.62 (1H, b); ^{13}C NMR (400 MHz, $CDCl_3$, 291 K) δ ppm: 12.64, 121.35, 148.17, 152.88, 177.92 (for –CHO); ESI-MS m/z: $[M+1]^{+1}$: 97.0 (molecular weight: 96.08 g/mol).

Conclusion

In conclusion of 5.1, The chemo-selectivity of Tollens' reagent for selective oxidation of heterocyclic and aromatic aldehyde, phenols, and methanol derivatives were studied.

- The Tollens' reaction of a mixture of two different molecules with aldehyde and phenol functionality resulted in both oxidation products, carboxylic acid, and bi-phenol. We could observe chemo-selectively bi-phenol formation simply by avoiding NaOH in the reaction mixture.
- The Tollens' reaction of hydroxybenzaldehydes resulted in the corresponding acid formation only and C-C coupled bi-phenol product formation was not observed.
- The Tollens' reaction of the aldehyde and methanol derivatives of heterocyclic compounds were studied. The Tollens' reaction of HMF (A) resulted in FFCA (2A) formation selectively (18% yield). To understand the mechanism of this experimental observation, we encountered chemo-selective oxidation of aldehyde and methanol derivatives of heteroaromatic compounds (total eight) using Tollens' reagent. All the products were characterized using FT-NMR (^{1}H and ^{13}C) spectroscopy, and ESI-Mass spectrometry. This investigation shows Tollens' reaction on A is chemo-selective and forms 2A by selective-oxidation of both aldehyde and alcohol functionality to corresponding acid and aldehyde, as proposed in path-2.

5.2 Interesting ways to mix Tollens' reagent with reducing agents

Introduction

The Tollens' reaction is traditionally performed in a glass test tube, resulting in oxidation product formation and metallic silver film formation.[6] This silver thin film formation is a side product of the reaction, which is two-dimensional growths of bulk Ag on the test tube wall. In the previous chapter, we have seen the role of the surface, especially plastic, quartz, etc., and its direct influence on the generation of the silver film. Our work has shown its relation to concurrently forming oxidized organic products. This part basically relates to curious experiments to mix reagents and observe silver formation.[7,8]

One can say that Tollens' reactions have been demonstrated as a variety of experiments, just by mixing Tollens' reagent with reducing agents in atypical ways, not limited to educational activities. Four different ways to mix Tollens' reagent with reducing agents, to carry out reactions discussed/presented here are:

(5.2.1) By carrying out the reactions directly on the TLC plate by co-spotting;

(5.2.2) reaction in sublimation assembly, By putting wet silver ammine complex on filter paper during sublimation of phenol;

(5.2.3) By dipping (melting point) capillary during silver film formation in the Tollens' reaction;

(5.2.4) by connecting vial containing Tollens' reagent and reducing agent solution using a paper strip.

5.2.1 TLC plate as a substrate for C-C oxidative reaction of phenol

Experimental

Experimental procedure

0.1 ml $AgNO_3$ solution (1.0 N in liquor ammonia) was spotted on a TLC plate using a micropipette. Similarly, **2,6-di-*tert*-butyl phenol** or **2-naphthol** (0.1 N in methanol) was spotted on it. This TLC plate was kept in the oven at different temperatures. After drying, the TLC plate was subjected to chromatographic development using a pet ether with 20% ethyl acetate.

Reaction conditions: The TLC plate was kept at 30°C, 50°C, 75°C, and 100°C in the oven.

Result and discussion

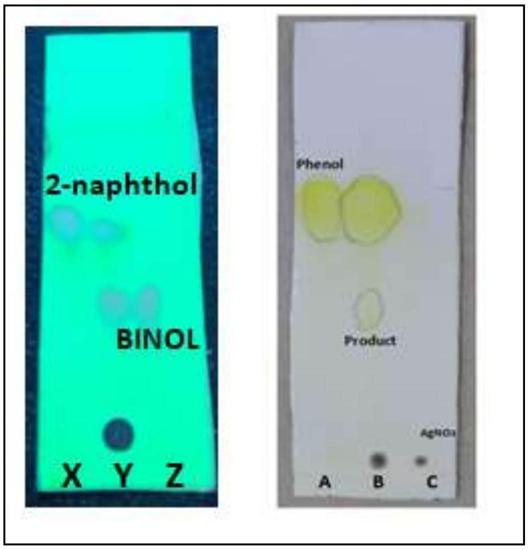


Figure F5.1: Photographs of developed TLC plate. Using 20% ethyl acetate in pet ether (X, Y, Z) and 2.5% ethyl acetate in pet ether (A, B, C)

The 2-naphthol solution in methanol was spotted on the baseline as X and Y. The BINOL was spotted on the baseline as Z. The silver ammine complex was co-spotted on Y, which resulted in the gray color silver staining. The TLC plate was kept in a preheated oven of 50°C for around 10 minutes. After drying, this TLC plate was chromatographed with 20% ethyl-acetate in pet-ether and stained with iodine, as shown in Figure 5.1. Herein coupling product BINOL (Rf=0.32) and unreacted 2-naphthol (Rf=0.52) were observed. Attempts were made to obtain a total conversion to BINOL by heating the TLC plate at 75°C, and 100°C (in the oven), but in vain. No appreciable change in the BINOL formation was observed, while tailing was observed when heating was done above 75°C temperature. TLC plate has been explored as a substrate to carry out Tollens' reaction of phenol. Similar efforts were reported in the literature for BINOL formation.[9]

The silver ammine complex was spotted on the baseline as B and C. The 2,6-di-*tert*butyl-phenol in methanol solution was co-spotted on B and spotted on the baseline as spot A. The spotting of the silver ammine complex on the TLC plate does not give instant staining (at 30°C). On the other hand, co-spotting with the 2,6-di-*tert*-butyl-phenol solution at room temperature resulted in instant yellowish coloration and gray-colored silver-staining. After drying, this TLC plate was chromatographed with 2.5% ethyl-acetate in pet-ether. TLC Plate was developed in an iodine chamber, as shown in Figure 5.1. Herein instant staining of silver was observed along with phenol (Rf=0.50) and coupling product formation 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-4,4'-diol (Rf= 0.81), which offers a new reaction scope for solvent-free conditions. The unreacted phenol was also observed. Products obtained from these reactions were not quantified or isolated or characterized separately. Characterization of reactants and products in this experiment is presented and discussed in chapter-2, with detailed FT-NMR (^{1}H and ^{13}C), FT-IR, and mass-spectroscopic analysis.

Conclusion: Traditionally TLC plate is used for monitoring the progress of the reaction and formation of some products. The present experiment explores it for carrying out C-C oxidative coupling reaction using a non-conventional way. This technique can be used not only for carrying a one-pot reaction but also to separate the observed product.

5.2.2 One-pot sublimation and coupling reaction of phenols on substrates

Experimental procedure

2-Naphthol (0.100 g, 0.0694 mmol) was added to an evaporating dish. This dish was covered with hollow cardboard. The silver ammine complex was prepared by dissolving silver nitrate (0.0600 g, 0.035 mmol) into 0.5 ml liquor ammonia. This freshly prepared silver ammine complex was sprinkled on a filter paper/cotton (as a substrate), kept over cardboard, and covered with a glass funnel, as shown in Figure 5.2. The evaporating dish was heated gradually in an oil bath to sublimate phenol. After almost complete sublimation, the assembly was kept aside for cooling, and the substrate was brought out. The substrate was washed with MDC to extract organic counterpart. This organic solid was purified using Column chromatography. Now the substrate, mainly containing silver, was dried for conductivity study.

Result and discussion

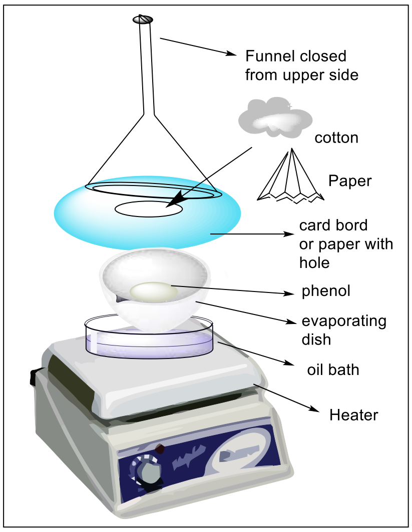


Figure F5.2: Modified sublimation assembly (cartoon image)

The sublimation of 2-naphthol was carried out using the setup shown in Figure F5.2. The silver staining on paper was observed. Under this condition, the purified gas phase of 2-naphthol gets converted to BINOL with around a 12% yield. By the controlling rate of sublimation yield of the conversion can be tuned.

- Similar results were observed with a cotton plug as a substrate.

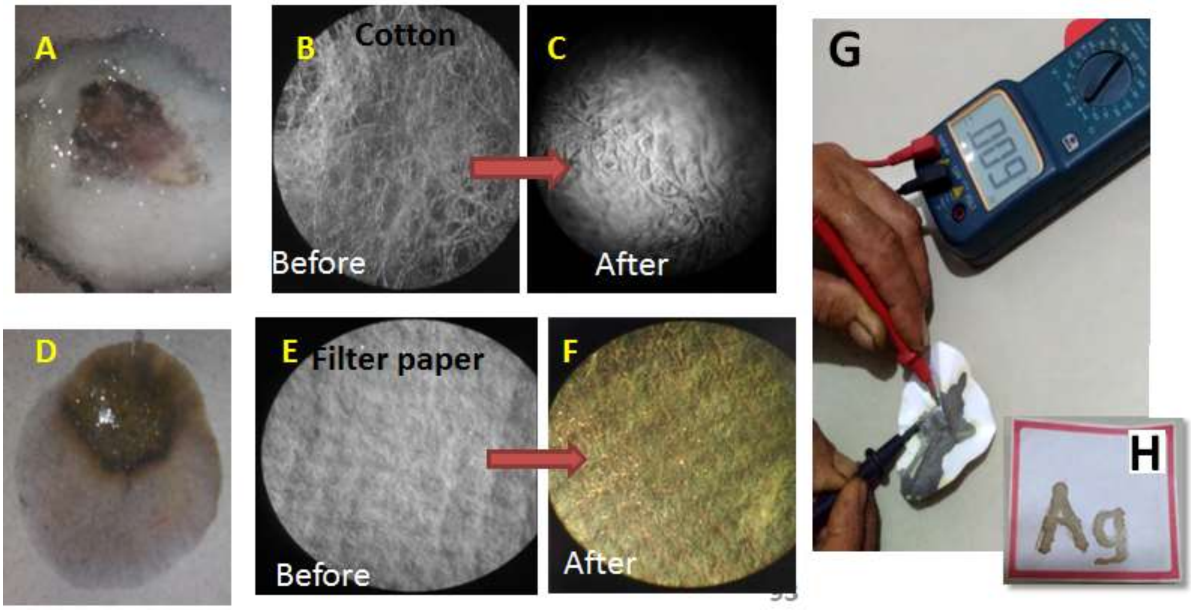


Figure 5.3: Photographs of silver stained paper (lower) and cotton (upper): A and D silver staining; microscopic images: B and E before reaction And C and F after reaction; G conductivity measurement on silver stained paper using multimeter; H selectively stained paper ('Ag')

- The same procedure/ methodology was explored for C-C oxidative coupling of 2,4-di-*tert*-butylphenol resulted in 10 % 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol.
- Isolated products were characterized using FT-NMR (^{1}H and ^{13}C), FT-IR spectroscopic, and mass-spectrometry analysis. The characterization data and spectra were similar to as shown in chapter-2.

The silver staining on the substrate was observed over both filter paper and cotton under a microscope. The coating of silver on the substrate (before/after) is clearly observed in Figure F5.3. The conductivity of stained paper was checked using a multimeter. It shows conducting behavior with 0.67 Ω/cm resistivity, comparable with reported conductive fabrics (0.22-0.80 Ω/cm).[8,10]

Clear observation of silver coating was carried by writing "Ag" on paper using a silver ammine complex. This paper was then kept in sublimation assembly. This resulted in silver staining only on the letter "Ag" as presented in Figure F5.3(H). Thus, this experiment reveals the feasibility of the reaction over a particular area on a substrate, boundary condition for mixing of the reagents.

Applications: The silver staining on different substrates obtained from this method can be used for a further application similar to reported electrically-conducting flexible fabrics synthesis[11], wearable electronics[12], solar equipment preparation, electromagnetic interference shielding[8,13], Cellulose coated SNP used for sensor[14], and e-textile technologies.[15]

Advantages and scope: This method has opened up the corridor to get chemically stable silver coating over the particular area, a low-cost method compared to literature. On the other hand, the reported techniques such as spray deposition/ metal-vapor phase deposition [16–18] have huge drawbacks due to the requirement of advanced techniques and high-temperature conditions. Using this method, by fluctuating silver complex dilution and other reaction conditions, one can mimic the staining to get desired flexible silver-coated wires covered on the high surface area, which graduates students can practice.

5.2.3 Selective deposition of silver on capillary

Experimental procedure

0.1 ml 0.1 N Sodium hydroxide Solution was added to the silver nitrate (0.01 N, 1.0 ml) solution, followed by liquor ammonia (2.67 N, 0.1 ml) solution to prepare the silver ammine complex. The solution of *D*-glucose (0.01 N, 1.0 ml) was added into the silver ammine complex solution containing vial and inserted capillary into it vertically. This reaction mixture was kept at room temperature for one day without disturbing.

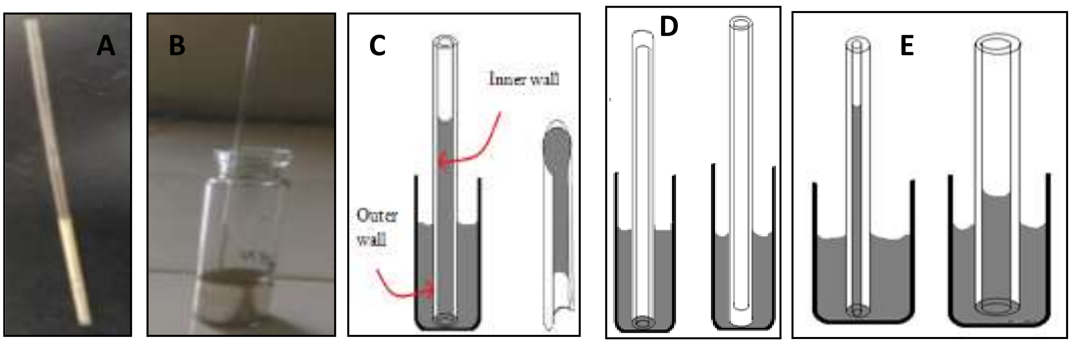
- The capillaries used areas listed here 1. Glass Capillary with both ends open, 2. Glass Capillary with both closed-end, 3. Glass Capillary with upper end closed, 4. narrow glass capillary, and 5. Plastic capillary with both ends open.

Result and discussion

Tollens' reaction of *D*-glucose was carried out by inserting a glass capillary in the vial, as shown in F5.4. The silver coating formation is noted. The probable gluconic acid product was not separated or characterized.

- In F5.4-B capillary with both ends open was dipped in the Tollens' reaction. Here, a selective silver coating is observed only on an inner surface of the capillary (and not the outer side) along with the inner walls of the vial, as shown in Figures F5.4-A and F5.4-C.
- This reaction was performed by keeping the capillary having closed from the upper end; As a result, absolutely no silver coating was noted on the outer side wall (convex) as well as the inner side wall of the capillary even though was dipped in the reaction mixture, as shown in Figure F5.4-D.
- This reaction was performed by keeping the capillary having a closed lower end; As a

Figure F5.4: Images of selective silver coating in capillary and set up; A. photograph of silver coated glass capillary ; B. reaction setup after 1 day; cartoon images of Glass capillaries: C. selective deposition of silver in inner wall; D. capillaries with only one open ends; E. effect of radius of capillary



result, absolutely no silver coating was noted on the outer side wall of the capillary dipped in the reaction mixture.

- This reaction was performed by keeping the capillary having closed from both ends; As a result, absolutely no silver coating was noted.
- The plastic capillary was inserted into the reaction instead of glass; absolutely no mirror formation was noted on either side of the plastic.
- The height of a silver mirror in the capillary was increased using a comparatively narrow capillary, as shown in Figure F5.4-F.

Probable reasons for selective deposition:

The basis of this lies in the fundamental concept of contact angle. Due to the large contact angle on the convex side of the capillary, the wettability is poor. Therefore the adhesiveness is also lacking, which resulted in the absence of a silver thin film on the outer surface of the capillary tube. That means nucleation or deposition of Ag^0 is favored in the present case for the higher radius of curvature surface.

Here the plastic used was of non-polar polymer and thus hydrophobic.[7,8] Being hydrophobic, large contact angle, and poor wettability, the adhesion is insufficient even to a concave meniscus; thus, The thin silver film was not observed on either side of the plastic capillary.

Scope of reaction: The silver mirror forming in the capillary is at a higher level than the reaction mixture, which can be used to show capillary action to students.

5.2.4 Mixing of Tollens' reagent with phenols on tissue paper

Experimental procedure

0.5 ml of liquor ammonia and 1.0 ml 0.01 N silver nitrate solution in water was mixed in a glass vial of capacity 2 ml. 1.5 ml of 2-naphthol solution (0.01 N in absolute ethanol) was taken in another similar glass vial. These two vials were kept 0.5 cm away from each other and connected by one tissue paper strip.

Result and discussion

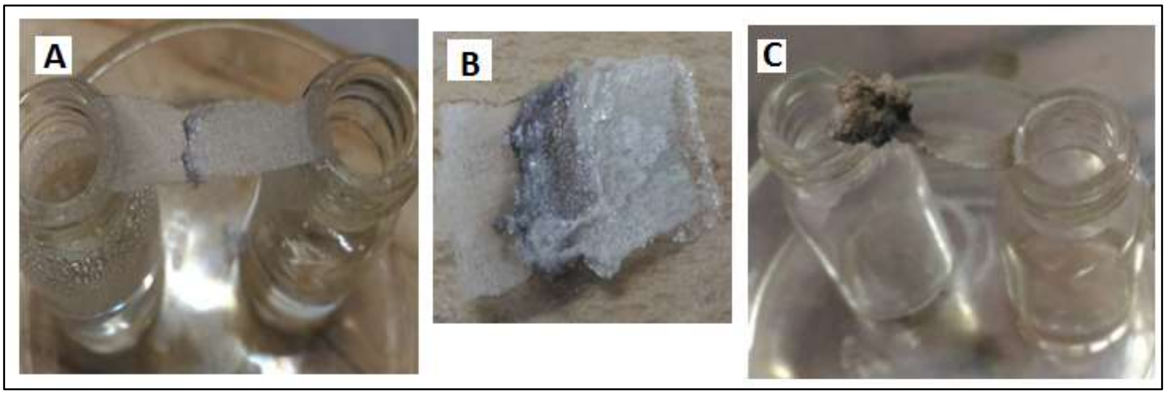


Figure F5.5: Photograph of A) mixing Tollens' reagent with 2-naphthol by strip joining both in different vial B) silver stained middle part of paper, C) After few hour reaction setup

The Tollens' reagent and 2-naphthol were kept in two different glass vials and connected using a tissue paper strip by dipping its' end in these solutions, as shown in Figure F5.5-A. The middle surface of the paper turned shiny after some time, where both solutions meet due to a rise in solution by capillary action, as shown in Figure F5.5-B. In addition, the precipitation of organic compounds near metallic silver formation was observed on keeping the strip for a long time, as shown in Figure F5.5-C.

C-C coupling reaction of 2,4-di-*tert*-butyl-phenol carried out with Tollens' reagent similarly resulted in the silver staining on a strip near the phenol solution. The black stained paper was separated and washed with water and MDC. The TLC of the extracted MDC solution was developed, and the 3,3',5,5'-tetra-*tert*-butyl-(1,1'-biphenyl)-2,2'-diol formation was confirmed. The products were not further characterized. The staining on paper was disappeared after the addition of nitric acid, and turbidity was observed on the addition of HCl. These observations support the formation of silver and C-C oxidative coupling in the middle part of the paper.

Conclusion

Section, 5.2 discloses different ways to mix Tollens' reagent with reducing agents for designing interesting experiments.

1) On co-spotting 2-naphthol/ 2,6-di-*tert*-butyl-phenol with Tollens' reagents over TLC plate the silver staining was observed. After TLC development, one can easily observe and monitor the formation of oxidative C-C coupled products.

2) In the modified sublimation assembly for phenol (2-naphthol/ 2,4-di-*tert*-butylphenol), silver staining can be obtained on a filter paper, if it is exposed to Tollens' reagent. The C-C oxidative coupling product was confirmed, after its separation. The purified products (with 10-12% yield) were characterized using FT-NMR (^{1}H and ^{13}C) spectroscopy, and mass-spectrometry analysis. This experiment reveals the feasibility of the reaction over a particular area on a substrate, where both reagents mix. This silver-stained paper was found to be conducive in nature (resistivity 0.67 Ω/cm).

3) Capillary dipped in the mixture of Tollens' reagent and *D*-glucose in a vial, has silver coating selectively on the inner side and not on the outer side.

4) The Tollens' reagent and phenol solution (2-naphthol/2,4-di-*tert*-butyl-phenol) taken in separate vials were mixed by dipping one end each of paper strip in them. The silver staining in the middle part of the strip was observed. The C-C coupling product was also confirmed in the middle part.

This method may be helpful for the demonstration/introduce redox reactions, the capillary action of the solution by silver deposition, chromatographic separation, sublimation, and silver coating over paper or conductive fabric. All these experiments were repeated many times, and wherever possible, yields obtained are quantitatively standardized.

Thus, different ways of mixing Tollens' reagent with reducing agents leads to not only in designing educational experiments but also help in developing technologically important applications.

5.3 Synthesis of Silver Nanoparticles (SNP)

Introduction

In the third part, Due to a challenging and fascinating field, the SNP were synthesized using modified Tollens' reagent and studied with various reducing agents.

In the era of nano-science, enormous research shows restricted growth of silver for nanoparticle synthesis.[19] Depending on the size and morphology, the Nanoparticles are used in catalysis, fuel cells, pigments, sensors, Bio-materials, and optoelectronic materials.[14,15,20,21] In particular, metal nanoparticles show unique spectroscopic, electronics, chemical, and physical properties depending upon size and morphology; one of them is SPR.[22] The Surface Plasmon resonance SPR is a quantum or measurement of oscillation of electron density produced due to strong interaction with electromagnetic waves to the metal.[22] This SPR is in UV-visible and near IR region makes it easier to analyze the formation of metal nanoparticles.[23] SPR of silver nanoparticles gives intense colors of solutions depending on the size of particles, which can be used as a key or most straightforward observation to conclude the results.

Herein, we demonstrate using a capping agent to get silver nanoparticles in a green way by modifying Tollens' reaction and UV-Visible spectroscopy and DLS particle size analysis.

Experimental

Materials and methods

- Formaldehyde, Glucose, Maltose, and Starch were used as the aldehydes. All chemicals used were of analytical grade quality, purchased commercially from Sigma-Aldrich, and Alfa Aesar, and used without further purification.
- The hydrodynamic size of nanoparticles was analyzed using Dynamic Light Scattering (DLS) technique using 90Plus Brookhaven instrument, using DLS laser (λ) 633 nm produced by solid-state He-Ne laser emitter (Lexel Laser Inc.) of 15 mW, and scattered light was detected at 90° scattering angle and 25°C (± 0.5°C) temperature by a photomultiplier.
- The UV-visible spectral analysis of the nanoparticle solutions was performed on a Perkin Elmer Lamada 35 instrument in the range of 200-800 nm wavelength, with a 1cm path length using a 4.0 ml quartz cuvette.

The procedure of modified Tollens' reaction:

0.1 ml, 0.1 N Sodium hydroxide Solution was added to the silver nitrate (1.0 N, 5.0 ml) solution, followed by liquor ammonia (0.2 ml) solution. 10.0 ml of PVP (1%) solution was added to prepare modified Tollens' reagent. 3.0 ml of this solution is mixed to 1.0 ml, 1.0 M glucose solution in a test tube and kept at room temperature (~30°C).

Procedure for synthesis of stable SNP:

The reaction was repeated with Formaldehyde, Maltose, and Starch solutions instead of glucose, where the solutions were heated for 5.0, 5.0, 10.0, and 20.0 minutes respectively. This reaction was also carried out by varying concentrations of these aldehyde solutions (1.0 M, 0.8 M, 0.6 M, 0.4 M, and 0.2 M).

10.0 ml, 0.5 mN Sodium hydroxide Solution, and 10.0 ml, 50.0 mN silver nitrate solution were mixed to 10.0 ml of PVP (1%) solution to prepare modified Tollens' reagent-II. In addition, 3.0 ml of this solution is mixed to 1.0 ml, 1.0 M glucose solution in a test tube and heated at 70° C in a water bath. These solutions were stored at room temperature in dark and used directly for DLS and UV-spectral analysis.

Result and discussion

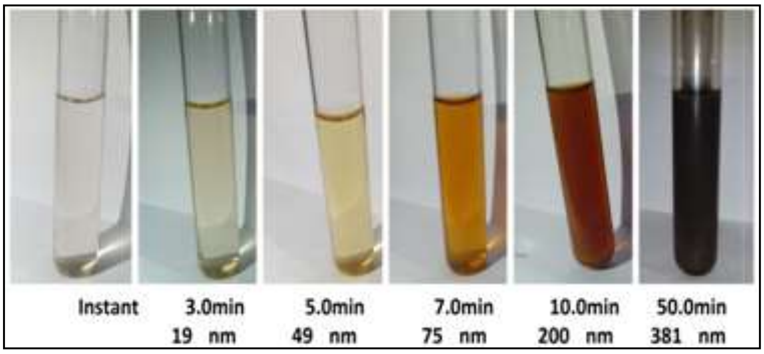


Figure F5.6: Photographs of SNP solution after different time interval and size of SNP

The Tollens' reaction of glucose was carried out in the presence of PVP, as shown in the above procedure. The color of solutions was varied from colorless to light yellow, dark yellow, orange, red, brown and black, as time passes, as shown in Figure F5.6. This solution was subjected to DLS analysis, and the hydrodynamic sizes of silver particles were observed in the nano-particle range, which confirmed silver nanoparticle formation. The hydrodynamic size of silver particles in the solution was analyzed rapidly after some time interval, and an increase in the size of nanoparticles from 19 nm to 381 nm was observed, after 3 to 50 minutes of preparation. After 60 minutes the silver mirror formation was observed, which shows the aggregation behavior of nanoparticles.

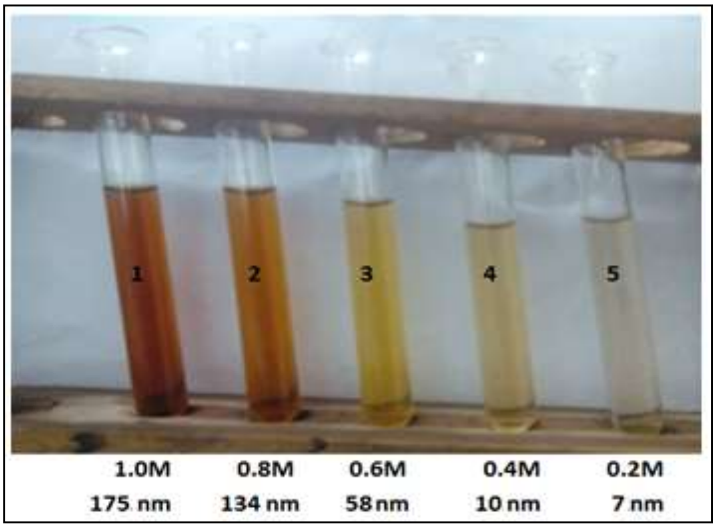


Figure F5.7: SNP formed after 10 min of performing modified Tollens' reaction by varying concentration of glucose and size of SNP

The reaction of modified Tollens' reagent was carried out by varying concentrations of glucose by 1.0 M, 0.8 M, 0.6 M, 0.4 M, and 0.2 M. Those solutions were resulted in red, orange, yellow, light yellow, and very pale yellow colors, respectively after 10 minutes of preparation, as shown in Figure F5.7. These solutions were subjected to DLS analysis, and the size of nanoparticles was observed at 176, 134, 59, 10, and 7 nm, respectively.

This analysis supported a decrease in concentrations resulted in smaller nanoparticles, as shown in Figure F5.7. Furthermore, these solutions were turned black and resulted in very thin silver film formation, due to aggregation of nanoparticles within some time (~1-2 hours), which presents their unstable nature.

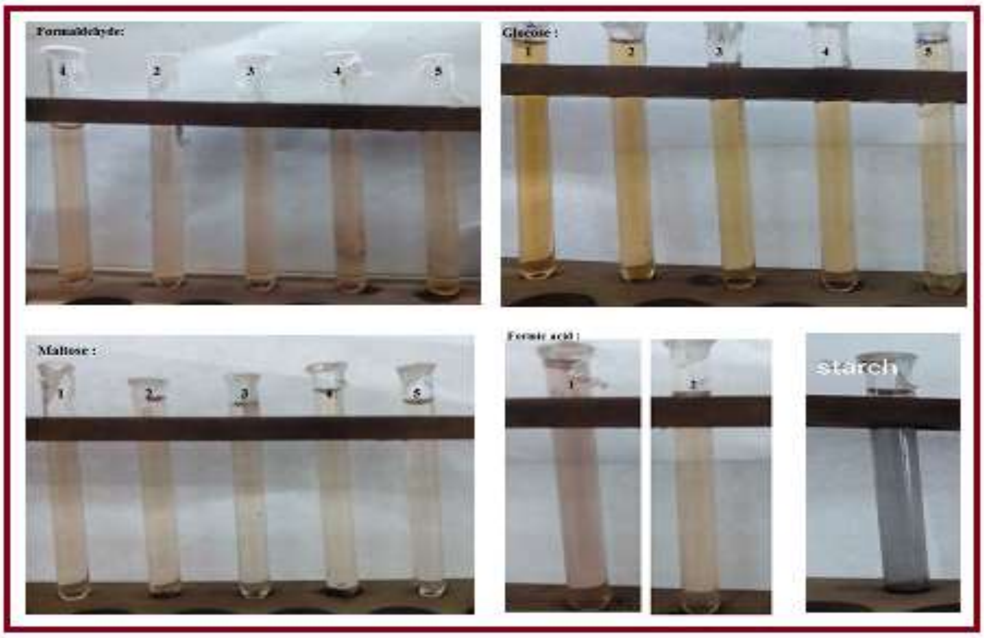


Figure F5.8: Solution of stable SNP synthesized by using solution of Formaldehyde, Glucose and Maltose (1.0 M 0.8 M, 0.6 M, 0.4 M, 0.2 M concentrations), Formic acid (1.0 M, 0.2 M) and starch (0.2 M).

The silver nanoparticles were synthesized using modified Tollens' reagent-II. In this method, diluted systems were used and ignoring ammonia and decreasing particle aggregation. To explore the effect of reducing agents on nanoparticles, the reaction of Formaldehyde, Glucose, Maltose, and Starch solutions was carried out with this reagent. These nanoparticles were found to be stable even for a week in the solution at room temperature. However, concentrations were observed critically in the previous case; thus, these reactions were carried out by varying concentrations (as shown in Figure F5.8).

The DLS study and UV-visible spectroscopy analysis (as shown in Figure F5.9) of these solutions support the formation of nanoparticles (size of SNP are noted in table T5.2).

The SNP is known for its unique property called surface Plasmon resonance effect, which gives absorption pattern mimics the shape, and colors of solution changes depending on SNP size. The nanoparticle size and corresponding colors of solutions were observed harmonious, depending on the oxidizability of aldehydes used. Absorbance at ~420 nm was observed in the UV-visible analysis of these solutions mimics the spherical shape of SNP as shown in Figure F5.9.

Table T5.2: Size of stable SNP synthesized by varying concentrations of reducing agents and colour of the solution

	Concentration	1.0 M	0.8 M	0.6 M	0.4 M	0.2 M
Reducing agent	Color	1	2	3	4	5
Glucose	Yellow	244 nm	69 nm	49 nm	12 nm	49 nm
Formaldehyde	Brownish Pink	128 nm	58 nm	27 nm	8 nm	7 nm
Maltose	Light brown	106 nm	54 nm	31 nm	14 nm	4 nm
Starch	Violet	400 nm	-	-	-	-

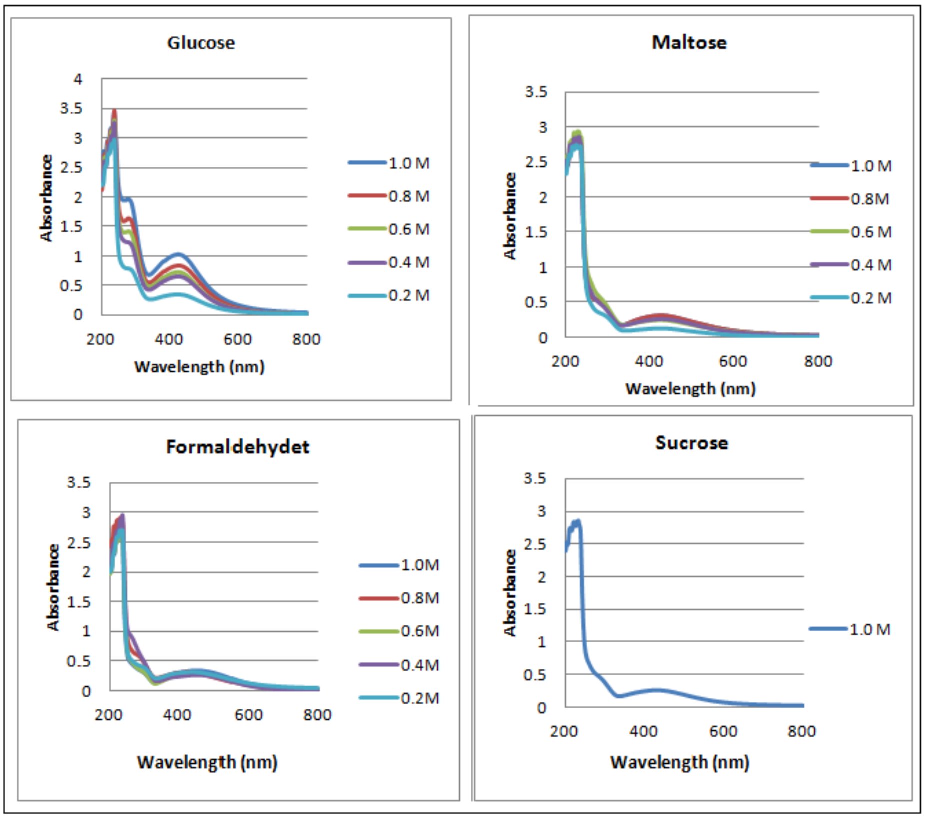


Figure F5.9: Images of UV-Visible spectra of stable SNP solution synthesized using the solution of Formaldehyde, Glucose, and Maltose, and sucrose in various concentrations

Scope: This experiment can make students aware of the nanoparticles, and the SPR concept and visualization make it enjoyable to the students.

Conclusion

In conclusion, the silver nanoparticles were synthesized by modifying traditional Tollens' reactions. These nano-particles were analyzed using DLS and UV-Spectroscopy. The silver nano-particle were observed using PVP (capping agent) in the Tollens' reaction mixture. The method for stable SNP synthesis was developed, and the aggregation behavior of unstable nanoparticles was also studied. These reactions can explain the correlation of sizes of SNP with colors of solutions and SPR property.

5.4 Summary

In summary, Extensional activities on Tollens' reactions were demonstrated in which 1st chemo-selectivity for oxidation was reported. In the 2nd part, different methodologies were demonstrated to mix Tollens' reagent and reducing agents, and in the 3rd part, silver nanoparticles were synthesized, as an activity not limited to **educational experiment.**

- The Tollens' reaction of a mixture of two different molecules with aldehyde and phenol functionality resulted in both oxidation products, carboxylic acid, and bi-phenol. We could observe chemo-selectively bi-phenol formation simply by avoiding NaOH in the reaction mixture.
- The Tollens' reaction of hydroxybenzaldehydes resulted in the corresponding acid formation only and C-C coupled bi-phenol product formation was not observed.
- The Tollens' reaction of HMF (A) resulted in FFCA (2A) formation selectively (18% yield). To understand the mechanism of this experimental observation, we carried out the oxidation of aldehyde and methanol derivatives of heteroaromatic compounds (total eight) using Tollens' reagent. This investigation shows Tollens' reaction on A is chemo-selective and forms 2A by selective-oxidation of both aldehyde and alcohol functionality to corresponding acid and aldehyde, as proposed in path-2.
- The Tollens' reactions were demonstrated by varying methodologies to mix Tollens' reagent with reducing agents;

  1) C-C oxidative coupling of 2-naphthol/ 2,6-di-*tert*-butyl-phenol was successfully obtained by co-spotting reagents on a TLC plate. 2) Coupling reactions were carried out, keeping Tollens' reagent containing filter paper (substrate) in a modified sublimation assembly of phenol, to obtain silver staining over the selected part of the paper. 3) By keeping capillaries in the reaction vessel, the selective inner side silver film formation in the capillary was obtained. 4) coupling reaction was also demonstrated by connecting a vial containing Tollens' reagent and phenol solution using a paper strip.

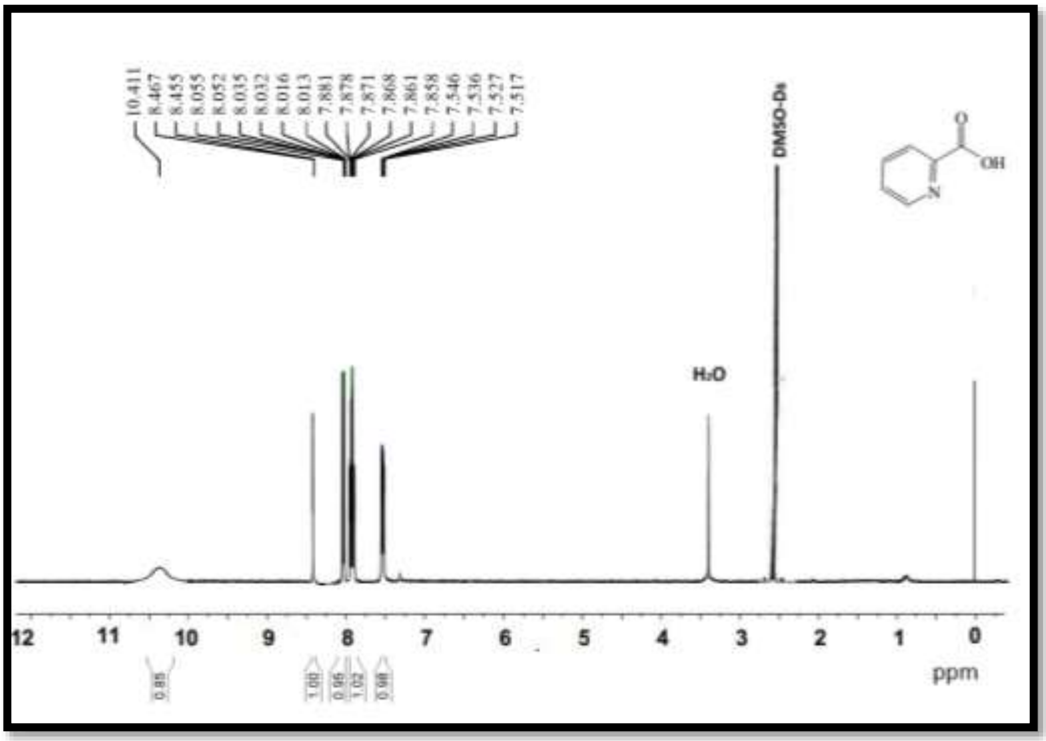
  This method may be helpful for the demonstration of redox reactions, capillary action, chromatography, sublimation, and silver coating. All these experiments were repeated many times, and wherever possible, yields obtained are quantitatively standardized.
- The silver nanoparticles were synthesized by modifying Tollens' reaction and using a PVP capping agent and analyzed using DLS and UV-Spectroscopic analysis. The method for stable SNP synthesis was developed, and the aggregation behavior of unstable nano-particle was also studied.

Overall, the work suggests that Tollens' reaction demonstrated experimentally may provide a general platform for developing educational activities, which will give hands-on practice of diverse areas in chemistry.

5.5 Spectral data

5.5.1 FT-NMR (^1H and ^{13}C) spectra

Figure F5.5.1 FT-NMR (^1H and ^{13}C) spectra of 2B



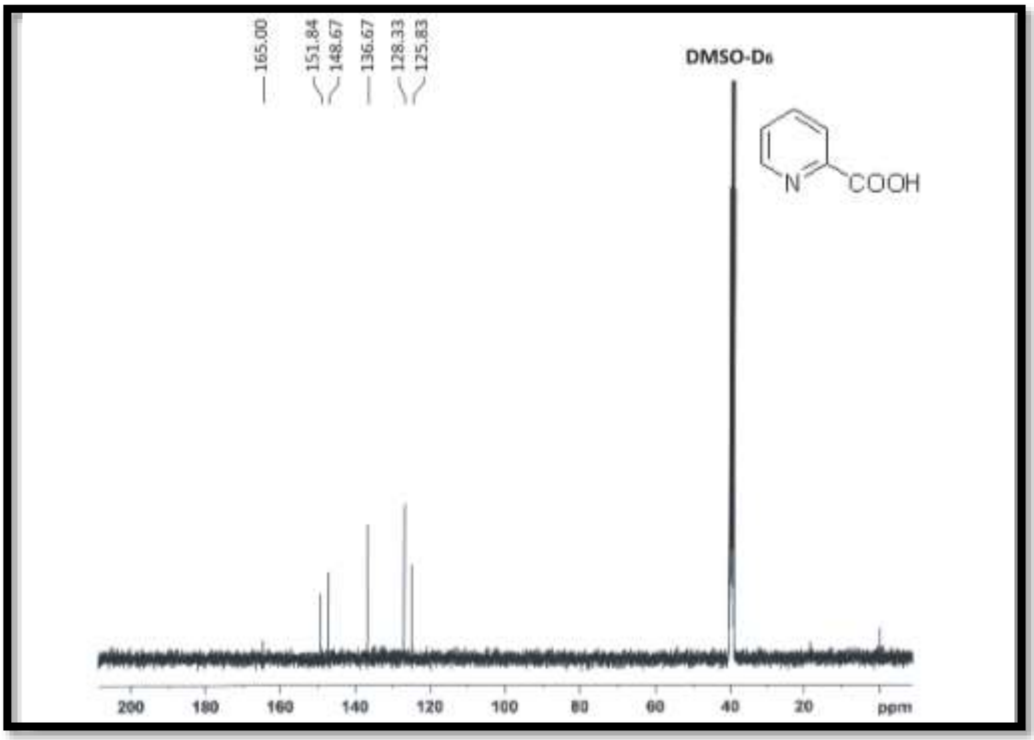
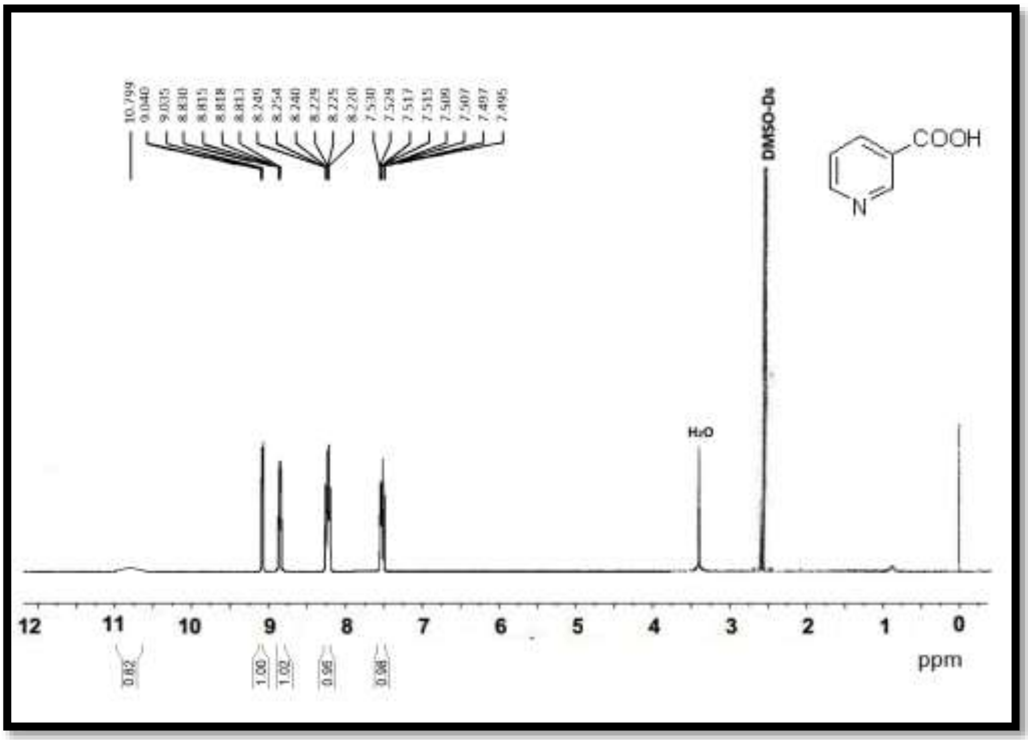


Figure F5.5.2 FT-NMR (^1H and ^{13}C) spectra of 2C



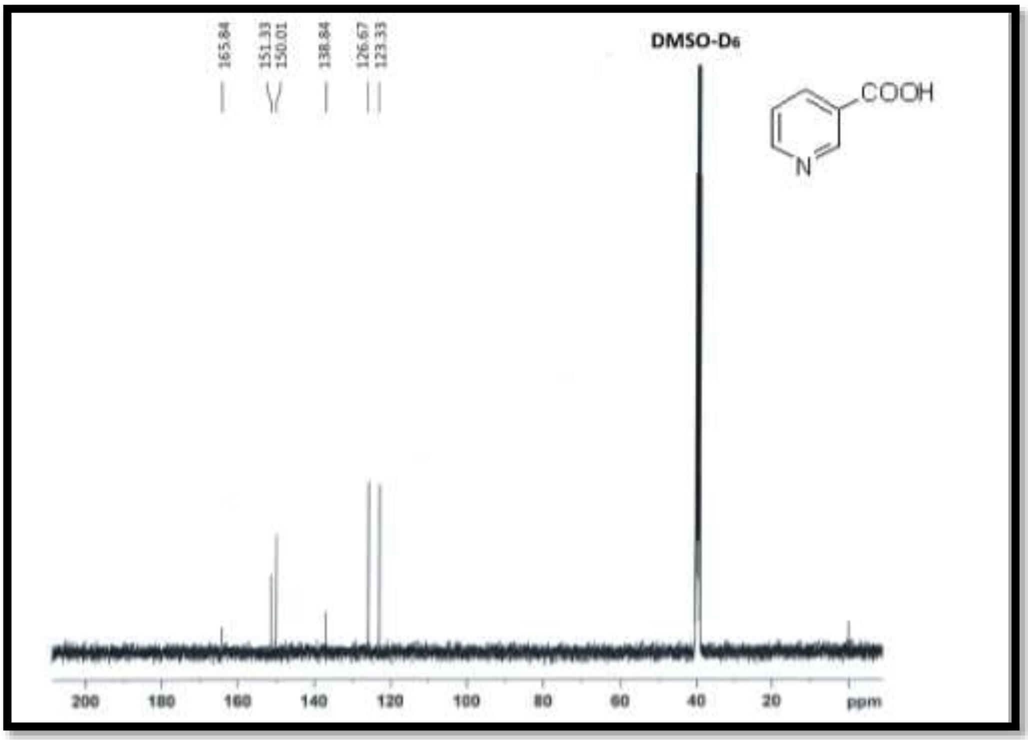
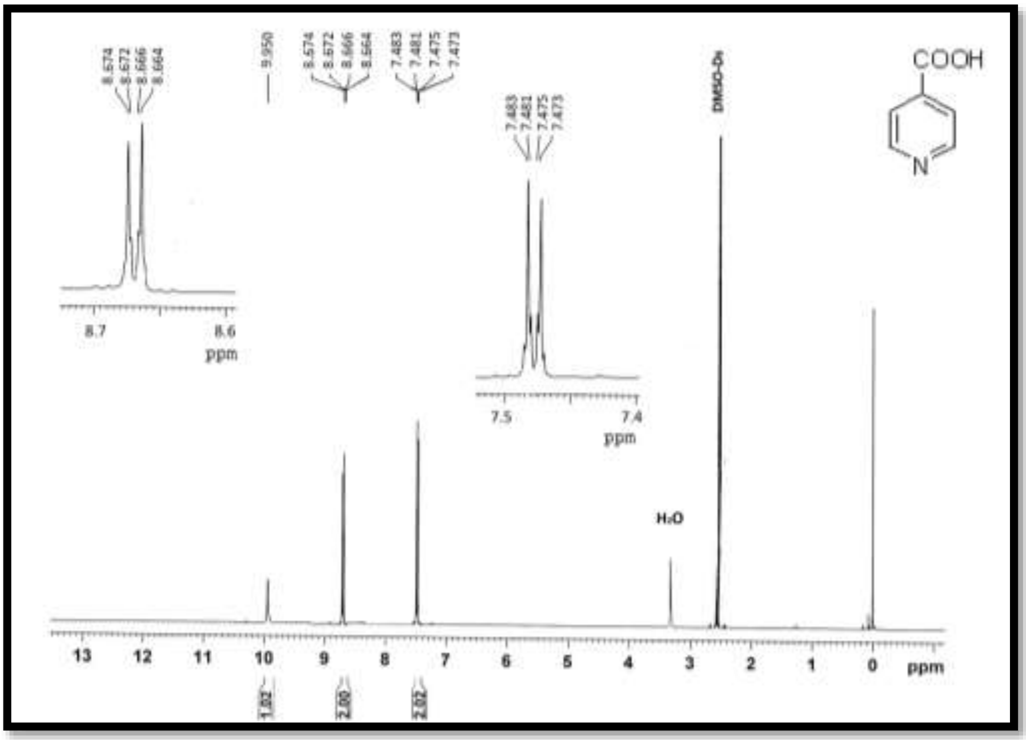


Figure F5.5.3 FT-NMR ([1]H and [13]C) spectra of 2D



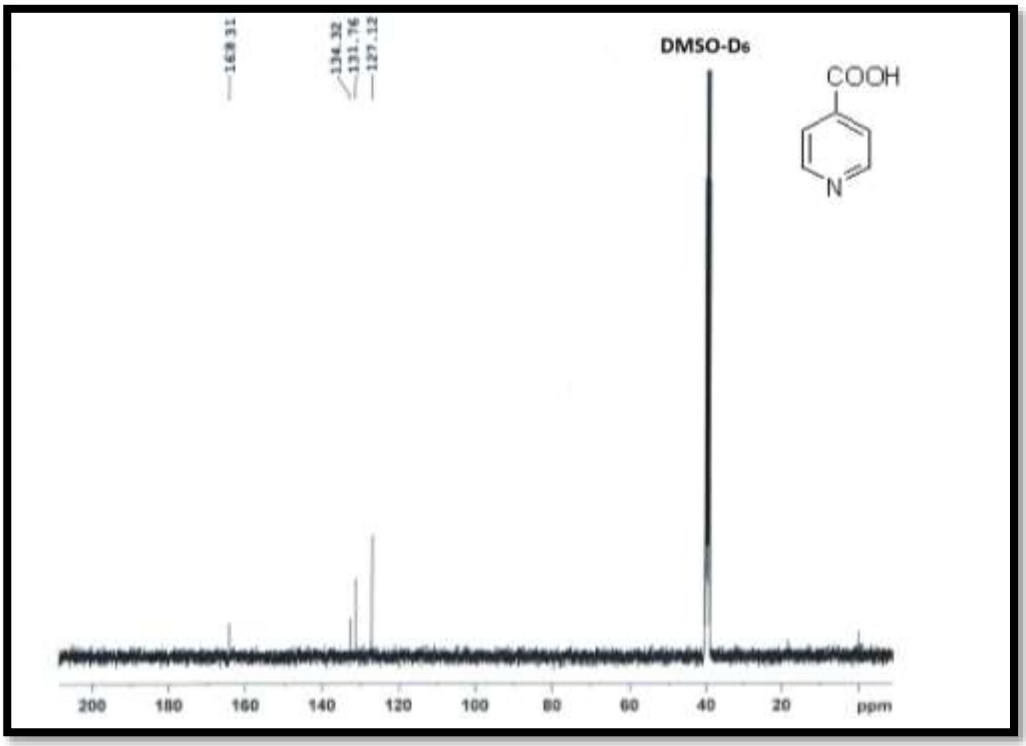
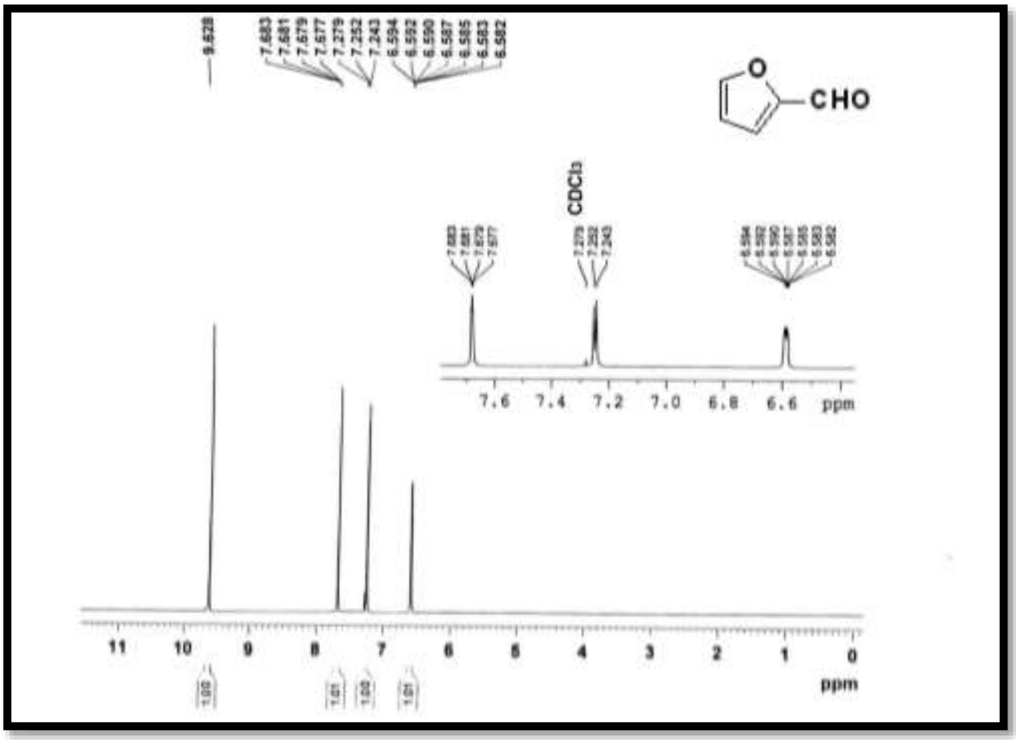


Figure F5.5.4 FT-NMR (^1H and ^{13}C) spectra of 1E



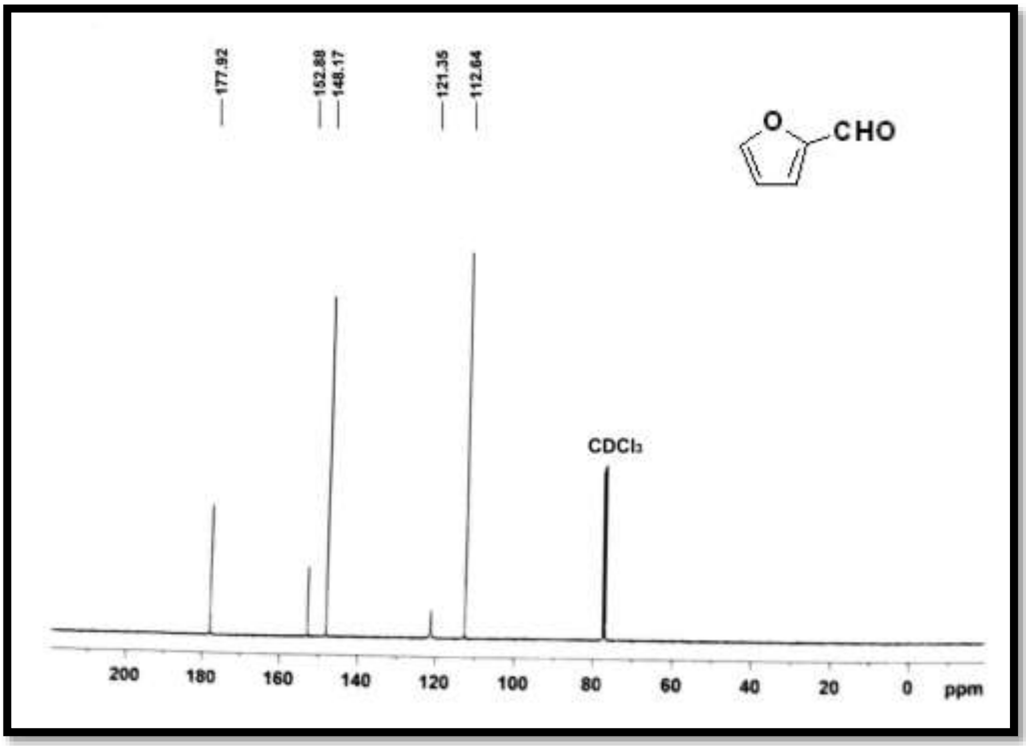
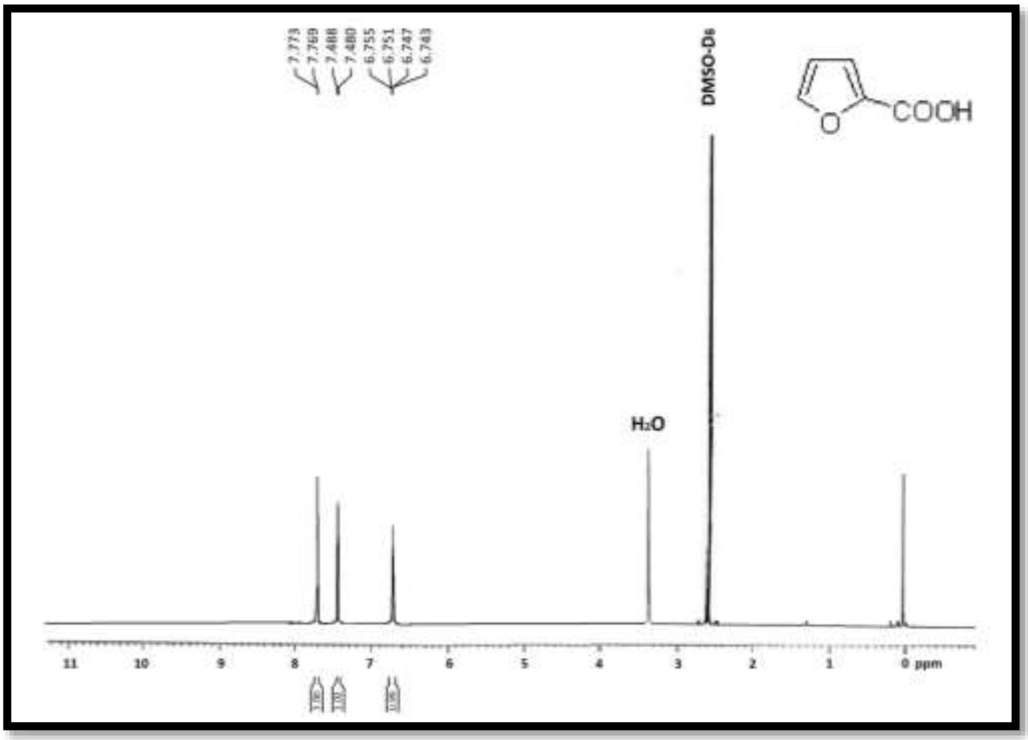


Figure F5.5.5 FT-NMR (^1H and ^{13}C) spectra of 2E



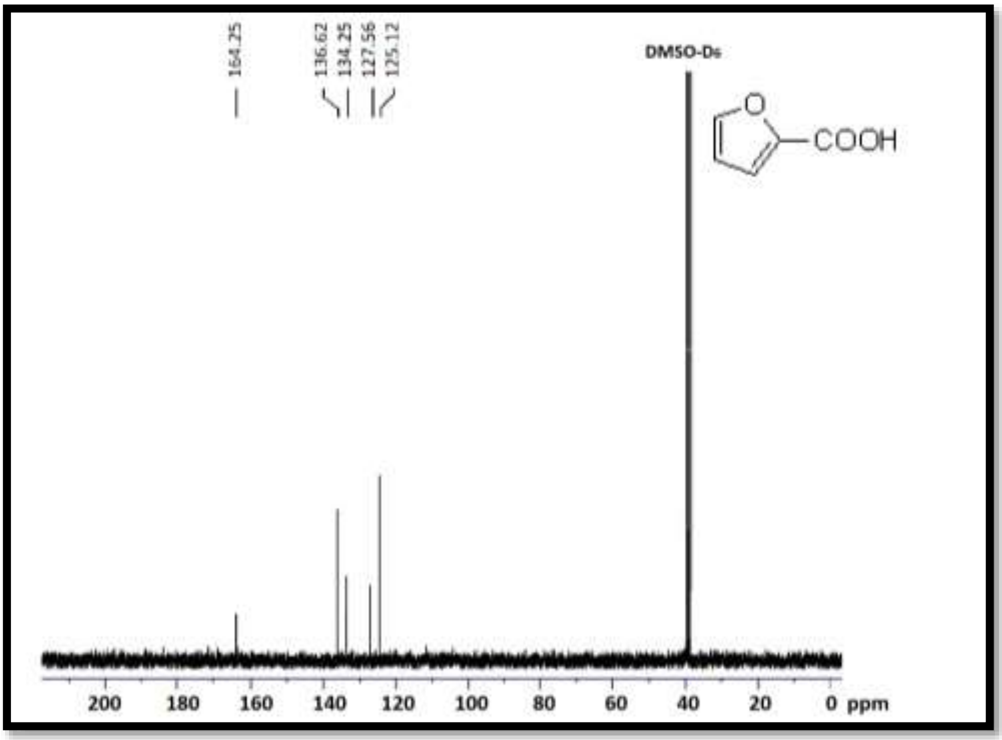
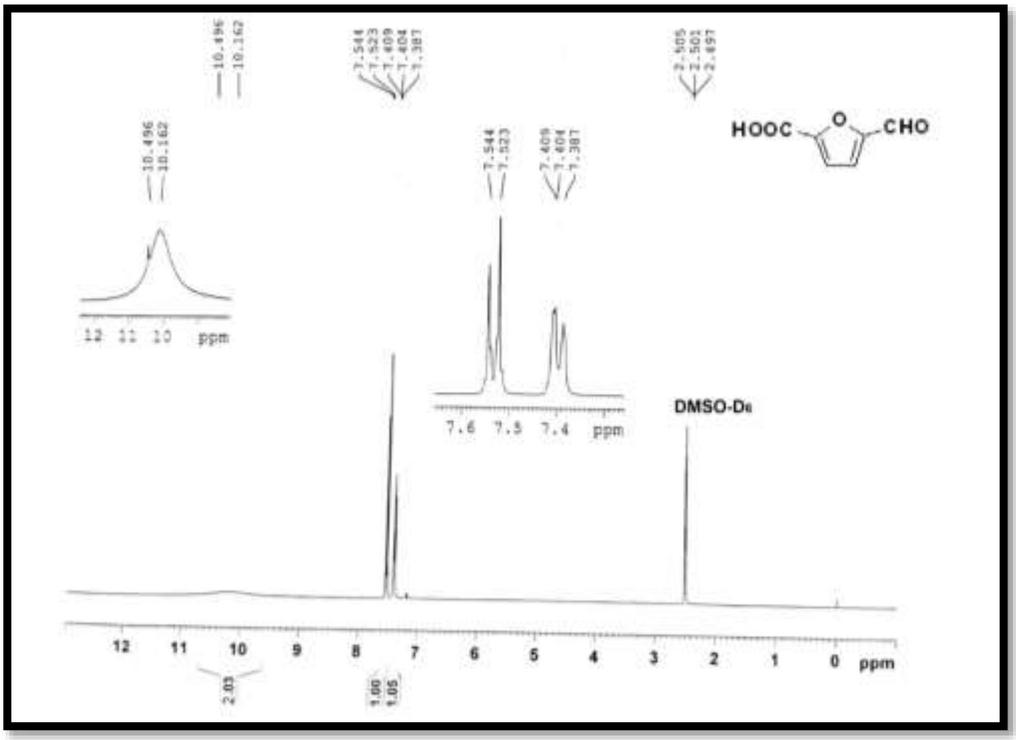
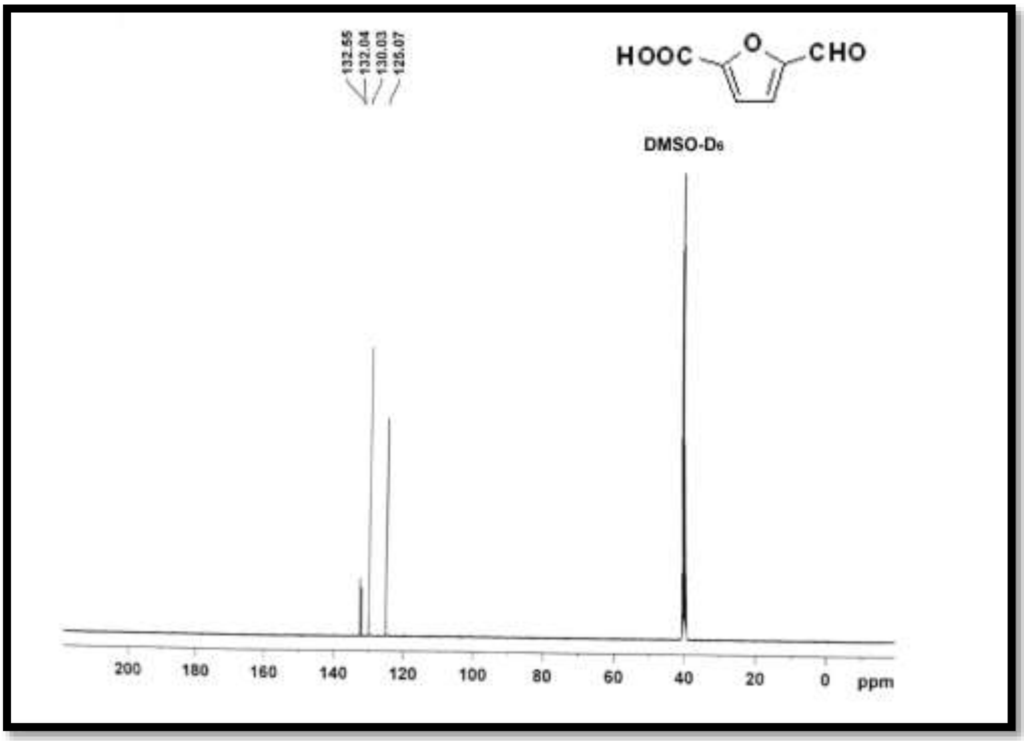


Figure F5.5.6 FT-NMR (^{1}H and ^{13}C) spectra of 2A





5.5.2 Mass spectra

Figure F5.5.7 ESI-MS spectraof 2B

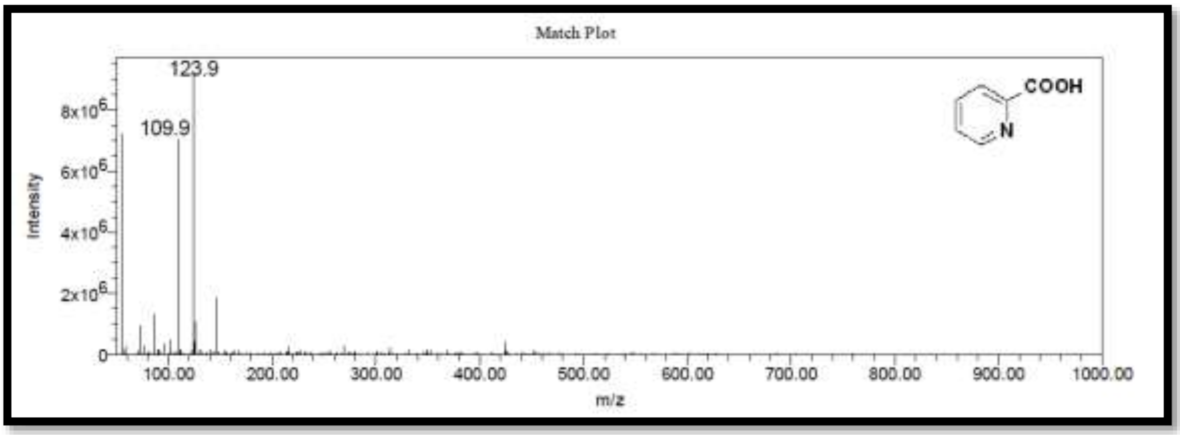


Figure F5.5.8 ESI-MS spectra of 2C

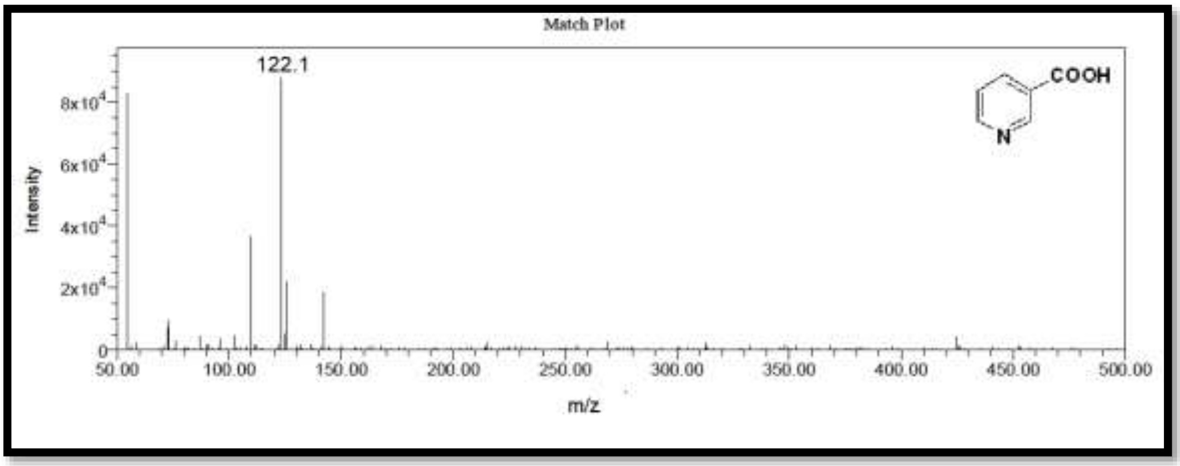


Figure F5.5.9 ESI-MS spectra of 2D

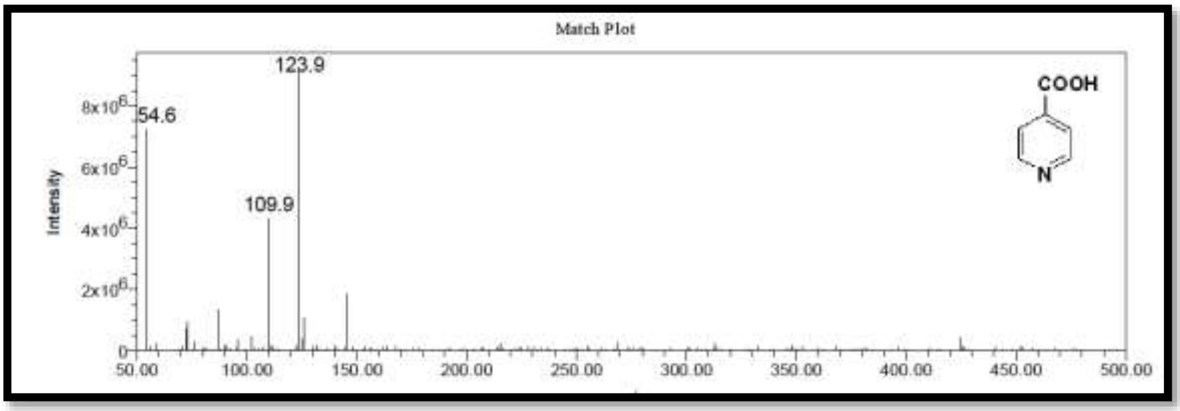


Figure F5.5.10 ESI-MS spectra of 1E

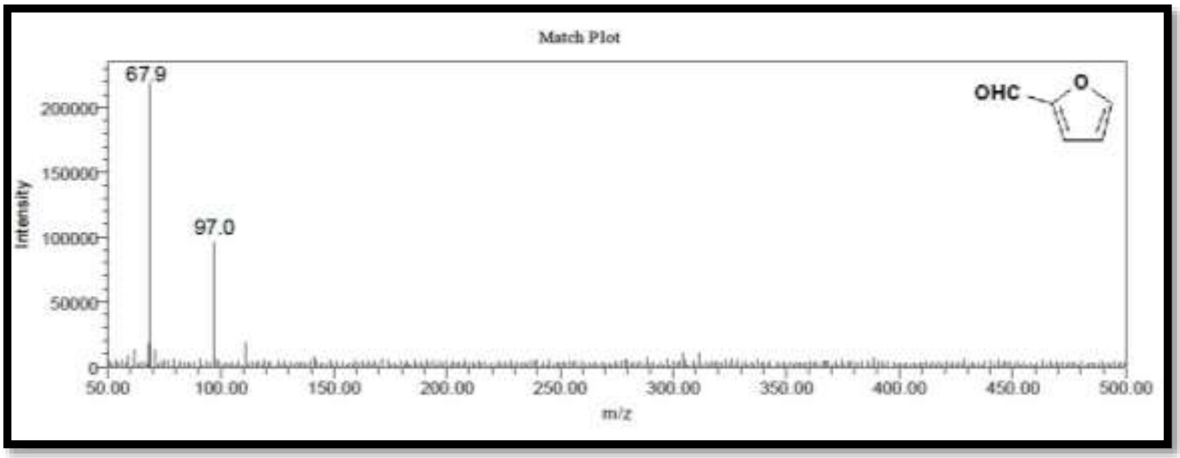


Figure F5.5.11 ESI-MS spectra of 2E

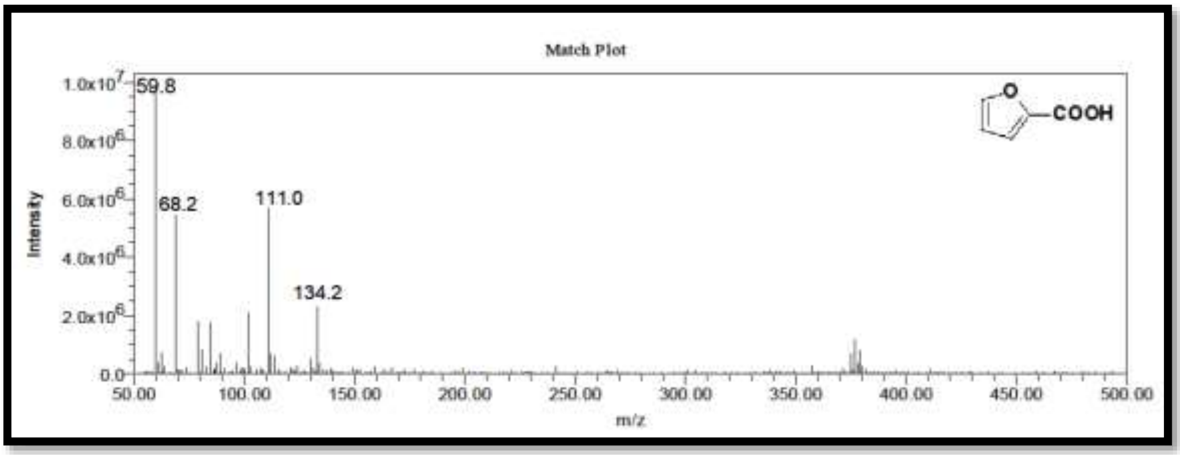
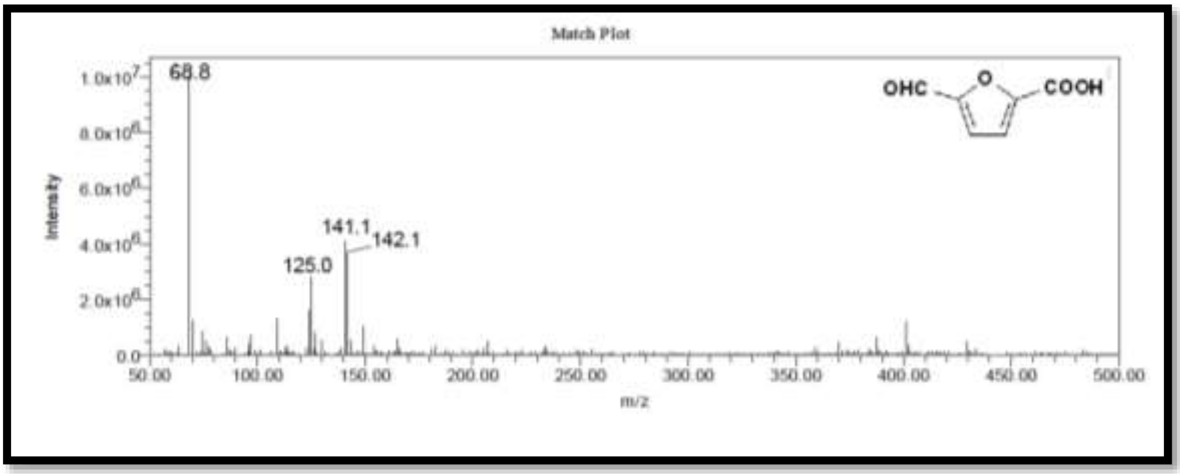


Figure F5.5.12 ESI-MS spectra of 2A



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