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RESEARCH ARTICLE

AMMONIUM NICKEL SULFATE (TUTTON'S SALT) MEDIATED RAPID AND FACILE SYNTHESIS OF SCHIFF BASE UNDER ENVIRONMENTAL FRIENDLY CONDITION

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Abstract

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In the present study a rapid and facile method for the synthesis of schiff bases (**3a-z & 3aa-af**) has been developed by using Ammonium Nickel Sulfate (ANS) (Tutton's Salt) as catalyst. Further more, the reaction is selective as only benzaldehydes are reacted where as acetophenone failed to perform this reaction. The present method is very rapid with simple work up and gives the products in good to excellent yield. The reaction is totally carried out under environmentally friendly condition by using green solvent MeoH and water in 1:1 ratio. Thus it is anticipated that the present newly developed method will give ample chemical space to the chemist to prepare the Schiff bases in rapid and envirnmentaly benign conditions.

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Introduction:-

Schiff bases are the compounds carrying imine or azomethine (–C=N–) functional group. They are the condensation products of primary amines with carbonyl compounds and were first reported by Hugo Schiff [1–3]. Schiff bases are most widely used organic compounds which exhibit numerous applications in various fields including analytical, biological and inorganic chemistry. Schiff bases have received immense importance in medicinal and pharmaceutical chemistry due to its broad spectrum of biological activities like anti-inflammatory [4–7], analgesic [5–8], antimicrobial [9, 10], anticonvulsant [11], antitubercular [12], anticancer [13, 14], antioxidant [15] and antihelmintic [16] etc. The nitrogen atom of azomethine may be involved in the formation of a hydrogen bond with the active centers of cell constituents and interferes in normal cell processes [17, 18]. Schiff bases are also used as catalysts, intermediates in organic synthesis, dyes, pigments, polymer stabilizers and corrosion inhibitors [19]. Although different research groups have attempted to develop various methods for the synthesis of schiff bases [20-25], these methods suffer from drawbacks such as prolonged reaction times, costly reagents and low yields. In view of the above, there is huge need for the devleopment of new methods for the sytnhesis of schiff bases under environmentally friendly conditions. We have developed a new protocol for the rapid preparation of Schiff's bases by using Ammonium Nickel Sulfate (Tutton's Salt) [26] as catalyst with short reaction times in high yields. Tutton's salts are a family of salts with the formula $M_2M'(SO_4)_2(H_2O)_6$ (sulfates) or $M_2M'(SeO_4)_2(H_2O)_6$ (selenates). These materials are double salts. (Which means they contains two different cations) [27]

Results and Discussion:-

Conventionally, Schiff's bases can be prepared by refluxing the amine and aldehyde in an organic solvent. For example, ethanol or methanol, with variations which are known, such as treatment of the same mixture at room

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temperature, refluxing the mixture in heptane in the presence of acetic acid, or azeotroping the mixture with benzene in a Dean Stark apparatus in the presence of acid [28]. In continuation of drug discovery programme we were in need for the synthesis of fluorine containing Schiff bases. When we tried the conventional as well as some reported methods for the synthesis of fluoroaniline based schiff bases we observed that the reactions are not upto the mark and in most of the cases we obtained the complex formation of mixture of the compounds and desired products were not obtianed. It might be due to high reactive of fluorine contining anilines which may be undergoing other reactions such as N-arylation via the fluorine-amine replacement (Undisclosed results). In our endeavours to get the schiff bases of fluoroanilines we found that the Tutton's salts particularly Ammonium Nickel Sulfate (ANS) has resulted the desired schiff bases of the fluoroanilines. For example the 2-fluoroaniline schiff bases with p-Touladehyde and benzaldehyde is got in good yield with easy seperation **Figure-1**. (The results of the fluoroanilines will be reported seperately as still work is in progress under drug discovery programme).

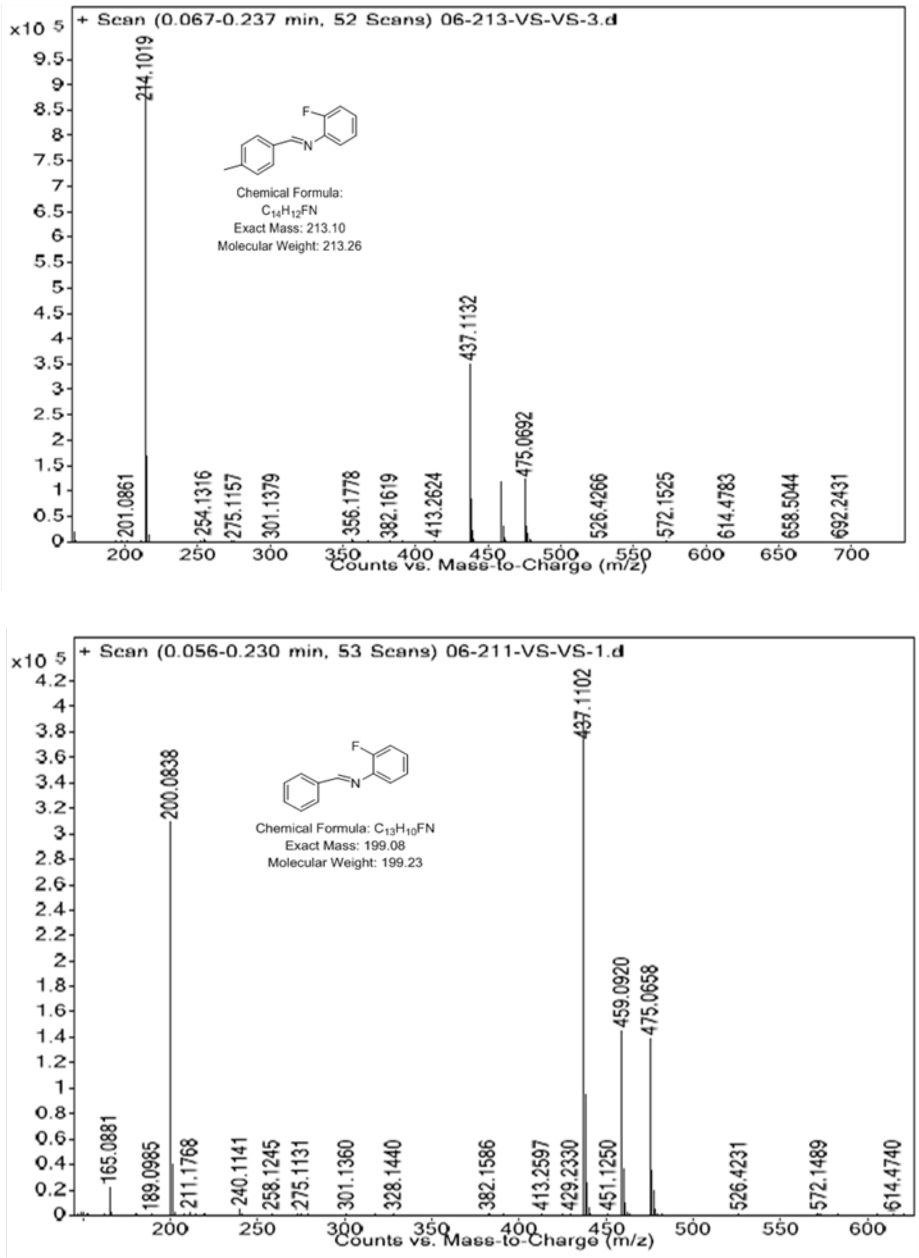
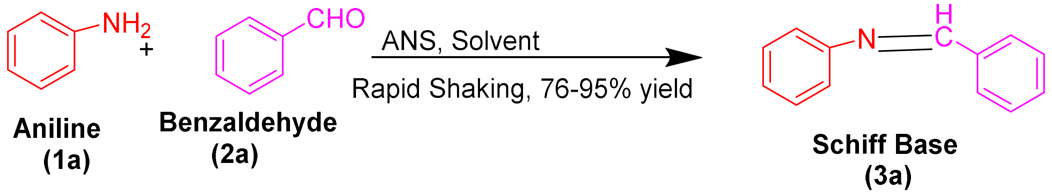


Figure1:- Mass spectra of fluoroanilines schiff bases.

With the new condition in hand which is usefull for our drug discovery programme, we thought to develop this new condition as an efficient and environmentally friendly method for the synthesis of Schiff bases and report to the scientific community. To further optimize our reaction conditions for the formtion of schiff base of benzaldehyde and aniline (**Scheme-1 and Figure-2**) we carried out several reaction conditions, the results are sumarized in **Table-1**.



Scheme-1:- Synthesis of Schiff base (**3a**) fomation from benzaldehyde and aniline.

To get the best optimized conditions for the formation of Schiff base (**3a**) using aniline (**1a**) with benzaldehyde (**2a**), we started first by taking various combinations of solvents with ANS. When we have taken THF/ANS/Reflux/4hr; THF/ANS/shaking for one minute no reaction is observed. When the DCM/ANS/Reflux/4hr ondition are used 10% product is obtained, where as DCM/ANS/shaking for one minute no reaction is observed. Similar results were observed when benzeene or tolulene were used as solvent. In the case of EtOAc/ANS/Reflux/4hr 20% product is obtained, where as in the case of EtOAc /ANS/shaking for one minute no reaction is observed. Suprisingly, when water is used as a solvent no reaction is observed as the reactant and catalysts are not miscible. Interestingly, when the reaction is carried out in protic solvent such as EtOH or MeOH the reaction is enourmously increaced (**Table-1, entries 12-15**). We finally decided to carried out the reaction in MeOH/Water (1:1) and found that reaction is efficiently working and the yield is improved very effectively. Thus finally we carried out the reaction in a sequential way i.e., the ANS (10%) soution is made in MeOH/Water (1:1) ratio and this solution is added to the methanolic solution of benzaldehyde and shaken well, finally to this mixture of ANS and Benzaldehyde solution the methaolic solution of aniline was added and shaken for few second, a repid precipitataion of the product is observed. Which has been confirm by its mass spectra. (**Fig-2**) Thus, in this work we develop a new rapid method for the preparation of Schiff bases. To the best of our knowledge and a literature search revealed that the synthesis of Schiff bases by using Ammonium Nickle Sulfate (ANS) has not been previously reported. (**Scheme-2**)

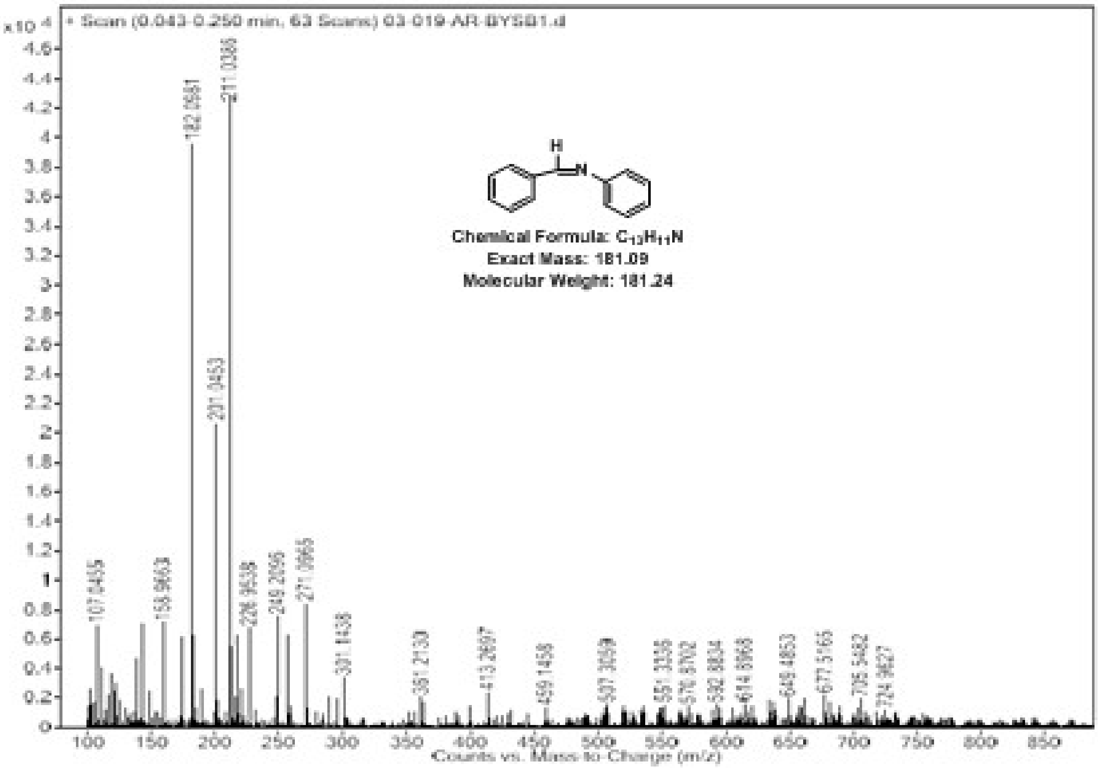


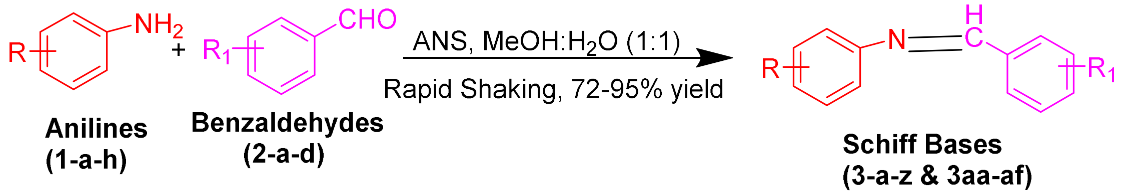
Figure 2:- Mass spectra of schiff base (3a) from benzaldehyde and aniline.

The generality of the reaction is examined by carriying out the reaction with substituted anilines (**1a-h**) and substituted benzaldehydes (**2-a-d**), the results indicate that the reactions with activtated anilines are more yielding when compare with electroron with drawing group on aniline, which produced less yield. The results are summarised in **Table-2**.

Table 1:- Optimization of Schiff base fomation from benzaldehyde and aniline.

S. No	**Solvent**	**Reaction condition**	**Yield %**
1	THF	ANS/ Reflux, 4 hr	NR
2	THF	ANS/ shaking for 1 minute*	NR
3	DCM	ANS/ Reflux, 4 hr	10
4	DCM	ANS / shaking for 1 minute	NR
5	Benzene	ANS / Reflux, 4 hr	10
6	Benzene	ANS / shaking for 1 minute	NR
7	Toulene	ANS / Reflux, 4 hr	10
8	Toulene	ANS/ shaking for 1 minute	NR
9	EtOAc	ANS / Reflux, 4 hr	20
10	EtOAc	ANS / shaking for 1 minute	NR
11	Water	ANS / Reflux, 4 hr	NR as the reactants are not miscible in water
12	Ethanol	ANS / Reflux, 4 hr	50
13	Ethanol	ANS / shaking for 1 minute	50
14	Methanol	ANS / Reflux, 4 hr	50
15	Methanol	ANS (1eq) / shaking for 1 minute	50
16	Methanol/Water (1:1)	ANS (1eq) / shaking for 1 minute	95
17	Methanol/Water (1:1)	ANS (50%) / shaking for 1 minute	95
18	Methanol/Water (1:1)	ANS (20%) / shaking for 1 minute	95
19	Methanol/Water (1:1)	ANS (10%) / shaking for 1 minute	95

Note: * The reaction is carried out by using the present sequence reaction i.e., aldehyde+ANS then amine solution addition in the solvent as given in the table: NR= No reaction.



Scheme 2:- Rapid Synthesis of Schiff Bases (**3a-z & 3aa-af**) catlyzed by Ammonium Nickel Sulfate (ANS).

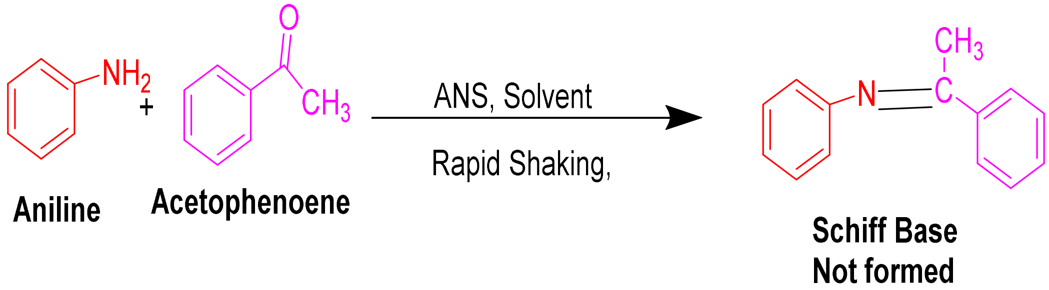
Table 2:- Rapaid Synthesis of Schiff Bases (**3a-z & 3aa-af**) catlyzed by Ammonium Nickle Sulfate (ANS).

S. No	**Anilines**	**Benzaldehydes**	**Product**	**Yield %**		**M. P (^{0}C)**	
				Present^a	**Conventional^b**	**Obtained**	**Reported**
1	Aniline (1a)	Benzaldehyde (2a)	3a	95	80	52-54	54-55
2	p-Toulidine (1b)	Benzaldehyde (2a)	3b	92	78	113-114	114-115
3	o-Toulidine (1c)	Benzaldehyde (2a)	3c	90	74	39-41	40-41
4	p-Anisidine (1d)	Benzaldehyde (2a)	3d	90	78	62-63	61-62
5	4-Hydroxyaniline (1e)	Benzaldehyde (2a)	3e	88	72	188-190	187-192
6	2-Nitroaniline (1f)	Benzaldehyde (2a)	3f	78	65	70-71	71-72
7	3-Nitroaniline (1g)	Benzaldehyde (2a)	3g	75	64	95-96	94-97
8	4-Nitroaniline (1h)	Benzaldehyde (2a)	3h	80	62	115-116	116-117

9	Aniline (1a)	Vaniline (2b)	3i	92	79	107-109	108-110
10	p-Toulidine (1b)	Vaniline (2b)	3j	88	76	119-120	118-121
11	o-Toulidine (1c)	Vaniline (2b)	3k	86	74	113-114	112-113
12	p-Anisidine (1d)	Vaniline (2b)	3l	88	76	134-137	135-136
13	4-Hydroxyaniline (1e)	Vaniline (2b)	3m	85	72	141-142	140-141
14	2-Nitroaniline (1f)	Vaniline (2b)	3n	75	62	51-53	52-53
15	3-Nitroaniline (1g)	Vaniline (2b)	3o	73	60	130-131	131-132
16	4-Nitroaniline (1h)	Vaniline (2b)	3p	72	60	159-160	160-161
17	Aniline (1a)	4-Chloro-benzaldehyde (2c)	3q	88	78	59-61	60-61
18	p-Toulidine (1b)	4-Chloro-benzaldehyde (2c)	3r	86	76	120-121	121-122
19	o-Toulidine (1c)	4-Chloro-benzaldehyde (2c)	3s	84	75	39-41	41-42
20	p-Anisidine (1d)	4-Chloro-benzaldehyde (2c)	3t	85	76	123-124	122-123
21	4-Hydroxyaniline (1e)	4-Chloro-benzaldehyde (2c)	3u	80	72	77-78	78-79
22	2-Nitroaniline (1f)	4-Chloro-benzaldehyde (2c)	3v	75	65	121-122	122-123
23	3-Nitroaniline (1g)	4-Chloro-benzaldehyde (2c)	3w	74	63	140-141	141-142
24	4-Nitroaniline (1h)	4-Chloro-benzaldehyde(2c)	3x	76	62	65-66	64-66
25	Aniline (1a)	2-Chloro-benzaldehyde (2d)	3y	87	78	52-53	53-54
26	p-Toulidine (1b)	2-Chloro-benzaldehyde (2d)	3z	85	74	77-78	78-79
27	o-Toulidine (1c)	2-Chloro-benzaldehyde (2d)	3aa	86	72	59-61	60-61
28	p-Anisidine (1d)	2-Chloro-benzaldehyde (2d)	3ab	88	75	156-157	157-158
29	4-Hydroxyaniline (1e)	2-Chloro-benzaldehyde (2d)	3ac	79	63	112-114	113-115
30	2-Nitroaniline(1f)	2-Chloro-benzaldehyde (2d)	3ad	74	60	113-115	114-116
31	3-Nitroaniline (1g)	2-Chloro-benzaldehyde (2d)	3ae	75	62	121-122	122-123
32	4-Nitroaniline(1h)	2-Chloro-benzaldehyde (2d)	3af	76	64	159-160	160-161

Note: [a] Present Reaction Condition: **Rapid with in one minute** [b] Conventional reaction Condition: H_2SO_4/MeOH/reflux, 4hr

Interrestingly, when the same reaction was carried out with acetophenone the desired product is observed instead of that, an unseperatable mass is observed. (**Scheme-3**)



Scheme 3:- Attempt for the Synthesis of Schiff base fomation from Acetophenone and aniline.

Mechanistically it is postulated or anticipated that the ANS solution of MeOH/Water is making the chelation with the oxygen atom of carbonyl group and polarising the carbonyl bond to facilitate the nucleophilic aniline to attack on the carbonyl group and later on upon dehydration gives the coorresponding schiff bases.

All the compounds are known compounds are characterised by MP, IR, NMR and Mass spectra. The data are found to be in agreement with the literature repoted data. The FTIR spectra of the synthesized Schiff bases (**3a-z & 3aa-af**) indicated medium intensity band observed between 2925-3120 cm^{-1} which are attributed to–CH stretching vibrations viz. Symmetric and Asymmetric of the aromatic ring. All these compounds showed a characteristic band in between 1584-1654 cm^{-1}, which is due to–CH=N-group (stretching). The three bands in the area of 1500-1600 cm^{-1} indicate aromatic C-H strechcing of the compound. A sharp band in the range of 1153-1193 cm^{-1} may be assigned to the aryl–C-N stretching vibration, additional band at 755-876 cm^{-1} for Schiff base containing chlorine attached to aromatic ring may be attributed to aryl C-Cl group. The Schiff base with group displayed strong band between 1487-1564 cm^{-1} and 1337-1365 cm^{-1} is due to nitro group. The ^{1}H-NMR spectrum of the synthesized Schiff base (**3a-z & 3aa-af**) shows broad signals between the 9.70-13.35 δ corresponds to the OH of the aromatic ring. The singlet peaks between 8.25-9.57 δ is due to imine proton of –CH=N. Aromatic protons appear between 6.48-8.44 δ. A singlet at 3.48-4.02 equivalents to 3H represents the OCH_3 protons. Whereas, the singlet's between 2.28-2.42 equivalent to 3 protons represent the methyl protons. Thus all the compounds are fully characterized and confirmed with their, Melting points, IR and ^{1}H-NMR spectra and are found to be in agreement with the reported literature values.

Furthermore, to compare the results of our developed method with the conventional acid catlyzed (H_2SO_4/MeOH/reflux, 4hr) synthesis of Schiff base (**3a-z & 3aa-af**) formation (**Table-2**) and we found that the acid catalyzed reactions are taking longer time and the yield is moderate, where as in our condition the reaction time is enourmously reduced to 240 fold i.e., from 240 minutes (4hr) to rapid with in one minute.

Concusion:-

Thus in conclusion we can say that we have developed a rapid and facile method for the synthesis of Sschiff bases (**3a-z & 3aa-af**) by using Ammonium Nickel Sulfate (ANS) as heterogenous catalyst. Further more, the rection is selective as only benzaldehyde are reacted where as aceophenone is fail to perform this reaction. The present method is very rapid with simple work up gives the products in good to excellent yield. The reaction is totally carried out in envirnmentally friendly condition by using green solvent MeoH and water in 1:1 ration. Thus it is anticipated that the present newly developed method will give ample chemical space to the chemist to prepare the Schiff bases in rapid and envirnmentaly benign conditions.

Experimental Data:-

All chemicals were obtained from commercial sources and used without further purification unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz for ^{1}H) in DMSO-d_6 with tetramethylsilane (TMS) as an internal standard. TLCs were performed on Merck TLC Silica gel 60 F254 plates eluting with EtOAc and developed with iodine. Melting points were determined in glass capillaries on a Mel-Temp 3.0. Mass spectra were measured on Bruker micrOTOF II or maXis (Bruker, Germany) instruments using electrospray ionization (HRESIMS). IR Spectrum was recorded on Perkin-Elmer Infrared spectrophotometer with NaCl.

General Representative Procedure for the Synthesis of Schiff Bases (3a-z & 3aa-af) by using ANS:-

To the solution of aromatic aldehyde (**2a-d**) (1 mmol) in 5 ml of methanol taken in a boiling tube was added 5 ml 10% ANS Solution in MeOH:Water (1:1) and shaken for few second. To this a solution of aromatic amine (**1a-h**) (1 mmol) in 5 ml of methanol made in separate boiling tube was added and shaken for few seconds. Rapidly the reaction mixture becomes solidified and was immediately poured into crushed ice and stirred for few minutes to get the precipitated product. (In few cases the precipitation has taken longer time). The precipitate is filtered off on buckner funnel to get the solid product which was dried over to get the crude product as solid. The crude products were recrystalized in methanol to get pure products.

Comparative Representative Procedure for the Synthesis of Schiff Bases (3a-z & 3aa-af) by using H_2SO_4:-

To the solution of aromatic aldehyde (**2a-d**) (1 mmol) and aromatic amine (**1a-h**) (1 mmol) in 10 ml of methanol, 2-3-drops of H_2SO_4 were added. The reaction mixture was reflused for 4 hr. After the completion of the reaction the rection mixture were immediately poured into crushed ice and stirred for few minutes to get the precipitated product. The precipitate is filtered off on buckner funnel to get the solid product which was dried over to get the crude product as solid. The crude products were recrystalized in methanol to get pure products.

The spetectral data of the synthesised schiff bases (**3a-z & 3aa-af**) are given below.

3a: Yellow solid: IR υ (cm^{-1}): 3049 (Ar, C-H), 1608 (s, C=N), 1530, 1492 (Ar, C-C); ^{1}H-NMR /DMSO, δ (ppm): 8.45 (s, 1 H), 7.92-7.23 (Ar-H, 10H).

3b: White solid: IR υ (cm^{-1}): 3052 (Ar, C-H), 1615 (s, C=N), 1543, 1486 (Ar, C-C). ^{1}H-NMR /DMSO, δ (ppm): 8.46 (s, 1H), 7.91-7.12 (Ar-H, 9H), 2.37 (s, 3H)

3c: White solid: IR υ (cm^{-1}): 3037 (Ar, C-H), 1607 (s, C=N), 1527, 1478 (Ar, C-C). ^{1}H-NMR /DMSO, δ (ppm): 8.54 (s, 1H), 7.91-7.12 (Ar-H, 9H), 2.31 (s, 3H).

3d: Orange solid: IR υ (cm^{-1}): 3018 (Ar, C-H), 1617 (s, C=N), 1580, 1526 (Ar, C-C). ^{1}H-NMR /DMSO, δ (ppm): 8.48 (s, 1H), 7.90-6.92 (Ar-H, 9H), 3.83 (s, 3H, OCH3).

3e: Pale Yellow solid: IR υ (cm^{-1}): 3321 (br, OH), 3110 (Ar, C-H), 1637 (s, C=N), 1890, 1535 (Ar, C-C). ^{1}H-NMR /DMSO, δ (ppm): 9.58 (s, 1H), 8.08 (s, 1H), 6.78-7.49 (ArH, 9H).

3f: Reddish Yellow solid: IR υ (cm^{-1}): 1595, 1575, 1500 (Ar-C=C-) 2925, (Ar-C-H), 2910 1623, (C=N-) 1456 9(s NO_2) and 1338, 1180(C-N). ^{1}H-NMR /DMSO, δ (ppm): 8.98 (s, 1H), 7.95 - 7.45 (ArH, 9H).

3g: Yellowish orange solid: IR υ (cm^{-1}): 1595, 1585, 1500 (Ar-C=C-), 2925, 2980 (Ar-C-H), 1628 (-C=N-), 1487 (s,-NO_2),1356 and 1185 (-C-N). ^{1}H-NMR /DMSO, δ (ppm): 8.77 (s, 1H), 7.90 - 7.34 (ArH, 9H).

3h: Yellow solid: IR υ (cm^{-1}): 1590, 1582, 1510 (Ar-C=C-), 3035, 2980 (Ar-C-H), 1622 (-C=N-), 1440 and 1355 (s,-NO_2) and 1178 (-C-N). ^{1}H-NMR /DMSO, δ (ppm): 8.92 (s, 1H), 8.21 (s, 1H), 7.48 (ArH, 9H).

3i: Yellow solid: IR υ (cm^{-1}): 3413 (=C-OH), 3090, 2935 (Ar-C-H), 1585 (-C=N), 1516 1428 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 9.44 (OH, 1H), 8.65 (-N=CH, 1H)-, 6.76-7.84 (m, 8H), 3.78 (s, 3H, -OCH_3).

3j: Yellow solid: IR υ (cm^{-1}): 3461 (=C-OH), 3086, 2939 (Ar-C-H), 1589 (-C=N), 1522 1432 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 13.35 (s, 1H, -OH), 8.93 (s, 1H, -CH=N-), 7.33 -6.91 (m, 7H, Ar-H), 3.94 (s, 3H, -OCH_3), 2.32 (s, 3H, -CH_3).

3k: Creamy solid: IR υ (cm^{-1}): 3552 (=C-OH), 3001, 2962 2939 (Ar-C-H), 1622 (-C=N), 1586, 1153 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 11.78 (O-H, 1H), 9.23 (s, 1H, H-C=N), 8.44-6.74 (m, 7H, Ar-H), 3.85 (s, 3H, -OCH_3), 2.28 (s, 3H, -CH_3).

3l: Gray solid: IR υ (cm^{-1}): 3378 (=C-OH), 3044, 2955 (Ar-C-H), 1592 (-C=N), 1506 1434 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 11.45 (O-H, 1H), 8.53 (s, 1H, HC=N), 8.28-6.21 (m, 7H, Ar-H), 4.02 (s, 3H, -OCH_3), 3.78 (s, 3H, -OCH_3).

3m: Brown Crystal: IR υ (cm^{-1}): 3248 (=C-OH), 3012, 2922 (Ar-C-H), 1588 (-C=N), 1516 1438 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 9.70 (1H, OH), 9.61(1H, OH) 8.42 s, 1H, HC=N) 7.49- 6.85 (m, 7H, Ar-H) 3.83 (s,3H, -OCH_3).

3n: White Solid: IR υ (cm^{-1}): 3124 (=C-OH), 3054, 2901(Ar-C-H), 1592 (-C=N), 1525 (NO_2), 1518-1460 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 9.92 (s, 1H, -OH,), 8.32 (s, 1H, HC=N), 8.34-6.74 (m, 7H, Ar-H), 3.82 (s, 3H, -OCH_3).

3o: Yellow solid: IR υ (cm^{-1}): 3235 (=C-OH), 3054, 2901(Ar-C-H), 1624 (-C=N), 1564 (NO_2), 1523, 1458 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 9.75 (s, 1H, -OH,), 8.55(s, 1H, HC=N), 8.16-6.54 (m, 7H, Ar-H), 3.92 (s, 3H, -OCH_3).

3p: Orange Solid: IR υ (cm^{-1}): 3354–3480 (OH), 1628 (1624 (-C=N), 1544, 1342 (NO_2), 1512 1424 (-C=C). ^{1}H-NMR /DMSO, δ (ppm): 9.88 (s, 1H, -OH,), 8.36 (s, 1H, HC=N), 8.08-6.90 (m, 7H, Ar-H), 3.80 (s, 3H, -OCH_3).

3q: Yellow solid: IR υ (cm^{-1}): 3044 (Ar, C-H), 1620 (s, C=N), 1524, 1498 (Ar, C-C).759 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.89 (S, 1H), 6.50-7.08 (Ar-H, 9H).

3r: Cream Solid: IR υ (cm^{-1}): 3020 (Ar, C-H), 1594 (s, C=N), 1530, 1492 (Ar, C-C).760(Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.45(s.lH), 7.13 -7.82(m.8H), 2.42 (s, 3H).

3s: White solid: IR υ (cm^{-1}): 2985 (Ar, C-H), 1624 (s, C=N), 1543, 1498 (Ar, C-C).783 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.25 (s.lH), 7.21 -7.88 (m.8H), 2.28 (s, 3H).
3t: Orange solid: IR υ (cm^{-1}): 3035 (Ar, C-H), 1625 (s, C=N), 1600, 1576 (Ar, C-C).825 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.42 (s, 1H), 7.83 -6.96 (8H, ArH), 3.87 (s, 3H, OCH_3).
3u: Brown Solid: IR υ (cm^{-1}): 3350 (br, OH), 3120 (Ar, C-H), 1654 (C=N), 1620, 1568 (Ar, C-C).795, (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 9.57 (s, 1H), 8.60 (s, 1H), 7.88 -6.85 (8H, ArH).
3v: Yellow solid: IR υ (cm^{-1}): 3065 (Ar, C-H), 1628 (C=N), 1333, 1505 (Ar, C-C), 1376 (NO_2), 815 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.83 (s,1H), 8.21-7.21 (8H, ArH).
3w: Yellow solid: IR υ (cm^{-1}): 3038 (Ar, C-H), 1608 (C=N), 1320, 1512 (Ar, C-C). 1378 (NO_2), 873 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.83 (s, 1H), 8.21-7.21 (8H, ArH).
3x: Yellow solid: IR υ (cm^{-1}): 3080 (Ar, C-H), 1625 (C=N), 1333, 1505 (Ar, C-C). 1376 (NO_2), 832 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.84 (s, 1H), 8.20-6.76 (m, 8H).
3y: White solid: IR υ (cm^{-1}): 3021 (Ar, C-H), 1604 (s, C=N), 1508, 1465 (Ar, C-C).774 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.75 ((S, 1H), 6.48-7.28(Ar-H, 9H).
3z: Yellow solid: IR υ (cm^{-1}): 3024 (Ar, C-H), 1625 (s, C=N), 1562, 1484 (Ar, C-C), 812 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.92 (1H, s, CH=N), 8.22–7.23 (8H, m, ArH), 2.38 (3H, s, CH_3).
3aa: Yellow solid: IR υ (cm^{-1}): 2967 (Ar, C-H), 1618 (s, C=N), 1548, 1475 (Ar, C-C), 795 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.57 (s. lH), 7.35 -7.91 (m.8H), 2.35 (s, 3H).
3ab: Orange solid: IR υ (cm^{-1}): 3045 (Ar, C-H), 1610 (s, C=N), 1621, 1553 (Ar, C-C), 828 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.95 (s, 1H), 8.22-6.98 (m, 8H), 3.85 (s, 3H, OCH_3).
3ac: Brown solid: IR υ (cm^{-1}): 3315 (br, OH), 3025 (Ar, C-H), 1618 (C=N), 1632, 1588 (Ar, C-C), 818 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 9.44 (s, 1H, OH) 8.38 (s, 1H), 6.76-7.20 (8H).
3ad: Yellow solid: IR υ (cm^{-1}): 2987 (Ar, C-H), 1615 (C=N), 1534, 1332 (Ar, C-C), 1365 (NO_2), 868 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.62 (s, 1H), 8.35-7.36 (8H, ArH).
3ae: Yellow solid: IR υ (cm^{-1}): 2995 (Ar, C-H), 1612 (C=N), 1528, 1338 (Ar, C-C), 1362 (NO_2), 856 (Ar-Cl). ^{1}H-NMR /DMSO, δ (ppm): 8.54 (s, 1H), 8.26-7.48 (8H, ArH).
3af: Yellow solid: IR υ (cm^{-1}): 3105, 3073 (Ar, C-H), 1600, (C=N), 1509, (C=C), 1337, 1193 (NO_2), 1049, 859,755 (C-Cl). ^{1}H-NMR /DMSO, δ (ppm): 9.12 (s, 1H), 6.50-7-02 (m, 8H).

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