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## Highly potential synthesis and characterization of new Schiff's bases derived from different di-amine and aromatic aldehyde compounds by using dichloro methane as a solvent at reflux condition within few hours

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### ABSTRACT

In this recent method a potential and significant synthesis of Schiff's base compounds were developed from various reactions of substituted aromatic aldehyde and di-amines; such as Salicylaldehyde, 3, 4-Tertiary butyl 2-Hydroxy benzaldehyde, Ethylene diamine, 2-Amino Pyridine, 1,2-di-amino Benzene, 1,3-Diamino Propane by using Dichloro methane as a solvent within few hours with excellent yields of products at reflux condition. Schiff's base compounds were characterized by means of IR, <sup>1</sup>H NMR spectroscopic data. Above Schiff's bases shows new series of medicinally important compounds. Advantage of this method is high yields of products, simplicity of reaction, no longer reaction time and easy workup procedure.

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### KEYWORDS

Salicylaldehyde;  
3,4-Tertiary butyl 2-hydroxy  
benzaldehyde;  
Ethylene diamine;  
2-Amino pyridine;  
1,2-diamino benzene;  
1,3-diamino propane;  
Dichloro methane.

### INTRODUCTION

Schiff's base compounds and their complexes have significant importance in chemistry. Every year number of reports is published on preparation of these compounds and their application in chemical reactions<sup>[1]</sup>. Such type of ligands represents vast utilized classes of new series of compounds in metal coordination chemistry<sup>[2]</sup>. The Schiff's base compounds and their complexes are widely applied in enantioselective cyclopropanation of styrene's<sup>[3]</sup>. Asymmetric addition of cyanide to aldehydes<sup>[4]</sup>. Schiff base compounds containing imines group (-RC=N-) are usually formed by the condensation of primary amine and Diamine with an active carbonyl compound in a methanol solvent<sup>[5]</sup>. Some synthesis methods have not been entirely satis-

factory owing to a number of drawbacks such as low yields and tedious workup procedures<sup>[6]</sup>. According to the tremendous scope of Schiff bases possesses an inherent imidazopyridine, with a high class of compounds of medicinal importance and oblige. Over the past few decades, significant research has been directed towards the development of new technologies for environmentally benign processes (green chemistry)<sup>[7]</sup>. The dipyriddy can attach two molecules of an alkyl-halide thus forming a bi-quaternary base. The method of preparation consisted in preparing first a quaternary base of pyridine and condensing two molecules of it to a dipyriddy compound by treatment with sodium amalgam and successive oxidation<sup>[8]</sup>. The deep Studies on a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists<sup>[9,10]</sup>. According to ligands, the

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Isoxazole Schiff bases, methyl salicylaldehyde and 4-methoxy salicylaldehyde with 3-amino-5-methyl Isoxazole potentiometrically titrated with their complexes with Cu(II) Ni(II), Co(II), Zn(II) and VO(IV)<sup>[11]</sup>. The Schiff base ligands have been prepared from carbonyl compounds within a short time, catalyzed by P<sub>2</sub>O<sub>5</sub> under solvent free conditions<sup>[12]</sup>. Considerable interest attached with the chemistry of Schiff bases<sup>[13]</sup>, obtained from heterocyclic aldehyde, also various heterocyclic Schiff bases having O,N and S donor atoms, have been reported by several scientists<sup>[14-16]</sup>. Most of the routes involve acylation reaction of a 2-aminomethylpyridine followed by cyclization with phosphorus oxychloride or polyphosphoric acid<sup>[17]</sup>. According to high yielding and environment proactive reactions, there some methods are significant for one pot synthesis of pyridil imidazo [1,5-a] pyridines catalyzed by K<sub>4</sub>FeCN<sub>6</sub> under free solvent conditions; which is technologically and economically attractive<sup>[18]</sup>. According to applications root from the facts that the Schiff's base are capable of chelating various metal ions and the resultant complexes possess a wide range of magnetic, photo physical, and electrochemical properties. Thus, the increment of synthetic methodologies for *N,N*-bidentate ligands is of paramount importance in chemistry. *N,N*-Bidentate ligands with mixed five- and six-membered heterocyclic are a high class of compounds in the pursuit of structural diversity for property performance. In particular, 1-pyridylimidazo [1,5-*a*] pyridines possess a bidentate structural feature with a pyridil unit directly next to a fused imidazo and have emerged as a new class of ligands<sup>[19,20]</sup>.

## RESULTS AND DISCUSSION

The deep and verified discussion was carried out for medicinally important evaluation of Schiff base compounds of Salicylaldehyde, 3,4-Tertiary butyl 2-hydroxy benzaldehyde, ethylene diamine, 2-Amino Pyridine, 1,2-di-amino Benzene, 1,3-diamino Propane were formed in dichloromethane as solvent at reflux condition. The rate of reaction of high yield was observed when higher molar ratios of both reactants were used. We are using here different types of substituted diamines and aldehyde for the synthesis of Schiff's bases within few hours. The special features of these efficient reaction is that

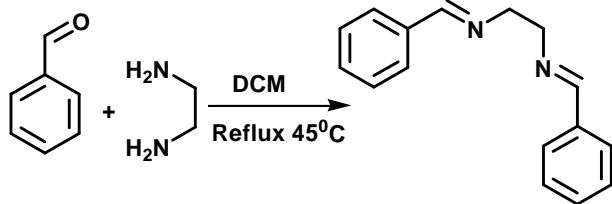
the reaction products were formed without using any type of catalytic amount. There was no requirement to use catalyst. In TABLE 1 here we may observe a series of new Schiff base compounds using Dichloro Methane (DCM) as solvent at reflux condition. We are kindly interested to report that the reaction of different diamines with substituted aldehyde was obtained as the corresponding Schiff base compounds in good to excellent yields within few hours without using any type of catalytic amount than some of the previously reported methods<sup>[21,22]</sup>. We may easily compare yield of product and product formation time (in hours) of reactions as shown in entry 4 & 5 in TABLE 1. In the reaction of entry 5 in TABLE 1 the salicylaldehyde is taken as (1 mol) and 2-amino pyridine is (1 mol) while in entry 1-4 the molar ratios of reactions are taken in (2:1) ratio respectively.

According to Scheme 1 and Scheme 2 there was a reactions of Schiff bases of ethylene diamine, benzaldehyde and reactions of 3,5 di tertiary butyl 2-hydroxy benzaldehyde with the help of these two (Scheme 1 and Scheme 2) schemes we may get series of high yielding and medicinally important compounds. It is great importances that yield of products are largely affected due to these types of series of diamines and aldehyde respectively; in DCM as solvent under reflux condition at 45°C temperatures without using any catalyst. Within few hours product formation occurs. As per study of past literature survey most of reactions extending the reaction time to several days. Possible and very simple reaction mechanism can be discussed as shown in following diagram.

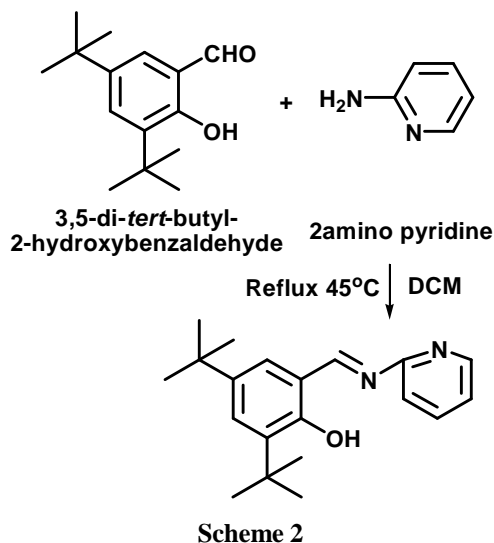
The structures of products were assigned by spectroscopic data from Chemdraw Software. In the IR spectra characteristic Schiff base compounds (C=N) stretching frequency and <sup>1</sup>H NMR may be observed.

## CONCLUSION

Schiff's base compounds have been synthesized from different aldehyde and Di-amine compounds without using any type of catalyst with excellent high yields within few hours at reflux condition. In shortly these reactions is having significant, mild and efficient base for synthesis of a new series of various Schiff's base compounds. Simply we have shown significant



Scheme 1



Scheme 2

path to synthesize a series of medicinally important compounds.

## EXPERIMENTAL

All the chemicals were purchased from Merck German chemically company in high quality standard and purity. IR spectra were recorded as KBr pellets on SHIMADZU spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> and DMSO with (400 MHz) spectrometer. Purity of all substances and reaction was monitored by TLC column chromatography using silica gel (60-120 mesh size).

### General procedure for preparation of schiff's base compounds

In a typical reaction, add a mixture of aldehyde (2 mol), Diamine (1 mol) was taken in 100 ml, round bottom flask containing 10-15 ml, of Dichloromethane. Dissolve complete reaction mixture by continuous stirring then add 2-4 porcelain pieces in round flask to avoid bumping. Reflux the reaction mixture for appropriate time. The progress of reaction was monitored on TLC (PE-EtOAc 7:3) portion; after completion of reaction,

TABLE 1 : Reactions of different benzaldehyde, Salicylaldehyde, 3,4-tertiary butyl 2-hydroxy benzaldehyde with different Diamines in DCM as solvent at reflux condition

Entry	Amine Substrate (2)	Aldehyde substrate (3)	Product (4)	Time in (Hrs:Minute)	Yield in %
1	Ethylene Diamine	Salicylaldehyde	A	6:14	87
2	1,3-Diamino Propane	Salicylaldehyde	B	6:04	89
3	1,2-Diamino Benzene	Salicylaldehyde	C	5:45	91
4	Ethylene Diamine	3,4-tertiary butyl 2-hydroxy benzaldehyde	D	5:20	86
5	2-Amino Pyridine	Salicylaldehyde	E	4:56	92
6	2-Amino Pyridine	3,5-tertiary butyl 2-hydroxy benzaldehyde	F	4:30	90
7	Ethylene Diamine	Benzilidene	G	2:39	93

filtered off the solid product and washes it with cold dichloromethane. The crude was further purified by recrystallisation in ethanol and the desired pure Schiff's base compounds were obtained in 83-93 % yield. Schiff's base compounds were identified and confirmed on the basis of spectroscopic data.

### Spectroscopic and analytical data for schiff base compounds

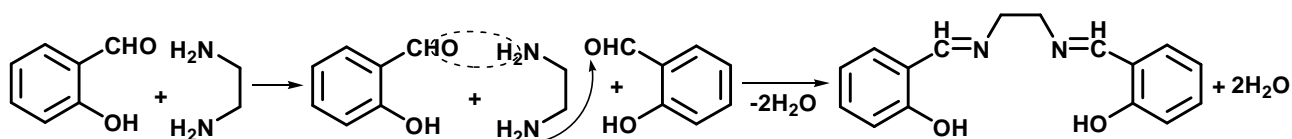
#### 2,2'-{ethane-1,2-diylbis [nitrilo (*E*) methylylidene]} diphenol (4a)

Color: bright shine yellow crystals, Melting Point: 134-136°C. FTIR (KBr pellets): 432.07, 476.43, 648.10, 748.41, 856.42, 976.98, 1019.41, 1042.56, 1149.61, 1200, 1284.63, 1374.33, 1416.73, 1459.20, 1496.81, 1576.86, 1632.80, 1798.68, 1941.42, 2926.11, 3056.31, 3600. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 3.92 (s, 4H), 6.90 (m, 4H), 7.24 (m, 4H), 8.34 (s, 2H), 13.22 (bs, 2H) Anal. Calcd. For C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.62; H, 6.01; N, 10.44; O, 11.93. Found C, 71.18; H, 5.81; N, 10.11; O, 11.13.

#### 2,2'-{propane-1,3-diylbis [nitrilo (*E*) methylylidene]} diphenol (4b)

Color: yellow crystals, Melting Point: 78-81°C. FTIR (KBr pellets): 462.93, 518.87, 567.09, 642.32, 663.53, 754.19, 777.43, 852.56, 883.43, 974, 1004, 1052, 1149, 1208, 1280, 1417, 1458, 1494, 1581, 1636, 1785, 1902, 2061, 2113, 2444, 2671, 2941, 3003, 3063, 3500.24. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 2.11 (dd, 2H), 3.72 (t, 4H), 6.92 (m, 4H), 7.31 (m, 4H), 8.37 (s, 2H), 13.43 (bs, 2H) Anal. Calcd. For C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.32; H, 6.43; N, 9.92; O, 11.33. Found C,

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Possible reaction mechanism

TABLE 2 : Synthesis of schiff's base compounds

Entry	Substituted Aldehyde	Product (4-a)	Time in (Hours: minutes)	Yield(%)
1			6:14	87
2			6:04	89
3			5:45	91
4			5:20	86
5			4:56	92
6			4:30	90
7			2:39	93

72.00; H, 6.06; N, 9.19; O, 10.82.

**2,2'-[1,3-phenylenebis [nitrilo(*E*) methylydene]] diphenol (4c)**

Color: bright orange crystals, Melting Point: -174-

176°C. FTIR(KBr): 438.82, 501, 582, 640, 759, 809, 857, 907, 975, 1037, 1110, 1152, 1193, 1231, 1278, 1368, 1404, 1453, 1484, 1562, 1614, 1810, 1887, 1952, 1942, 1997, 2054, 2108, 2262, 2661, 2988, 3059, 3400.52 <sup>1</sup>H NMR (200.13 CDCl<sub>3</sub>): 6.90-

7.42(m,12H), 8.65(s,2H), 13.09(s,2H). Anal. Calcd. For  $C_{20}H_{16}N_2O_2$ : C, 75.93; H, 5.10; N, 8.86; O, 10.11. Found C, 75.21; H, 4.80; N, 8.16; O, 9.94.

**6,6'-((1E,1'E)-(propane-1,3-diylbis (azanylylide-  
ne))bis(methanylylidene))bis(2,4-di-tert-  
butylphenol) (4d)**

Color: bright yellow crystals, Melting Point: 184-186°C. FTIR (KBr): 444.61, 513, 587, 644, 709, 772, 836, 878, 975, 1040, 1132, 1206, 1270, 1319, 1362, 1440, 1468, 1592, 1627, 2866, 2905, 2956, 3500.56.  $^1H$  NMR (200.13  $CDCl_3$ ): 1.28 (s, 18H), 1.43(s,18H), 3.91(s,2H), 7.07(s,2H), 7.37(s,2H), 8.38(s,2H), 13.65(bs,2H). Anal. Calcd. For  $C_{32}H_{48}N_2O_2$ : C, 78.00; H, 9.82; N, 5.69; O, 6.49. Found C, 77.45; H, 9.35; N, 5.12; O, 6.00.

**2-[(E)-(pyridin-2-ylimino) methyl] phenol (4e)**

Color: dark orange crystals, Melting Point: -74-76°C. FTIR (KBr pellets): 452, 503, 577, 623, 676, 756, 786, 846, 914, 956, 997, 1112, 1146, 1187, 1280, 1351, 1410, 1430, 1462, 1497, 1554, 1586, 1607, 1838, 1957, 2057, 2109, 2384, 2433, 2484, 2560, 2597, 2732, 2801, 2862, 2930, 3052, 3206.76, 3400.15  $^1H$  NMR (200.13  $CDCl_3$ ): 7.01(m,2H), 7.25-7.52(m,4H), 7.77(dd,1H), 8.49(d,1H), 9.44(s, 1H), 13.46(s, 1H) Anal. Calcd. For  $C_{12}H_{10}N_2O$ : C, 72.71; H, 5.08; N, 14.13; O, 8.07. Found C, 72.11; H, 4.81; N, 13.77; O, 7.86.

**2,4-di-tert-butyl-6-[(E)-(pyridin-2-ylimino) methyl] phenol (4f)**

Color: yellow crystals, Melting Point: 115-118°C. FTIR (KBr pellets):430.07, 466.33, 640.1048.41, 850.40, 970.18, 1010, 1032.56, 1138.61, 1200, 1270.63, 1354, 1400, 1450, 1480, 1570, 1630, 1790.48, 2926.11, 3056.31, 3600.  $^1H$  NMR (200.13 MHz  $CDCl_3$ ):3.92(s, 4H), 6.84(m,4H), 7.20(m, 4H), 8.30 (s, 2H), 13.20 (bs, 2H) Anal. Calcd. For  $C_{20}H_{26}N_2O$ : C, 77.38; H, 8.44; N, 9.02; O, 5.15. Found C, 77.02; H, 8.04; N, 8.76; O, 4.86.

**N,N'-bis [(1E)-phenyl ethylene] ethane-1,2-di-  
amine (4g)**

Color: bright yellow crystal, Melting Point: 124-126°C. FTIR (KBr pellets):432, 476.02, 649, 746, 858, 976, 1022, 1032, 1151, 1203, 1284, 1374, 1421, 1462, 1490, 1544, 1622, 1748, 1943, 2928, 3040,

3501. Anal. Calcd. For  $C_{16}H_{16}N_2$ : C, 81.32; H, 6.82; N, 11.85. Found C, 81.00; H, 6.14; N, 11.28.

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