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## Novel One-Pot Synthesis of Schiff Base Compounds Derived From Different Diamine & Aromatic Aldehyde Catalyzed by P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> Under Free-Solvent Condition at Room Temperature

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### ABSTRACT

A potential method for one-pot synthesis of Schiff base compounds derived from different aldehyde and Di-amine compounds like substituted aromatic aldehyde and Diamines; 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 catalytic amount of P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> have catalyzed the ligand formation in dry media under free-solvent condition at room temperature. This type of excellent method avoids use of hazardous solvents, longer reaction time and tedious work up procedure. Advantage of this efficient method is excellent yield of products in crystalline form, short reaction time, simplicity of work up procedure and no use of any type of hazardous solvents. Simply this reaction is environmentally Proctive (non polluted) and economically attractive method for synthesis of Schiff base compound. All these Schiff base compounds were characterized by means of IR, <sup>1</sup>H-NMR and their Elemental analysis as (C, H, N, and O) spectral analysis data. Above Schiff base compounds shows inherent new generation of series of pharmaceutically important compounds.

**Keywords:** Salicylaldehyde, 3, 4-Tertiary butyl 2-Hydroxy Benzaldehyde, Ethylene Diamine, 2-Amino Pyridine, 1, 2-Diamino Benzene, 1, 3-Diamino Propane, Dichloro Methane and P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>.

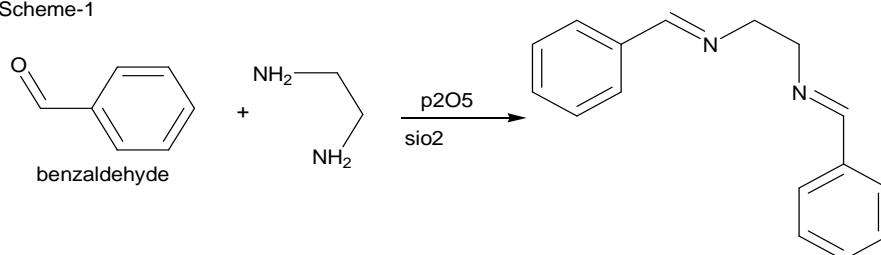
### INTRODUCTION

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

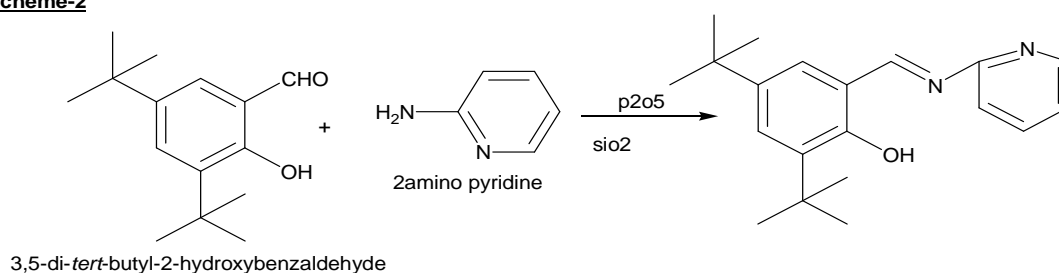
are widely applied in enantioselective cyclopropanation of styrene's<sup>3</sup>. Asymmetric addition of cyanide to aldehydes<sup>4</sup>. Schiff base compounds containing imines group (-RC=N-) are usually formed by the condensation of primary amine and Diamine with an active carbonyl compound in a methanol solvent<sup>5</sup>. Some synthesis methods have not been entirely satisfactory 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 dipyrindyl 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 dipyrindyl 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 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>14,15,16</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>.

### Reactions:

Scheme-1



Scheme-2



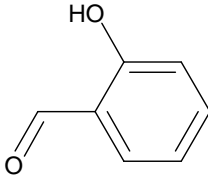
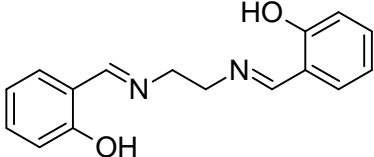
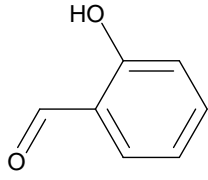
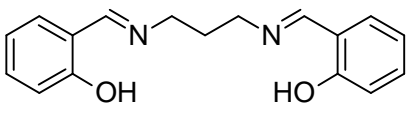
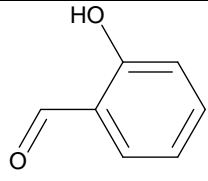
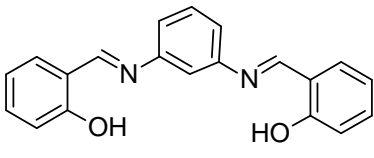
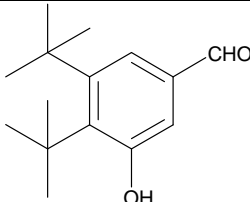
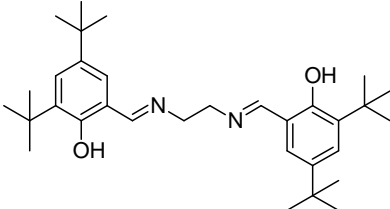
## EXPERIMENTAL SECTION

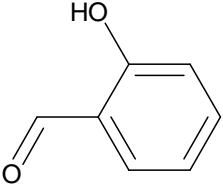
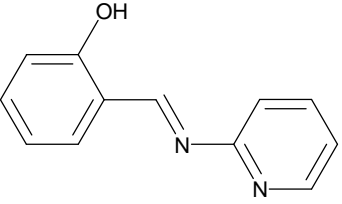
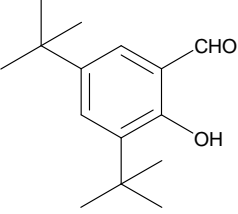
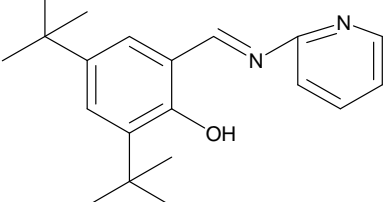
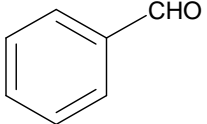
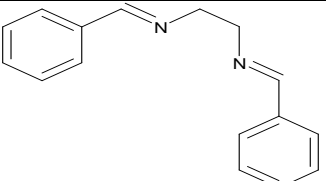
All the chemicals were purchased from Merck German chemically company in high quality standard and purity. IR spectra were recorded as KBr pellets on SHIMADZU spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> and DMSO with (400 MHz) spectrometer. Purity of all substances and reaction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

**General Procedure For Preparation of Schiff's Base Compounds:**

In a detailed discussion of reaction, a mixture of benzaldehyde (2 mmol), amine (2mmol) and P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> mixture (0.4 g, 2mol % of P<sub>2</sub>O<sub>5</sub>/benzaldehyde) was grounded together in a mortar. The resulting mixture was placed in a flask and mechanically stirred for 30-35 minutes. The progress of reaction was monitored on TLC. After completion of reaction ethanol (40-50 ml) was added to reaction mixture, filtered off the solid product and washed with cold methanol. The crude product was further purified and recrystallised in petroleum ether/ diethyl ether. Desired Schiff base compounds are obtained up to 92 % yield<sup>21</sup>.

**Table -2: Synthesis of Scheff's Base Compounds**

Entry	Substituted Aldehyde	Product (4-a)	Time in (minutes)	Yield (%)
1	 salicylaldehyde		16:14	88
2	 salicylaldehyde		26:04	90
3	 salicylaldehyde		15:45	92
4	 3,4-di- <i>tert</i> -butyl-5-hydroxybenzaldehyde		15:20	88

5	 salicylaldehyde		14:56	93
6	 3,5-di- <i>tert</i> -butyl-2-hydroxybenzaldehyde		19:30	92
7	 benzaldehyde		13:39	92

### Spectroscopic and Analytical Data for Schiff Base Compounds:

**2, 2'-{ethane-1, 2-diylbis [nitrilo (*E*) methylidene]} diphenol No. [4-a]:** Colour: bright shine yellow crystals, Melting Point: 134-136 °C. FTIR (KBr pellets): 432.09, 476.40, 648.11, 748.43, 856.45, 977.02, 1019.38, 1042.52, 1149.59, 1200, 1284.60, 1374.30, 1416.71, 1459.18, 1496.84, 1576.89, 1632.83, 1798.70, 1941.44, 2926.13, 3056, 3600. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 3.90(s, 4H ), 6.88(m,4H), 7.22(m,4H), 8.32 (s, 2H), 13.20 (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, 5.80; N, 10.10; O, 11.15.

**2, 2'-{propane-1, 3-diylbis [nitrilo (*E*) methylidene]} diphenol [4-b]:** Colour: yellow crystals, Melting Point: 78-81 °C. FTIR (KBr pellets): 462.90, 518.85, 567.13, 642.30, 663.51, 754.17, 777.41, 852.54, 883.41, 976, 1007, 1050, 1147, 1206, 1278, 1415, 1456, 1492, 1579, 1634, 1783, 1900, 2060, 2111, 2441, 2670, 2940, 3002, 3061, 3500.22. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): d 2.09(dd, 2H), 3.70(t, 4H), 6.90(m,4H), 7.29(m,4H), 8.35(s, 2H), 13.41(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, 72.00; H, 6.05; N, 9.17; O, 10.80.

**2,2'-{1,3-phenylenebis[nitrilo(*E*)methylidene]}diphenol [4-c]:** Colour: bright orange crystals, Melting Point: -174-176 °C. FTIR(KBr): 438.80, 500, 581, 642, 758, 810, 858, 906, 974, 1036, 1113, 1153, 1192, 1230, 1277, 1369, 1402, 1452, 1482, 1563, 1612, 1808, 1886, 1950, 1940, 1995, 2052, 2106, 2260, 2662, 2986, 3058, 3400.52. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 6.88-7.40(m, 12H), 8.63(s, 2H), 13.07(s, 2H). Anal. Calcd. For C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 75.93; H, 5.10; N, 8.86; O, 10.11. Found C, 75.20; H, 4.79; N, 8.14; O, 9.92.

**6,6'-((1*E*,1'*E*)-(propane-1,3-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butyl phenol) [4-d]:** Colour: bright yellow crystals, Melting Point: 184-186 °C. FTIR (KBr): 444.60, 512, 588, 643, 707, 771, 835, 877, 976, 1039, 1131, 1205, 1271, 1318, 1361, 1441, 1469, 1591, 1626, 2867, 2904, 2955, 3500. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 1.27(s, 18H), 1.41(s, 18H), 3.90(s, 2H), 7.06(s, 2H ), 7.36(s, 2H), 8.37(s, 2H), 13.64(bs, 2H). Anal. Calcd. For C<sub>32</sub>H<sub>48</sub>N<sub>2</sub>O<sub>2</sub>: C, 78.00; H, 9.82; N, 5.69; O, 6.49. Found C, 77.44; H, 9.34; N, 5.11; O, 6.00.

**2-[(*E*)-(pyridin-2-ylimino) methyl] phenol [4-e]:** Colour: dark orange crystals, Melting Point: -74-76 °C. FTIR (KBr pellets): 451, 502, 576, 622, 675, 755, 785, 845, 913, 955, 996, 1111, 1145, 1186, 1279, 1349, 1411, 1429, 1461, 1497, 1552, 1585, 1606, 1837, 1956, 2056, 2108, 2383, 2432, 2483, 2559, 2596, 2731, 2800, 2861, 2929, 3051, 3205.76, 3400.12. <sup>1</sup>H NMR (200.13 MHz CDCl<sub>3</sub>): 7.00(m, 2H), 7.24-7.51(m, 4H),

7.76(dd,1H), 8.48(d,1H), 9.43(s, 1H), 13.45(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, 72.10; H, 4.80; N, 13.76; O, 7.85.

**2, 4-di-tert-butyl-6-[(E)-(pyridin-2-ylimino) methyl] phenol [4-f]:** Colour: yellow crystals, Melting Point: 116-118 °C. FTIR (KBr pellets):430.05, 466.31, 640, 1048.41, 850.41, 970.16, 1010, 1032.54, 1138.60, 1200, 1270.61, 1353, 1400, 1451, 1481, 1571, 1631, 1790.46, 2926.10, 3056.31, 3600.  $^1H$  NMR (200.13 MHz CDCl<sub>3</sub>):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, 77.01; H, 8.03; N, 8.74; O, 4.84.

**N, N'-bis [(1E)-phenyl ethylene] ethane-1, 2-diamine [4-g]:** Colour: bright yellow crystal, Melting Point: 123-126 °C. FTIR (KBr pellets):431, 476.01, 648,745, 858, 976, 1022, 1032, 1151, 1203, 1284, 1373, 1420, 1461, 1489, 1542, 1621, 1747, 1941, 2927, 3040

## RESULTS AND DISCUSSION

In a typical reaction substituted aldehyde was treated with different types of amines and diamines; such as Salicylaldehyde, 3, 4-Tertiary butyl 2-Hydroxy Benzaldehyde, Ethylene Diamine, 2-Amino Pyridine, 1, 2-Di-amino Benzene, 1, 3-Diamino Propane in the presence of P<sub>2</sub>O<sub>5</sub> supported on SiO<sub>2</sub> as catalyst without using any solvent by crushing in a mortar at room temperature within few minutes. There is no requirement to use any solvent. P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> was used as catalyst in solvent-free media. Here we are kindly interested to report that the reaction of different substituted aldehyde, amines and di-amines obtained as corresponding Schiff base compounds in excellent yields, in shorter time under free solvent condition at room temperature. The desired results are indicated in Table-1, as shown in Table-1, vast and new series of different Schiff's base compounds were synthesized using P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> as catalyst in solvent free media by crushing in a mortar, at room temperature. In comparison, the reaction of Salicylaldehyde, 3,4-tertiery butyl 2-hydroxy benzaldehyde with 2-amino pyridine, ethylene diamine in absence of catalyst as shown at entry no.[8,9] in Table-1, found very low yield of compound and longer reaction time while to verify detailed study, the progress of this methodology, various diamines with different substituted aldehyde were treated in the presence of P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> the desired results of such studies are mentioned in Table-1Entry(1-7). In Table-1 Entry [5] the salicylaldehyde is taken as (1 mol) and 2-amino pyridine is (1 mol) while in Entry No. [1, 2, 3 & 4] the molar ratios of reactions are taken in (2:1) ratio respectively. According to scheme (1 & 2) we may easily obtain a vast series of excellent high yield products and pharmaceutically important compounds by using P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> as catalyst under free solvent condition at room temperature. In scheme (1, 2 & 3) the reaction is formed by using Dichloromethane as solvent at reflux condition.

**Table-1: Reactions of different benzaldehyde, Salicylaldehyde, 3, 4-tertiery butyl 2-hydroxy benzaldehyde with different Di-amines in DCM as solvent at reflux condition.**

Entry	Amine Substrate (2)	Aldehyde Substrate (3)	Product (4)	Time in (Minute)	Yield in %
1	Ethylene Di-amine	Salicylaldehyde	A	16:14 sec.	88
2	1,3-Diamino Propane	Salicylaldehyde	B	26:04 sec.	90
3	1,2-Diamino Benzene	Salicylaldehyde	C	15:45 sec.	92
4	Ethylene Di-amine	3,4-tertiery butyl 2-hydroxy benzaldehyde	D	15:20 sec.	88
5	2-Amino Pyridine	Salicylaldehyde	E	14:56 sec.	93
6	2-Amino Pyridine	3,5-tertiery butyl 2-hydroxy benzaldehyde	F	19:30 sec.	92
7	Ethylene Diamine	Benzilidene	G	13:39 sec.	92
8	Ethylene Di-amine	3,4-tertiery butyl 2-hydroxy benzaldehyde	D	4 Hours20 min	72
9	2-Amino Pyridine	Salicylaldehyde	E	6 hours 34 min	79

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

In a typical reaction mild and significant Schiff base compound have been synthesized from different aldehyde and Diamine compounds using P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> as catalyst with excellent yield of products within few minutes by crushing in a mortar at room temperature under free solvent condition. In short these types of reactions are environ mentally Proctive, technically and economically attractive. Gives high yield of products, short reaction time without using any type of hazardous solvent. Simply we have shown significant path to synthesize a variety of new series of medicinally important and excellent scientific future based Schiff base compounds. , 3500. Anal. Calcd. For C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>: C, 81.32; H, 6.82; N, 11.85. **Found** C, 81.00; H, 6.14; N, 11.28.

### Acknowledgements

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