

An Efficient Method for Chemoselective Reduction of Nitro Compounds Using Bimetallic Fe-Ni NPs/H₃PW₁₂O₄₀·xH₂O System

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The selective reduction of nitro compounds by treatment with bimetallic Fe-Ni nanoparticles (NPs) and tungstophosphoric acid hydrate (H₃PW₁₂O₄₀·xH₂O) in H₂O is reported. The method has been applied to a broad range of nitro compounds with different sensitive functionalities, including halides, carbonyl, hydroxyl, aldehyde, methyl, acetyl, nitrile, and ester substituents with excellent yields. The reaction yielded single product in all cases with very high yield. The simple experimental procedure and easy purification make the protocol advantageous.

Keywords: Amines; Bimetallic Fe-Ni NPs; Chemoselective reduction.

INTRODUCTION

Reduction of the nitro compounds to amines which find applicability in diverse fields including dyes, pharmaceuticals, agrochemicals, photographic, antioxidants, and conducting polymers, is a very useful synthetic transformation.¹⁻³ To date, there are vast arrays of reagents which can be used to convert nitro compounds to their corresponding amines. Conventional methods of reduction of nitro compounds use hydrogenation, electron-transfer, electrochemical and hydride transfer conditions.^{4,5}

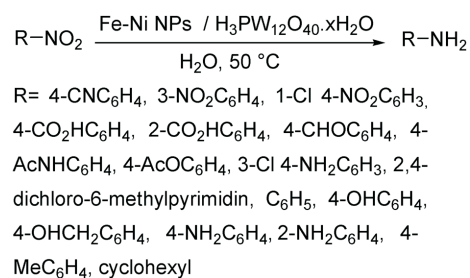
These methods involve activated metal catalysis^{6,7} and transition-metal-catalyzed hydrogenation,^{8,9} although the latter often employs harsh reaction conditions affecting other reduction-sensitive functionalities such as halides, ketones, aldehydes, esters, and nitriles in addition to the nitro substituent.¹⁰⁻¹² The reduction of nitroarenes employing stoichiometric reagents are often associated with unwanted side products, such as hydroxylamine.^{13,14} Therefore, the catalytic hydrogenation of nitroarenes has been actively pursued using many readily available metal catalysts such as copper, gold, iron, palladium, platinum, and rhodium immobilized on solid supports,¹⁵⁻³³ and several hydrogen sources have been utilized, including hydrogen gas,^{34,35} silanes,³⁶⁻³⁸ and hydrazine derivatives.³⁹⁻⁴²

In contrast to the costly metal catalysts mentioned above, iron is one of the most economical and environmentally friendly metal catalysts.⁴³ The selective reduction of aryl nitro compounds using iron powder and dilute acid^{44,45} have been reported as efficient methods for the synthesis of aryl amines in good yields. However, notable disadvantages

to these methods include high reaction temperatures, relatively long reaction times, and the incompatibility of acid-sensitive functional groups. The use of milder conditions, for example, acetic acid as solvent, has been reported, but high temperatures and longer reaction times are still required^{46,47} and metals such as indium, tellurium, and samarium are needed. Other reagents reported for this reaction include sodium borohydride,⁴⁸ ruthenium carbonyl,⁴⁹ hydrazine hydrate,⁵⁰ ionic liquids,⁵¹ and Raney nickel.⁵² Most of the above systems lack chemoselectivity and often yield a mixture of products.

Nanomaterials are more effective than conventional reagents because of their extremely small size and tremendous surface area-to-volume ratio. In continuation of our interest in exploring the utility of nanoparticles in organic synthesis,⁵³ in the present work we would like to report an efficient and chemoselective method for the reduction of various nitro compounds to the corresponding amines by treatment with bimetallic Fe-Ni NPs/H₃PW₁₂O₄₀·xH₂O system (Scheme 1).

Scheme 1 Reduction of different nitro compounds



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RESULTS AND DISCUSSION

Initially to search for the optimum reaction condition, reducing agent, solvent, and temperature, *p*-nitrobenzotrile was considered as test substrate. The reaction was carried out with different reducing agents in various acidic media, and diverse molar ratios of reactants at different temperatures. In continuation of our interest in exploring the utility of green solvents in organic synthesis,⁵⁴ we would like to study the reduction reaction of various nitro compounds to the corresponding amines in H₂O. When *p*-nitrobenzotrile reacted with iron powder/HCl or AcOH *p*-aminobenzotrile was produced after 24 and 2.5 hours with 60 and 90% isolated yields respectively (Table 1, entries 1-2). By applying the same conditions as mentioned above and using bimetallic Fe/Ni NPs as reducing agent, the product was obtained with 95 and 35% isolated yields after 30 minutes (Table 1 entries 3-4). Using HOAc leads to formation of by products (Table 1, entry 4). *p*-Aminobenzotrile was obtained after 24 hours in the presence of iron powder/tungstophosphoric acid hydrate with 50% isolated yield (Table 1 entry 5), but in the presence of bimetallic Fe-Ni NPs/tungstophosphoric acid hydrate was obtained after 20 min with 95% isolated yield (Table 1, entry 6). When *p*-nitrobenzotrile reacted with Raney nickel and NaBH₄ no desired product was obtained (Table 1, entries 7-8). After screening different reducing agents in different acidic media, bimetallic Fe-Ni NPs in the presence

of tungstophosphoric acid hydrate has been found to be the most suitable reducing agent (in H₂O at 50 °C) for the reaction in terms of reaction time and yield (Table 1, entry 6). In an effort to develop better reaction conditions, different molar ratios of nitro compound/reducing agent/acid and different temperatures were screened for the reduction of *p*-nitrobenzotrile to *p*-aminobenzotrile in the presence of bimetallic Fe-Ni NPs/tungstophosphoric acid hydrate in H₂O. The yield of the reaction does not decrease drastically when the reaction was performed at room temperature (Table 1, entry 9). The molar ratio of bimetallic Fe-Ni NPs as reducing agent plays an important role in the reduction reaction. *p*-Aminobenzotrile was obtained after 24 hours with 50% isolated yield, by using 1:0.25:1 molar ratio of nitro compound/reducing agent/acid (Table 1, entry 10). To improve amine formation, different volume ratio of EtOH as a green solvent was added to the reaction mixture at various temperature (Table 1, entries 11-16). According to this study, performing the reduction reaction in different volume ratio of EtOH/H₂O does not lead to higher conversion. On the basis of this study, H₂O was chosen as solvent for further experiments.

Encouraged by the convenient reduction of *p*-cyanonitrobenzene with Fe-Ni nanoparticles/tungstophosphoric acid hydrate, we have investigated the reactions of bimetallic Fe-Ni nanoparticles/tungstophosphoric acid hydrate system with various nitro compounds. The reductions

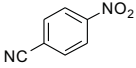
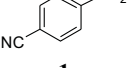
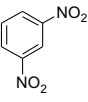
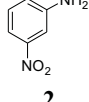
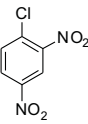
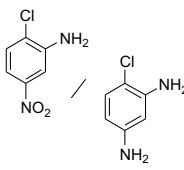
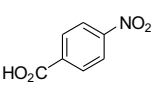
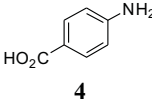
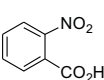
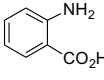
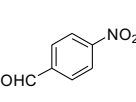
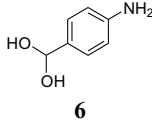
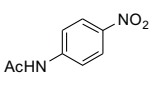
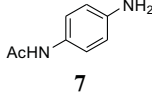
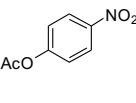
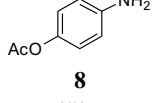
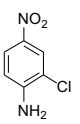
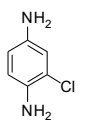
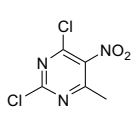
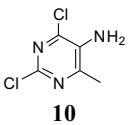
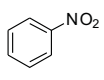

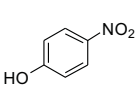
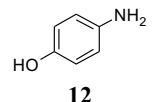
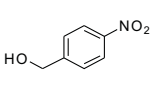
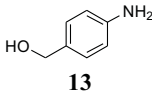
Table 1. Reduction of *p*-cyanonitrobenzene with bimetallic Fe-Ni NPs and other different reducing agent at various reaction conditions

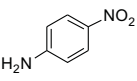
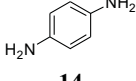
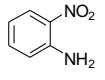
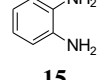
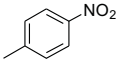
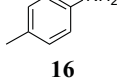
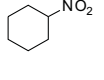
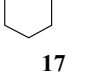
Entry	Reducing agent	Acid	Solvent EtOH/H ₂ O	Molar ratio N/R/A ^[b]	Temp (°C)	Time (h)	Conversion (%)
1 ^[a]	Fe	HCl	H ₂ O	1:3:9.7	50	24	60
2 ^[a]	Fe	HOAc	H ₂ O	1:3:8.7	50	2.5	90
3	Fe/Ni NPS	HCl	H ₂ O	1:3:9.7	50	0.5	95
4	Fe/Ni NPS	HOAc	H ₂ O	1:3:8.7	50	0.5	35
5 ^[a]	Fe	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	H ₂ O	1:3:1	50	24	50
6	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	H ₂ O	1:3:1	50	20(min)	98
7	RaneyNi	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	H ₂ O	1:3:1	50	24	5
8	NaBH ₄	none	EtOH	1:0.25:0	50	24	0
9	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	H ₂ O	1:3:1	rt	0.5	95
10	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	H ₂ O	1:2.5:1	rt	24	50
11	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	1:1	1:3:1	rt	20	100
12	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	10:1	1:3:1	rt	18	90
13	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	10:1	1:3:1	70	0.5	100
14	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	10:1	1:2:1	70	24	80
15	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	10:1	1:1:1	70	24	50
16	Fe/Ni NPS	H ₃ PW ₁₂ O ₄₀ ·xH ₂ O	10:1	1:3:1	50	0.5	100

[a] Bulk Fe powder was used as reducing agent.

[b] N/R/A: Nitro compound/ Reducingagent/Acid

Table 2. Reduction of different nitro compounds with bimetallic Fe-Ni NPs/H₃PW₁₂O₄₀·xH₂O in H₂O

Entry	Substrate	Product	Time (min)	Isolated yield (%)
1		 1	20	98
2		 2	30	95
3		 3	30	85/10
4		 4	20	98
5		 5	30	60
6		 6	30	65
7		 7	30	95
8		 8	20	92
9		 9	30	95
10		 10	10	95
11 ^[a]		 11	30/60	60/95
12		 12	60	97
13		 13	60	85

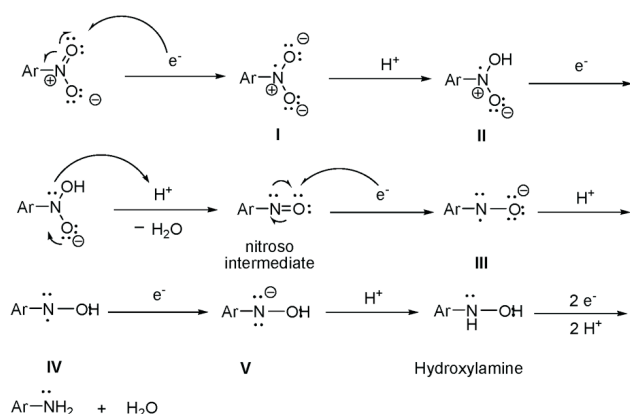
14		 14	45	93
15		 15	40	95
16		 16	60	96
17		 17	30	98

[a] The second number corresponds to reaction which was carried out at 90 °C.

of different substituted nitro compounds to the corresponding amines in high yields and selectivity over other labile substituents indicate the generality of this system as tabulated in Table 2. In the course of this process, several sensitive functional groups such as -CN, -Cl, -COOH, -CHO, -NHAc, -OAc, -OH, -CH₂OH, -NH₂, -CH₃ remained unaffected. Entries 3 and 9 (Table 2) demonstrate the selective reduction of the aryl nitro substituent over the aryl halide, with good to excellent yields without any dehalogenation which was often encountered with several procedures such as hydrogenation.^{1,2} Furthermore, carbonyl substituted aromatic nitro compound showed remarkable selectivity to give the corresponding anilines without further reduction of carbonyl group (Table 2, entries 4-8). Since H₂O has been found to be the most suitable solvent for the reaction in terms of reaction time and yield, reduction of 4-nitrobenzaldehyde was led to isolation of the corresponding aryl amine in its hydrated form (Table 2 entry 6). It is noteworthy that only one nitro group of 1,3-dinitro benzene was reduced, even by using 1:6:1 molar ratio of dinitro compound: reducing agent: tungstophosphoric acid hydrate instead of 1:3:1 molar ratio (Table 2, entry 2). 1-Chloro-2,4-dinitro-benzene by using 1:3:1 molar ratio of 1-chloro-2,4-dinitro-benzene:reducing agent:tungstophosphoric acid hydrate converted to 2-chloro-5-nitro-phenylamine and 4-chloro-benzene-1,3-diamine with 85% and 10% isolated yield respectively (Table 2, entry 3). Surprisingly, even by increasing the molar ratio of reducing agent, the ratio of two reduced products does not change. Entry 10 demonstrates the tolerance of chlorine on a heterocyclic ring with a yield of 95%. Among the various aromatic nitro

compounds tested, the aromatic nitro compounds with electron withdrawing substituent gave excellent yields in a very short time (Table 2, entries 1-10). Electron withdrawing substituents can partially stabilize the radical anions **I** and **III** which are formed through accepting electron action (Scheme 2). Several aromatic nitro compounds containing electron-donating groups, were successfully converted into their corresponding amines with a prolonged reaction time (Table 2, entries 12-16). The position of the substituents on the phenyl ring of nitro compounds affected the reaction rate slightly. In spite of the same electronic effects of $-\text{COOH}$ on *para* and *ortho* positions, 2-nitro-benzoic acid was reduced more slowly than 4-nitro-benzoic acid, because of steric effects of $-\text{COOH}$ on *ortho* position (e.g. compare entries 4 and 5). As the inductive effect of $-\text{NH}_2$ in *ortho* position is more effective than *para* position, 2-nitro-phenylamine was reduced more quickly than 4-nitro-phenylamine (e.g. compare entries 14 and 15). Because of incomplete reduction of nitro benzene (as an aromatic nitro compound without any electron withdrawing and electron donating effects) at 50 °C, complete conversion was obtained after 60 min at 90 °C (Table 2, entry 11). Likewise, nitrocyclohexane as an aliphatic nitro compound react similarly and provide good yield of cyclohexylamine in short reaction time (Table 2, entry 17).

Scheme 2 Mechanism of the reduction of nitro compounds



These results indicate that the Fe-Ni NPs/ $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ can successfully reduce the aromatic and aliphatic nitro compounds to the corresponding aryl and alkyl amines.

Iron is abundant, inexpensive, environmentally benign reducing agent for nitroarenes,^{6,55} but iron itself is not

able to complete the reduction reaction (Table 1, entry 5). Bimetallic NP_s generally exhibit unusual chemical properties which are different from those of the bulk material or their individual constituents and have a number of fascinating potential applications in areas such as catalysis.⁵⁶ The high reducing property exhibited by bimetallic Fe-Ni NP_s proceeds through transfer of one electron from the nano sized Fe⁰ on the surface of Ni⁰ to the substrate. Although the role of Ni is still not clarified, it is assumed that nickel can act as an effective catalyst.⁵⁷

A literature survey reveals that reduction of nitro compounds by iron in acidic media, which is shown in Scheme 2, proceeds by single electron transfer (SET) mechanism to form amines through intermediate stages involving nitroso intermediates, which are often reduced further to the corresponding amines.⁵⁸

The mechanism starts with transfer of an electron from iron to the double bonded nitrogen to form the radical anion (**I**). After transferring the second electron to the protonated radical anion (**II**), protonation was followed by elimination of water, which leads to the formation of nitroso intermediate. The same sequence is repeated again to get the intermediate **III-V** and then hydroxylamine. Finally, addition of two electrons to hydroxylamine breaks the N-O bond which leads to formation of the anions of the product. Protonation of the corresponding anions in acidic media produces amine and water. The detailed mechanism is still unclear, and will be investigated by further experiments.

The synthesis of bimetallic Fe-Ni NP_s is very simple, it can be performed by the method described previously.⁵⁹

In conclusion, we have demonstrated that the bimetallic Fe-Ni NP_s/ $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ system mediates an efficient and mild reduction of aromatic and aliphatic nitro compounds to the corresponding amines. The present method could be a practical alternative to the conventional method. The notable advantages of this methodology are: selectivity of the reduction of nitro compound in the presence of other reducible or hydrogenolysable groups, simple manipulation, rapid reduction at relatively low temperature, the use of environmentally benign solvent and cheap reagents, high yields of amines, avoidance of using strong acid medium, less expensively.

EXPERIMENTAL

General: All starting materials were obtained from commercial suppliers, and were used without further purification. An-

alytical TLC was performed on Merck DC precoated TLC plates with 0.25-mm Kieselgel 60 F254. Visualization was performed with a 254-nm UV lamp. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer in CDCl_3 and acetone- d_6 . All melting points were measured with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Thermo Nicolet spectrometer. Mass spectra were recorded with a Varian mat Bremen CH7A and Agilent Technologies (HP) 5973 Network Mass Selective Detector instruments at 70 eV. All products were known compounds and characterized by IR and ^1H NMR spectra and comparison of their melting points (or those of the derivatives) with known compounds. Bimetallic Fe-Ni NPs were prepared and purified by the method described previously.⁵⁹

Typical procedure for reduction of *p*-cyanonitrobenzene

To a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (2.882 g, 1 mmol) in H_2O (10 mL), *p*-cyanonitrobenzene (0.148 g, 1 mmol) and Fe-Ni NPs (0.343 g, 3 mmol) were added. The resulting suspension was stirred at 50 °C for 20 min. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered to remove the Fe-Ni NPs residue, neutralized with NaHCO_3 (2×10 mL) and washed with EtOAc (2×25 mL). The organic extracts were washed with H_2O (2×25 mL), dried over Na_2SO_4 , and concentrated to give the crude solid *p*-aminobenzonitrile (Table 2, Entry 1). The crude product was recrystallized from ethylacetate obtaining 0.1156 g of pure 4-aminobenzonitrile (98% yield).

***p*-Aminobenzonitrile (1):** mp 82.5–84 °C (Lit. 83–85 °C).⁶⁰ ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.8$ Hz, 2H, Ph), 6.67 (d, $J = 8.8$ Hz, 2H, Ph), 4.24 (brs, 2H, NH_2). ^{13}C NMR (100 MHz, CDCl_3): δ 150.5, 133.8, 120.2, 114.4, 100.1. FT-IR (KBr, cm^{-1}): 3477, 3370, 3211, 2213, 1625, 1602, 1514, 1316, 1175, 838, 830, 696, 546. MS (EI): m/z (%) 118 [M^+], 91 [$\text{M}^+ - \text{CN}$]. **3-Nitroaniline (2):** mp 110–112 °C (Lit. 111–113 °C).⁶¹ ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.6$ Hz, 1H, Ph), 7.52 (s, 1H, Ph), 7.30 (t, $J = 8$ Hz, 1H, Ph), 6.98 (d, $J = 7.2$ Hz, 1H, Ph), 4.03 (brs, 2H, NH_2). ^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 147.4, 130.0, 120.6, 113.2, 109.1. FT-IR (KBr, cm^{-1}): 3432, 3325, 1624, 1523, 1483, 1348, 1264, 868, 817, 792, 736, 670. MS (EI): m/z (%) 138 [M^+], 92 [$\text{M}^+ - \text{NO}_2$]. **2-Chloro-5-nitroaniline (3):** mp 119 °C (Lit. 119 °C).⁶² ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 2.4$ Hz, 1H, Ph), 7.56 (dd, $J = 8.6$ Hz, $J = 2.4$ Hz, 1H, Ph), 7.41 (t, $J = 8.4$ Hz, 1H, Ph), 4.42 (brs, 2H, NH_2). FT-IR (KBr, cm^{-1}): 3430, 3339, 3109, 1633, 1509, 1482, 1350, 1328, 1041, 868, 736. MS (EI): m/z (%) 172 [M^+], 174 [$\text{M}^+ + 2$], 126 [$\text{M}^+ - \text{NO}_2$], 90 [$(\text{M}^+ - \text{NO}_2) - \text{Cl}$]. **4-Aminobenzoic acid (4):** mp 184–185 °C (Lit. 185–186 °C).⁵⁸ ^1H NMR (400 MHz, acetone- d_6): δ 7.78 (d, $J = 8.8$ Hz, 2H, Ph), 6.71 (d, $J = 8.8$ Hz, 2H, Ph). ^{13}C NMR (100 MHz, acetone- d_6): δ 167.2,

153.0, 131.5, 119.2, 112.8. FT-IR (KBr, cm^{-1}): 3460, 3387, 3364, 3227, 2958, 2827, 2667, 2557, 1665, 1624, 1600, 1537, 1442, 1422, 1311, 1291, 1174, 849, 771, 616. MS (EI): m/z (%) 137 [M^+], 120 [$\text{M}^+ - \text{OH}$], 92 [$\text{M}^+ - \text{CO}_2$]. **2-Aminobenzoic acid (5):** mp 143–145 °C (Lit. 144–145 °C).⁵⁸ FT-IR (KBr, cm^{-1}): 3476, 3378, 3297, 2925, 1671, 1616, 1589, 1413, 1243, 1160, 753. MS (EI): m/z (%) 137 [M^+], 119 [$\text{M}^+ - \text{OH}$], 92 [$\text{M}^+ - \text{CO}_2$]. **(4-Aminophenyl)methanediol (6):** FT-IR (KBr, cm^{-1}): 3456, 3362, 3223, 1596, 1566, 1519, 1162, 739. **4-Aminoacetanilide (7):** mp 162–163 °C (Lit. 162–164 °C).⁶³ FT-IR (KBr, cm^{-1}): 3370, 3281, 3125, 3064, 1664, 1601, 1552, 1512, 1333, 1266, 829, 522. MS (EI): m/z (%) 151 [M^+], 136 [$\text{M}^+ - \text{NH}_2$], 108 [$\text{M}^+ - \text{COMe}$]. **4-Acetoxyaniline (8):** Mp 72–73 °C (Lit. 73 °C).⁶⁴ FT-IR (KBr, cm^{-1}): 3456, 3378, 2958, 2924, 2855, 1754, 1609, 1508, 1369, 1220, 1195, 1013, 906, 828, 741, 517. **2-Chlorobenzene-1,4-diamine (9):** mp 62–65 °C (Lit. 62–66 °C).⁶⁵ FT-IR (KBr, cm^{-1}): 3420, 3411, 3394, 3334, 3219, 1617, 1605, 1504, 1435, 1303, 1235, 1164, 1147, 1039, 863, 818, 726, 677, 583. MS (EI): m/z (%) 141 [M^+], 143 [$\text{M}^+ + 2$], 107 [$\text{M}^+ - \text{Cl}$]. **2,4-Dichloro-6-methylpyrimidin-5-amine (10):** mp 101–103 °C.⁶⁶ FT-IR (KBr, cm^{-1}): 3472, 3371, 3215, 1621, 1555, 1527, 1405, 1354, 1248, 1208, 1111, 920, 851, 729, 538. MS (EI): m/z (%) 178 [M^+], 182 [$\text{M}^+ + 4$], 180 [$\text{M}^+ + 2$], 142 [$\text{M}^+ - \text{Cl}$], 106 [$\text{M}^+ - 2\text{Cl}$]. **Aniline (11):** Liquid. FT-IR (neat, cm^{-1}): 3431, 3356, 3215, 3072, 3035, 1621, 1601, 1498, 1277, 1174, 725, 692, 503. **4-Aminophenol (12):** mp 186–188 °C (Lit. 187–189 °C).⁶³ ^1H NMR (400 MHz, acetone- d_6): δ 8.20 (brs, 1H, OH), 6.79 (d, $J = 8.4$ Hz, 2H, Ph), 6.55 (d, $J = 8.4$ Hz, 2H, Ph), 3.00 (brs, 2H, NH_2). ^{13}C NMR (100 MHz, acetone- d_6): δ 115.2, 143.8, 153.1. FT-IR (KBr, cm^{-1}): 3341, 3281, 3219, 3030, 2920, 2810, 2682, 2592, 1614, 1510, 1474, 1386, 1255, 1238, 1168, 1092, 968, 826, 750. **4-Aminobenzyl alcohol (13):** Mp 90–92 °C (Lit. 90–92 °C).⁶⁷ FT-IR (KBr, cm^{-1}): 3395, 3363, 3219, 3015, 2913, 2847, 1613, 1517, 1466, 1316, 1252, 1178, 1119. **Benzene-1,4-diamine (14):** mp 139–140 °C (Lit. 139–141 °C).⁶⁸ FT-IR (KBr, cm^{-1}): 3409, 3373, 3306, 3199, 3011, 1629, 1516, 1263, 831, 718, 513. MS (EI): m/z (%) 108 [M^+]. **Benzene-1,2-diamine (15):** mp 101–102 °C (Lit. 101–104 °C).⁶⁸ ^1H NMR (400 MHz, CDCl_3): δ 6.78–6.73 (m, 4H, Ph), 3.37 (s, 4H, 2NH_2). ^{13}C NMR (100 MHz, CDCl_3): δ 134.7, 120.3, 116.7. FT-IR (KBr, cm^{-1}): 3385, 3364, 3293, 3191, 1633, 1592, 1501, 1458, 1274, 1147, 927, 748. MS (EI): m/z (%) 108 [M^+]. ***p*-Toluidine (16):** mp 40–41 °C (Lit. 40–41 °C).⁶⁷ ^1H NMR (400 MHz, CDCl_3): δ 7.01 (d, $J = 8.0$ Hz, 2H, Ph), 6.65 (d, $J = 8.4$ Hz, 2H, Ph), 3.48 (brs, 2H, NH_2), 2.28 (s, 3H, Me). ^{13}C NMR (100 MHz, CDCl_3): δ 143.8, 129.8, 127.8, 115.3, 20.5. FT-IR (KBr, cm^{-1}): 3417, 3335, 3219, 3009, 2912, 2858, 1621, 1515, 1279, 1268, 1177, 812, 505. **Cyclohexanamine (17):** Liquid. FT-IR (neat, cm^{-1}): 3350, 3276,

2927, 2855, 1584, 1448, 1379, 1340, 1078, 959, 927, 844. MS (EI): m/z (%) 99 [M^+], 97 [M^+-2].

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