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Nickel Catalyzed Amidation reaction in the Synthesis of Azaphenoxazine Carboxamides

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ABSTRACT

*We synthesize 3-chloro-1-azaphenoxazine compound **1** by the condensation of 2-aminophenol and 2, 3, 5-trichloropyridine in aqueous basic medium. Compound **1** was then coupled with five different amides via nickel catalyzed amidation reaction to afford compound **2-6**. The structures of the synthesized compounds were established based on their analytical and spectra data. The synthesized compounds were further evaluated for antimicrobial activity on different gram- positive and gram- negative bacteria's.*

Keywords: Synthesis, phenoxazine derivatives, antimicrobial activity, nickel catalyst.

INTRODUCTION

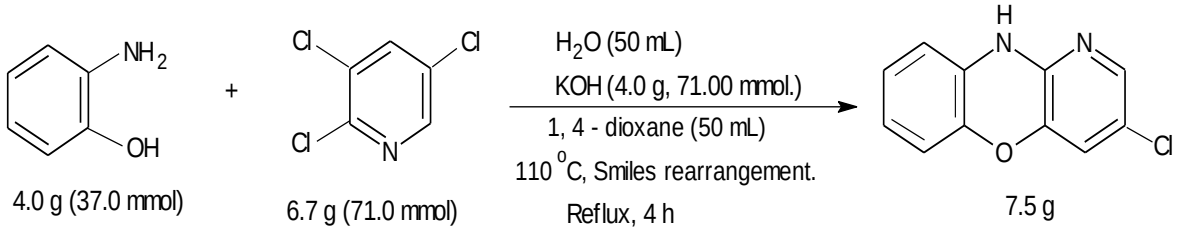
Nickel-catalyzed carbon-nitrogen bonds [1-3] via cross-coupling reactions represent a powerful means for the preparation of numerous important products in pharmaceutical, biological and material sciences [4, 5]. The major advantages of nickel based catalyst are; their lower cost [6], high catalytical activity for various chloroarenenes having an electron-withdrawing/donating groups, and there is no appreciable side-reaction with the phosphine-bound aryls which is often unavoidable in most other metal catalyzed coupling reactions like palladium [7]. In nickel-catalyzed cross-couplings, both Ni (0) and Ni (II) reagents are employed as Ni catalyst sources, but the Ni (0) species are generally regarded as being catalytically active. Although utilizing Ni (0) reagents, such as Ni $(COD)_2$ and $Ni(PPh_3)_4$ as catalysts is the simplest and most direct route. However, could be difficult to handle and manipulate because of their high air sensitivity and thermal instability. By contrast, nickel (II) compounds are readily available and conveniently handled, as pre-catalysts and are more preferred from a practical point of view. Certainly, the nickel (II) as pre-catalyst needs to first be activated (i.e, converted *in situ* to zerovalent nickel) in reaction systems because the active nickel(0) species is essential for nickel-catalyzed processes [8]. Different from the palladium (II), however, the added ligands, solvents, or bases in reaction systems are normally insufficient to reduce Ni (II) to Ni (0) [9]. Thus, the treatment of nickel (II) precatalysts with external reducing agents like zinc dust [10-12], butyl lithium, Grignard reagent [13, 14] and NaH [15-17] becomes indispensable. Recently we were interested in exploring new nickel (II)-catalyzed protocols for C-N bond-forming reaction, where the use of external reducing agents would be avoided. Hence, in the present study we wish to report the amidation of 3-chloro-1-azaphenoxazine using $NiCl_2(PPh_3)_2$ complexes without introducing the use of any external

reducing agents. This new protocol provides an extremely convenient, highly efficient and less expensive alternative for the synthesis of 3-amido derivatives of monoazaphenoxazines.

MATERIALS AND METHODS

All the reagents used in this study were of analytical grade and were used without further purification. All the amidation reactions were carried out under a nitrogen atmosphere. 2, 3, 5-trichloropyridine, 2-aminophenol, trichloroacetamide, urea, benzamide, nitrobenzamide, potassium trioxocarbonate(iv), *ter*-butylhydroxide, nickel(II)chloride, ethyl acetate and triphenylphosphine ligand were all purchased from Zayo-Sigma Chemical Company (Plateau, Nigeria) in sure-seal bottles and were used as received. Distilled water was degassed by brief 30 sec sonication under vacuum. The synthesized 3-amido-derivatives were purified by column chromatography using Merck's Silica Gel (60-230 Mesh). Melting points (mp) were determined with a Fisher-Johns apparatus and were uncorrected. All mass spectra were recorded on Shimadzu LK-9000 Mass spectrophotometer. All IR spectra were acquired on a Shimadzu model 8400S Spectrophotometer (ν max. in cm^{-1}). ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker DRX-400 spectrophotometer in DMSO at 400 and 100 MHz respectively using TMS as an internal standard. All chemical shifts were reported on δ Scale.

Synthesis of 3-chloro-1-azaphenoxazine (1): To a solution of 4.0 g, 0.07 mol of potassium hydroxide in 50 mL of distilled water, 4.0 g, 0.04 mol of 2-aminophenol was added. The mixture was warmed until the materials dissolved. Thereafter, freshly prepared 6.7 g, 0.04 mol of 2, 3, 5-trichloropyridine in 50 mL of 1, 4- dioxane was added in drops during a period of 15 min. The entire mixture was refluxed for 4 hours. At the end of the reflux period, the mixture was poured into a beaker, diluted with water to the 500 mL mark, placed in a chip of ice and cooled overnight. On filtering, the unreacted 0.6 g, 0.01mol of 2-aminophenol was first recovered and recrystallized from ethanol. The filtrate after collecting impure 2-aminophenol was further chilled, filtered and the residue crystallized from aqueous ethanol. Cream coloured plates of 3-chloro-1-azaphenoxazine were obtained. The cream coloured plates of 3-chloro-1-azaphenoxazine obtained was dissolved in 4 mL of dichloromethane to make slurry of it in a 50 mL glass tumbler. The glass tumbler containing the slurry of the 3-chloro-1-azaphenoxazine was then placed in a TLC tank containing 15 mL of diethyl ether. The TLC tank was covered tightly without intrusion of air and left undisturbed for two weeks for the crystals to grow. At the end of the two weeks, glistening cream coloured needle-like crystals of **1** (7.1 g, 0.07 mol) were obtained. Yield 89 %; m.p. 286 - 289 ^{O}C; IR [ν , cm^{-1}, KBr]: 3368(C-H, Ar-H), 2360 (N-H str), 1658 (>C=C, >C=N), 448 (C-Cl), 408 (C-O-C); ^{1}HNMR [400 MHz, DMSO]: δ 8.40 (d, j= 2.30 Hz, 1H, NH), δ 8.46 (d, j= 2.26 Hz, 2H, H(2), H(4); ^{13}CNMR [100 MHz, DMSO]: δ 129.6 (C of aromatic ring), 130.5 (C=N, C-2), 131.2 (C=C, C-8), 131.8 (C-Cl, C-3), 139.5 – 147.6 (C=C, C4-C6); MS m/z: 96 (5), 108 (6), 203 (7), 219 (M^{+}, 100); exact mass Calcd for $C_{11}H_7ON_2Cl$ 218.5000, found 219.1038.

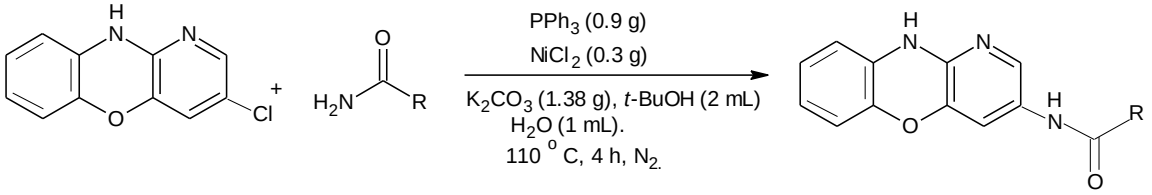


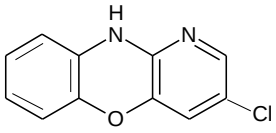
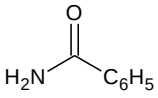
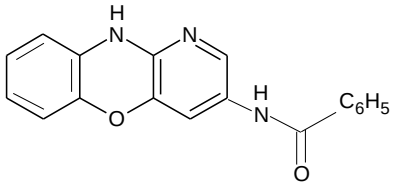
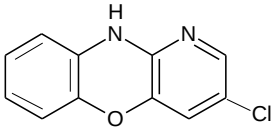
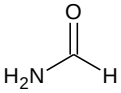
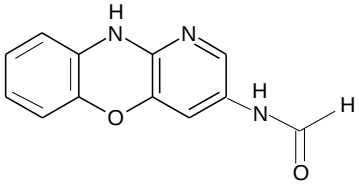
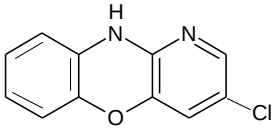
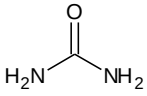
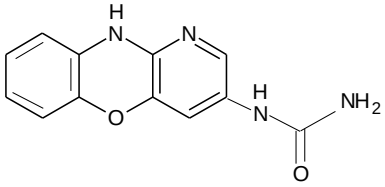
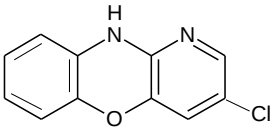
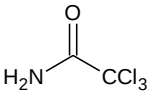
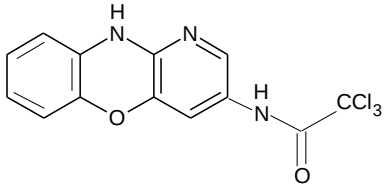
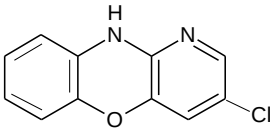
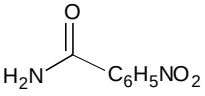
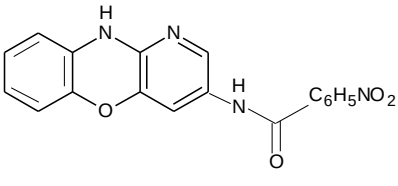
Scheme 1. Synthesis of the 3-chloro-1-azaphenoxazine

General Procedure for the synthesis of 1-azaphenoxazine carboxamides: An oven dried 250 mL two-necked flask which was equipped with a magnetic stir bar and fitted with a teflon septum was charged with 0.3 g, 0.001 mol nickel (II) chloride and 0.9 g, 0.001 mol triphenyphosphine ligand. The vessel was evacuated and backfilled with nitrogen (this process was repeated thrice) and the 2 mL of *ter*-butanol and

1mL of degassed water were added via syringe. After the addition of the degassed water, the solution was heated to 80 ^{O} C for I minute. Thereafter, the solid reactants, 1.38 g, 0.01 mol of potassium trioxocarbonate (IV), compound **1** and the amide which was used for the amidation was added to the solution without extruction of air. The septum was replaced with a Teflon screw cap. The set up was then stirred at 110 ^{O}C for four 4 h under nitrogen until compound **1** had been completely consumed. The reaction mixture was then cooled to room temperature, diluted with ethyl acetate, washed with water and concentrated in vacuo. Purification of the crude product by silica gel column chromatography, gave the desired product.

Table 1. Coupling of 3-chloro-1-azaphenoxazine with various amides (i.e amidation reaction), with melting point and percentage yield of the various products).



Entry	3-chloro-1-azaphenoxazine	Amide	Product	Yield	mp
1				85.00	210 -212 ^{o} C
2				85.00	208 -209 ^{o} C
3				62.00	248 -250 ^{o} C
4				98.00	288 -290 ^{o} C
5				84.00	287 -289 ^{o} C

Synthesis of 3-Benzamido-1-azaphenoxazine (2): Following the general procedure, a mixture of 0.3 g, 0.001 mol of nickel(II)chloride, 0.9 g, 0.001 mol of triphenylphosphine ligand, 1.38 g, 0.01 mol of potassium trioxocarbonate(iv), 7.2 g, 0.03 mol of 3-chloro-1-azaphenoxazine, 4.0 g, 0.03 mol benzamide, 1 mL of water and 2 mL of *ter*-butylhydroxide was heated to 110 ^{o} c for 3h under nitrogen atmosphere. Purification of the crude product by silica gel column chromatography gave compound **2**. Yield 85%; m.p.210 - 212^{O}C; IR [ν , max, cm^{-1}, KBr]: 3369 cm^{-1} (C-H , Ar-H), 3191 and 3071 (N-H), 1655 (C=O, amide, C=N and C=C), 1403 and 1303 (C-C str), 1030 (C-N str), and 707 (C-O-C); ^{1}H-NMR [400 MHz, DMSO]: δ 7.24, (td, J= (3.72, 6.41, 5.35)Hz, 2H, 2NH), 7.46 (m, 2H, H (2), H (4), 7.88 (t, 3H, H6, H7, H8); ^{13}CNMR [100 MHz, DMSO]: δ 129.3 ppm (C of Aromatic ring), 129.6 (C=N, C-2), 131.8 (C=C, C-8), 133.7 (C=O, amide). MS (m/z) 105(5), 245(3), 296(2), 303(M^{+}, 100); exact mass calcd for $C_{11}H_7N_2ONCOC_6H_5$ is 303.0000, found 303.1023

Synthesis of 3-Methanamido-1-azaphenoxazine (3): Following the general procedure, a mixture of 0.3 g, 0.001 mol of nickel(II)chloride, 0.9 g, 0.003 mol of triphenylphosphine ligand, 1.38 g, 0.01 mol of potassium trioxocarbonate(iv), 19.4 g, 0.09 mol of 3-chloro-1-azaphenoxazine, 4.0 g, 0.09 mol of formamide, 1 mL water and 2 mL *ter*-butylhydroxide was heated to 110 ^{o} c for 3h under nitrogen. Purification of the crude product by silica gel column chromatography gave the desired product. Yield 82 %; m.p.208 - 209 ^{O}C; IR [ν max, cm^{-1}, KBr]: 3352 (C-H stretch of the aromatic system), 3053 (N-H str), 1596 (C=O of the carbonyl (amide), C=N and C=C), 692 (C-O-C); ^{1}H-NMR [400 MHz, DMSO]: δ 7.24 (td, j=(2.99, 7.40)Hz, 2H, 2NH), δ 7.40 (m, 4H, H2, H4, H8, H9); ^{13}CNMR [100 MHz, DMSO]: δ 129.2 ppm (C of aromatic ring), 129.3 (C=N, C-2), 129.4 (C=C, C-8), 133.7 (C=O, amide), 133.9 (C-H) , 137.3 (C=C, C-4); MS m/z: 137(1), 178(15), 210(3), 219(7), 227(M^{+}, 100) exact mass calcd for $C_{11}H_7NHONNHCHO$ 227.0000, found 227.1520

Synthesis of 3-Aminomethanamido-1-azaphenoxazine (4): Following the general procedure, a mixture of 0.3 g, 0.001 mol nickel(II)chloride, 0.9 g, 0.003 mol triphenylphosphine ligand, 1.38 g, 0.01 mol potassium trioxocarbonate(iv), 14.56 g, 0.07 mol of 3-chloro-1-azaphenoxazine, 4.0 g, 0.07 mol urea, 1 mL water and 2 mL *ter*-butylhydroxide was heated to 110 ^{o} c for 3h under nitrogen. Purification of the crude product by silica gel column chromatography gave the desired product. Yield 62 %; m.p. 248 - 250 ^{O}C; IR [ν max, cm^{-1}, KBr]: 3419 (C-H str, A-H), 1650 (C=O, C=N and C=C), 1083 (C-N), 673 (C-O-C). ^{1}H-NMR [400 MHz, DMSO]: δ 7.24, (ddt, J (1.83, 4.56, 7.55)Hz, 2H, 2NH), 7.39 (m, 3H, H7, H8, H9); ^{13}CNMR [100 MHz, DMSO]: δ 129.3 (Ar-C), 129.4 (C=N, C-2), 129.6 (C=C, C-8), 133.7 (>C=O, amide), 137.1 (C-NH$_2$); MS m/z: 198(3), 209(7), 225(10). 242 (M^{+}, 100) exact mass Calcd. For $C_{11}H_7N_2ONHCONH_2$ 242.0000 found 242.1562

Synthesis of 3-Trichloromethanamido-1-azaphenoxazine (5) : Following the general procedure, a mixture of 0.3 g, 0.001 mol nickel(II)chloride , 0.9 g, 0.003 mol triphenylphosphine ligand, 1.38 g, 0.01 mol potassium trioxocarbonate (iv), 5.32g, 0.02 mol 3-chloro-1-azaphenoxazine, 4g, 0.02 mol trichloroacetamide, 1 mL water and 2 mL *ter*-butylhydroxide was heated to 110 ^{o} c for 3h under nitrogen. Purification of the crude product by silica gel column chromatography gave the desired product. Yield 98 %; IR [ν max, cm^{-1}, KBr]: 3414 (C-H str. of the aromatic system), 3073 (N-H), 1676 (C=O str. of the amide, C=N and C=C), 1022 (C-N), 823(C-Cl), 823 (C-O-C); ^{1}H-NMR [400 MHz, DMSO]: δ 7.24 (ddt (J=2.42, 6.04, 7.56)Hz, 2H, 2NH), 7.39 (dd, J=(2.06, 3.86)Hz, 3H, H6, H7, H8); ^{13}CNMR [100 MHz, DMSO]: δ 129.3 (C of aromatic ring), 129.4 (C=N, C-2), 129.6 (C=C-8), 132.0 (C-Cl), 132.1 (C=C, C-3)132.6 (C=C, C-7), 133.8 (C=O, amide), 137.2 (C=C, C-4); MS m/z: 198(7), 215(6), 298(10), 344 (M^{+}, 100) exact mass Calcd for $C_{11}H_7N_2ONHCOCI_3$ 344.5001 found 344.5212

Synthesis of 3-(4-nitrobenzamido)-1-azaphenoxazine (6) : Following the general procedure, a mixture of nickel (II) chloride (0.3 g, 0.001 mol), 0.9 g, 0.003 mol triphenylphosphine ligand , 1.38 g potassium trioxocarbonate (iv), 5.28 g, 0.02 mol 3-chloro-1-azaphenoxazine, 1.0 g, 0.02 mol nitrobenzamide, 1 mL water and 2 mL *ter*-butylhydroxide was heated to 110 ^{O}c for 3h under nitrogen. Purification of the crude

product by silica gel column chromatography gave the desired product. Yield 84 %; IR [ν max, cm^{-1}, KBr]: 3442 (C-H str of the aromatic system), 3182 and 3078 cm^{-1} (N-H), 1672 (>C=O str of the carbonyl, >C=N and C=C str), 1529 (C-C), 1365 (C-NO_2), 1122 (C-N), 713 (C-O-C). ^{1}H-NMR [400 MHz, DMSO]: δ 7.20 (S, 2H, 2NH), δ 7.34(S, 2H, H6, H7); ^{13}CNMR [100 MHz, DMSO]: δ 126.3 (C of aromatic ring), 129.5 (C=N, C-2), 130.5 (C=C, C8), 133.7 (C=O, amide), 139.4 (C=C, C-9),166.3 (C-NO_2); MS m/z: 221(3), 285(7), 312(3), 364(m^+, 100) exact mass Calcd. For $C_{11}N_7N_2ONHCOC_6H_5NO_2$ found 364.1012. The Scheme and results

Antibacterial Screening: Various concentration of the extract was prepared. Nutrient agar plate was also prepared following the manufacturers instruction. These plates were dried in hot air oven and each of the test organisms were separately inoculated unto each plate. They were labelled, using agar borer, five different holes or wells were made; one central well and four satellite wells each having the same distance from the other. Each of the wells or holes were labelled according to their concentrations and filled to the brim, covered and incubated overnight (24 h). Each of the wells were observed for zones of inhibition and were measured. Results were then recorded (Table 2).

Table 2: Antibacterial Activity of the Synthesized Phenoxazine Derivatives (MIC, µg mL^{-1})

Entry	3-chloro-1-azaphenoxazine/ 3-amido derivatives	*S. typhi*	*S. aureus*	*E. coli*	*K. pneumonia*	*S. pyogenes*	*P. aeruginosa*
1	3-chloro-1-azaphenoxazine	**2.5**	**15.0**	**5.0**	**5.0**	**15.0**	**5.0**
2	3-Benzamido-1-azaphenoxazine	**15**	**2.5**	**15**	**2.5**	**15**	**15**
3	3-Methanamido-1-azaphenoxazine	**15.0**	**2.50**	**15.0**	**2.50**	**5.00**	**15.0**
4	3-Aminomethanamido-1-azaphenoxazine	**2.50**	**15.0**	**5.00**	**15.0**	**5.00**	**1.25**
5	3-Trichloromethanamido-1-azaphenoxazine	**1.25**	**15.0**	**1.25**	**1.25**	**15.0**	**15.0**
6	3-(4-nitrobenzamido)-1-azaphenoxazine	**15.0**	**2.50**	**2.50**	**1.25**	**2.50**	**15.0**
7	Ampicillin	**15.0**	**2.5**	**15.0**	**1.25**	**1.25**	**5.00**

RESULTS AND DISCUSSION

2-aminophenol on reaction with 2, 3, 5 –trichloropyridine yielded 3-chloro-1-azaphenoxazine **1**. In IR spectrum of compound **1**, the absorption band characteristic for N-H group was identified at 2360 cm^{-1}. The bands at C=C and C=N absorption were identified at 1658 cm^{-1}. In the ^{1}HNMR spectrum the peak at δ 8.40 ppm was due to NH (j= 2.30 Hz, 1H). The spectrum also displayed a two proton doublet at δ 8.46 ppm which may be assigned to H (2) and H (4) respectively. Furthermore, in the ^{13}CNMR spectrum, the peak at δ 129.6 ppm appeared due to C of aromatic compound, the peak at δ 130.5 ppm was due to (C=N, C-2) and the peak at δ 131.8 ppm was due to (C-Cl) confirmed the formation of compound **1.** Compound **1** with benzamides yielded 3-benzamido-1-azaphenoxazine **2.** In the IR spectrum of compound **2**, the bands at 1655 cm^{-1} (>C=O of amide, C=N and C=C), 707 cm^{-1} (C-O-C), 3191 and 3071 cm^{-1} (N-H) were observed. In the ^{1}HNMR spectra of compound **2** the peak at δ 7.24 ppm was due to NH (j = (3.72, 6.41,

5.35) Hz, 2H, 2NH). The spectrum also displayed a two proton multiplets at δ 7.41 ppm which were assigned to H (2) and H (4). In the ^{13}CNMR spectrum, the peak at δ 129.3 ppm was due to (C of aromatic ring) and the peak at δ 133.7 ppm was due to (C=O, of amide) which confirmed the formation of compound **2.** Compound **1** with formamide yielded 3-methanamido-1-azaphenoxazine **3.** In IR spectrum of compound **3,** the band at 3053 cm^{-1} (N-H), 692 cm^{-1} (C-O-C) and 1596 cm^{-1} (C=O, of amide) were observed. In the ^{1}HNMR spectrum, the peak at δ 7.24 ppm was observed due to N-H (j = (2.99, 7.40) Hz, 2NH). The spectrum also displayed a four proton peak at δ 7.40 ppm which was assigned to H (2), H (4), H (8) and H (9). In the ^{13}CNMR spectrum, a peak at δ 129.2 ppm was due to (C of aromatic ring) and the peak at 133.7 ppm was due to (> C = O of amide), confirmed the formation of compound **3.** Compound **1** with urea (ethanamide) yielded 3-aminomethanamido-1-azaphenoxazine **4.** In IR spectrum of compound **4**, the absorption band characteristics for C= O, amide group was identified at 1650 cm^{-1}. The ^{1}HNMR spectrum peak at δ 7.24 ppm was due to NH (j = 1.83, 4.56, 7.55) Hz, 2NH). The spectrum also displayed a three proton multiplets at δ 7.39 ppm were assigned to H (7) H (8) and H (9). In the ^{13}CNMR spectrum, a peak at δ 129.3 ppm appeared due to (C of aromatic ring), δ 133.7 ppm (C =O, amide) and δ 137.1 ppm due to (C-NH_2) confirmed the formation of compound **4.** Compound **1** with trichloroacetamide furnished 3-Trichloromethanamido-1-azaphenoxazine **5**. In IR spectrum of compound **5** the bands at 3073cm^{-1} was due to (N-H), 1676 cm^{-1} for (C = O of amide) and 823 cm^{-1} (C-Cl) were observed. In the ^{1}HNMR spectrum, the peak at δ 7.24 ppm was due to NH (j = (2.42, 6.04, 7.56) Hz, 2H, 2NH). The spectrum also displayed a three proton doublet of doublet (dd) at δ 7.39 ppm which were assigned to H (6) H (7) and H (8). In the ^{13}CNMR spectrum, a peak at δ 129.4 ppm appeared due to (C of aromatic ring), δ 129.4 ppm (C=N, C-2), δ 132.0 ppm due to (C-Cl) and δ 133.8 ppm (C=O of amide) confirmed the formation of compound **5.** Coupling compound **1** with nitrobenzamide furnished 3-(4-nitrobenzamide)-1-azaphenoxazine **6.** In IR spectrum of compound **6** the bands at 1672cm-1 for (C=O of amide), 3182 and 3078 cm^{-1} for NH-str were observed. In the ^{1}HNMR spectrum the peak at δ 7.20 ppm was due to NH (2H, 2NH). The spectrum also displayed a two proton singlet at δ 7.39 ppm were assigned to H (6) and H (7). In the ^{13}CNMR spectrum, a peak at δ 126.4 ppm appeared due to (C of aromatic ring), δ 129.5 ppm (C=N, C-2), δ 133.3 ppm (C=O of amide) and 166.3 ppm (C-NO_2) confirmed the formation of compound **6.** Mass spectra of all the synthesized compounds were showed appropriate parent ion peaks corresponding to their molecular weight respectively.

APPLICATIONS

The synthesized phenoxazine derivatives generally posses very good antimicrobial activity with minimum inhibitory concentration (MIC) in the range of 1.25 – 5.00 µg mL^{-1}. The best activity against the selected bacteria was observed for the nitro substituted 3-amido derivative of phenoxazine, compound **6,** which is slightly less potent than the standard drug 'ampicillin' that was used. This antimicrobial analysis result reveals that these studies may contribute to the development of novel antibiotics against the selected bacteria.

CONCLUSIONS

The antimicrobial analysis result revealed that all the synthesized phenoxazine derivatives showed considerable and varied activity against the selected microorganisms (bacteria). Structure activity relationship (SAR) study of the substitution pattern of the phenoxazine derivative reveals that electron releasing group decreases the activity while electron withdrawing group on the ring increases the activity remarkably. The compound **6** with a nitro group exhibits the highest activity which is slightly less potent than the standard ampicillin. Chlorine substituted phenoxazine compound **5** has a weaker antimicrobial activity than the nitro substituted one due to the less electron withdrawing ability of the chlorine. Although, these two compounds (compounds **5** and **6**) possess stronger antibacterial activity than others. The compounds **1, 2, 3** and **4** with less electron withdrawing group shows less activity respectively.

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