

Synthesis, Antimicrobial And Anticorrosive Activities Of N⁴-Substituted Benzylidene-N¹-(2-Bromo-3-Phenylallylidene)-2-Chlorobenzene-1,4-Diamine Derivatives

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Abstract

A series of N⁴-substituted benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine derivatives (1-22) was synthesized and characterized by physicochemical and spectral means. The synthesized compounds were evaluated in vitro for their antimicrobial activity against different Gram-positive and Gram-negative bacterial and fungal strains by the tube dilution method. Results of antimicrobial screening indicated that compound 5 was the most active antimicrobial agent (pMIC₅₀ = 1.83 μM/ml). The anticorrosive activity of synthesized compounds by weight loss technique indicated that compound 20 showed appreciable corrosion inhibitory efficiency of 95.89 % and low corrosion rate of 1.42 at 24 h.

Keywords: Schiff base, Antimicrobial, Anticorrosive

1. INTRODUCTION

Antibacterial agents inhibit the growth and survival of microorganism without any serious toxicity to the host. The clinical utility of currently available antibiotics are severely declined from the market within a span of 5-year due to the development of resistance by the microorganism towards antibiotic. This necessitated the search for novel antimicrobial agents [1].

The study of mild steel corrosion phenomena has become important particularly in acidic media because of the increased industrial applications of acid solutions. The important fields of application are acid pickling, industrial cleaning, acid descaling, oil well acid in oil recovery and the petrochemical processes. Among the acid solutions, hydrochloric acid is one of the most widely used agents. Due to the exposure of mild steel to corrosive environments, they are susceptible to different types of corrosion mechanisms; therefore, the use of corrosion inhibitors to prevent metal dissolution is inevitable [2].

Corrosion inhibition efficiency of organic compounds is related to their adsorption properties. The adsorption of these molecules depends mainly on certain physicochemical properties of the corrosion inhibitor such as the presence of hetero atoms including: oxygen, sulfur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on the metal surface. The selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and wide variety of corrosive environment. As a result, several types of corrosion inhibitors were developed to fit the different types of corrosion processes and also the medium where the corrosion takes place [3].

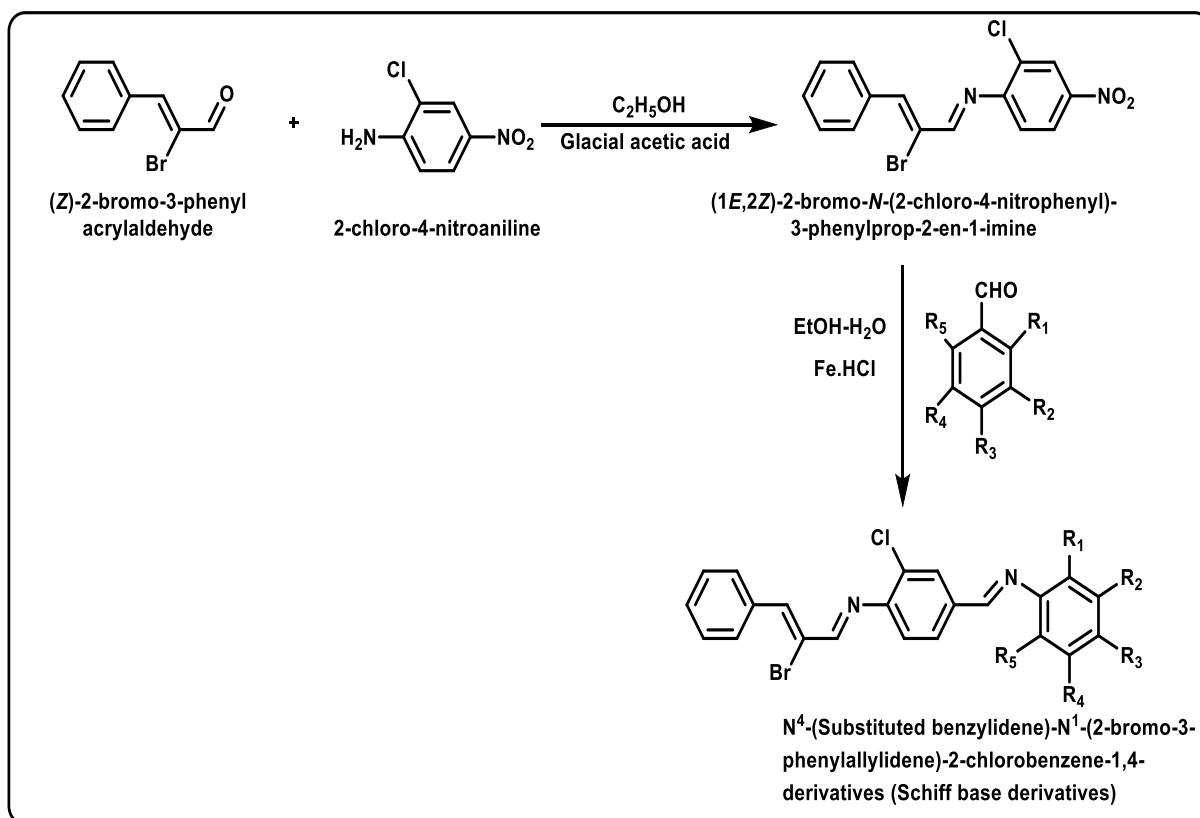
The synthesis of Schiff base derivatives and investigation of their chemical and biological behavior has gained more importance in recent decades. Schiff bases are reported to show a variety of biological activities including antibacterial [4], antifungal [5], antiamebic [6], anthelmintic [7], anticorrosive [8] and anticancer [9]. In light of above, in the present study, we hereby report the synthesis, and antimicrobial and anticorrosive activities of Schiff bases derived from N-(2-bromo-3-phenylallylidene)-2-chloro-4-nitrobenzenamine.

2. EXPERIMENTAL PART

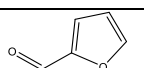
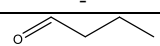
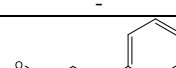
2.1. Material and instruments

The starting material, for the research work were obtained from commercial sources and were used without further purification. Reaction progress was monitored by Thin Layer Chromatography (TLC) making use of silica gel G plates. Melting points were determined in one end open capillary tubes on a melting point apparatus (Sunbim, made in India).

¹H-Nuclear Magnetic Resonance (¹H-NMR) spectra were determined by Bruker Avance II 400 MHz spectrometer in appropriate deuterated solvents and are expressed in parts per million (δ , ppm) downfield from tetramethyl silane (internal standard). ¹H-NMR data are given as multiplicity (s, singlet; m, multiplet) and number of protons. Infrared (IR) spectra were recorded on Bruker 12060280, Software: OPUS 7.2.139.1294 spectrometer in the range (600-4000 cm⁻¹). Mild steels having different composition used for the corrosion study in acidic medium such as C 0.054, Mn 0.26, Cr 0.056, Cu 0.010, Ti 0.002, S 0.017, P 0.019, Mo 0.018, Si 0.015, Ni 0.009 and remained iron. All the specimen was utilized for weight loss test with dimensions 1 x 3 cm and then polished with different grades (100, 200, 400, 600, 1000) of emery papers and finally dried with help of hot air dryer and then stored into vacuum desiccators.



Scheme 1. Synthesis of N⁴-substituted benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine Schiff base derivatives

Comp.	R	R ₁	R ₂	R ₃	R ₄	R ₅
1	-	H	H	OH	H	H
2	-	Cl	H	H	H	H
3	-	H	H	Br	H	H
4	-	NO ₂	H	H	H	H
5	-	Cl	H	Cl	H	H
6	-	OCH ₃	H	H	H	H
7	-	H	NO ₂	H	H	H
8	-	H	NO ₂	H	H	H
9	-	N(CH ₃) ₂	H	N(CH ₃) ₂	H	H
10	-	OH	H	H	H	H
11	-	H	H	H	H	H
12	-	H	H	OH	H	H
13		-	-	-	-	-
14	-	H	H	OCH ₃	H	H
15		-	-	-	-	-
16	-	OCH ₃	OCH ₃	H	H	H
17	-	OCH ₃	OH	H	H	H
18		-	-	-	-	-

19	-	H	H	Cl	H	H
20	-	H	H	N(C ₂ H ₅) ₂	H	H
21	-	H	H	NO ₂	H	H
22	-	OCH ₃	H	H	H	H

2.2. Synthetic Procedure for synthesis of N⁴-substituted benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine derivatives (1-22)

Step 1:- Synthesis of (N-(2-bromo-3-phenylallylidene)-2-chloro-4-nitrobenzenamine (I)

α -Bromo cinnamaldehyde (0.5 mol) and o-chloro p-nitroaniline (0.5 mol) in ethanol (50 ml) was added with few drops of glacial acetic acid and refluxed for 4-5 h. Then, the reaction mixture was cooled and the resultant precipitate was separated, washed, dried followed by recrystallization with suitable solvent.

Step 2:- Synthesis of Schiff base derivatives (11)

Hydrochloric acid (4.5 mmol) was added to a mixture of intermediate I (0.72 mmol), substituted benzaldehyde (0.72 mmol) and iron powder (7.32 mmol) in 24 ml of ethanol-water (2:1 v/v) solution. The reaction mixture was heated to 65 °C for 2 h before being filtered while hot (monitored by TLC) then it was extracted with dichloromethane (2x20 ml) and the dry product obtained after evaporation of dichloromethane was recrystallized using suitable solvent.

2.3. Biological studies

2.3.1. In vitro antimicrobial evaluation

The synthesized Schiff bases were evaluated for their in vitro antimicrobial activity against Gram positive bacteria (Staphylococcus aureus and Bacillus subtilis), Gram negative bacteria (Escherichia coli, Pseudomonas aeruginosa and Salmonella enterica) and fungal strains (Candida albicans and Aspergillus niger) by tube dilution method using cefadroxil (antibacterial) and ketoconazole (antifungal) as standard drugs. The stock solutions of 100 μ g/ml for the standard and test drugs were prepared in DMSO. The serial dilutions (50, 25, 12.5, 6.25, 3.12, 1.65, μ g/ml) for the test and standard drugs were prepared in double strength Nutrient broth I.P. (for bacteria) and Sabourad dextrose broth I.P. (for fungus). The bacterial cultures were incubated at 37 °C \pm 2 for 24 h and fungal cultures C. Albicans were incubated at 37 °C \pm 2 for 48 h and A. Niger at 25 °C \pm 2 for 7 days. The results of antimicrobial activity were reported in time of MIC (minimum inhibitory concentration i.e. minimum conc. of compound required to complete growth inhibition) values.

2.3.2. Anticorrosive evaluation

The corrosion medium was prepared by dilution of 1.0 M HCl of analytical grade 37% with double distilled water. The test solutions were made up by dilution of 0.5 ml Schiff base derivatives with 500 ml of 1.0 M HCl solution to make 1000 ppm solution (stock solution). The desired concentrations (100, 500, 1000 ppm) of Schiff base derivatives were prepared from stock solution of 1000 ppm.

The gravimetric method (weight loss) is most widely used in many corrosion monitoring programmes. The weight loss study has been carried out in 1.0 M HCl solution. Firstly, all mild steel samples were cut in to 1 x 3 cm then scraped with emery paper of different grade (100-1000) and washed with double distilled water, rinsed with acetone and finally dried between filter paper then weighted. The weight loss study was carried out in 30 ml of 1.0 M HCl solution filled in 50 ml beaker in presence and absence of various concentration of inhibitor for 12 h and 24 h. After the immersion of sample in test solution, specimens were put out side and washed with double distilled water and acetone, dried and weighed again. This process of weight loss study was carried out in triplicate and then average weight loss was calculated. The percentage corrosion inhibition efficiency (1) and surface coverage (2) were calculated using following equations:

$$\eta_w = \frac{w_o - w_i}{w_o} \times 100 \dots \dots \dots (1)$$

$$\theta = \frac{w_o - w_i}{w_o} \dots \dots \dots (2)$$

Where, w_o and w_i are the weight loss value of mild steel in absence and presence of test respectively.

The corrosion rate (3) of mild steel was calculated by using equation:

$$C_R \text{ (mmy}^{-1}\text{)} = \frac{87.6 \times W}{AtD} \dots \dots \dots (3)$$

Where w is weight loss of mild steel in mg, A is area of sample (cm^2), t is exposure time (h) and D is density of mild steel (g cm^{-3}) [10].

3. RESULTS & DISCUSSION

3.1. Chemistry

A series of novel N⁴-substituted benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine derivatives (1-22) was synthesized using synthetic procedure outlined in **Scheme 1**.

The reaction of α -bromo cinnamaldehyde and 2-chloro-4-nitrobenzamine resulted in formation of (N-(2-bromo-3-

phenylallylidene)-2-chloro-4-nitrobenzenamine which on reduction in presence of iron powder and hydrochloric acid followed by treatment with various aromatic/heteroaromatic aldehydes resulted in the formation of title compounds (**1-22**) [11].

The physicochemical properties of the synthesized compounds are presented in **Table 1**.

Table 1 The physicochemical properties of synthesized compounds

Comp.	Mol. Formula	M. Wt.	mp (°C)	R _f Value ^a	% Yield
1	C ₂₂ H ₁₆ BrClN ₂	423.73	120-122	0.25	72.50
2	C ₂₂ H ₁₅ BrCl ₂ N ₂	458.82	158-160	0.30	62.35
3	C ₂₂ H ₁₅ Br ₂ ClN ₂	502.63	160-162	0.32	70.75
4	C ₂₂ H ₁₅ BrClN ₃ O ₂	468.73	180-182	0.22	80.56
5	C ₂₂ H ₁₄ BrCl ₃ N ₂	492.62	192-194	0.25	59.25
6	C ₂₃ H ₁₈ BrClN ₂ O	453.76	178-180	0.30	73.25
7	C ₂₂ H ₁₅ BrClN ₃ O ₂	468.73	180-182	0.32	73.58
8	C ₂₄ H ₂₁ BrClN ₃	465.06	198-200	0.34	70.26
9	C ₂₄ H ₂₀ BrClN ₂ O ₂	483.78	164-166	0.36	71.21
10	C ₂₂ H ₁₆ BrClN ₂ O	439.73	152-154	0.38	68.35
11	C ₂₂ H ₁₆ BrClN ₂	423.73	188-190	0.40	65.36
12	C ₂₂ H ₁₅ BrCl ₃ N ₂	458.18	200-202	0.50	72.35
13	C ₂₀ H ₁₄ BrClN ₂ O	413.69	170-172	0.34	65.25
14	C ₂₃ H ₁₃ BrClN ₂ O	467.87	168-170	0.46	78.25
15	C ₁₉ H ₁₈ BrClN ₂	389.72	160-162	0.26	65.35
16	C ₂₄ H ₂₀ BrClN ₂ O ₂	483.78	164-166	0.24	68.23
17	C ₂₃ H ₁₈ BrClN ₂ O ₂	469.76	204-206	0.38	74.25
18	C ₂₄ H ₁₈ BrClN ₂	449.77	190-192	0.32	71.23
19	C ₂₂ H ₁₅ BrCl ₂ N ₂	458.18	180-182	0.24	70.25
20	C ₂₇ H ₄₈ BrClN ₃	530.05	172-174	0.28	69.12
21	C ₂₂ H ₁₅ BrClN ₃ O ₂	468.73	168-170	0.56	68.21
22	C ₂₃ H ₁₈ BrClN ₂ O	453.76	184-186	0.70	72.21

^aTLC mobile phase-Benzene

The structures of the synthesized Schiff bases (**1-22**) were confirmed by IR (ATR) and ¹H-NMR spectral studies, which are in agreement with the proposed molecular structures. The appearance of IR stretching vibration at 3032-3169 cm⁻¹ and 1456-1615 cm⁻¹ in the spectra of synthesized compounds (**1-22**) indicated the presence of C-H and C=C groups respectively.

The IR bands in the range of 1310-1362 cm⁻¹ indicated the presence of N=CH in the spectra of all synthesized compounds. The appearance of IR stretching vibration at 695-810 and 640-693 cm⁻¹ in the spectra of all synthesized compounds indicated the presence of C-Cl and C-Br group respectively. The most of the synthesized compounds showed multiplet at δ 6.81-8.23 ppm due to presence of aromatic protons. The conjugated carbon protons appeared as doublets in range of δ 7.6-8.4 ppm. The -OCH₃ protons appeared as singlet at δ 3.86 ppm. The phenolic group proton appeared in the range of δ 11-13 ppm.

N⁴-benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine

(**Compound 1**). Mol. Formula C₂₂H₁₆BrClN₂, R_f 0.25, Yield 72.50 %, brown powder, mp 122-124 °C. IR spectrum (ATR, cm⁻¹): 1451 (C=C str., phenyl nucleus), 3160 (C-H str., phenyl nucleus), 651 (C-Cl str.), 638 (C-Br str.), 1389 (-N=CH str.), 1595 (C=C str.), 3565 (OH str., phenol)

N⁴-(2-chlorobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 2).

Mol. Formula C₂₂H₁₅BrCl₂N₂, R_f 0.30, Yield 62.35 %, brown powder, mp 160-162 °C. IR spectrum (ATR, cm⁻¹): 1615 (C=C str., phenyl nucleus), 3169 (C-H str., phenyl nucleus), 695 (C-Cl str.), 640 (C-Br str.), 1362 (-N=CH str.), 1615 (C=C str.); ¹H-NMR spectrum, δ, ppm.; (CDCl₃, ppm): 7.15-7.56 m, (12H, Ar-H), 7.50 s, (2H, CH₂), 6.85 s, (1H, CH)

N⁴-(4-bromobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 3).

Mol. Formula C₂₂H₁₅Br₂ClN₂, R_f 0.32, Yield 70.75 %, yellow powder, mp 162-164 °C. IR spectrum (ATR, cm⁻¹): 1623 (C=C str., phenyl nucleus), 3090 (C-H str., phenyl nucleus), 739 (C-Cl str.), 671 (C-Br str.), 1310 (-N=CH str.), 1623 (C=C str.), 701 (C-Br str.); ¹H-NMR spectrum, δ, ppm.; (CDCl₃, ppm): 7.29-7.37 m, (12H, Ar-H), 7.37 s, (2H, CH₂), 6.84 s, (1H, CH)

N⁴-(2-nitrobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 4).

Mol. Formula C₂₂H₁₅BrClN₃O₂, R_f 0.22, Yield 80.56 %, brown powder, mp 182-184 °C. IR spectrum (ATR, cm⁻¹): 1447 (C=C str., phenyl nucleus), 3086 (C-H str., phenyl nucleus), 705 (C-Cl str.), 637 (C-Br str.), 1323 (-N=CH str.), 1624 (C=C str.), 1545 (C-NO₂ str.); ¹H-NMR spectrum, δ, ppm.; (CDCl₃, ppm): 7.22-8.23 m, (12H, Ar-H), 7.50 s, (2H, CH₂), 7.08 s, (1H, CH)

N⁴-(2,4-dichlorobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 5).

Mol. Formula C₂₂H₁₄BrCl₃N₂, R_f 0.25, Yield 59.25 %, yellow powder, mp 194-196 °C. IR spectrum (ATR, cm⁻¹): 1469 (C=C str., phenyl nucleus), 3119 (C-H str., phenyl nucleus), 747 (C-Cl str.), 693 (C-Br str.), 1376 (-N=CH str.), 1654 (C=C str.)

N⁴-(2-methoxybenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 6). Mol. Formula C₂₃H₁₈BrClN₂O, Rf 0.30, Yield 73.25 %, brown powder, mp 178-180 °C. IR spectrum (ATR, cm⁻¹): 1595 (C=C

str., phenyl nucleus), 3139 (C-H str., phenyl nucleus), 818 (C-Cl str.), 642 (C-Br str.), 1364 (-N=CH str.), 1662 (C=C str.), 2850 (C-H str., OCH₃)

N⁴-(3-nitrobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 7). Mol. Formula C₂₂H₁₅BrClN₃O₂, Rf 0.32, Yield 73.58 %, brown-red powder, mp 182-185 °C. IR spectrum (ATR, cm⁻¹): 1625 (C=C str., phenyl nucleus), 3077 (C-H str., phenyl nucleus), 781 (C-Cl str.), 654 (C-Br str.), 1320 (-N=CH str.), 1625 (C=C str.), 1577 (C-NO₂ str.)

N⁴-(4-(dimethylamino)benzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 8). Mol. Formula C₂₄H₂₁BrClN₃, Rf 0.34, Yield 70.26 %, yellow powder, mp 198-200 °C. IR spectrum (ATR, cm⁻¹): 1456 (C=C str., phenyl nucleus), 3032 (C-H str., phenyl nucleus), 726 (C-Cl str.), 631 (C-Br str.), 1310 (-N=CH str.), 1592 (C=C str.), 2797 (NCH₃)₂ str.); ¹H-NMR spectrum, δ, ppm; (CDCl₃, ppm): 6.72-7.39 m, (12H, Ar-H), 7.79 s, (2H, CH₂), 7.09 s, (1H, CH), 2.64 s, (6H, CH₃)

2-bromo-3-phenylallylideneamino)-3-chlorophenylimino)methyl)-3-ethoxyphenol (Compound 9). Mol. Formula C₂₄H₂₀BrClN₂O₂, Rf 0.36, Yield 71.21 %, brown-yellow powder, mp 166-168 °C. IR spectrum (ATR, cm⁻¹): 1625 (C=C str., phenyl nucleus), 3285 (C-H str., phenyl nucleus), 804 (C-Cl str.), 634(C-Br str.), 1395 (-N=CH str.), 1625 (C=C str.), 2839 (OH str., phenol nucleus)

2-bromo-3-phenylallylideneamino)-3-chlorophenylimino)methyl) phenol (Compound 10). Mol. Formula C₂₂H₁₆BrClN₂O, Rf 0.38, Yield 68.35 %, cream powder, mp 154-156 °C. IR spectrum (ATR, cm⁻¹): 1611 (C=C str., phenyl nucleus), 3106 (C-H str., phenyl nucleus), 810 (C-Cl str.), 663 (C-Br str.), 1386, (-N=CH str.), 1611 (C=C str.), 2844 (OH str., phenol nucleus); ¹H-NMR spectrum, δ, ppm; (CDCl₃, ppm): 7.01-7.43 m, (12H, Ar-H), 8.18 s, (2H, CH₂), 7.1 s, (1H, CH), 4.14 s, (1H, OH)

N⁴-benzylidene-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 11). Mol. Formula C₂₂H₁₆BrClN₂, Rf 0.40, Yield 65.36 %, brown-dark powder, mp 190-192 °C. IR spectrum (ATR, cm⁻¹): 1620 (C=C str., phenyl nucleus), 3102 (C-H str., phenyl nucleus), 807 (C-Cl str.), 634(C-Br str.), 1351 (-N=CH str.), 1620 (C=C str.), 2753 (-CHO str.)

N⁴-(3-chlorobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 12). Mol. Formula C₂₂H₁₅BrCl₂N₂, Rf 0.50, Yield 72.35 %, dark brown powder, mp 202-204 °C. IR spectrum (ATR, cm⁻¹): 1430 (C=C str., phenyl nucleus), 3081 (C-H str., phenyl nucleus), 773 (C-Cl str.), 628 (C-Br str.), 1337, (-N=CH str.), 1677 (C=C str.); ¹H-NMR spectrum, δ, ppm; (CDCl₃, ppm): 7.13-7.50 m, (12H, Ar-H), 7.50 s, (2H, CH₂), 7.2 s, (1H, CH)

N¹-(2-bromo-3-phenylallylidene)-2-chloro-N⁴-(furan-2-ylmethylene)benzene-1,4-diamine (Compound 13). Mol. Formula C₂₀H₁₄BrClN₂O, Rf 0.34, Yield 65.25 %, purple powder, mp 170-172 °C. IR spectrum (ATR, cm⁻¹): 1651 C=C str., phenyl nucleus), 3094 (C-H str., phenyl nucleus), 792 (C-Cl str.), 661 (C-Br str.), 1331, (-N=CH str.), 1651 (C=C str.), 2229 (C-H str., furan); ¹H-NMR spectrum, δ, ppm; (CDCl₃, ppm): 7.24-7.29 m, (11H, Ar-H), 7.47 s, (2H, CH₂), 7.24 s, (1H, CH), 1.61 s, (4H, C₂H₅)

N⁴-(4-methoxybenzylidene)-N¹-((2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 14). Mol. Formula C₂₃H₃₂BrClN₂O, Rf 0.46, Yield 78.26 %, yellow powder, mp 168-170 °C. IR spectrum (ATR, cm⁻¹): 1599 C=C str., phenyl nucleus), 3153 (C-H str., phenyl nucleus), 825 (C-Cl str.), 635 (C-Br str.), 1304 (-N=CH str.), 1677 (C=C str.), 2832 (C-H str., -OCH₃)

N¹-((2-bromo-3-phenylallylidene)-N⁴-butylidene-2-chlorobenzene-1,4-diamine (Compound 15). Mol. Formula C₁₉H₁₈BrClN₂, Rf 0.26, Yield 65.35 %, yellow powder, mp 162-164 °C. IR spectrum (ATR, cm⁻¹): 1617 (C=C str., phenyl nucleus), 3111 (C-H str., phenyl nucleus), 794 (C-Cl str.), 640 (C-Br str.), 1307, (-N=CH str.), 1617(C=C str.), 2881 (C-H str., alkyl chain); ¹H-NMR spectrum, δ, ppm; (CDCl₃, ppm): 7.13-7.29 m, (8H, Ar-H), 7.48 s, (2H, CH₂), 7.13 s, (1H, CH), 1.2 s, (1H, CH₃)

N⁴-(3,4-dimethoxybenzylidene)-N¹-((2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 16). Mol. Formula C₂₄H₂₀BrClN₂O₂, Rf 0.24, Yield 68.23 %, brown powder, mp 164-164 °C. IR spectrum (ATR, cm⁻¹): 1436 (C=C str., phenyl nucleus), 3121 (C-H str., phenyl nucleus), 787 (C-Cl str.), 637 (C-Br str.), 1351 (N=CH str.), 1670 (C=C str.), 2834 (C-H str., -OCH₃)

2-Bromo-3-phenylallylideneamino)-3-chlorophenylimino)methyl)-2-methoxyphenol (Compound 17). Mol. Formula C₂₃H₁₈BrClN₂O₂, Rf 0.38, Yield 74.25 %, dark purple powder, mp 204-206 °C. IR spectrum (ATR, cm⁻¹): 1436 (C=C str., phenyl nucleus), 3116(C-H str., phenyl nucleus), 752 (C-Cl str.), 662 (C-Br str.), 1392 (-N=CH str.), 1691 (C=C str.),

3575 (OH str., phenol nucleus), 2839 (C-H str., -OCH₃); ¹H-NMR spectrum, δ, ppm.; (CDCl₃, ppm): 6.81-7.29 m, (11H, Ar-H), 7.45 s, (2H, CH₂), 7.1 s, (1H, CH), 4.36 s, (1H, OH)

N¹-(2-Bromo-3-phenylallylidene)-2-chloro-N⁴-(3-phenylallylidene)benzene-1,4-diamine (Compound 18). Mol. Formula C₂₄H₁₈BrClN₂, Rf 0.32, Yield 71.23 %, red brown powder, mp 188-190 °C. IR spectrum (ATR, cm⁻¹): 1600 (C=C str., phenyl nucleus), 3141 (C-H str., phenyl nucleus), 803 (C-Cl str.), 634 (C-Br str.), 1350 (-N=CH str.), 1661 (C=C str.); ¹H-NMR spectrum, δ, ppm.; (CDCl₃, ppm): 7.13-7.33 m, (13H, Ar-H), 7.47 s, (2H, CH₂), 7.13 s, (1H, CH), 6.48 s, (4H, CH₃)

N⁴-(4-chlorobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 19). Mol. Formula C₂₂H₁₅BrCl₂N₂, Rf 0.24, Yield 70.25 %, brown powder, mp 180-182 °C. IR spectrum (ATR, cm⁻¹): 1487 (C=C str., phenyl nucleus), 3135 (C-H str., phenyl nucleus), 755 (C-Cl str.), 687 (C-Br str.), 1409 (-N=CH str.), 1680 (C=C str.)

N⁴-(4-(diethylamino)benzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 20). Mol. Formula C₂₇H₄₈BrClN₃, Rf 0.28, Yield 69.12 %, brown-red powder, mp 172-174 °C. IR spectrum (ATR, cm⁻¹): 1442 (C=C str., phenyl nucleus), 3092 (C-H str., phenyl nucleus), 777 (C-Cl str.), 653 (C-Br str.), 1328 (-N=CH str.), 1571 (C=C str.), 2857 (C-H str., -(NC₂H₅)₂)

N⁴-(4-nitrobenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 21). Mol. Formula C₂₂H₁₅BrClN₂O₂, Rf 0.56, Yield 68.21 %, dark powder, mp 168-170 °C. IR spectrum (ATR, cm⁻¹): 1443 (C=C str., phenyl nucleus), 3115 (C-H str., phenyl nucleus), 738 (C-Cl str.), 644 (C-Br str.), 1399 (-N=CH str.), 1629 (C=C str.), 1502 (C-NO₂ str.)

N⁴-(3-methoxybenzylidene)-N¹-(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine (Compound 22). Mol. Formula C₂₃H₁₈BrClN₂O, Rf 0.70, Yield 72.21 %, red-brown powder, mp 184-186 °C. IR spectrum (ATR, cm⁻¹): 1487 (C=C str., phenyl nucleus), 3128 (C-H str., phenyl nucleus), 782 (C-Cl str.), 692 (C-Br str.), 1353 (-N=CH str.), 1643 (C=C str.), 2826 (C-H str., OCH₃ str.)

3.2. In vitro antimicrobial screening

The synthesized Schiff bases were evaluated for antimicrobial potential by tube dilution method [12]. The results of antimicrobial activity were reported in terms of MIC (minimum inhibitory concentration) values presented in **Table 2**. Antimicrobial screening results indicated that the compound **2** (MIC_{sa} = 0.58 x 10⁻² μM/ml) and compound **5** (MIC_{bs} = 0.52 x 10⁻² μM/ml) were most active against *S. aureus*, and *B. subtilis* respectively. The maximum activity had been shown by compound **7** (MIC_{pa} = 0.55 x 10⁻² μM/ml) against *P. aeruginosa* and compound **13** (MIC_{se & ec} = 0.56 x 10⁻² μM/ml) against *S. enterica* and *E. coli* respectively. From the antifungal screening results, compound **5** and **9** (MIC_{ca} = 0.58 x 10⁻² μM/ml) and compound **6** (MIC_{an} = 0.57 x 10⁻² μM/ml) were found to be most potent against *C. albicans* and *A. niger*, respectively. The compound **5** exhibited broad spectrum of antimicrobial activity and may be taken as a lead compound for development of new antimicrobial agent.

Table 2 Minimum inhibitory concentration (MIC = μM/ml x 100) of synthesized compounds (1-22)

Compounds	Minimum Inhibitory Concentration (MIC)						
	Bacterial Strains					Fungal Strains	
	Gram positive		Gram negative			CA	AN
	SA	BS	PA	SE	EC		
1	2.36	0.57	1.17	1.18	0.58	1.17	0.78
2	0.58	1.16	1.18	0.58	1.12	1.18	1.12
3	1.15	0.58	1.09	1.17	0.64	1.16	1.18
4	1.20	0.59	1.63	2.38	1.25	0.63	1.22
5	1.10	0.52	0.55	1.10	1.17	0.58	1.15
6	1.08	1.02	1.11	0.56	0.59	1.11	0.57
7	2.20	0.57	0.55	1.12	1.13	0.68	1.12
8	1.21	0.62	0.63	1.25	0.65	1.23	1.21
9	1.16	1.10	1.11	0.63	1.11	0.58	0.68
10	2.40	0.58	1.22	1.22	1.18	1.25	0.62
11	1.20	1.19	0.59	2.41	0.62	0.62	1.22
12	2.25	1.10	1.15	1.15	1.15	0.59	1.15
13	2.26	1.05	1.12	0.56	0.56	1.15	1.12
14	1.24	1.22	0.63	0.63	1.24	1.26	0.63
15	1.20	0.63	1.25	1.25	0.63	1.25	1.25
16	1.19	0.62	0.62	1.28	1.25	0.63	1.25
17	2.21	0.55	0.56	1.12	1.12	0.65	1.25
18	1.07	0.68	1.25	1.52	1.02	0.85	1.12
19	1.19	1.23	1.12	0.95	1.42	0.65	0.65
20	2.31	1.08	0.86	1.15	0.76	1.25	0.75
21	2.29	0.72	0.75	0.85	0.68	1.22	0.64
22	1.13	1.18	1.05	1.08	0.85	1.21	1.05
Std.	1.72 ^a	1.72 ^a	1.72 ^a	1.72 ^a	1.72 ^a	2.04 ^b	2.04 ^b

^aCefadroxil^bFluconazole

SA: Staphylococcus aureus; EC: Escherichia coli; BS: Bacillus subtilis; PA: Pseudomonas aeruginosa; SE: Salmonella enterica; CA: Candida albicans; AN: Aspergillus niger

A

3.3. Anticorrosive screening

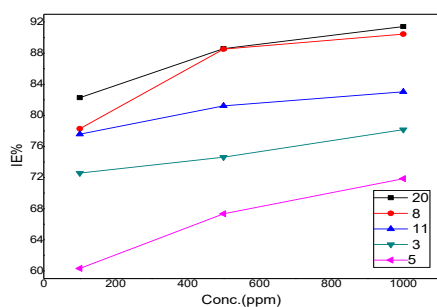
The most active antimicrobial compounds, **3**, **5**, **8**, **11** and **20** were investigated for their corrosion inhibitory potential at various concentrations by weight loss technique [13] for mild steel in 1.0 M HCl at 35°C. The anticorrosion activity results of selected compounds were presented in terms of corrosion inhibition efficiency after 12 h and 24 h in **Table 3** and **Table 4** respectively. The graph of inhibition efficiency vs concentration of inhibitors at 35°C for 12 h, 24 h indicated in **Fig. 1 (a, b)**. The graph between corrosion rate vs concentration at 35°C for 12 h and 24 h are presented in **Fig. 2 (a, b)**. The graph between surface area coverage vs concentration at 35°C for 12 h, 24 h are presented in **Fig. 3 (a, b)**. The results of inhibition efficiency after 12 h and 24 h at 35°C indicated that all the tested compounds exhibited good corrosion inhibiting potential especially compound **20** which showed corrosion inhibitory efficiency of 95.89 % and low corrosion rate of 1.42 at 24 h. It is also evident from the corrosion inhibition study results that the corrosion rate decreases with increasing concentration of inhibitor.

Table 3 Corrosion inhibition efficiency of synthesized compounds at 35°C for 12 h

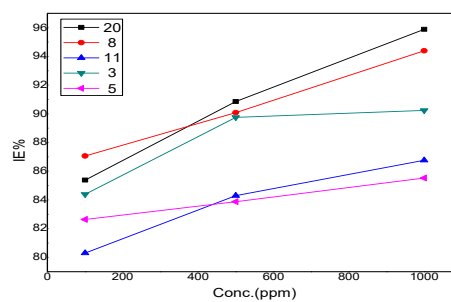
S. NO.	Inhibitors	Conc. ppm	Weight Before	Weight After	Weight Loss	Corrosion Rate	Inhibition Efficiency	Surface Area Coverage
1	20	Blank	1.126	0.951	0.175	55.44	----	----
		100	1.091	1.060	0.031	9.82	82.28	0.82
		500	1.121	1.101	0.020	6.33	88.57	0.88
		1000	1.079	1.064	0.015	4.75	91.42	0.91
2	8	Blank	1.107	0.950	0.157	49.74	----	----
		100	1.100	1.080	0.020	6.33	78.28	0.78
		500	1.112	1.094	0.018	5.70	88.53	0.88
		1000	1.115	1.100	0.015	4.75	90.44	0.90
3	11	Blank	1.135	0.970	0.165	52.78	----	----
		100	1.095	1.058	0.037	11.72	77.57	0.77
		500	1.133	1.102	0.031	9.82	81.21	0.81
		1000	1.124	1.096	0.028	8.87	83.03	0.83
4	3	Blank	1.142	0.945	0.197	62.41	----	----
		100	1.101	1.047	0.054	17.10	72.58	0.72
		500	1.139	1.089	0.050	15.84	74.61	0.74
		1000	1.112	1.069	0.043	13.62	78.17	0.78
5	5	Blank	1.088	0.889	0.199	63.05	----	----
		100	1.122	1.043	0.079	25.03	60.30	0.60
		500	1.103	1.038	0.065	20.59	67.33	0.67
		1000	1.096	1.040	0.056	17.74	71.85	0.71

Table 4 Corrosion inhibition efficiency of synthesized compounds at 35°C for 24 h

S. NO.	Inhibitors	Conc. ppm	Weight Before	Weight After	Weight Loss	Corrosion Rate	Inhibition Efficiency	Surface Area Coverage
1	20	Blank	1.116	0.903	0.219	33.90	----	----
		100	1.108	1.074	0.032	5.70	85.38	0.85
		500	1.123	1.096	0.020	3.96	90.86	0.90
		1000	1.102	1.093	0.009	1.42	95.89	0.95
2	08	Blank	1.135	0.903	0.232	36.75	---	----
		100	1.116	1.086	0.030	4.75	87.06	0.87
		500	1.123	1.100	0.023	3.64	90.08	0.90
		1000	1.120	1.107	0.013	2.05	94.39	0.94
3	11	Blank	1.140	0.815	0.325	51.48	----	----
		100	1.149	1.085	0.064	10.13	80.30	0.80
		500	1.151	1.100	0.051	8.07	84.30	0.84
		1000	1.126	1.083	0.043	6.81	86.76	0.86
4	03	Blank	1.129	0.924	0.205	32.47	----	----
		100	1.092	1.060	0.032	5.06	84.39	0.84
		500	1.122	1.101	0.021	3.32	89.75	0.89
		1000	1.115	1.095	0.020	3.16	90.24	0.90
5	05	Blank	1.086	0.844	0.242	38.33	----	----
		100	1.114	1.072	0.042	6.65	82.64	0.82
		500	1.120	1.081	0.039	6.17	83.88	0.83
		1000	1.122	1.087	0.035	5.54	85.53	0.85

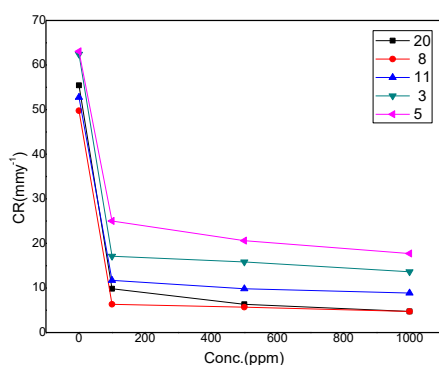


(a)

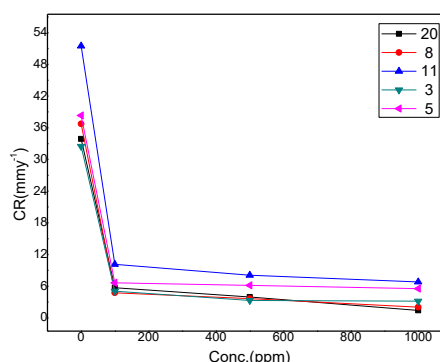


(b)

Fig. 1 Graph between inhibition efficiency vs concentration of inhibitor for 12 h (a) and 24 h (b)

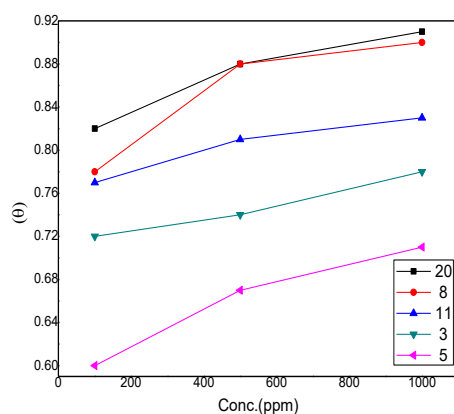


(c)

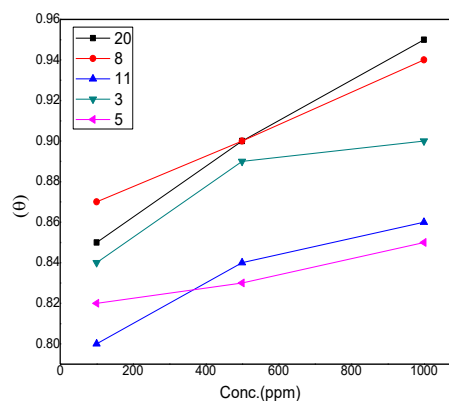


(d)

Fig. 2 Graph of corrosion rate vs concentration of inhibitor at 12 h (c) and 24 h (d)



(e)



(f)

Fig. 3 Graph of Surface area coverage (θ) vs concentration of inhibitor at 12 h (e) and 24 h (f)

3.4. Structure Activity Relationship

The structure activity relationship for antimicrobial and anticorrosive activities of synthesized N^4 -substituted benzylidene- N^1 -(2-bromo-3-phenylallylidene)-2-chlorobenzene 1,4-diamine (Schiff base) derivatives are indicated in **Fig. 4**. In general the compounds substituted with electron withdrawing groups on the phenyl ring resulted in enhanced antimicrobial activity [14]. The compounds **5** having three substituted chloro group exhibited high activity against *B. subtilis*, *C. albicans* and *P. aeruginosa*. The compound **20** having diethyl amino substituted at the p-position of phenyl ring exhibited the maximum anticorrosion activity [15].

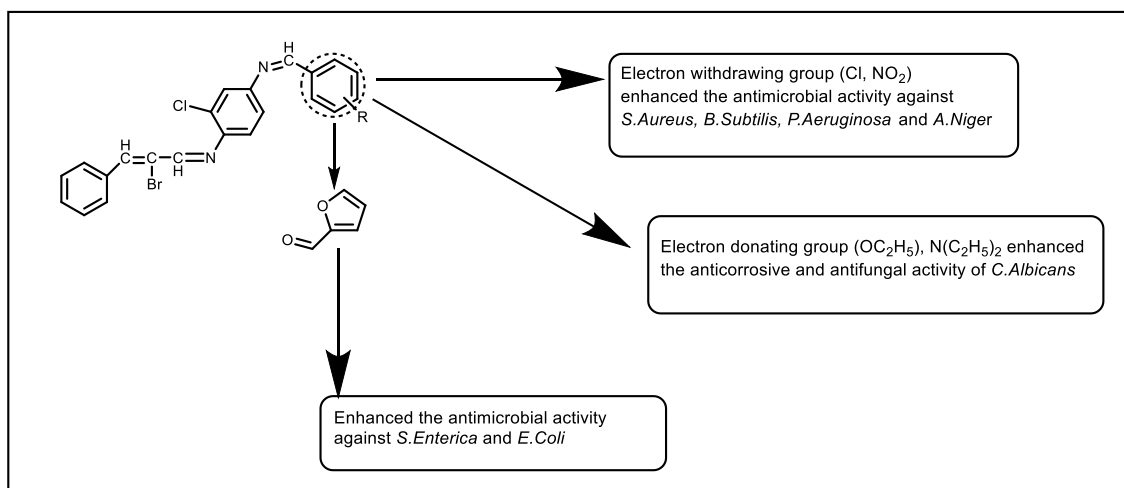


Fig. 4 SAR of antimicrobial and anticorrosive activities of synthesized compounds

4. Summary & CONCLUSION

In the present study, a series of N^4 -substituted benzylidene- N^1 -(2-bromo-3-phenylallylidene)-2-chlorobenzene-1,4-diamine Schiff base derivatives (**1-22**) was synthesized in appreciable yield and its chemical structure were confirmed by IR (ATR) and $^1\text{H-NMR}$ spectral studies. The synthesized Schiff base derivatives were evaluated for their antimicrobial activity by tube dilution method. Antimicrobial evaluation results demonstrated that compounds (**2, 5, 6, 7, 9** and **13**) were found to be the most active against different microbial species (**Fig. 5**). The anticorrosive evaluation of most active antimicrobial compounds by weight loss method indicated that compound **20** was found to be most active agent at 35°C (**Fig. 6**).

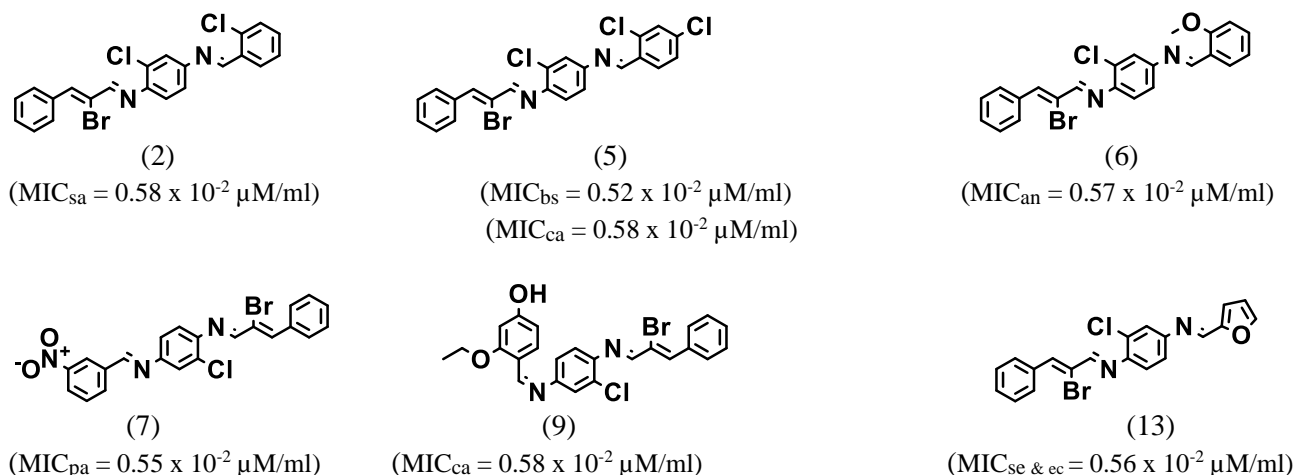
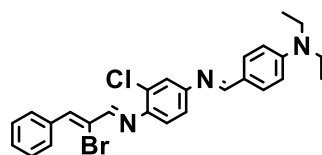


Fig. 5 Most active antimicrobial compounds with their MIC value



IE % 95.89 % for 24 h

Fig. 6 Most active anticorrosive compound with corrosion inhibition efficiency (IE %)

Abbreviations

SA: Staphylococcus aureus; EC: Escherichia coli; BS: Bacillus subtilis; PA: Pseudomonas aeruginosa; SE: Salmonella enterica; CA: Candida albicans; AN: Aspergillus niger; MIC: Minimum Inhibitory Concentration

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Authors' Contributions

Authors MK, MH and SY have designed synthesized and carried out the antimicrobial activity; SY, AS and AK carried out the anticorrosive activity; RM carried out the structure activity relationship of synthesised compounds; MK helped in critical revision of the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analysed during the current study are available from the corresponding author upon reasonable request.

Ethics approval and consent to participate

Not applicable

Conflict of interest

The authors declare no conflict of interest

Consent for publication

All authors of the research paper have approved the manuscript for submission

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