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Synthesis of Highly Functionalized Angular Azaphenoxazines and Related Benzo Analogues *via* Suzuki-Miyaura Cross-Coupling Reaction

U.C. OKORO, M.A. EZEOKONKWO*, E.A. UJAH and R.N. NWELOKE

Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka 410002, Nigeria

*Corresponding author: Tel: +234 8035486024; E-mail: mercy.ezeokonkwo@unn.edu.ng

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Highly functionalized angular azaphenoxazines and the benzo analogues have been prepared following the Suzuki-Miyaura protocol, which consists in the palladium catalyzed coupling of 11-amino-6-chloro-8,10-diazabenzo[a]phenoxazin-5-one, 6-chloro-11-azabenzo[a]phenoxazin-5-one, 6-chlorobenzo[a]phenoxazin-5-one and 6-chlorodibenzo[a,j]phenoxazin-5-one respectively with various boronic acids at 110 °C in DMF-toluene. The corresponding products were obtained in trace to excellent yields in the presence of piperazine ligand and K_2CO_3 as base. The structures of the newly synthesized compounds were established by spectral analysis.

Keywords: Azaphenoxazines, Benzo analogues, Palladium catalyzed coupling, Suzuki-Miyaura cross-coupling, Boronic acids.

INTRODUCTION

Interest in phenoxazine and its derivatives has remained unabated mostly because of their several applications as dyes and drugs. They exhibit strong biological activities, which ranges from antidepressant [1], antitumor [2], anticancer [3], to antibacterial [4], antituberculosis [5] and schizophrenia agents [6]. Among the several other applications of phenoxazine derivatives are their uses as acid-base indicators [7], biological stains [8], laser dyes [9] and as chromophoric compounds [10]. There are a good number of methods of preparing derivatives of phenoxazines in the literature. However, the use of the Suzuki-Miyaura protocol in the synthesis of phenoxazine derivatives is entirely new. Moreover, the protocol has been found to be a convenient and powerful tool for construction of carbon-carbon bonds under mild reaction conditions [11,12]. It has high functional group tolerance [13-16] and the reaction partner, boronic acids are commercially available and stable to heat, water and oxygen [16,17]. Other known advantages of the Suzuki-Miyaura coupling are the ease of handling and separating [11,16] by products from its reaction mixtures and the amenability of the reaction conditions to the industrial synthesis [17].

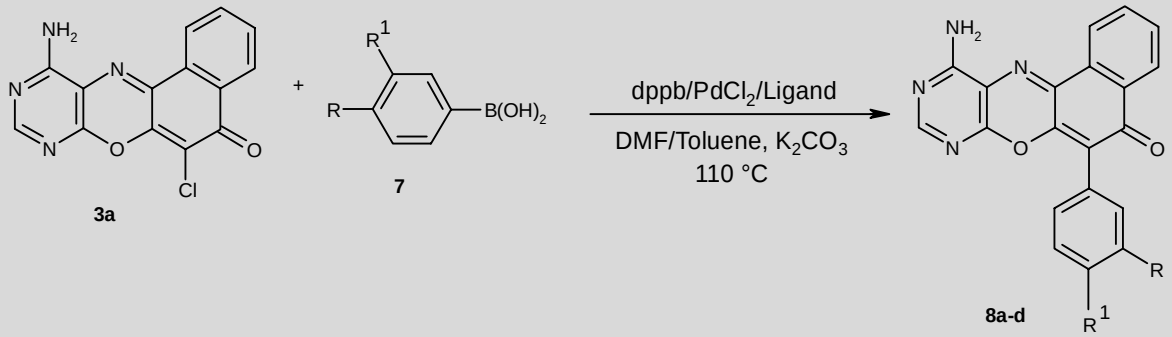
The utility of Suzuki-Miyuara protocol has been successfully demonstrated in a wide range of synthetic applications, including in polymers [16], natural products [16,18,19], ligands [16], pharmaceuticals [16,18], biologically important molecules [20,21] and fine chemicals [18]. It has also been used in the synthesis of many biaryl compounds utilize in structure/activity relationship [17]. Some oligophenothiazines [22], the sulphur analogue of phenoxazine have also been prepared using the Suzuki-Miyaura reaction. In view of the biological importance of phenoxazines and the various advantages of Suzuki-Miyaura cross-coupling reaction attempt has been made to synthesize the functionalized angular azaphenoxazine derivatives and the benzo analogues using the Suzuki-Miyaura cross-coupling reaction.

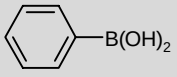
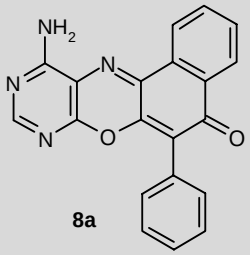
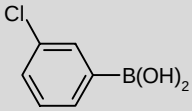
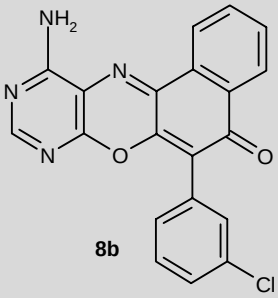
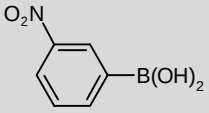
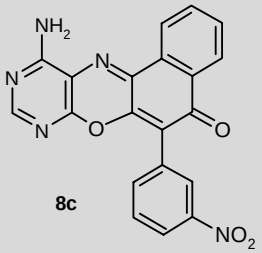
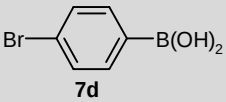
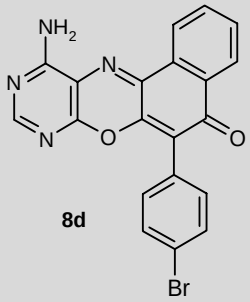
We herein report a successful Suzuki-Miyaura cross-coupling reaction of angular azaphenoxazines/the benzo analogues and arylboronic acids using 1,4-*bis*(diphenylphosphino)butane-palladium(II) chloride (dppb/$PdCl_2$), as catalyst, 1,4-*bis*(2-hydroxy-3,5-di-*tert*-butlbenzyl)piperizine as ligand, potassium carbonate as base and dimethyl formamide (DMF)/toluene mixture as solvent. The reaction afforded well functionalized angular azaphenoxazine derivatives **8-9** and the benzo analogues **10-11** in trace to excellent yields (Tables 1-4).

EXPERIMENTAL

The phenylboronic acids, 1,4-*bis*(diphenylphosphinobutane)palladium(II) chloride and piperizine used in this work were purchased from Sigma-Aldrich chemical Co. 2,4-Dichloro-1,4-naphthoquinone, 4,5-diamino-6-hydroxypyrimidine and 2-amino-3-hydroxypyridine were purchased from Fluka Chemical Co. Aniline, 2-naphthol, tin(II) chloride, sodium nitrite, sodium acetate and *o*-aminophenol were purchased from Lab. Tech. Chemicals. All the chemicals were used as purchased without further purification. Analytical grade DMF and toluene, were used for all the reactions. NMR spectra were

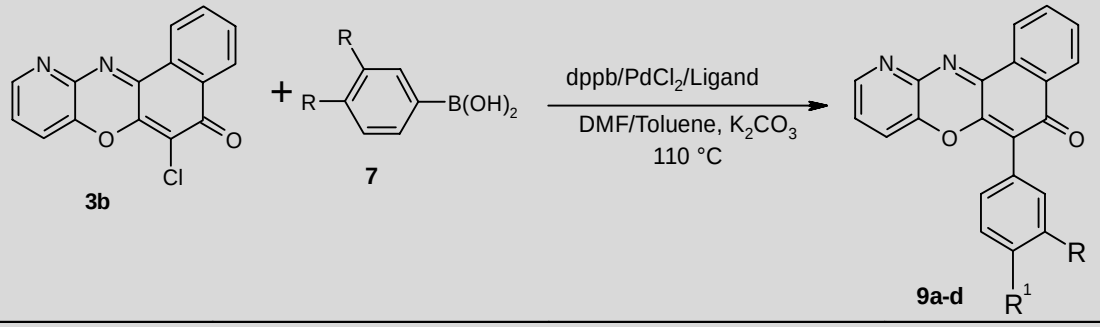
TABLE-1
SUZUKI-MIYAURA CROSS-COUPLING OF 11-AMINO-6-CHLORO-8,10-DIAZABENZO[a]PHENOXAZIN-5-ONE (**3a**) WITH ARYLBORONIC ACIDS (**7**)

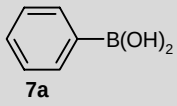
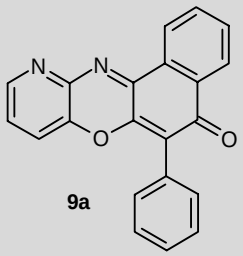
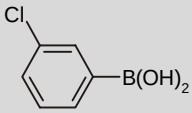
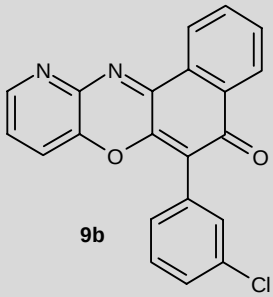
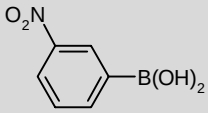
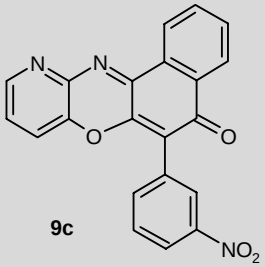
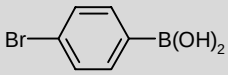
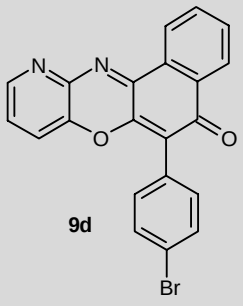


Entry	Boronic acid	Product	Yield (%)
1	 **7a**	 **8a**	85 %
2	 **7b**	 **8b**	70 %
3	 **7c**	 **8c**	30 %
4	 **7d**	 **8d**	99 %

recorded on Varian NMR Mercury-200BB. Chemical shifts are in δ using tetramethyl silane as internal standard. Mass spectra analyses were done on Gas chromatographic Mass spectrophotometer (GCMS) Shimadzu. Infrared spectra were determined on Shimadzu FTIR 8400S Spectrometer using KBr pellets. UV-visible spectra were recorded on a JENWAY 6405 UV/VIS spectrometer using 1 cm quartz cells. Melting Points were determined on Fisher-Johns melting point apparatus and were uncorrected. The compound 1,4-*bis*(2-hydroxy-3,5-di-tetrabutylbenzyl)piperizine was prepared according to literature procedure [23]. Some of the intermediates used were synthesized also using literature procedures [24-26].

TABLE-2
SUZUKI-MIYAURA CROSS-COUPLING OF 6-CHLORO-11-AZABENZO[a]PHENOXAZIN-5-ONE (**3b**) WITH ARYLBORONIC ACIDS (**7**)

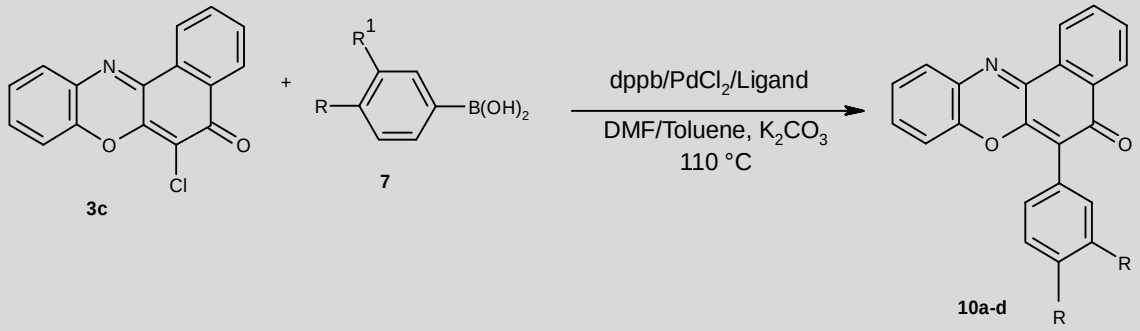


Entry	Boronic acid	Product	Yield (%)
1	 **7a**	 **9a**	Traces
2	 **7b**	 **9b**	Traces
3	 **7c**	 **9c**	48 %
4	 **7d**	 **9d**	Traces

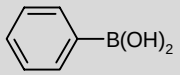
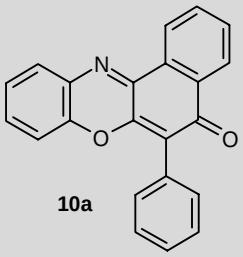
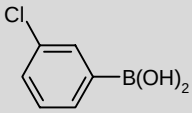
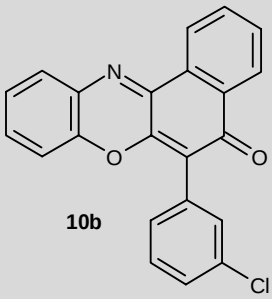
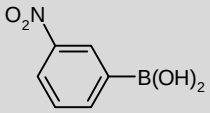
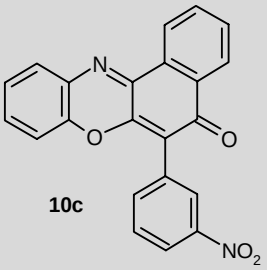
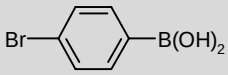
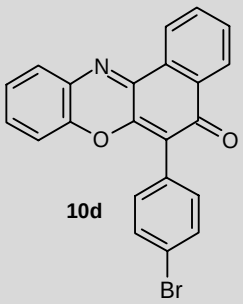
General procedure: Synthesis of angular azaphenoxazines **3a**, **3b** and benzo analogues **3c**, **3d** and ligand.

11-Amino-6-chloro-8,10-diazabenzo[a]phenoxazin-5-one (3a): This compound was prepared according to literature [23] with little modification. A mixture of 4,5-diamino-6-hydroxypyrimidine (0.555 g, 0.0044 mol), sodium carbonate (0.47, 0.0044 mol) and benzene/dimethyl formamide (10:1) in 100 mL two-necked round bottomed flask was refluxed on a water bath at 80-85 °C for 45 min, while being stirred. 2,3-Dichloro-1,4-naphthoquinone (1 g, 0.0044 mol) was added to the mixture and refluxed further at the same temperature for 8 h. The reaction was monitored with thin layer chromatography (TLC) paper in an interval of 1 h until the reaction comes to completion. The colour of the reaction mixture changed from light brown to

TABLE-3
SUZUKI-MIYAURA CROSS-COUPLING OF 6-CHLOROBENZO[a]PHENOXAZIN-5-ONE (**3c**) WITH ARYLBORONIC ACIDS (**7**)

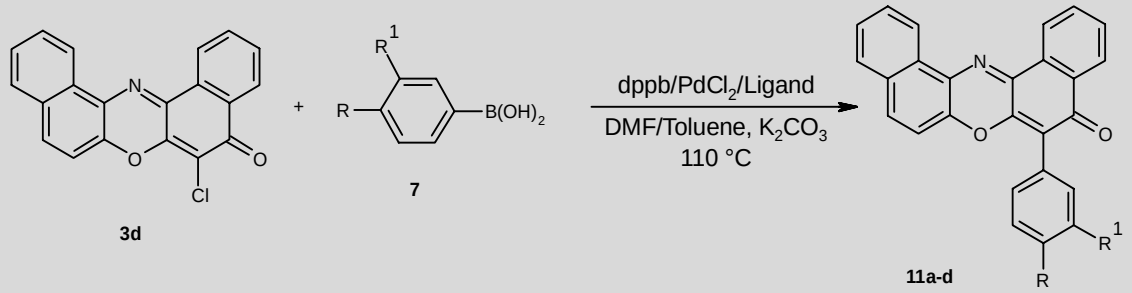


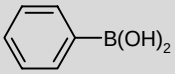
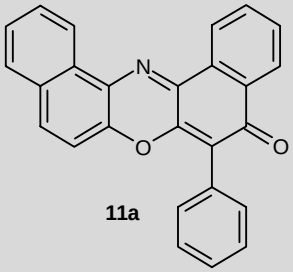
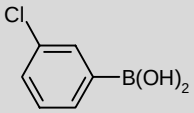
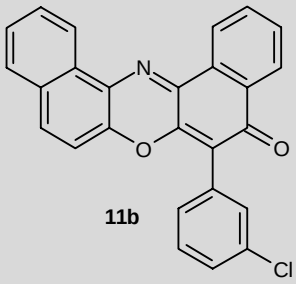
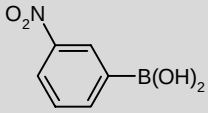
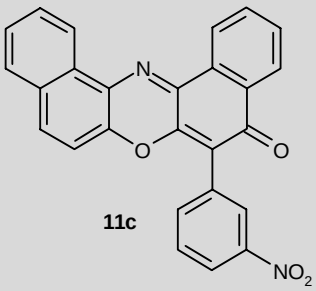
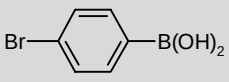
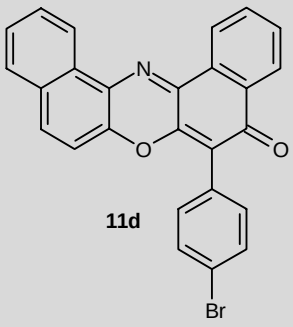
3c **7** **10a-d**

Entry	Boronic acid	Product	Yield (%)
1	 **7a**	 **10a**	30 %
2	 **7b**	 **10b**	80 %
3	 **7c**	 **10c**	60 %
4	 **7d**	 **10d**	80 %

greenish yellow to red and finally to deep red as the reaction progressed. At the end of the reaction, the solvent was allowed to evaporate leaving slurry. Ice chips were added to the slurry and reddish crystalline powder was obtained after filtration. The product was recrystallized from benzene. The yield was 80 %. Melting point is 158-160 °C. UV-visible (acetone): λ_{max} 311 (4.046), 425 (2.961), 500 (1.608) nm. IR (KBr, ν_{max}, cm^{-1}): 3400, 3100, 3000, 1615, 1556, 1275. ^{1}H NMR (DMSO-d_6): δ 8.2 (1H, s), 7.8 (4H, m), 3.5(2H, s), 1.5 (DMSO-d_6). ^{13}C NMR (DMSO-d_6): δ 205 C=O), 176 (C-9), 145 (C-11), 134 (C-2), 131 (C-3), 127 (C-6), 29 (DMSO-d_6). MS: *m/z* (rel int.) 95 M^+ -$C_{10}H_4NO_2Cl$, 100), 271 (m^+ -NH_2, 70), 244 (M^+ -CO, 30).

TABLE-4
SUZUKI-MIYAURA CROSS-COUPLING OF 6-CHLORODIBENZO[a,j]PHENOXAZIN-5-ONE (**3d**) WITH ARYLBORONIC ACIDS (**7**)



Entry	Boronic acid	Product	Yield (%)
1	 **7a**	 **11a**	85 %
2	 **7b**	 **11b**	Traces
3	 **7c**	 **11c**	51 %
4	 **7d**	 **11d**	Traces

6-Chloro-11-azabenzo[a]phenoxazin-5-one (3b): 6-Chloro-11-azabenzo[a]phenoxazin-5-one was prepared according to the literature [25]. Yellowish brown solid. m.p.: 231-232 °C. UV-visible (DMF, nm): 305 (3.8767), 340 (3.936), 445 (3.820). IR (KBr, ν_{max}, cm^{-1}): 1760, 1097-1221. ^1H NMR (400 MHz, acetone): δ 5.8-6.8 (m, 1H, 4H), 8.29 (m, 1H, 10H), 8.01-7.68 (m, 5H, 9H, 8H, 3H, 2H, 1H). ^{13}C NMR (acetone): δ 205.52-205.34 (C=O), 147.2-124.59 (aromatic carbon).

6-Chlorobenzo[a]phenoxazin-5-one (3c): This compound was prepared according to the literature [23]. Data for the compound: Brown solid. m.p.: 176 °C. UV-visible (acetone, nm): 322 (1.035), 326 (1.048), 360 (1.158), 497 (2.532), 657

(2.113). IR (KBr, ν_{max}, cm^{-1}): 2930, 1668, 1266. ^1H NMR (400 MHz, DMSO-d_6): δ 8.1 (m, 4H), 7.6 (m, 4H). ^{13}C NMR (DMSO-d_6): δ 205 (C=O).

6-Chlorodibenzo[a,j]phenoxazin-5-one (3d): 1-Amino-2-naphtholhydrochloride [25,26] (4.9 g, 25 mmol) was placed in benzene (30 mL) containing DMF (20 mL). Anhydrous sodium acetate (2.05, 25 mmol) was added and the mixture refluxed for about 45 min to enhance a complete dissolution of the hydrochloride. A solution of 2,3-dichloro-1,4-naphthoquinone (5.68, 25 mmol) in benzene (120 mL) was poured into the mixture and refluxed for 6 h. The mixture was cooled to room temperature and the solvent removed by distillation to near dryness. Dark red slurry formed was washed well with water and filtered. The resulting residue was recrystallized with benzene to give reddish brown crystals of 6-chlorodibenzo [a,j]phenoxazin-5-one. m.p.: 210 °C. UV-visible (DMF, nm): 490 (3.366), 335 (3.750), 305 (3.825). IR (KBr, ν_{max}, cm^{-1}): 1717 (C=O), 1096-1221 (C-O-C). ^1H NMR (400 MHz, acetone): δ 8.86 (m, 1H, 4-CH), 8.14 (m, 1H, 8-CH), 8.13 (m,1H, -CH), 7,91 (s, 1H,13-CH), 7.90 (s, 1H, 2-CH), 7.89 (s, 1H, 3-CH), 7.34 (s, 1H, 9-CH), 7.01 (s, 10-CH), 6.75 (s, 4-CH), 6.51 (1H, 12-CH). ^{13}C NMR (acetone): δ 205.52-205.32 (C=O), 147.25-124.59 (aromatic carbon).

1,4-*Bis*(2-hydroxy-3,5-di-tetrabutylbenzyl)piperizine ligand: 1,4-*Bis*(2-hydroxy-3,5-di-tetrabutylbenzyl)piperizine was prepared according to literature procedure [22]. Yield: 85 %. m.p.: 260 °C.

General procedure for the synthesis of functionalized angular azaphenoxazines 8a-c, 9a-c and related benzo analogues 10a-c, 11a-c: A two-necked 100 mL flask equipped with a magnetic stirrer was charged with 1,4-*bis*(2-hydroxy-3,5-di*tert*butylbenzyl)piperazine (0.0005 g, 0.01 mmol), dppb/$PdCl_2$ (0.006 g, 0.01 mmol) and a mixture of DMF (2 mL)/toluene (3 mL). After starring the mixture for 5 min, an intimate mixture of phenoxazine derivative (0.5 mmol), arylboronic acid (0.75 mmol) and potassium carbonate (0.5 mmol) was added to it. The mixture was heated at 110 °C in an oil bath for 24 h. After the refluxing period, the solvent was evaporated under reduced pressure. The residue was extracted with diethyl ether (2 × 6mL) or acetone as the case may be. After evaporation under reduced pressure, the residue was recrystallized from ethanol to give the products of interest **8a-c**, **9a-c**, **10a-c** and **11a-c**.

11-Amino-6-phenyl-8,10-diazabenzo[a]phenoxazin-5-one (8a): Extracted with acetone. Brown solid. m.p.: 78-80 °C. UV-visible (acetone, nm): 322 (1.035), 326 (1.048), 360 (1.158), 463 (2.718), 529 (3.106). IR (KBr, ν_{max}, cm^{-1}): 3392, 2925, 1663, 1601, 1289. ^1H NMR (400 MHz, DMSO-d_6): δ 8.2 (s, 1H), 7.6-7.8 (m, 4H), 7.0-7.2 (m, 4H), 3.5 (m, 2H). MS: *m/z* (rel int.) 57 (M^+, 100), 265 (M^+, 15), 235 (M^+, 25), 219 (M^+, 40).

11-Amino-6-(3-chlorophenyl)-8,10-diazabenzo[a]phenoxazin-5-one (8b): Extracted with acetone. Reddish-brown solid. m.p.: 160-162 °C. UV-visible (acetone, nm): 322 (1.035), 360 (1.158), 497 (2.534). IR (KBr, ν_{max}, cm^{-1}): 3418, 2926, 1666, 1582, 1467, 1334. ^1H NMR (400 MHz, DMSO-d_6): δ 8.3 (s, 1H), 7.9-8.1 (m, 4H), 7.0-7.6 (m, 4H), 3.7 (m, 2H). MS: *m/z* (rel int.) 55 (M^+, 100), 264 (M^+, 30), 97 (M^+, 50).

11-Amino-6-(3-nitrophenyl)-8,10-diazabenzo[a]phenoxazin-5-one (8c): Extracted with acetone. Reddish-brown solid. m.p.: 76 °C. UV-visible (acetone, nm): 322 (1.035) 326 (1,048), 498 (2.528). IR (KBr, ν_{max}, cm^{-1}): 3398, 2925, 1673, 1594, 1535, 1348. ^1H NMR (400 MHz, DMSO-d_6): δ 8.8 (s, 1H), 8.0 (m, 4H), 7.0-7.7 (m, 4H), 3.6 (m, 2H). MS: *m/z* (rel int.) 55 (M^+, 100), 264 (M^+, 20), 207 (M^+, 10).

11-Amino-6-(4-bromophenyl)-8,10-diazabenzo[a]phenoxazin-5-one (8d): Extracted with acetone. Green solid. m.p.: 101-102 °C. UV-visible (acetone, nm): 322 (1.035), 326 (1.048), 360 (1.158), 427 (2.877). IR (KBr, ν_{max}, cm^{-1}): 3404, 2929, 1668, 1600, 1483, 1286. ^1H NMR (400 MHz, DMSO-d_6): δ 8.2 (s, 1H), 7.7-7.9 (m, 4H), 7.4-7.6 (m, 4H), 3.6 (m, 2H). ^{13}C NMR (acetone): δ 205 (C=O). MS: *m/z* (rel int.) 262 (M^+, 100), 344 (M^+, 40), 263 (M^+, 90).

6-Phenyl-11-azabenzo[a]phenoxazin-5-one (9a): Extracted with diethyl ether. Yellowish brown resin. UV-visible (acetone, nm): 322 (3.319), 326 (3.240). IR (KBr, ν_{max}, cm^{-1}): 2863-2976 (C-H), 1123 (C-O-C). MS: *m/z* (rel int.) 324 (M^+, 100), 297 (M^+, -CO, 10).

6-(3-Chlorophenyl)-11-azabenzo[a]phenoxazin-5-one (9b): Extracted with diethyl ether. Reddish brown resin. UV-visible (acetone, nm): 359 (3.975), 492 (4.039). IR (KBr, ν_{max}, cm^{-1}): 2924 (C-H), 1718 (C=O). MS: *m/z* (rel int.) 300 (M^+, -CO, 10), 333 (M^+, $-C_2H_2$, 3), 324 (M^+, -Cl, 10), 247 (M^+, PhCl, 17).

6-(3-Nitrophenyl)-11-azabenzo[a]phenoxazin-5-one (9c): Extracted with diethyl ether. Reddish brown resin. UV-visible (acetone, nm): 389 (3.561), 488 (3.957), 488 (3.957). IR (KBr, ν_{max}, cm^{-1}): 2926 (C-H), 1718 (C=O), 1527 (C=O), 1227 (C-O-C). MS: *m/z* (rel int.) 342 (M^+, -CO, 29), 342 (M^+, $-NO_2$, 10).

6-(4-Bromophenyl)-11-azabenzo[a]phenoxazin-5-one (9d): Extracted with diethyl ether. Brown resin. UV-visible (acetone, nm): 389 (3.896), 572 (3.874). IR (KBr, ν_{max}, cm^{-1}): 3010 (C-H), 1718 (C=O), 1372-1221 (C-N), 1097 (C-O-C). MS: *m/z* (rel int.) 248 (M^+, -PhBr, 100).

6-Phenylbenzo[a]phenoxazin-5-one (10a): Extracted with acetone. Reddish brown solid. m.p.: 94 °C. UV-visible (acetone, nm): 322 (1.035), 360 (1.158), 495 (2.543). IR (KBr, ν_{max}, cm^{-1}): 2925, 1665, 1603, 1528, 1374, 1281.

6-(3-Chlorophenyl)benzo[a]phenoxazin-5-one (10b): Extracted with acetone. Reddish brown crystals. m.p.: 116-118 °C. UV-visible (acetone, nm): 322 (1.035), 360 (1.158), 449 (2.8o1), 557 (3.046). IR (KBr, ν_{max}, cm^{-1}): 2923, 1669, 1578, 1471, 1288. ^1H NMR (400 MHz, DMSO-d_6): δ 8.1-7.9 (m, 4H), 7,4-7.7 (m, 4H), 7.2 (m, 4H). ^{13}C NMR (acetone): δ 205 (C=O), 184 [(C- 6-(2], 145 [(C-6-(4)], 134 [(C-6-(1)], 132 (C-6), 130 (C-8), 129 (C-11), 128 (C-1), 126 (C-3).

6-(3-Nitrophenyl)benzo[a]phenoxazin-5-one (10c): Extracted with acetone. Brown oily resin. UV-visible (acetone, nm): 322 (1.035), 360 (1.158), 444 (1.528), 498 (2.528). IR (KBr, ν_{max}, cm^{-1}): IR (KBr, cm^{-1}): 2924, 1672, 1534, 1274. ^1H NMR (400 MHz, DMSO-d_6): δ 8.1-8.3 (m, 4H), 7.6-7.8 (m, 4H), 7.2-7.4 (m, 4H). ^{13}C NMR (acetone): δ 205 (C=O).

6-(4-Bromophenyl)benzo[a]phenoxazin-5-one (10d): Extracted with acetone. Dark green solid. m.p.: 94-95 °C. UV-visible (acetone, nm):322 (1.035), 449 (2.801). IR (KBr, ν_{max}, cm^{-1}): 2925, 1671, 1590, 1482, 1298. ^1H NMR (400 MHz, DMSO-d_6): δ 7.6-7.8 (m, 4H), 7.4 (m, 4H), 7.1-7.3 (m, 4H).

^{13}C NMR (acetone): δ 205.4 (C=O), 185 [(C-6-(2)], 182 [(C-6-(4)], 179 [(C-6-(1)], 144 (C-6), 131.7 (C-8), 134 (C-8), 132 (C-10), 131 (C-1), 130 (C-2), 126 (C-3).

6-Phenyldibenzo[a,j]phenoxazin-5-one (11a): Extracted with diethyl ether. Green powder. m.p.: 240 °C. UV-visible (acetone, nm): 321 (3.534, 326 (3.438). IR (KBr, ν_{max}, cm^{-1}): 2921 (C-H), 1661 (C=O), 1287(C-O-C). MS: *m/z* (rel int.) 345 (M^+, CO, 100), 296 (M^+, Ph, 62), 373 (M^+, 10).

6-(3-Chlorophenyl)dibenzo[a,j]phenoxazin-5-one (11b): Extracted with diethyl ether. Reddish brown resin. UV-visible (acetone, nm): 326 (3.803). IR (KBr, ν_{max}, cm^{-1}): 3009 (C-H), 1717 (C=O), 1368 (C-N), 1221 (C-O-C). MS: *m/z* (rel int.) 347 (M^+, C_2H_2Cl, 100), 295 (M^+, PhCl, 100).

6-(3-Nitrophenyl)dibenzo[a,j]phenoxazin-5-one (11c): Extracted with diethyl ether. Reddish brown resin. UV-visible (acetone, nm): 327 (3.711). IR (KBr, ν_{max}, cm^{-1}): 2926 (C-H), 1718 (C=O), 1527 (NO_2), 1227 (C-N). MS: *m/z* (rel int.) 384 (M^+, CO, 3), 345 (M^+, $C_2H_2.NO_2$, 100), 364 (M^+, C_4H_6).

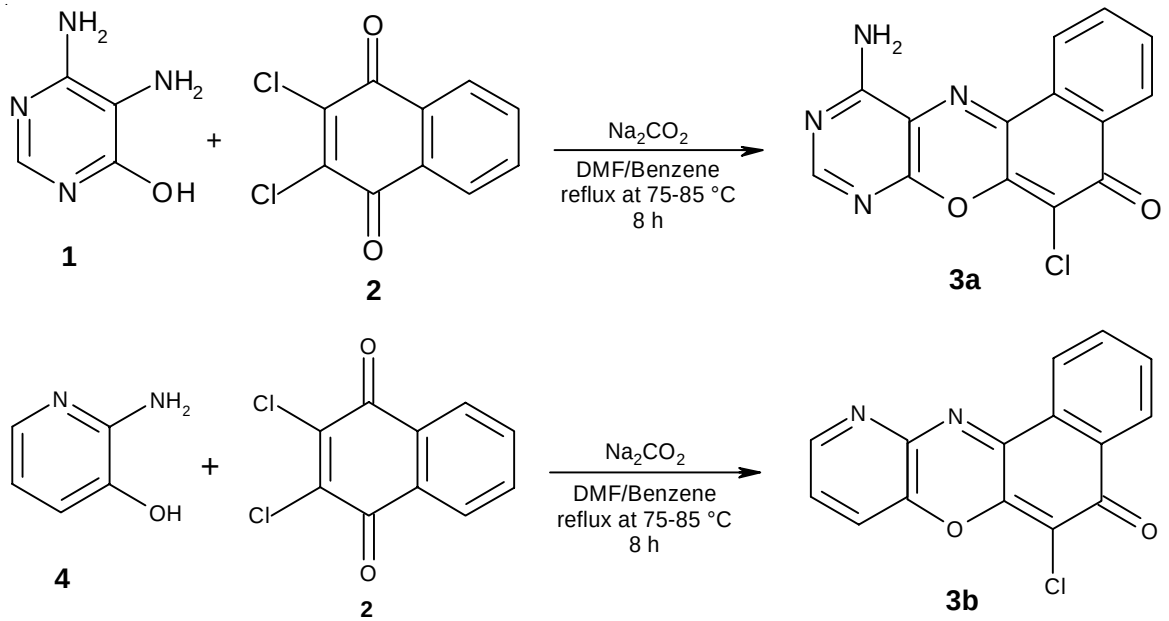
6-(4-Bromophenyl)dibenzo[a,j]phenoxazin-5-one (11d): Extracted with diethyl ether. Reddish brown resin. UV-visible (acetone, nm): 327 (3.814). IR (KBr, cm^{-1}): 3190 (C-H), 1722 (C=O). MS: *m/z* (rel int.) 296 (M^+, PhBr, 10), 345 (M^+, C_2H_2Br, 100).

RESULTS AND DISCUSSION

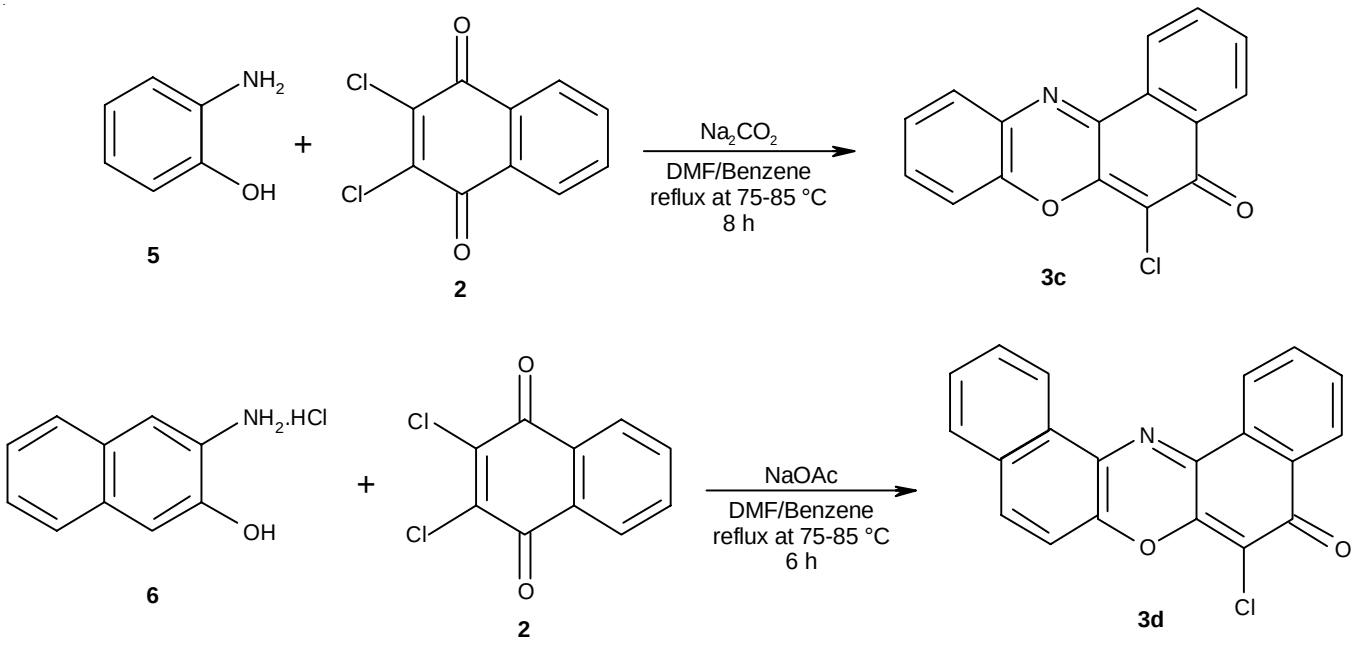
Base catalyzed condensation of 4,5-diamino-6-hydroxypyrimidine (**1**) with 2,3-dichloro-1,4-naphthoquinone (**2**) in dimethyl formamide/benzene gave 11-amino-6-chloro-8,10-dibenzo[a]phenoxazin-5-one (**3a**). Similarly, reaction of compound **2** with 2-amino-3-hydroxypyridine (**4**) furnished 6-chloro-11-azabenzo[a]phenoxazin-5-one (**3b**) in good yield (**Scheme-I**). When 2,3-dichloro-1,4-naphthoquinone (**2**) condensed with 2-aminophenol (**5**) under similar reaction condition, a yellowish brown crystals of 6-chlorobenzo[a]phenoxazin-5-one (**3c**) was obtained. In a similar reaction, 1-amino-2-naphthol hydrochloride (**6**) condensed with compound **2** in the presence of sodium acetate to give 6-chlorodibenzo[a,j]-phenoxazin-5-one (**3d**) (**Scheme-II**).

Treatment of compounds **3a-d** with various boronic acids (**7**) gave the corresponding derivatives (**8-11**) under the Suzuki-Miyuara protocol. In Table-1, the reaction of aryl boronic acids having electron-withdrawing groups with 11-amino-6-chloro-8,10-diazabenzo[a]phenoxazin-5-one (**3a**) gave the desired products in excellent yields under the reaction conditions (entries 1-4), while the nitro substituted aryl boronic acid reacted with **3a** to give low yield (entry 3). For 6-chloro-11-azabenzo[a]phenoxazin-5-one (**3b**) very poor yields were obtained when reacted with the aryl boronic acids (Table-2 entries 1-4). However, the nitro substituted aryl boronic acid gave the highest yield of 48 % (Table-2 entry 3). 6-Chlorobenzo[a]phenoxazin-5-one (**3c**) reacted with bromo- and chloro- aryl boronic acids to give the desired products in excellent yields (Table-3 entries 2 and 4), whereas the nitro aryl boronic acid gave slightly lower yield (Table-3 entry 3). Poor yield was obtained when **3c** reacted with the phenyl boronic acid (Table-3 entry 1). Similarly, the reaction of 6-chlorodibenzo [a,j]phenoxazin-5-one (**3d**) with bromo- and chloro- aryl boronic acids gave a very poor yield (Table-4 entries 2 and 4). When **3d** was reacted with unsubstituted phenyl boronic acid, an excellent yield was obtained (Table-4 entry 1). Reaction of **3d** with nitro phenyl boronic acid gave a moderate yield (Table-4 entry 3).

Structures were assigned to the newly prepared compounds based on spectral data. The UV-visible spectrum of compound **8a** showed absorption maxima at 322 (1.-35), 326 (1.048) and 360 (1.158) nm which are characteristics of phenoxazine compounds and a peak at 529 (3.106) which is consistent with the brown colour of the compound. In the IR spectrum of compound **8a**, there are peaks at 3392 cm^{-1} due to N-H stretch of primary amine and at 2925 cm^{-1} for -C-H stretch. There are also peaks at 1664 cm^{-1} for C=O stretch of ketone, 1601 cm^{-1} for -C=N stretch and at 1289 cm^{-1} for aromatic C-O-C of



Scheme-I: Synthesis of angular azaphenoxazines **3a** and **3b**



Scheme-II: Synthesis of angular benzophenoxazine analogues **3c** and **3d**

phenoxazine compounds. The ^{1}H NMR of compound **8a** showed characteristic absorption of phenyl moiety at δ 7.2-7.8 and that of amino proton at δ 3.5. Compound **10a** which is the benzo analogue of compound **8a** showed absorption bands in the UV-visible spectrum at 322 (1.035) and 360 (1.158) nm which are characteristics of phenoxazine compounds. There is also an absorption maximum at 495 (2.543) nm which is in good agreement with the observed visible complementary colour (reddish brown) of the compound. The infrared spectrum of compound **10a** showed characteristic peaks at 2925 cm^{-1} for C-H aromatics and at 1668 cm^{-1} for ketone carbonyl. It is noteworthy that the ^{1}H NMR of compound **10a** could not be obtained due to insolubility challenges. However, the remaining spectra data are in agreement with the structures of the newly synthesized compounds (**8a-d**, **9a-d**, **10a-d** and **11a-d**).

Conclusion

Highly funtionalized angular azaphenoxazines and the benzo analogues have been prepared through the cross coupling reaction of monoazabenzo-, diazabenzo and benzo-phenoxazines with aryl boronic acids. The compounds were characterized using UV/visible spectroscopy, mass spectroscopy, infrared, ^{1}H NMR and ^{13}C NMR spectroscopy. The spectral analysis confirmed the structures of the synthesized compounds.

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