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A simplified green approach for the synthesis of arylquinoxalines under solvent-free and clay-catalysed conditions

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Abstract

A friendly benign, green, rapid and facile strategy for the synthesis a series of arylquinoxalines was achieved by condensation of aromatic 1,2-diamines with arylglyoxals under clay-catalyzed as an inexpensive and eco-friendly catalyst using grindstone chemistry. Significant decreases in reaction times and high yields have been observed by this green chemistry approach in comparison to the previously reported approaches using toxic solvents and reflux conditions. The improved method, described herein, is economical, environmentally friendly, easily-operated due to solvent-free and easy work-up conditions.

Keywords: Solvent-free; clay catalyst; quinoxalines; 1,2-diamines; arylglyoxals; condensation reactions.

Introduction

Nitrogen-containing heterocyclic compounds are important for both chemists and biochemists due to their biological activities [1]. Quinoxalines have been used as antitumor [2], antibacterial [3,4] and antidepressant for human health and as receptor antagonists [5,6]. Although there are a number of methods for the synthesis of substituted quinoxalines [6,7], the most common methods involve the condensation of 1,2-diamine and 1,2-dicarbonyl compounds [9], oxidation-trapping of α-hydroxy ketones with 1,2-diamines and oxidative coupling of epoxides with ene-1,2-diamines [10].

In recent years use of inorganic solids as reaction media in organic reactions has been developed [11-15]. Clay minerals which occur abundantly in nature and have high surface area are used as catalyst and reaction medium through last decades. The synthesis of heterocyclic compounds such as aziridines [16], benzimidazoles [17], flavones [18], quinoxalines [19], pyrazines and pyrimidines [20] under solvent-free or catalyzed conditions using clay minerals have been reported. In continuation of our ongoing research leading to the regioselective synthesis of arylquinoxaline derivatives [21-25], we became interested in the development of an efficient and a facile method for synthesis of quinoxalines by reaction of arylglyoxals with 1,2-diamine compounds under solventless and clay-catalysed conditions with good to excellent yields.

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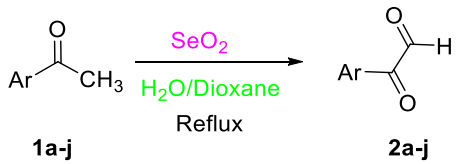
Green chemistry is fundamentally concerned with the prevention of pollution by waste minimization and the avoidance of hazardous and toxic reagents in the reactions and application of chemical products [26]. Solvent-free as an economical and environmentally friendly approach have rapidly become a part of intense research activity and key technic for pharmaceutical research. This avoids problems associated with the use of extra chemicals and the waste removal of harmful solvents [27].

In continuation of our interest in the synthesis of novel heterocyclic compounds [28-38], herein we were prompted to use a solvent-free methodology for the synthesis of arylquinoxalines from aromatic 1,2-diamines and arylglyoxals under solvent-free conditions in the presence of clay as a catalysed.

Results and discussion

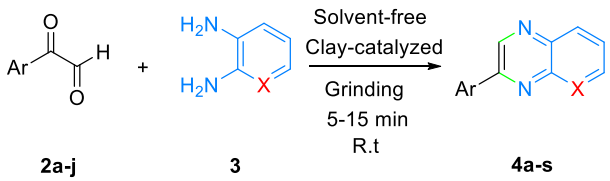
The substituted arylglyoxals **2a-j** were prepared by oxidation of related acetophenones **1a-j** using SeO_2, in dioxane/water as solvent system under reflux condition [39] (Scheme 1).



a; Ar = C_6H_5
b; Ar = 4-$O_2NC_6H_4$
c; Ar = 4-ClC_6H_4
d; Ar = 4-FC_6H_4
e; Ar = 3-$MeOC_6H_4$
f; Ar = 4-BrC_6H_4
g; Ar = 4-$MeOC_6H_4$
h; Ar = (3-MeO)(4-MeO)C_6H_3
i; Ar = 4-$C_6H_5C_6H_4$
j; Ar = (3-MeO) (4-OH)C_6H_3

Scheme 1. Synthesis of arylglyoxals **2a-j**

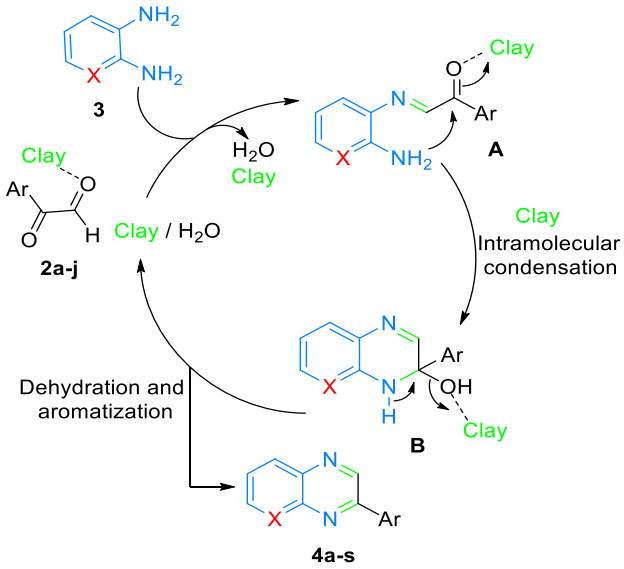
Condensation of arylglyoxals **2a-j** with aromatic diamines **3** under clay-catalysed solvent free grinding conditions at room temperature gave the corresponding quinoxalines **4a-s** in excellent yields (Scheme 2).



X = CH, N Clay = K10 or KFS montmorillonite

Scheme 2. Condensation of diamines with arylglyoxals under clay-catalysed grinding conditions

It seems that the more active amino group will react with the formyl group of arylglyoxal in the first step. Then the condensation of the keto group of arylglyoxal with the other amino group and following the loss of two molecules of water will cause the formation of final product (Scheme 3).

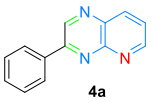
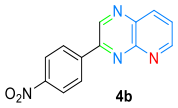
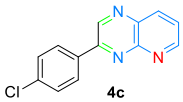
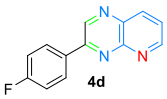
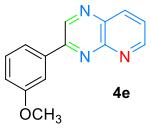
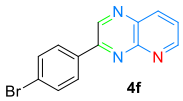
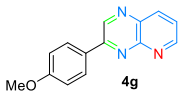
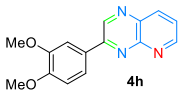
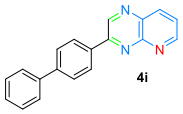


Scheme 3. Suggested mechanism for the synthesis of quinoxaline derivatives **4a-s**

We have previously reported [23,24], that the condensation of diamines with arylglyoxals was also carried out under reflux using DMF as solvent, but the reaction did not proceed in some cases and significant increase in reaction times and decrease in yields have been observed in comparison with clay-catalysed solventless condition.

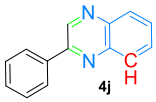
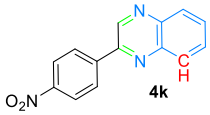
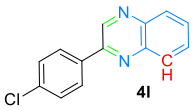
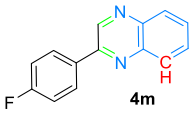
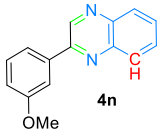
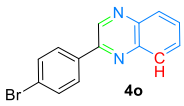
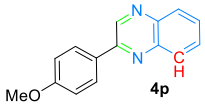
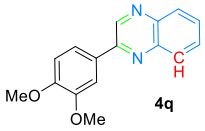
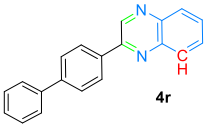
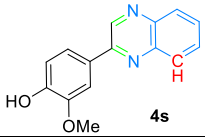
The reaction conditions and yields for condensation of 2,3-diaminopyridine and phenylenediamine with arylglyoxals or α-hydroxyketones under both reflux [23,24,40], and clay-catalyzed solventless conditions are listed in Table 1 and 2 respectively.

Table 1. Reaction conditions for condensation of 2,3-diaminopyridine with arylglyoxals

Entry	Pyrido pyrazines (4a-i, X = N)	Synthesis under reflux condition (lit. [23])			Synthesis under solventless condition		
		Reaction time (h)	M.p. (ºC)	Yield[a] (%)	Reaction time (min)	M.p. (ºC)	Yield[a] (%)
1	 **4a**	8	97	69	5	98	93
2	 **4b**	6	212	81	3	210	89
3	 **4c**	7	173	79	4	170	93
4	 **4d**	6	152	95	8	155	98
5	 **4e**	8	104	74	4	102	92
6	 **4f**	6.5	193	93	4	194	96
7	 **4g**	N.R	-	-	3	136	93
8	 **4h**	N.R	-	-	2	141	96
9	 **4i**	N.R	-	-	10	180	95

[a]Isolated yield

Table 2. Reaction conditions for condensation of phenylenediamine with arylglyoxals

Entry	2-Arylquinoxaline (4a-s, X = CH)	Synthesis under reflux conditions (lit. [24,40])			Synthesis under solventless conditions		
		Reaction time (h)	M.p. (°C)	Yield[a] (%)	Reaction time (min)	M.p. (°C)	Yield[a] (%)
1	 4j	3	76	83	4	77-78	92
2	 4k	N.R	-	-	4	184	89
3	 4l	6	138	73	4	140	86
4	 4m	N.R	-	-	5	112	96
5	 4n	N.R	-	-	4	74	93
6	 4o	6	135	81	4	132	98
7	 4p	6	92	78	3	94	86
8	 4q	5	105	92	2	103	94
9	 4r	N.R	-	-	15	103	87
10	 4s	N.R	-	-	3	133	95

[a]Isolated yield

Experimental

All chemicals used in this text were obtained from Arcos and Merck companies and were used without further purification. Melting points were determined on a Philip Harris C4954718 apparatus and are uncorrected. The progress of the reactions were monitored by thin layer chromatography (TLC) on Merck's

silica gel plates. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR instrument using KBr discs. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained at room temperature with Bruker AM-400 spectrometer using TMS as internal standard and $CDCl_3$ as solvent. Microanalyses were performed on a Leco Analyzer 932.

General procedure for the synthesis of arylglyoxals 2a-j

Selenium dioxide (10 mmol) was dissolved in a mixture of dioxane (60 mL) and water (5 mL) by stirring at 50-55 ^{o}C. Then acetophenone **1a-j** (10 mmol) was added to the solution, and the resulting mixture was stirred under reflux for 4 h. The hot mixture was filtered to remove the selenium, and the solvent was evaporated under vacuum to give a yellow oil, which was recrystallized by hot water to give the desired products **2a-j** as their hydrates.

General procedure for the synthesis of quinoxalines 4a-s under clay-catalysed and solvent-free conditions

A mixture of arylglyoxal (2 mmol), diamine (2 mmol) and clay (1 g) were thoroughly mixed in a mortar by grinding them together at room temperature for several minutes till the completion of reaction as indicated by TLC using $CHCl_3$/MeOH (20:1) as eluent. The product was extracted by CH_2Cl_2 (10 mL), washed with water and dried (Na_2SO_4). Removal of the solvent and recrystallization of the residue from ethanol gave the pure products in 86-98% yields.

3-Phenylpyrido[2,3-*b*]pyrazine (4a)

Brown solid, yield: 93%, m.p: 98 ^{o}C (lit. [23], m.p: 97 ^{o}C); FT-IR (KBr): ν 3052, 1589, 1546, 1442, 1313, 1231, 957, 837, 761, 687, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (1H, s, Ar), 9.22 (1H, d, J = 4.2 Hz, Ar), 8.53 (1H, d, J = 8.4 Hz, Ar), 8.40-8.34 (2H, m, Ar), 7.74 (1H, dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, Ar), 7.65-7.50 (3H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.41, 152.95, 149.43, 145.08, 140.08, 136.79, 135.18, 131.63, 129.35, 128.31, 124.69; Anal. Calcd. for $C_{13}H_9N_3$: C, 75.35; H, 4.38; N, 20.28; Found: C, 75.45; H, 4.21; N, 20.01.

3-(4-Nitrophenyl)pyrido[2,3-*b*]pyrazine (4b)

Brown solid, yield 89%, m.p: 210 ^{o}C (lit. [23], m.p: 212 ^{o}C); FT-IR (KBr): ν 3068, 1603, 1542, 1511, 1483, 1454, 1353, 1324, 1304, 855, 787 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (1H, s, Ar), 9.28 (1H, bd, J = 4.2 Hz, Ar), 8.59 (1H, bs, overlapped with doublet at δ 8.55, Ar), 8.55 (2H, d, J = 9 Hz, Ar), 8.46 (2H, d, J = 9 Hz, Ar), 7.82 (1H, dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.18, 152.18, 150.40, 149.34, 143.95, 141.43, 138.46, 137.65, 128.94, 125.75, 124.35; Anal. Calcd. for $C_{13}H_8N_4O_2$: C, 61.90; H, 3.20; N, 22.21; Found: C, 61.80; H, 3.36; N, 22.55.

3-(4-Chlorophenyl)pyrido[2,3-*b*]pyrazine (4c)

Green solid, yield 93%, m.p: 170 ^{o}C (lit. [23], m.p: 173 ^{o}C); FT-IR (KBr): ν 3061, 1593, 1587, 1539, 1479, 1453, 1401, 1304, 1206, 1091, 1009, 837, 788, 557 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (1H, s, Ar), 9.21 (1H, bs, Ar), 8.51 (1H, d, J = 7.8 Hz, Ar), 8.31 (2H, d, J = 8.4 Hz, Ar), 7.74 (1H, dd, J_1 = 8.1 Hz, J_2 = 3.9 Hz, Ar), 7.57 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.01, 153.78, 150.03, 144.24, 139.08, 137.84, 136.92, 133.89, 129.58, 129.38, 124.95; Anal. Calcd. for $C_{13}H_8ClN_3$: C, 64.61; H, 3.34; N, 17.39; Found: C, 64.53; H, 3.22; N, 17.69.

3-(4-Fluorophenyl)pyrido[2,3-*b*]pyrazine (4d)

Brown solid, yield 95%, m.p: 155 °C (lit. [23], m.p: 152 °C); FT-IR (KBr): ν 1601, 1545, 1515, 1484, 1410, 1307, 1273, 1233, 1161, 1118, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (1H, s, Ar), 9.21 (1H, bs, Ar), 8.52 (1H, d, J = 8.4 Hz, Ar), 8.38 (2H, bt, J = 8.4 Hz, Ar), 7.74 (1H, dd, J_1 = 8.1 Hz, J_2 = 4.2 Hz, Ar), 7.30 (2H, d, J = 8.7 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.50, 154.23, 150.34, 144.10, 138.64, 136.69, 130.25, 130.138, 124.80, 116.47, 116.26; Anal. Calcd. for $C_{13}H_8FN_3$: C, 69.48; H, 3.32; N, 18.77; Found: C, 69.33; H, 3.58; N, 18.66.

3-(3-Methoxyphenyl)pyrido[2,3-*b*]pyrazine (4e)

Brown solid, yield 92%, m.p: 102 °C (lit. [23], m.p: 104 °C); FT-IR (KBr): ν 3050, 1600, 1565, 1544, 1488, 1466, 1426, 1301, 1242, 1178, 829, 793 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.48 (1H, s, Ar), 9.22 (1H, d, J = 4.2 Hz, Ar), 8.53 (1H, d, J = 8.1 Hz, Ar), 7.99 (1H, s, Ar), 7.88 (1H, d, J = 7.8 Hz, Ar), 7.75 (1H, dd, J_1 = 8.1 Hz, J_2 = 4.2 Hz, Ar), 7.51 (1H, t, J = 7.8 Hz, Ar), 7.10 (1H, d, J = 8.4 Hz, Ar), 3.97 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.49, 154.86, 153.60, 150.00, 144.89, 139.30, 138.59, 136.87, 130.19, 124.74, 120.45, 118.11, 112.64, 55.63; Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71; Found: C, 70.71; H, 4.79; N, 17.62.

3-(4-Bromophenyl)pyrido[2,3-*b*]pyrazine (4f)

Brown solid, yield 96%, m.p: 194 °C. (lit. [23], m.p: 193 °C); FT-IR (KBr): ν 3060, 1586, 1588, 1539, 1479, 1397, 1304, 1206, 1119, 1072, 1006, 837, 825, 788 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.46 (1H, s, Ar), 9.22 (1H, s, Ar), 8.52 (1H, d, J = 8.1 Hz, Ar), 8.25 (2H, d, J = 8.4 Hz, Ar), 7.75 (1H, d, J = 7.8 Hz, Ar), 7.74 (2H, d, J = 8.7 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.01, 153.79, 149.80, 144.31, 139.42, 136.98, 134.25, 132.58, 129.61, 126.48, 124.97; Anal. Calcd. for $C_{13}H_8BrN_3$; C, 54.57; H, 2.82; N, 14.69; Found: C, 54.33; H, 2.91; N, 14.71.

3-(4-Methoxyphenyl)pyrido[2,3-*b*]pyrazine (4g)

Brown solid, yield 93%, m.p: 136 °C; FT-IR (KBr): ν 2924, 1606, 1568, 1454, 1254, 1172, 1022, 840, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.34 (1H, s, Ar), 8.20-8.11 (2H, m, Ar), 7.83-7.74 (3H, m, Ar), 7.49 (1H, t, J = 7.8 Hz, Ar), 7.09 (1H, dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, Ar), 3.96 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21, 154.32, 154.27, 144.06, 138.10, 114.76, 114.68, 92.49, 55.49; Anal. Calcd. for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71; Found: C, 70.91; H, 4.52; N, 17.66.

3-(3,4-Dimethoxyphenyl)pyrido[2,3-*b*]pyrazine (4h)

Brown solid, yield 96%, m.p: 141 °C; FT-IR (KBr): ν 2998, 1597, 1517, 1453, 1250, 1230, 1170, 1022, 841,792, 491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (1H, s, Ar), 9.17 (1H, dd, J_1 = 4.5 Hz, J_2 = 1.8 Hz, Ar), 8.47 (1H, dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, Ar), 8.09 (1H, d, J = 2.1 Hz, Ar), 7.85 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, Ar), 7.68 (1H, dd, J_1 = 8.4 Hz, J_2 = 4.5 Hz, Ar), 7.04 (1H, d, J = 8.4 Hz, Ar), 4.07 (3H, s, OCH_3), 4.00 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 152.95, 151.93, 149.92, 146.05, 144.17, 138.17, 136.36, 128.57, 124.35, 121.06, 110.98, 110.54, 59.28, 56.09; Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72: Found: C, 67.55; H, 5.01; N, 15.66.

3-([1,1-Byphenyl]4-yl)-pyrido[2,3-*b*]pyrazine (4i)

Brown solid, yield 95%, m.p: 180 °C; FT-IR (KBr): ν 3056, 1563, 1537, 1480, 1453, 1403, 1301, 842, 771, 728,

693, 567 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.55 (1H, s, Ar), 9.24 (1H, bs, Ar), 8.54 (1H, bd, J = 7.6 Hz, Ar), 8.49 (2H, d, J = 8 Hz, Ar), 7.86 (2H, d, J = 8 Hz, Ar), 7.73 (3H, d, J = 7.6 Hz, Ar), 7.53 (2H, d, J = 7.2 Hz, Ar), 7.45 (1H, d, J = 7.2 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.30, 170.71, 154.51, 144.30, 143.05, 140.03, 130.55, 127.90, 127.21, 127.00, 124.70, 123.05, 120.97, 120.51, 120.50, 120.05, 120.00, 117.70, 116.62; Anal. Calcd. for $C_{19}H_{13}N_3$: C, 80.54; H, 4.62; N, 14.83; Found: C, 80.44; H, 4.79; N, 14.75.

2-Phenylquinoxaline (4j)
Brown solid, yield 78%, m.p: 77-78 ºC (lit. [40], 75-76 ºC); FT-IR (KBr): ν 2925, 1605, 1519, 1537, 1420, 846, 766, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.34 (1H, s, Ar), 8.22-8.11 (4H, m, Ar), 7.82-7.74 (2H, m, Ar), 7.58-7.54 (3H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.82, 143.33, 142.27, 141.55, 136.75, 130.25, 130.16, 129.60, 129.51, 129.12, 129.09, 127.52; Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58; Found: C, 81.48; H, 4.63; N, 13.44.

2-(4-Nitrophenyl)quinoxaline (4k)
Brown solid, yield 89%, m.p: 184 ºC; FT-IR (KBr): ν 2924, 1598, 1514, 1486, 1343, 853, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.42 (1H, s, Ar), 8.45 (2H, d, J = 9.2 Hz, Ar), 8.41 (2H, d, J = 9.2 Hz, Ar), 8.23-8.18 (2H, m, Ar), 7.88-7.85 (2H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.21, 149.20, 142.60, 142.23, 142.14, 142.03, 130.72, 130.07, 130.02, 124.33, 120.88, 120.81, 120.40, 120.32; Anal. Calcd. for $C_{14}H_9N_3O_2$: C, 66.93; H, 3.61; N, 16.73; Found: C, 66.79; H, 3.78; N, 16.62.

2-(4-Cholorophenyl)quinoxaline (4l)
Brown solid, yield 86%, m.p: 140 ºC (lit. [23], m.p: 138 ºC); FT-IR (KBr): ν 2963, 2936, 2834, 1580, 1489, 1452, 1427, 1313, 1093, 832, 755, 699, 548 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.29 (1H, bs, Ar), 8.15-8.12 (4H, m, Ar), 7.77 (2H, bs, Ar), 7.53 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.55, 142.77, 142.23, 141.60, 136.57, 135.13, 130.46, 129.77, 129.58, 129.37, 129.14, 128.74; Anal. Calc. for $C_{14}H_9ClN_2$: C, 69.86; H, 3.77; N, 11.64; Found: C, 69.66; H, 3.81; N, 11.71.

2-(4-Fluorophenyl)quinoxaline (4m)
Brown solid, yield 96%, m.p: 112 ºC (lit. [40], m.p: 120-121 ºC); FT-IR (KBr): ν 2926, 1602, 1491, 1423, 1229, 836, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.29 (1H, s, Ar), 8.22-8.17 (2H, m, Ar), 8.14-8.10 (2H, m, Ar), 7.28-7.22 (2H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.04, 150.87, 142.84, 142.59, 141.34, 132.96, 131.08, 130.31, 129.95, 129.84, 129.21, 116.73; Anal. Calcd. for $C_{14}H_9FN_2$: C, 74.99; H, 4.05; N, 12.49; Found: C, 74.97; H, 4.08 ; N, 12.43.

2-(3-Methoxyphenyl)quinoxaline (4n)
Brown solid, yield 93%, m.p: 74 ºC; FT-IR (KBr): ν 2935, 1605, 1519, 1430, 1324, 1250, 827, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.33 (1H, s, Ar), 8.17 (1H, dd, J_1 = 8 Hz, J_2 = 1.6 Hz, Ar), 8.13 (1H, dd, J_1 = 8 Hz, J_2 = 1.6 Hz, Ar), 7.82-7.75 (4H, m, Ar), 7.49 (1H, t, J = 8 Hz, Ar), 7.09 (1H, dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, Ar), 3.95 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.34, 151.67, 143.47, 142.27, 141.69, 138.21, 130.31, 130.20, 129.67, 129.62, 129.15, 119.93, 116.24, 112.69, 55.50; Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86; Found: C, 76.12; H, 5.28; N, 11.74.

2-(4-Bromophenyl)quinoxaline (4o)
Brown solid, yield 98%, m.p: 132 ºC (lit. [24], m.p: 135 ºC); FT-IR (KBr): ν 3050, 2921, 1586, 1510, 1485, 1312,

1072, 1009, 828, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.32 (1H, s, Ar), 8.15-8.09 (4H, m, Ar), 7.84-7.70 (4H, m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.58, 142.65, 142.20, 141.53, 135.53, 132.33, 130.50, 129.83, 129.58, 129.09, 128.96, 125.01; Anal. Calcd. for $C_{14}H_9BrN_2$: C, 58.97; H, 3.18; N, 9.82; Found: C, 58.74; H, 3.35; N, 9.77.

2-(4-Methoxyphenyl)quinoxaline (4p)

Brown solid, yield 86%, m.p: 94 ^oC (lit. [24], m.p: 92 ^oC); FT-IR (KBr): ν 3056, 2934, 2833, 1606, 1520, 1324, 1250, 1073, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.30 (1H, s, Ar), 8.18 (2H, d, J = 8.4 Hz, Ar), 8.15-8.08 (2H, m, Ar), 7.78-7.69 (2H, m, Ar), 7.08 (2H, d, J = 8.4 Hz, Ar), 3.90 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.49, 151.40, 143.00, 142.27, 141.14, 130.21, 129.36, 129.22, 129.08, 129.03, 128.98, 114.60, 55.43; Anal. Calcd. for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86; Found: C, 76.39; H, 5.01; N, 11.74.

2-(3,4-Dimethoxyphenyl)quinoxaline (4q)

Brown solid, yield 94%, m.p: 103 ^oC (lit. [24], m.p: 105 ^oC); FT-IR (KBr): ν 3057, 2925, 2836, 1598, 1518, 1461, 1430, 1285, 1250, 1026, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.33 (1H, s, Ar), 8.18-8.11 (2H, m, Ar), 7.89 (1H, s, Ar), 7.82-7.74 (3H, m, Ar), 7.05 (1H, d, J = 8.4 Hz, Ar), 4.08 (3H, s, OCH_3), 4.00 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.26, 151.19, 149.74, 143.00, 142.12, 141.12, 130.30, 129.39, 129.27, 129.19, 129.00, 120.50, 111.15, 110.17, 56.10, 56.04; Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52; Found: C, 72.02; H, 5.41; N, 10.63.

2-[(1,1-Byphenyl)-4-yl]quinoxaline (4r)

Brown solid, yield 87%, m.p: 103 ^oC; FT-IR (KBr): ν 2925, 1605, 1519, 1537, 1420, 846, 766, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.42 (1H, s, Ar), 8.33 (2H, dt, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar), 8.20 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar), 8.17 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar), 7.86-7.81 (3H, m, Ar), 7.73-7.71 (3H, m, Ar), 7.51 (2H, tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, Ar), 7.43 (1H, tt, J_1 = 7.6 Hz, J_2 = 2.4 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.49, 143.25, 143.02, 142.42, 141.55, 140.25, 135.60, 130.67, 130.38, 129.64, 129.59, 129.11, 128.95, 127.98, 127.88, 127.19; Anal. Calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92; Found: C, 85.11; H, 4.87; N, 9.80.

2-Methoxy-4-(quinoxaline-2-yl)phenol (4s)

Brown solid, yield 95%, m.p: 133 ^oC; FT-IR (KBr): ν 2924, 1590, 1520, 1431, 1277, 1250, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.32 (1H, s, Ar), 8.14 (2H, td, J_1 = 8.4 Hz, J_2 = 1.6 Hz, Ar), 7.88 (1H, d, J = 1.6 Hz, Ar), 7.79 (1H, td, J_1 = 7.2 Hz, J_2 = 1.6 Hz, Ar) 7.75 (1H, td, J_1 = 6.8 Hz, J_2 = 1.6 Hz, Ar), 7.72 (1H, dd, J_1 = 8 Hz, J_2 = 2 Hz, Ar), 7.11 (1H, d, J = 8.4 Hz, Ar), 6.14 (1H, s, OH), 4.08 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.46, 148.07, 147.42, 143.11, 142.25, 141.20, 130.24, 129.31, 129.09, 121.14, 114.86, 109.73, 56.16; Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10; Found: C, 71.33; H, 4.65; N, 11.21.

Conclusion

We have reported a rapid and facile method for the synthesis of arylquinoxalines by condensation of 1,2-diamines with arylglyoxals under solvent free conditions using clay as an easily recoverable and low-cost catalyst. The procedure may be used for the synthesis of other heterocyclic compounds through condensation reactions. The improved strategies

described herein is economical, environmentally friendly, easily-operated due to solvent-free and easy work-up condition.

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