An Efficient Synthesis of Quinoxaline Derivatives Mediated by Stannous Chloride

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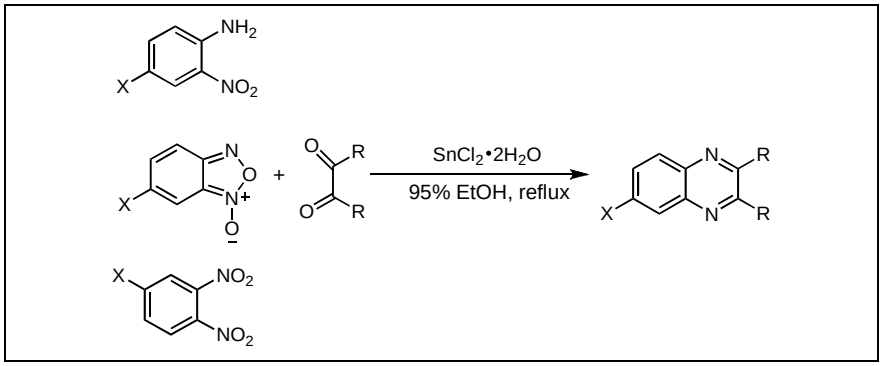

Various biologically important quinoxaline derivatives were efficiently synthesized in excellent yields by the reaction of 1,2-diketones and 2-nitroaniline, benzofuroxan or 1,2-dinitrobenzene promoted by $SnCl_2 \cdot 2H_2O$. The role of stannous chloride is acting as both reductive agent and catalyst in this synthesis. This new method has the advantages of accessible starting materials, convenient manipulation, short reaction time and high yields.

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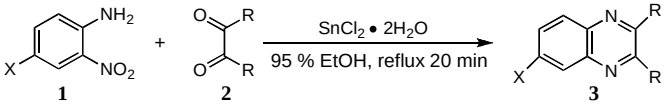
INTRODUCTION

Quinoxaline derivatives are an important class of nitrogen-containing heterocycles and they constitute useful intermediates in organic synthesis. Quinoxaline derivatives are well known in the pharmaceutical industry and have been shown to possess a broad spectrum of biological activities such as antibacterial, anti-inflammatory, antiviral and anticancer activity [1]. Besides this, it has been reported for their application in dyes [2], efficient electroluminescent materials [3], organic semiconductors [4], building blocks for the synthesis of anion receptor [5], cavitands [6], dehydroannulenes [7], and DNA cleaving agents [8]. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines. By far, the most common method is the condensation of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2-12 h giving 34-85% yields [9]. Recently, many improved methods have been reported for the synthesis of quinoxalines derivatives including the Bi-catalyzed oxidative coupling of epoxides and ene-1,2-diamines [10], from α-hydroxy ketones via a tandem oxidation process using $Pd(OAc)_2$ [11] and MnO_2 [12] as catalyst, cyclization of α-arylimino oximes of α-dicarbonyl compounds under reflux in acetic anhydride [13], the condensation of *o*-phenylene diamines and 1,2-dicarbonyl compounds in MeOH/AcOH under microwave irradiation [14] or using molecular iodine as the catalyst [15] and solid phase synthesis [16]. Nevertheless, most of these methods suffer from unsatisfactory product yields, critical product isolation procedures, expensive and detrimental metal precursors, expensive and inaccessible starting materials, and harsh reaction conditions, which limit their use under the aspect of environmentally benign processes.

The use of stannous chloride in organic synthesis has been known for a long time. In recent years, stannous chloride has received considerable attention as an inexpensive, nontoxic, readily available catalyst for various organic reactions [17] under mild and convenient conditions to afford the corresponding products in excellent yields with high selectivity. In this letter, we report the synthesis of quinoxalines by the reaction of 2-nitroanilines and 1,2-dicarbonyl compounds mediated by $SnCl_2 \cdot 2H_2O$ (Scheme 1).

Scheme 1



RESULTS AND DISCUSSION

We began our study of the reaction shown in Scheme 1 by optimizing the reaction conditions for the preparation of **3a**. A summary of the optimization experiments is provided in Table 1. The results showed that at room temperature, no reaction takes place (Table 1, entry 1). To our delight, under reflux the reaction proceeded smoothly in high yield. To find the optimum ratio of substrates with reductive agent, the reaction

was carried out in 95% EtOH using ratio of substrates with reductive agent from 1:1 to 1:6 (Table 1, entries 4,5,6,7,3,8), leading to **3a** in 0%, 0%, 85%, 89%, 97%, 85%, respectively. We concluded the best ratio of substrates with reductive agent is 1:5. Moreover, different organic solvents were further investigated as shown in Table 1, we concluded that 95% EtOH was the best solvent for this reaction.

Table 1

Optimization of temperature, ratio and solvents in the synthesis of **3a**

Entry	Solvent	T/°C	Ratio of **1a**: catalyst	Time /min	Yield (%)
1	EtOH	r.t	1:5	120	0
2	EtOH	60	1:5	120	10
3	EtOH	reflux	1:5	20	97
4	EtOH	reflux	1:1	90	0
5	EtOH	reflux	1:2	90	0
6	EtOH	reflux	1:3	20	85
7	EtOH	reflux	1:4	20	89
8	EtOH	reflux	1:6	20	85
9	CH_3CN	reflux	1:5	120	65
10	DMF	90	1:5	20	90
11	Acetone	reflux	1:5	20	68
12	$CHCl_3$	reflux	1:5	60	13
13	MeOH	reflux	1:5	270	95
14	EtOH	reflux	1:5	270	93

In order to demonstrate the efficiency and the applicability of the present method, we performed the reaction of a variety of 2-nitroanilines **1** and 1,2-diketones **2** with stannous chloride in refluxing 95% ethanol. The results are summarized in Table 2. As shown in Table 2, for series of **1** and **2**, either the aromatic ring containing electron-withdrawing groups (such as halides) or electron-donating groups (such as alkyl group), reacted well with stannous chloride to give the corresponding products **3** in high yields under the same reaction conditions. So we concluded that no obvious effects from the electronic nature of the aromatic ring substrates were observed in the above reactions.

Table 2

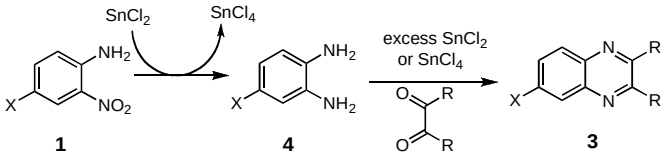
The Synthesis of Quinoxalines by the Reaction of 2-Nitroanilines and 1,2-Dicarbonyl Compounds Mediated by $SnCl_2{\cdot}2H_2O$

Product	X	R	Isolated yield (%)[a]
3a	H	C_6H_5	97
3b	H	4-$CH_3C_6H_4$	91
3c	H	Furan-2-yl	95
3d	CH_3	C_6H_5	93
3e	CH_3	4-$CH_3C_6H_4$	96
3f	CH_3	Furan-2-yl	91
3g	F	C_6H_5	92
3h	F	4-$CH_3C_6H_4$	95
3i	F	Furan-2-yl	93
3j	Br	C_6H_5	92
3k	Br	4-$CH_3C_6H_4$	93
3l	Br	Furan-2-yl	91
3m	CH_3O	C_6H_5	97

[a] The ratio of $SnCl_2{\cdot}2H_2O$, **1** and **2** is 5 : 1 : 1, in 95 % EtOH, reflux for 20 min.

Although a detailed mechanism of the above reaction has not yet been clarified, the formation of quinoxaline derivatives can be explained by the tentative mechanism presented in Scheme 2. The intermediates in this transformation were 1,2-diaminobenzenes **4**, which were generated *in situ* by reduction of the 2-nitroanilines **1** by stannous chloride and subsequently reacted with 1,2-diketones to give the target compounds **3**. In this reaction, stannous chloride was oxidized to tin tetrachloride. This species or the excess of stannous chloride present in the reaction medium can catalyze the cyclization of 1,2-diaminobenzenes with 1,2-diketones.

Scheme 2



To support this, we studied the stannous chloride or tin tetrachloride catalyzing the cyclization of 1,2-diaminobenzene with 1,2-diketone (Scheme 3). The results are summarized in Table 3. As shown in Table 3, both stannous chloride and tin tetrachloride have high efficiency catalyzing this reaction. Other Lewis acid or Brönsted acid can also catalyze this cyclization.

Scheme 3

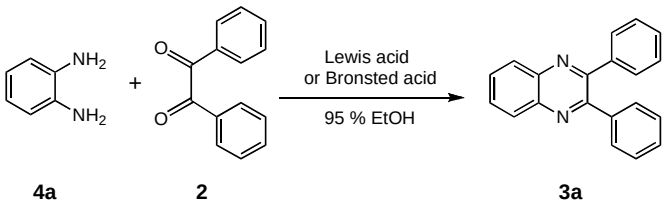


Table 3

The results of cyclization of 1,2-diaminobenzene with 1,2-diketone catalyzed by acid[a]

Entry	Catalyst	Temperature (°C)	Time (min.)	Yield (%)[b]
1	No	reflux	45	60
2	$SnCl_2{\cdot}2H_2O$	reflux	15	93
3	$SnCl_4{\cdot}5H_2O$	reflux	15	94
4	$AlCl_3$	reflux	15	92
5	$CoCl_2{\cdot}6H_2O$	reflux	65	86
6	$FeCl_3{\cdot}6H_2O$	reflux	15	77
7	$CaCl_2$	reflux	15	80
8	TsOH	r.t	2	92
9	H_2SO_4	reflux	20	81
10	HCl	reflux	30	89

[a] All reactions were performed at 1 mmol scale using 10 mol% of catalyst in 10 mL of 95% EtOH. [b] Isolated yields

Moreover, the reaction of benzofuroxan **5** and 1,2-dicarbonyl compound **2** with the same reagent afforded quinoxalines **3** (Scheme 4) and the results are summarized in Table 4.

Scheme 4

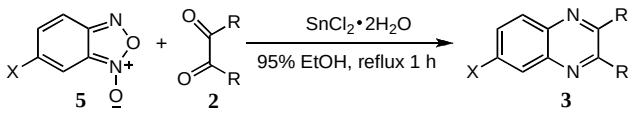


Table 4

The Synthesis of Quinoxalines by Reaction of Benzofuroxanes and 1,2-Dicarbonyl Compounds Mediated by $SnCl2{\cdot}2H_2O$

Product	X	R	Isolated yield (%)[a]
3a	H	C_6H_5	95
3n	H	4-$CH_3OC_6H_4$	95
3c	H	Furan-2-yl	95
3o	F	4-$CH_3OC_6H_4$	97
3i	F	Furan-2-yl	96
3p	Cl	C_6H_5	95
3q	Cl	4-$CH_3OC_6H_4$	99
3r	Cl	Furan-2-yl	98
3s	H	4-BrC_6H_4	97
3t	F	4-BrC_6H_4	93
3u	Cl	4-BrC_6H_4	95

[a] The ratio of $SnCl_2{\cdot}2H_2O$, **4** and **2** is 5 : 1 : 1, in 95 % EtOH, reflux for 1 h.

However, treatment of 1,2-dinitrobenzene **6** and 1,2-dicarbonyl compounds **2** with $SnCl_2{\cdot}2H_2O$ in 95 % EtOH under the same reaction conditions, the desired products quinoxalines **3** were obtained in good yields (Scheme 5). The results are summarized in Table 5.

Scheme 5

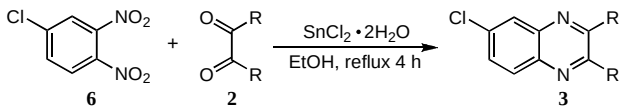


Table 5

The Synthesis of Quinoxalines by the Reaction of 1,2-Dinitrobenzenes and 1,2-Dicarbonyl Compounds Mediated by $SnCl_2{\cdot}2H_2O$

Product	R	Isolated yield (%)[a]
3p	C_6H_5	94
3q	4-$CH_3OC_6H_4$	98
3u	4-BrC_6H_4	94
3r	Furan-2-yl	94

[a] The ratio of $SnCl_2{\cdot}2H_2O$, **6** and **2** is 5 : 1 : 1, in 95 % EtOH, reflux for 4 h.

The structures of products **3** were confirmed by IR, ^1H NMR and HRMS.

In summary, a series of substituted quinoxalines were synthesized *via* reductive cyclization of 1,2-dicarbonyl compounds with 2-nitroanilines or benzofuroxanes or 1,2-dinitrobenzenes induced by $SnCl_2{\cdot}2H_2O$. The advantages of this new method are the easily accessible starting materials, convenient manipulation, short reaction time and high yields.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer. ^1H NMR spectra were measured on a Bruker DPX-400 M Hz spectrometer using TMS as internal standard, DMSO-d_6 as solvent. High resolution mass spectra were obtained using TOF-MS instrument.

General procedure for the synthesis of quinoxaline 3. The general procedure for the synthesis of quinoxaline is represented as follow: $SnCl_2{\cdot}2H_2O$ (15 mmol) was added to a solution of 1,2-dicarbonyl compound (3 mmol) and 2-nitroaniline or benzofuroxan or 1,2-dinitrobenzene (3 mmol) in 95 % ethanol (10 mL) at r.t. The mixture was stirred at refluxing for 2-4 h. When the reaction was completed, the mixture was poured into 3 % HCl aqueous (100 mL). The solid that separated was collected by filtration, washed with water, and then recrystallized from ethanol to afford pure quinoxaline **3**.

2,3-Diphenylquinoxaline (**3a**). This compound was obtained as solid with mp 124-126 °C (Lit. [15a] 126-127 °C); IR (KBr) ν: 3056, 1504, 1495, 1478, 1441, 1395, 1347, 1290, 1247, 1219, 1177, 1155, 1142, 1128, 1075, 1058, 1022, 977, 928, 817, 801, 771, 730, 697 cm^{-1}. ^1H nmr (DMSO-d_6): 7.34-7.43 (m, 6H, ArH), 7.45-7.50 (m, 4H, ArH), 7.88-7.91 (m, 2H, ArH), 8.15-8.19 (m, 2H, ArH).

2,3-Di(4-methylphenyl)quinoxaline (**3b**). This compound was obtained as solid with mp 142-143 °C (Lit. [18] 144-145 °C); IR (KBr) ν: 3029, 2912, 1611, 1555, 1539, 1514, 1474, 1407, 1393, 1343, 1307, 1248, 1222, 1212, 1184, 1141, 1110, 1055, 1019, 976, 951, 819, 761, 723 cm^{-1}. ^1H nmr (DMSO-d_6): 2.33 (s, 6H, 2 × CH_3), 7.18 (d, J = 8.0 Hz, 4H, ArH), 7.39 (d, J = 8.0 Hz, 4H, ArH), 7.85-7.89 (m, 2H, ArH), 8.11-8.15 (m, 2H, ArH).

2,3-Di(furan-2-yl)quinoxaline (**3c**). This compound was obtained as solid with mp 129-130 °C (Lit. [19] 131-132 °C); IR (KBr) ν: 3107, 3061, 1571, 1537, 1499, 1489, 1479, 1449, 1400, 1336, 1226, 1171, 1163, 1139, 1129, 1089, 1077, 1059, 1033, 1009, 993, 913, 887, 762, 751 cm^{-1}. ^1H nmr (DMSO-d_6): 6.71-6.75 (m, 4H, ArH), 7.88-7.90 (m, 2H, ArH), 7.91-7.93 (m, 2H, ArH), 8.10-8.13 (m, 2H, ArH).

6-Methyl-2,3-diphenylquinoxaline (**3d**). This compound was obtained as solid with mp 112-113 °C (Lit. [20] 115-116 °C); IR (KBr) ν: 3054, 2975, 1619, 1556, 1497, 1484, 1445, 1419, 1400, 1345, 1308, 1287, 1201, 1138, 1078, 1060, 1023, 979, 833, 775, 752, 703 cm^{-1}. ^1H nmr (DMSO-d_6): 2.61 (s, 3H, CH_3), 7.34-7.40 (m, 6H, ArH), 7.46-7.48 (m, 4H, ArH), 7.74 (d, 1H, J = 8.4 Hz, ArH), 7.96 (s, 1H, ArH), 8.06 (d, 1H, J = 8.4 Hz, ArH).

6-Methyl-2,3-di(4-methylphenyl)quinoxaline (**3e**). This compound was obtained as solid with mp 128-130 °C (Lit. [15a] 135.5-136 °C); IR (KBr) ν: 3029, 2916, 1611, 1554, 1533, 1514, 1487, 1455, 1405, 1378, 1324, 1305, 1252, 1204, 1183, 1142, 1110, 1056, 1018, 979, 834, 819, 795, 748, 721 cm^{-1}. ^1H nmr (DMSO-d_6): 2.33 (s, 6H, 2 × CH_3), 2.59 (s, 3H, CH_3), 7.18 (d,

4H, *J* = 8.0 Hz, ArH), 7.37 (d, 4H, *J* = 8.0 Hz, ArH), 7.70 (d, 1H, *J* = 8.4 Hz, ArH), 7.92 (s, 1H, ArH), 8.02 (d, 1H, *J* = 8.4 Hz, ArH).

2,3-Di(furan-2-yl)-6-methyl-quinoxaline (**3f**). This compound was obtained as solid with mp 175-177 °C (Lit. [21] 176 °C); IR (KBr) *ν*: 3114, 1619, 1568, 1528, 1489, 1382, 1336, 1216, 1169, 1152, 1079, 1064, 1016, 991, 913, 887, 824, 754 cm^{-1}. ^1H nmr (DMSO-d_6): 2.59 (s, 3H, CH_3), 6.68-6.72 (m, 4H, ArH), 7.73 (d, 1H, *J* = 8.4 Hz, ArH), 7.89-7.94 (m, 3H, ArH), 8.00 (d, 1H, *J* = 8.4 Hz, ArH).

6-Fluoro-2,3-diphenylquinoxaline (**3g**). This compound was obtained as solid with mp 130-132 °C; IR (KBr) *ν*: 3047, 1620, 1561, 1542, 1497, 1479, 1446, 1437, 1345, 1285, 1243, 1224, 1205, 1183, 1153, 1115, 1074, 1059, 1025, 980, 961, 866, 834, 822, 802, 776, 758, 701, 695 cm^{-1}. ^1H nmr (DMSO-d_6): 7.37-7.41 (m, 6H, ArH), 7.47-7.49 (m, 4H, ArH), 7.82-7.87 (m, 1H, ArH), 7.95-7.98 (m, 1H, ArH), 8.24-8.28 (m, 1H, ArH). HRMS [Found: m/z 300.1061 (M^+), cacld for $C_{20}H_{13}FN_2$: M, 300.1063]

6-Fluoro-2,3-di(4-methylphenyl)quinoxaline (**3h**). This compound was obtained as solid with mp 112-114 °C; IR (KBr) *ν*: 3031, 2918, 1616, 1560, 1541, 1515, 1481, 1458, 1397, 1343, 1247, 1205, 1183, 1154, 1117, 1054, 1019, 981, 960, 864, 837, 818, 756, 721 cm^{-1}. ^1H nmr (DMSO-d_6): 2.34 (s, 6H, 2 × CH_3), 7.19 (d, 4H, *J* = 8.4 Hz, ArH), 7.38 (d, 4H, *J* = 8.4 Hz, ArH), 7.38-7.83 (m, 1H, ArH), 7.91-7.94 (m, 1H, ArH), 8.20-8.24 (m, 1H, ArH). HRMS [Found: m/z 328.1362 (M^+), cacld for $C_{22}H_{17}FN_2$: M, 328.1376]

6-Fluoro-2,3-di(furan-2-yl)-quinoxaline (**3i**). This compound was obtained as solid with mp 116-117 °C; IR (KBr) *ν*: 3115, 1619, 1566, 1536, 1486, 1329, 1216, 1171, 1114, 1079, 1063, 1016, 992, 968, 913, 890, 868, 833, 755 cm^{-1}. ^1H nmr (DMSO-d_6): 6.71-6.77 (m, 4H, ArH), 7.80-7.85 (m, 1H, ArH), 7.90-7.94 (m, 3H, ArH), 8.17-8.21 (m, 1H, ArH). HRMS [Found: m/z 280.0645 (M^+), cacld for $C_{16}H_9FN_2O_2$: M, 280.0648]

6-Bromo-2,3-diphenylquinoxaline (**3j**). This compound was obtained as solid with mp 116-117 °C (Lit. [22] 124-125 °C); IR (KBr) *ν*: 3055, 1593, 1546, 1497, 1445, 1393, 1341, 1285, 1250, 1238, 1221, 1191, 1182, 1159, 1075, 1061, 1024, 976, 915, 902, 874, 829, 801, 768, 724, 697 cm^{-1}. ^1H nmr (DMSO-d_6): 7.35-7.43 (m, 6H, ArH), 7.47-7.49 (m, 4H, ArH), 8.03 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz, ArH), 8.12 (d, 1H, *J* = 8.8 Hz, ArH), 8.41 (d, 1H, *J* = 2.0 Hz, ArH). HRMS [Found: m/z 360.0266 (M^+), cacld for $C_{20}H_{13}N_2{}^{79}Br$: M, 360.0262].

6-Bromo-2,3-di(4-methylphenyl)quinoxaline (**3k**). This compound was obtained as solid with mp 174-176 °C; IR (KBr) *ν*: 3056, 2916, 1608, 1594, 1546, 1513, 1470, 1422, 1404, 1391, 1337, 1278, 1245, 1181, 1138, 1110, 1056, 1018, 977, 908, 874, 841, 819, 791, 724 cm^{-1}. ^1H nmr (DMSO-d_6): 2.33 (s, 6H, 2 × CH_3), 7.19 (d, 4H, *J* = 8.0 Hz, ArH), 7.39 (d, 4H, *J* = 8.0 Hz, ArH), 7.99 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.6 Hz, ArH), 8.08 (d, 1H, *J* = 8.8 Hz, ArH), 8.37 (d, 1H, *J* = 1.6 Hz, ArH). HRMS [Found: m/z 388.0563 (M^+), cacld for $C_{22}H_{17}BrN_2$: M, 388.0575]

6-Bromo-2,3-di(furan-2-yl)-quinoxaline (**3l**). This compound was obtained as solid with mp 131-133 °C; IR (KBr) *ν*: 3113, 1591, 1566, 1535, 1496, 1484, 1468, 1410, 1334, 1256, 1219, 1198, 1163, 1151, 1128, 1089, 1076, 1062, 1053, 1030, 1017, 992, 928, 911, 871, 830, 756, 741 cm^{-1}. ^1H nmr (DMSO-d_6): 6.73-6.78 (m, 4H, ArH), 7.93-7.96 (m, 2H, ArH), 8.00 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.0 Hz, ArH), 8.05 (d, 1H, *J* = 8.8 Hz, ArH), 8.35 (d, 1H, *J* = 2.0 Hz, ArH). HRMS [Found: m/z 339.9841 (M^+), cacld for $C_{16}H_9BrN_2O_2$: M, 339.9847]

6-Methoxy-2,3-diphenylquinoxaline (**3m**). This compound was obtained as solid with mp 154-156 °C (Lit. [23] 154-155 °C); IR (KBr) *ν*: 3058, 2960, 1617, 1559, 1496, 1483, 1438, 1410, 1351, 1331, 1286, 1235, 1205, 1166, 1158, 1125, 1079, 1060, 1024, 976, 932, 835, 781, 771, 753, 704 cm^{-1}. ^1H nmr (DMSO-d_6): 3.99 (s, 3H, CH_3O), 7.33-7.41 (m, 6H, ArH), 7.44-7.49 (m, 4H, ArH), 7.52-7.56 (m, 2H, ArH), 8.06 (d, 1H, *J* = 10.0 Hz, ArH).

2,3-Di(4-methoxyphenyl)quinoxaline (**3n**). This compound was obtained as solid with mp 140-142 °C (Lit. [19] 145.5-146 °C); IR (KBr) *ν*: 3055, 2962, 2931, 1606, 1577, 1515, 1475, 1458, 1392, 1344, 1298, 1250, 1170, 1138, 1111, 1057, 1028, 1013, 975, 832, 810, 792, 767 cm^{-1}. ^1H nmr (DMSO-d_6): 3.79 (s, 6H, 2 × CH_3O), 6.95 (d, 4H, *J* = 8.4 Hz, ArH), 7.46 (d, 4H, *J* = 8.4 Hz, ArH), 7.84 (dd, 2H, J_1 = 6.4 Hz, J_2 = 3.6 Hz, ArH), 8.11 (dd, 2H, J_1 = 6.4 Hz, J_2 = 3.2 Hz, ArH).

6-Fluoro-2,3-bis(4-methoxyphenyl)quinoxaline (**3o**). This compound was obtained as solid with mp 146-147 °C; IR (KBr) *ν*: 3067, 2932, 1607, 1577, 1563, 1538, 1513, 1483, 1463, 1414, 1343, 1304, 1292, 1251, 1226, 1208, 1175, 1160, 1119, 980, 961, 885, 839, 796, 787, 758 cm^{-1}. ^1H nmr (DMSO-d_6): 3.79 (s, 6H, 2 × CH_3O), 6.95 (d, 4H, *J* = 8.8 Hz, ArH), 7.44-7.47 (m, 4H, ArH), 7.75-7.79 (m, 1H, ArH), 7.87-7.91 (m, 1H, ArH), 8.16-8.20 (m, 1H, ArH). HRMS [Found: m/z 360.1268 (M^+), cacld for $C_{22}H_{17}FN_2O_2$: M, 360.1274].

6-Chloro-2,3-diphenylquinoxaline (**3p**). This compound was obtained as solid with mp 118-119 °C (Lit. [24] 119-121 °C); IR (KBr) *ν*: 3055, 1606, 1593, 1551, 1497, 1472, 1444, 1393, 1341, 1286, 1251, 1239, 1221, 1192, 1182, 1159, 1068, 1024, 976, 919, 873, 830, 802, 725, 712, 694 cm^{-1}. ^1H nmr (DMSO-d_6): 7.35-7.43 (m, 6H, ArH), 7.47-7.49 (m, 4H, ArH), 7.92 (dd, 1H, J_1 = 1.6 Hz, J_2 = 8.8 Hz, ArH), 8.20 (d, 1H, *J* = 8.8 Hz, ArH), 8.26 (d, 1H, *J* = 1.6 Hz, ArH).

6-Chloro-2,3-di(4-methoxyphenyl)quinoxaline (**3q**). This compound was obtained as solid with mp 147-148 °C; IR (KBr) *ν*: 3074, 2961, 2935, 2838, 1607, 1576, 1535, 1512, 1466, 1441, 1394, 1342, 1304, 1286, 1257, 1247, 1172, 1109, 1071, 1026, 978, 922, 877, 844, 837, 799, 692 cm^{-1}. ^1H nmr (DMSO-d_6): 3.79 (s, 6H, 2 × CH_3O), 6.95 (d, 4H, *J* = 8.0 Hz, ArH), 7.46 (d, 4H, *J* = 8.8 Hz, ArH), 7.85 (dd, 1H, J_1 = 2.0 Hz, J_2 = 8.8 Hz, ArH), 8.13 (d, 1H, *J* = 8.8 Hz, ArH), 8.18 (d, 1H, *J* = 2.0 Hz, ArH). HRMS [Found: m/z 376.0985 (M^+), cacld for $C_{22}H_{17}ClN_2O_2$: M, 376.0979].

6-Chloro-2,3-di(furan-2-yl)-quinoxaline (**3r**). This compound was obtained as solid with mp 128-129 °C (Lit. [25] 122 °C); IR (KBr) *ν*: 3062, 1602, 1565, 1549, 1528, 1479, 1414, 1398, 1378, 1333, 1254, 1218, 1200, 1156, 1082, 1065, 1015, 988, 938, 912, 876, 823, 783, 752 cm^{-1}. ^1H nmr (DMSO-d_6): 6.74-6.78 (m, 4H, ArH), 7.89 (dd, 1H, J_1 = 1.6 Hz, J_2 = 8.8 Hz, ArH), 7.93-7.96 (m, 3H, ArH), 8.12 (d, 1H, *J* = 8.8 Hz, ArH), 8.19 (d, 1H, *J* = 2.0 Hz, ArH).

2,3-Bis(4-bromophenyl)quinoxaline (**3s**). This compound was obtained as solid with mp 188-189 °C (Lit. [26] 188-190 °C); IR (KBr) *ν*: 3058, 1585, 1557, 1541, 1521, 1487, 1475, 1389, 1342, 1219, 1125, 1068, 1047, 1007, 975, 842, 827, 818, 803, 760, 746, 721 cm^{-1}. ^1H nmr (DMSO-d_6): 7.45 (d, *J* = 8.4 Hz, 4H, ArH), 7.62 (d, *J* = 8.4 Hz, 4H, ArH), 7.92 (dd, J_1 = 3.2 Hz, J_2 = 6.4 Hz, 2H, ArH), 8.26 (dd, J_1 = 6.0 Hz, J_2 =8.8 Hz, 2H, ArH).

2,3-Bis(4-bromophenyl)-6-fluoroquinoxaline (3t). This compound was obtained as solid with mp 160-161 °C; IR (KBr) *ν*: 3057, 1618, 1585, 1558, 1539, 1475, 1390, 1341, 1245, 1217, 1204, 1155, 1111, 1072, 1047, 1009, 979, 958, 865, 843, 833,

814, 767, 722 cm^{-1}. ^1H nmr (DMSO-d_6): 7.44 (d, J = 8.4 Hz, 4H, ArH), 7.62 (d, J = 8.4 Hz, 4H, ArH), 7.84-7.89 (m, 1H, ArH), 7.98 (dd, 1H, J_1 = 2.0 Hz, J_2 = 9.2 Hz, ArH), 8.26 (dd, 1H, J_1 = 6.0 Hz, J_2 =8.8 Hz, ArH). HRMS [Found: m/z 455.9253 (M^+), cacld for $C_{20}H_{11}Br_2FN_2$: M, 455.9273].

2,3-Bis(4-bromophenyl)-6-chloroquinoxaline (**3u**). This compound was obtained as solid with mp 166-167 °C; IR (KBr) ν: 3069, 1601, 1585, 1558, 1540, 1487, 1464, 1389, 1339, 1244, 1192, 1177, 1071, 1048, 1009, 975, 921, 877, 842, 829, 817, 788, 721 cm^{-1}. ^1H nmr (DMSO-d_6): 7.44 (d, J = 8.4 Hz, 4H, ArH), 7.63 (d, J = 8.4 Hz, 4H, ArH), 7.94 (dd, J_1 = 1.2 Hz, J_2 = 9.2 Hz, 1H, ArH), 8.20 (d, J =8.8 Hz, 1H, ArH). HRMS [Found: m/z 471.8957 (M^+), cacld for $C_{20}H_{11}Br_2ClN_2$: M, 471.8977].

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