Synthesis of quinoxalines catalysed by cetyltrimethyl ammonium bromide (CTAB) in aqueous media

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A facile and simple method has been developed for the condensation of 1,2-diaminobenzenes with α-bromoketones to form quinoxalines with good yields using cetyltrimethyl ammonium bromide (CTAB) in aqueous media. The efficiency of this reaction was demonstrated by the compatibility with nitro, methyl, methoxy, fluoro chloro bromo and furanyl groups. The important features of the methodology are broad substrate scope, simple workup, and no requirement for metal catalysts.

Keywords: quinoxaline, cetyltrimethyl ammonium bromide (CTAB), aqueous media

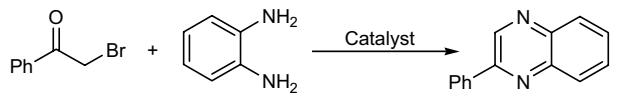
Quinoxaline derivatives have shown a broad spectrum of biological activities such as anticancer, anthelmintic, antifungal and insecticidal agents.[1] The quinoxaline ring is present in a number of antibiotics such as echinomycin, levomycin, and actinomycin, which are known to inhibit the growth of gram-positive bacteria and are also active against various transplantable tumours.[2,3] They have also found applications as dyes,[4] efficient electroluminescent materials,[5] organic semiconductors,[6] dehydroannulenes,[7] cavitands[8] and chemically controllable switches.[9] Thus, a large number of procedures have been developed for the construction of quinoxaline derivatives involving condensation of 1,2-diamines with 1,2-diketones,[10,11] oxidation-trapping of α-hydroxyketones with 1,2-diamines,[12-14] 1,4-addition of 1,2-diamines to diazenylbutenes,[15] $POCl_3$-mediated heteroannulation of α-nitroketene *N*,*S*-anilinoacetals,[16] oxidative coupling of epoxides with ene-1,2-diamines,[17] cyclisation–oxidation of phenacyl bromides and *o*-phenylenediamines through solid-phase synthesis[18,19] or high temperature and pressure[20,21] (150 °C and 20 psi) by microwave irradiation or using $HClO_4{\cdot}SiO_2$[22] as heterogeneous catalyst. Nevertheless, most of these methods suffer from drawbacks such as unsatisfactory yields, difficult experimental procedures, expensive and harmful reagents and harsh reaction conditions. Therefore, the development of environmentally benign, efficient and high-yielding methods for the synthesis of quinoxalines remains a highly desirable goal in organic synthesis.

In continuation of our efforts to develop green synthetic routes for the formation of C–C and carbon–heteroatom bond,[23-32] we report here a green, simple and practical method for the synthesis of quinoxaline derivatives from α-bromoketones and 1,2-diaminobenzenes catalysed by CTAB in aqueous media.

At the onset of the research, the efficacy of various catalysts was investigated in the model reaction between α-bromoketone **1a** and 1,2-diaminobenzene **2a** under different reaction conditions (Table 1). The results showed that CTAB was superior with respect to product yields. Entry 1 shows the control reaction without addition of any catalyst, in this case 2-phenylquinoxaline **3a** was obtained in low yield. We next planned to determine the influence of solvent on the rate and yield of the model reaction. As shown in Table 1, the presence of organic solvents lowers the reaction rate (Table 1, entries 9–12). So we chose to perform this reaction in aqueous media. The structure of **3a** was characterised by ^{1}H NMR, ^{13}C NMR, IR and by comparison with authentic samples prepared by a literature procedure.

With the optimised conditions in place, the reactions of various α-bromoketones with different 1,2-diaminobenzenes were examined to explore the scope and generality of this protocol for the synthesis of various quinoxalines and the results are summarised in Table 2.

Table 1 Synthesis of 2-phenylquinoxaline under different reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Yield/%[b]
1	none	H_2O	29
2	SDS	H_2O	52
3	TBAF	H_2O	50
4	TBAI	H_2O	51
5	TMAB	H_2O	64
6	CTAB	H_2O	81
7	CTAB	H_2O	53[c]
8	CTAB	H_2O	70[d]
9	CTAB	EtOH	60
10	CTAB	CH_3CN	59
11	CTAB	1,4-dioxane	61
12	CTAB	DMSO	70

[a]All the reactions were run with α-bromoketone **1a** (1.0 mmol), 1,2-diaminobenzene **2a** (1.2 mmol) and catalyst (25 mol%) in water (5 mL) at reflux for 8 h.
[b]Isolated yield.
[c]5 mol%.
[d]10 mol%.

As shown in Table 2, the substitutent groups on the aromatic ring of the α-bromoketone had no obvious effect on the yields. It was observed that the α-bromoacetophenones with electron-donating functionality as well as electron-withdrawing functionality undergo condensation reactions with 1,2-diaminobenzenes equally well to afford the corresponding products in good to excellent yields. When employing the more hindered α-methylphenacyl bromide and 1,2-diaminobenzenes, moderate to good yields were also obtained (Table 2, entries 8, 17 and 22). Compared with the unsubstitued diamine, the reaction of most aromatic diamines bearing two substituents with α-bromoketones gave slightly lower product yields (Table 2, entries 11–22). The results showed that the scope of the reaction is quite broad and the conditions are tolerant of various functional groups such as nitro, methyl, methoxy, fluoro, chloro, bromo and furan groups.

In conclusion, we have developed an eco-friendly synthesis of quinoxalines catalysed by CTAB in water. Compared to previous reported methodologies, the present protocol features broad substrate scope, good yields, simple workup and has no requirement for metal catalysts. Further investigations on the

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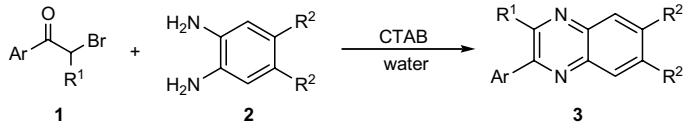
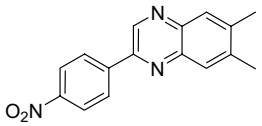
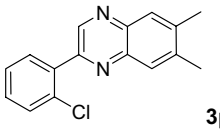
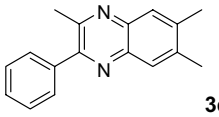
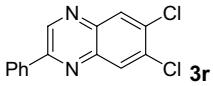
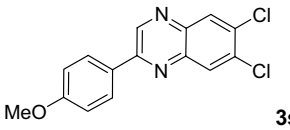
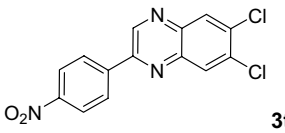
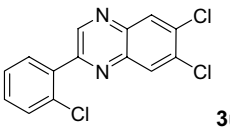
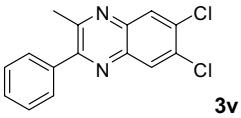
Table 2 Synthesis of quinoxalines using CTAB in water[a]



1 **2** **3**

Entry	α-Bromoketone		R^2	Products	Yield/%[b]
	Ar	R^1			
1	C_6H_5	H	H	**3a**	81[c]
2	*p*-ClC_6H_4	H	H	**3b**	92
3	*p*-BrC_6H_4	H	H	**3c**	95
4	*p*-$MeOC_6H_4$	H	H	**3d**	96[c]
5	*p*-MeC_6H_4	H	H	**3e**	87[c]
6	*p*-$NO_2C_6H_4$	H	H	**3f**	81
7	*o*-ClC_6H_4	H	H	**3g**	90
8	C_6H_5	Me	H	**3h**	71
9	2-furyl	H	H	**3i**	80
10	*p*-FC_6H_4	H	H	**3j**	88
11	C_6H_5	H	Me	**3k**	89[c]
12	*p*-ClC_6H_4	H	Me	**3l**	81
13	*p*-BrC_6H_4	H	Me	**3m**	85
14	*p*-$MeOC_6H_4$	H	Me		80

Table 2 *Continued*

Entry	α-Bromoketone		R^2	Products	Yield/%[b]
	Ar	R^1			
15	*p*-$NO_2C_6H_4$	H	Me		71
16	*o*-ClC_6H_4	H	Me	 **3p**	85
17	C_6H_5	Me	Me	 **3q**	52
18	C_6H_5	H	Cl	 **3r**	81
19	*p*-$MeOC_6H_4$	H	Cl	 **3s**	75
20	*p*-$NO_2C_6H_4$	H	Cl	 **3t**	70
21	*o*-ClC_6H_4	H	Cl	 **3u**	60
22	C_6H_5	Me	Cl	 **3v**	85

[a]All reactions were run with α-bromoketone **1** (1.0 mmol), 1,2-diaminobenzene **2** (1.2 mmol), CTAB (25 mol%, 0.25 mmol) and water (5 mL) at reflux for 24 h.
[b]Isolated yield.
[c]The reaction was carried out for 8 h.

reaction mechanism, scope and limitations of these reactions and a biological evaluation of the new class of compounds are under way.

Experimental

Chemicals were purchased and used without further purification. Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected. IR spectra were recorded on a Bruker-EQUINOX55 spectrometer. Mass spectra (EI, 70 ev) were measured with SHIMADZU GCMS-QP2010 Plus instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 300 instrument using $CDCl_3$ or DMSO-d_6 or acetone-d_6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts were given in δ relative to TMS, the coupling constants *J* are given in Hz. Elemental analysis was determined on a Carlo-Erba 1108 instrument. Column chromatography was performed using EM Silica gel 60 (300–400 mesh). All known products were identified by comparison with authentic samples.

General synthetic procedure for synthesis of 2-substituted quinoxalines of **3a–o**

To a mixture of α-bromoketone **1** (1 mmol) and 1,2-diaminobenzene **2** (1.2 mmol), CTAB (25 mol%) was added in water (5 mL) under reflux. The reaction was monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate (3 × 10 mL), the organic layer washed with brine (3 × 10 mL), and then dried over anhydrous Na_2SO_4 and concentrated. The product was separated and purified by column chromatography on silica gel (300–400 mesh) using an ethyl acetate/petrol mixture as the eluent to afford a pure product. When necessary, the products are purified by recrystallising with an ethyl acetate/petrol mixture.

2-Phenylquinoxaline (**3a**): Solid, m.p. 74–76 °C (lit.[33] 75–76 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56–7.59 (m, 3H), 7.77–7.81 (m, 2H), 8.13–8.23 (m, 4H), 9.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.4, 127.7, 129.0, 129.3, 129.5, 130.0, 130.1, 136.5, 141.4, 142.1, 143.2, 151.5.

2-(4-Chlorophenyl)quinoxaline (**3b**): Solid, m.p. 12–128 °C (not reported);[22] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.56 (m, 2H), 7.56–7.81 (m, 2H), 8.11–8.18 (m, 2H), 9.31 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.7, 129.1, 129.4, 129. 6, 129.7, 130.4, 135.1, 136.6, 141.6, 142.2, 142.8, 150.5.

2-(4-Bromophenyl)quinoxaline (**3c**): Solid, m.p. 136–139 °C (not reported);[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63–7.66 (m, 2H), 7.74–7.76 (m, 2H), 8.02–8.11 (m, 2H), 9.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.91, 128.89, 129.09, 129.51, 129.73, 130.40, 132.25, 135.47, 141.57, 142.10, 142.70, 150.48.

2-(4-Methoxyphenyl)quinoxaline (**3d**): Solid, m.p. 100–101 °C (lit.[33] 99–100 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 7.05–7.08 (m, 2H), 7.71–7.75 (m, 2H), 8.07–8.18 (m, 4H), 9.28 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.4, 114.5, 128.9, 129.0, 129.0, 129.2, 129.3, 130.1, 141.2, 142.3, 143.0, 151.3,161.4.

2-(4-Methylphenyl)quinoxaline (**3e**): Solid, m.p. 93–94 °C (lit.[33] 90–91 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.71–7.77 (m, 2H), 8.09–8.16 (m, 4H), 9.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 127.3, 129.0, 129.2, 129.4, 129.8, 130.1,133.8, 140.4, 141.3, 142.2, 143.2, 151.7.

2-(4-Nitrophenyl)quinoxaline (**3f**): Solid, m.p. 188–191 °C (not reported);[34] ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.90–7.93 (m, 2H), 8.13–8.16 (m, 2H), 8.39–8.42 (m, 2H), 8.56–8.59 (m, 2H), 9.67 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 124.6, 129.2, 129.36, 129.9, 131.4, 131.5, 141.8, 142.0, 142.4, 144.4, 148. 9, 149.4.

2-(2-Chlorophenyl)quinoxaline (**3g**): Solid, m.p. 86–88 °C (not reported);[35] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.48 (m, 2H), 7.55–7.74 (m, 2H),7.81–7.84 (m, 2H), 8.16–8.19 (m, 2H), 9.22 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.4, 129.1, 129.5, 130.1, 130.2, 130.2,1 30.7, 131.8, 132.5, 136.4, 141.2, 142.2, 146.1, 152.3.

2-Methyl-3-phenyl-quinoxaline (**3h**): Solid, m.p. 54–56 °C (lit.[11] 56 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.77 (s, 3H), 7.48–7.52 (m, 3H), 7.63–7.66 (m, 4H), 7.69–7.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 24.3, 128.2, 128.5, 128.8, 128.9, 129.1, 129.2, 129.7, 138.9, 140.9, 141.1, 152.4, 154.8.

2-(2-Furanyl)quinoxaline (**3i**): Solid, m.p. 98–99 °C (lit.[33] 97–98 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.61–6.62 (m, 1H), 7.30–7.31 (m, 1H), 7.67–7.75 (m, 3H), 8.04–8.10 (m, 2H), 9.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.8, 112.5, 129.2, 129.2, 129.3, 130.5, 141.2, 142.0, 142.1, 143.8, 145.1, 151.5.

2-(4-Fluorophenyl)quinoxaline (**3j**): Solid, m.p. 120–122 °C (lit.[33] 120–121 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21–7.27 (m, 2H), 7.75–7.78 (m, 2H), 8.09–8.21 (m, 4H), 9.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.16 (d, $^2J_{CF}$ = 21.3 Hz), 129.07, 129.43 (d, $^3J_{CF}$ = 8.25 Hz), 129.46, 129.54, 130.36, 132.84 (d, $^3J_{CF}$ = 3.45 Hz), 141.4, 142.1, 142.9, 150.7, 164.2 (d, $^1J_{CF}$ = 248.93 Hz).

6,7-Dimethyl-2-phenylquinoxaline (**3k**): Solid, m.p. 127–129 °C (lit.[33] 128–129 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 6H), 7.49–7.55 (m, 3H), 7.84 (s, 1H), 7.89 (s, 1H), 8.14–8.18 (m, 2H), 9.21 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 20.3, 127.3, 128.1, 128.6, 129.0, 129.8, 137.0, 140.1, 140.5, 140.7, 141.1, 142.3, 150.9.

6,7-Dimethyl-2-(4-chlorophenyl)quinoxalin (**3l**): Solid, m.p. 160–163 °C (not reported);[36,37] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 6H), 7.49 (d, *J* = 8.57 Hz, 2H), 7.82 (s, 1H), 7.85 (s, 1H), 8.09 (d, *J* = 8.57 Hz, 2H), 9.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 20.4, 128.1, 128.5, 128.5, 129.2, 135.4, 136.1, 140.4, 140.5, 141.0, 141.0, 141.8, 149.6.

6,7-Dimethyl-2-(4-bromophenyl)quinoxalin (**3m**): Solid, m.p. 140–142 °C (lit.[38] 141–142 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 6H), 7.66 (d, *J* = 8.7 Hz, 2H); 7.83 (s, 1H), 7.86 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 9.16 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 20.4, 124.5, 128.1, 128.5, 128.8, 132.2, 135.9, 140.4, 140.6, 141.0, 141.1, 141.8, 149.7.

6,7-Dimethyl-2-(4-methoxyphenyl)quinoxaline (**3n**): Solid, m.p. 126–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 6H), 3.89 (s, 3H), 7.06 (d, *J* = 8.57 Hz, 2H), 7.82 (s, 1H), 7.85 (s, 1H), 8.13 (d, *J* = 8.57 Hz,2H), 9.17 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.2, 20.3, 55.3, 114.4, 128.0, 128.4, 128.7, 129.5, 139.5, 140.0, 140.58, 141.1, 142.0, 150.5, 161.1. MS (EI, 70 eV) *m/z* (%): 266 (M^+ + 2, 2), 265 (M^+ + 1, 19), 264 (M^+, 100), 249 (32). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.29; H, 6.07; N, 10.65%.

6,7-Dimethyl-2-(4-nitrophenyl)quinoxaline (**3o**): Solid, m.p. 197–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (s, 6H), 7.88 (s, 1H), 7.91 (s, 1H), 8.33 (d, *J* = 9.11 Hz,2H), 8.38 (d, *J* = 9.11 Hz, 2H), 9.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 20.4, 124.2, 128.0, 128.2, 128.7, 141.1, 141.1, 141.5, 141.6, 141.8, 142.9, 148.2, 148.5. MS (EI, 70 eV) *m/z* (%): 281 (M^+ + 3, 2), 280 (M^+ + 1, 19), 279 (M^+, 100), 103 (42). Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.87; H, 4.72; N, 15.09%.

6,7-Dimethyl-2-(2-Chlorophenyl)quinoxaline (**3p**): Solid, m.p. 96–98 °C; IR (KBr) ν_{max}/cm^{-1}: 3044, 2917, 1736, 1482, 1439, 1035, 755; ^{1}H NMR (300 MHz, $CDCl_3$): 2.50–2.51 (m, 6H), 7.40–7.44 (m, 2H), 7.51–7.52 (m, 1H), 7.69–7.72 (m, 1H), 7.89–7.91 (m, 2H), 9.10 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 20.4, 127.1, 127.3, 128.1, 128.5, 130.1, 130.5, 131.8, 132.5, 136.7, 140.2, 140.8, 141.1, 145.1, 151.3; MS (EI, 70 eV) *m/z* (%): 270 (M^+ + 2, 26), 268 (M^+, 72), 233 (100), 134 (15), 103 (28). Anal. Calcd for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42. Found: C, 71.64; H, 4.96; N, 10.27%.

2,6,7-Trimethyl-3-phenylquinoxaline (**3q**): Solid, m.p. 92–95 °C (not reported);[39] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H), 2.49 (s, 3H), 2.75 (s, 3H), 7.48–7.52 (m, 3H), 7.63–7.66 (m, 2H), 7.80 (s, 1H), 7.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 20.4, 24.2, 127.3, 128.2, 128.4, 128.7, 128.9, 139.3, 139.5, 139.9, 140.1, 140.1, 151.3, 153.8.

6,7-Dichloro-2-phenylquinoxaline (**3r**): Solid, m.p. 153–156 °C (not reported);[40] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.61 (m, 3H), 8.19–8.22 (m, 2H), 8.26 (s, 1H), 8.30 (s, 1H), 9.34 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.6, 129.3, 129.8, 130.2, 130.8, 134.1, 136.1, 140.3, 141.1, 144.3, 152. 7.

6,7-Dichloro-2-(4-methoxyphenyl) quinoxaline (**3s**): Solid, m.p. 199–201 °C; IR (KBr) ν_{max}/cm^{-1}: 2920, 2417, 1460, 1260, 1180, 1114, 837; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.1 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 8.19 (s, 1H), 8.22 (s, 1H), 9.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.5, 114.7, 128.4, 129.1, 129.7, 129.9, 133.3, 134.7, 139.9, 141.1, 144.0, 152.2. 161.9; MS (EI, 70 eV) *m/z* (%): 308 (M^+ + 4, 11), 306 (M^+ + 2, 63), 304 (M^+, 100), 289 (21), 133 (19). Anal. Calcd for $C_{15}H_{10}C_{l2}N_2O$: C, 59.04; H, 3.30; N, 9.18. Found: C, 59.16; H, 3.43; N, 9.27%.

6,7-Dichloro-2-(4-nitrophenyl) quinoxaline (**3t**): Solid, m.p. 223–225 °C; IR (KBr) ν_{max}/cm^{-1}: 2921, 2398, 1733, 1458, 1348, 1110, 859; ^{1}H NMR (300 MHz, acetone-d_6): δ 8.39 (d, *J* = 8.7 Hz, 2H), 8.43 (s, 2H), 8.53 (d, *J* = 8.7 Hz, 2H), 9.68 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6): δ 124.10, 128.86 (× 2), 130.02, 130.41, 134.08, 134.39, 140.92, 141.77, 145.04, 205.22, 205.48; MS (EI, 70 eV) *m/z* (%): 323 (M^+ + 4, 11), 321 (M^+ + 2, 62), 319 (M^+, 100), 289 (26), 144 (22), 77 (32). Anal. Calcd for $C_{14}H_7Cl_2N_3O_2$: C, 52.53; H, 2.20; N, 13.13. Found: C, 52.41; H, 2.29; N, 13.22%.

6,7-Dichloro-2-(2-chlorophenyl)quinoxaline (**3u**): Solid, m.p. 113–115 °C; IR (KBr) ν_{max}/cm^{-1}: 3048, 2918, 1453, 1316, 1112, 939, 752; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.57 (m, 3H), 7.70–7.72 (m, 1H), 8.28 (s, 1H), 8.29 (s, 1H), 9.22 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.6, 129.9, 130.2, 130.4, 131.2, 131.9, 132.5, 134.7, 134.9, 135.8, 140.0, 141.0, 147.1, 153.3; MS (EI, 70 eV) *m/z* (%): 314 (M^+ + 6, 3), (312 (M^+ + 4, 24), 310 (M^+ + 2, 68), 308 (M^+, 77), 275 (52), 273 (100), 109 (35). Anal. Calcd for $C_{14}H_7Cl_3N_2$: C, 54.32; H, 2.28; N, 9.05. Found: C, 54.49; H, 2.17; N, 8.96%.

2-Methyl-6,7-dichloro-3-phenylquinoxaline (**3v**): Solid, m.p. 151–153 °C (not reported);[39] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.78 (s, 3H), 7.54–7.56 (m, 3H), 7.64–7.65 (m, 2H), 8.17 (s, 1H), 8.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 128.6, 128.96, 129.1, 129.4, 129.8, 133.6, 134.1, 138.2, 139.7, 139.9, 154.0, 155.9.

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