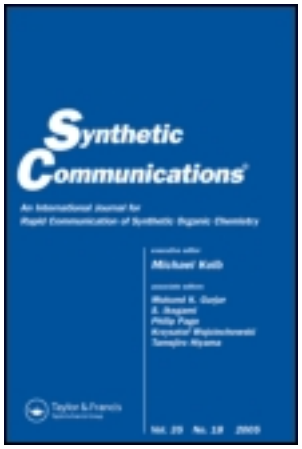

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Glycerin and $CeCl_3 \cdot 7H_2O$: A New and Efficient Recyclable Reaction Medium for the Synthesis of Quinoxalines

A. Venkat Narsaiah [a] & J. Kranthi Kumar [a]

[a] Organic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India

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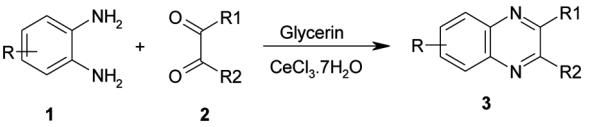
GLYCERIN AND $CeCl_3 \cdot 7H_2O$: A NEW AND EFFICIENT RECYCLABLE REACTION MEDIUM FOR THE SYNTHESIS OF QUINOXALINES

A. Venkat Narsaiah and J. Kranthi Kumar
Organic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India

GRAPHICAL ABSTRACT



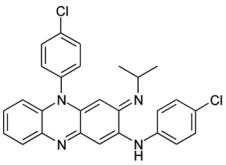
1 2 3

Abstract *An efficient and environmentally benign process for the synthesis of quinoxalines has been developed using glycerine–cerium chloride as a reaction medium. This method is applicable to a variety of diketones and 1,2-phenylenediamines to afford the corresponding quinoxaline derivatives in excellent yields. The reaction medium was recovered and reused for further reactions without any problem.*

Keywords $Cecl_3 \cdot 7H_2O$; diketones; glycerine; *ortho*-phenylenediamines; quinoxalines

INTRODUCTION

Quinoxalines are a versatile class of nitrogen-containing heterocyclic compounds, 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 including antibacterial, antiviral, anti-inflammatory, anticancer, and kinase inhibitory activities.[1,2] In addition, quinoxaline derivatives have been evaluated as anthelmintic agents, semiconductors, dyes, and biocides.[3] Therefore, a variety of synthetic strategies have been developed for the preparation of substituted quinoxalines.



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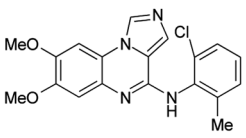

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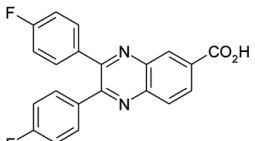

Hit-2-anti-HCV

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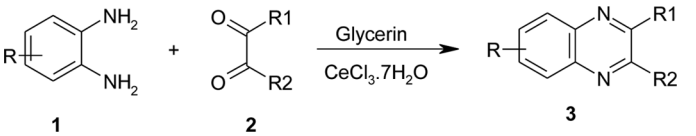
Address correspondence to A. Venkat Narsaiah, Organic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India. E-mail: vnakkirala2001@yahoo.com

Conventionally, quinoxaline synthesis can be achieved by the reaction of *ortho*-pheny lenediamine with two-carbon synthones such as α-dicarbonyls,[4–8] α-halogeno carbonyls, α-hydroxycarbonyls, α-azocarbonyls, epoxides, and α,β-dihalides.[9–16] Among the reported procedures, the most common method is the condensation of aryl-1,2-diamine with 1,2-diketone in refluxing ethanol or acetic acid[17–22] or using different catalysts and reaction conditions.[23–28] However, many of these methods suffer from several drawbacks, such as drastic reaction conditions, use of polar solvents [e.g., AcOH, EtOH, dimethylsulfoxide (DMSO)], expensive and toxic metal catalysts [e.g., $Pd(OAc)_2$ and $RuCl_2(PPh_3)_3$–[2,2,6,6-tetramethylpiperidin-1-yl]oxyl (TEMPO)], tedious workup procedures, and unsatisfactory yields, which limit their use.[29–31] Therefore, the development of simple, convenient, environmentally benign, and improved method for the synthesis of quinoxalines derivatives would certainly be useful in generating combinatorial libraries for drug discovery. Recently, Silvera et al. reported glycerine–$CeCl_3 \cdot 7H_2O$ as a new and efficient recyclable reaction medium for the synthesis of bis(indole) methanes,[32] and we demonstrated this system for the synthesis of Hantzsch pyridines.[33]

RESULTS AND DISCUSSION

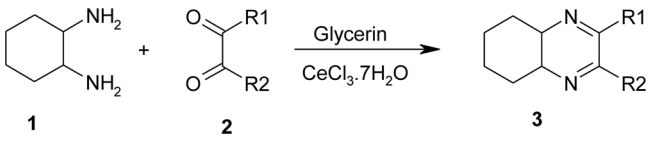
Herein, we report an efficient and environmentally friendly protocol for the synthesis of quinoxaline derivatives using glycerine–$CeCl_3 \cdot 7H_2O$ as a reaction medium. Initially, we chose the benzil and 1,2-phenylenediamine as standard reactants to establish the best reaction conditions for this transformation. In a typical experiment, equimolar amounts of benzil and 1,2-phenylenediamine were reacted in gylcerine (2 mL) using $CeCl_3 \cdot 7H_2O$ as catalyst to obtain the corresponding product 2,3-diphenylquinoxaline (**3a**) in excellent yields, as shown in the Scheme 1.

We have examined the effect of temperature, amount of catalyst $CeCl_3 \cdot 7H_2O$, and reaction time using glycerine as a solvent. It was found that when using 0.5 equivalents of $CeCl_3 \cdot 7H_2O$ and 2.0 mL of glycerine at room temperature, the reaction proceeded slowly and 70% yield was obtained after stirring for 24 h. However, when the mixture was heated at 60 °C and 75 °C, the desired product was obtained in very good to excellent yields after 8 and 4 h, respectively. At higher temperature (100 °C), the reaction was completed within 4.0 h but in poor yield. The effect of the amount of the catalyst was also studied. The observation shows that when $CeCl_3 \cdot 7H_2O$ was used in 0.5 equivalents and 0.1 equivalents, the same yield was obtained after 4 h of stirring at 75 °C. On the other hand, using 1 equivalent of $CeCl_3 \cdot 7H_2O$ was tested but there was no increase in yield or reduction in reaction time. When the reaction was performed in glycerine without $CeCl_3 \cdot 7H_2O$, at room



1 2 3

Scheme 1. General reaction for the synthesis of quinoxalines with aromatic-1,2-diamines.



Scheme 2. General reaction for the synthesis of quinoxalines with alicyclic-1,2-diamines.

temperature or with heating, no product formation was observed. The ideal reaction conditions for this condensation were 0.1 equivalent of $CeCl_3 \cdot 7H_2O$ (10 mol%) and 75 °C in glycerine (Scheme 2 and Table 1).

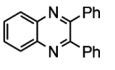
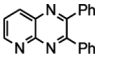
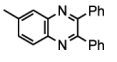
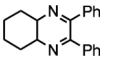
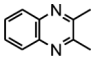
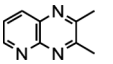
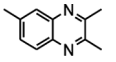
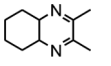
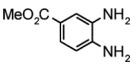
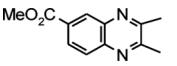
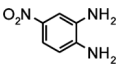
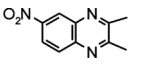
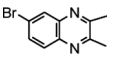
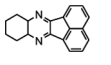
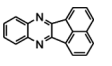
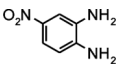
This protocol was extended to other aromatic diketones, including benzil and acenaphthylene-1,2-dione, and aliphatic carbonyls, including biacetyl. In a similar manner, the aromatic diamines such as *ortho*-phenylene diamine (**3a, 3e, 3m**), 4-methylbenzene-1,2-diamine (**3c** and **3g**), 4,5-dimethyl benzene-1,2-diamine (**3r, 3s, 3u**), 4-notrobenzene-1,2-diamine (**3j** and **3n**), pyridine-2,3-diamine (**3b, 3f, 3q**), 4-bromobenzene-1,2-diamine (**3k, 3t, 3v**), methyl-3,4-diaminobenzoate (**3i, 3o, 3p**), and alicyclic diamine such as cyclo hexene-1,2-diamine (**3d, 3h, 3l**) have been studied. The scope and generality of this procedure is illustrated with respect to various diketo carbonyls and 1,2-diamines, and the results are presented in Table 2. In general, the condensation takes place faster when the reaction was carried out between aromatic diketones and *ortho*-phenylenediamines. In a similar manner, the reaction between aliphatic diketones and alicyclic diamines was comparatively slower with lesser yields. All the reactions were completed within 4 to 6 h at 75 °C. The products were obtained in 75% to 95% yields. The structures of the products were identified by their ^{1}H NMR, infrared (IR), and mass spectral analysis.

The glycerin/$CeCl_3 \cdot 7H_2O$ mixture can be successfully reused up to five times with excellent results. Accordingly, treatment of benzil (**1**) with *ortho*-phenylenediamine (**2**) in presence of 10 mol% of $CeCl_3 \cdot 7H_2O$ in glycerine at 75 °C afforded 2,3-diphenyl quinoxalines (**3a**) in 95% yield (entry 1, Table 2). The product **3a** was simply extracted with ethyl acetate (2 × 10 mL), and the glycerin/$CeCl_3 \cdot 7H_2O$ mixture was reused for further reactions up to four times without any problem. The product was obtained in 95, 93, 93, and 90% yields respectively in successive cycles.

Table 1. Optimization of reaction conditions for the synthesis of quinoxalines

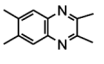
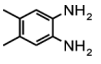
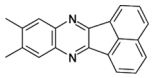
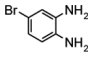
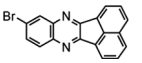
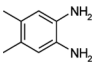
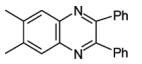
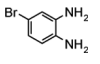
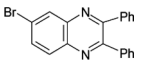
Entry	Solvent	$CeCl_3 \cdot 7H_2O$	Temp. (°C)	Time (h)	Yield (%)
1	Glycerin	0.5	rt	24	70
2	Glycerin	0.5	60	8.0	78
3	Glycerin	0.5	75	4.0	95
4	Glycerin	0.5	100	4.0	80
5	Glycerin	0.1	75	4.0	95
6	Glycerin	1.0	75	4.0	95
7	Glycerin	0	rt	24	0
8	Glycerin	0	75	24	0

Table 2. Glycerin- and $CeCl_3 \cdot 7H_2O$-catalyzed synthesis of quinoxalines

No.	Diamine	Diketone	Product (**3a–3v**)[a]	Reaction time (h)	Yield[b] (%)
a				4.0	95
b				4.0	92
c				4.0	95
d				6.0	88
e				5.0	90
f				5.0	84
g				5.0	85
h				6.0	75
i				5.0	83
j				6.0	81
k				5.0	83
l				5.5	85
m				4.5	92
n				5.5	84
o				5.0	86
p				5.0	85
q				5.0	86

(*Continued*)

Table 2. Continued

No.	Diamine	Diketone	Product (**3a–3v**)[a]	Reaction time (h)	Yield[b] (%)
r				6.0	85
s				5.0	91
t				5.0	85
u				4.0	95
v				4.5	86

[a]All the products were identified by their ^{1}H NMR, IR, and mass.
[b]Yields were isolated and not optimized.

CONCLUSION

In conclusion, we have demonstrated an efficient and environmentally friendly protocol for the synthesis of quinoxalines using a new catalyst system (glycerine–$CeCl_3 \cdot 7H_2O$) via the coupling of diketo carbonyls with 1,2-diamines. The method is very simple, clean, and applicable to a variety of reactants such as aromatic, hetero aromatic, aliphatic, and alicyclic systems.

EXPERIMENTAL

Melting points were recorded on Buchi R-535 apparatus. IR spectra were recorded on a Perkin-Elmer Fourier transform (FT)–IR 240-c spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded on Gemini-200 and Varian Bruker-300 spectrometers in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

General Procedure for the Synthesis of Quinoxalines

The catalyst $CeCl_3 \cdot 7H_2O$ (37 mg, 0.1 mmol) were added to a mixture of diketone (210 mg, 1.0 mmol) and diamine (128 mg, 1.1 mmol) in glycerine (2.0 mL) at room temperature. The resulting reaction mixture was stirred at 75 °C for a period of 4 to 6 h (Table 2). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature. Ethyl acetate (10 mL) was added to the reaction mixture and stirred well, the ethyl acetate layer was separated by decantation, and the process was repeated. The combined organic layers were washed with

water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude products, which were purified by column chromatography using silica gel (60–120 mesh). All the pure products were identified by their IR, ^{1}H NMR, and mass spectroscopic data.

Spectral Data for All Compounds

2,3-Diphenylquinoxaline (3a). IR (KBr): υ 3384, 3056, 2934, 1659, 1595, 1541, 1474, 1442, 1394, 1344, 1248, 1216, 1174, 1053, 977, 925, 872, 798, 768, 725, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.25–7.35 (m, 6H), 7.45–7.55 (m, 4H), 7.75 (q, 2H, $J = 6.0$ Hz), 8.35 (d, 2H, $J = 6.0$ Hz); EIMS m/z (%): 283 (m^{+1} 100), 256 (10), 205 (10), 179 (35), 140 (28), 128 (18), 104 (10), 91 (15), 79 (50), 76 (20), 52 (10).

2,3-Diphenylpyrido-[2,3-*b*]-pyrazine (3b). IR (KBr): υ 3413, 3058, 2923, 2853, 1592, 1549, 1433, 1385, 1338, 1242, 1189, 1123, 1070, 1020, 973, 922, 806, 776, 740, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.25–7.40 (m, 6H), 7.45–7.55 (m, 2H), 7.58–7.63 (m, 2H), 7.75 (q, 1H, $J = 6.5$ Hz), 8.50 (dd, 1H, $J = 3.5$, 10.0 Hz), 9.12–9.20 (m, 1H); EIMS m/z (%): 284 (m^{+1} 100), 281 (12), 270 (15), 242 (20), 223 (10), 205 (10), 189 (15), 179 (35), 159 (20), 145 (20), 117 (30), 103 (40), 82 (56), 77 (10), 51 (10).

6-Methyl-2,3-diphenylquinoxaline (3c). IR (KBr): υ 3419, 3054, 2922, 1665, 1591, 1485, 1447, 1342, 1250, 1208, 1172, 1060, 1022, 978, 875, 832, 773, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.63 (s, 3H), 7.25–7.35 (m, 5H), 7.45–7.55 (m, 5H), 7.89–8.08 (m, 3H).; EIMS m/z (%): 297 (m^{+1} 100), 145 (20), 105 (15), 60 (20).

2,3-Diphenyl-4a,5,6,7,8,8a-hexahydroquinoxaline (3d). IR (KBr): υ 3386, 2937, 2856, 1661, 1595, 1552, 1488, 1443, 1316, 1288, 1262, 1212, 1174, 1089, 1056, 979, 916, 850, 793, 766, 741, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.35–1.45 (m, 3H), 1.50–1.62 (m, 2H), 1.85–1.95 (m, 1H), 2.50 (d, 1H, $J = 6.0$ Hz), 2.80 (d, 1H, $J = 3.0$ Hz), 7.15–7.28 (m, 6H), 7.32–7.42 (m, 4H); EIMS m/z (%): 289 (m^{+1} 100), 288 (10), 241 (10), 171 (10), 165 (15), 151 (10), 104 (60), 102 (30), 79 (25), 67 (35), 54 (10).

2,3-Dimethylquinoxaline (3e). IR (KBr): υ 3380, 2941, 2885, 1647, 1428, 1397, 1324, 1208, 1164, 1044, 989, 922, 856, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 6H), 7.60–7.70 (m, 2H), 7.90–8.01 (m, 2H); EIMS m/z (%): 158 (m^+ 70), 143 (10), 130 (10), 118 (10), 117 (100), 102 (10), 90 (15), 89 (12), 77 (20), 76 (35), 75 (12), 61 (12), 50 (18), 41 (10).

2,3-Dimethylpyrido-[2,3-b]-pyrazine (3f). IR (neat): υ 3376, 2994, 2947, 1641, 1599, 1560, 1461, 1395, 1313, 1238, 1191, 1151, 1108, 1041, 995, 918, 830, 796, 713, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.78 (s, 3H), 2.83 (s, 3H), 7.58–7.68 (m, 1H), 8.35 (d, 1H, $J = 5.0$ Hz), 9.05 (d, 1H, $J = 3.0$ Hz).; EIMS m/z (%): 159 (m^+ 48), 144 (10), 118 (58), 105 (12), 91 (15), 77 (52), 61 (100), 50 (18), 41 (66).

2,3,6-Trimethylquinoxaline (3g). IR (KBr): υ 3388, 2940, 1620, 1563, 1494, 1442, 1399, 1367, 1325, 1255, 1200, 1113, 1044, 988, 832, 769, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.58 (s, 3H), 2.70 (s, 6H), 7.45 (d, 1H, $J = 7.0$ Hz), 7.70 (s, 1H), 7.83 (d, 1H, $J = 7.0$ Hz); EIMS m/z (%): 173 (m^{+1} 100), 146 (10), 132 (10), 91 (25), 76 (15).

2,3-Dimethyl-4a,5,6,7,8,8a-hexahydroquinoxaline (3h). ^{1}H NMR ($CDCl_3$): δ 0.92 (s, 6H), 1.30–1.45 (m, 4H), 1.55–1.70 (m, 6H); EIMS m/z (%): 164 (m^+ 100), 140 (20), 114 (10), 98 (10), 82 (10), 56 (10), 43 (15).

Methyl-2,3-Dimethylquinoxaline-6-carboxylate (3i). IR (KBr): υ 3384, 2943, 2886, 1712, 1658, 1442, 1400, 1343, 1307, 1263, 1198, 1095, 1046, 992, 918, 854, 765, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.75 (s, 6H), 3.99 (s, 3H), 7.98 (d, 1H, $J = 6.5$ Hz), 8.25 (d, 1H, $J = 6.5$ Hz), 8.68 (s, 1H); EIMS m/z (%): 217 (m^+ 100), 191 (20), 177 (12), 102 (25).

2,3-Dimethyl-6-nitroquinoxaline (3j). IR (KBr): υ 3383, 2941, 1617, 1525, 1403, 1342, 1197, 1163, 1111, 1045, 995, 919, 847, 821, 744, 711, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.80 (s, 6H), 8.09 (d, 1H, $J = 7.0$ Hz), 8.44 (d, 1H, $J = 7.0$ Hz), 8.88 (s, 1H); EIMS m/z (%): 204 (m^{+1} 100), 194 (10), 179 (10), 171 (15), 164 (10), 158 (10), 155 (15), 145 (20), 112 (10), 72 (10).

6-Bromo-2,3-dimethylquinoxaline (3k). IR (KBr): υ 3406, 3085, 3020, 2950, 1597, 1573, 1480, 1440, 1415, 1398, 1366, 1322, 1250, 1159, 1127, 1054, 1015, 963, 913, 889, 828, 777, 707, 671 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 6H), 7.70 (d, 1H, $J = 7.0$ Hz), 7.82 (d, 1H, $J = 7.0$ Hz), 8.12 (s, 1H); EIMS m/z (%): 237 (m^+ 100), 211 (10), 171 (10), 155 (20), 145 (10), 115 (10).

7a,8,9,10,11,11a-Hexahydroacenaphtho-[1,2-b]-quinoxaline (3l). IR (KBr): υ 3387, 3064, 2938, 1661, 1592, 1449, 1323, 1211, 1172, 1110, 1045, 996, 927, 874, 794, 719, 641 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.48–1.62 (m, 3H), 1.90–2.05 (m, 3H), 2.55 (d, 2H, $J = 6.0$ Hz), 3.08–3.18 (m, 2H), 7.68 (t, 2H, $J = 6.0$ Hz), 7.95 (d, 4H, $J = 6.0$ Hz).

Acenaphtho-[1,2-*b*]-quinoxaline (3m). IR (KBr): υ 3386, 2939, 2856, 1646, 1428, 1299, 1208, 1108, 1043, 992, 923, 857, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.71 (d, 2H, $J = 6.0$ Hz), 7.83 (t, 2H, $J = 6.0$ Hz), 8.08 (d, 2H, $J = 6.0$ Hz), 8.18 (d, 1H, $J = 6.0$ Hz), 8.41 (d, 2H, $J = 6.0$ Hz).

6-Nitro-2,3-diphenylquinoxaline (3n). IR (KBr): υ 3381, 3061, 2937, 1660, 1594, 1518, 1448, 1398, 1341, 1210, 1170, 1111, 1050, 995, 980, 907, 874, 767, 720, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.30–7.45 (m, 6H), 7.95 (d, 4H, $J = 7.0$ Hz), 8.25 (d, 1H, $J = 7.0$ Hz), 8.54 (d, 1H, $J = 7.0$ Hz), 9.08 (s, 1H); EIMS m/z (%): 328 (m^{+1} 65), 298 (30), 265 (25), 255 (20), 233 (45), 225 (20), 211 (35), 194 (10), 178 (35), 171 (40), 164 (10), 149 (10), 131 (15), 115 (20), 105 (100), 75 (30).

Methyl-2,3-diphenylquinoxaline-6-carboxylate (3o). IR (KBr): υ 3384, 2942, 1715, 1651, 1445, 1309, 1256, 1178, 1107, 1045, 920, 856, 761, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.02 (s, 3H), 7.30–7.40 (m, 6H), 7.48–7.58 (m, 4H), 8.16 (d, 1H, $J = 7.0$ Hz), 8.34 (d, 1H, $J = 7.0$ Hz), 8.87 (s, 1H).; EIMS m/z (%): 341 (m^{+1} 100), 267 (10), 253 (10), 232 (10), 190 (15), 110 (20), 60 (20).

Methylacenaphtho-[1,2-*b*]-quinoxaline-9-carboxylate (3p). IR (KBr): υ 3360, 2923, 2853, 1709, 1618, 1517, 1435, 1368, 1299, 1231, 1105, 1046, 986, 907, 824, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.05 (s, 3H), 7.87 (t, 2H, $J = 7.0$ Hz), 8.10 (d, 2H, $J = 7.0$ Hz), 8.20 (d, 1H, $J = 7.0$ Hz), 8.30 (d, 1H, $J = 7.0$ Hz), 8.43 (d, 2H, $J = 7.0$ Hz), 8.39 (s, 1H); EIMS m/z (%): 313 (m^{+1} 20), 279 (10), 265 (10), 247

(20), 237 (25), 219 (45), 207 (35), 191 (100), 177 (25), 171 (30), 167 (25), 160 (10), 149 (10), 131 (15), 115 (30).

Compound (3q). IR (KBr): υ 3383, 2940, 2850, 1620, 1563, 1494, 1442, 1399, 1367, 1325, 1255, 1200, 1158, 1113, 1095, 1044, 988, 907, 833, 769, 677 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.68–7.72 (m, 1H), 7.82–7.90 (m, 2H), 8.12–8.18 (m, 2H), 8.40 (d, 1H, $J = 6.0$ Hz), 8.01–8.10 (m, 2H), 9.12 (s, 1H); EIMS m/z (%): 255 (m^+ 25), 233 (56), 225 (18), 211 (33), 194 (15), 178 (30), 171 (65), 149 (20), 131 (25), 115 (15), 105 (100), 75 (28).

2,3,6,7-Tetramethylquinoxaline (3r). IR (KBr): υ 3383, 2940, 2850, 1620, 1563, 1494, 1442, 1399, 1367, 1325, 1255, 1200, 1158, 1113, 1095, 1044, 988, 907, 833, 769, 677 cm^{-1}; ^{1}HNMR ($CDCl_3$): δ 7.68–7.72 (m, 1H), 7.82–7.90 (m, 2H), 8.12–8.18 (m, 2H), 8.40 (d, 1H, $J = 6.0$ Hz), 8.01–8.10 (m, 2H), 9.12 (s, 1H); EIMS m/z (%): 255 (m^+ 25), 233 (56), 225 (18), 211 (33), 194 (15), 178 (30), 171 (65), 149 (20), 131 (25), 115 (15), 105 (100), 75 (28).

9,10-Dimethylacenaphtho-[1,2-*b*]-quinoxaline (3s). IR (KBr): υ 3386, 2939, 2856, 1646, 1428, 1299, 1208, 1108, 1043, 992, 923, 857, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.52 (s, 6H), 7.81 (t, 2H, $J = 6.0$ Hz), 7.90 (s, 2H), 8.20 (d, 2H, $J = 6.0$ Hz), 8.39 (d, 2H, $J = 6.0$ Hz); EIMS m/z (%): 282 (m^+ 100), 256 (25), 221 (10), 195 (15), 171 (10), 136 (20), 111 (10), 84 (20).

9-Bromoacenaphtho-[1,2-*b*]-quinoxaline (3t). IR (KBr): υ 3341, 3056, 2937, 2879, 1642, 1571, 1495, 1408, 1384, 1315, 1254, 1201, 1159, 1101, 1094, 1005, 975, 908, 846, 761, 679 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.50–7.60 (m, 2H), 7.80–7.99 (m, 6H), 8.30 (s, 1H); EIMS m/z (%): 333 (m^{+1} 100), 253 (40), 230 (10), 204 (10), 180 (10), 152 (10), 126 (15), 104 (20), 81 (10), 56 (20).

6,7-Dimethyl-2,3-diphenylquinoxaline (3u). IR (KBr): υ 3386, 2939, 2856, 1646, 1428, 1299, 1208, 1108, 1043, 992, 923, 857, 758 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.52 (s, 6H), 7.81 (t, 2H, $J = 6.0$ Hz), 7.90 (s, 2H), 8.20 (d, 2H, $J = 6.0$ Hz), 8.39 (d, 2H, $J = 6.0$ Hz); EIMS m/z (%): 310 (m^+ 25), 233 (10), 156 (100), 132 (20), 105 (30), 94 (10), 76 (25), 68 (15), 56 (10).

6-Bromo-2,3-diphenylquinoxaline (3v). IR (KBr): υ 3408, 3056, 2935, 1662, 1590, 1506, 1486, 1445, 1348, 1252, 1204, 1185, 1061, 1008, 973, 895, 812, 779, 632 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25–7.40 (m, 6H), 7.50–7.75 (m, 5H), 8.50 (d, 1H, $J = 6.0$ Hz), 9.19 (brs, 1H); EIMS m/z (%): 360 (m^+ 100), 281 (15), 204 (20), 127 (30), 104 (10), 76 (20), 56 (20).

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