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Magnetic Fe_3O_4 Nanoparticles as New, Efficient, and Reusable Catalysts for the Synthesis of Quinoxalines in Water

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A novel, environmentally friendly procedure has been developed for the synthesis of quinoxaline derivatives in the presence of magnetic Fe_3O_4 nanoparticles. The reaction between 1,2-diamines and 1,2-dicarbonyl compounds was carried out in water to afford quinoxaline derivatives in high yield. The catalyst can be recovered by the use of an external magnet and reused for five cycles with almost consistent activity.

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Introduction

Environmentally friendly chemical processes involving clean organic reactions in the absence of harmful organic solvents are highly encouraged. Performing organic reactions in aqueous media has attracted much attention because water is easily handled on high scale and is abundant, non-toxic, environmentally friendly, and economical compared with organic solvents. Moreover, in many cases, due to hydrophobic effects, using water as a solvent not only accelerates reaction rates but also enhances reaction selectivities.[1–3] Therefore, the development of a recyclable catalyst that functions in water is highly desirable.

Quinoxaline derivatives are an attractive class of compounds because of their wide range of biological and pharmaceutical properties such as antitumor,[4] antimicrobial,[5] antimycobacterial,[6] antibacterial,[7] antileishmanial,[8] and anti-hyperglycemic activities.[9] Furthermore, these compounds can be used as dyes,[10] electroluminescent materials,[11] photoinitiators,[12] and used in luminescence studies.[13] Besides these, the quinoxaline nucleus is a part of several antibiotics such as echinomycin, levomycin, and actinomycin that are known to inhibit the growth of gram-positive bacteria and are active against various transplantable tumours.[14] Due to their wide range of activity and importance, a variety of methods for the synthesis of quinoxaline derivatives have been developed, including the reaction of α-keto oximes and 1,2-diamines,[15] oxidative coupling of epoxides and ene-1,2-diamines,[16] the coupling of α-diazoketones with aryl 1,2-diamines,[17] reductive cyclization of 1,2-dicarbonyl compounds with 2-nitroanilines,[18] oxidative cyclization of α-hydroxyketones with *o*-phenylenediamines,[19] heteroannulation of nitroketene *N*,*S*-aryliminoacetals with $POCl_3$,[20] the reaction of α-haloketones with aromatic 1,2-diamines,[21] intramolecular cyclization of dialdimines,[22] and the reaction of aryl-1,2-diamines and diethyl bromomalonate.[23]

Moreover, quinoxaline derivatives can also be successfully obtained from the direct condensation of 1,2-dicarbonyl compounds and aryl 1,2-diamines. This is the most simple and straightforward route for their synthesis. A variety of catalysts such as oxalic acid,[24] montmorillonite K-10,[25] polyaniline-sulfate salt,[26] cerium(IV) ammonium nitrate,[27] sulfamic acid,[28] Wells-Dawson heteropolyacid,[29] bismuth(III) triflate,[30] indium chloride,[31] ionic liquid 1-*n*-butylimidazolium tetrafluoroborate,[32] zirconium tetrakis(dodecyl sulfate),[33] molecular iodine,[34] and gallium(III) triflate[35] have been employed to effect this transformation. Although these methods are suitable for specific synthetic conditions, sometimes, these methods suffer from one or more disadvantages such as long reaction times, high temperature, use of costly catalysts, high catalyst loading, use of toxic solvents, and the requirement of microwave irradiation or ultrasound irradiation.[36] Thus, it is still a challenge to explore an environmentally benign synthetic methodology for this class of compound.

Recently, nanometre-scale metal oxides have attracted a great deal of attention due to their unique properties and potential applications in organic synthesis. In comparison with other transition metal oxides extensively used, iron-based catalysts are inexpensive, environmentally benign, and relatively non-toxic. Magnetic Fe_3O_4 nanoparticles, in particular, can be conveniently removed after the reaction by simple magnetic separation. It has been demonstrated to be an efficient catalyst for various useful chemical transformations, including aza-Sakurai[37] and Suzuki reactions,[38] synthesis of α-aminonitriles[39] and sulfonamides,[40] reduction of carbonyl compounds to alcohols,[41] protection of alcohols and phenols with HMDS,[42] and selective *N*-monoalkylation of aromatic amines with benzylic alcohols.[43] Considering the above points and in continuation of our work on the development of new synthetic methodologies,[44–48] we report here a green, mild, and practical method for the synthesis of quinoxaline derivatives from 1,2-diamines and 1,2-dicarbronyl compounds catalyzed by nano-Fe_3O_4 in water (Scheme 1).

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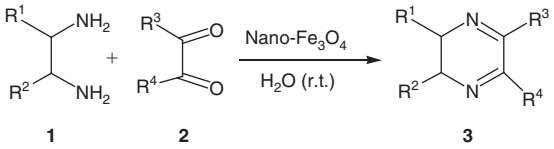


1 2 3

Scheme 1. Synthesis of quinoxalines catalyzed by nano-Fe_3O_4.

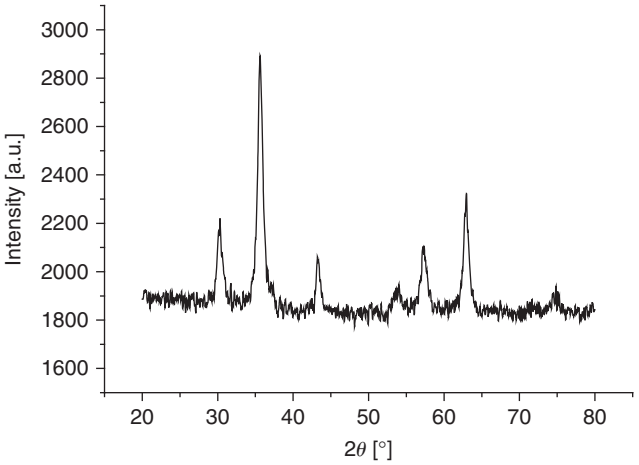


Fig. 1. The X-ray powder diffraction pattern of Fe_3O_4 nanoparticles.

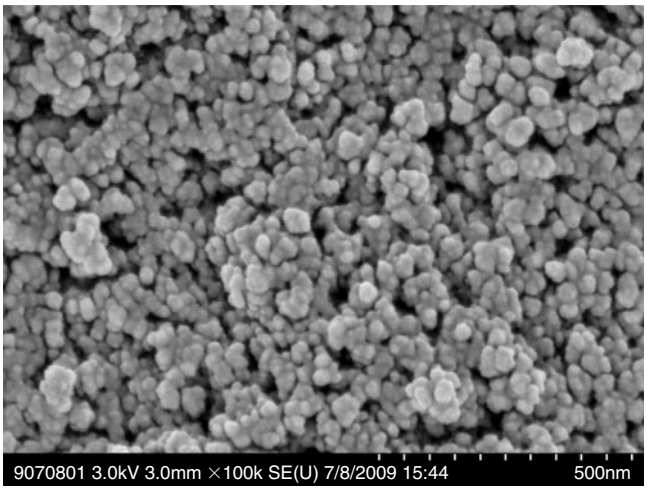


Fig. 2. The transmission electron microscopy image of morphology of Fe_3O_4 nanoparticles.

Results and Discussion

The X-ray diffraction pattern (Fig. 1) showed that all diffraction peaks are basically consistent with the standard data for the Fe_3O_4 structure (JCPDS card file No. 3–863), and no other unexpected peaks are present. The sample powder has an average particle diameter of 20 nm, which was estimated from Scherrer's formula using peak width at half height of the X-ray diffraction. The nanoparticles prepared were round in shape, with an average diameter of 20 nm as confirmed by transmission electron microscopy (Fig. 2), substantially consistent with the results estimated from Scherrer's formula. The results showed that the sample prepared by this method is a uniform distribution of spherical particles with no obvious aggregation.

In the initial experiment, we investigated the condensation reaction of benzil and *o*-phenylenediamine using different nanometre-scale metal oxides in water and the results are displayed in Table 1. As shown in Table 1, 11 nanometre-scale metal oxides were tested at room temperature and it was found that Fe_3O_4 showed the best catalytic activity.

Table 1. Influence of different nano catalysts for the condensation of benzil and *o*-phenylenediamine

Reaction conditions: *o*-phenylenediamine (1 mmol), benzil (1 mmol), catalyst (10 mol-%), H_2O (5 mL), 2.5 h, room temperature

Entry	Catalyst	Yield [%][A]
1	ZnO	60
2	CuO	45
3	MgO	40
4	Al_2O_3	65
5	In_2O_3	60
6	Y_2O_3	65
7	α-Fe_2O_3	65
8	γ-Fe_2O_3	60
9	TiO_2	60
10	ZrO_2	55
11	Fe_3O_4	95

[A]Yield refers to isolated pure products.

Table 2. Optimization of reaction conditions

Reaction conditions: *o*-phenylenediamine (1 mmol), benzil (1 mmol), solvent (5 mL), room temperature

Entry	Catalyst [mol-%]	Solvent	Time [h]	Yield [%][A]
1	10	None	4.0	30
2	10	Toluene	2.5	50
3	10	CH_2Cl_2	2.5	65
4	10	AcOEt	2.5	40
5	10	CH_3CN	2.5	85
6	10	EtOH	2.5	93
7	0	H_2O	4.0	30
8	1	H_2O	2.5	80
9	5	H_2O	2.5	82
10[B]	10	H_2O	2.5	95, 94, 93, 92, 92, 90
11	20	H_2O	2.5	96

[A]Yield refers to isolated pure products.
[B]Catalyst was reused five times.

In the studies regarding the effect of various solvents, the above reaction was conducted in the presence of Fe_3O_4 with various solvents such as toluene, dichloromethane, acetonitrile, ethyl acetate, ethanol, and water. The results indicated that the solvents had a significant effect on the product yield (Table 2). In general, non-polar solvents such as toluene, dichloromethane, and ethyl acetate afforded low yields. The best conversion was observed when the reaction was performed in water. Moreover, we found that the yields were obviously affected by the amount of Fe_3O_4 loaded. When 1, 5, 10, and 20 mol-% of Fe_3O_4 were used, the yields were 80, 82, 95, and 96%, respectively (Table 2, entries 8–11). Therefore, 10 mol-% of Fe_3O_4 was sufficient, however utilizing 20 mol-% of catalyst did not increase the yield significantly. In addition, in the absence of catalyst, the reaction was slow and gave unsatisfactory yield of quinoxaline (Table 2, entry 7). The above results showed that Fe_3O_4 was essential for high yield, and the best results were obtained when the reaction was carried out with 10 mol-% of Fe_3O_4 in water at room temperature.

Recyclability of the catalyst was also investigated. After completion of the reaction of benzil and *o*-phenylenediamine, the

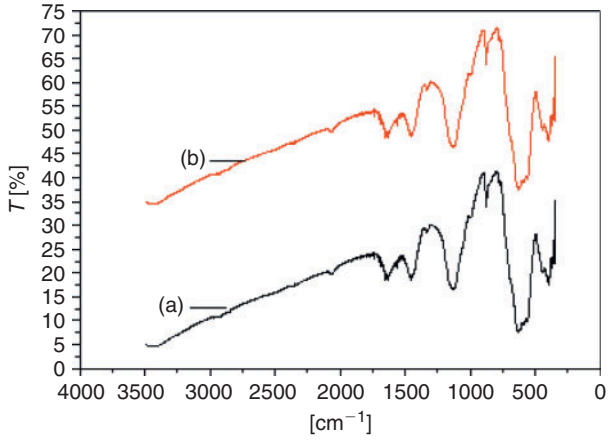


Fig. 3. IR spectrum of nano-Fe_3O_4 (a) before use and (b) after reuse five times.

catalyst was recovered from the reaction mixture simply by applying an external magnet. The recovered catalyst was then added to fresh substrates under the same experimental conditions for five runs without a noticeable decrease in the product yield and its catalytic activity (Table 2, entry 10). Infrared (IR) spectra of fresh and used nano-Fe_3O_4 catalyst confirmed the fact that the structure and morphology of the catalyst remained the same after recycling (Fig. 3).

To evaluate the scope and limitation of this procedure, we extended our study to structurally modified 1,2-diamines and 1,2-dicarbonyl compounds. The results are summarized in Table 3. As shown in Table 3, mono- and disubstituted aryl 1,2-diamines reacted with 1,2-diketone compounds to give the corresponding quinoxaline derivatives in high yield. The reaction proceeded very cleanly at room temperature and no undesirable side-reactions were observed. Aryl-1,2-diamines bearing an electron-withdrawing functionality such as a nitro group, showed slightly weaker reactivity than those containing electron-neutral or electron-donating groups. The reactions also proceed well when an aliphatic 1,2-diamine was used in the reaction (Table 3, entry 17). Under similar conditions, several 1,2-dicarbonyl compounds such as furil, acenaphthene-1,2-quinone, and phenylglyoxal also reacted with 1,2-diamines to afford the corresponding quinoxalines in high yield.

Conclusions

In summary, we have demonstrated that nanopowder Fe_3O_4 can be used as a magnetically recyclable catalyst for the synthesis of quinoxaline derivatives via the direct condensation of 1,2-diamines and 1,2-dicarbonyl compounds in water. This methodology offers the competitive advantages of mild reaction conditions, high product yields, the use of a benign solvent, easy separation and reuse of the catalyst, and a simple workup procedure.

Experimental

Surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument. X-ray diffraction analysis was carried out using a PANalytical X′Pert Pro X-ray diffractometer. Melting points were determined using an X-4 apparatus and are uncorrected. IR spectra were obtained using a Bruker-TENSOR 27 spectrometer instrument. NMR spectra were taken with a Bruker DRX-500 spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C) using $CDCl_3$ as the solvent with TMS as the internal standard. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer.

Preparation of Magnetic Fe_3O_4 Nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by the chemical coprecipitation method. $FeCl_2{\cdot}4H_2O$ (5 g) and $FeCl_3{\cdot}6H_2O$ (12.50 g) were dissolved into 65 mL deionized water followed by adding 2.0 mL of concentrated hydrochloric acid. The resulting solution was dropped into 650 mL of 1.5 mol L^{-1} NaOH solution under vigorous stirring at 70°C. The obtained magnetic nanoparticles were separated from solution by a powerful magnet and the precipitate was washed until free of chlorine ions, filtered, and dried.

*General Procedure for the Synthesis of Quinoxaline Derivatives (**3**)*

A mixture of 4-nitrobenzene-1,2-diamine (1 mmol), benzil (1 mmol), and Fe_3O_4 (0.1 mmol) in water (5 mL) was stirred at room temperature. After completion of the reaction (monitored by TLC), a conventional permanent magnet (0.5–0.7 T) was applied to the outside of the reaction flask to separate the catalyst from the solution. The crude product was filtered, washed with cold water, and dried. Further purification was carried out, if needed, by short column chromatography on silica gel eluting with ethyl acetate/petroleum ether (2:8 v/v) to obtain pure 6-nitro-2,3-diphenylquinoxaline (Table 3, entry 13) as a yellow solid.

The spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR) and elemental analytical data of all compounds are given below.

2,3-Diphenylquinoxaline (Table 3, Entry 1)

ν_{max} (KBr)/cm^{-1} 3060, 1505, 1493, 1441, 1395, 1346, 1220, 1142, 1022, 770. δ_H 7.35–7.43 (m, 6H), 7.52–7.56 (m, 4H), 7.76–7.80 (m, 2H), 8.20–8.23 (m, 2H). δ_C 128.3, 128.9, 129.3, 130.0, 130.1, 139.2, 141.3, 153.5. Anal. Calc. for $C_{20}H_{14}N_2$: C 85.08, H 5.00, N 9.92. Found: C 85.21, H 5.16, N 10.05%.

2,3-Bis-(4-bromophenyl)quinoxaline (Table 3, Entry 2)

ν_{max} (KBr)/cm^{-1} 3058, 1590, 1558, 1542, 1488, 1390, 1342, 1215, 1125, 1068, 1048, 1007, 975, 760. δ_H 7.35–7.43 (m, 4H), 7.58–7.54 (m, 4H), 7.75–7.82 (m, 2H), 7.78–7.82 (m, 2H). δ_C 123.5, 129.2, 130.3, 131.4, 131.6, 137.6, 141.2, 151.9. Anal. Calc. for $C_{20}H_{12}Br_2N_2$: C 54.58, H 2.75, N 6.36. Found: C 54.75, H 2.92, N 6.20%.

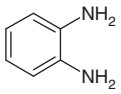
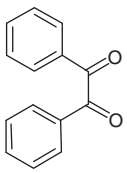
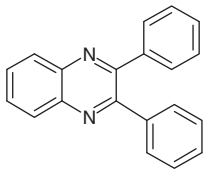
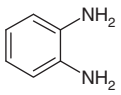
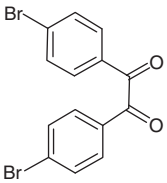
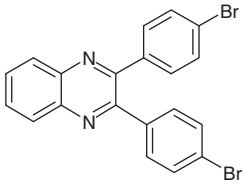
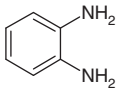
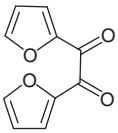
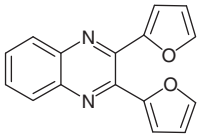
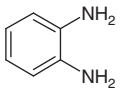
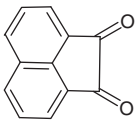
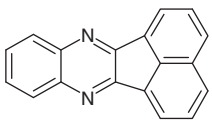
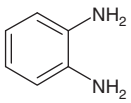
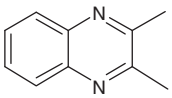
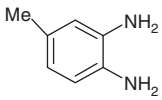
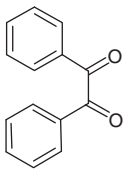
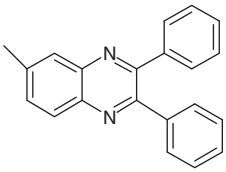
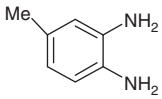
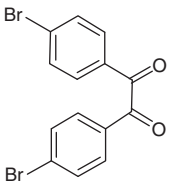
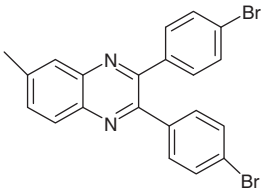
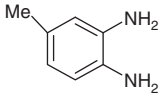
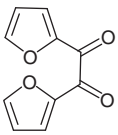
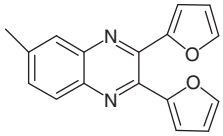
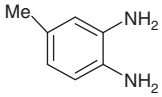
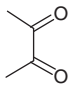
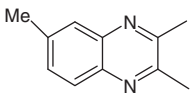
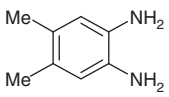
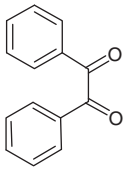
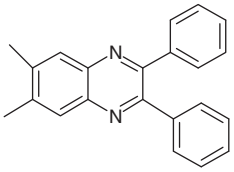
2,3-Di-furan-2-ylquinoxaline (Table 3, Entry 3)

ν_{max} (KBr)/cm^{-1} 3059, 1566, 1536, 1498, 1484, 1450, 1400, 1170, 1140, 1129, 1090, 755. δ_H 6.48–6.55 (m, 2H), 6.66 (d, J 3.5, 2H), 7.56 (d, J 1.5, 2H), 7.61–7.66 (m, 2H), 8.07–8.12 (m, 2H). δ_C 111.9, 113.0, 129.1, 130.3, 140.5, 142.6, 144.2, 150.8. Anal. Calc. for $C_{16}H_{10}N_2O_2$: C 73.27, H 3.84, N 10.68. Found: C 73.02, H 3.18, N 10.50%.

Acenaphtho[1,2-b]quinoxaline (Table 3, Entry 4)

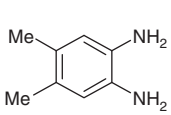
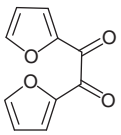
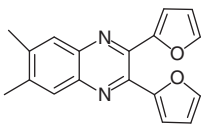
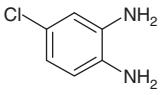
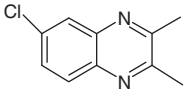
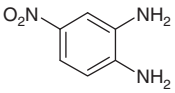
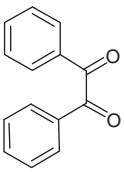
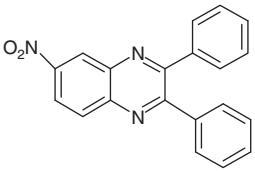
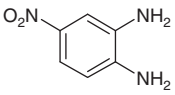
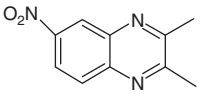
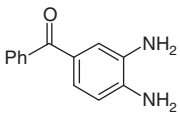
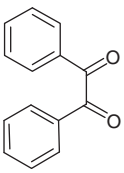
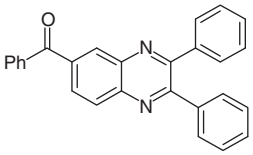
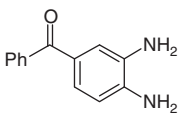
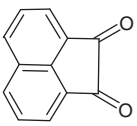
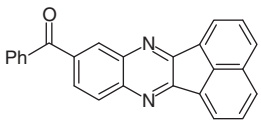
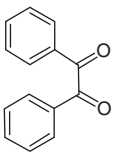
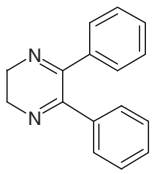
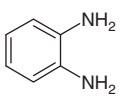
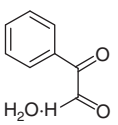
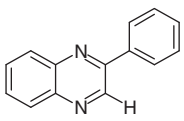
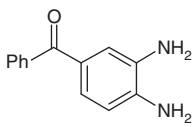
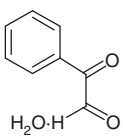
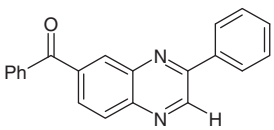
ν_{max} (KBr)/cm^{-1} 1614, 1572, 1481, 1435, 1418, 1300, 1207, 1095, 1031, 831. δ_H 7.76–7.78 (m, 2H), 7.84–7.87 (m, 2H), 8.12 (d, J 8.0, 2H), 8.21–8.24 (m, 2H), 8.44 (d, J 7.0, 2H). δ_C 125.6, 126.7, 127.1, 128.1, 128.8, 129.5, 130.1, 133.2, 142.5, 145.4. Anal. Calc. for $C_{18}H_{10}N_2$: C 85.02, H 3.96, N 11.02. Found: C 84.88, H 4.09, N 10.90%.

Table 3. Scope for nano-Fe_3O_4-catalyzed synthesis of quinoxaline derivatives

Entry	Diamine	Dicarbonyl	Product	Time [h]	Yield [%][A]	m.p. [°C]
1				2.5	95	125–126(126–127[27])
2				3.0	85	190–191(188–189[18])
3				2.0	95	131–132(131[27])
4				3.0	95	243–245(242–245[30])
5				2.5	95	105–107(105–106[15])
6				2.5	96	116–117(115–117[24])
7				2.5	95	184–185(185–186[32])
8				2.0	94	176–177(175–177[18])
9				2.5	95	90–91(88–90[49])
10				5.0	90	176–177(176–178[51])

(*Continued*)

Table 3. (Continued)

Entry	Diamine	Dicarbonyl	Product	Time [h]	Yield [%][A]	m.p. [°C]
11				3.0	92	135–136(134–136[30])
12				2.0	90	84–86(85–86[29])
13				6.0	80	193–194(193–194[32])
14				3.5	90	135–136(134–135[50])
15				5.0	88	141–142(140–142[35])
16				4.0	89	245–246
17				3.0	90	161–162(160–162[24])
18				1.0	93	78–79(79–80[19])
19				1.5	86	132–134(133[52])

[A]Isolated yield.

2,3-Dimethylquinoxaline (Table 3, Entry 5)

ν_{max} (KBr)/cm^{-1} 1491, 1400, 1363, 1317, 1256, 1211, 1165, 989, 904, 762. δ_H 2.73 (s, 6H), 7.65–7.68 (m, 2H), 7.96–7.99 (m, 2H). δ_C 23.6, 128.7, 129.2, 141.5, 153.0. Anal. Calc. for $C_{10}H_{10}N_2$: C 75.92, H 6.37, N 17.71. Found: C 76.05, H 6.52, N 17.90%.

6-Methyl-2,3-diphenylquinoxaline (Table 3, Entry 6)

ν_{max} (KBr)/cm^{-1} 2923, 1618, 1445, 1419, 1344, 1137, 1058, 1022, 979, 827, 704. δ_H 2.64 (s, 3H), 7.34–7.39 (m, 6H), 7.52–7.54 (m, 4H), 7.63 (dd, *J* 8.5, 1.5, 1H), 7.98 (s, 1H), 8.09 (d, *J* 8.5, 1H). δ_C 22.0, 127.7, 128.3, 128.5, 128.9, 129.0, 129.9, 129.9, 132.7, 138.5, 138.6, 139.4, 140.8, 141.0, 152.4, 153.1.

Anal. Calc. for $C_{21}H_{16}N_2$: C 85.11, H 5.44, N 9.45. Found: C 85.30, H 5.61, N 9.28%.

2,3-Bis-(4-bromophenyl)-6-methylquinoxaline (Table 3, Entry 7)

ν_{max} (KBr)/cm^{-1} 3020, 2975, 1620, 1590, 1485, 1341, 1216, 1074, 979, 832, 758, 670. δ_H 2.60 (s, 3H), 7.35–7.41 (m, 4H), 7.45–7.50 (m, 4H), 7.60 (d, *J* 8.5, 2H), 7.90 (s, 1H), 8.03 (d, *J* 8.5, 2H). δ_C 22.0, 123.4, 123.5, 127.9, 128.5, 131.3, 131.5, 132.6, 137.8, 139.5, 141.0, 141.2, 150.9, 151.5. Anal. Calc. for $C_{21}H_{14}Br_2N_2$: C 55.54, H 3.11, N 6.17. Found: C 55.72, H 2.98, N 6.36%.

2,3-Di-furan-2-yl-6-methylquinoxaline (Table 3, Entry 8)

ν_{max} (KBr)/cm^{-1} 3110, 1618, 1569, 1529, 1490, 1448, 1336, 1215, 1170, 1152, 1134, 1062, 1018, 991, 759. δ_H 2.60 (s, 3H), 6.56 (s, 2H), 6.63 (s, 2H), 7.59 (d, *J* 8.5, 1H), 7.62 (s, 2H), 7.93 (s, 1H), 8.03 (d, *J* 8.5, 1H). δ_C 21.9, 111.9, 112.6, 112.8, 128.0, 128.6, 132.8, 139.1, 140.7, 141.1, 141.9, 142.6, 144.0, 144.1, 150.9. Anal. Calc. for $C_{17}H_{12}N_2O_2$: C 73.90, H 4.38, N 10.14. Found: C 74.06, H 4.55, N 9.98%.

2,3,6-Trimethylquinoxaline (Table 3, Entry 9)

ν_{max} (KBr)/cm^{-1} 2924, 1448, 1400, 1328, 1126, 1072, 993, 831, 773. δ_H 2.56 (s, 3H), 2.71 (s, 6H), 7.49 (d, *J* 8.5, 1H), 7.75 (s, 1H), 7.86 (d, *J* 8.5, 1H). δ_C 22.1, 23.4, 23.5, 127.7, 128.2, 131.4, 139.5, 139.9, 141.5, 152.8, 153.7. Anal. Calc. for $C_{11}H_{12}N_2$: C 76.71, H 7.02, N 16.27. Found: C 76.53, H 7.20, N 16.09%.

6,7-Dimethyl-2,3-diphenylquinoxaline (Table 3, Entry 10)

ν_{max} (KBr)/cm^{-1} 1658, 1448, 1344, 1334, 1211, 1024, 1004, 871, 702. δ_H 2.54 (s, 6H), 7.34–7.43 (m, 6H), 7.50–7.55 (m, 4H), 7.95 (s, 2H). δ_C 20.2, 127.9, 128.3, 128.8, 129.6, 139.2, 140.0, 140.2, 152.2. Anal. Calc. for $C_{22}H_{18}N_2$: C 85.13, H 5.85, N 9.03. Found: C 85.29, H 6.05, N 8.92%.

2,3-Di-furan-2-yl-6,7-dimethylquinoxaline (Table 3, Entry 11)

ν_{max} (KBr)/cm^{-1} 3425, 2982, 1606, 1568, 1442, 880, 745. δ_H 2.52 (s, 3H), 6.52–6.54 (m, 2H), 6.61–6.63 (m, 2H), 7.56–7.65 (m, 2H), 7.78–7.85 (m, 2H). δ_C 39.9, 115.6, 131.2, 131.7, 147.7, 159.1, 160.1, 160.2, 163.1. Anal. Calc. for $C_{18}H_{14}N_2O_2$: C 74.47, H 4.86, N 9.65. Found: C 74.30, H 5.01, N 9.79%.

6-Chloro-2,3-dimethylquinoxaline (Table 3, Entry 12)

ν_{max} (KBr)/cm^{-1} 1604, 1481, 1325, 1261, 1065, 950, 804. δ_H 2.74 (s, 3H), 2.75 (s, 3H), 7.63 (dd, *J* 2.5, 9.0, 1H), 7.93 (d, *J* 9.0, 1H), 7.99 (d, *J* 2.5, 1H). δ_C 23.5, 23.6, 121.5, 121.6, 130.1, 130.3, 134.6, 140.1, 141.0, 154.0, 154.1. Anal. Calc. for $C_{10}H_9ClN_2$: C 62.35, H 4.71, N 14.54. Found: C 62.51, H 4.89, N 14.35%.

6-Nitro-2,3-diphenylquinoxaline (Table 3, Entry 13)

ν_{max} (KBr)/cm^{-1} 2923, 2852, 1521, 1446, 1433, 1398, 1336, 1207, 1128, 1072, 1055, 1026, 906, 810, 767. δ_H 7.38–7.41 (m, 4H), 7.45 (t, *J* 7.0, 2H), 7.59 (t, *J* 7.0, 4H), 8.32 (d, *J* 9.0, 1H), 8.56 (dd, *J* 9.0, 2.5, 1H), 9.10 (d, *J* 2.5, 1H). δ_C 123.3, 125.4, 128.3, 129.5, 129.6, 129.7, 129.8, 130.6, 137.9, 138.0, 139.7, 143.4, 147.7, 155.5, 156.1. Anal. Calc. for $C_{20}H_{13}N_3O_2$: C 73.38, H 4.00, N 12.84. Found: C 73.50, H 4.18, N 12.66%.

2,3-Dimethyl-6-nitroquinoxaline (Table 3, Entry 14)

ν_{max} (KBr)/cm^{-1} 1616, 1577, 1521, 1483, 1404, 1432, 1165, 1070, 947, 846. δ_H 2.79 (s, 3H), 2.80 (s, 3H), 8.10 (d, *J* 9.0, 1H), 8.44 (dd, *J* 2.5, 9.0, 1H), 8.88 (d, *J* 2.5, 1H). δ_C 23.7, 23.9, 122.7, 125.3, 130.3, 140.4, 144.1, 147.5, 156.7, 157.6. Anal. Calc. for $C_{10}H_9N_3O_2$: C 59.11, H 4.46, N 20.68. Found: C 59.30, H 4.30. N 20.51%.

(2,3-Diphenyl-quinoxaline-6-yl)-phenylmethanone (Table 3, Entry 15)

ν_{max} (KBr)/cm^{-1} 1660, 1444, 1400, 1348, 1269, 1126, 1076, 1058, 1024, 975, 877, 696. δ_H 7.33–7.41 (m, 5H), 7.52–7.57 (m, 6H), 7.63–7.68 (m, 1H), 7.91 (d, *J* 7.5, 2H), 7.98 (d, *J* 7.5, 1H), 8.28 (d, *J* 8.5, 1H), 8.30 (d, *J* 8.5, 1H), 8.54 (s, 1H). δ_C 128.3, 128.5, 128.9, 129.1, 129.2, 129.7, 129.8, 130.1, 132.4, 132.8, 134.8, 137.1, 138.2, 138.5, 138.6, 140.1, 142.9, 154.6, 155.1, 195.7. Anal. Calc. for $C_{27}H_{18}N_2O$: C 83.92, H 4.69, N 7.25. Found: C 84.05, H 4.88, N 57.06%.

Acenaphtho[1,2-b]quinoxaline-9-ylphenylmethanone (Table 3, Entry 16)

ν_{max} (KBr)/cm^{-1} 1647, 1616, 1558, 1444, 1302, 1263, 1101, 1002, 889, 775, 713. δ_H 7.56 (t, *J* 7.5, 2H), 7.65 (t, *J* 7.5, 1H), 7.87–7.91 (m, 2H), 7.94 (d, *J* 7.0, 2H), 8.18 (t, *J* 8.5, 2H), 8.28 (d, *J* 8.0, 1H), 8.35 (d, *J* 8.0, 1H), 8.45 (d, *J* 7.0, 1H), 8.52 (d, *J* 7.0, 1H), 8.62 (s, 1H). δ_C 122.3, 122.6, 128.5, 128.9, 129.4, 129.9, 130.0, 130.1, 130.2, 131.3, 132.8, 136.9, 137.4, 137.6, 140.3, 143.3, 155.0, 155.6, 159.9. Anal. Calc. for $C_{25}H_{14}N_2O$: C 83.78, H 3.94, N 7.82. Found: C 83.96, H 4.12, N 7.65%.

5,6-Diphenyl-2,3-dihydropyrazine (Table 3, Entry 17)

ν_{max} (KBr)/cm^{-1} 1610, 1552, 1492, 1442, 1336, 1300, 1267, 1230, 1035, 989, 896. δ_H 3.71 (s, 4H), 7.23–7.27 (m, 4H), 7.29–7.32 (m, 2H), 7.38–7.40 (m, 4H). δ_C 46.3, 128.3, 128.6, 130.1, 138.2, 160.8. Anal. Calc. for $C_{16}H_{14}N_2$: C 82.02, H 6.02, N 11.96. Found: C 81.89, H 5.88, N 11.80%.

2-Phenylquinoxaline (Table 3, Entry 18)

ν_{max} (KBr)/cm^{-1} 1616, 1545, 1488, 1446, 1313, 1290, 1209, 1126, 1049, 1028, 956, 769, 688. δ_H 7.54 (t, *J* 7.5, 1H), 7.59 (t, *J* 7.5, 2H), 7.76 (t, *J* 8.0, 1H), 7.80 (t, *J* 8.0, 1H), 8.14 (d, *J* 8.0, 1H), 8.17 (d, *J* 8.0, 1H), 8.21 (d, *J* 7.5, 2H), 9.34 (s, 1H). δ_C 127.5, 129.0, 129.1, 129.5, 129.6, 130.2, 136.7, 141.5, 142.3, 143.3, 151.8. Anal. Calc. for $C_{14}H_{10}N_2$: C 81.53, H 4.89, N 13.58. Found: C 81.68, H 5.05, N 13.40%.

Phenyl-(3-phenylquinoxaline-6-yl)methanone (Table 3, Entry 19)

ν_{max} (KBr)/cm^{-1} 1652, 1590, 1569, 1456, 1294, 1255, 1172, 1112, 1028, 972, 885, 684. δ_H 7.54–7.68 (m, 6H), 7.91 (d, *J* 7.5, 2H), 8.25–8.28 (m, 4H), 8.50 (s, 1H), 9.42 (s, 1H). δ_C 127.7, 128.5, 129.2, 130.0, 130.1, 130.2, 130.7, 132.3, 132.8, 136.2, 137.0, 137.8, 140.5, 144.1, 144.3, 153.2, 195.5. Anal. Calc. for $C_{21}H_{14}N_2O$: C 81.27, H 4.55, N 9.03. Found: C 81.45, H 4.38, N 9.19%.

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