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Synthesis of Quinoxaline Derivatives Using TiO_2 Nanoparticles as an Efficient and Recyclable Catalyst

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TiO_2 nanoparticles were synthesized and characterized by SEM and XRD techniques. The TiO_2 nanoparticles were employed as a recyclable, inexpensive and efficient catalyst for the synthesis of substituted quinoxalines in high to excellent yields and in relatively short duration.

Key Words : TiO_2 Nanoparticles, Quinoxalines, *o*-Phenelendiamines, 1,2-Diketones

Introduction

In recent years, transition metal nanoparticles are used as efficient catalysts for various synthetic organic transformations due to their high surface area to volume ratio and coordination sites which are mainly responsible for their catalytic activity.[1,2]

Titanium dioxide nanoparticles (nano-TiO_2) are certainly one of the most interesting metal oxides because it has surface properties which enable organic reactions to occur. It has been proved to be a good catalyst because of its high activity, non-toxicity, strong oxidizing power, easy availability, reusability, and long term stability.[3-5] Likewise, nano-titanium dioxide is a versatile material for various kinds of industrial applications related to catalysis, photocatalysis for pollutant elimination or organic synthesis, photovoltaics, sensors, and paints.[6] In order to prepare nanocrystalline TiO_2 with significant properties, several processes have been developed over the last decade and can be classified as liquid process (hydrothermal,[7] sol-gel[8]), solid state processing routes (mechanical alloying/milling,[9] mechanochemical[10]), and other routes such as laser ablation.[11] From the above methods, the sol-gel method is normally used for preparation of nanometer TiO_2 powder.

Quinoxaline derivatives have found applications as antibacterial agents possessing a wide range of activities. For example, echinomycin, leromycin and actinomycin have proven to be an efficient antibacterial and growth-inhibiting material. They exhibit a diverse range of biological properties, such as antitumor,[12] cytotoxic,[13] antiviral, *anti*-inflammatory, and kinase inhibitor properties.[14]

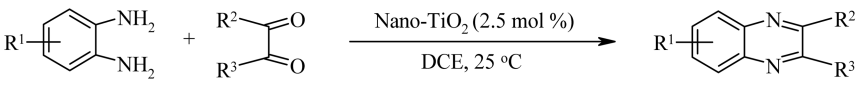
Based on the significant applications of quinoxaline compounds in both medicinal and industrial fields, several synthetic strategies have been developed for the preparation of substituted quinoxalines by condensation of aryl 1,2-diamines with ketones, α-halo-β-ketoesters, α-hydroxyketones and 1,2-diketones.[15-19] A number of methods have been reported for the generating quinoxaline derivatives using stoichiometric or catalytic Lewis acids such as $Ga(OTf)_3$,[20] alumina,[21] SBA-Pr-SO_3H[22] and $Bi(OTf)_3$.[23] Different heterogeneous transition-metal catalysts such as sulfated TiO_2-P25,[24] Ni nanoparticles,[25] Fe_3O_4 nanoparticles,[26] and ZrO_2/M_xO_y/MCM-41[27] have been used for this purpose.

Nevertheless, some of these methods suffer from long reaction time, low product yields, expensive and detrimental metal precursors for preparation of catalyst, using complex or poorly available catalyst and harsh reaction conditions which limit their use.

As part of our research on chemical transformations,[28] we here report the preparation of a recyclable and highly effective homogeneous nanocatalyst TiO_2 for the synthesis of substituted quinoxalines in high to excellent yields in dichloroethane at room temperature (Scheme 1).

Results and Discussion

In this study, we prepared nano-TiO_2 by the sol-gel method using titanium tetra-isopropoxide, deionized water, ethanol and HNO_3 under ultrasonic irradiation. The X-ray diffraction pattern (Fig. 1) showed that the diffraction angle and intensity of the characteristic peaks of the samples are well consistent with the standard data for the TiO_2 nanoparticle structure. The value of 52 nm was calculated from XRD data for average particle diameter of this nanocrystallin TiO_2 using Scherrer's equation.[29] The nanoparticles prepared were round in shape, with an average diameter of



Scheme 1. Synthesis of the quinoxaline derivatives using of nano-TiO_2.

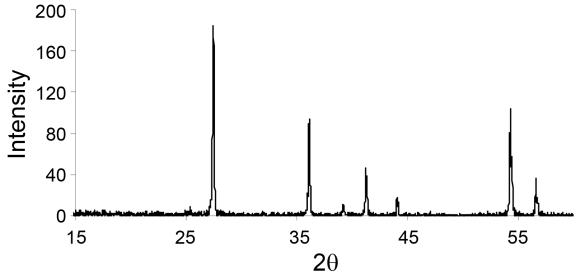


Figure 1. X-ray diffraction pattern of TiO_2 nanoparticles.

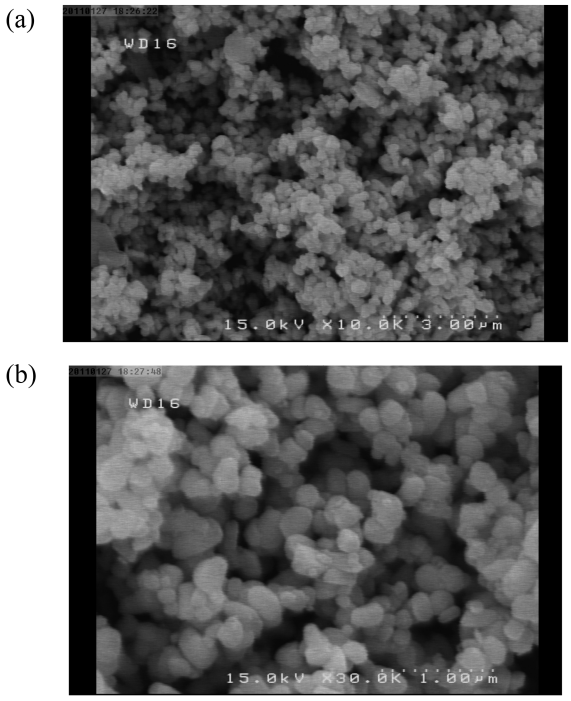


Figure 2. FE-SEM micrographs of synthesis TiO_2 nanoparticle (a) low magnification, (b) high magnification.

50 nm as measured by field emission-scanning electron microscopy (FE-SEM; Fig. 2), substantially consistent with the results estimated from Scherrer's formula. The results showed that the sample prepared by this method has a uniform distribution of spherical particles with no obvious aggregation.

To choose the most appropriate medium in this heterocyclization reaction and to understand the influence of different variables in this reaction, several components were studied. We accomplished the reaction under standard conditions employing *o*-phenylenediamine (1.1 mmol) and benzil (1.0 mmol) as a representative model in the presence of a catalytic amount of different titanium dioxides [commercially available bulk TiO_2 (CM-TiO_2), and conventionally sol-gel-prepared TiO_2 nanoparticles (Nano-TiO_2)] at room temperature in dichloroethane (DCE) to afford the corresponding 2,3-diphenylquinoxaline (Table 1, entries 1 and 2). The Nano-TiO_2 was found to be superior to the CM-TiO_2 in terms of yields and reaction times. Nano-TiO_2 gave 2,3-diphenylquinoxaline in excellent yield within 15 min, while CM-TiO_2 afforded it in longer time (35 min).

Table 1. Formation of 2,3-Diphenylquinoxaline with Different Catalysts[a]

Entry	Catalyst	mol % of catalyst	Time (min)	Yield (%)[b]
1	Nano-TiO_2	5	15	99
2	CM-TiO_2	5	35	90
3	Nano-ZnO	5	60	87
4	Nano-ZrO_2	5	45	89
5	Nano-SiO_2	5	25	89
6	Nano-TiO_2	1	60	93
7	Nano-TiO_2	2	25	95
8	Nano-TiO_2	2.5	15	99

[a]Reaction conditions: 1,2-phenylenediamine (1.1 equiv), benzyl (1.0 equiv), catalyst (different mol %), DCE, 25 °C. [b]Yields refer to isolated pure products.

Table 2. Effect of the Solvent on the Synthesis of 2,3-Diphenylquinoxaline Using a Catalytic Amount of Nano-TiO_2[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	DCE	15	99
2	DCM	90	90
3	CH_3CN	120	90
4	H_2O	120	40
5	EtOH	120	85

[a]Reaction conditions: 1,2-phenylenediamine (1.1 mmol), benzil (1.0 mmol), TiO_2 nanoparticles (2.5 mol %), solvent (5.0 mL), 25 °C. [b]Yields refer to isolated pure products.

Next, we studied the effect of nano-ZnO, nano-ZrO_2 and nano-SiO_2 on the quinoxaline formation (Table 1, entries 3-5). However, their catalytic activities were much lower than nano-TiO_2.

We also found that the amount of catalyst had an effective influence on the reaction course. As shown in Table 1, 2.5 mol % of catalyst gave the best result (Table 1, entries 1 and 6-8).

In order to optimize the protocol, we explored the influence of different solvents such as DCE, CH_2Cl_2, EtOH, H_2O and CH_3CN (Table 2). The results clearly showed that DCE is the most efficient solvent as the highest yield of 2,3-diphenylquinoxaline was obtained.

To investigate the generality of this method, various 1,2-diketones were reacted with different substituted *o*-phenylenediamines (Table 3). In general, all reactions were very clean and the quinoxaline derivatives were obtained in high to excellent yields under the optimized reaction conditions. All products were characterized by IR, ^1H and ^{13}C-NMR and MS spectra, melting point and compared with literature data.

As summarized in Table 3, both electron-rich and electron-deficient *o*-phenylenediamines were effective in this process. When *o*-phenylenediamines are substituted at the 4-position with electron-donating (ED) groups, higher rates and yields are observed than the ones bearing electron-withdrawing (EW) groups at that position. For example, 4-nitro-1,2-phenylenediamine afforded the product in 90 min with 80% yield (entry 4), whereas methyl and methoxy

Table 3. Synthesis of Quinoxaline Derivatives Catalyzed by Nano-TiO_2[a]

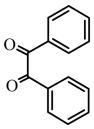
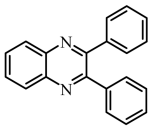
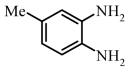
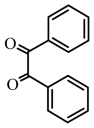
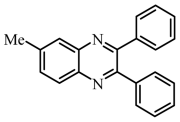
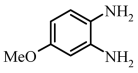
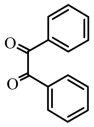
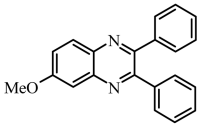
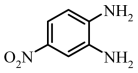
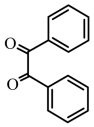
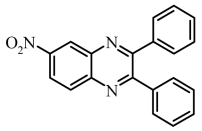
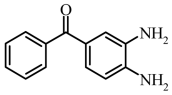
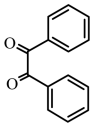
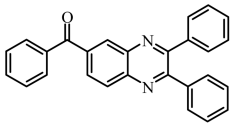
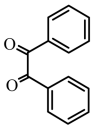
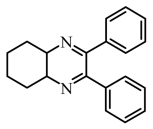
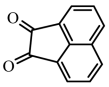
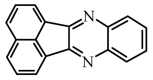
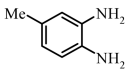
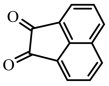
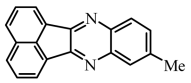
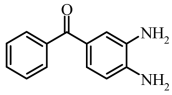
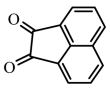
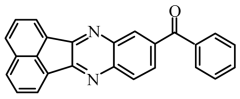
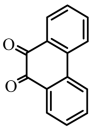
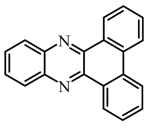
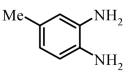
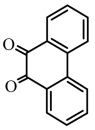
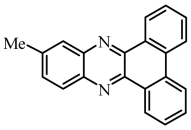
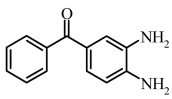
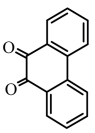
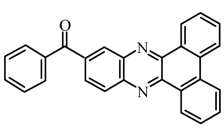
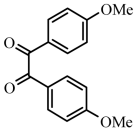
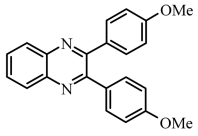
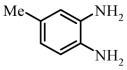
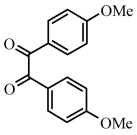
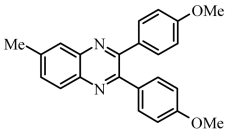
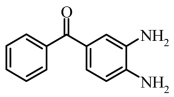
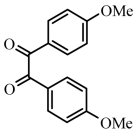
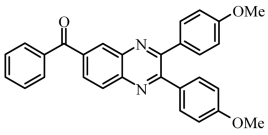
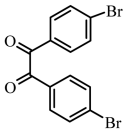
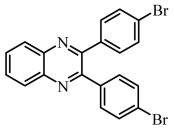
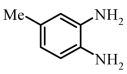
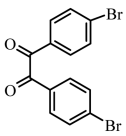
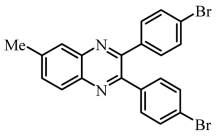
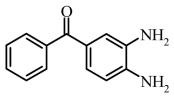
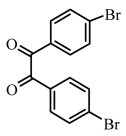
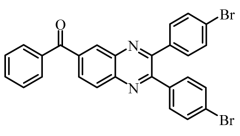
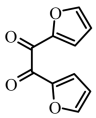
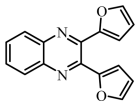
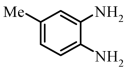
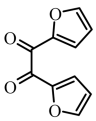
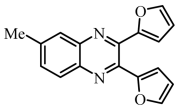
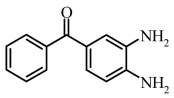
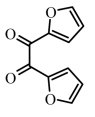
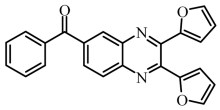
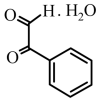
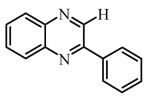
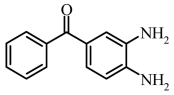
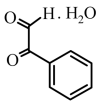
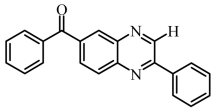
Entry	1,2-Diamine	1,2-Diketone	Product[b]	Time (min)	Yield (%)[c]	mp (°C) (Literature)	Ref.
1				15 (15)[d]	99 (97)[d]	128-130 (130-131)	20
2				15	95	114-116 (116-117)	20
3				15	97	160-162 (156-158)	30
4				90	80	188-191 (190-192)	20
5				90	91	137-139 (140-142)	20
6				45	70	168-170 (168-172)	25
7				30	95	240-242 (242-245)	23
8				30	91	230-232 (233-235)	31
9				40	93	242-244 (245-246)	26
10				20	90	227-229 (228-230)	32
11				25	91	220-221	-
12				35	90	245-247	-

Table 3. Continued

Entry	1,2-Diamine	1,2-Diketone	Product[b]	Time (min)	Yield (%)[c]	mp (°C) (Literature)	Ref.
13				60	96	147-149 (148-150)	33
14				60	92	124-126 (125-127)	33
15				90	94	161-163	33
16				10	97	188-190 (190-191)	26
17				10	92	183-185 (184-185)	26
18				30	99	203-206 (203-204)	31
19				20	93	132-134 (131-132)	34
20				40	93	114-116 (112-114)	34
21				75	91	128-130	-
22				15	90	76-77 (78-79)	26
23				70	90	130-132 (132-134)	26

[a]Reaction conditions: 1,2-phenylenediamine (1.1 mmol), 1,2-diketone (1 mmol), Nano-TiO_2 (2.5 mol %), DCE, 25 °C. [b]Products were characterized by IR, ^{1}H, ^{13}C-NMR and mass spectroscopy and melting point. [c]Yields refer to isolated products. [d]Reaction was recorded on 10 mmol scale.

Table 4. Comparison of the Catalyst Effects in the Synthesis of 2,3-Diphenyel-quinoxaline at Room Temperature

Entry	Catalyst	mol % of catalyst	Time (min)	Yield (%)	Ref.
1	Nano-TiO_2	2.5	15	99	-
2	TiO_2-SO_4^{2-}	5	5	99	24
3	Nano-Ni	10	10	98	25
4	Nano-Fe_3O_4	10	150	95	26
5	Nano-TiO_2	12	15	94	35

Table 5. Recycling of TiO_2 Nanoparticles

Run No.	1	2	3	4
Time (min)	15	15	17	17
Yield (%)[a]	95	92	89	87

[a]Yields refer to isolated products.

substituted 1,2-phenylenediamines gave the expected quinoxaline in 15 min with 95 and 97% yield, respectively (entries 2 and 3). Substituted benzil also reacted smoothly with 1,2-phenylenediamines, to give high yielded of the corresponding quinoxalines (Table 3, entries 13-18).

In order to show the advantages and limitations of this protocol, we have compared some of our results with those reported in the literature (Table 4). Nano-TiO_2 is an effective catalyst for this reaction in terms of the amount of catalyst and reaction time in comparison with other catalysts. Although nano-TiO_2 was previously used as a catalyst for this reaction (entry 5), but their preparation of nanoparticles required the use of $TiCl_4$ which liberates HCl as a toxic waste as well as the use of higher amount of catalyst (12 mol %) compared to our method (entry 1).

The reusability of the catalyst was investigated. After completing the model reaction, the catalyst was recovered by filtration, washed with dichloromethane, and dried at 70 °C in air. The regenerated catalyst was used for consecutive runs under the same substrate and reaction conditions. The recycling results show that the catalyst was still highly efficient after the fourth run (Table 5).

Conclusion

In summary, TiO_2 nanoparticles with diameter of 50 nm was successfully synthesized *via* sol-gel method and used as eco-friendly (non-toxic, recyclable), easily available, inexpensive and efficient homogeneous catalyst for the synthesis of quinoxaline derivatives in high to excellent yields with relatively short reaction times. The simplicity of operation, easy work-up procedure, and high yields are some other advantageous.

Experimental

Starting materials used in the reactions were supplied commercially from Aldrich or Merck Chemical Co. Nuclear magnetic resonance spectra were recorded on a Bruker DRX-400 AVANCE spectrometer in $CDCl_3$ or DMSO as solvent. Melting points were determined on an electrothermal apparatus and were uncorrected. Mass spectra were obtained on an Agilent technologies instrument and IR spectra were determined on a Shimadzu instrument. Powder X-ray diffraction data were obtained using ShimadzuXD-D1 diffractometer using Cu Kα radiation (λ = 1.5418 Å). Nanosize and morphology of the ZnO nanoparticles were observed under TESCAN MV2300T/40 Field Emission-Scanning Electron Microscope (FE-SEM).

Synthesis of Nanocatalyst. In a typical process, 5 mL of titanium tetra-*n*-butoxide was dissolved in 5 mL anhydrous alcohol, and ultrasonically dispersed to produce a mixture. Meanwhile, 5 mL of water and 1 mL of HNO_3 (65%) were added to another 20 mL of absolute ethanol in turn to form an ethanol-nitric acid-water mixture solution. The $Ti(OBu)_4$-C_2H_5OH solution was slowly added dropwise to the ethanol-nitric acid-water solution under ultrasonic irradiation in a sonication cell in 15 min to carry out a hydrolysis. Then, a semitransparent sol was gained after continuously ultrasoning for 1 h. Subsequently, the sonication was conducted so that the temperature was raised from 25 to 80 °C at the end of the reaction. The obtained precipitates were separated by filtering, washing for several times with de-ionized water and anhydrous alcohol, drying at 70 °C in the air for about 12 h to produce dry gel powder after grinding. Finally, nano-TiO_2 was obtained by calcined the dry gel precursor at 480 °C for 2 h in air. The TiO_2 nanoparticles were characterized by FE-SEM and XRD techniques.

Typical Procedure for Synthesis of Quinoxaline Derivatives. Nano-TiO_2 (0.002 g, 2.5 mol %) was added to a mixture of *o*-phenylenediamine (0.124 g, 1.1 mmol) and benzil (0.21 g, 1 mmol) in 5 mL of DCE and the mixture was stirred at room temperature. After completion of the reaction (as monitored by TLC), the catalyst was filtered, washed with dichloromethane. The solvent was removed under reduced pressure, and crude product was purified by recrystallization from ethanol or acetone/water, in some cases by column chromatography on silica gel with *n*-hexane:EtOAC (20:1) as an eluent to afford the pure product (yield: 0.28 g (99%)). The product was characterized by IR, ^1H, ^{13}C-NMR and mass spectrums, melting point and compared with literature data. Furthermore, we accomplished the reaction in large scale synthesis of 2,3-diphenylquinoxaline with 11 mmol of *o*-phenylenediamine, 10 mmol of benzil and 2.5 mol % nano-TiO_2. Usual work-up and purification afforded a white solid of 2,3-diphenylquinoxaline at the same time (2.73 g, 9.70 mmol, 97%).

Some of the selected compounds' spectroscopic data

2,3-Diphenylquinoxaline. (Table 3, entry 1) IR (KBr): 3051, 1630, 1528, 1348, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19-8.23 (m, 2H), 7.78-7.83 (m, 2H), 7.52-7.57 (m, 4H), 7.34-7.41 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 153.49 (C), 141.25 (C), 139.09 (C), 129.98 (CH), 129.85 (CH), 129.22 (CH), 128.82 (CH), 128.29 (CH); MS: *m/z* (EI) 282 (M^+), 205, 140, 127, 103, 76, 50.

Acenaphtho[1,2-*b*]quinoxaline. (Table 3, entry 7) IR

(KBr): 3060, 1640, 1614, 1571, 1480, 1431, 1297, 1205, 1103, 835, 768, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, 2H, J = 7.2 Hz), 8.21-8.24 (m, 2H), 8.10 (d, 2H, J = 7.2 Hz), 7.84 (t, 2H, J = 7.2 Hz), 7.76-7.79 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 154.08 (C), 141.26 (C), 136.51 (C), 131.80 (C), 130.01 (C), 129.59 (CH), 129.49 (CH), 129.24 (CH), 128.67 (CH), 121.88 (CH); MS: *m/z* (EI) 254 (M^+), 227, 200, 151, 127, 100, 77.

Dibenzo[*a*,*c*]phenazine. (Table 3, entry 10) IR (KBr): 3035, 1608, 1501, 1356, 1039, 770, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.39 (dd, 2H, J = 6.4, J = 1.6 Hz), 8.55 (d, 2H, J = 7.6 Hz), 8.32-8.35 (m, 2H), 7.85-7.88 (m, 2H), 7.79-7.82 (m, 2H), 7.73-7.77 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.41 (C), 142.16 (C), 132.02 (C), 130.28 (CH), 129.73 (CH), 129.44 (CH), 127.91 (CH), 126.25 (CH), 122.89 (CH); MS: *m/z* (EI) 280 (M^+), 253, 225, 176, 140, 50.

11-Methyl-dibenzo[*a*,*c*]phenazine. (Table 3, entry 11) IR (KBr): 3065, 1623, 1503, 1361, 755, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.35-9.38 (m, 2H), 8.53 (d, 2H, J = 8 Hz), 8.19 (d, 1H, J = 7.2 Hz), 8.19 (d, 1H, J= 8.4 Hz), 8.07 (s, 1H), 7.76-7.79 (m, 2H), 7.71-7.75 (m, 2H), 7.65-7.68 (m, 1H), 2.68 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.19 (C), 142.14 (C), 141.62 (C), 140.69 (C), 140.35 (C), 132.38 (CH), 131.96 (C), 131.77 (C), 130.35 (C), 130.31 (C), 130.12 (CH), 129.99 (CH), 22.08 (CH_3); MS: *m/z* (EI) 294 (M^+), 240, 190, 147, 90.

Dibenzo[*a*,*c*]phenazine-11-yl-phenyl-methanone. (Table 3, entry 12) IR (KBr): 3068, 1656, 1601, 1328, 1257, 749, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (d, 1H, J = 7.6 Hz), 9.37 (d, 1H, J = 8 Hz), 8.71 (s, 1H), 8.59 (d, 2H, J = 7.6 Hz), 8.35-8.47 (m, 2H), 7.99 (d, 2H, J = 7.2 Hz), 7.63-7.88 (m, 5H), 7.59 (t, 2H, J = 7.2 Hz); ^{13}C NMR (400 MHz, $CDCl_3$): δ 195.90 (C), 143.72 (C), 141.06 (C), 137.97 (C), 137.37 (C), 132.93 (CH), 132.86 (CH), 132.63 (C), 132.21 (C), 131.04 (CH), 130.80 (CH), 130.23 (CH), 129.93 (CH), 129.45 (CH), 128.59 (CH), 128.16 (CH), 126.74 (CH), 126.39 (CH), 123.05 (CH), 123.03 (CH); MS: *m/z* (EI) 384 (M^+), 307, 279, 227, 201, 175, 151, 105, 77.

2,3-Bis(4-bromophenyl)quinoxaline. (Table 3, entry 16) IR (KBr): 3049, 1587, 1540, 1485, 1394, 1340, 1066, 829, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.16-8.20 (*m*, 2H), 7.80-7.84 (m, 2H), 7.52-7.55 (m, 4H), 7.41-7.44 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 151.9, 141.3, 137.7, 131.7, 131.4,130.4, 129.2, 123.7; MS: *m/z* (EI) 440 (M+2), 438 (M^+), 359, 280, 178, 151, 102, 76.

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References

1. Jiang, Y.; Decker, S.; Mohs, C.; Klabunde, K. J. J. *Catal.* **1998**, *180*, 24. (b) Lucas, E.; Decker, S.; Khaleel, A.; Seitz, A.; Fultz, S.; Ponce, A.; Li, W.; Carnes, C.; Klabunde, K. *J. Chem. Eur. J.* **2001**, *7*, 2505.
2. (a) Schlogl, R.; Abd Hamid, S. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 1628. (b) Kantam, M. L.; Laha, S.; Yadav, J.; Choudary, B. M.; Sreedhar, B. *Adv. Synth. Catal.* **2006**, *348*, 867. (c) Kantam, M. L.; Laha, S.; Yadav, J.; Sreedhar, B. *Tetrahedron Lett.* **2006**, *47*, 6213.
3. Yamazaki, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2955.
4. Reich, H. J.; Chow, F.; Peake, S. L. *Synthesis* **1978**, *2*, 299.
5. Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688.
6. Klyachko, N. L.; Klibanov, A. M. *Appl. Biochem. Biotechnol.* **1992**, *37*, 53.
7. (a) Yuan, Z. Y.; Su, B. L. *Colloids Surf. A* **2004**, *241*, 173. (b) Nian, J. N.; Teng, H. *J. Phys. Chem. B* **2006**, *110*, 4193.
8. (a) Bischoff, B. L.; Anderson, M. A. *Chem. Mater.* **1995**, *7*, 1772. (b) Jung, H. S.; Shin, H.; Kim, J. R.; Kim, J. Y.; Hong, K. S.; Lee, J. K. *Langmuir* **2004**, *20*, 11732.
9. (a) Kim, D. H.; Hong, H. S.; Kim, S. J.; Song, J. S.; Lee, K. S. *J. Alloys Compd.* **2004**, *375*, 259. (b) Xiaoyan, P.; Xueming, M. *Mater. Lett.* **2004**, *58*, 513.
10. (a) Guimaraes, J. L. Abbate, M.; Betim, S. B.; Alves, M. C. M. *J. Alloys Compd.* **2003**, *352*, 16. (b) Kamei, M.; Mitsuhashi, T. *Surf. Sci.* **2000**, *463*, L609.
11. Matsubara, M.; Yamaki, T.; Itoh, H.; Abe, H.; Asai, K. Jpn. *J. Appl. Phys.* **2003**, *42*, (5A Pt 2) L479.
12. Corona, P.; Carta, A.; Loriga, M.; Vitale, G.; Paglietti, G. *Eur. J. Med. Chem.* **2009**, *44*, 1579.
13. Tanimori, S.; Nishimura, T.; Kirihata, M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4119.
14. Shaabani, A.; Maleki, A. *Chem. Pharm. Bull.* **2008**, *56*, 79.
15. Corona, P.; Vitale, G.; Loriga, M.; Paglietti, G. *Farmaco* **2000**, *55*, 77.
16. Hassan, S. Y.; Khattab, S. N.; Bekhit, A. A. Adel Amer, *Bio. Med. Chem. Lett.* **2006**, *16*, 1753.
17. Woo, G. H. C.; Snyder, J. K.; Wan, Z. K. *Prog. Heterocycl. Chem.* **2002**, *14*, 279.
18. Mizuno, T.; Wei, W. H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134.
19. Crossley, J. C.; Johnston, L. A. *Chem. Commun.* **2002**, *10*, 1122.
20. Cai, J. J.; Zou, J. P.; Pan, X. Q.; Zhang, W. *Tetrahedron Lett.* **2008**, *49*, 7386.
21. Mohsenzadeh, F.; Aghapoor, K.; Darabi, H. R. *J. Braz. Chem. Soc.* **2007**, *18*, 297.
22. Mohammadi Ziarani, Gh.; Badiei, A.; Haddadpour, M. *International J. Chem.* **2011**, *3*, 87.
23. Yadav, J. S.; Reddy, B. V. S.; Premalatha, K.; Shankar, K. S. *Synthesis* **2008**, 3787.
24. Krishnakumar, B.; Velmurugan, R.; Jothivel, S.; Swaminathan, M. *Catal. Commun.* **2010**, *11*, 997.
25. Kumar, A.; Kumar, S.; Saxena, A.; De, A.; Mozumdar, S. *Catal. Commun.* **2008**, *9*, 778.
26. Lü, H. Y.; Yang, Sh. H.; Deng, J.; Zhang, Zh. H. *Aust. J. Chem.* **2010**, *63*, 1290.
27. Ajaikumar, S.; Pandurangan, A. *Appl. Catal. A: Gen.* **2009**, *357*, 184.
28. Alinezhad, H.; Salehian, F.; Biparva, P. *Syn. Commun.* **2011**, In Press.
29. Cullity, B. D. *Elements of X-ray d*iffraction*; vol. 1, Addison-Wesley, USA, 1978.
30. Zhao, Zh.; Wisnoski, D. D.; Wolkenberg, S. E.; Leister, W. H.; Wang, Y.; Lindsley, C. W. *Tetrahedron Lett.* **2004**, *45*, 4873.
31. Hou, J. T.; Liu, Y. H.; Zhang, Zh. H. J. *Heterocyclic Chem.* **2010**, *47*, 703.
32. Zare, A.; Hasaninejad, A.; Parham, A.; Moosavi-Zare, A. R.; Khedri, F.; Parsaee, Z.; Abdolalipoor-Saretoli, M.; Khedri, M.; Roshanakar, M.; Deisi, H. *J. Serb. Chem. Soc.* **2010**, *75*, 1315.
33. Bhosale, R. S.; Sarda, S. R.; Ardhapure, S. S.; Jadhav, W. N.; Bhusare, S. R.; Pawar, R. P. *Tetrahedron Lett.* **2005**, *46*, 7183.
34. Guo, W. X.; Jin, H. L.; Chen, J. X.; Chen, F.; Ding, J. C.; Wu, H. Y. *J. Braz. Chem. Soc.* **2009**, *20*, 1674.
35. Mirjalili, B. F.; Akbari, A. *Chin. Chem. Lett.* **2011**, *22*, 753.