An Efficient Silica Supported Fluoroboric Acid Catalysed Synthesis of Quinoxaline Derivatives

D. Y. BHOSALE[1], F. K. CHATE[2], B. N. CHATE[2]

[1]Department of Chemistry, S. M. D. B. S. College, Miraj, Dist Sangli, MH, India
[2]Department of Chemistry, Sanjeevanee Mahavidhyalaya, Chapoli, Dist Latur, MH, India
***Corresponding Author E-Mail:** bhosaledhiraj317@rediffmail.com

Received: 24.03.2018 ***Accepted: 23.04.2018*** ***Published Online 15.06.2018***
https://doi.org/10.30731/ijcps.7.3.2018.17-26

Abstract

*Synthesis of some new quinoxqline derivatives (**3a-p**) from the reaction between substituted 1,2 diketone and substituted 1,2 diamino arene by using silica supported fluoroboric acid as an heterogeneous catalyst and PEG as a green solvent. Reaction route reported herein carries the attractive features like clean, mild, efficient acidic condition with short reaction time with quantitative yield of the product. Thus, this method flashes the combo of simple and efficient synthesis with easy isolation and purification of the desire product.*

Keywords: Quinoxaline, 1,2 diketone, 1,2 diamine, HBF_4-SiO_2, PEG

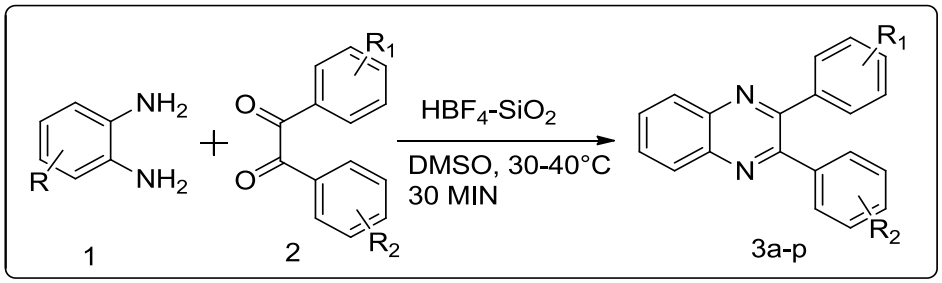
Introduction

Quinoxalines are incredibly valuable intermediate for the improvement of biologically and pharmacologically interested molecule. Bezimidazole derivatives showed broad spectrum in the field of medicinal chemistry including antibacterial,[1] antiviral,[2] antifungal,[3] antihyperglycemic,[4] and anticancer.[5] In addition quinoxaline derivatives have been evaluated as photoinitiators,[6] electroluminescent,[7] dyes[8] and in luminescent studies.[9] The well-known interest in the molecule containing benzimidazole scaffold has provoked widespread studies for their synthesis.

Due to the huge collection of applications, different synthetic roots have been developed for the synthesis of quinoxaline derivatives. It includes the reaction of 1,2-diamines and α-keto-oximes,[10] the coupling of α-diazoketones with aryl 1,2-diamines,[11] oxidative coupling of ene-1,2-diamines and epoxides,[12] reaction of aromatic 1,2-diamines with α-haloketones,[13] reaction of diethyl bromomalonate with aryl-1,2-diamines,[14] and reductive cyclization of 2-nitroanilines with 1,2-dicarbonyl,[15] intramolecular cyclization of dialdimines,[16] and oxidative cyclization of o-phenylenediamines with α-hydroxyketones.[17]

Number of oxidative reagents are used for the synthesis of qninoxaline like DDQ,[18] Oxone,[19] benzofuroxan,[20] MnO2,[21] benzoquinone,[22] NaHSO3,[23] Pb(OAc)4,[24] tetracyanoethylene,[25] have been engaged. Although, day by day several synthetic route have been developed for the synthesis of quinoxalineby using variety of catalyst such as $CuSO_4.5H_2O$,[26] oxalic acid,[27] CAN,[28] $KHSO_4$,[29] sulfamic acid,[30] Yb(OTf)3,[31] Zn2+-K10-clay,[32] DABCO,[33] o-iodoxybenzoic acid,[34] $HClO_4$–SiO_2,[35] polyaniline-sulfate salt,[36] Zr(DS)4[37]. Along with this literature observation also flash on the solvent system used for the synthesis of quinoxalines.[38-40] On the basis of above observed literature, there is a need to create a new mode for the synthesis of quinoxaline derivatives. Answer to this demand herein we report a new method

for the synthesis of quinoxaline derivatives by employing HBF_4-SiO_2 as a heterogeneous catalyst (**Scheme 1**).



Scheme 1: *Synthesis of 2,3-diphenylquinoxaline derivatives (**3a-p**).*

Experimental

Materials and Methods

All the chemicals were used laboratory grade and purified previously to use. Melting points of all synthesized compounds were recorded in open capillary tubes and are uncorrected. IR spectra were recorded in KBr pellets on FTIR Shimadzu spectrophotometer, and ^{1}H NMR spectra in were scanned on an AVANCE 300 MHz spectrometer using DMSO and TMS as an internal standard. The MS were recorded on an EI-Shimadzu-GC-MS spectrometer. Elemental analysis was carried out on a Carlo Ebra 106 Perkin-Elmer model 240 analyzer.

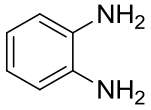
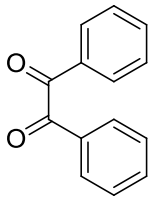
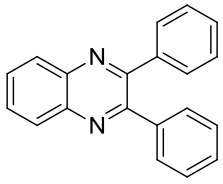
Preparation of Tetrafluoroboric Acid Adsorbed on Silica Gel (HBF_4-SiO_2)

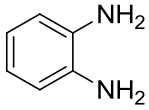
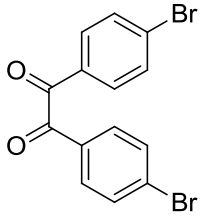
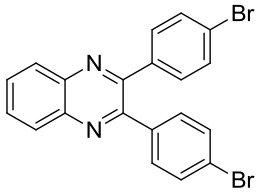
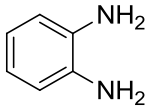
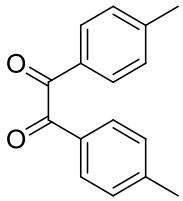
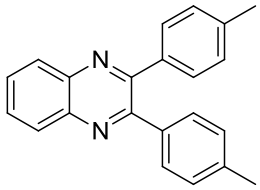
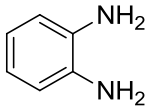
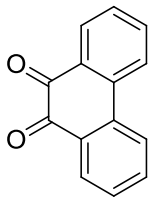
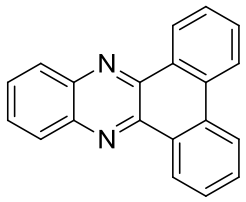
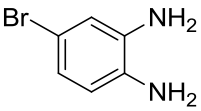
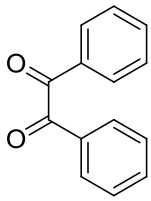
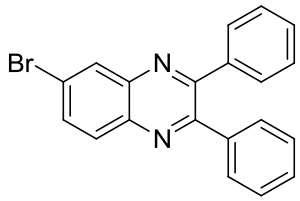
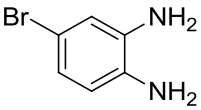
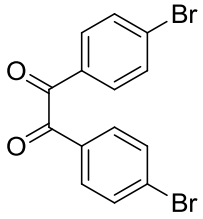
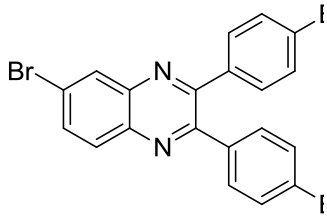
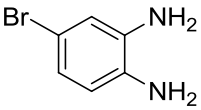
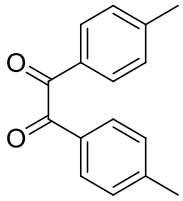
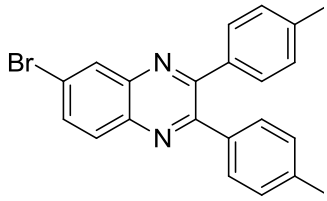
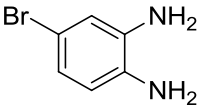
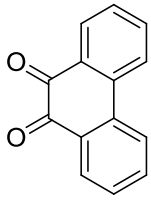
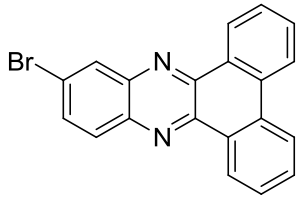
The heterogeneous catalyst HBF_4-SiO_2 was prepared by the report reported method.[41] A mixture of silica gel (26.7 g, 300–400 mesh) and 40% aq. HBF_4 (3.3 g, 8.25 mL, 15 mmol) in diethyl ether (75 ml) was stirred for 3 hrs. Concentrate the mixture and dried the residue under vacuum at 100 °C for 72 hrs to afford HBF_4-SiO_2 (0.5 mmol HBF_4/g) as a free-flowing power.

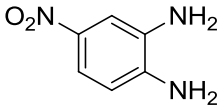
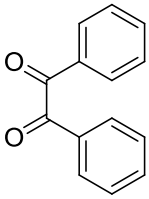
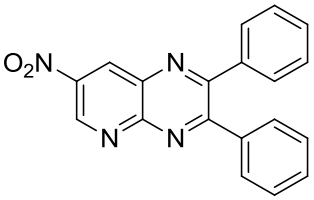
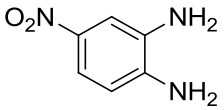
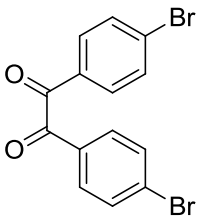
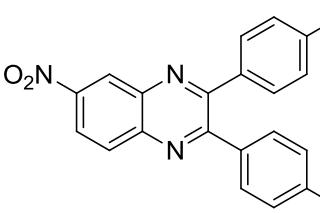
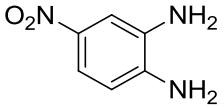
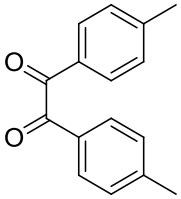
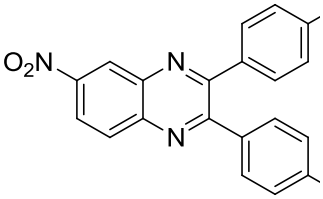
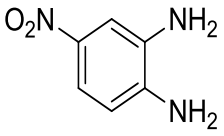
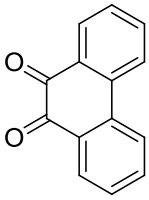
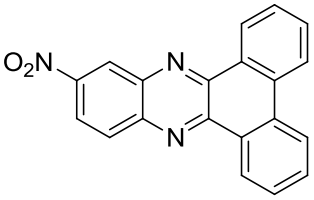
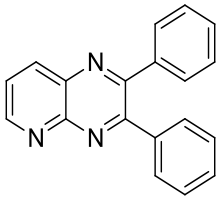
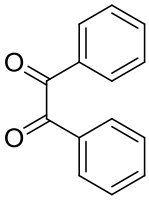
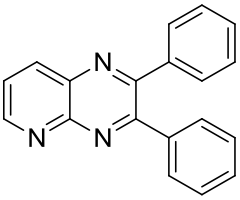
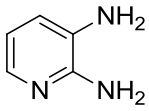
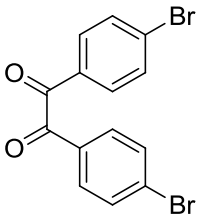
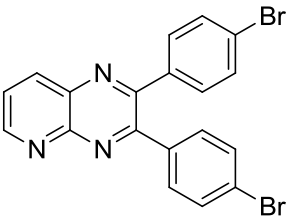
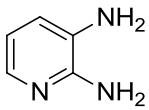
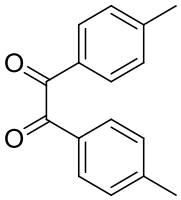
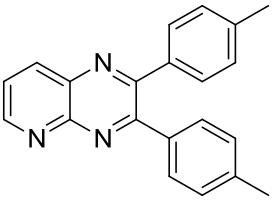
General procedure for the preparation of 2,3-diphenylquinoxaline derivatives (3a-p)

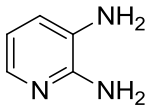
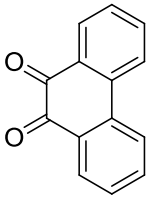
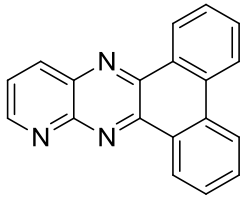
Equimolar mixture of 1,2 diketone 1 (0.1 mmol), 1,2 diamino arene (o.1 mmol) and HBF_4-SiO_2 (0.20 g, 0.1 mmol) in DMSO (10 ml) was stirred at 60-70 °C for an appropriate time (monitored by TLC). After completion of reaction, reaction mixture cooled at room temperature, poured in cold water and washed with $CHCl_3$. The obtained crude product was recrystallize by aq. Acetic Acid. Finally melting point of the final product was compared those of the authentic sample and found to be ideal. Further, by spectral characterization structural determination of the newly synthesized compounds was done.

Table 1: The scope of various substituents for the synthesis of quinoxaline derivatives.

Entry	1,2-diamine	1,2-Diketone	Product	Time (min)	Yield (%)
3a				12	92

3b				20	85
3c				15	90
3d				22	87
3e				20	88
3f				24	82
3g				17	89
3h				22	85

3i				20	80
3j				21	86
3k				18	80
3l				22	83
3m				19	81
3n				18	80
3o				23	86

3p				20	80

Spectral data of newly synthesized compounds

2,3-diphenylquinoxaline (3a)

IR (KBr): υ 3138, 1686, 1566, 1535, 1481, 1372, 1298 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H, *J* = 8 Hz), 7.67 (d, 2H, *J* = 10 Hz), 7.62-7.39 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.84, 141.39, 137.52, 129.64, 128.93, 127.25, 126.37, 125.88; MS: m/z 282 (M^+); Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08 (85.31); H, 5.00 (4.83); N, 9.92 (10.11).

2,3-bis(4-bromophenyl)quinoxaline (3b)

IR (KBr): υ 3093, 1665, 1556, 1542, 1440, 1385, 1291 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95-7.80 (m, 8H), 7.74-7.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.37, 142.61, 136.17, 132.40, 131.75, 130.89, 130.26, 129.37, 128.64, 120.53; MS: m/z 439 (M^+); Anal. calcd. for $C_{20}H_{12}Br_2N_2$: C, 54.58 (54.29); H, 2.75 (2.46); Br, 36.31 (36.72); N, 6.36 (6.81).

2,3-di-p-tolylquinoxaline (3c)

IR (KBr): υ 3084, 2970, 1666, 1572, 1519, 1450, 1337, 1284 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93-7.67 (m, 4H), 7.52 (d, 2H, *J* = 10 Hz), 7.48 (d, 2H, *J* = 10 Hz), 7.30 (d, 2H, *J* = 8 Hz), 7.28 (d, 2H, *J* = 8 Hz), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.34, 142.67, 135.97, 131.38, 130.22, 128.42, 126.84, 125.23, 124.06, 122.54; MS: m/z 310 (M^+); Anal. calcd. For $C_{22}H_{18}N_2$: C, 85.13 (85.6); H, 5.85 (5.24); N, 9.03 (9.78).

dibenzo[a,c]phenazine (3d)

IR (KBr): υ 3148, 1659, 1582, 1555, 1460, 1334, 1310 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, 2H, *J* = 8 Hz), 8.24 (d, 2H, *J* = 10 Hz), 7.88-7.48 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.52, 131.63, 130.71, 130.64, 129.27, 128.13, 127.81, 126.27, 124.08, 123.40, 122.10; MS: m/z 280 (M^+); Anal. calcd. for $C_{20}H_{12}N_2$: C, 85.69 (85.19); H, 4.31 (4.57); N, 9.99 (9.62).

6-bromo-2,3-diphenylquinoxaline (3e)

IR (KBr): υ 3070, 1664, 1590, 1520, 1450, 1392, 1348 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.92 (d, 1H, *J* = 7.0Hz), 7.56 (d, 1H, *J* = 7.0Hz), 7.50-7.36 (m, 4H), 7.30 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.15, 152.48, 142.63, 140.75, 138.19, 130.58, 129.46, 128.67, 128.77, 126.34, 120.39, 118.81; MS: m/z 360 (M^+); Anal. calcd. for $C_{20}H_{13}BrN_2$: C, 66.50 (66.27); H, 3.63 (3.42); Br, 22.12 (22.74); N, 7.75 (7.31).

6-bromo-2,3-bis(4-bromophenyl)quinoxaline (3f)

IR (KBr): υ 3132, 1678, 1548, 1563, 1434, 1390, 1286 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89-7.42 (m, 8H), 8.23 (s, 1H), 7.72 (d, 1H, *J* = 7.0 Hz), 7.42 (s, 1H, *J* = 7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.76, 158.34, 143.95, 139.42, 135.28, 133.62, 132.58, 131.86, 130.83, 129.71, 122.39, 119.62; MS: m/z

517 (M^+); Anal. calcd. for $C_{20}H_{11}Br_3N_2$: C, 46.28 (46.63); H, 2.14 (2.57); Br, 46.18 (46.35); N, 5.40 (5.11).

6-bromo-2,3-di-p-tolylquinoxaline (3g)

IR (KBr): υ 3143, 2968, 1688, 1546, 1572, 1462, 1350, 1310 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.84 (d, 1H, *J* = 7 Hz), 7.56 (s, 1H, *J* = 7 Hz), 7.84-7.36 (m, 8H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.68, 156.48, 143.34, 140.96, 136.58, 134.33, 132.26, 131.72, 130.57, 120.64, 118.55, 20.82; MS: m/z 388 (M^+); Anal. calcd. For $C_{22}H_{17}BrN_2$: C, 67.88 (67.25); H, 4.40 (4.73); Br, 20.53 (20.17); N, 7.20 (7.63).

11-bromodibenzo[a,c]phenazine (3h)

IR (KBr): υ 3137, 1642, 1568, 1538, 1472, 1364, 1288 cm^{-1}; ^1H NMR (400 MHz, CDCl3): δ 8.90 (d, 2H, *J* = 10 Hz), 8.84 (d, 2H, *J* = 10 Hz), 8.76 (d, 2H, *J* = 12 Hz), 8.23 (s, 1H), 7.88 (d, 2H, *J* = 12 Hz), 7.85 (d, 1H, *J* = 8 Hz), 7.56 (d, 1H, *J* = 8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.67, 140.71, 133.64, 132.25, 131.63, 130.83, 129.38, 128.76, 128.07, 127.46, 122.15, 118.68; MS: m/z 358 (M^+); Anal. calcd. for $C_{20}H_{11}BrN_2$: C, 66.87 (66.42); H, 3.09 (3.34); Br, 22.24 (22.73); N, 7.80 (7.28).

6-nitro-2,3-diphenylquinoxaline (3i)

IR (KBr): υ 3061, 1660, 1594, 1518, 1448, 1398, 1341 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, 1H, *J* = 8 Hz), 8.59 (d, 1H, *J* = 8 Hz),7.95 (d, 2H, *J* = 10 Hz), 7.82 (d, 2H, *J* = 10), 7.68 (s, 1H), 7.43-7.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.32, 157.66, 144.85, 138.27, 130.83, 130.08, 129.62, 128.96, 128.26, 127.54, 124.84, 122.30; MS: m/z 327 (M^+); Anal. calcd. for $C_{20}H_{13}O_2N_3$: C, 73.38 (73.56); H, 4.00 (4.26); N, 12.84 (12.64); O, 9.78 (9.32).

2,3-bis(4-bromophenyl)-6-nitroquinoxaline (3j)

IR (KBr): υ 3048, 1643, 1551, 1536, 1412, 1416, 1309 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, 1H, *J* = 8 Hz), 8.67 (d, 1H, *J* = 8 Hz), 8.29-7.63 (m, 8H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.21, 155.73, 140.15, 136.36, 130.12, 129.78, 129.32, 128.48, 128.05, 127.28, 123.51, 121.73; MS: m/z 485 (M^+); Anal. calcd. for $C_{20}H_{11}Br_2O_2N_3$: C, 49.52 (49.23); H, 2.29 (2.61); Br, 32.94 (32.72); N, 8.66 (8.34); O, 6.60 (6.16).

6-nitro-2,3-di-p-tolylquinoxaline (3k)

IR (KBr): υ 3048, 2983, 1656, 1576, 1536, 1433, 1382, 1269 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, 1H, *J* = 8 Hz), 8.56 (d, 1H, *J* = 8 Hz), 7.98 (d, 2H, *J* = 10 Hz), 7. 82 (d, 2H, *J* = 10 Hz), 7.52 (s, 1H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.86, 158.38, 141.56, 140.29, 137.26, 133.67, 130.74, 129.46, 128.59, 127.13, 121.73, 24.10; MS: m/z 355 (M^+); Anal. calcd. For $C_{22}H_{17}O_2N_3$: C, 74.35 (74.66); H, 4.82 (4.53); N, 11.82 (11.42); O, 9.00 (9.37).

11-nitrodibenzo[a,c]phenazine (3l)

IR (KBr): υ 3078, 1642, 1581, 1517, 1462, 1370, 1288 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, 1H, *J* = 8 Hz), 8.65 (d, 1H, *J* = 8 Hz), 7.99 (d, 4H, *J* = 10 Hz), 7.83 (d, 4H, *J* = 10 Hz), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.39, 142.74, 140.80, 131.25, 130.86, 130.15, 129.06, 128.86, 127.47, 126.68, 121.73, 120.96; MS: m/z 325 (M^+); Anal. calcd. For $C_{20}H_{11}O_2N_3$: C, 73.84 (73.63); H, 3.41 (3.82); N, 12.92 (12.45); O, 9.84 (9.37d).

2,3-diphenylpyrido[2,3-b]pyrazine (3m)

IR (KBr): υ 3037, 1676, 1590, 1546, 1478, 1386, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, 1H, *J* = 10 Hz), 7.81 (d, 1H, *J* = 10 Hz), 7.59-7.38 (m, 10H), 7.33 (d, 1H, *J* = 10 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.22, 154.73, 150.48, 148.84, 140.62, 138.56, 132.16, 130.74, 129.34, 128.08, 127.47, 126.19; MS: m/z 283 (M^+); Anal. calcd. For $C_{19}H_{13}N_3$: C, 80.54 (80.37); H, 4.62 4.57); N, 14.83 (14.38).

2,3-bis(4-bromophenyl)pyrido[2,3-b]pyrazine (3n)

IR (KBr): υ 3072, 1659, 1562, 1550, 1448, 1364, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, 1H, *J* = 10 Hz), 8.54 (d, 1H, *J* = 10 Hz), 7.86 (d, 2H, *J* = 8 Hz), 7.68 (d, 2H, *J* = 8 Hz), 7.48 (m, 4H), 7.36 (s, 1H, *J* = 10 Hz), 7.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.87, 156.98, 152.67, 150.52, 146.74, 136.14, 132.82, 131.43, 130.74, 128.08, 126.27, 124.33; MS: m/z 440 (M^+); Anal. calcd. For $C_{19}H_{11}Br_2N_3$: C, 51.73 (51.29); H, 2.51 (2.72); Br, 36.23 (36.18); N, 9.53 (9.86).

2,3-di-p-tolylpyrido[2,3-b]pyrazine (3o)

IR (KBr): υ 3060, 2997, 1683, 1540, 1571, 1466, 1352, 1244 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, 1H, *J* = 10 Hz), 8.63 (d, 1H, *J* = 10 Hz), 7.78 (d, 2H, *J* = 8 Hz), 7.57 (d, 2H, *J* = 8 Hz), 7.38 (m, 4H), 7.21 (d, 1H, *J* = 10 Hz), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.52, 152.71, 152.67, 145.34, 135.62, 133.08, 132.84, 130.37, 128.19, 127.46, 125.38, 22.44; MS: m/z 311 (M^+); Anal. calcd. For $C_{21}H_{17}N_3$: C, 81.00 (81.26); H, 5.50 (5.67); N, 13.49 (13.84).

dibenzo[f,h]pyrido[2,3-b]quinoxaline (3p)

IR (KBr): υ 3127, 1653, 1568, 1582, 1494, 1381, 1268 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8. 87 (d, 2H, *J* = 8 Hz), 8.71 (d, 1H, *J* = 10 Hz), 8. 41 (d, 2H, *J* = 8 Hz), 7.88 (d, 2H, *J* = 8 Hz), 7.80 (d, 2H, *J* = 8 Hz), 7.43 (d, 1H, *J* = 10 Hz), 7.20 (d, 1H, *J* = 10 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.75, 142.38, 130.18, 129.62, 128.57, 128.23, 127.22, 126.85, 126.13, 125.78, 124.30, 123.67; MS: m/z 281 (M^+); Anal. calcd. For $C_{19}H_{11}N_3$: C, 81.12 (81.67); H, 3.94 (3.48); N, 14.94 (14.52).

Results and Discussion

The route adopted for the synthesis of the title compound was flashed in the **scheme 1**. By using the method reported elsewhere in the literature[41] the heterogeneous catalyst HBF_4-SiO_2 was prepared and used in the above scheme. The structures of compounds (**3a-p)** were confirmed by the IR, ^1H NMR and Mass spectral analysis. For the quantitative yield of the final product (**3a-p)**, the model reaction was observed in different criterion. Optimization of the synthetic rout was arranged in order to achieve the Green Chemistry Principles. On that way firstly we try to carry out the same synthesis without catalyst and without solvent. Here we find out that the reaction cannot be proceeding at RT as well as in higher temperature also. But by increasing temperature and introducing the heterogeneous catalyst HBF_4-SiO_2, the % yield of the newly synthesized compounds is increased (**Entry 6, Table 1**).

Table 2: Optimization of reaction in different reaction condition.

Entry	Catalyst	Temp (°C)	Time (min)[a]	Yield (%)[b]
1	No Catalyst	RT	>120	0
2	No Catalyst	120	>120	0

3	HBF_4-SiO_2 (5% mole %)	RT	40	5
4	HBF_4-SiO_2 (5% mole %)	60	15	65
5	HBF_4-SiO_2 (5% mole %)	80	22	80
6	HBF_4-SiO_2 (10% mole %)	60	12	92
7	HBF_4-SiO_2 (20% mole %)	60	18	80

[a] Reaction progress monitored by thin-layer chromatography (TLC)
[b] Yields refer to isolated yield

Furthermore, we carry out the same reaction in different reaction solvent including water to find out the solvent influence and also to enhance the % yield of the final product. At the end of this experiment we observed that the % of the final product is greather that means above 87% when we use the heterogeneous catalyst with PEG-400 as a green catalyst (**Entry 6, Table 2**). Thus, after completion of the reaction, catalyst was reuse after simple filtration and washed thoroughly with ethanol. This optimized condition focus the green reaction media using heterogeneous catalyst and green solvent for the synthesis of 2,3-diphenylquinoxaline derivatives (**3a-p**).

Table 2: Influence of the solvent on the reaction.

Entry	Solvent	Time(min)[a]	Yield(%)[b]
1	Water	>60	12
2	EtOH	>30	74
3	CH_3CN	>30	58
4	DMF	>30	65
5	PEG-400	12	92

[a] Reaction progress monitored by thin-layer chromatography (TLC)
[b] Yields refer to isolated yield

Conclusion

In summary, by using different substituted 1,2-diketones and 1,2-diamine here we report a new synthetic rout for the synthesis of 2,3-diphenyl quinoxaline derivatives. The reported methods incorporate the provisions which are the building blokes of the Green Chemistry, like simple, efficient, eco-friendly method. Among these, the ambient condition is also favorable for the high reaction rate with excellent product yield. With the use of heterogeneous catalyst herein we use PEG-400 as a green solvent which focus the reaction route as a green and safe process and achieve both economic and environmental advantages and also explore in feature for the different organic synthesis.

References

[1] A. Jaso, B. Zarranz, I. Aldana, A. Monge, *J Med Chem.* 2005, 48, 2019–2025.
[2] C. Zie, Z. Zhang, B. Yang, G. Song, H. Gao, L. Wen, C. Ma, *Tetrahedron*. 2015, 71, 1831-1837.

[3] G. Aguirre, H. Cerecetto, R. DiMaio, M. Gonzales, M. E. M. A. Alfaro, A. Jaso, B. Zarranz, M. A. Ortega, I. Aldana, A. Monge-Vega, *Bioorg Med Chem Lett.* 2004, 14, 3835–3839.
[4] P. Y. Pawar, S. B. Bhise, *Asian J Chem.* 2008, 20, 1473-1481.
[5] S-B. Lee, Y. I. Park, M-S. Dong, Y-D. Gong, *Bioorg Med Chem Lett.* 2010, 20, 5900–5904.
[6] D. K. Balta, S. Keskin, F. Karasu, N. Arsu, *Prog Org Coat.* 2007, 60, 207-210.
[7] G. Bernardo, M. A. Esteves, A. M. Guerreiro, B. Gigante, J. Morgado, *Opt Mater.* 2008, 31, 320-327.
[8] P. Thirumurugan, D. Muralidharan, P. T. Perumal, *Dyes Pigments*. 2009, 81, 245-253.
[9] F. S. Mancilha, B. A. D. Neto, A. S. Lopes, P. F. Moreira, F. H. Quina, R. S. Goncalves, J. Dupont, *Eur J Org Chem.* 2006, 4924-33.
[10] A. Shaabani, A. Maleki, *Chem Pharm Bull.* 2008, 56, 79-81.
[11] J. S. Yadav, B. V. S. Reddy, Y. G. Rao, A. V. Narsaiah, *Chem Lett.* 2008, 37, 348-349.
[12] S. Antoniotti, E. Dunach, *Tetrahedron Lett.* 2002, 43, 3971-3973.
[13] H-W. Wu, G-S. Yang, *Chinese J Org Chem.* 2008, 28, 2132-2136.
[14] P. Haldar, B. Dutta, J. Guin, J. K. Ray, *Tetrahedron Lett*. 2007, 48, 5855-5857.
[15] D-Q. Shi, G-L. Dou, S-N. Ni, J-W. Shi, X-Y. Li, *J Heterocycl Chem.* 2008, 45, 1797-1801.
[16] B. J. E. Reich, A. K. Justice, B. T. Beckstead, J. H. Reibenspies, S. A. Miller, *J Org Chem.* 2004, 69, 1357-1359.
[17] R. S. Robinson, R. J. K. Taylor, *Synlett.* 2005, 1003-1005.
[18] J. J. vanden Eynde, F. Delfosse, P. Lor, Y. van Haverbeke, *Tetrahedron* 1995, 51, 5813-5818.
[19] P. L. Beaulieu, B. Hache, E. von Moos, *Synthesis.* 2003, 11, 1683-1692.
[20] F. Patzold, F. Zeuner, T. H. Heyer, H-J. Niclas, *Synth Commun.* 1992, 22, 281-284.
[21] I. Bhatnagar, M. V. George, *Tetrahedron.*1968, 24, 1293-1298.
[22] E. Verner, B. A. Katz, J. R. Spencer, D. Allen, J. Hataye, W. Hruzewicz, H. C. Hui, A. Kolesnikov, Y. Li, C. Luong, A. Martelli, K. Radika, R. Rai, M. She, Shrader, W. P. A. Sprengeler, S. Trapp, J. Wang, W. B. Young, R. L. Mackman, *J Med Chem.* 2001, 44, 2753-2771.
[23] M. A. Weidner-Wells, K. A. Ohemeng, V. N. Nguyen, S. Fraga-Spano, M. J. Macielag, H. M. Werblood, B. D. Foleno, G. C. Webb, J. F. Barrett, D. J. Hlasta, *Bioorg Med Chem Lett.* 2001, 11, 1545-1553.
[24] F. F. Stephens, J. D. Bower, *J Chem Soc.* 1949, 2971-2972.
[25] H. Chikashita, S. Nishida, M. Miyazaki, Y. Morita, K. Itoh, *Bull Chem Soc Jpn.* 1987, 60, 737-746.
[26] M. M. Heravi, S. Taheri, K. Bakhtiari, H. A. Oskooie. *Catal commun.* 2007, 211-214.
[27] A. Hasaninejad, A. Zare, M. R. Mohammadizadeh, M. Shekouhy, *Arkivoc.* 2008, 8, 28–35.
[28] S. V. More, M. N. V. Sastry, C. F. Yao, *Green Chem.* 2006, 8, 91-95.
[29] H. A. Oskooie, M. M. Heravi, K. Bakhtiari, S. Taheri, *Monatsh Chem.* 2007, 138, 875–877.
[30] H. R. Darabi, S. Mohandessi, K. Aghapoor, F. Mohsenzadeh, *Catal Commun.* 2007, 389–392.
[31] L. Wang, J. Liu, H. Tian, C. Qian, *Synth Commun.* 2004, 34, 1349–1357.
[32] A. Dhakshinamoorthy, K. Kanagaraj, K. Pitchumani, *Tetrahedron Lett*. 2011, 52, 69-73.
[33] H. M. Meshram, G. S. Kumar, P. Ramesh, B. C. Reddy, *Tetrahedron Lett.* 2010, 51, 2580-2585.
[34] M. M. Heravi, K. Bakhtiari, M. H. Tehrani, N. M. Javadi, H. A. Oskooie, *Arkivoc*. 2006, 16, 16–22.
[35] B. Das, K. Venkateswarlu, K. Sunnel, A. Majhi, *Tetrahedron Lett.* 2007, 48, 5371-5374.

[36] C. Srinivas, C. N. S. S. P. Kumar, V. J. Rao, S. Palaniappan, *J Mol Cat A: Chem* 2006, 265, 228–231.
[37] A. Hasaninejad, A. Zare, M. A. Zolfigol, *synth commun.* 2009, 39, 569-579.
[38] N. P. Xekoukoulotakis, M. C. P. Hadjiantonious, A. J. Maroulis, *Tetrahedron Lett.* 2000, 41, 10299-10302.
[39] Z. Zhao, D. D. Wisnoski, S. E. Wolkenberg, W. H. Leister, Y. Wang, C. W. Lindsley, *Tetrahedron Lett*. 2004, 45, 4873-4876.
[40] R. S. Bhosale, S. R. Sarda, S. S. Ardhapure, W. N. Jadhav, S. R. Bhusare, R. P. Pawar, *Tetrahedron Lett*. 2005, 46, 7183-7186.
[41] Y-H. Liu, X-Y. Tao, L-Q. Lei, Z-H. Zhang, *Synth Commun.* 2009, 39, 580-589.