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Synthesis and application of polyvinylimidazole-based Brønsted acidic ionic liquid grafted silica as an efficient heterogeneous catalyst in the preparation of quinoxaline derivatives

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Abstract: Two types of polymer-grafted silica based on polyvinylimidazole Brønsted acidic ionic liquids were prepared and used as new heterogeneous catalysts for the preparation of pharmaceutically important quinoxaline derivatives. These catalysts were characterized by thermogravimetric analysis, FT-IR spectroscopy, and titration. They could be recycled without considerable loss in their catalytic activity. High efficiency of the catalysts along with short reaction times, high yields, easy purification, recyclability, and simple procedure are among the advantages of these catalytic systems.

Key words: Polymeric ionic liquid grafted silica, heterogeneous catalyst, quinoxaline

1. Introduction

In contrast to high temperature melts, which are commonly referred to as molten salts, ionic liquids (ILs) are defined as salts that melt below 100 °C and whose melts are composed of discrete ions. Ionic liquids have no measurable vapor pressure, and hence can emit no volatile organic compounds. This new chemical group can reduce the use of hazardous and polluting organic solvents due to these kinds of properties. ILs have found an increasing number of applications in some technological fields such as catalysis,[1] electrochemistry and analytical chemistry,[2–4] nanotechnology,[5] biotechnology,[6–8] and polymer science.[9–11]

Brønsted acidic ionic liquids (BAILs) are a group of ILs with special importance because they possess the proton acidity and characteristic properties of an ionic liquid simultaneously. BAILs can replace traditional liquid acid catalysts such as H_2SO_4 and HCl that are often toxic, corrosive, and difficult to separate and recover from products of reaction despite their high catalytic activity. These kinds of catalysts have attracted the attention of researchers in many organic reactions, such as esterification,[12] alkylation,[13] acylation,[14] nitration,[15] Mannich reaction,[16] Beckmann rearrangement,[17] quinoline synthesis,[18] and Ritter reaction.[19] However, in addition to the advantages of ILs, there are some disadvantages in application of these materials in reactions. ILs are expensive; therefore, for many applications it is desirable to minimize the amount of ILs used in reaction systems. On the other hand, ILs are viscose materials and using them in reaction systems can induce mass transfer limitations. Although the IL used as catalyst maybe recyclable by distillation of the product from the resulting mixture, simpler catalyst separation processes remain a challenge. These problems can be overcome by immobilizing a thin film of polymeric ionic liquid (PIL) onto a support.

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PILs have found an important role in some fields of material science. PILs are polymers that contain at least one ionic center covalently bonded with a polymer backbone. PILs combine the unique properties of ILs with the flexibility and properties of macromolecular architectures and provide novel properties and functions. These properties provide a wide variety of applications in some fields but there are only a few reports in the literature on the application of PILs as catalyst.[20−22]

Immobilization of PILs on supports like silica offers a number of advantages. According to the literature, some supported PILs were synthesized, characterized, and used in analytical chemistry, particularly in HPLC, SPE, microextraction, coating, sorption of bioactive compounds, and also as stationary phase.[23−25] However, there are few reports in the literature on the use of supported PILs as catalyst.[26,27] On the other hand, these kinds of catalysts can be recovered from the reaction mixture by simple filtration and the product solution is not contaminated. These kinds of properties provide a good domain for catalysis activity of supported PILs.

Quinoxaline derivatives are important groups of nitrogen-containing heterocyclic compounds. They are well known in the pharmaceutical industry as important precursors with biological activities such as antimicrobial,[28] antiviral,[29,30] and anticancer activity.[31] Moreover, their applications as dyes,[32,33] efficient electroluminescent materials,[34] building blocks for the synthesis of organic semiconductors,[35] and DNA cleaving agents[36] have been reported. Many synthetic methods have been developed for quinoxaline derivatives. Quinoxaline derivatives can be synthesized from tetrazospiro compounds[37] and usually by the condensation of aryl 1,2-diamines with 1,2-dicarbonyl compounds in the presence of an acidic catalyst. For this transformation, several catalysts have been reported, including p-toluene sulfonic acid (PTSA),[38] oxalic acid,[39] polyaniline-sulfate salt,[40] sulfamic acid,[41] ceric(IV) ammonium nitrate,[42] [Hbim] BF_4,[43] Brønsted-acidic ionic liquid [TMPSA].HSO_4,[44] and graphite.[45] However, a number of these methods suffer from some limitations such as using strong acidic conditions, tedious work-up procedures, low yield, and long reaction times. Thus, it seems desirable to find a more efficient and milder protocol for the synthesis of quinoxalines.

As an extension of our previous work on heterogeneous catalysts based on polymeric support and polymer grafted silica,[46−52] herein we report the synthesis and characterization of two types of polyvinylimidazole-based Brønsted acidic ionic liquid grafted silica and their application as heterogeneous catalysts in the synthesis of quinoxaline derivatives with various substrates. The quinoxaline derivatives are important precursors in pharmaceutical chemistry.

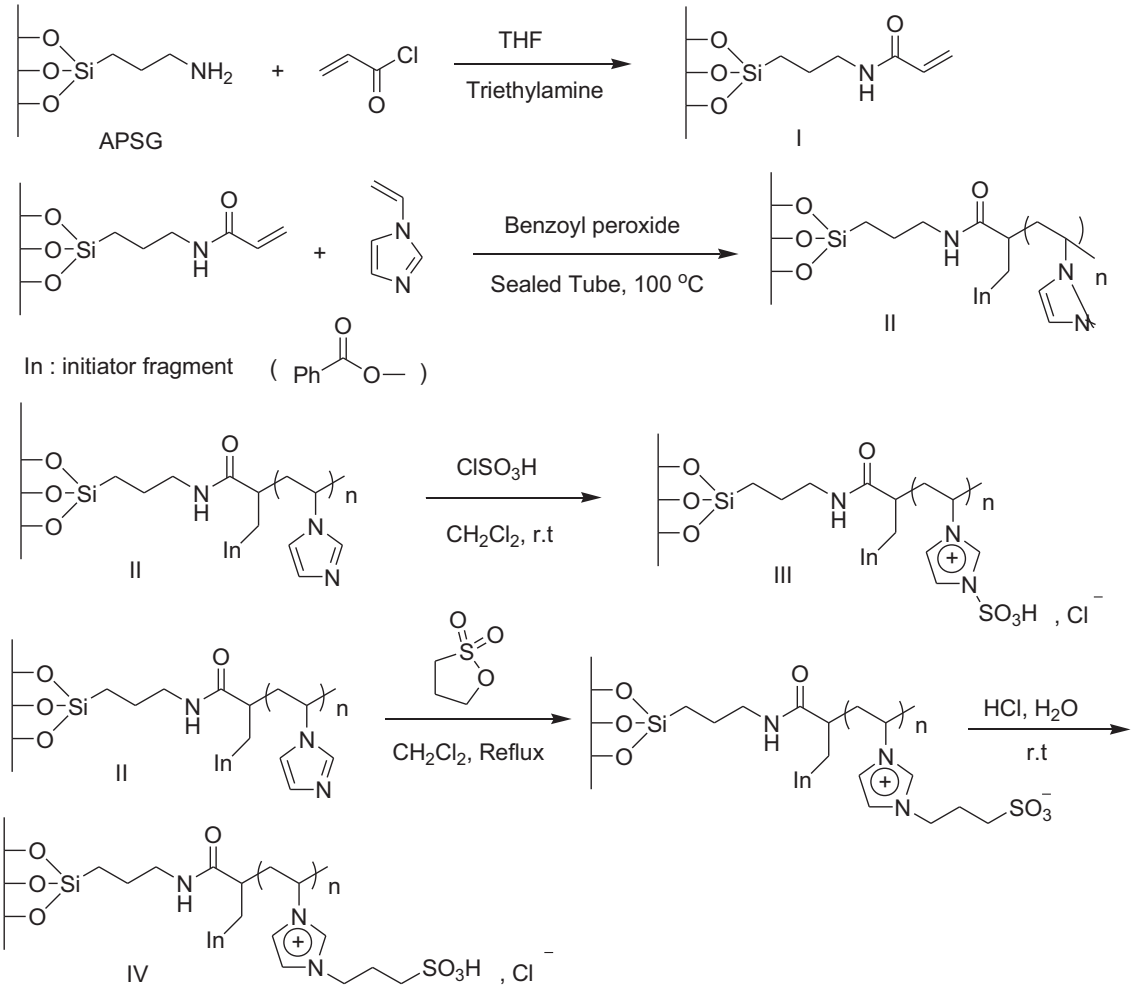
2. Results and discussion

2.1. Synthesis and characterization of supported catalysts

The catalysts were designed by the sequence of reactions given in the Scheme.

Acrylamidopropyl silica gel (I) was obtained by the reaction of aminopropyl silica gel (APSG) with acryloyl chloride. Figure 1 shows the FT-IR of compound I. The appearance of bands at 1627 cm^{-1} (carbon–carbon double bond stretching), 1103 cm^{-1} (Si–O stretching), 1662 cm^{-1} (amide I), 1558 cm^{-1} (amide II), and 3421 cm^{-1} (N–H stretching) confirmed that the reaction between the amino group of APSG and acryloyl chloride had occurred.

Poly (*N*-vinylimidazole) modified silica gel (II) was obtained by free-radical copolymerization between acrylamidopropylsilica (I) and vinylimidazole monomer in the presence of benzoyl peroxide as an initiator. Figure 2 shows the FT-IR spectrum of (II). The appearance of bands at 1512 cm^{-1} and 1650 cm^{-1} (imidazole ring), 1103 cm^{-1} (Si–O stretching), and 1550 cm^{-1} (amide), and disappearance of the double bond confirmed that the copolymerization reaction had occurred.



Scheme. Preparation of silica supported polymeric Brønsted acidic ionic liquid catalysts.

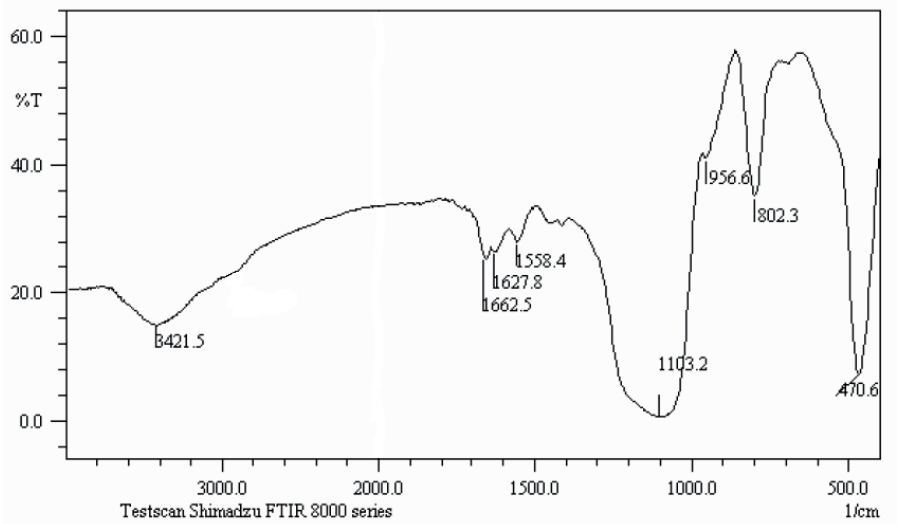


Figure 1. FT-IR spectrum of acrylamidopropyl silica (I).

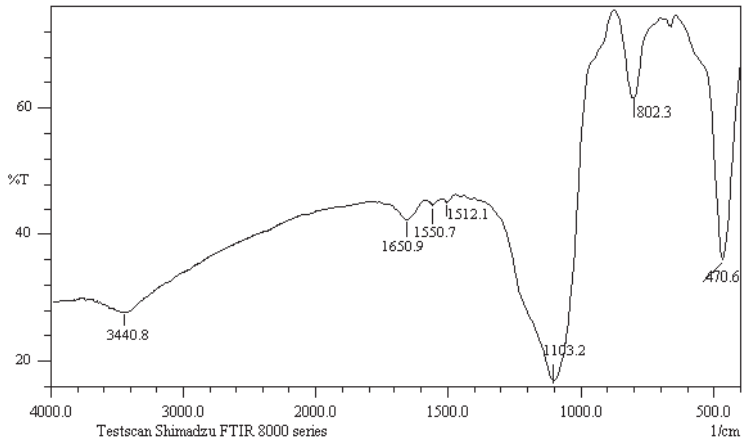


Figure 2. FT-IR spectrum of polyvinylimidazole grafted silica (II).

The amount of polymer grafted on the surface of silica was determined by thermogravimetric method and was found to be 1.5 mmol of poly (*N*-vinylimidazole) per gram of the functionalized silica gel.

Polyvinylimidazole-based Brønsted acidic ionic liquid grafted silica (III) was prepared by the reaction between poly(*N*-vinylimidazole) grafted silica (II) and chlorosulfonic acid at room temperature. The capacity of catalyst III was determined, by acid-base back titration method, to be 0.80 mmol of $-SO_3H$ per gram. The thermal stability of III was determined by thermogravimetric method. As shown in Figure 3, the weight loss begins at about 200 °C and ends at around 600 °C. Obviously the thermal stability is high, and this is important for the catalyst application.

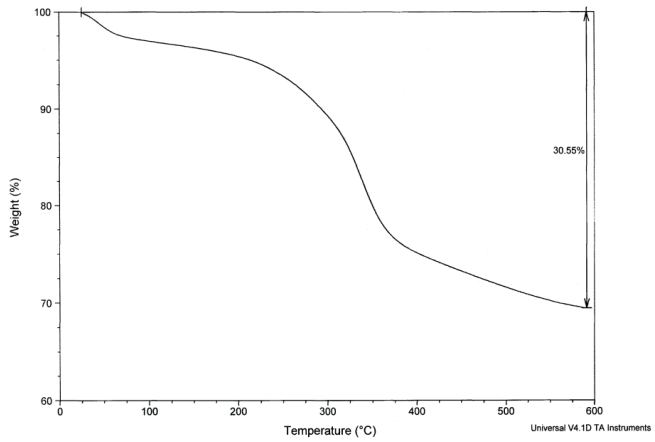


Figure 3. Thermogravimetric spectra of catalyst III.

Catalyst IV, which was prepared by the reaction of poly (*N*-vinylimidazole) grafted silica (II) and 1,3-propanesultone, was treated with hydrochloric acid. The capacity of this catalyst was also determined by titration method to be 0.65 mmol of SO_3H per gram.

A broad band at 1000–1250 is due to overlapping of Si–O and S=O stretching vibrations. The S=O stretching vibration band is hidden under that of Si–O as shown in Figure 4.

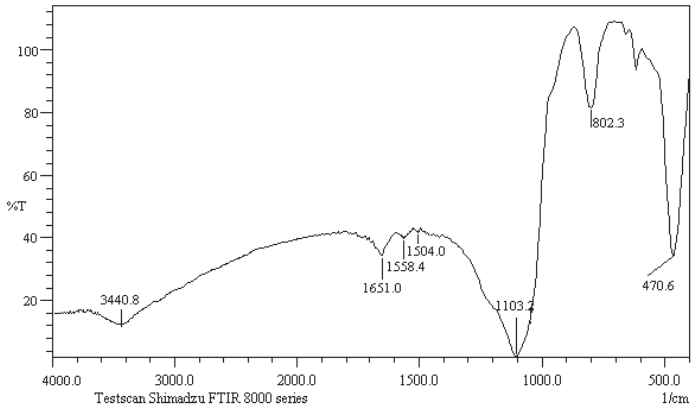
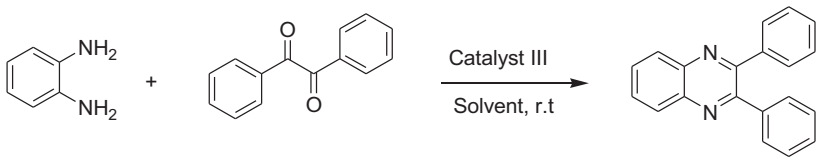


Figure 4. FT-IR spectrum of catalyst III.

2.2. Catalytic activity of the catalysts in the synthesis of quinoxaline derivatives

The activity of catalyst III was examined in the synthesis of quinoxaline derivatives. The reaction of *o*-phenylenediamine and benzil was initially studied as a model reaction. The reaction conditions were optimized and the results are presented in Table 1. It was found that the best solvent for this reaction was EtOH, in which 100% conversion of benzil within 1 h using 0.5 mol% of the catalyst at room temperature was obtained (Table 1, entry 8).

Table 1. Optimization of the reaction conditions for preparation of quinoxaline derivatives using catalyst III.



Entry	Solvent	Molar ratio of the catalyst	Catalyst amount (g)	Time (h)	Conversion %[a]
1	H_2O	3 mol%	0.039	1	40
2	MeOH	3 mol%	0.039	1	85
3	EtOH	3 mol%	0.039	1.5	100
4	THF	3 mol%	0.039	2	50
5	DMF	3 mol%	0.039	1	80
6	CH_2Cl_2	3 mol%	0.039	2	30
7	EtOH	1 mol%	0.013	1.25	90
8	EtOH	0.5 mol%	0.006	1	100
9	EtOH	0.3 mol%	0.004	1.6	95
10	EtOH	0.2 mol%	0.003	1.6	95
11	EtOH	0.1 mol%	0.001	2	60

Reaction conditions: benzil (1 mmol), *o*-phenylenediamine (1 mmol), solvent (4 mL), catalyst (0.1–3 mol%) at room temperature, [a] Conversion based on benzil

To survey the generality of the catalytic protocol, we investigated the reaction using a variety of α-diketones and 1,2-diamines under the optimized condition.

Table 2. Synthesis of quinoxalines in the presence of catalyst III.[a]

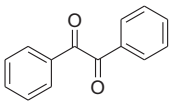
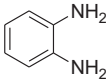
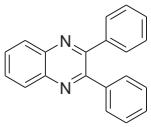
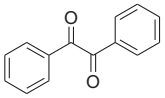
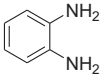
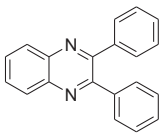
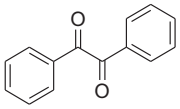
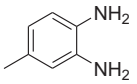
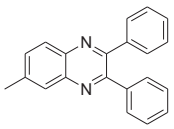
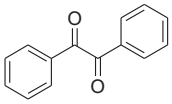
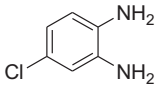
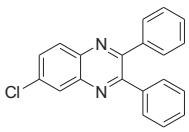
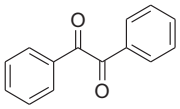
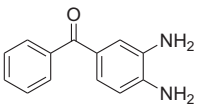
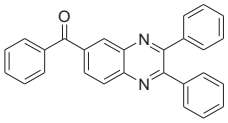
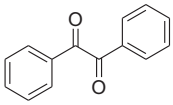
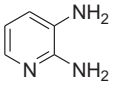
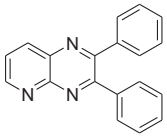
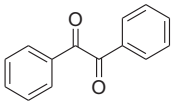
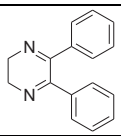
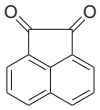
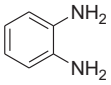
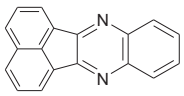
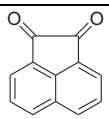
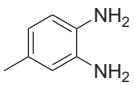
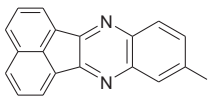
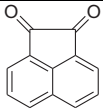
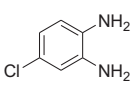
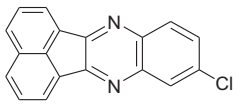
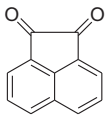
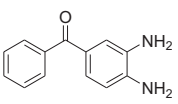
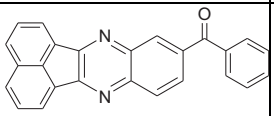
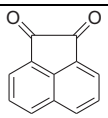
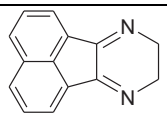
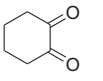
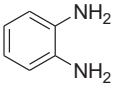
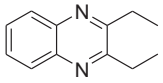
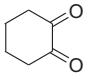
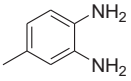
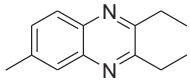
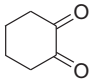
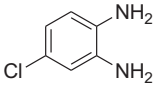
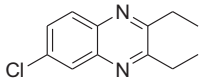
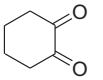
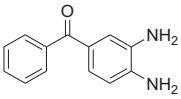
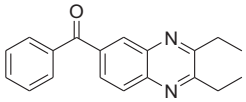
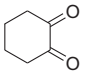
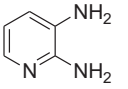
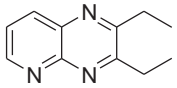
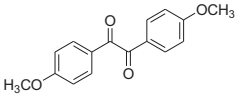
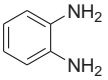
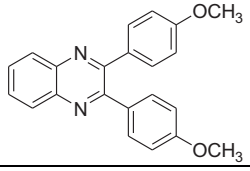
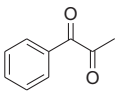
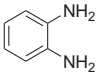
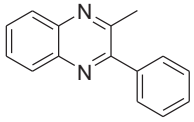
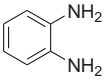
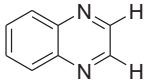
Entry	α-Diketone	1,2-Diamine	Product	Time (h)	Yield %
1				5	30[b]
2				1	97
3				1	90
4				1	85
5				1	60
6				0.5	50
7				1	60
8				0.25	97
9				0.25	95
10				0.75	93
11				1	85

Table 2. Continued.

Entry	α-Diketone	1,2-Diamine	Product	Time (h)	Yield %
12				0.25	97
13				0.16	98
14				0.16	97
15				0.16	95
16				0.5	95
17				0.5	97
18				1	70
19				0.25	98
20				1	30

[a] Diketone (1 mmol), diamine (1 mmol), EtOH (5 mL), catalyst (0.5 mol%), room temperature, [b] Without catalyst

The results are shown in Table 2. In the absence of any catalyst the reaction occurred with low speed and yield. For series of diketones and diamines, the majority of the corresponding quinoxalines were obtained in high yields and acceptable times at room temperature.

In order to see the effect of three carbon spacer arm in the efficiency of the catalyst, in a series of reactions catalysts III and IV were compared. As seen in Table 3, the efficiency of catalyst III is higher than that of IV.

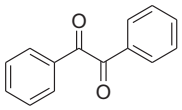
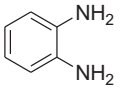
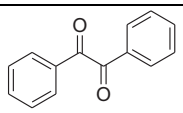
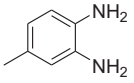
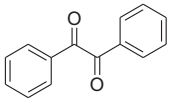
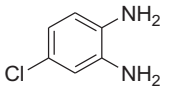
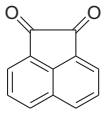
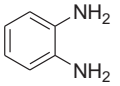
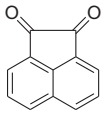
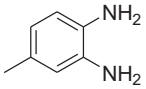
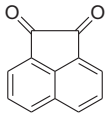
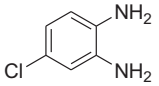
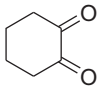
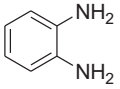
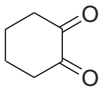
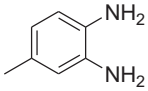
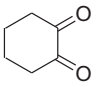
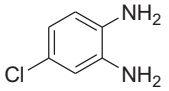
Table 4 shows a comparison of catalyst III with some of the previous heterogeneous catalysts reported in the literature for preparation of quinoxaline derivatives. Short reaction times with excellent yields, lower amount of the catalyst, and recyclability are among the characteristics of this new catalyst.

2.3. Recycling of the catalysts

Recycling of catalysts is important from economic and environmental points of view. The reaction of benzil and benzene-1,2-diamine was run as a model reaction using catalysts III and IV. When the reaction was finished,

the mixture was filtered. The catalysts were washed and dried under vacuum and then used in the next reaction cycle with a new portion of reagents without any pretreatment.

Table 3. Comparison of catalysts III and IV in synthesis of quinoxaline derivatives.

Entry	Diketone	Diamine	Catalyst (III)		Catalyst (IV)	
			Time (h)	Yield %	Time (h)	Yield %
1			1	97	1.83	93
2			1	90	2	80
3			1	85	2	80
4			0.25	97	1	90
5			0.25	95	1.3	90
6			0.75	93	1.3	90
7			0.16	98	0.25	96
8			0.16	97	0.5	85
9			0.16	95	0.5	85

Reaction conditions: α-Diketone (1 mmol), 1,2-diamine (1 mmol), EtOH (5 mL), catalyst III (0.5 mol%), catalyst IV (1 mol%), room temperature

The catalysts obtained in this way were reused 6 consecutive times without any significant loss in their activities. The results are shown in Table 5.

In conclusion, two types of heterogeneous catalysts based on polymeric Brønsted acidic ionic liquid grafted silica were synthesized and characterized by FT-IR spectroscopy, thermogravimetry, and titration. These catalysts were used efficiently in the preparation of quinoxaline derivatives. The catalysts were easily separated

from the reaction mixture by filtration and were recyclable. The effect of spacer arm on the activity of these two catalysts was studied.

Table 4. Preparation of 2,3-diphenylquinoxaline under different heterogeneous catalysts reported in the literature.

Entry	Catalyst	Reaction conditions	Yield %	Reference
1	Catalyst III	0.5 mol%/EtOH/1 h/rt	97	-
2	$SbCl_3/SiO_2$	2.5 mol%/MeOH/1 h/rt	97	53
3	Silica bonded S-sulfonic acid	3.4 mol%/H_2O, EtOH/rt/5 min	96	55
4	Graphite	2 mol%/EtOH/1 h/rt	92	45
5	Carbon–MoO_3–TiO_2	3 mol%/H_2O, EtOH/15 min/40 °C	82	54
6	Amberlyst 15	24 mol%/H_2O/19 min/70 °C	92	56
7	Montmorillonite K-10	10 mol%/H_2O/2.5 h/rt	100	58
8	Nano-Fe_3O_4	10 mol%/H_2O/2.5 h/rt	95	57

Table 5. Recyclability of catalysts III and IV in the synthesis of 2,3-diphenylquinoxaline.

Run	Catalyst III		Catalyst IV	
	Time (h)	Yield %	Time (h)	Yield %
1st	1	97	1.5	93
2nd	1	97	1.5	93
3rd	1	97	1.5	90
4th	1.25	95	2	85
5th	1.25	95	2	85
6th	1.5	90	2	80
7th	2	85	2.5	78

3. Experimental

3.1. General

Substrates were purchased from Fluka, Merck, or Aldrich. Aminopropylsilica was supplied by Fluka AG. The products were purified by column chromatography or recrystallization from appropriate solvents and were identified by comparison of their melting points, IR, and NMR spectral data with those reported for the known samples. Progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates. FT-IR spectra were recorded on a Shimadzu FT-IR-8000 spectrophotometer. The spectra of solids were obtained using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra of products in $CDCl_3$ and CCl_4 were recorded on a Bruker Avance DPX instrument (250 MHz). Chemical shifts are reported in ppm (δ) downfield from TMS. TGA thermograms were recorded on a PerkinElmer instrument with N_2 carrier gas and the rate of temperature change of 20 °C/min was used.

3.2. Preparation of the catalysts

3.2.1. Preparation of acrylamidopropylsilica (I)

Acrylamidopropylsilica was prepared by the reaction between aminopropyl silica gel (APSG) and acryloyl chloride according to the previous procedure.[46,47] The aminopropylsilica (10 g, 9.5 mmol amino groups) was suspended in dry THF (200 mL) and the suspension cooled to 0 °C. Triethylamine (1.5 g, 0.015 mol) was added, followed by propenoyl chloride (1.1 g, 0.012 mol) over 1 h. The temperature of the reaction reached 5 °C at

the end of the addition. The thick slurry was then stirred at 0 °C for a further 4 h and the modified silica isolated by filtration and washed with THF (100 mL), water (2 × 100 mL), and THF (100 mL). The obtained solid was then dried in an oven at 50 °C for 24 h.

3.2.2. Preparation of poly (*N*-vinylimidazole) grafted silica (II)

To a 10-mL sealed tube was added a suspension of acrylamidopropylsilica (4 g) in 8 mL of fresh *N*-vinylimidazole (88.3 mmol) and recrystallized benzoyl peroxide (0.01 g). The tube was sealed under argon atmosphere and the mixture was heated at 100 °C in an oven for 15 h. The product was Soxhlet-extracted with 200 mL of $CHCl_3$ for 24 h, followed by washing with 200 mL of methanol and then acetone (2 × 100 mL), and dried for 12 h under vacuum.

3.2.3. Preparation of polyvinylimidazole-based Brønsted acidic ionic liquid grafted silica (III)

A flask was charged with 2 g of poly (*N*-vinylimidazole) grafted silica in 10 mL of dry CH_2Cl_2 and then chlorosulfonic acid (3 mmol, 0.2 mL) was added dropwise over 5 min at room temperature. The reaction mixture was stirred for 2 h, and CH_2Cl_2 was decanted. The residue was washed with CH_2Cl_2 and an adequate amount of water. The solid obtained was dried in an oven at 80 °C for 24 h.

3.2.4. Preparation of polyvinylimidazole-based Brønsted acidic ionic liquid grafted silica (IV)

A flask was charged with 2 g of poly (*N*-vinylimidazole) grafted silica in 10 mL of dry CH_2Cl_2 and 1,3-propanesultone (3 mmol, 0.26 mL) was added dropwise over 15 min under reflux condition. The reaction mixture was stirred for 10 h. Then the supernatant was decanted. The residue was washed with CH_2Cl_2 and an adequate amount of water. The solid obtained was dried in an oven at 80 °C for 24 h. Then the formed solid (2 g) was added to a flask of 5 mL of water, and equal molar hydrochloric acid was slowly dropped into the flask at room temperature and stirred for 12 h. Finally, the formed solid was washed with ether, acetone, and water and dried in a vacuum oven at 80 °C for 24 h.

3.3. General procedure for preparation of quinoxaline derivatives

To a mixture of 1,2-diketone (1 mmol) and 1,2-diamine (1 mmol) in 4 mL of ethanol was added catalyst III (0.006 g, 0.5 mol%) or catalyst IV (0.017 g, 1 mol%). The reaction mixture was stirred at room temperature for the appropriate time. The progress of the reaction was followed by TLC. Upon completion, the product and the catalyst were separated easily from each other by simple filtration. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography with petroleum ether (bp 60 °C) and ethyl acetate (in some cases recrystallization was used). The obtained quinoxalines were identified by their ^{1}H NMR and ^{13}C NMR spectra and comparison of their melting points with those of the authentic samples.

Selected spectral data for products of Table 2:

2,3-Diphenylquinoxaline (table 2, entry 1): White solid; mp 127–128 °C (Lit.[57] 125–126 °C); IR (KBr, cm^{-1}): 3059, 1620, 1558; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.3–7.4 (m, 6H, Ar-H), 7.5–7.6 (m, 4H, Ar-H), 7.7–7.8 (m, 2H, Ar-H), 8.1–8.2 (m, 2H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 128.3, 128.8, 129.2, 129.8, 129.9, 139.1, 141.2, 153.5.

2,3-Diethylquinoxaline (Table 2, entry 13): White solid; mp 51–53 °C (Lit.[43] 51–52 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.6 (t, J = 7.5 Hz, 6H, CH_3), 3.2 (q, J = 7.5 Hz, 4H, CH_2), 7.8–7.9 (m, 2H, Ar-H), 8.2–8.3 (m, 2H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.6, 28.4, 128.5, 128.7, 141.0, 157.3

6-Methyl-2,3-Diethylquinoxaline (Table 2, entry 14): White solid; mp 40–43 °C (Lit.[43] 41–42 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.4 (t, J = 7.5 Hz, 6H, CH_3), 2.5 (s, 3H, CH_3), 3.0 (q, J = 7.5 Hz, 4H, CH_2), 7.5 (dd, J = 8.5, 1.9 Hz, 1H, CH), 7.8 (s, 1H, CH), 7.9 (d, J = 8.5 Hz, 1H, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.6, 12.6, 21.7, 28.2, 28.3, 127.3, 127.9, 130.9, 139.0, 139.3, 140.9, 156.2, 157.0.

Supplementary information: Supplementary data (^{1}H and ^{13}C NMR spectra of products) are available at the end of this manuscript.

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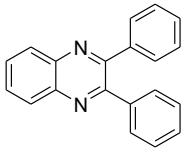
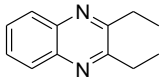
Supplementary Material

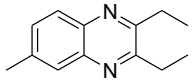
1. Characterization data of some of the compounds



2,3-Diphenylquinoxaline (Table 2, entry 1): White solid; mp 127–128 °C (Lit.[57] 125–126 °C); IR (KBr, cm^{-1}): 3059, 1620, 1558; ^1H NMR (250 MHz, $CDCl_3$): δ = 7.3–7.4 (m, 6H, Ar-H), 7.5–7.6 (m, 4H, Ar-H), 7.7–7.8 (m, 2H, Ar-H), 8.1–8.2 (m, 2H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 128.3, 128.8, 129.2, 129.8, 129.9, 139.1, 141.2, 153.5.

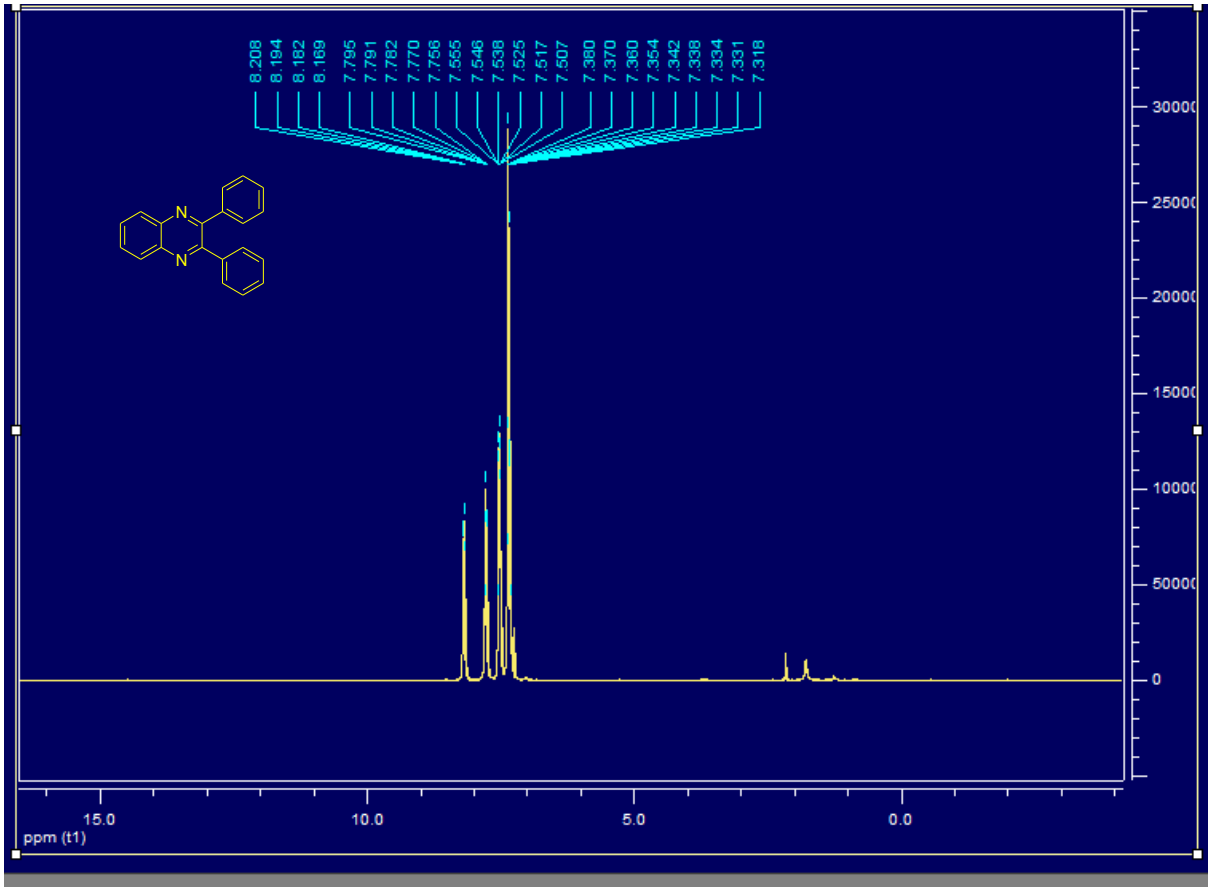


2,3-Diethylquinoxaline (Table 2, entry 13): White solid; mp 51–53 °C (Lit.[43] 51–52 °C); ^1H NMR (250 MHz, $CDCl_3$): δ = 1.6 (t, *J* = 7.5 Hz, 6H, CH_3), 3.2 (q, *J* = 7.5 Hz, 4H, CH_2), 7.8–7.9 (m, 2H, Ar-H), 8.2–8.3 (m, 2H, Ar-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.6, 28.4, 128.5, 128.7, 141.0, 157.3.

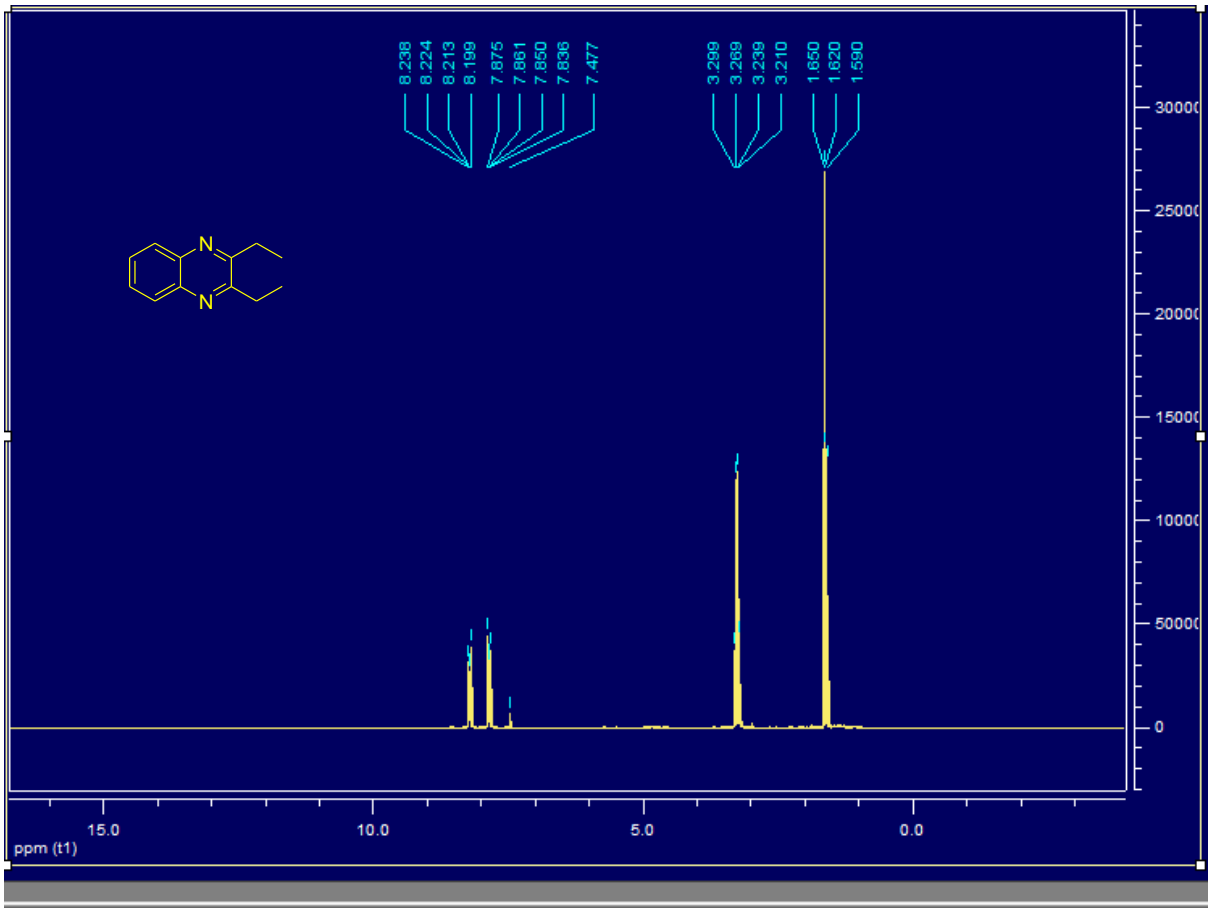


6-Methyl-2,3-Diethylquinoxaline (Table 2, entry 14): White solid; mp 40–43 °C (Lit.[43] 41–42 °C); ^1H NMR (250 MHz, $CDCl_3$): δ = 1.4 (t, *J* = 7.5 Hz, 6H, CH_3), 2.5 (s, 3H, CH_3), 3.0 (q, *J* = 7.5 Hz, 4H, CH_2), 7.5 (dd, *J* = 8.5, 1.9 Hz, 1H, CH), 7.8 (s, 1H, CH), 7.9 (d, *J* = 8.5 Hz, 1H, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 12.6, 12.6, 21.7, 28.2, 28.3, 127.3, 127.9, 130.9, 139.0, 139.3, 140.9, 156.2, 157.0.

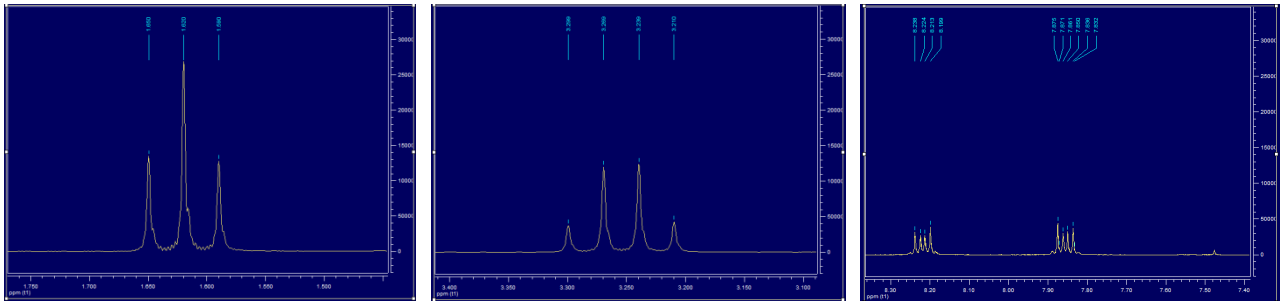
2. Original ^{1}H and ^{13}C NMR spectra of some of the compounds.



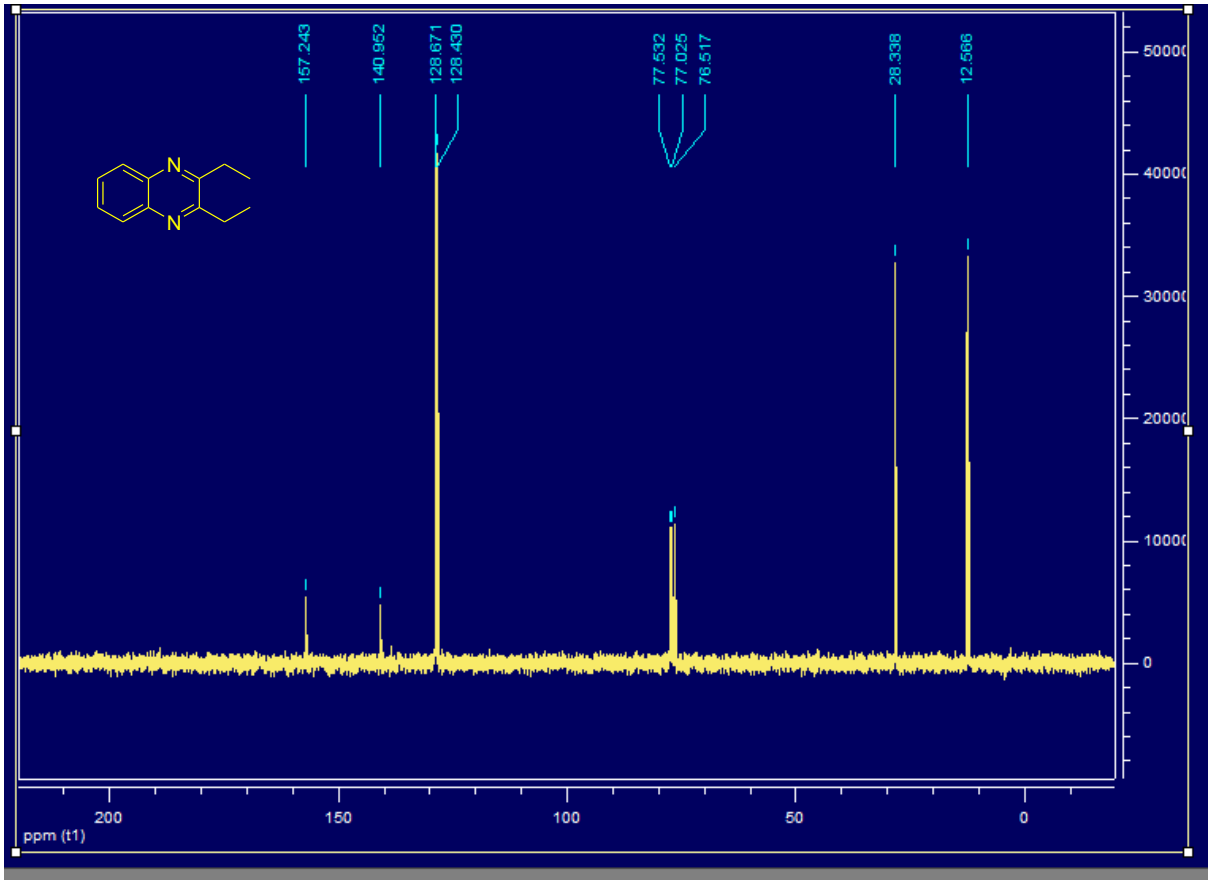
Scheme S1. ^{1}H NMR spectrum of 2, 3-diphenylquinoxaline.



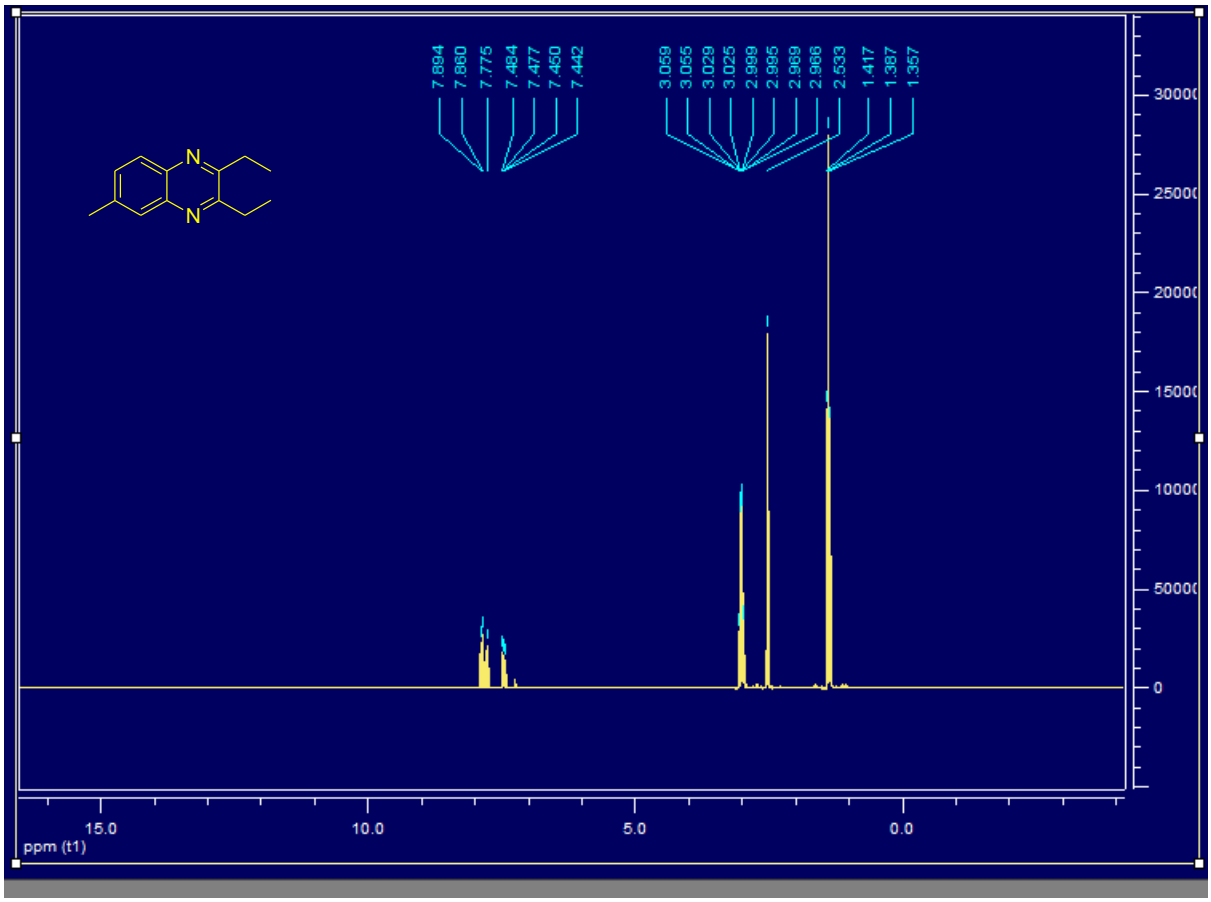
Scheme S2. ^{1}H NMR spectrum of 2,3-diethylquinoxaline.



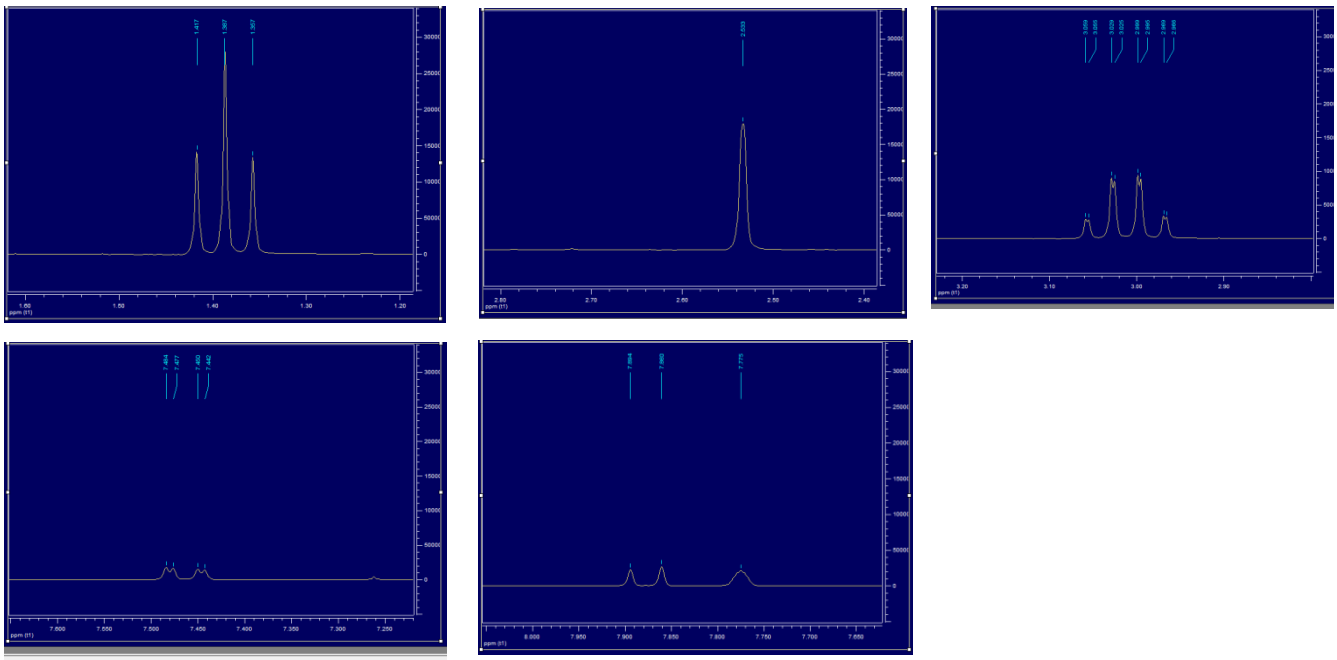
Scheme S3. Expanded ^{1}H NMR spectrum of 2,3-diethylquinoxaline.



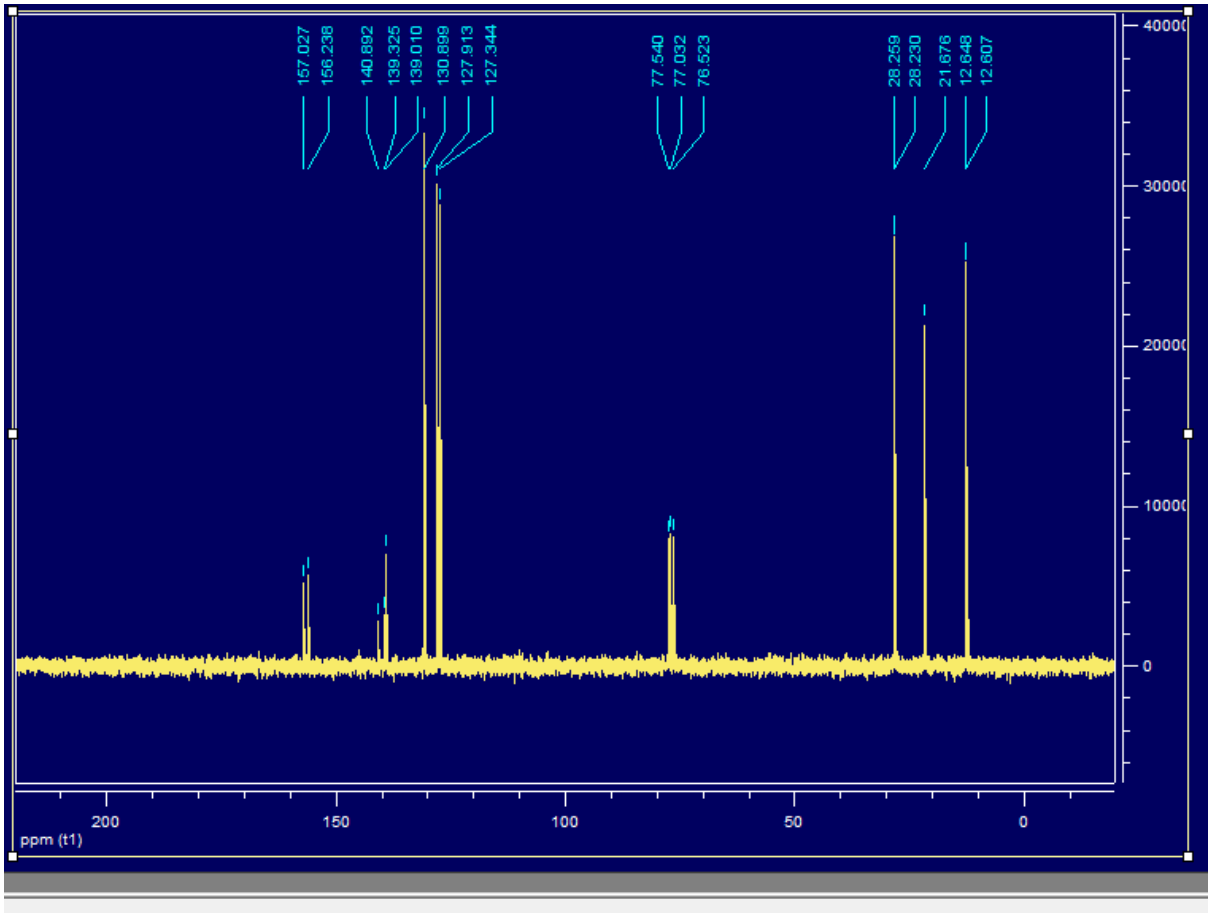
Scheme S4. ^{13}C NMR spectrum of 2,3-diethylquinoxaline.



Scheme S5. ^{1}H NMR spectrum of 6-methyl-2,3-diethylquinoxaline.



Scheme S6. Expanded ^{1}H NMR spectrum of 6-methyl-2,3-diethylquinoxaline.



Scheme S7. ^{13}C NMR spectrum of 6-methyl-2,3-diethylquinoxaline.