$NH_3(CH_2)_6NH_3SiF_6$ catalyzed highly efficient synthesis of benzimidazoles, benzoxazoles, benzothiazoles, quinoxalines and pyrimidin-2-ones/thiones

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Herein, we describe a simple, highly efficient and environmentally friendly protocol for the synthesis of benzimidazoles, benzoxazoles, benzothiazoles, 3,4-dihydropyrimidin-2-ones/ thiones and quinoxalines derivatives using hybrid crystal $NH_3(CH_2)_6NH_3SiF_6$ as a catalyst. Use of recyclable catalyst, easy work-up procedure, excellent yields, short reaction times and scalability are the important practical features of the present protocol.

Introduction

The quinoxaline derivatives have found applications as as antiviral, anti-inflammatory, antibacterial, kinase inhibitory properties, antiprotozoal, antibiotics such as echinomycin, leromycin and actinomycin [1-4]. As well, quinoxaline moieties have found applications in macrocyclic receptors [5], building blocks in the synthesis of organic semiconductors [6-7], and DNA cleaving agents [8]. In late years, several synthetic strategies have been developed for the preparation of quinoxalines using diverse catalysts such as Fe_3O_4@SiO_2-imid-PMA^n magnetic porous nano sphere [9], ZrO_2 Al_2O_3[10], nanoparticle-supported Cobalt (Co

NPs) [11], RHA-SO_3[12], cell-[pmim]HSO_4 [13], $VOSO_4$ [14].

Compounds bearing benzimidazole, benzoxazole and benzothiazole moieties are of great interest in medicinal area, as they show various and significant biological and pharmacological attributes such as antibiotic, anti-inflammatory, anti-parasitic, anti-stress, ulcer, anticancer, gram-positive antibacterial and antiviral attributes [15]. In recent times, several catalysts and reagents such as Fe(III)-schiff base/SBA-15 [16] and PSA [17] have been reported for the synthesis of benzimidazole, benzoxazole and benzothiazole.

The 3,4-dihydropyrimidin-2-ones/thiones, which have been synthesized by a multicomponent reaction, are very important heterocyclic motif in the realm of natural and synthetic organic chemistry due to possessing different biological and pharmacological activities, such as antibacterial [18], antitumor[19] and antiviral [20] properties. Several improved methods have been reported for the preparation of 3,4-dihydropyrimidin-2-(1H)-ones/thiones using various catalysts such as [Et_3N-SO_3H]HSO_4 [21], calix[8]arene sulfonic acid [22], sulfated polyborate [23], nano-YAl_2O_3:Eu^{3+} [24], Fe_3O_4/SiO_2-NH-ligand-Bi(III) nano catalyst [25], $Fe_{3-x}Ti_xO_4$@SO_3H [26], $TiCl_3OTf$-[bmim]Cl [27], [Dsbim]Cl [28] and $Cr(NO_3)_3 \cdot 9H_2O$ [29].

Based on this knowledge and in continuation of our work [30] towards development of simple, mild, eco-friendly reaction protocol, we explored the potential of $NH_3(CH_2)_6NH_3SiF_6$ as a catalyst for the synthesis of benzimidazoles, benzoxazoles, benzothiazoles, 3,4-dihydro pyrimidin-2-ones/ thiones and quinoxalines.

Results and Discussion

General information for the catalyst

The hexylenediammonium hexafluoro silicate $NH_3(CH_2)_6NH_3SiF_6$ single crystal has been synthesised by slow evaporation of aqueous solution containing $NH_2(CH_2)_6NH_2$ and H_2SiF_6 [31]. This compound belong to the family of alkylenediammoniums halogeno metallates compounds of the general formula $NH_3(CH_2)_nNH_3MX_6$ (IV) (M: Sn, Si, Te; X: Cl, Br, I and F) that have attracted more attention because of their important chemical and physical properties [32]. Some of these compounds have been found to be interesting for the study of crystal dynamic and phase transition involving hydrogen bonds as well as the reorientation motions of alkylammoniums cations [33]. $NH_3(CH_2)_6NH_3SiF_6$ was characterized by X-ray diffraction analysis. The catalyst was crystallized in the triclinic system with $P\bar{1}$ (Z = 4) as space group [a = 5.8965 (2) Å, b = 13.6946 (5) Å, c = 14.4945 (5) Å; α = 91.379 (2)°, β = 93.8 4 (1)°, γ = 90.906 (2)° and V = 1168.53 (7) $Å^3$]. All characteristic structural data of this compound have been recently published [31].

The crystal structure of this compound has been found to be built up from inorganic anions SiF_6^{2-} that were arranged to form sheets parallel to (001), which are linked into a three-dimensional network by the organic cations $^{+}NH_3(CH_2)_6NH_3^{+}$ through intermolecular N-H….F hydrogen bonding contacts (Figure 1) that provide a linkage between cationic $^{+}NH_3(CH_2)_6NH_3^{+}$ and SiF_6^{2-} anionic entities. The hydrogen bonds involved (donors and acceptors) ensure the three-dimensional cohesion of the atomic arrangement.

The symmetry codes : (i) –x, 1−y, −z ; (ii) −x, 2−y, −z ; (iii) −x, 1−y, 1−z ; (iv) −x, 2−y, 1−z. The asymmetric unit cell of $NH_3(CH_2)_6NH_3SiF_6$ salt consists of one anion (Si1) and one cation together with half of each of two cations and two anions (Si2) and (Si3) located on inversion centers.

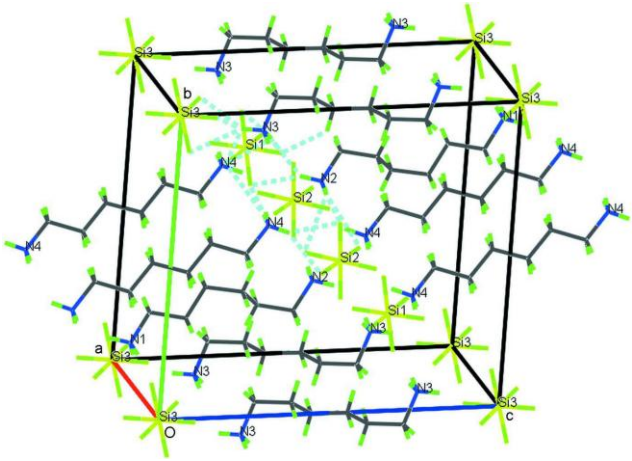


Figure 1. The three dimensional plot of the $NH_3(CH_2)_6NH_3SiF_6$ compound, showing inorganic sheets linked through N–H….F hydrogen bonds to the organic layers (dashed lines).

In the crystal structure of this compound, two silicon atoms [Si2 (0, 1/2, 1/2); Si3 (0, 0, 0)] are located at inversion centers of the $P\bar{1}$ space group. Each silicon atom is surrounded by six fluorine anions in a slightly distorted SiF_6^{2-} octahedral geometry. The unit cell contains one hexylenediammonium cation and two halves of cations located about an inversion centre. The organic cations fill the space between the inorganic sheets, forming a three-dimensional network by N-H….F hydrogen bonds.

The catalytic activity of Catalyst

1. Synthesis of benzimidazole 3, benzoxazole 4 and benzothiazole 5.

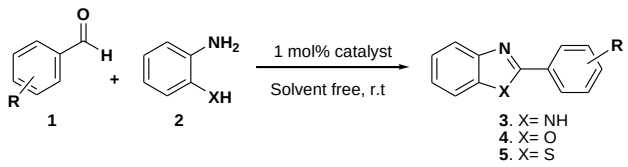
At first, the condensation reaction between benzaldehyde **1a** with 1,2-phenylenediamine **2a** was studied as a model reaction (Scheme 1) and the optimization of the reaction conditions was performed using various amounts of $NH_3(CH_2)_6NH_3SiF_6$ in various solvents at room temperature. As shown in Table 1, in the absence of a catalyst, only 12% yield of the desired product was obtained even after longer reaction time (Table 1, entry 1). Solvent-free conditions at room temperature using 1 mol % (2.60 mg) of catalyst (Table 1, entry 13) are the best condition for this reaction. The generality of the described protocol was explored by reacting different substituted aromatic aldehydes with o-phenyl

enediamine, o-aminothiophenol or o-amino phenol. The reaction affords respectively benzimidazole **3**, benzoxazole **4** and benzothiazole **5** (Scheme 1) in good to excellent yields in shorter times (Table 2).

Table 1. The effect of solvent and different amounts of $NH_3(CH_2)_6NH_3SiF_6$ on the synthesis of benzimidazole **3a**[a]

Entry	Catalyst (mol%)	Solvent (1 mL)	Time[b] (min)	Yield (%)[c]
1	-	EtOH	240	12
2	5	EtOH	15	90
3	5	MeOH	20	91
4	5	Butanol	55	60
5	5	Isopropanol	35	76
6	5	CH_3CN	60	71
7	5	THF	100	62
8	5	AcOEt	30	84
9	5	Solvent free	6	92
10	4	Solvent free	6	93
11	3	Solvent free	4	93
12	2	Solvent free	4	95
13	1	Solvent free	4	96

[a]Reaction conditions: Benzaldehyde **1a** (1 mmol), o-phenylene diamine **2a** (1 mmol), room temperature. [b]Time reported in min monitored by thin layer chromatography (TLC). [c]Isolated yield.



Scheme 1. Synthesis of compounds **3**, **4** and **5** derivatives catalyzed by $NH_3(CH_2)_6NH_3SiF_6$.

2. Synthesis of 3,4-dihydropyrimidin-2-thione and 3,4-dihydropyrimidin-2-ones/thiones 8.

To standardize the reaction conditions, a model reaction of benzaldehyde **1a**, acetylacetone **6a** and urea **7a** was initially carried out under different conditions in the presence of catalytic amount of $NH_3(CH_2)_6NH_3SiF_6$ (Scheme 2, Table 3).

Table 2. $NH_3(CH_2)_6NH_3SiF_6$ catalyzed synthesis of benzimidazole, benzothiazoles and benzoxazoles[a].

Product	R	X	Time[b] (min)	Yield[a](%)
3a	H	NH	4	96
3b	4-Cl	NH	4	94
3c	4-Me	NH	6	92
3d	4-NO_2	NH	2	98
4a	H	O	7	98
4b	4-Cl	O	5	95
4c	4-Me	O	7	98
4d	4-NO_2	O	5	96
4e	2-OH	O	2	99
5a	H	S	6	93
5b	4-Cl	S	6	90
5c	4-Me	S	5	90
5d	4-NO_2	S	7	97

[a]Isolated yields. [b]Time reported in min monitored by TLC.

Table 3. Optimization of catalyst amount and solvent in the synthesis of pyrimidine-2-one **8a**[a].

Entry	Catalyst (mol%)	Solvent (1 mL)	Time[b] (min)	Yield (%)[c]
1	without	EtOH	45	39
2	4	MeOH	10	84
3	4	Butanol	33	67
4	4	Isoprop	11	64
5	4	CH_3CN	14	54
6	4	THF	26	45
7	4	AcOEt	24	45
8	4	EtOH	7	91
9	3	EtOH	7	92
10	2	EtOH	7	95
12	1	EtOH	7	94

[a]Reaction conditions:: benzaldehyde **1a** (1 mmol), acetoacetate **6a** (1 mmol) and urea **7a** (1.5 mmol), $NH_3(CH_2)_6NH_3SiF_6$, 1mL solvent, at 40°C. [b]Time reported in min monitored by thin layer chromatography (TLC). [c]Isolated yield

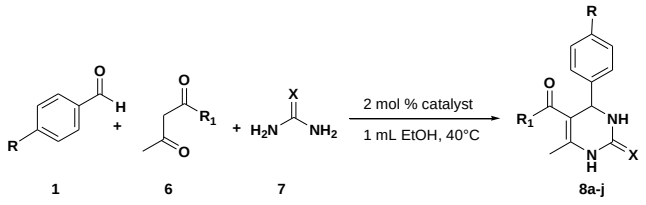
It was found that only a 39% amount of product **8a** was obtained in the absence of catalyst even after 45 min (Table 3, entry 1). It

was found that the best condition is using 2 mol % of the catalyst under EtOH at 40°C (Table 3, entry 10).

A general method has now been developed for the synthesis of 3,4-dihydropyrimidin-2-thione and 3,4-dihydro pyrimidin-2-one **8a-j** catalyzed by $NH_3(CH_2)_6NH_3SiF_6$ as a heterogeneous catalyst (Scheme 2), the obtained results are summarized in Table 4. In all the cases the corresponding 3,4-dihydropyrimidin-2-thione and 3,4-dihydro pyrimidin-2-one **8a-j** were obtained in good to excellent yield (90-99%) after 2-50 min.

3. Synthesis of quinoxalines 10.

Initially, the condensation of o-phenylene diamine **2a** with benzile **9** was used as model reaction (Scheme 3). We investigated the effect of various solvents (EtOH, MeOH and water) and catalyst amounts (1-5 mol %) at room temperature for optimization the conditions (Table 5).



Scheme 2. Synthesis of 3,4-dihydropyrimidin-2-one/ thione **8a-j** catalyzed by $NH_3(CH_2)_6NH_3SiF_6$.

It was found that only 47% yield of product **10a** was obtained when grinding for 10 minutes in the absence of any catalyst (Table 5, entry 1). The best result was achieved by carrying out the condensation in the presence of 1 mol% (2.60 mg) of $NH_3(CH_2)_6NH_3SiF_6$ in 1 mL methanol (Table 5, entry 10).

Table 4. Synthesis of 3,4-dihydropyrimidin-2-thione and 3,4-dihydropyrimidin-2-one **8a-h** catalyzed by $NH_3(CH_2)_6NH_3SiF_6$.

Product	R	R_1	X	Time[b] (min)	Yield[a] %
8a	H	Me	O	7	95
8b	H	OEt	O	45	90
8c	Cl	OEt	O	45	91
8d	Cl	OEt	S	50	90
8e	NO_2	OEt	O	12	99
8f	MeO	OEt	O	30	98
8g	MeO	OEt	S	15	95
8h	$N(Me)_2$	OEt	O	2	92

[a]Isolated yields. [b]Time reported in min monitored by TLC.

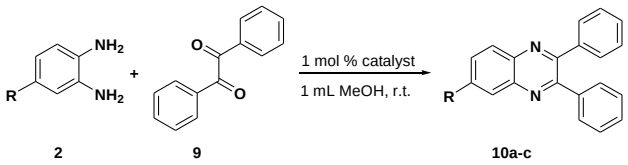
Table 5. Optimization of the reaction conditions for the synthesis of 2,3-diphenylquinoxaline **10a**.[a]

Entry	Catalyst (mol%)	Solvent (1 mL)	Time[b] (min)	Yield (%)[c]
1	-	EtOH	10	47
2	5	EtOH	3	87
3	5	H_2O	11	43
4	5	MeOH	2	90
5	4	MeOH	2	92
6	3	MeOH	2	93
7	2	MeOH	2	93
8	1	MeOH	2	93

[a]Reaction conditions: o-phenylenediamine **2a** (1 mmol) and benzile **9** (1 mmol), room temperature. [b]Time reported in min monitored by thin layer chromatography (TLC). [c]Isolated yield.

To examine the generality of this methodology, various 1,2-diamine derivatives **2** were reacted with benzile **9** (Scheme 3). As evident from the table, most of the examined

substrates provide good to excellent yields of compounds **10a-c** in shorter times (Table 6).



Scheme 3. Reaction of benzile with 1,2-diamine catalyzed by $NH_3(CH_2)_6NH_3SiF_6$.

All prepared products are known compounds [16,34-40] and were identified by comparing their ^1H NMR and ^{13}C NMR data with authentic samples reported in the literature.

The recycling of the catalyst was also studied. For this, the catalyst was filtered, separated, washed with methanol and dried at 80°C for 45 min and then the residual catalyst as such was reused without loss of any significant catalytic activity. The structure and aspect of the catalyst remains unchanged after recovery and reuse. We observed that the recovered catalyst could be used for six successive runs with a slight decrease in activity as indicated in Table 7. The reusability of the catalyst was also investigated on the models reactions for the synthesis of compounds **3a**, **8a** and **10a**.

Table 6. Condensation of 1,2-phenylenediamine **2** with benzile **9** catalyzed by NH_3 $(CH_2)_6NH_3SiF_6$ in MeOH at room temperature.

Product	R	Time[b] (min)	Yield[a] %
10a	H	2	93
10b	Me	3	94
10c	NO_2	7	99

[a]Isolated yields. [b]Time reported in min monitored by TLC.

Table 7. Recycling of $NH_3(CH_2)_6NH_3SiF_6$ in the synthesis of the compounds **3a**, **8a** and **10a**

Run	**3a**		**8a**		**10a**	
	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]
1	4	96	7	95	2	93
2	4	96	7	95	2	93
3	4	94	7	94	2	91
4	4	90	7	92	2	90
5	4	90	7	90	2	90
6	4	90	7	90	2	89

[a]Isolated yield.

In order to compare the efficiency of our catalyst with respect to the other catalysts [9-12,18,22-26,41-42] reported for the synthesis of benzimidazole, benzothiazole, benzoxazole, 3,4-dihydro pyrimidin-2-thione, 3,4-dihydro pyrimidin-2-one and quinoxaline, the results are tabulated in Table 8. As it is clear from Table 8, $NH_3(CH_2)_6NH_3SiF_6$ has remarkably improved the synthesis of these compounds in different terms (reaction time, yield and amount of catalyst).

Conclusions

In conclusion, we have developed an highly yield, environmentally friendly and mild condition protocol for the synthesis of medicinally important heterocycles such as the quinoxalines, benzimidazoles, benzoxazoles, benzothiazoles and 3,4-dihydropyrimidin-2-ones/thiones catalyzed by hybrid crystal $NH_3(CH_2)_6NH_3SiF_6$ under solvent-free or ecological solvent conditions. To our delight, $NH_3(CH_2)_6NH_3SiF_6$ catalyzed reactions not only required shorter reaction times but also provided

the desired products in good to excellent yields with low catalyst loading.

Table 8. Comparison of $NH_3(CH_2)_6NH_3SiF_6$ with the reported catalysts for the synthesis of these compounds.

Catalyst [Ref.]	Conditions	Time (min)	Yield %
$NH_3(CH_2)_6NH_3SiF_6$	1 mol% solvent free, rt	2-7	90-99
CuO-np/SiO_2 [41]	10 mol %, 10 mL, MeOH, rt	240-840	68–93
ZnO PNs [34]	5 mg; solvent free, or in EtOH, rt	2-8	90–99
CeO_2 NPs [42]	10 mol%, H_2O, rt	20-40	58–97
$NH_3(CH_2)_6NH_3SiF_6$	2 mol%, 1 mL EtOH, 100 °C	2-50	90-99
$[Et_3N–SO_3H]HSO_4$ [22]	(0.014g, 0.05 mmol), solvent free, 70 °C	15-100	86-98
Calix[8]arene sulfonic acid [23]	0.2 mol%, 3 mL EtOH, reflux	20-48	67-93
Sulfated polyborte [24]	5wt%, solvent free, 100°C	20-45	83-94
Nano $YAl_2O_3:Eu^{3+}$ [25]	2.5 mmol, 5 mL EtOH, 80°C	110	71-92
Fe_3O_4/SiO_2-NH-ligand -Bi(III) nano catalyst [26]	0.05g, solvent free, 100 °C	30	70-95
$NH_3(CH_2)_6NH_3SiF_6$	1 mol%, 1 mL MeOH, rt	2-7	93-99
Fe_3O_4@SiO_2-imid-PMA magnetic porous nanosphere [9]	0.03 g, 0.5 mol%, 5 mL EtOH, rt	5-25	89-95
ZrO_2-Al_2O_3 [10]	0.03g, 10 mL EtOH, 80°C	20	90-91
Co NPs [11]	1 mol%, 5 mL EtOH, rt	90	88-98
RHA-SO_3H [12]	15 mg, solvent free, rt	5-30	90-98

Experimental part

Materials

All the chemicals used were purchased from Sigma-Aldrich and were used as such. All products are known, and were identified by comparison of spectral and physical data with the literature. Melting points were measured with a Buchi melting-point apparatus and are uncorrected. ^1H NMR (300 MHz) and ^{13}C NMR(75 MHz) spectra were recorded on a Brucker spectrometer in DMSO-d_6.

***General procedure for the synthesis of catalyst*:** The catalyst single crystal has been recently synthesized by slow evaporation of aqueous solution containing NH_2-$(CH_2)_6NH_2$ and H_2SiF_6 by the following method: the solid hexane-1,6-diamine $NH_2(CH_2)_6NH_2$ (percentage $\geq$ 99%) was primarily dissolved in the necessary distilled water and then was mixed with the stoichiometric amounts (1:1) to H_2SiF_6 (percentage = 34% in weight).

The obtained solution was taken under room temperature for evaporation. The colorless single crystals were so obtained (Yield 85%).

***General procedure for the preparation of benzimidazoles 3, benzoxazoles 4 and benzothiazoles 5*:** Aldehyde (1 mmol), o-phenyl enediamine, o-amino thiophenol or o-amino phenol (1 mmol) and 1 mol % (2.60 mg) of $NH_3(CH_2)_6NH_3SiF_6$ were stirred, in free solvent conditions, at room temperature for the appropriate time (Table 3). The progress of the reaction was monitored by TLC hexane/ethyl

acetate (70:30) as eluent. After completion of the reaction, the crude reaction mixture was dissolved in EtOH, and the catalyst was separated out by simple filtration. The product was recrystallized from ethanol to give respectively benzimidazoles **3**, benzoxazoles **4** and benzothiazoles **5** in high yields (90–98%, Table 3).

2-phenyl-1H-benzimidazole **3a**. Yield 98%. M.p.: 291-292 ^{o}C (Lit.[16] 292-294 ^{o}C). ^{1}H NMR δ 12.93 (s, 1H, NH); 7.17-8.18 (m, 9H, ArH). ^{13}C NMR δ 151.7; 144.3; 135.5; 130.6; 130.3; 129.4; 126.9; 123.0; 122.2; 119.3; 111.8.

2-(4-chlorophenyl)-1H-benzimidazole **3b** Yield 97%. M.p.: 287-289 ^{o}C (Lit.[16] 288-290 ^{o}C). ^{1}H NMR δ 12.99 (s, 1H, NH); 7.19-8.18 (m, 8H, ArH). ^{13}C NMR δ 150.6; 135.0; 131.2; 129.5; 129.4; 129.3; 128.8; 128.6; 123.3; 119.4; 111.9.

2-(p-tolyl)-1H-benzimidazole **3c**. Yield 95%. M.p.: 276-278 ^{o}C (Lit.[16] 275-276 ^{o}C). ^{1}H NMR δ 12.80 (s, 1H, NH), 7.15-8.06 (m, 8H, ArH); 2.35 (s. 3H. CH_3). ^{13}C NMR δ 151.9; 140.1; 129.9; 129.8; 129.5; 127.9; 126.8; 126.4; 122.8; 119.1; 111.6; 21.4.

2-(4-nitrophenyl)-1H-benzimidazole **3d**. Yield 99%. M.p.: 317-319 ^{o}C (Lit.[16] 318-320 ^{o}C). ^{1}H NMR δ 8.81 (s, 1H, NH); 6.52-8.40 (m, 8H, ArH). ^{13}C NMR δ 153.9; 148.8; 145.4; 142.8; 134.4; 129.9; 129.3; 127.9; 124.3; 117.5; 115.5.

2-phenyl benzoxazole (**4a**). Yield 98%. M.p.:100-102^{o}C (Lit.[34] 100-102 ^{o}C). ^{1}H NMR δ 6.79-8.03 (m, 9H, ArH). ^{13}C NMR δ 159.8; 151.6; 138.4; 136.8; 131.7; 129.9; 129.6; 129.3; 127.8; 119.9; 116.4.

2-(4-chlorophenyl) benzoxazole **4b**. Yield 97%. M.p.: 144-145 ^{o}C (Lit.[34] 144-146 ^{o}C). ^{1}H NMR δ 6.78-8.05 (m, 8H, ArH). ^{13}C NMR δ 158.3; 151.8; 137.9; 136.2; 135.7; 130.9; 129.2; 129.1; 128.1; 119.5; 116.9.

2-(p-tolyl) benzoxazole **4c**. Yield 96%. M.p.: 88-90 ^{o}C (Lit.[34] 88-89 ^{o}C). ^{1}H NMR δ 6.79-7.56 (m, 8H, ArH); 2.33 (s, 3H, CH_3). ^{13}C NMR δ 159.5; 151.6; 138.4; 134.4; 134.3; 130.2; 129.7; 129.3; 127.6; 119.9; 116.9; 21.6.

2-(4-nitrophenyl) benzoxazole **4d**. Yield 99%. M.p.: 261-262 ^{o}C (Lit.[16] 262-264 ^{o}C). ^{1}H NMR δ 6.81-8.34 (m, 8H, ArH). ^{13}C NMR δ 157.5; 152.2; 149.1; 142.5; 137.4; 130.2; 129.0; 127.3; 124.3; 119.8; 116.8.

2-(4-hydroxyphenyl) benzoxazole **4e**. Yield 98%. M.p.: 220-221 ^{o}C (Lit.[34] 220-223 ^{o}C). ^{1}H NMR δ 13.78 (s, 1H, OH); 6.83-7.60 (m, 8H, ArH). ^{13}C NMR δ 162.1; 151.6; 135.4; 133.3; 132.8; 130.5; 129.7; 129.1; 128.5; 124.5; 119.2; 116.9.

2-phenyl benzothiazole **5a**. Yield 97%. M.p.: 111-113 ^{o}C (Lit.[16] 110-114 ^{o}C). ^{1}H NMR δ 7.42-8.08 (m, 9H, ArH). ^{13}C NMR δ 167.8; 154.0; 134.9; 133.3; 131.9; 129.9; 127.7; 126.0; 123.4; 122.2; 114.7.

2-(4-chlorophenyl) benzothiazole **5b**. Yield 94%. M.p.: 114-116 ^{o}C (Lit.[16] 114-116 ^{o}C). ^{1}H NMR δ 7.29-8.11 (m, 8H, ArH). ^{13}C

NMR δ 166.4; 153.9; 136.5; 132.1; 129.9; 128.7; 127.3; 126.2; 123.4; 122.9, 114.6.

2-(p-tolyl) benzothiazole **5c**. Yield 90%. M.p.: 85-87 ^{o}C (Lit.[34] 86-89 ^{o}C). ^{1}H NMR δ 7.29-8.06 (m, 8H, ArH); 2.33 (s, 3H, CH_3). ^{13}C NMR δ 167.8; 154.1; 141.9; 134.8; 130.7; 130.3; 127.5; 127.0; 125.8; 123.1; 114.8; 21.4.

2-(4-nitrophenyl) benzothiazole **5d**. Yield 99%. M.p.: 226-227 ^{o}C (Lit.[16] 227-229 ^{o}C). ^{1}H NMR δ 6.51-8.21 (m, 8H, ArH). ^{13}C NMR δ 159.4; 149.7; 148.3; 141.7; 132.2; 130.3; 128.8; 127.6; 124.9; 122.9; 115.1.

***Typical experimental procedure for the preparation of 3,4-dihydropyrimidin-2(1H)-ones/thiones* 8:** A mixture of thiourea or urea (1.5 mmol), aldehyde (1 mmol), β-ketoester (1 mmol) and 2 mol % (5.20 mg) of $NH_3(CH_2)_6NH_3SiF_6$ in ethanol (1 ml) was stirred at 100°C for a specified time (Table 6) . The progress of the reaction was monitored by thin layer chromatography (TLC). The resulted reaction mixture was cooled to room temperature, diluted with ethanol (2 x 10 mL) and stirred for 5 min. Then, the catalyst was separated by simple filtration, the solvent was evaporated and recrystallized from ethanol to afford pure 3,4-dihydropyrimidin-2(1H)-ones/thiones **8** as yellow/white solids. The catalyst from filtrate was recovered by the procedure mentioned below.

5-acetyl-6-methyl-4-phenyl-3,4 dihydro pyrimidin-2(1H)-one **8a**. Yield 95%. M.p.: 237-239°C (lit.[38] 238-239°C). ^{1}H NMR δ 9.16 (s, 1H, NH); 7.71 (s, 1H, NH); 7.20-7.30 (m, 5H, ArH); 5.12 (d, 1H, *J* = 3 Hz, CH); 2.22 (s, 3H, CH_3). ^{13}C NMR δ 165.0; 152.6; 148.8; 145.5; 129.0; 127.7; 126.8; 99.7; 54.4; 30.7; 19.5.

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8b**. Yield 90%. M.p.: 208-210°C (lit.[36] 207-208°C). ^{1}H NMR δ 9.16 (s, 1H, NH); 7.71 (s, 1H, NH); 7.21-7.32 (m, 5H, ArH); 5.12 (s, 1H, CH); 3.97 (q, 2H, OCH_2); 2.22 (s, 3H, CH_3); 1.1 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 165.8; 152.6; 145.4; 129.0; 128.8; 127.7; 126.8; 99.7; 59.6; 54.4; 17.6; 14.5.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo 1,2,3,4-tetrahydropyrimidine-5-carboxylate **8c**. Yield 91%. M.p.: 212-214°C (lit.[35] 212-214°C). ^{1}H NMR δ 9.28 (s, 1H, NH); 7.73 (s, 1H, NH); 7.09-7.55 (m, 4H, ArH); 5.57 (s, 1H, CH); 3.89 (q, 2H, OCH_2); 2.27 (s, 3H, CH_3); 0.98 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 151.6; 150.0; 141.4; 133.1; 130.7; 129.2; 128.4; 97.9; 59.6; 51.6; 18.1; 14.3.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-thio -xo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8d**. Yield 90%. M.p.: 186-188°C (lit.[37] 186-188°C). ^{1}H NMR δ 9.22 (s, 1H, NH); 7.75 (s, 1H, NH); 7.21-7.38 (m, 4H, ArH); 5.12 (s, 1H, CH); 3.97 (q, 2H, OCH_2); 2.22 (s, 3H, CH_3); 1.07 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 165.7; 152.4; 149.2; 144.2; 132.0; 128.8; 128.6; 99.3; 59.7; 53.8; 18.2; 14.5.

Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8e**.

Yield 99%. M.p.: 210-212°C (lit.[35] 211-212°C). ^{1}H NMR δ 9.32 (s, 1H, NH); 7.86 (s, 1H, NH); 7.47-7.56 (m, 4H, ArH); 5.26 (s, 1H, CH); 3.97 (q, 2H, OCH_2); 2.24 (s, 3H, CH_3); 1.09 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 165.5; 158.1; 152.4; 149.8; 139.5; 130.7; 124.3; 98.6; 59.9; 54.1; 18.3; 14.5.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8f** Yield 98%. M.p.: 200-202°C (lit.[39] 200-202°C). ^{1}H NMR δ 9.10 (s, 1H, NH); 7.64 (s, 1H, NH); 6.83-7.13 (m, 4H, ArH); 5.07 (s, 1H, CH); 3.96 (q, 2H, OCH_2); 3.69 (s, 3H, OCH_3); 2.21 (s, 3H, CH_3); 1.07 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 165.9; 158.9; 152.6; 148.4; 137.5; 127.8; 114.2; 100.1; 59.6; 55.5; 53.8; 18.2; 14.5.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8g** Yield 95%. M.p.: 153-155°C (lit.[39] 153°C). ^{1}H NMR δ 9.11 (s, 1H, NH); 7.63 (s, 1H, NH); 6.83-7.13 (m, 4H, ArH); 5.07 (s, 1H, CH); 3.96 (q, 2H, OCH_2); 3.69 (s, 3H, OCH_3); 2.21 (s, 3H, CH_3); 1.1 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 165.8; 158.9; 152.6; 148.4; 137.5; 127.9; 114.2; 100.1; 59.6; 55.5; 53.8; 18.2; 14.5.

Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **8h**. Yield 92%. M.p.: 228-230°C (lit.[39] 228-230°C). ^{1}H NMR δ 9.05 (s, 1H, NH); 7.68 (s, 1H, NH); 6.61-7.56 (m, 4H, ArH); 5.01 (s, 1H, CH); 3.97 (q, 2H, OCH_2); 3.02 (s, 3H, NCH_3); 3.02 (s, 3H, NCH_3); 2.20 (s, 3H, CH_3); 1.11 (t, 3H, $OCH_2\underline{CH_3}$). ^{13}C NMR δ 190.3; 165.9; 152.7; 150.2; 147.9; 133.1; 127.3; 112.7; 111.5; 100.4; 59.6; 53.7; 18.2; 14.6.

***General procedure for the preparation of quinoxalines* 10:** Aldehyde (1 mmol), o-phenylenediamine (1 mmol) and 1 mol % (2.60 mg) of NH_3 $(CH_2)_6NH_3SiF_6$ were stirred in methanol (1 ml), at room temperature for the appropriate time (Table 8). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the crude reaction mixture was dissolved in ethyl acetate and the catalyst was separated out by simple filtration. The quinoxalines **10** were recrystallized from ethanol.

2,3-diphenylquinoxaline **10a.** Yield 93%. M.p.: 126-128°C (lit.[40] 126-127°C). ^{1}H NMR δ 7.32-7.37 (m, 6H); 7.43-7.46 (m, 4H); 7.83-7.86 (m, 2H); 8.11-8.14 (m, 2H). ^{13}C NMR δ 153.5; 140.9; 139.2; 132.0; 130.9; 130.2; 129.2; 128.5.

6-methyl-2,3-diphenylquinoxaline **10b**. Yield 94%. M.p.: 122-124°C (lit.[40] 120-122°C). ^{1}H NMR δ 2.47 (s, 3H); 7.28-7.44 (m, 5H); 7.44-7.66 (m, 4H); 7.66-7.69 (m, 2H); 7.90-7.99 (m, 2H). ^{13}C NMR δ 153.3; 141.0; 139.3; 133.0; 130.1; 129.1; 128.8;127.9; 21.8.

6-nitro-2,3-diphenylquinoxaline **10c**. Yield 99%. M.p.: 140-142 °C (lit.[40] 140-142 °C). ^{1}H NMR δ 7.32-7.49 (m, 5H); 8.29-8.32 (m, 4H); 8.48-8.52 (m, 2H); 8.85-8.86 (m, 2H).

^{13}C NMR δ 156.5; 143.4; 139.6; 138.4; 136.0; 131.2; 130.2; 129.9; 125.3.

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