Hybrid crystal NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ as an efficient catalyst for the synthesis of benzoxazoles, benzimidazoles and benzothiazoles under solvent-free conditions

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ABSTRACT
An easy synthetic protocol for the synthesis of biologically active benzimidazole, benzothiazole and benzoxazole derivatives has been demonstrated using a hybrid crystal NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ as a mild and efficient heterogeneous catalyst. Short reaction times, solvent-free conditions, good to excellent yields, easy reusability and use of an eco-friendly catalyst are some of the significant attributes of the present method.

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Introduction
The benzimidazole, benzoazole and benzothiazole skeletons may be found in numerous pharmaceutical agents with a diverse spectrum of biological properties (1–4). They are considered as privileged structures in the medicinal chemistry field (5) and are found in a large variety of natural products. They have been used as antiviral (6), anti-microbial (7), anti-tumor (8), anti-inflammatory (9), anti-convulsant (10), anti-ulcer (11), antihelminthic (12a), anti-hypertensive (12b) and anti-analgesic (12c) agents. Moreover, their application in the field of advanced materials is worthy of note (13). The protocols usually followed for their synthesis involve condensation of ortho-esters (14–15), nitriles (16), aldehydes (17–18), carboxylic acids (19), amides (20) and esters (21) with ortho-substituted aminoaromatic, in the presence of different acids or catalysts such as Pd-catalyzed oxidative cyclization (22), base-assisted reaction of 1,1-dibromoethanes (23), different hetero-polyacid catalysts (24), In(OTf)$_3$ (25), Cu-np/SiO$_2$ (26), iron phthalocyanine (27), nanoCeO$_2$ (28), nanosolid acids (29), CuFe$_2$O$_4$ (30), Fe(NO$_3$)$_3$/Tempo (31), RHA-SO$_3$H (32) and Fe(III)-Schiff base/SBA-15 (33). Therefore, there is a strong demand for a more effective, simple and environmentally friendly process for the synthesis of these heterocycles.

In order to develop such processes, it was used in the present synthetic protocols, the butane-1,4-diammonium hexafluorosilicate NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ as a solid catalyst; that is a novel hybrid compound (34) that belongs to the family of alkylenediammonium halogenometalate salts of the general formula NH$_3$(CH$_2$)$_n$NH$_3$MX$_6$ (IV) (M: Sn, Te; X: Cl, Br, I and F) that have recently attracted considerable attention due to their important chemical and physical properties (35–38). Generally, the hexafluorosilicate NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ salts were less studied in comparison with other hexahalogenometalate salts of the general formula NH$_3$(CH$_2$)$_n$NH$_3$MX$_6$ (IV) (M: Sn, Te; X: Cl, Br, I) (38–42). But, the monoalkylammonium hexafluorosilicate compounds have extensively been studied and some of them have been found to be of interest for the study of crystal dynamic and phase transition involving hydrogen bonds as well as the reorientation motions of alkylammoniums cations (39–42). The synthesis of complex NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ is a practical way
to produce heterogeneous catalyst with the associated advantages such as easy catalyst separation, possible recycling, high activity and selectivity.

In the present study, we report the synthesis of benzimidazole, benzoxazole and benzothiazole derivatives by condensation of 1,2-phenylenediamine, ortho-aminophenol and ortho-aminothiophenol with various aromatic aldehydes using NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ as an efficient catalyst in free solvent conditions.

**Results and discussion**

The NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ crystal has been recently synthesized and characterized by X-ray diffraction (34). The crystal structure of this compound has been determined in the triclinic system with $P$1 ($Z = 1$) as space group and $a = 5.796$ (1) Å, $b = 5.889$ (1) Å, $c = 7.774$ (2) Å and $α = 87.02$ (1)$°$, $β = 82.15$ (1)$°$ and $γ = 61.87$ (1)$°$, $V = 231.79$ (8) Å$^3$ as parameters of the crystal unit cell.

The molecular structure of the NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ compound is given in Figure 1. The crystal structure of this little compound has been found to be built up from inorganic anions SiF$_2^{-}$ linked to the organic cations $^{+}$NH$_3$(CH$_2$)$_4$NH$_3$ through N–H…F hydrogen bonds producing an infinite two-dimensional layer parallel to (0 1 1) (Figure 2).

The intermolecular hydrogen bonding contacts N–H…F types provide a linkage between cationic entities $^{+}$NH$_3$(CH$_2$)$_4$NH$_3$ and SiF$_2^{-}$ anionic complexes. The hydrogen bonds involved (donors and acceptors) ensure the three-dimensional cohesion of the atomic arrangement. The unit cell of the NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ compound contains only one organic cation $^{+}$NH$_3$(CH$_2$)$_4$NH$_3$ and one slightly distorted SiF$_2^{-}$ anion. In this structure, all

**Figure 1.** The molecular structure of the NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ compound with the atom-labeling scheme as has been determined. The symmetry codes are: (i) $-x+1$, $-y+1$, $-z+1$; (ii) $x+1$, $-y$, $-z$.

**Figure 2.** The three-dimensional plot of the NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ compound, showing inorganic sheets linked through N–H…F hydrogen bonds to the organic layers (dashed lines) (34).
atoms have been found to be in general positions, except the silicon atom Si which has been located at a crystallographic center of inversion (1/2, 0, 0) of the $P1$ space group. The silicon atom was surrounded by six fluorine atoms building a slightly distorted SiF$_2$ octahedron. In addition, the center of the bond C$_2$–C$_2$ (i) [with (i) being a symmetry code: $-x+1$, $-y+1$, $-z+1$] was also situated on another crystallographic center of inversion.

Working on a series of new alkylenediammonium halogenometallate compounds, we found it interesting to study the efficiency of the hybrid compound NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ as heterogeneous solid catalysts for the preparation of benzoxazoles, benzothiazoles and benzimidazoles. At first, 1,2-phenylenediamine 1a and benzaldehyde 2a were selected as the model substrates to investigate the best reaction conditions (Scheme 1). Then several reaction conditions were tried to accomplish this reaction and the efficiency of the reaction was found to be influenced by the quantity of the catalyst and solvent at room temperature. In the absence of a catalyst, only 12% yield of the desired product was obtained even after longer reaction time (Table 1, entry 1). However, in the presence of the catalyst the product 3a was obtained in 93% yield and only after 14 min (Table 1, entry 2). Next, the optimization of reaction conditions was undertaken to increase the yield of the product using various solvents, which showed a prominent influence on reaction time and yields to obtain the desired product (Table 1, entries 3–8). It was also found that the reaction proceeded efficiently without solvent and resulted in high yields of the desired product (Table 1, entries 9–13). Furthermore, the catalytic efficiency of NH$_3$(CH$_2$)$_4$NH$_3$SiF$_6$ was examined using different amounts of this catalyst. Interestingly, the yield of 3a was significantly increased to 98% by employing 1 mol% of the catalyst, without solvent, at room temperature (Table 1, entry 13). The opportunity of applying solvent-free conditions is an environmentally significant benefit of the procedure.

The generality of the procedure was evaluated for the synthesis of benzimidazole 3, benzoxazole 4 and benzothiazole 5 derivatives by condensation of different 1,2-phenylene diamine, 1,2-aminophenol and 1,2-aminothiophenol with substituted aldehydes (Scheme 2). As shown in Table 2, good to excellent yields were obtained for these reactions. The reactivity of 1 with

| Entry | Catalyst (mol%) | Solvent (1 mL) | Time (min) | Yield (%) |
|-------|----------------|----------------|------------|-----------|
| 1     |               | EtOH           | 240        | 12        |
| 2     | 5             | EtOH           | 14         | 93        |
| 3     | 5             | MeOH           | 10         | 93        |
| 4     | 5             | Butanol        | 23         | 80        |
| 5     | 5             | Isopropanol    | 30         | 77        |
| 6     | 5             | CH$_2$CN       | 40         | 67        |
| 7     | 5             | THF            | 25         | 69        |
| 8     | 5             | ACOEt          | 15         | 79        |
| 9     | 5             | Solvent free   | 4          | 94        |
| 10    | 4             | Solvent free   | 4          | 94        |
| 11    | 3             | Solvent free   | 4          | 95        |
| 12    | 2             | Solvent free   | 4          | 95        |
| 13    | 1             | Solvent free   | 4          | 98        |

*Reaction conditions: benzaldehyde (1a, 1 mmol), o-phenylenediamine (2a, 1 mmol), room temperature.

*Time reported in min monitored by thin layer chromatography (TLC).

Table 2. Substrate scope for synthesis of desired heterocycles derivatives.

| Product | R | X | Time min$^a$ | Yield %$^b$ | Melting point (°C) |
|---------|---|---|--------------|-------------|--------------------|
| 3a      | H | NH| 4            | 98          | >266 – 292–294     |
| 3b      | Cl| NH| 2            | 97          | >266 – 288–290     |
| 3c      | Me| NH| 6            | 95          | >266 – 275–276     |
| 3d      | NO$_2$| NH| 2            | 99          | >266 – 318–320     |
| 4a      | H | S | 4            | 97          | 112–113 – 110–114  |
| 4b      | Cl| S | 5            | 94          | 114–116 – 114–116  |
| 4c      | Me| S | 5            | 99          | 226–227 – 227–229  |
| 4d      | NO$_2$| S | 5            | 99          | 100–102 – 100–102  |
| 5a      | H | O | 5            | 98          | 144–145 – 144–146  |
| 5b      | Cl| O | 3            | 97          | 88–90 – 88–89      |
| 5c      | Me| O | 6            | 96          | 89–90 – 88–89      |
| 5d      | NO$_2$| O | 5            | 99          | 261–262 – 262–264  |
| 5e      | OH| O | 2            | 98          | 220–221 – 220–223  |

*Isolated yields.

*Time reported in min monitored by TLC.

Table 3. Reusability of the catalyst in the synthesis of 2-phenyl benzimidazole 3a.

| Run | Time (min) | Yield (%)$^a$ |
|-----|------------|--------------|
| 1   | 4          | 98           |
| 2   | 4          | 97           |
| 3   | 4          | 97           |
| 4   | 4          | 96           |
| 5   | 4          | 95           |
| 6   | 4          | 95           |

*Isolated yields.
aldehyde derivatives 2 appear to be not controlled by
electronic effects. Indeed, the reaction with both elec-
tron-rich and electron-deficient aldehydes is good and
affording benzimidazole 3, benzoazole 4 and benzo-
azole 5 in high yields (Scheme 2). The prepared products
are known compounds and were confirmed by comparing
the \(^1\text{H}\) NMR and \(^13\text{C}\) NMR spectral data with authentic
samples reported in the literature (33, 43).

The recycling of the catalyst was also studied. For this,
the catalyst was filtered, separated, washed with metha-
nol and dried at 80°C for 45 min and then the residual
catalyst as such was reused without loss of any signifi-
cant catalytic activity. The structure and aspect of the cat-
alyst remains unchanged after recovery and reuse. In
the case of the model reaction, the catalyst was recovered
and reused six times without any significant changes in
the yield and the reaction time (Table 3).

In order to compare the capability and efficiency of our
catalyst with respect to the previously reported cat-
alysts in the literature (26, 29, 33, 43–44), the results for
the synthesis of benzimidazoles, benzoazoles and
benzoxazoles employing these catalysts are tabulated
in Table 4. As it is clear from the Table, \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{SiF}_6\)
is more efficient than the others.

### Conclusion

In conclusion, an efficient and mild one-pot protocol for
the synthesis of benzimidazoles, benzoazoles and ben-
zoazoles using a crystal \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{SiF}_6\) as a catalyst in
free solvent has been developed. The use of the crystal as
reusable heterogeneous catalyst, solvent-free conditions,
excellent product yields and shorter reaction time make
this protocol practical and environment-friendly. In
addition, the preliminary toxicity evaluation has showed
that the catalyst is non-toxic at low concentration levels.
The study on the exact mechanism of \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{SiF}_6\)
applicable to the preparation of these heterocycle deriva-
tives is underway in our laboratory.

### Experimental

#### Chemicals and apparatus

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 taken on a KOFLER hot stage apparatus and are
uncorrected. \(^1\text{H}\) NMR and \(^13\text{C}\) NMR spectra were
recorded on a Brucker 300-MHz 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 \(\text{NH}_2-
(\text{CH}_2)_4\text{NH}_2\) and \(\text{H}_2\text{SiF}_6\) by the following method: the solid
butane-1,4-diamine \(\text{NH}_2(\text{CH}_2)_4\text{NH}_2\) (percentage ≥99%)
was primarily dissolved in the necessary distilled water
and then was mixed with the stoichiometric amounts
(1:1) to \(\text{H}_2\text{SiF}_6\) (percentage = 34% in weight). The
obtained solution was taken under room temperature
for evaporation. The colorless single crystals were so
obtained

#### General procedure for the preparation of
benzimidazoles, benzoazoles and
benzoxazoles

Aldehyde (1 mmol), o-phenylenediamine, o-amino thio-
phenol or o-amino phenol (1 mmol) and 1 mol %
(2.32 mg) of \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{SiF}_6\) were stirred, in free
solvent conditions, at room temperature for the appro-
piate time (Table 2). The progress of the reaction was
monitored by TLC hexane/ethyl acetate (70:30) as
eluent. After completion of the reaction, the crude reac-
tion mixture was dissolved in EtOH, and the catalyst was
separated out by simple filtration. The product was
recrystallized from ethanol to give respectively

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### Table 4. Comparative synthesis of desired heterocycles using the reported catalysts versus \(\text{NH}_3(\text{CH}_2)_4\text{NH}_3\text{SiF}_6\).

| Catalyst | Amount of catalyst/reaction conditions | Time | Yield % |
|----------|----------------------------------------|------|---------|
| \(\text{FeCl}_3/\text{montmorillonite K-10}\) | 1 mol% solvent free, RT | 2–6 min | 90–99 |
| Fe(III)–Schiff base/SBA-15 (33) | 0.01 g, 0.0014 mmol (0.01 based on metal ion), water, reflux | 3 h | 79–92 |
| ZnBr\(_2\)/ABM (44b) | 100 mg, 5 mL, toluene, 111°C | 10–25 min | 83–96 |
| Indion 190 resin (44b) | 10% weight, 5 mL, EtOH, 70°C | 4 h | 78–92 |
| Nano-ZnO (29) | 10 mol%, 10 mL, EtOH, reflux | 80–100 min | 64–88 |
| CuO-np/SiO\(_2\) (26) | 10 mol %, 10 mL, MeOH, RT | 4–14 h | 68–93 |
| ZnO PNs (43) | 5 mg: solvent free, or in EtOH, RT | 2–8 min | 90–99 |
| r-Butyl hypochloride (44c) | 2 mmol, 10 mL CH\(_2\)CN, reflux | 1–4 h | 65–92 |
| AMs-ZnBr\(_2\) (44d) | Toluene, air, 110°C | 10–25 min | 81–96 |
| PIFA (44e) | 1.05 equiv, 3 mL EtOH , 800°C, μW | 15 min | 59–90 |
| Cu NPs/SiO\(_2\) (44f) | 10 mol%, methanol, RT | 4–8 h | 72–86 |
| CeO\(_2\) NPs (44g) | 10 mol%, H\(_2\)O, RT | 20–40 min | 58–97 |
| PPTA (44h) | 10 mol%, water, 70°C | 1–5 h | 60–97 |
| FeCl\(_3\)/montmorillonite K-10 (44i) | 10%w/w, CH\(_2\)OH, condensation, ultrasonic irradiation | 0.7–5 h | 33–95 |
benzimidazole 3, benzothiazole 4 and benzoazole 5 in high yields (90–99%, Table 2).

Disclosure statement
No potential conflict of interest was reported by the authors.

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