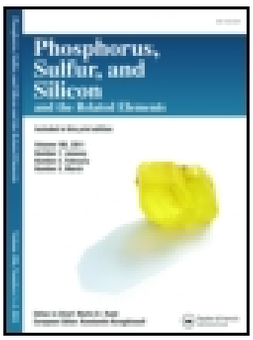

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Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

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To cite this article: Sushil R. Mathapati, Komal N. Patil, Sujit S. Mathakari, Appasaheb W. Suryawanshi & Arvind H. Jadhav (2021): Fluorinated phosphoric acid as a versatile effective catalyst for synthesis of series of benzimidazoles, benzoxazoles and benzothiazoles at room temperature, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2020.1871345

To link to this article: https://doi.org/10.1080/10426507.2020.1871345

Published online: 15 Jan 2021.

PHOSPHORUS, SULFUR, AND SILICON AND THE RELATED ELEMENTS
https://doi.org/10.1080/10426507.2020.1871345

Fluorinated phosphoric acid as a versatile effective catalyst for synthesis of series of benzimidazoles, benzoxazoles and benzothiazoles at room temperature

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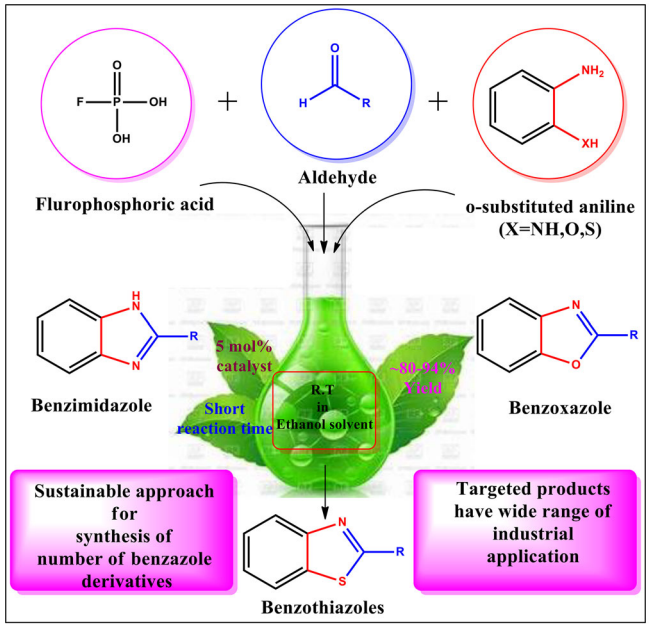
ABSTRACT

The present work describes synthesis of a series of benzimidazoles, benzoxazoles and benzothiazoles through the cyclization of 1, 2-phenylenediamine, 2-aminothiophenol, or 2-aminophenol with aryl, aliphatic and heteroaryl aldehydes. The present synthetic protocol is very much efficient in presence of 5 mol % fluorophosphoric acid as a catalyst in ethanol solvent at room temperature. Shorter reaction time, simple work-up technique, high yields and easy availability are specific compensations of the present synthetic approach.

ARTICLE HISTORY
Received 18 August 2020
Accepted 30 December 2020

KEYWORDS
Fluorophosphoric acid; cyclization; room temperature; benzimidazoles; benzoxazoles; benzothiazoles

GRAPHICAL ABSTRACT



Introduction

The use of nonmetallic acid catalysts has gained pronounced importance in the organic synthesis field. Amongst various nonmetallic acid catalysts, sulfonic acid and phosphoric acid have gained superior attraction than to achieve desired organic transformations. Phosphoric acid shows lower acidic strength compared to sulfonic acid and have always been the second choice of the researchers as a catalyst. Thus, there is a need to enhance the acidic properties of phosphoric acid. The literature suggested that introduction of electron-withdrawing moieties such as fluorine at phosphorus atom in in phosphoric acid molecule could possibly increase the acidic nature of phosphoric acid.[1]

Thus, fluorinated catalysts have gained additional attention of researchers and its applications have undergone rapid growth.[2–4] Fluorinated phosphoric acids offer enhanced properties such as higher stability, greater acidity and less nucleophilicity than the corresponding phosphoric acids. This feature makes fluorinated phosphoric acids capable of removing water from the reactive centers and thus,

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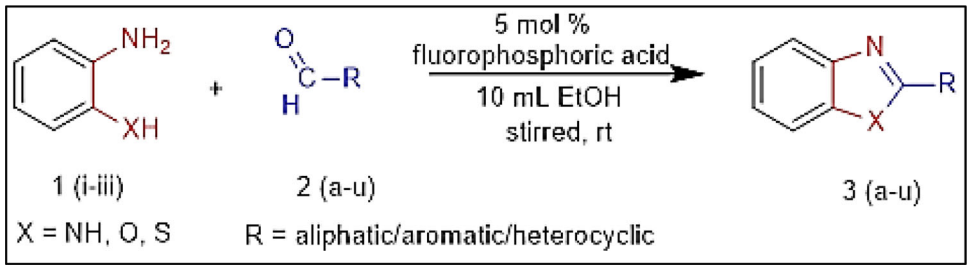


Scheme 1. Synthetic Route to the products, 3.

Table 1. Comparative study of various catalysts with respective to fluorophosphoric acid for the synthesis of benzimidazole.[a]

Entry	Catalyst	Solvent	Reaction Time[b] (h)	Yield[c] (%)
a	Catalyst free	Ethanol	48 & 14[d]	13 & 60[d]
b	Fluorophosphoric acid	Solvent free	28	16
c	Fluorophosphoric acid	Ethanol	2.2	93
d	PPA	Ethanol	10	61
e	DPA	Ethanol	8.2	63
f	Sulfamic acid	Ethanol	8	70
g	Chlorosulfonic Acid	Ethanol	6.4	35 + 53[e]
h	Phosphosulfonic acid	Ethanol	3	86

[a]**Reaction conditions:** o-Phenylenediamine (0.01 mol), benzaldehyde (0.01 mol), solvent 10 mL, 5 mol % catalyst, stir at room temperature;
[b]Monitored by TLC;
[c]Isolated yield;
[d]Reaction carried out at 60 °C;
[e]Yield of di-substituted benzimidazole by-product.

maintaining high catalytic activity.[1] Additionally, P-F bond in the fluorinated phosphoric acids offers importance in the field of pharmaceuticals.[5] The literature shows that fluorinated phosphoric acids such as fluorophosphoric acid exhibit potential applications as green and efficient catalysts for numerous organic transformations.[6–9]

Five membered heterocycles containing a C = N bond such as benzimidazole, benzoxazole and benzothiazole are important structural scaffold in natural products as well as pharmaceutical and agrochemical compounds.[10,11] These small molecules have received a significant amount of attention for their biological and therapeutic activities[12,13] such as antifungal,[14] anticancer,[15] antibiotic,[16] antiviral,[17] anti-Parkinson[18] and antimicrobial[19] activities. The reports display that these types of organic moieties may also act as a ligand and play an important role in asymmetric transformations.[20]

With regards to above context, numerous techniques are reported for the synthesis of such heterocycles by using dissimilar catalytic agents such as $ZrOCl_2$ $8H_2O$,[21] SiO_2-$ZnCl_2$,[22] $In(OTF)_3$,[23] different heteropolyacid catalysts[24] and ionic liquid catalytic synthesis.[25] Lengthways, various chemical reagents such as aldehydes,[26] acid chlorides,[27] carboxylic acids,[28] esters,[29] nitriles[30] and amides[31] can be condensed with o-substituted (NH_2/OH/SH) amino aromatic compounds in the presence of diverse catalysts. On the other hand, some of them do suffer from several downsides such as requirement of long reaction time, side product formation, tedious work up procedure, unsatisfactory yields, need of additional amount of catalyst, necessity of expensive tools and cumbersome experimental procedure. Therefore, the development of an efficient, simple and high yield protocol for the synthesis of such biological active moieties is still required.

Herein, we extend our interest toward the development of novel and cleaner methods for classical synthesis of benzimidazoles and other heterocycles.[32–36] Earlier, we have reported catalytic the application of fluorophosphoric acid for the synthesis of dihydropyrimidinones which presented better activity with respect to the concerned reaction.[1] The results obtained encouraged us to extend our study and scope of fluorophosphoric acid as a catalyst in various organic transformations. Accordingly, we report a proficient approach for the synthesis of benzimidazoles, benzoxazoles and benzothiazoles using fluorophosphoric acid catalyst at room temperature. The reported fluorophosphoric acid catalyst offered some advantages in comparison to reported catalysts such as easy availability, nonmetallic acidic character, effective and efficient even at room temperature. The current approach was found be highly selective, effective and yielded the desired product with satisfactory yield within short reaction period.

Results and discussion

The synthetic methodology adopted to obtain the targeted benzimidazole, benzoxazole and benzothiazole derivatives is represented in Scheme 1. Targeted molecules have been synthesized from o-substituted (NH_2/OH/SH) amino-aromatics and various substituted aldehydes (aromatic/aliphatic/heterocyclic) in the attendance of catalytic amount (5 mol %) of fluorophosphoric acid under optimized reaction conditions.

In order to outline the optimized reaction parameters for the condensation reaction, initially we screened and evaluated effect of diverse catalysts and solvents as well. In addition to this, effect of catalyst loading and reaction temperature has also been investigated. A model reaction has been conducted concerning o-phenylenediamine and benzaldehyde in the presence of different catalysts and solvents at diverse temperatures and the results are summarized in Tables 1 and 2.

When the neat reaction (without any catalyst) was performed in ethanol solvent at room temperature, it did not produce satisfactory yield (Table 1, entry a). The neat reaction was also performed at 60 °C keeping the rest of the conditions constant which resulted in a moderate yield of the desired product (Table 1, entry a). These control experiments suggested that the reaction did not proceed at room temperature as efficiently as at an elevated temperature of 60 °C in the absence of a catalyst and that a catalyst-free

Table 2. Influence of various reaction parameters on fluorophosphoric acid catalyzed reaction between o-phenylenediamine and benzaldehyde.[a]

Entry	Amount of Fluorophosphoric Acid	Solvent	Reaction Temp. (°C)	Reaction Time[b] (h)	Yield[c] (%)
i	2.5 mol.%	EtOH	r. t.	7.4	48
ii	5 mol.%	EtOH	r. t.	2.2	93
iii	7.5 mol.%	EtOH	r. t.	2.4	91
iv	10 mol.%	EtOH	r. t.	4.0	80
v	5 mol.%	EtOH	40	3.3	86
vi	5 mol.%	EtOH	60	3.3	72
vii	5 mol.%	MeOH	r. t.	6.0	70
viii	5 mol.%	DMF	r. t.	7.2	66
ix	5 mol. %	H_2O	r. t.	12.0	53
x	5 mol.%	THF	r. t.	15.0	40
xi	5 mol.%	Toluene	r. t.	18.0	28

[a]**Reaction conditions:** *o*-Phenylenediamine (0.01 mol), benzaldehyde (0.01 mol), solvent 10 mL;
[b]Monitored by TLC;
[c]Isolated yield.

protocol did not work for this transformation. Additionally, the reaction was performed in the presence of fluorophosphoric acid catalyst under similar reaction conditions in a solvent free environment at room temperature, showing an unsatisfactory result (Table 1, entry b). This suggests that presence of a solvent is equally important and plays a crucial role in obtaining an acceptable yield of benzimidazole. Further, when the reaction was performed in the presence of fluorophosphoric acid at room temperature, we could achieve 93% yield of benzimidazole in a reaction time of 2.2 h in ethanol as a solvent (Table 1, entry c). This demonstrated that a catalyst is essentially required in order to obtain higher yield of product even at room temperature. Further, the reaction was conducted under similar condition in presence of Polyphosphoric acid (PPA) as a catalyst which resulted in 61% yield toward benzimidazole (Table 1, entry d). Dodecyl phosphonic acid (DPA) was also employed as a catalyst which led to the formation of benzimidazole in 63% yield (Table 1, entry e). The obtained results indicated that both, PPA and DPA as a catalyst was unable to effectively yield the desired product benzimidazole at room temperature. Meanwhile, the catalytic activity of sulfamic acid and chlorosulfonic acid was also investigated and the reactions ended up with 70% and 88% yield of the anticipated product, respectively (Table 1, entries f & g). The results revealed that these catalysts to some extent were capable of achieving admirable yield toward benzimidazole at room temperature. However, a long duration of 8 h and 6.4 h, respectively was required in order to achieve these yields. Furthermore, the chlorosulfonic acid catalyzed reaction produced mixture of mono and di-substituted benzimidazoles with 35% and 53% yield of corresponding derivative (Table 1, entry g). Phosphosulfonic acid catalyst was also taken into account for the catalytic application for the planned synthesis. This acid catalyst produced a remarkable 86% yield of desired product within 3 h. It seems to be an efficient catalyst but still not as good when compared to fluorophosphoric acid.

Fluorophosphoric acid showcased the most prominent results as compared to the rest of the acid catalysts. Thus, fluorophosphoric acid was considered as a catalyst of choice in the present work. In order to determine the optimal conditions to carry out reaction between benzaldehyde and o-phenylenediamine using fluorophosphoric acid as a catalyst, few controlled experiments were performed, the results of which are listed in Table 2. Initially, the influence of catalyst loading on the throughput of the present reaction at room temperature was evaluated. To begin with at 2.5 mol% of fluorophosphoric acid, the reaction resulted in the formation of the benzimidazole product with 48% yield at room temperature in ethanol solvent after 7.4 h reaction time (Table 2, entry i). 2.5 mol% of catalyst loading was not sufficient to obtain an acceptable yield of the desired product. Further, when the same reaction was performed with 5 mol% catalyst loading and while keeping the rest of the parameters constant, the catalyst amount provided sufficient active sites for the reaction to effectively yield 93% of desired product in just 2.2 h (Table 2, entry ii). Additionally, the reaction was also performed by employing 7.5 mol% and 10 mol% catalyst which led to the formation of 91% and 80% yield of product in 2.4 h and 4 h, respectively (Table 2, entries iii & iv). The yield obtained with 7.5 mol% was reliable with respect to 5 mol% catalyst, however, the time required for achieving the yield was comparatively more. However 10 mol. % catalyst failed to achieve an additional yield. At a higher loading of catalyst, yield of the desired benzimidazole was observed to decrease which could possibly be due to undesirable increased acidity of the catalyst. Hence, we observed that the concentration of catalyst in the reaction also played an important role in the formation of benzimidazoles and 5 mol. % catalyst loading was adequate for achieving admirable conversion and yield toward benzimidazole.

Likewise, the influence of temperature on the fluorophosphoric acid catalyzed reaction between benzaldehyde and o-phenylenediamine was also studied in detail. The reaction was performed by employing 5 mol% catalyst in ethanol solvent at room temperature, 40 °C and 60 °C. The reaction performed at room temperature displayed better yield of 93% in just 2.2 h. However, at higher temperatures, the reaction system produced some by-products[26,32,37] and thus lowered the yield of benzimidazole (Table 2, entries v & vi). Thus, room temperature was considered as an optimum temperature for the present reaction. In conclusion, with aspects of energy efficiency, the present fluorophosphoric acid catalyzed reaction can be considered greener.

Additionally, as solvent can also drastically affect the reaction under investigation, study of solvent effect was considered necessary. Hence, we have scanned various solvents such

as methanol (MeOH), dimethyl formamide (DMF), water (H_2O), tetrahydrofuran (THF) and toluene for same reaction with optimized reaction condition. Among these solvents, 10 mL ethanol was the most prominent solvent for the present fluorophosphoric acid catalyzed reaction system which yielded 93% benzimidazole. Methanol and DMF solvents produced moderate benzimidazole yield of 70% & 66%, respectively (Table 2, entries vii & viii). Continually, the same reaction was also performed in H_2O, tetrahydrofuran (THF) and toluene solvent at room temperature. The results obtained revealed that these solvents proved to be inactive for this synthetic protocol. These reactions produced unsatisfactory yields of selective benzimidazole (Table 2, entries ix, x & xi). Thus, the results showed that ethanol solvent was very suitable for the present reaction catalyzed using fluorophosphoric acid and thus ethanol was used for the further studies.

The control experiments performed for the synthesis of benzimidazoles by varying different reaction parameters revealed that with equimolar amount of o-phenylenediamine and benzaldehyde in 10 mL ethanol solvent and in presence of 5 mol% of fluorophosphoric acid catalyst at room temperature displayed the most useful results. Therefore, these parameters were considered as optimized reaction conditions. With these optimized conditions, the generality of the method was estimated from the reaction of o-phenylenediamine, o-aminophenol and o-aminothiophenol with diverse aldehydes and obtained results are summarized in Table 3.

All entries mentioned in Table 3 clearly indicated that, under optimized reaction condition all substituted aldehydes readily reacted with o-phenylenediamine, o-aminophenol as well as o-aminothiophenol and generated good to better yield of respective benzimidazoles, benzoxazoles and benzothiazoles. Under the similar circumstances, aliphatic, aromatic as well as heterocyclic aldehydes showed acceptable reactivity without any significant difference in the product yield and reaction time. Moreover, the results reveal that aromatic aldehydes with different substitution (electron donating/electron withdrawing) at ortho, meta or para positions showed comparable results with respect to the formation of targeted moieties. These results illustrated that the reaction under study at optimized reaction condition in presence of fluorophosphoric acid as a catalyst has the ability to tolerate other functional groups such as methyl, methoxy, nitro and halides. Thus, the substituted functionalities are preserved throughout the course of reaction. The derivatives of benzimidazole, benzoxazole and benzothiazole were synthesized in good to excellent yields and structural confirmation of synthesized compounds were performed by various advanced spectroscopic techniques such as FT-IR, ^{1}H NMR, ^{13}C NMR and Mass spectroscopy. Physical and spectral data of known compounds are in agreement with those reported in the literature.[38–44]

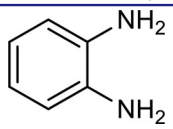
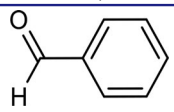
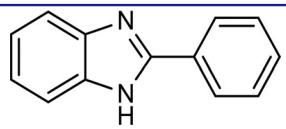
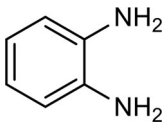
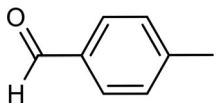
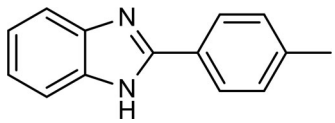
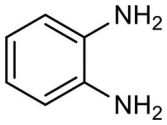
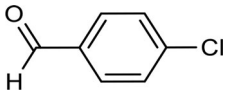
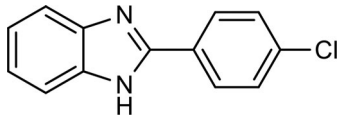
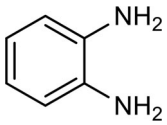
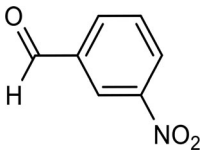
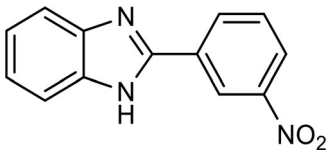
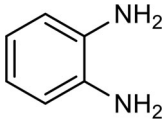
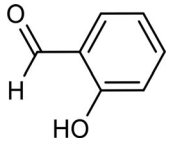
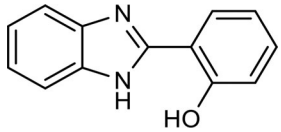
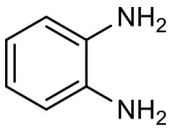
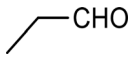
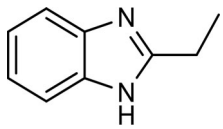
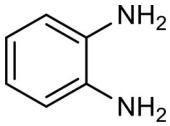
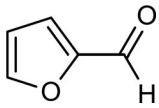
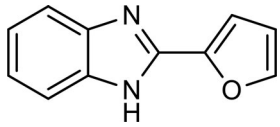
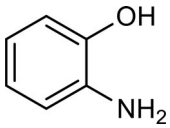
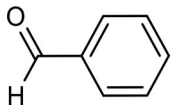
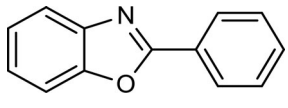
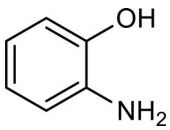
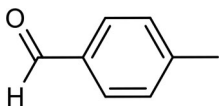
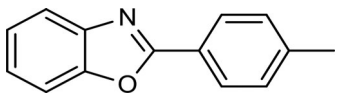
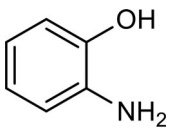
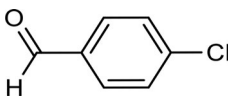
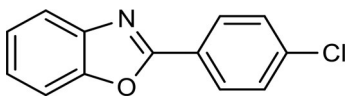
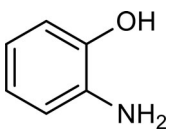
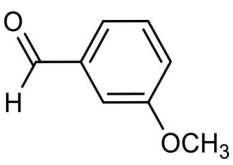
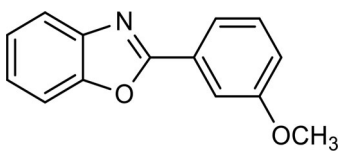
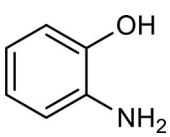
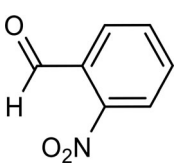
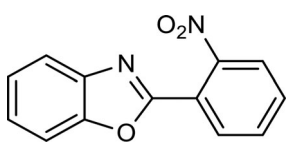
Comparison of the present work with the previous literature for the synthesis of series of benzimidazoles, benzoxazoles and benzothiazoles

The present work is compared with the previous literature and the results are displayed in Table 4. Even though various catalysts exist that displayed appreciable catalytic performance, certain drawbacks were encountered such as requirement of high temperature, harsh solvent. Precisely, the reaction of *o*-Nitroaniline and benzyl acohol performed by Sarkar *et al.* in the presence of the $Co(acac)_2$/NaOBu resulted in the formation of benzimidazole in an 73% yield at 135 °C for 24 h in the presence of 1,4-dioxane solvent (Table 4, entry 1).[45] The $Co(acac)_2$ catalyst system worked well in the presence of NaOBu as a base to yield the desired product at high temperature and long reaction time of 24 h.[45] Another study reported the synthesis of benzimidazole by reacting benzene-1,2-diamine with benzaldehyde in presence of tungstate-based imidazolium ILs ($[BMIm]_2[WO_4]$).[46] The catalyst afforded the target product in good yield (80%) at the cost of high temperature of 100 °C and long reaction time (Table 4, entry 2).[46] Interestingly, in the present work the authors could successfully synthesize benzimidazole in the presence of fluorophosphoric acid as a catalyst. The catalyst effectively yielded 93% desired product at room temperature in just couple of hours (Table 4, entry 3).

Additionally, there are reports on synthesis of benzoxazoles using various catalytic systems. Yuan *et al.* used imidazolium chloride to synthesize benzoxazoles from 2-Aminophenols and N,N-dimethylbenzamide.[47] The catalyst could yield 86% of the desired product in 10 h of reaction time and high reaction temperature (Table 4, entry 4).[47] Further, with an aim to synthesize benzoxazoles in high yield, Tran and group synthesized Brønsted acidic ionic liquid (BAIL) gel by grafting the surface of TEOS with Brønsted acidic ionic liquid.[48] The BAIL catalyst displayed 98% yield toward benzoxazole in just 5 h of reaction time (Table 4, entry 5).[48] However, the catalyst required high temperature of 130 °C to produce desired product in high yields (Table 4, entry 5).[48] Further, $[BMIm]_2[WO_4]$ catalyst resulted in formation of benzoxazole in 82% yield at harsh reaction condition (Table 4, entry 6).[46] Additionally, the synthesis of $[BMIm]_2[WO_4]$ catalyst was a multi-step process.[46] In comparison to the reported works, catalytic amount of flurophosphoric acid used in the present work yielded 90% of benzoxazole at room temperature in just 2.4 h of reaction time (Table 4, entry 7).

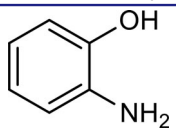
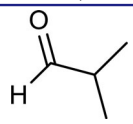
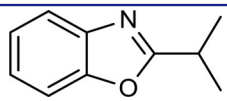
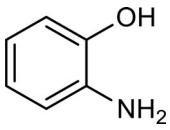
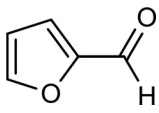
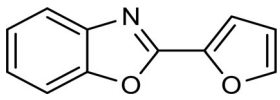
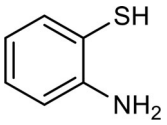
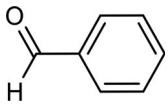
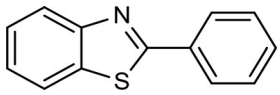
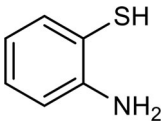
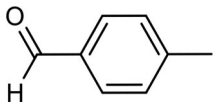
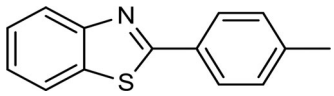
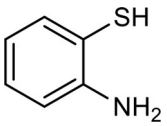
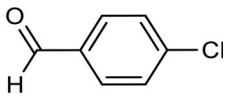
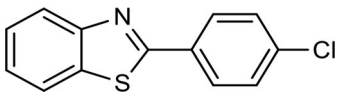
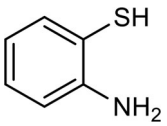
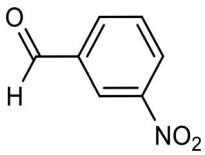
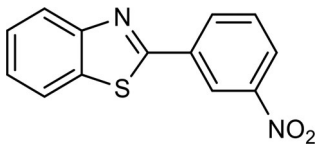
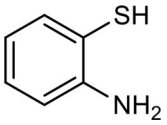
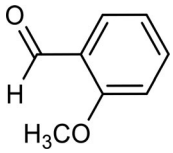
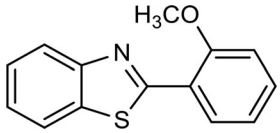
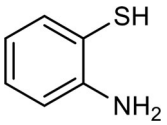
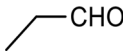
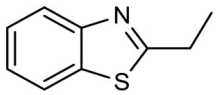
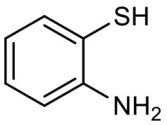
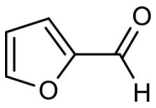
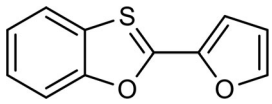
Benzothiazole was also catalytically synthesized in good yield by several researchers. Yuan *et al.* used 2-amino-benzenethiol and N,N-dimethylbenzamide to synthesize benzothiazole in presence of catalytic amount of imidazolium chloride.[47] The catalyst yielded 79% desired product at 140 °C and the reaction time required was 10 h (Table 4, entry 8).[48] Song and coauthors reported $[BMIm]_2[WO_4]$ catalyst for producing benzothiazoles in 85% yield at high reaction temperature (Table 4, entry 9).[46] Further, Tran *et al.* synthesized Brønsted acidic ionic liquid (BAIL) Gel in an attempt to obtain high yields of benzothiazole.[48] The catalyst with high acidic character yielded 91% of desired product (Table 4, entry 10).[48] However, the reaction system was run at high temperature of about 130 °C.[48] In contrary to the reported work, the fluorophosphoric acid in the present work produced benzothiazoles in high yield at room temperature (Table 4, entry 11). Therefore, from the above discussion we could consider that fluorophosphoric acid catalyst in the present work offered

Table 3. Synthesis of 2-substituted benzimidazole, benzoxazole, and benzothiazoles.[a]

Entry	Amino aromatic compound	Aldehyde	Product	Yield[b] (%)	Time[c] (h)	M.P[d](°C)	Ref.
a				93	2.2	290-291	32
b				94	2.1	223-224	32
c				88	2.5	292-293	32
d				87	3	146-147	32
e				85	3	240-241	32
f				80	3.4	175-176	42
g				90	3	289-290	39
h				90	2.4	102-103	38
i				88	2.4	115-116	43
j				86	3.2	144-145	40
k				83	3.5	73-74	43
l				82	4	90-91	40

(*continued*)

Table 3. Continued.

Entry	Amino aromatic compound	Aldehyde	Product	Yield[b] (%)	Time[c] (h)	M.P[d](°C)	Ref.
m				80	3.5	148-149	38
n				87	3	86-87	43
o				92	2.4	109-110	41
p				87	2.5	84-86	41
q				90	2.4	116-117	41
r				86	3.4	199-200	43
s				82	4	102-103	41
t				80	4.2	251-252[d]	41
u				88	3	103-104	41

[a]**Reaction conditions**: amino aromatic compound (0.01 mol), various aldehyde (0.01 mol), EtOH 10 mL, 5 mol % Fluorophosphoric acid;
[b]Isolated yield;
[c]Monitored by TLC;
[d]Boiling point (at 760 mm Hg).

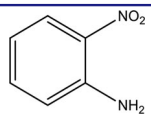
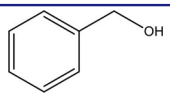
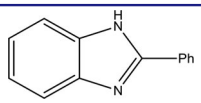
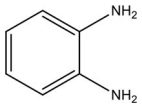
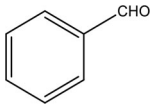
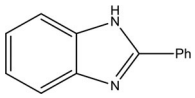
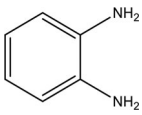
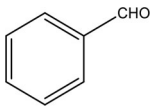
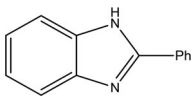
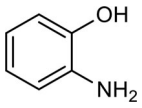
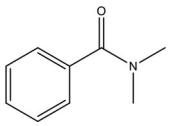
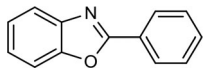
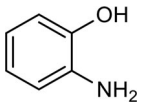
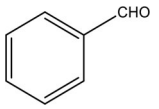
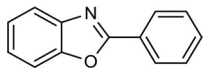
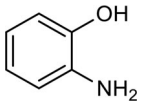
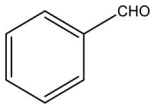
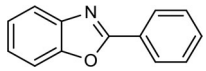
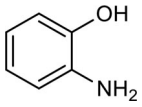
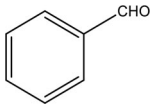
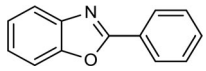
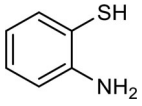
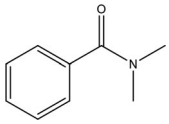
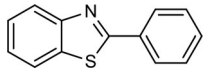
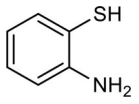
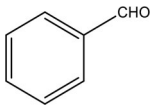
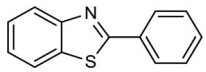
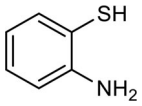
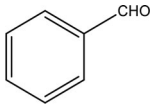
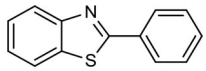
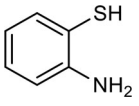
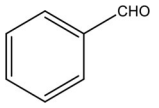
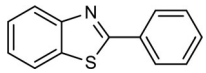
some advantages in comparison to the reported catalysts such as easy availability, nonmetallic acidic character, effective and efficient even at room temperature. The current approach was found be highly selective, effective and yielded the desired product with satisfactory yield within short reaction period.

Experimental

Materials and characterization techniques

Fluorophosphoric acid (95%) was purchased from Sigma Aldrich. All necessary reagents and solvents were used without additional distillation. All the chemicals were obtained from commercial chemical supplier and used without further purification. The melting points of all the compounds were determined in open capillary tubes and are uncorrected. The IR spectra of the compounds were recorded on a Perkin-Elmer spectrophotometer in KBr pellets. ^{1}H-NMR spectra were recorded on Varian Gemini (400 MHz) spectrometer using dimethyl sulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as an internal standard.^{13}C-NMR spectra were recorded on 50 MHz in DMSO solvent. The reactions were monitored by thin layer

Table 4. Comparative study of synthesis of series of benzimidazoles, benzoxazoles and benzothiazoles with the literature.

Entry	Substrate 1	Substrate 2	Catalyst	Product	Temp (°C)	Time (h)	Solv.	Yield (%)	Ref.
1			$Co(acac)_2$/ NaOBu		135	24	1,4-Dioxane	73	45
2			$[BMIm]_2[WO_4]$		100	7	1,4-Dioxane	80	46
3			Fluorophosphoric acid		25	2.2	EtOH	93	Present work
4			Imidazolium chloride		160	10	–	86	47
5			Bail gel		130	5	Solvent free	98	48
6			$[BMIm]_2[WO_4]$		100	5	1,4-Dioxane	82	46
7			Fluorophosphoric acid		25	2.4	EtOH	90	Present work
8			Imidazolium chloride		140	10	–	79	48
9			$[BMIm]_2[WO_4$		100	5	1,4-Dioxane	85	46
10			Bail gel		130	6	Solvent free	91	48
11			Fluorophosphoric acid		25	2.4	EtOH	92	Present work

chromatography (TLC) on silica gel plates. The crude products obtained were purified by column chromatography over silica gel and the purity of the compounds has been mentioned in the spectral data.

General procedure for synthesis of benzimidazoles/ benzoxazoles/benzothiazoles

A mixture of o-substituted amino-aromatics 1(i-iii) (0.1 mol) and aldehydes 2(a-u) (0.1 mol) was added in 100 mL round bottom flask containing ethanol (10 mL). A known catalytic amount of fluorophosphoric acid was added in the above solution. The resulting reaction mixture was stirred at room temperature for an appropriate time. After completion of the reaction, it was monitored by TLC (hexane/ethyl acetate 90:10). The work-up was performed for the reaction mixture by diluting it with ice cold water and extracting it by ethyl acetate. The organic layer was separately collected and evaporated under vacuum on rotary evaporator to obtain solid crude product. The obtained solid product was further

purified by recrystallization with hot ethanol and by passing sample through a short column of silica gel whenever required.

Spectral data of selective synthesized products

2-Phenyl- 1H-benzimidazole (3a)- (Purity- 97%): **^{1}H-NMR** (DMSO-d_6, in δ ppm): 8.20 (d, 2H, J = 6.0 Hz), 7.65-7.59 (m, 4H), 7.50-7.48 (m, 1H), 7.22 (m, 2H), 5.20 (s, 1H, NH); **^{13}C-NMR** (DMSO-d_6, in δ ppm): 113.26, 118.68, 122.71, 123.90, 125.69, 129.20, 129.89, 130.84, 135.11, 145.52, 152.50. **IR** (KBr, in cm^{-1}): 3220, 2280, 1672, 1400, 1275, 1119, 970, 738; **Mass** (m/z): 194 [M^+].

2-(2- Hydroxyphenyl)-1H- benzimidazole (3e)- (Purity- 98%): **^{1}H NMR** (DMSO-d_6, in δ ppm): 7.92 (dd, 1H, J = 7.6, 1.4 Hz), 7.78 (d, 1H, J = 7.6 Hz), 7.65 (d, 1H, J = 7.4 Hz), 7.48 – 7.40 (m, 1H), 7.32–7.26 (m, 2H), 7.10–7.06 (m, 2H)), 4.91 (brs, 1H, OH), 5.19 (s, 1H, NH); **^{13}C NMR** (DMSO-d_6, in δ ppm): 156.18, 149.80, 140.55, 135.10, 132.05, 131.79, 129.55, 128.71, 127.64, 124.04, 123.18, 121.19, 117.09; **IR** (KBr, in cm^{-1}): 3560, 3390, 2185, 1640, 1610, 1090, 940, 762; **Mass** (m/z): 211 [M^+].

2-(Furan-2-yl)-1H-benzo[d]imidazole **(3 g)**- (Purity- 97%): **^{1}H NMR** (DMSO-d_6, in δ ppm): 7.96 (d, 1H, J = 1.2) , 7.65 (d, 1H, J = 6.4), 7.52 (d, 1H, J = 6.4 Hz), 7.30-7.21 (m, 2H), 6.92-6.80 (m, 2H), 5.24 (s, 1H, NH); **^{13}C NMR** (DMSO-d_6, in δ ppm): 145.84, 144.86, 143.60, 140.03, 122.48, 115.30, 112.93, 109.97; **IR** (KBr, in cm^{-1}): 3408, 2927, 2860, 1700, 1619, 1555, 1462, 1380, 1201, 1071, 768, 585; **Mass** (m/z): 184 [M^+].

2-Phenyl benzoxazole (3 h)- (Purity- 95%): **^{1}H NMR** ($CDCl_3$, in δ ppm): 8.30-8.24 (m, 2H), 7.79-7.73 (m, 1H), 7.58-7.53 (m, 1H), 7.46-7.39 (m, 3H), 7.35-7.30 (m, 2H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 163.70, 152.02, 142.51, 132.06, 129.10, 128.34, 127.20, 125.09, 123.98, 120.40, 111.05; **IR** (KBr, in cm^{-1}): 3452, 2920, 1622, 1565, 1260, 756; **Mass** (m/z): 196 [M + 1].

2-(3-Methoxyphenyl)benzoxazole **(3k)**- (Purity- 94%): **^{1}H NMR** ($CDCl_3$ in δ ppm): 7.80-7.71 (m, 3H), 7.62-7.56 (m, 1H), 7.42 (t, 1H, J = 8.2 Hz), 7.36-7.30 (m, 2H), 7.08-6.95 (m, 1H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 164.20, 162.01, 151.29, 144.02, 131.26, 127.69, 124.58, 123.89, 119.32, 118.98, 117.57, 110.09, 55.87. **IR** (KBr, in cm^{-1}): 3005, 2962, 2865, 1660, 1504, 1480, 1254, 1084, 780, 669, 630; **Mass** (m/z): 226.23 [M + 1].

2-isopropylbenzo[d]oxazole **(3 m)**- (Purity- 94%): **^{1}H NMR** ($CDCl_3$, in δ ppm): 7.82 (d, 1H, *J = 8.0 Hz*), 7.67 (d, 1H, *J = 8.2 Hz*), *7.51–7.39 (m, 2H),* 3.42-3.36 (hept, 1H, *J = 6.8 Hz*), 1.50 (d, 6H, *J = 6.8 Hz*); **^{13}C NMR** ($CDCl_3$, in δ ppm): 176.48, 152.19, 143.0, 126.32, 124.81, 121.95, 119.89, 33.49, 21.97. **IR** (KBr, in cm^{-1}): 3135, 2954, 2902, 2862, 1648, 1542, 1500, 1264, 1063, 778, 670; **Mass** (m/z): 162 [M + 1].

2-(furan-2-yl)benzoxazole **(3n)**- (Purity- 96%): **^{1}H NMR** ($CDCl_3$ in δ ppm): 7.75-7.69 (m, 1H), 7.58-7.55 (m, 1H), 7.48-7.43 (m, 1H), 7.35-7.29 (m, 2H), 7.18 (d, 1H, J = 3.8 Hz), 6.60-6.58 (m, 1H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 155.28, 150.51, 148.00, 141.89, 139.75, 125.38, 123.99, 120.30, 115.04, 111.75, 110.25; **IR** (KBr, in cm^{-1}): 2945, 2886, 1715, 1624, 1574, 1460, 1378, 1221, 1070, 760, 582; **Mass** (m/z): 186 [M + 1].

2-Phenyl benzothiazole (3o)- (Purity- 95%): **^{1}H NMR** ($CDCl_3$, in δ ppm): 8.20-8.16 (m, 3H), 7.80 (d, 1H, J = 8.0 Hz), 7.55-7.50 (m, 4H), 7.38-7.34 (m, 1H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 169.20, 155.02, 135.09, 133.90, 132.04, 130.12, 128.24, 126.80, 124.92, 123.44, 121.90; **IR** (KBr, in cm^{-1}): 3103, 2940, 1660, 1487, 1365, 1238, 875, 754, 682; **Mass** (m/z): 212 [M + 1].

2-(4-Chlorophenyl)benzothiazole (3q)- (Purity- 94%): **^{1}H NMR** ($CDCl_3$, in δ ppm): 8.20 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.5 Hz, 1H), 7.48–7.33 (m, 4H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 168.02, 155.45, 137.71, 134.98, 132.60, 130.01, 128.58, 125.29, 124.89, 123.6, 120.78; **IR** (KBr, in cm^{-1}): 3119, 3025, 1654, 1593, 1463, 1248, 864, 682; **Mass** (m/z): 245 [M^+].

2-Ethylbenzothiazole (3t)- (Purity- 94%): **^{1}H NMR** ($CDCl_3$ in δ ppm): 8.05 (d, J = 8.2 Hz, 1H), 7.85 (dd, J = 8.2, 1.2 Hz, 1H), 7.52-7.45 (m, 1H), 7.30-7.21 (m, 1H), 3.06 (q, J = 7.4, 2H), 1.50 (t, J = 7.4, 3H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 168.20, 150.12, 138.64, 124.85, 124.60, 121.89, 119.05, 27.41, 12.08; **IR** (KBr, in cm^{-1}): 3404, 2980, 2942, 2880, 1560, 1485, 1420, 1296, 1052, 940, 767, 685; **Mass** (m/z): 164 [$M + 1^+$].

2-(Furan-2-yl)-benzothiazole (3 u)- (Purity- 95%): **^{1}H NMR** ($CDCl_3$ in δ ppm): 8.47 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 3.5 Hz, 1H), 7.62 (dd, J = 14.3, 6.8 Hz, 2H), 7.40 (t, J = 7.6 Hz, 1H), 7.20-7.12 (m, 1H); **^{13}C NMR** ($CDCl_3$, in δ ppm): 158.25, 153.72, 148.76, 144.70, 134.26, 126.47, 125.11, 123.30, 121.51, 112.55, 111.40; **IR** (KBr, in cm^{-1}): 2982, 2860, 1704, 1645, 1564, 1470, 1367, 1222, 1044, 785, 578; **Mass** (m/z): 202 [M^+].

Conclusions

In summary, we demonstrated that fluorophosphoric acid catalyst offered an efficient, selective route to synthesize series of benzimidazoles, benzoxazoles and benzothiazoles from 1, 2-phenylenediamine, o-aminophenol and o-aminothiophenol with aliphatic, aromatic as well as heterocyclic aldehydes. The study suggested that 5 mol% fluorophosphoric acid could effectively catalyzed these reactions in ethanol solvent at room temperature in just reaction time of 2.2-4.2 h with admirable yields. The high yields obtained are comparable to those reported in the literature. Additionally, as compared with the works reported for the synthesis of series of benzimidazoles, benzoxazoles and benzothiazoles, the present work holds certain merits. Precisely, the fluorophosphoric acid could be considered as inexpensive catalyst in comparison to that of metal-based catalyst. There are several problems associated with of metal-based catalyst such as stability and acidity. Conversely, fluorophosphoric acid is stable and offered the required acidity for driving the reaction into the forward direction. Therefore, reported protocol could be considered as an efficient, inexpensive synthetic approach for producing moderate to excellent yields of targeted molecules not only at academic level but also can be

looked upon as a choice for scale-up reactions with wide ranging applications.

Acknowledgements

Authors are thankful to the management and principals of their respective colleges for encouragement & assistance. They are also thankful to IICT Hyderabad and Solapur University for proving spectral data.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

The authors would like to acknowledge CNMS, Jain University and Nano Mission, DST, Government of India, for financial support SR/NM/NS-20/2014. The authors also gratefully acknowledge Centre for Nano and Material Sciences (CNMS), JAIN University, Bangalore for partially funding support through the basic research grant of JAIN (No.II(39)/17/005/2017SG).

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