

# Pentafluorophenylammonium Triflate: A Mild, Efficient and Reusable Catalyst for the Synthesis of 2-Arylbenzothiazole and 2-Arylbenzothiazoline Derivatives in a Green Chemical Approach

ARUP DATTA

Department of Chemistry, Shibpur Dinobundhoo Institution (College), 412/1, G. T. Road (South),  
Howrah-711102, Shibpur, West Bengal, India.

\*Corresponding Author E-mail: arupdattadb@gmail.com

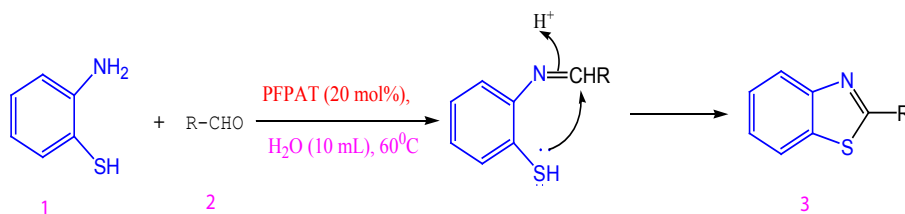
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## ABSTRACT

In this work, one pot, simple and environmentally benign effective synthesis of 2-substituted benzothiazole and benzothiazoline derivatives are described in presence of PFPAT (pentafluorophenylammonium triflate) catalyst in water successfully. A series of benzothiazole derivative were synthesized by the reaction between 2-aminothiophenol and various aldehydes in good yields. Recyclability of the catalyst is observed for four times without loss of its activity in aqueous medium.

**Keywords:** Pentafluorophenylammonium triflate, Reusable catalyst, 2-Arylbenzothiazole, Aqueous medium.



## INTRODUCTION

Environment friendly green reaction medium has been given large importance in academic and industrial procedure.<sup>1</sup> Keeping the environment in mind volatile, hazardous, toxic organic solvents are continuously replaced by green solvent like water<sup>2</sup> and ionic liquids<sup>3</sup> in organic

transformation. It is well known that water act as a green reaction medium because it is easily available in huge quantities, containing high polarity and assembles activity of the hydrophobic part<sup>4</sup> and that's why the profound catalytic activity is noticeable in water medium. 2-Aryl benzothiazole derivatives are sulphur and nitrogen containing heterocycles create an attraction because of their immense biological

activity in a broad range. The benzothiazole nucleus possesses large pharmacological activity like anti-cancer, anti-viral, antitumor, anti-convulsant.<sup>5</sup> Benzothiazolyl moiety act as a  $\beta$ -amyloid for the treatment of Alzheimer disease. The compounds like 2-(4'-dimethylaminophenyl)-benzothiazole and 2-(4'-aminophenyl)-benzothiazole show inhibitory activity against human ovarian and renal cell lines. Derivative 2-(3', 4'-dimethoxyphenyl)-5-fluorobenzothiazole is used against breast, lung and colon cancer. Beside this, benzothiazole derivative is helpful for the treatment of anti-parasitics, anti-tuberculosis diseases.<sup>6</sup>

There are numerous methods are available to design the benzothiazolyl moiety put condensation method is very common where *o*-aminothiophenols are reacted with acid derivatives<sup>7</sup> like acid chloride,<sup>8</sup> ester,<sup>9</sup> nitriles.<sup>10</sup> In the Second method, *o*-aminothiophenols are reacted with aldehydes using different catalyst in either different solvents or solvent less reaction medium to synthesize 2-arylbenzothiazole derivatives through condensation process. Catalyst like CAN,<sup>11</sup> [Pmlm] Br,<sup>12</sup> MnO<sub>2</sub>/SiO<sub>2</sub>,<sup>13</sup> Sc(OTf)<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>,<sup>14</sup> H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/Zr(HPO<sub>4</sub>)<sub>2</sub>,<sup>15</sup> *p*-TsOH,<sup>16</sup> and bakers' yeast,<sup>17</sup> were used to develop the benzothiazole and some benzothiazoline derivatives.<sup>18</sup> Reaction between *o*-aminothiophenol and aromatic aldehydes in microwave irradiation through direct method was also documented.<sup>19</sup> Some catalyst such as CBr<sub>4</sub>, tin-modified monoammonium phosphate fertilizer, acacia concinna bio-catalyst and riboflavin catalyst were applied to develop benzothiazole derivatives in recent years.<sup>20</sup> However, most procedures have some of disadvantages that are hazardous, carcinogenic solvents like chloroform,<sup>21</sup> DMSO,<sup>22</sup> MeCN,<sup>23</sup> dioxane<sup>24</sup> were applied, expensive and toxic catalyst<sup>25</sup> were used, recyclability of the catalyst was noticeable in a few papers<sup>26</sup> and in most papers multistep reaction and complex purification technique were accommodated<sup>27</sup>.

So it is very important to switchover above difficulties and come up with new simple, eco-friendly and efficient methods to develop 2-substituted benzothiazole and benzothiazoline derivatives with green catalyst. In recent study PFPAT (C<sub>6</sub>F<sub>5</sub>NH<sub>3</sub>OTf) worked well as a novel organocatalyst in the conversion of esterification of carboxylic acid and enol silyl ether formation.<sup>28</sup> However, still now there is no application of this novel organocatalyst as a Brønsted acid in aqueous medium to develop

these derivatives. Here I report the synthesis of benzothiazole and also benzothiazoline derivatives using PFPAT catalyst through a condensation method in water.

## EXPERIMENTAL

Chemicals were purchased from SRL India and Spectrochem Pvt. Ltd. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz instrument. From Aldrich chemical company NMR solvents CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub> and TMS as the internal standard were purchased. Electrical melting point apparatus were used to determine the melting point. Perkin Elmer Spectrophotometer was used to study FT-IR spectra. Thin layer chromatography was used to monitor the reaction. For recrystallisation, aqueous ethanol was used as solvent.

### Preparation of the PFPAT catalyst

In toluene 25 mmol pentafluoroaniline and 25 mmol trifluoromethane sulphonic acid were added and stirred for 30 min at 0-5°C temperature. The solvent was evaporated after completion of the reaction under vacuum. Then crude product was collected and washed with hexane to produce the pure catalyst.<sup>31c</sup>

### General Procedure

In a round-bottomed flask substituted benzaldehyde (1 mmol, 2) and *ortho*-aminothiophenol (1.2 mmol, 1) were mixed and dissolved in 10 mL water. Then PFPAT (0.2 mmol) catalyst was added. It was stirred in oil bath at 60°C for the appropriate time. The reaction was monitored by silica coated thin layer chromatography plate in presence of MeCO<sub>2</sub>Et and petroleum ether solvent. The reaction completed within 4.5-6 h confirmed by the developing brown spot in iodine chamber. Then the crude product was cooled and filtered. Crude product was washed with minimum volume of mixture of ethylacetate and petroleum ether. Finally the washed product was crystallized directly from hot aqueous ethanol (80%). The filtrate containing PFPAT was regenerated and directly used by adding it into the reactants. Character analysis of the product (3a-o) and (4a-c) were compared by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR data with authentic known compounds.

### Selected characterization data for synthesized compounds

#### 2-(2'-Chlorophenyl)-benzothiazole (Entry 8, Table 3)

White color solid, FT-IR (KBr, cm<sup>-1</sup>): 3435,

2363, 1423, 1266, 1053 and 755, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.21-8.18 (m, 1H), 8.12 (dd, 1H), 7.94 (dd, 1H), 7.54-7.49 (m, 2H), 7.44-7.38 (m, 3H) <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 164.2, 152.5, 136.1, 132.7, 132.3, 131.7, 131.1, 130.8, 127.1, 126.3, 125.4, 123.5, 121.4. Analytical calculation for C<sub>13</sub>H<sub>8</sub>CINS (%): C: 63.54; H: 3.28; N: 5.70, Found: C: 63.41; H: 3.12; N: 5.59.

### 2-(2'-Hydroxyphenyl)-benzothiazole (Entry 2, Table 5)

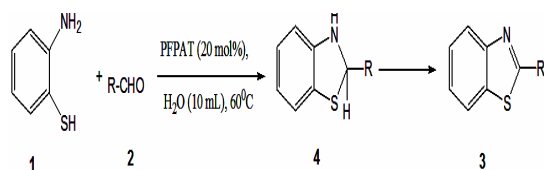
White color solid, IR (KBr, cm<sup>-1</sup>): 3437, 2923, 2372, 1580, 1477, 1210 and 742, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 12.52 (brs, 1H), 8.00 (brd, 1H), 7.91 (brd, 1H), 7.71 (dd, 1H), 7.51 (dt, 1H), 7.40 (dt, 2H), 7.11 (dd, 1H), 6.97 (dt, 1H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 169.4, 158.0, 151.9, 132.8, 132.6, 128.4, 126.7, 125.6, 122.2, 121.5, 119.5, 117.9, 116.8. Analytical calculation for C<sub>13</sub>H<sub>9</sub>NOS (%): C: 68.70; H: 3.99; N: 6.16; Found: C: 68.59; H: 3.82; N: 6.04.

### 2-(2'-Chlorophenyl)-benzothiazoline (Entry 1, Table 4)

White color solid, FT-IR (KBr, cm<sup>-1</sup>): 3344, 3063, 2371, 1573, 1462, 1240, 1033 and 734, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.77-7.71 (m, 1H), 7.40-7.31 (m, 1H), 7.28-7.18 (m, 2H), 7.04 (dd, 1H), 6.95 (dt, 1H), 6.79-6.71 (m, 2H), 6.66 (s, 1H, C<sub>2</sub> proton), 4.43 (brs, 1H, N-H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 146.1, 140.0, 131.6, 129.6, 129.3, 127.4, 127.3, 126.3, 125.5, 122.0, 121.1, 110.4, 65.6. Analytical calculation for C<sub>13</sub>H<sub>10</sub>CINS (%): C: 63.02; H: 4.07; N: 5.65; Found: C: 62.92; H: 3.95; N: 5.51.

## RESULTS AND DISCUSSIONS

To find out the optimization condition of the benzothiazole formation, first the reaction was carried out between 2-aminothiophenol (1 mmol) and 4-chlorobenzaldehyde (1 mmol) as model substrates under different conditions to investigate the influence of catalyst in aqueous medium.



Scheme 1. Synthesis of 2-arylbenzothiazoles in presence of 20 mol% PFPAT catalyst in water

The reaction mixture was heated with different amount of the PFPAT catalyst in water at variable temperature and the result were summarized in Table 1. It was noticeable that the initiation of the reaction depends on the amount of catalyst PFPAT and also temperature. The reaction was very slow without catalyst at 60°C and same situation repeated when catalyst (20 mol%) was used at room temperature but both reactions were continued for 8 h separately. (Entries 1 and 2, Table 1).

Table 1: Study of optimization of the reaction for the formation of 2-(4'-chlorophenyl)-benzothiazole (3f) in different mol% of catalyst PFPAT (Entry 6, Table 3)

Entry	PFPAT (mol%)	Conditions	Time (h)	<sup>a</sup> Yield (%)
1.	0	Oil bath 60°C, H <sub>2</sub> O	8	20
2.	20	Room temp, H <sub>2</sub> O	8	30
3.	05	Oil bath 60°C, H <sub>2</sub> O	10	40
4.	10	Oil bath 60°C, H <sub>2</sub> O	8	48
5.	15	Oil bath 60°C, H <sub>2</sub> O	7.5	56
6.	15	Oil bath 80°C, H <sub>2</sub> O	7	62
7.	20	Oil bath 50°C, H <sub>2</sub> O	8	70
8.	20	Oil bath 60°C, H <sub>2</sub> O	5.5	90
9.	20	Oil bath 80°C, H <sub>2</sub> O	5.5	89
10.	25	Oil bath 50°C, solvent free	8	52
11.	25	Oil bath 60°C, H <sub>2</sub> O	5.0	90
12.	25	Oil bath 80°C, H <sub>2</sub> O	5.0	91

<sup>a</sup>Isolated Yield

It was noticeable that in this model reaction the gradual increase of the mol% of PFPAT at 60°C temperature, the overall yield of the reaction gradually increases. Investigating reaction completed within 5.5 h and maximum yield 90% was isolated (Entry 8, Table 1). Below temperature 60°C very low yields was seen but above 60°C no improved yield was observed (Entries 9 and 12, Table 1). Low yields may be attributed due to benzothiazoline generation along with benzothiazole and also present of unreacted aldehyde in the reaction medium. (Entry 7, Table 1).

Table 2: Solvent effect for the formation of compound 2-(4'-chlorophenyl)-benzothiazole (3f) (Entry 6, Table 3)

Entry	Solvent (10 mL)	<sup>a</sup> Conditions	Time (h)	<sup>b</sup> Yield (%)
1.	Toluene	Oil bath, 60°C	8	32
2.	THF	Oil bath, 60°C	8	40
3.	MeCN	Oil bath, 60°C	8	42
4.	EtOH	Oil bath, 60°C	8	50
5.	AqEtOH(1:1)	Oil bath, 60°C	5.5	60
6.	H <sub>2</sub> O	Oil bath, 60°C	5.5	90
7.	NIL	Oil bath, 60°C	8	30

<sup>a</sup>Condition: PFPAT catalyst 20 mol%, <sup>b</sup>Isolated Yield

Solvent effect has been studied to finalize the optimization condition in this reaction. So to investigate the various solvent effects the reaction was carried out between 2-aminothiophenol and 4-chlorobenzaldehyde in presence of 20 mol% of PFPAT catalyst at 60°C. Examination reveals that the highest yield of the product in the reaction was observed in water medium (Entry 6, Table 2) and even in aqueous alcoholic medium (1:1), moderate yield was obtained (Entry 5, Table 2). Finally conclusion has been made that 20 mol% of Bronsted acid catalyst PFPAT worked well at 60°C temperature in aqueous medium to synthesize the excellent product (3) yields.

After the evaluation of the generality of the model reaction then various 2-substituted benzothiazole derivatives were synthesized under the optimized reaction condition. Here both electron donating and withdrawing groups were involved but no distinct difference in the percentage yield was observed in the product that means all the substrates reacted uniformly with 2-aminothiophenol under this reaction condition. Rate of the reaction depends on the substituent nature of the aldehyde although all reactions completed within 6 hours. Here *m*-nitro, *p*-chloro, *o*-nitro and *o*-methoxy benzaldehyde (Entries 1, 6, 7 and 11, Table 3) gave good yield at comparatively short reaction time on the other hand *p*-methoxy, *p*-hydroxy, *p*-N, N-dimethylamino benzaldehyde gave slight lower yield even after 6 h of the reaction. It may be attributed because of lower electrophilic nature of aldehydes group present in substituted benzaldehyde. For heteroaromatic aldehydes this methods works equally well and the results are represented in entry 10, Table 3.

It was noted that benzothiazoline was generated under this reaction condition when reaction took place between *o*-hydroxybenzaldehyde and *o*-aminothiophenol and the stability of the benzothiazoline may be attributed by intramolecular hydrogen bonding which prevents the aerial oxidation to generate benzothiazole derivatives. Since reaction between *o*-hydroxybenzaldehyde and *o*-aminothiophenol stops at the benzothiazoline stage so conversion of benzothiazole of *o*-hydroxybenzaldehyde was carried out at high temperature under the same reaction condition (Scheme 3).

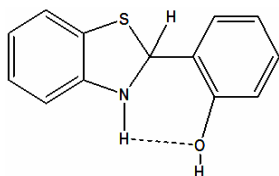
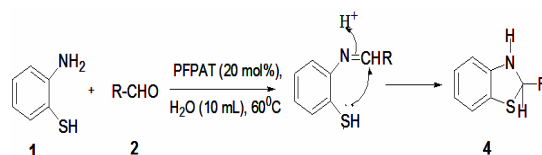
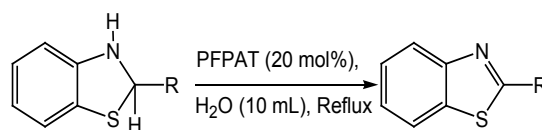


Fig. 1. Intramolecular hydrogen bonding stability of the 2-hydroxy benzothiazoline derivative

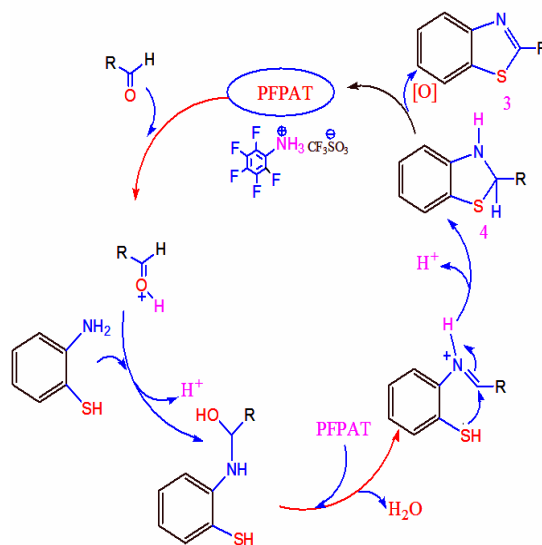


Scheme 2. Synthesis of benzothiazoline in presence of 20 mol% PFPAT catalyst at 60°C in water



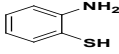
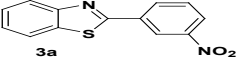
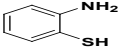
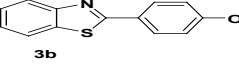
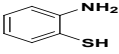
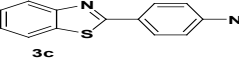
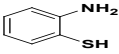
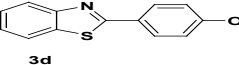
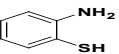
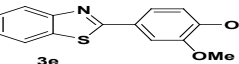
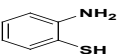
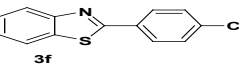
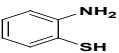
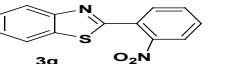
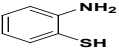
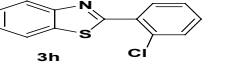
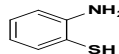
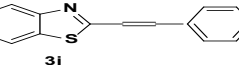
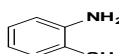
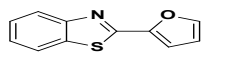
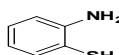
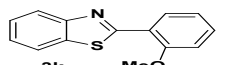
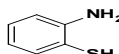
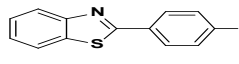
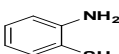
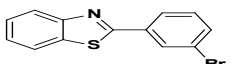
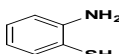
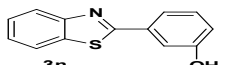
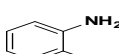
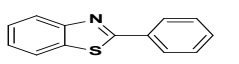
Scheme 3. Conversion of 2-substitutedbenzothiazolines to 2-substitutedbenzothiazoles

From the above discussion author conclude that the 2-substituted benzothiazole no N-H peak at 4-4.5ppm and no C<sub>2</sub>-H peak at approximately 6.33-6.70 ppm in <sup>1</sup>HNMR spectra was obtained from oxidation of benzothiazoline intermediate because isolation was done of the benzothiazoline derivatives from the following aldehydes like 2-chloro, 2-hydroxy and 4-nitrobenzaldehydes. It was achieved when the reaction was continued for a shorter time period (Table 4).  $\delta$  value at 4.43ppm brs and 6.66ppm singlet in proton NMR spectra indicates N-H proton and C<sub>2</sub>-H present respectively in 2-(2'-Chlorophenyl)-benzothiazoline compound (4a) (Entry 1, Table 4). Author has done one experiment in anaerobic condition (absence of oxygen) only benzothiazoline was isolated and benzothiazole never obtained although the reaction was continued for longer time under this reaction condition. So oxygen was essential for oxidation from benzothiazoline to benzothiazole.



Scheme 4. General mechanism for the formation of benzothiazole derivative


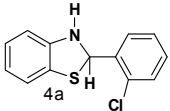

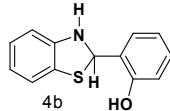

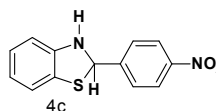
Table 3: Synthesis of 2-substituted benzothiazoles catalysed by PFPAT

Entry	<i>o</i> -Aminothiophenol (1)	Ar-CHO (2)	2-Aryl-benzothiazoles (3)	Time (h)	Isolated yield (%)	Ref
1.		3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	 3a	4.5	88	17
2.		4-OHC <sub>6</sub> H <sub>4</sub> CHO	 3b	06	80	19
3.		4-N,NMe <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	 3c	06	82	29
4.		4-OMeC <sub>6</sub> H <sub>4</sub> CHO	 3d	06	81	29
5.		4-OH-3-OMeC <sub>6</sub> H <sub>3</sub> CHO	 3e	06	85	19
6.		4-ClC <sub>6</sub> H <sub>4</sub> CHO	 3f	5.5	90	30
7.		2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	 3g	4.5	86	15
8.		2-ClC <sub>6</sub> H <sub>4</sub> CHO	 3h	06	85	19
Entry	<i>o</i> -Aminothiophenol (1)	Ar-CHO (2)	2-Aryl-benzothiazoles (3)	Time (h)	Isolated yield (%)	Ref
9.		C <sub>6</sub> H <sub>7</sub> CHO	 3i	05	85	19
10.		C <sub>4</sub> H <sub>3</sub> OCHO	 3j	5.0	85	31
11.		2-OMeC <sub>6</sub> H <sub>4</sub> CHO	 3k	5.0	86	15
12.		4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	 3l	6.0	88	19
13.		3-BrC <sub>6</sub> H <sub>3</sub> CHO	 3m	5.0	89	19
14.		3-OHC <sub>6</sub> H <sub>4</sub> CHO	 3n	5.0	87	19
15.		C <sub>6</sub> H <sub>5</sub> CHO	 3o	5.0	88	19

The plausible mechanistic pathway is depicted in Scheme 4 to generate 2-arylbenzothiazole derivatives using *o*-aminothiophenol and substituted aldehydes. Since PFPAT acts as a Bronsted acid in aqueous medium so in the first step protonation takes place at the carbonyl oxygen centre which

makes more electrophilicity of the carbonyl carbon. Intermediate 4 was obtained by the reaction with *o*-aminothiophenol and then benzothiazole derivative 3 was generated by oxidation of intermediate 4 and details mechanism shown in Scheme 4.

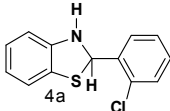
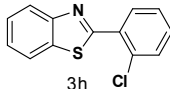
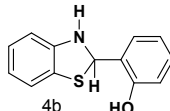
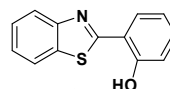
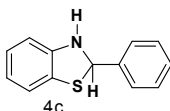
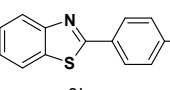
**Table 4: Synthesis of 2-arylbenzothiazolines**

Entry	<i>o</i> -Aminothiophenol (1)	Ar-CHO (2)	2-Arylbenzothiazolines (4)	Time (h)	Isolated yield (%)	Ref
1.		2-ClC <sub>6</sub> H <sub>4</sub> CHO		03	78	18
2.		2-OHC <sub>6</sub> H <sub>4</sub> CHO		5.5	75	19
3.		4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO		03	88	18

Recycling of catalyst is very important in organic reactions and as well as in commercial purpose. So recycle activity studied of PFPAT catalyst in this reaction. The catalyst is soluble in water and it was recovered by evaporation of the filtrate. Then it was washed with hexane and dried under vacuum. PFPAT catalyst was reused in the next four consecutive reactions maintaining the same reaction conditions. Investigation reveals that there were no major loss of its efficacy of catalyst even after using four times in the reaction and it is clearly represented in graphical method Fig. 2. The following advantages of this work were observed

in contrast with other reported procedures such as (a) environmentally benign reaction and cheap reaction procedure (b) pentafluoroaniline and triflic acid were used to prepare PFPAT very easily<sup>31c</sup> (c) isolation and purification of the product was very simple (d) catalyst was used four times without loss of its efficacy (e) solid crude compound was crystallized from hot aqueous ethanol directly after separation of catalyst by simple filtration from aqueous medium (f) no need of column chromatography for purification step and (g) this protocol may be used to prepare benzothiazole derivatives in large scales in near future.

**Table 5: Synthesis of 2-substitutedbenzothiazolines to 2-substitutedbenzothiazoles**

Entry	2-Arylbenzothiazoline (4)	2-Arylbenzothiazole (3)	Time (h)	Isolated yield (%)	Ref	M.P. (°C)	
						Obs	Rep
1.			08	72	18	84-85	82
2.			10	70	19	124-126	126
3.			06	80	19	228-230	230

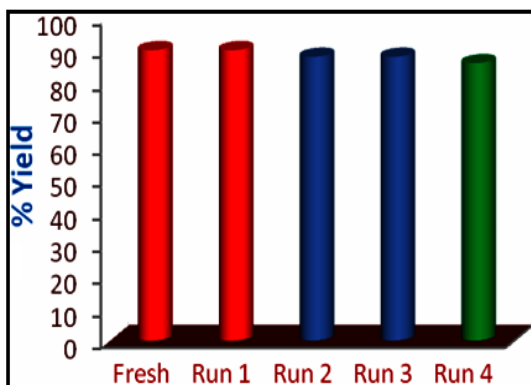


Fig. 2. Graphical representation of yields of the reaction carried out by using reused catalyst PFPAT for the formation of 2-(4'-Chlorophenyl)-benzothiazole (Table 3, 3f)

### CONCLUSION

In this reaction a simple, mild and eco-friendly reaction is reported in presence

of an effective, inexpensive and recyclable organocatalyst for the synthesis of benzothiazole and benzothiazoline derivatives in excellent and moderate yield respectively. In addition this protocol has a tolerance in case of various electron donating and withdrawing substituents which gave high yield of benzothiazole and moderate yield of benzothiazoline. Details mechanism is narrated in this work. It is hoped that in near future this procedure will be useful in terms of academically and industrially.

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### Conflict of Interest

No conflict of interest regarding this article.

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