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Urea nitrate–catalyzed C-N and C-S bond formation: A mechanochemical approach for 5-chloro-2-arylbenzo*[d]* thiazole derivatives

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Abstract

A series of substituted 5-chloro-2-arylbenzo*[d]*thiazoles were synthesized using 4-chloro-2-aminothiophenol and aromatic aldehydes in the presence of urea nitrate as a catalyst using the mechanochemical grindstone technique. This protocol was effectively carried out under metal-free conditions at room temperature, and the desired products were obtained in high to excellent yields in short reaction time (30–60 s). The structure of all the synthesized derivatives was confirmed by spectral characterization. The designed protocol has several benefits like eco-friendly, solvent-free, high yields, easy workup, and recyclability of catalyst. The catalyst was reusable at least four times without significant loss of activity. The good functional group tolerance with a series of derivatives has been demonstrated.

1 | INTRODUCTION

Heterocyclic compounds are pervasive to various sectors of life. They are the most felicitous structural units in pharmaceutical chemistry as the presence of heteroatoms augments their properties [1,2]. Among the heterocyclic compounds, N- and S-bearing scaffolds are of much interest for the researchers [3,4]. One of the prominent heterocyclic moieties, benzothiazole (BT) possesses a thiazole ring, fused with a benzene ring, and serves as a fundamental building block in several organic syntheses and acts as a chief model for the development of numerous therapeutic and potent agents [5–7]. It possesses a plethora of biological and industrial applications, namely antimicrobial [8], anticonvulsant [9], anti-HIV [10], antidiabetic [11], antiparkinson [12], antiproliferative [13], falciparum inhibitors [14], anti-leishmanial [15], *Mycobacterium tuberculosis* shikimate kinase inhibitor [16], polymer chemistry [17], clothing textiles [18], pesticides [19], corrosion inhibitors [20], and so on. Some biologically active scaffolds based on 2-aryl benzothiazole are illustrated in Figure 1.

Due to their pleiotropic nature and immense importance in biological and other related fields, they have drawn the attention of researchers and chemists all across the world. Several synthetic pathways have been designed from time to time for the synthesis of 2-arylbenzothiazole derivatives to enhance their yield and to make the protocol eco-friendly. Still, there is a huge upsurge to design a facile and green procedure for the fabrication of 2-arylbenzothiazole derivatives. Here in, we have employed a green and efficient protocol by grinding of 5-chloro-2-aminothiophenol with different aromatic aldehydes under solvent-free conditions in the presence of urea nitrate as a catalyst.

Urea nitrate is a user-friendly catalyst and easy to prepare. Previously, it has been used to catalyze a range of chemical reactions including regioselective nitration [21], imino Diels–Alder reaction [22], cleavage of oximes under microwave irradiation [23], aromatization of

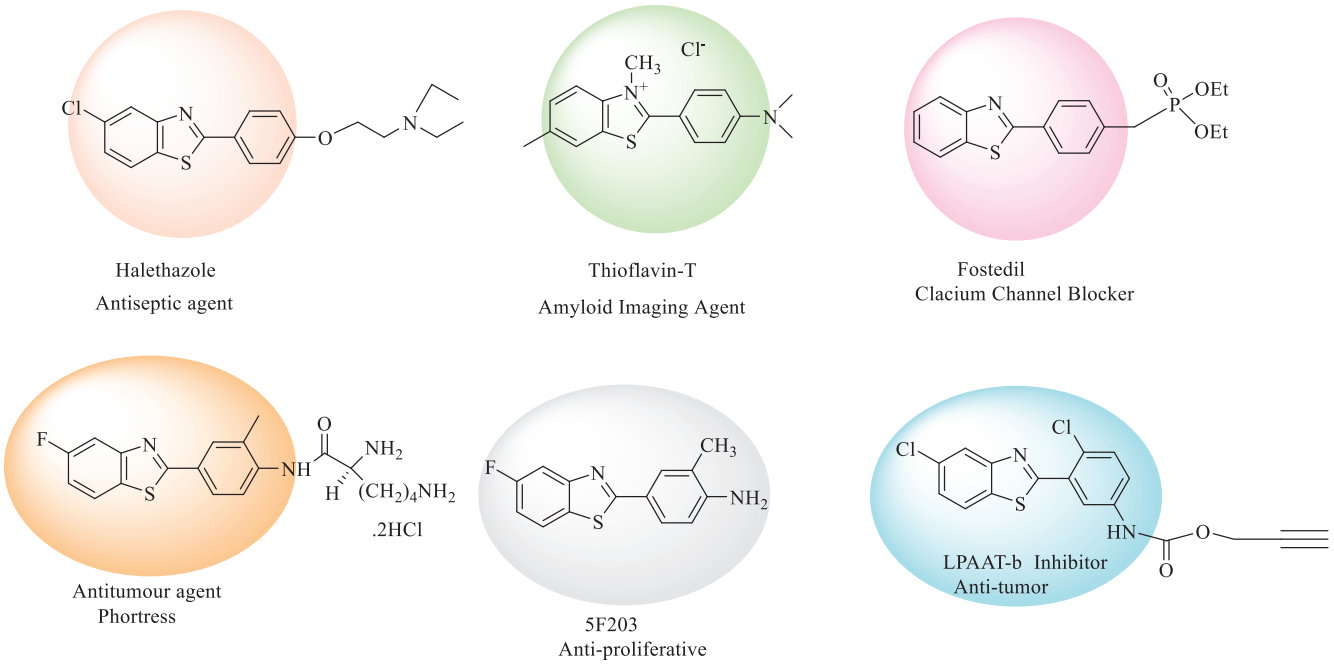


FIGURE 1 Biologically active compounds having 2-arylbenzothiazole scaffolds [Colour figure can be viewed at wileyonlinelibrary.com]

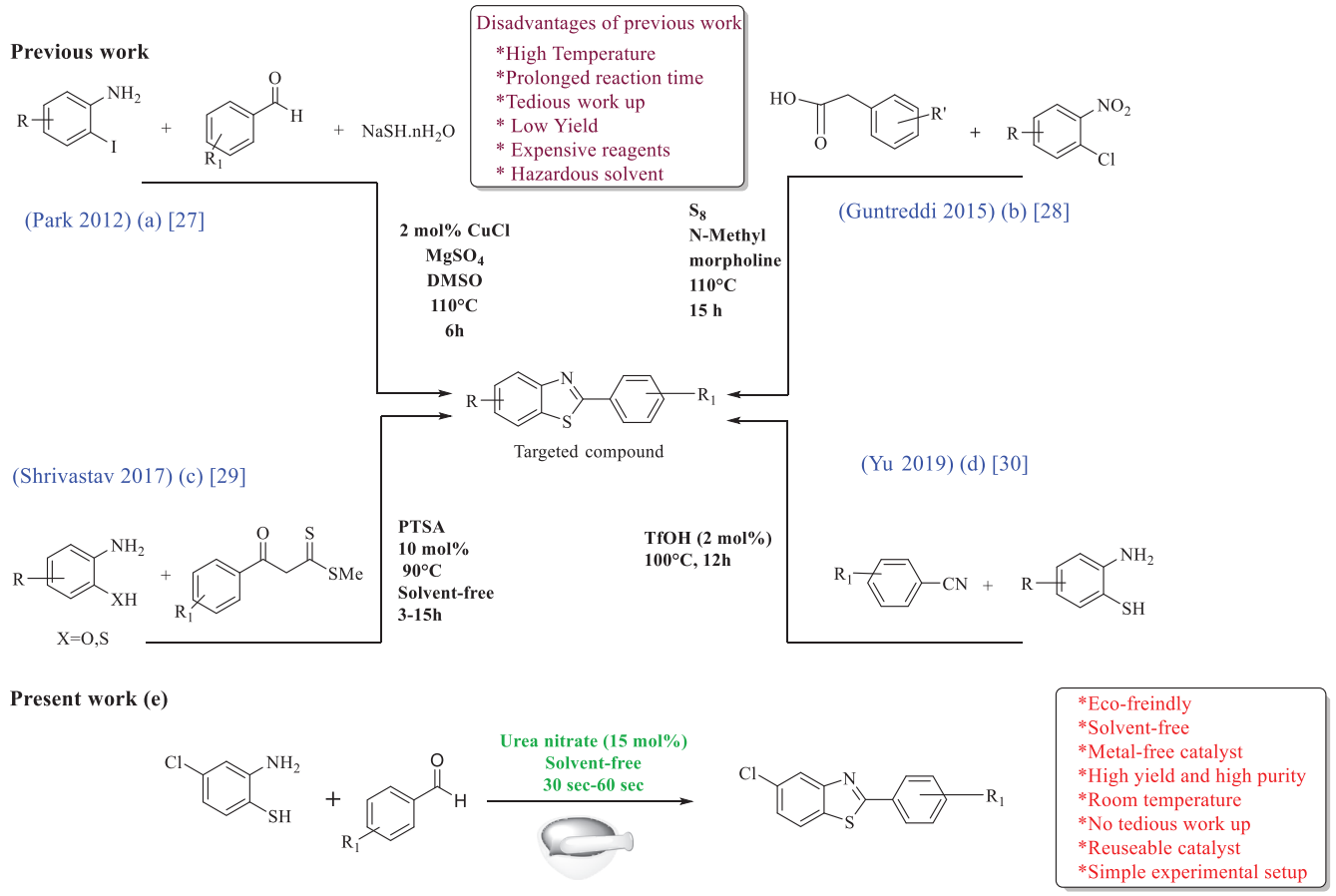
1,4-dihydropyridines [24], and so on. It has also been used to synthesize diversely substituted 2-aryl benzothiazole derivatives by our research group [25], and inspiring from the results and outcomes of our exhaustive literature study [26], we have designed an efficient approach for the synthesis of some new 5-chloro-2-arylbenzothiazole derivatives which has not been reported so far. Several researchers and organic chemists have introduced different pathways for the synthesis of 5-chloro-2-arylbenzo*[d]*thiazole derivatives under diverse reaction conditions using different precursors illustrated in Scheme 1. Park et al. synthesized substituted 2-arylbenzothiazole analogues using substituted 2-iodoanilines, aldehydes, and $NaSH{\cdot}nH_2O$ catalyzed by 2 mol% of CuCl in the presence of $MgSO_4$ and DMSO as a solvent Scheme 1a [27]. Furthermore, the desired product was synthesized by Guntreddi and coworkers [28] using *o*-chloro nitroarenes and aryl acetic acid by the sulfur-mediated decarboxylative redox cyclization Scheme 1b. Another alternative strategy for 2-arylbenzothiazole scaffolds was designed by Srivastav et al. using diversely substituted 2-aminothiophenol with β-oxodithioesters Scheme 1c [29]. Yu and coworkers have synthesized 5-chloro-2-arylbenzothiazole derivatives from 4-chloro-2-aminothiophenol with nitriles Scheme 1d [30]. In addition to all these methods, Senapak et al. devised similar derivatives from 2-aminothiophenol with aromatic aldehydes using Brönsted acid-surfactant-combined ionic liquid (BASILs) [bsdodecim][OTf] as a catalyst in water and tert-butyl hydroperoxide (TBHP) as an oxidant [31]. Similarly, Shah and group synthesized them in the presence of catalytic amount of $Na_2S_2O_5$ using DMF as a solvent and refluxing for 2 h [32]. All of these synthetic protocols have their own merits but include harsh reaction conditions, long reaction time (2–15 h), tedious workup, poor yield, experimental setup, hazardous solvents, high catalyst loading, and costly substrates for the synthesis of catalyst, while our synthetic protocol comprises of several benefits, namely cost-effectiveness, eco-friendly, rapid process, solvent-free, avoid tedious work up, and no need of tough experimental setup and gave high yield of products Scheme 1e.

A comparative study of present protocol with the previously reported literature for the synthesis of 5-chloro-2-aryl benzothiazole derivatives using 4-chloro-2-aminothiophenol with aromatic aldehydes has been illustrated in (Table 1).

2 | RESULTS AND DISCUSSION

2.1 | Chemistry

In progression to our research efforts toward the development of synthetic methodologies for the biologically active 2-arylbenzothiazole and 1,2-disubstituted benzimidazole derivatives [25,34] herein, we have reported a simple and facile synthesis for 5-chloro-2-arylbenzothiazole derivatives from 4-chloro-2-aminothiophenol with substituted



SCHEME 1 Synthesis of substituted 5-chloro-2-phenylbenzo*[d]*thiazole (present and previous approaches) [Colour figure can be viewed at wileyonlinelibrary.com]

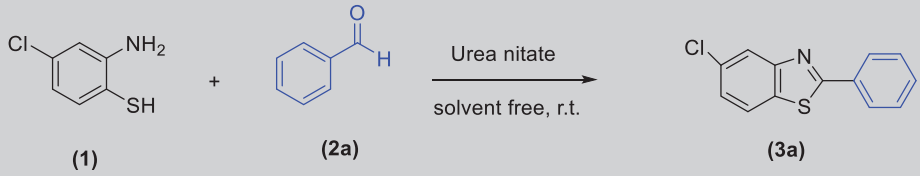
TABLE 1 A comparative study of the present work with different catalysts for the synthesis of 5-chloro-2-aryl benzothiazole derivatives using 4-chloro-2-aminothiophenol and aromatic aldehydes

Entry	Catalyst	Reaction conditions	Yields (%)	Reference
1	[bsdodecim][OTf] (1 mL)	Tert-butyl hydroperoxide (TBHP), stirring at room temperature for 1.5 h	73–81%	Senapak et al. [31]
2	$Na_2S_2O_5$	DMF, reflux, 2 h	41–93%	Shah et al. [32]
3	$RuCl_3$ (0.05 equivalent)	[bmim]PF_6, air, 80°C, 0.5 h	76–88%	Fan et al. [33]
8	Urea nitrate (15 mol%)	Solvent-free, grinding, rt	87–94%	Present work

aromatic aldehydes under green reaction conditions using urea nitrate as a catalyst by simple grinding method (Scheme 1e). Urea nitrate is a low-cost, easy to prepare, and neutralized by water, but it should be tackled with care as being unstable in the presence of moisture and liberates nitric acid [35–36]. It reduces the reaction time by providing solid H^+ ion. The reaction protocol was initiated using 5 mol% of urea nitrate catalyst via mechanochemical grinding in a mortar and pestle in solvent-free conditions with 4-chloro-2-aminothiophenol and benzaldehdye. The progression of reaction was envisioned by the change in color and monitored by TLC. The desired product was obtained in high yields in just few mins. Furthermore, the catalyst loading was studied by successively increasing the catalyst amount to 15 mol%. The results obtained were encouraging, and excellent yields were obtained in short reaction time (Table 2). Further increase in the concentration of catalyst resulted in no change in the yield of reaction.

As per the previously reported literature [25,37], urea nitrate gave good results under solvent-free conditions. Keeping this in mind and also from environmental point of view, we did not examine the reaction under different solvents. With the optimized conditions in hand, a

TABLE 2 Effect of catalyst loading on the model reaction



S. No.	Catalyst loading	Time	Yield (%)
1	No catalyst	10 min	50
2	5 mol%	5 min	80
3	10 mol%	2 min	88
4	12 mol%	1 min	89
5	15 mol%	30 s	92
6	20 mol%	30 s	92

TABLE 3 Synthesis of 2-aryl benzothiazole derivatives in the presence of urea nitrate as the catalyst

				M.P. (°C)	
Entry	**Aldehyde**	**Symbol for product**	**Yield (%)**	**Observed**	**Literature**
1	C_6H_5	**3a**	92	132–134°C	135°C [32]
2	4-OCH_2CH_3 C_6H_4	**3b**	92	124–126°C	128°C [32]
3	4-CH_2CH_3 C_6H_4 (novel)	**3c**	95	90–93°C	–
4	Furfural	**3d**	87	120–121°C	121°C [32]
5	Thiophene	**3e**	88	118–119°C	120°C [32]
6	4-OMe C_6H_4	**3f**	90	147–148°C	148°C [32]
7	4-F C_6H_4	**3g**	93	111–112°C	113–114°C [38]
8	4-Cl C_6H_4	**3h**	94	155–156°C	158°C [32]
9	4-CN C_6H_4	**3i**	89	168–170°C	–
10	3-Cl C_6H_4	**3j**	91	140°C	142–144°C [39]
11	2,5-$(OMe)_2C_6H_3$ (novel)	**3k**	89	102–103°C	–
12	2-Br	**3l**	87	115°C	112–114°C [29]

variety of aldehydes having electron withdrawing and donating substituents and heteroaromatic aldehydes were examined, and all gave high yields irrespective of the nature of substituents (Table 3). These results proved that urea nitrate is efficient toward liquid as well as solid aldehydes. The compounds (**3a–l)** were synthesized and characterized by spectral characterization techniques.

The present work has several benefits like cost-efficient, solvent-free, avoid tedious work up, no need of experimental set up, reusability and recyclability of catalyst. The probable mechanism for the reaction suggested that Schiff base was formed as an intermediate that on intramolecular cyclization gave the desired product. The formation of Schiff base was achieved by the activation of carbonyl group of aldehyde due to urea nitrate. This activated aldehyde reacted with the amino group of thiophenol and formed Schiff base under aerobic conditions which resulted in the formation of desired 2-aryl benzothiazole derivatives (Scheme 2).

2.2 | Recovery and reuse of catalyst

The catalyst urea nitrate is soluble in water and could be easily recovered from the reaction mixture. After completion of the reaction, the ice-cold water was poured to the crude reaction mixture and stirred for some time. A solid mass was seen and filtered. The water was evaporated under reduced pressure to recover urea from the filtrate that can be reused further to make urea nitrate. This

SCHEME 2 Proposed mechanism for the formation of substituted 2-arylbenzothiazole using urea nitrate as a catalyst [Colour figure can be viewed at wileyonlinelibrary.com]

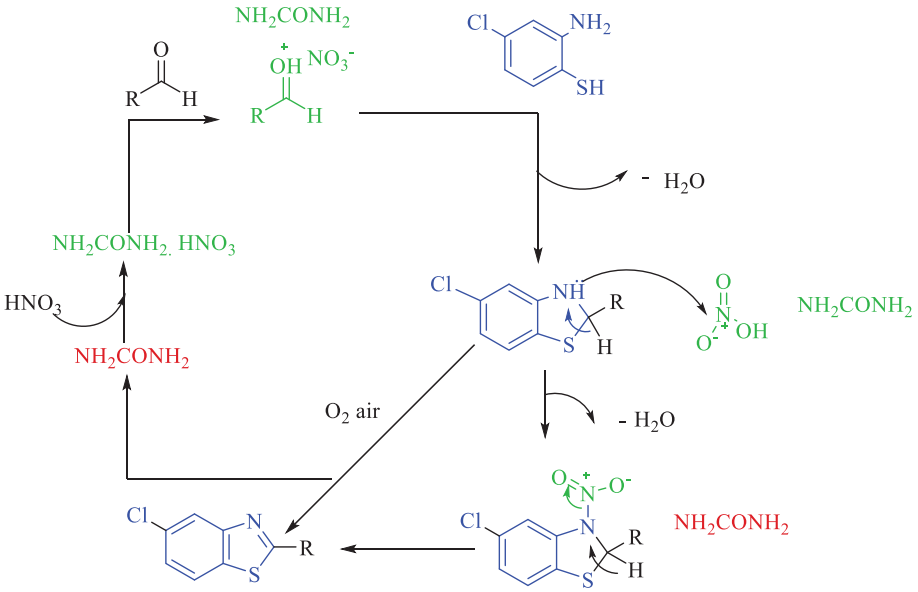


TABLE 4 Recyclability of urea nitrate catalyst for the synthesis of substituted 2-arylbenzothiazole

Catalyst cycle	Fresh	I	II	III	IV	V	VI
Isolated yield	95%	93%	90%	87%	82%	80%	75%

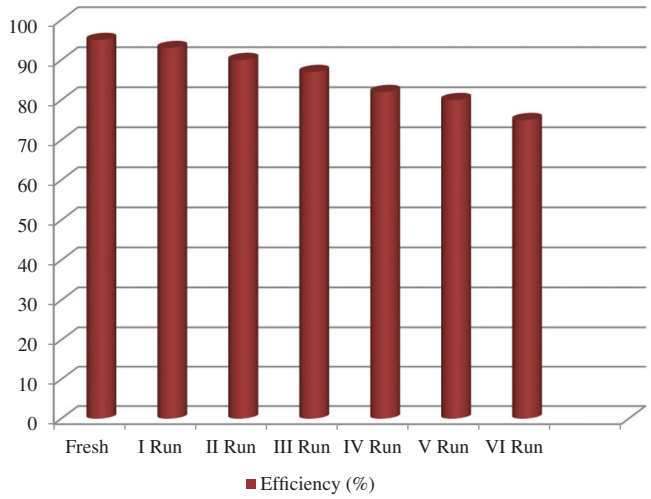


FIGURE 2 Graphical representation of urea nitrate reusability [Colour figure can be viewed at wileyonlinelibrary.com]

recovered urea was further converted to urea nitrate for its reuse as a catalyst. The catalytic efficiency has been appended below in Table 4 and Figure 2.

3 | EXPERIMENTAL DESIGN

3.1 | General

All the chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and Hi-Media and used without further purification. 4-Chloro-2-aminothiophenol was purchased from Sigma-Aldrich. An agate mortar and pestle was used for the synthesis and cleaned with ethanol and acetone. Melting points were recorded in open capillary tubes and were uncorrected. The FT-IR spectrum was analyzed using KBr pellets on a Bruker FT-IR spectrometer. The ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were examined on a Bruker Avance II 500 spectrometer. Tetramethylsilane (TMS) is used as an internal standard and DMSO-d_6 and $CDCl_3$ as a solvent. The purity of synthesized compounds was confirmed by thin layer chromatography (TLC) using silica gel G as an adsorbent and eluting with hexane: ethyl acetate. The catalyst urea nitrate was synthesized from the previously reported literature [37].

3.2 | General procedure for synthesis of 2-arylbenzothiazoles (3a–l)

4-Chloro-2-aminothiophenol (1 mmol), aromatic aldehyde, and urea nitrate (15 mol%) were grounded together in a mortar and pestle under solvent-free conditions at room temperature. In all the cases, initially reactant became a pasty mass on grinding and then converted to fine powder. A drastic change in color and physical state appeared in just few seconds (30–60 s; Figure 3). The completion of reaction was monitored by TLC. The catalyst was separated from the reaction mixture by pouring

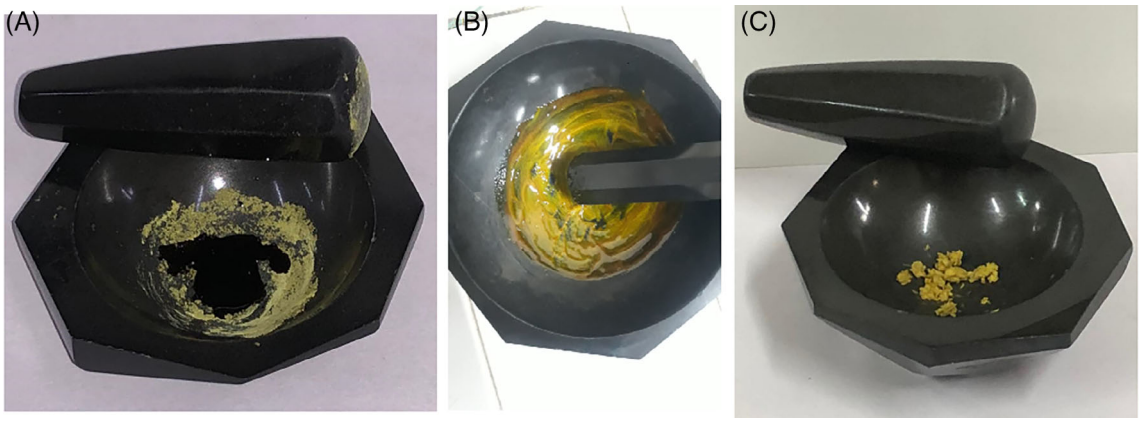


FIGURE 3 Reaction between 4-chloro-2-aminothiophenol and 2-thiophene carbaldehdye in the presence of catalytic amount of urea nitrate. A, reactants with catalyst before reaction; B, during grinding, the reaction mixture became pasty mass; C, after the reaction, the pasty mass turned into powder [Colour figure can be viewed at wileyonlinelibrary.com]

ice-cold water to it and stirred for 30 min. The solid residue left after filtration was recrystallized with ethanol.

3.3 | Spectral characterization

3.3.1 | 5-Chloro-2-phenylbenzo*[d]* thiazole (3a)

White solid; yield 92%; m.p. 132–134°C; IR(KBr): 2925, 1620, 1485, 1421, 1050, 755 cm^{-1}; ^1H NMR (500 MHz, $DMSOd_6$) δ 7.19 (d, J = 3 Hz, 2H), 7.33–7.37(m, 2H), 7.52 (s, 1H), 7.64 (s, 1H), 8.20–8.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 122.4, 122.6, 122.8, 124.3, 126.1, 129.62, 129.64, 130.22, 130.29, 131.9, 133.8, 154.8, 168.9; MS (EI): m/z 245.01 [M^+].

3.3.2 | 5-Chloro-2-(4-ethoxyphenyl)benzo *[d]*thiazole (3b)

Yellow solid; yield 92%; m.p. 124–126°C; IR(KBr): 3030, 2925, 2890, 1637, 1485, 1398, 1261, 1050, 790 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, 3H, OCH_2CH_3), 4.20 (q, J = 6.8 Hz, 2H, OCH_2CH_3), 6.50 (d, J = 7.65 Hz, 1H, Ar-H), 7.06 (dd, J = 50 Hz, 8 Hz, 1H, Ar-H), 7.25–7.36 (m, 1H, Ar-H), 7.45(d, J = 7.9 Hz, 1H, Ar-H), 7.78 (d, J = 8.3 Hz, 1H, Ar-H), 7.98(d, J = 7.95 Hz, 2H, Ar-H), ^{13}C NMR (125 MHz,$CDCl_3$) δ 14.8, 63.7, 114.7, 114.9, 122.6, 125.1, 125.8, 128.5, 128.7, 129.2, 129.7, 155, 158.3, 161.6, 169.8; MS (EI): m/z 289.03 [M^+].

3.3.3 | 5-Chloro-2-(4-ethylphenyl)benzo *[d]*thiazole (3c)

Light mehandi green; yield 95%; m.p. 90–93°C; IR(KBr): 2957, 1648, 1449, 1321, 1250, 980, 790 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 7.5 Hz, 3H, CH_2CH_3), 2.61–2.69 (q, J = 7.3 Hz, 2H, CH_2CH_3), 7.25–7.34 (m, 3H, Ar-H), 7.77(d, J = 8.35 Hz, 1H, Ar-H), 7.97–8.03(m, 3H, Ar-H), ^{13}C NMR (125 MHz, DMSO d_6) δ 15.5, 28.8, 125.4, 127.2, 127.6, 128.2, 128.6, 130.7, 132.2, 133.2, 137.9, 143.5, 155.0, 170.1; MS (EI): m/z 273.04 [M^+].

3.3.4 | 5-Chloro-2-(furan-2-yl)benzo*[d]* thiazole (3d)

Light yellow solid; yield 87%; m.p. 120–121°C; IR(KBr): 2895, 1742, 1554, 1421, 1232, 1150, 980, 780 cm^{-1}; ^1H NMR: (500 MHz, DMSO d_6) δ 7.16 (dd, J = 8.5 Hz, 1 Hz, 1H,), 7.26 (dd, J = 6.5 Hz, J = 2 Hz, 1H), 7.30–7.36 (m, 1H), 7.58 (dd, 1H, J = 7 Hz, 1 Hz), 7.59–7.60 (m, 1H), 7.89 (dd, J = 8 Hz, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO d_6) δ 117.1, 122.7, 124.8, 125.3, 125.6, 127.0, 128.1, 129.0, 141.4, 149.2, 154.5; MS (EI): m/z 235.69 [M^+].

3.3.5 | 5-Chloro-2-(thiophen-2-yl) benzothiazole (3e)

Golden yellow solid; yield 88%; m.p. 118–119°C; IR(KBr): 2945, 1625, 1456, 1374, 1219, 1046, 775 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, J = 5 Hz, 3.75 Hz), 7.31 (dd, J = 8.5 Hz, 2 Hz, 1H), 7.51 (dd, J = 5 Hz, 1.1 Hz, 1H), 7.64 (dd, J = 3.75 Hz, 1.1 Hz, 1H); 7.72 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 1.95 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.8, 125.3, 127.0, 128.1, 129, 129.8, 132.4, 132.9, 154.5, 163.1; MS (EI): m/z 251.75 [M^+].

3.3.6 | 5-Chloro-2-(4-methoxyphenyl) benzo*[d]*thiazole (3f)

White solid; 90% yield; m.p. 147–148°C; IR(KBr): 2921, 2850, 1662, 1558, 1445, 1211, 1090, 759 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$)] δ 3.8 (s, 3H, CH_3-H), 7.26 (dd, J = 8.79 Hz, 1.33 Hz, 2H, Ar-H), 7.46 (dd, J = 8.5 Hz, 1.8 Hz, 1H, Ar-H), 7.54 (dd, J = 7.5 Hz, 1 Hz, 1H, Ar-H), 7.8 (dd, J = 8.7 Hz, 1.5 Hz, 2H, Ar-H), 7.9 (dd, J = 1.83, 0.5 Hz, 1H, Ar-H); ^{13}C NMR (125 MHz,$CDCl_3$) δ 55.8, 114.2, 114.5, 121.2, 122.9, 124.5, 127.3, 128.8, 129.2, 130.5, 134, 150.7, 160.4, 167.1; MS (EI): m/z 275.02 [M^+].

3.3.7 | 5-Chloro-2-(4-fluorophenyl)benzo*[d]*thiazole (3g)

White solid; 93% yield; m.p. 111–112°C; IR(KBr): 2975, 1664, 1451, 1402, 1210, 1096, 780 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$)] δ 7.24–7.31 (m, 3H, Ar-H), 7.55 (d, J = 1 Hz, 1H, Ar-H), 7.65 (d, J = 7.5 Hz, 1H, Ar-H), 7.73 (d, J = 7.5 Hz, 1H, Ar-H), 8.02 (d, J = 1 Hz, 1H, Ar-H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.08, 115.1, 119.4, 122.4, 122.6, 122.7, 127.8, 129.1, 130.9, 136.3, 153.6, 160.1, 168.9; MS (EI): m/z 263.71 [M^+].

3.3.8 | 5-Chloro-2-(4-chlorophenyl)benzo*[d]*thiazole (3h)

White solid; 93% yield; m.p. 155–156°C; IR (KBr): 2949, 1596, 1450, 1332, 1218, 1154, 1042 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$)] δ 7.33 (dd, J = 8.5 Hz, 2 Hz, 1H, Ar-H), 7.43–7.45 (m, 2H, Ar-H), 7.76 (d, J = 8.5 Hz, 1H, Ar-H), 7.95–7.98 (m, 2H, Ar-H), 8.01 (d, J = 1.9 Hz, 1H, Ar-H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 122.3, 123.1, 125.8, 128.7, 129.3, 131.7, 132.5, 133.2, 137.4, 154.9, 168.4; MS (EI): m/z 278.97 [M^+].

3.3.9 | 5-Chloro-2-(4-cyanophenyl)benzo*[d]*thiazole (3i)

White solid; 89% yield; m.p. 168–170°C; IR (KBr): 2972, 2250, 1630, 1455, 1232, 1178, 1042, 980, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$)] δ 7.41 (dd, J = 8.55 Hz, 2.0 Hz, 1H, Ar-H), 7.78–7.80 (m, 2H, Ar-H), 7.84 (d, J = 8.5 Hz, 1H, Ar-H), 8.08 (d, J = 1.95 Hz, 1H, Ar-H), 8.17–8.19 (m, 2H, Ar-H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.5, 118.1, 122.5, 123.5, 126.6, 128.0, 132.8, 132.9, 133.5, 137.0, 154.8, 167.1; MS (EI): m/z 270.73 [M^+].

3.3.10 | 5-Chloro-2-(3-chlorophenyl)benzo*[d]*thiazole (3j)

Light yellow; solid; 91% yield; m.p. 140°C; IR (KBr): 2972, 2250, 1630, 1455, 1232, 1178, 1042, 980, 743 cm^{-1}; ^{1}H NMR (500 MHz, $DMSOd_6$)] δ 7.40–7.44 (m, 2H, Ar-H), 7.50 (dd, J = 8.55 Hz, 2.1 Hz, 2H, Ar-H), 8.12 (d, J = 1.95 Hz, 1H, Ar-H), 8.13–8.16 (m, 2H, Ar-H), 8.18 (d, J = 0.25 Hz, 1H, Ar-H), ^{13}C NMR (125 MHz, DMSO d_6) δ 116.3, 116.5, 122.1, 123.7, 125.5, 129.0, 129.6, 131.3, 133.2, 154.2, 168.3; MS (EI): m/z 278.97 [M^+].

3.3.11 | 5-Chloro-2-(2,5-dimethoxyphenyl)benzo*[d]*thiazole (3k)

White solid; 89% yield; m.p. 102–103°C; IR (KBr): 3050, 2950, 1455, 1232, 1205, 1148, 1022, 850, 758 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$)] δ 3.90 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 6.99 (d, J = 9 Hz, 1H, Ar-H), 7.03 (dd, J = 9 Hz, 3 Hz, 1H, Ar-H), 7.32 (dd, J = 8.5 Hz, 2 Hz, 1H, Ar-H), 7.80 (d, J = 8.5 Hz, 1H, Ar-H), 8.05 (m, 2H, Ar-H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.0, 56.4, 112.6, 113.4, 119.2, 121.9, 122.4, 122.5, 125.1, 131.8, 134.5. 151.9, 152.9, 153.9, 164.7; MS (EI): m/z 305.78 [M^+].

3.3.12 | 5-Chloro-2-(2-bromophenyl)benzo*[d]*thiazole (3l)

Light yellow; solid; 87% yield; m.p. 140°C; IR (KBr): 2872, 1530, 1475, 1272, 1168, 1032, 950, 745, 650 cm^{-1}; ^{1}H NMR (500 MHz, DMSO d_6)] δ 7.51–7.58 (m, 4H, Ar-H), 7.78 (dd, J = 7.7 Hz, 1.4 Hz, 1H, Ar-H), 8.16 (dd, J = 7.6 Hz,1.95 Hz, 1H, Ar-H), 8.30–8.82 (s, 1H, Ar-H), ^{13}C NMR (125 MHz, DMSO d_6) δ 120.7, 121.2, 122.9, 124.9, 127.6, 127.7, 130.6, 130.7, 131.7, 132.0, 134.1, 154.5, 167.8; MS (EI): m/z 324.62 [M^+].

4 | CONCLUSION

The search of privileged structures in drug discovery is a hastily emerging area in synthetic chemistry. For this, designing of an eco-benign protocol is inevitable. In lieu of this, a facile, green, cost-effective pathway for biologically active scaffold has been designed using 4-chloro-2-aminothiophenol with aromatic aldehydes catalyzed by urea nitrate. 5-Chloro-2-aryl benzo*[d]*thiazole derivatives were synthesized through eco-friendly pathway in significant yields in a very short period of reaction time. The present work is highly beneficial as it involved a low-cost robust catalyst, solvent-free, easy work up, no waste generation, metal-free, and no need of column chromatography. Moreover, the developed synthetic pathway will be helpful to fabricate diversely substituted benzothiazole derivatives as it has good compatibility with all types of

aldehydes. In assessment, this one-pot synthesis is found to be an efficient method to synthesize diversely substituted 2-aryl benzothiazole derivatives. The simple experimental setup is supposed to be highly potential for the synthesis of complex molecules.

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DATA AVAILABILITY STATEMENT

Data available on request due to privacy/ethical restrictions. The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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SUPPORTING INFORMATION

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