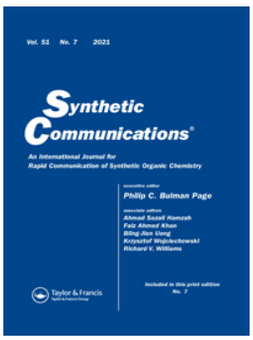

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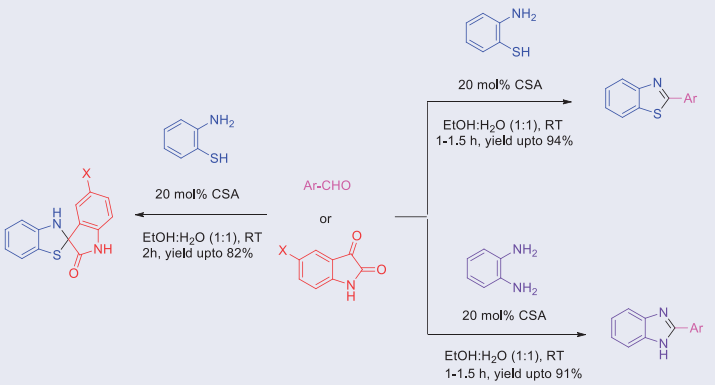
ABSTRACT

A simple, mild, eco-friendly, general, and convenient approach has been developed for the synthesis of structurally diverse 2-arylbenzothiazole derivatives from the reactions of 2-aminothiophenol and various aromatic aldehydes using camphor sulfonic acid a low cost, commercially available, efficient organo-catalyst in aqueous ethanol at room temperature. Under the same optimized conditions, a series of 2-arylbenzimidazoles was also synthesized starting from *o*-phenylenediamines and various aldehydes whereas synthesis of 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-ones was accomplished from the reactions of 2-aminothiophenol and substituted isatins.

GRAPHICAL ABSTRACT



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2-arylbenzimidazoles; 2-arylbenzothiazoles; camphor sulfonic acid; 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-ones; organocatalysis

Introduction

Benzothiazole and benzimidazole skeletons are very common in naturally occurring bioactive compounds (Figure 1).[1–8] Many commercially available drug molecules bearing

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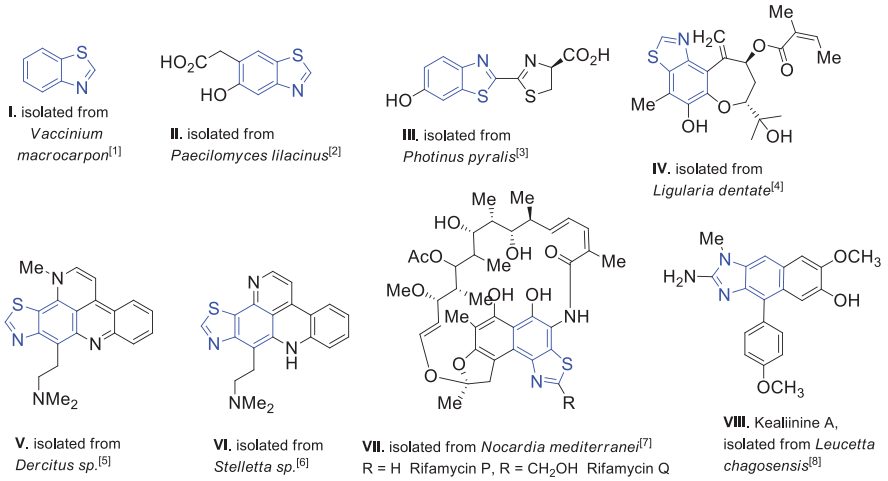


Figure 1. Naturally occurring bioactive compounds containing benzimidazole or benzothiazole skeleton.

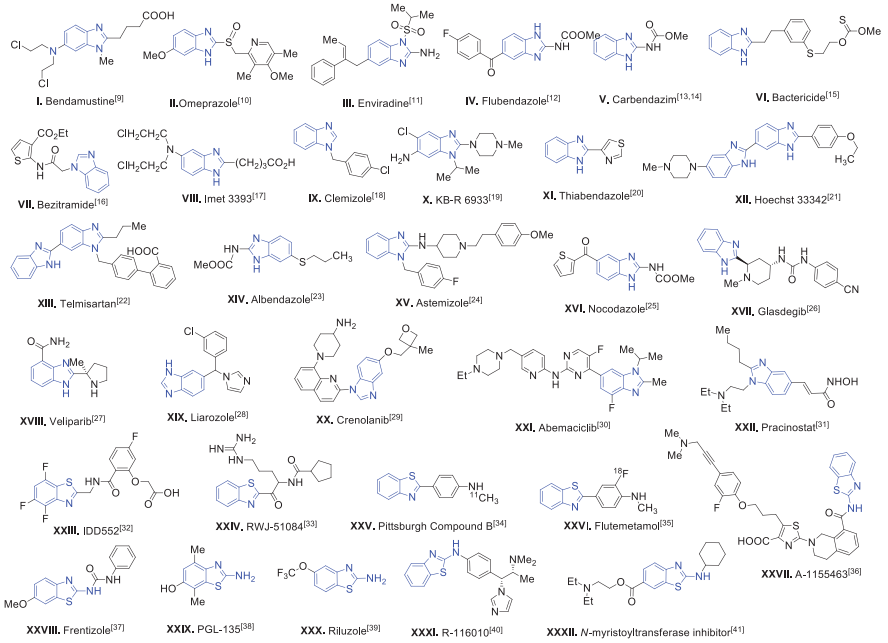


Figure 2. Important drug molecules containing benzimidazole or benzothiazole moieties.

benzothiazole or benzimidazole as the main structural unit (Figure 2).[9–41] Recent studies revealed that various synthetic benzothiazole or benzimidazole derivatives possess significant biological efficacies such as anti-oxidant, anti-tumor, anti-cancer, anti-proliferative, anti-anxiety, etc. activities (Figure 3).[42–71]

After noticing the huge biological importance of benzothiazole as well as benzimidazole derivatives, scientists were motivated to synthesize a variety of such derivatives under various reaction conditions. Among many others, during the last two decades,

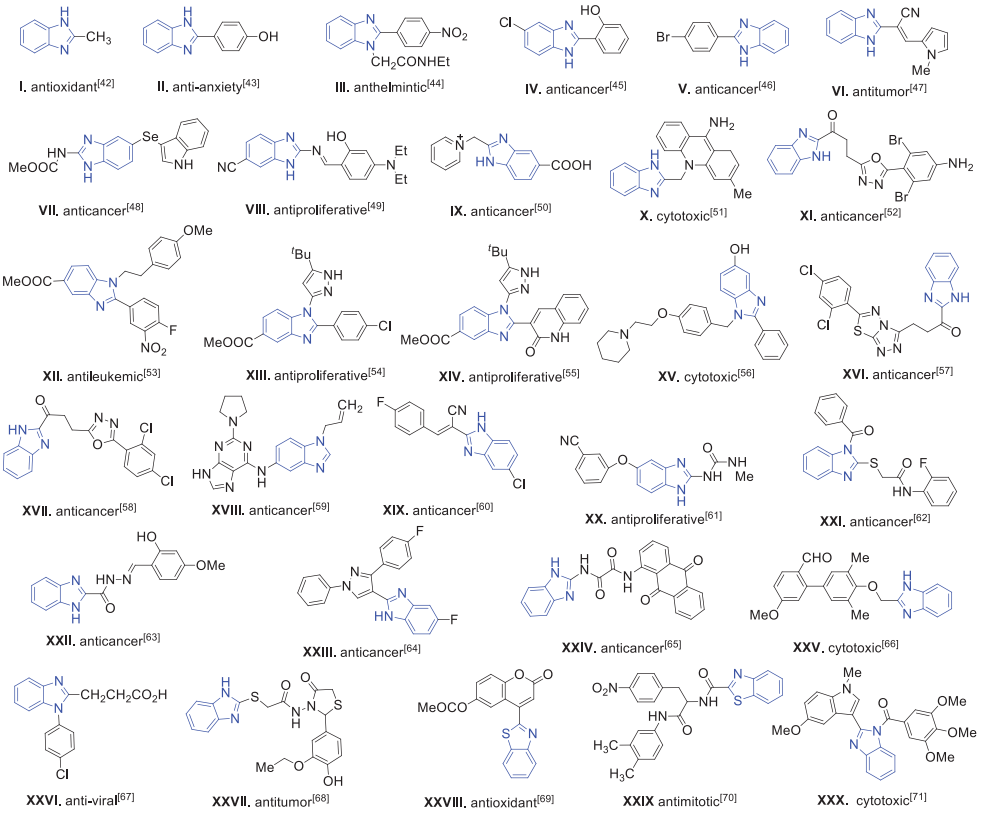


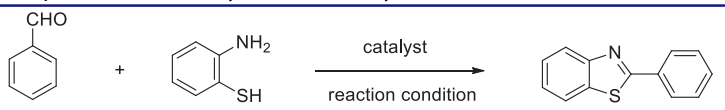
Figure 3. Glimpse of bioactive synthetic benzimidazole and benzothiazole derivatives.

both 2-arylbenzothiazoles and 2-arylbenzimidazoles gained huge attention. As a result, a large number of methods were reported for the synthesis of 2-arylbenzothiazoles from the reactions of various aromatic aldehydes and 2-aminothiophenol in the presence of a variety of homogeneous or heterogeneous catalysts under various reaction conditions (Table 1).[72–91] On the other hand, 2-arylbenzimidazoles were synthesized from the reactions of various aromatic aldehydes and *o*-phenylenediamine by using various catalytic systems under diverse reaction conditions (Table 2).[92–131] Though these reported protocols have some merits still many of them are suffering in terms of green chemistry perspectives due to the use of metal-containing catalysts and toxic organic solvents. Moreover, in some cases, high catalyst loading, heating, microwave-irradiation, ball milling, visible light, etc. were required additionally. Besides, all these reported methods are focused only on a particular scaffold, that is, either synthesis of 2-arylbenzothiazoles or 2-arylbenzimidazoles.

Therefore, search for an efficient and general route for the synthesis of both 2-arylbenzothiazoles as well as 2-arylbenzimidazoles by using a metal-free organocatalyst under greener conditions still remains a valid exercise.

Under these environmentally conscious days, metal-free organocatalysts have gained tremendous attention due to their environmental friendliness.[131–136] Among many others, camphor sulfonic acid (CSA) has also come out as an efficient, low cost,

Table 1. Reported protocols for the synthesis of 2-arylbenzothiazoles. .



1 2 3

Entry	Catalyst	Solvent	Temp.	Time	Yield (%)[REF]
1	*β*-CD	H_2O	60–65 °C	4–10 h	81[72]
2	30%H_2O_2/37%HCl	EtOH	RT	45 min	90[73]
3	NH_4Cl	CH_3OH:H_2O	RT	30 min	84[74]
4	12 W blue LED	EtOAc	RT	6 h	91[75]
5	SnP_2O_7	EtOH	Reflux	10 min	95[76]
6	*Acacia concinna*	Neat	MW	4 min	93[77]
7	PIFA	EtOH	MW, 80 °C	15 min	87[78]
8	I_2	Neat	MW	3 min	92[79]
9	H_2O_2 (30 %)/ CAN	Neat	50 °C	13 min	97[80]
10	*tert*-butyl hypochlorite	CH_3CN	Reflux	2.5 h	88[81]
11	$HClO_4$/PANI	EtOH	Reflux	2 h	85[82]
12	Nano-ZnO	Neat	Ball-mill	30 min	91[83]
13	PTSA	H_2O	70 °C	5 h	97[84]
14	$Sm(OTf)_3$	EtOH:H_2O	55 °C	2 h	89[85]
15	I_2	DMF	100 °C	25 min	88[86]
16	Baker's Yeast	CH_2Cl_2	RT	24 h	80[87]
17		Glycerol	RT	30 min	92[88]
18	CAN	MeOH	RT	10 h	75[89]
19	$ZnBr_2$-ABM	Toluene	110 °C	75 min	69[90]
20	*L*-Proline	Neat	MW	1 h	99[91]
21	CSA	EtOH:H_2O	28–32 °C	1 h	93[this work]

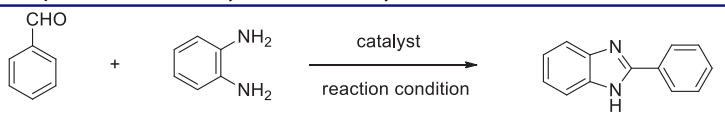
TBHP: tert-Butyl hydroperoxide; CAN: ceric ammonium nitrate; $HClO_4$/PANI: perchloric acid/doped polyaniline; PTSA: para-toluene sulfonic acid; ABM: animal bone meal.

commercially available organocatalyst.[137] In continuation of our strong interest in organo-catalyzed protocols,[138–143] in this communication we wish to report camphor sulfonic acid-catalyzed a simple, efficient, and general method for the synthesis of 2-arylbenzothiazoles, 2-arylbenzimidazoles, and 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-one derivatives in aqueous ethanol at room temperature (Schemes 1 and 2).

Results and discussion

To optimize the reaction condition, we carried out a series of trial reactions between freshly distilled benzaldehyde (**1a**; 1 mmol) and 2-aminothiophenol (**2**; 1 mmol) under various reaction conditions at ambient temperature. At first, we performed the reaction under catalyst as well as solvent-free conditions at room temperature which produced only a trace amount of the desired product after 4 h (Table 3, entry 1). Less than 10% yield was observed under catalyst-free conditions in water after 4 h (Table 3, entry 2). After obtaining poor yields under catalyst-free conditions we realized the necessity of a suitable catalyst to promote this reaction. Initially, in continuation of our strong interest with mandelic acid as catalyst, for this reaction also we employed 20 mol% mandelic acids as catalyst in water which afforded 53% of 2-phenylbenzo[*d*]thiazole (**3a**) after 2 h (Table 3, entry 3). Using the same amount of catalyst in ethanol, we obtained **3a** with a 62% yield after 2 h (Table 3, entry 4). The same reaction in methanol (Table 3, entry 5)

Table 2. Reported protocols for the synthesis of 2-arylbenzimidazoles.



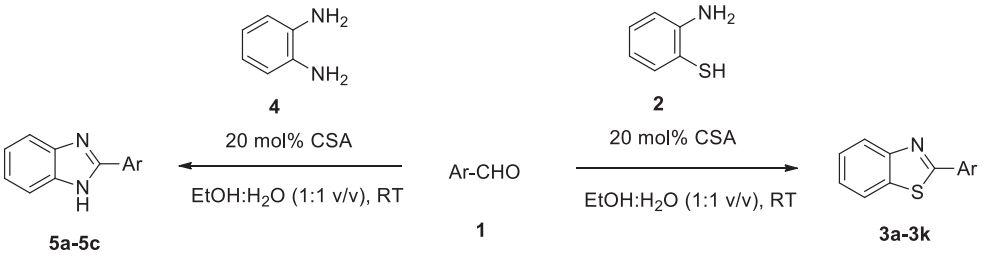
1 4 5

Entry	Catalyst	Solvent	Temp.	Time	Yield (%)[REF]
1	SBSA	H_2O	RT	25 min	97[92]
2	p-TsOH	DMF	80 °C	10 min	85[93]
3	$NaHSO_3$	DMAc	MW	10 min	88[94]
4	CAN	dry DCM	Reflux	45 min	75[95]
5	$FeCl_3/Al_2O_3$	DMF	25 °C	2 h	86[96]
6	$ZnCl_2$-SiO_2	Neat	MW	5 min	94[97]
7	CAN	PEG-400	50 °C	2 h	98[98]
8	Fe/MgO	MeOH	RT	25 min	92[99]
9	$La(OTf)_3$	CH_3CN-H_2O	RT	3 h	86[100]
10	*L*-Proline, pH 4.2	H_2O	Reflux	5 h	97[101]
11	$LaCl_3$	CH_3CN	RT	3 h	88[102]
12	$Zn(OTf)_2$	EtOH	Reflux	8 h	94[103]
13	Oxalic acid	Neat	MW	4 min	95[104]
14	Blue LEDs (7 W)	MeOH	RT	7 h	96[105]
15	NH_4Cl	$CHCl_3$	RT	4 h	94[43]
16	$Er(OTf)_3$	Neat	80 °C	5 h	78[106]
17	tert-butyl nitrite	THF	RT	2 h	75[107]
18	[Cu(BHPPDAH)H_2O]	EtOH	RT	2 h	95[108]
19	NH_4Cl	EtOH	80–90 °C	2.5 h	63[109]
20	Na_3AlF_6	EtOH	RT	11 h	80[110]
21	$K_4[Fe(CN)_6]$ grinding	Neat	RT	—	97[111]
22	PbO_2	Neat	RT	10 min	94[112]
23	H_3BO_3	H_2O	RT	30 min	92[113]
24	$[bmim]PF_6$	H_2O	Reflux	2 h	92[114]
25	Fe_3O_4 NPs	EtOH	RT	4 h	86[115]
26	$Co(OH)_2$ /CoO	EtOH	RT	6 h	93[116]
27	$MnZrO_2$-450	EtOH	80 °C	60 min	95[117]
28	Pt/TiO_2	Mesitylene	Reflux	24 h	78[118]
29	RuO_2-MoO_3	EtOH	Reflux	55 min	90[119]
30	$Ce(NO_3)_3.6H_2O$	DMF	80 °C	1.5 h	93[120]
31	$CoCl_2.6H_2O$	CH_3CN	RT	4 h	81[121]
32	$LaCl_3$	CH_3CN	RT	3 h	88[122]
33	MgI_2	EtOAc	RT, hν	6 h	93[123]
34	$MgCl_2.6H_2O$	DMF	60 °C	100 min	93[124]
35	YCl_3	CH_3CN	RT	3 h	88[125]
36	$[Epty]BF_4$	Neat	MW	20 min	90[126]
37	Amberlite IR-120	Neat	MW	4 min	92[127]
38	H_5IO_6-SiO_2	CH_3CN	RT	20 min	94[128]
39	Glacial acetic acid	Neat	MW	25 min	92[129]
40	$CuFe_2O_4$ NPs	Toluene	110 °C	24 h	94[130]
41	CSA[a]	EtOH:H_2O	28–32 °C	1 h	87[this work]

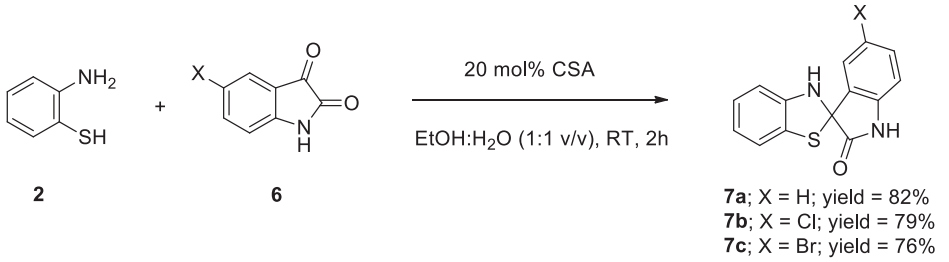
[a]Instead of benzaldehyde we have used *p*-chlorobenzaldehyde.

BHPPDAH: *N*,*N*-bis(2-hydroxylphenyl)pyridine-2,6-diarboxamide; CAN: ceric ammonium nitrate; SBSA: silica boron sulfonic acid.

or acetonitrile (Table 3, entry 6) as solvent afforded 59% or 38% yields respectively. Slight better yield (72%) was obtained aqueous-ethanol (1:1 v/v) as solvent through the time required still 2 h (Table 3, entry 7). From these preliminary studies, it was established that aqueous-ethanol may be the best suitable solvent to carry out this reaction. But we were unsatisfied with the performance of mandelic acid for this reaction and that is why we reinvestigated the catalytic efficiency of some other metal-free organo-

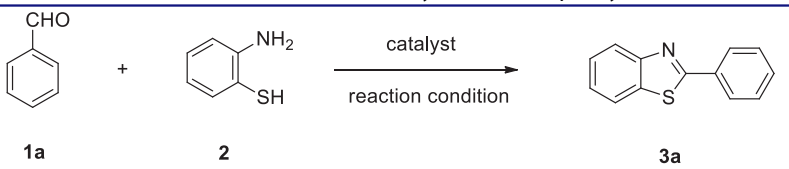


Scheme 1. CSA-catalyzed synthesis of 2-arylbenzothiazoles and 2-arylbenzimidazoles at room temperature.



Scheme 2. CSA-catalyzed synthesis of 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-ones at room temperature.

Table 3. Optimization of reaction conditions for the synthesis of 2-phenylbenzo[*d*]thiazole.



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)[a,b]
1.	Catalyst-free	Neat	4	trace
2	Catalyst-free	H_2O	4	10
3	Mandelic acid (20)	H_2O	2	53
4	Mandelic acid (20)	EtOH	2	62
5	Mandelic acid (20)	MeOH	2	59
6	Mandelic acid (20)	MeCN	2	38
7	Mandelic acid (20)	H_2O:EtOH	2	72
8	Itaconic acid (20)	H_2O:EtOH	2	66
9	Palmitic acid (20)	H_2O:EtOH	2	54
10	CSA (20)	H_2O:EtOH	1	93
11	CSA (15)	H_2O:EtOH	1	82
12	CSA (25)	H_2O:EtOH	1	93

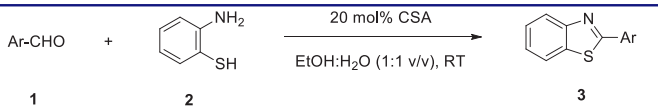
[a]Reaction conditions: benzaldehyde (**1**; 1 mmol) and 2-aminothiophenol (**2**; 1 mmol) in the absence or presence of a catalytic amount of camphor sulfonic acid in neat/4 mL of water/ethanol/methanol/aqueous ethanol at 28–32 °C; [b]isolated yields.

catalysts. When we employed 20 mol% of itaconic acid (Table 3, entry 8) or palmitic acid (Table 3, entry 9) as a catalyst in aqueous-ethanol it produced 66% or 54% of **3a** respectively after 2 h. When we employed 20 mol% camphor sulfonic acid (CSA) as a catalyst in aqueous ethanol, surprisingly, the reaction completed within just 1 h and

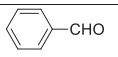
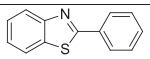
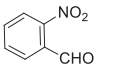
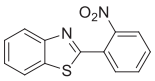
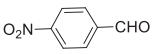
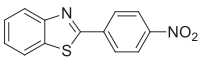
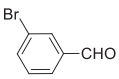
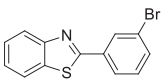
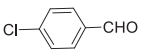
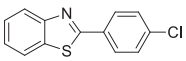
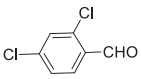
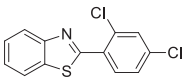
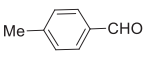
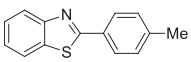
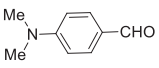
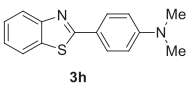
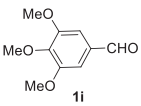
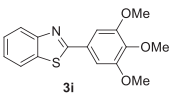
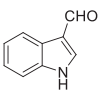
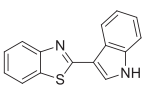
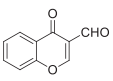
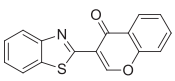
yielded 93% of the desired product (Table 3, entry 10). We then standardized the amount of required catalyst by maintaining other parameters remain fixed. More than 10% less product (82%) was isolated using 15 mol% of CSA (Table 3, entry 11) whereas no significant improvement was observed in the product formation even after increasing the catalyst amount to 25 mol% (Table 3, entry 12). Therefore, it was optimized that 20 mol% of camphor sulfonic acid (CSA) is sufficient for the efficient synthesis of 2-phenylbenzo[*d*]thiazole (**3a**) from the unimolar reaction of benzaldehyde (**1a**) and 2-aminothiophenol (**2**) in aqueous ethanol at room temperature (Table 3, entry 10). To check the generality of our developed protocol we were interested to synthesize a series of other derivatives of 2-arylbenzothiazoles under the same optimized reaction conditions. It is our delight to mention that we were successful to synthesize ten other derivatives of 2-arylbenzothiazoles (**3 b-3k**) with excellent yields (74-94%) from the reactions of various aromatic aldehydes (**1b–1k**) and 2-aminothiophenol (**2**) (Table 4, entries 2-11). Aldehydes with both electron-withdrawing as well as donating substituent underwent smoothly and afforded the desired products with excellent yields. It may be due to steric reason *o*-nitrobenzaldehyde (Table 4, entry 2) yielded a lesser product than *p*-nitrobenzaldehyde (Table 4, entry 3). Heteroaryl aldehydes such as indole-3-carboxaldehyde (Table 4, entry 10) and chromone-3-carboxaldehyde (Table 4, entry 11) also produced the desired products with excellent yields. To extend the scope of our developed protocol, we then planned to carry out the reactions between aldehydes (**1**, 1 mmol) and *o*-phenylenediamine (**4**, 1 mmol) instead of 2-aminothiophenol (**2**) under the same reaction conditions which afforded the corresponding 2-arylbenzimidazoles (**5a**-**5c**) with excellent yields (79–91%) within 90 min (Table 5, entries 1–3). Moreover, under the same optimized reaction conditions synthesis of 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-ones (**7a–7c**) was also achieved from the reaction of 2-aminothiophenol (**2**; 1 mmol) and isatins (**6**; 1 mmol) with excellent yields (76–82%) (Scheme 2).

All the synthesized compounds were obtained pure just by simple filtration and washing the crude products subsequently with aqueous ethanol. No column chromatographic purification was required. We were successful to synthesize 2-phenylbenzo[*d*]thiazole (**3a**; 1.77 g, 84%) in gram scale within 3 h from the reactions of freshly distilled 10 mmol benzaldehyde (**1a**; 1.06 g) and 10 mmol 2-aminothiophenol (**2**; 1.25 g) using 20 mol% CSA (0.46 g) in aqueous ethanol (20 ml) at room temperature. All the synthesized compounds were well characterized by the detailed physical as well as spectroscopic analyses of ^{1}H NMR, ^{13}C NMR, and HRMS. It is also noted worthy to mention that we were able to form a single crystal of one derivative, that is, compound **7a**. ORTEP view of the compound **7a** is shown in Figure 4. In this ORTEP small spheres of arbitrary radii represent H atoms. Figure 5 shows the packing view of molecules down *a*-axis within the unit cell of compound **7a**. From the X-ray structure, it is confirmed that the molecules in the unit cell are bound by the intermolecular N–H … O hydrogen bonds (Figure 6). A plausible mechanism for the formation of 2-arylbenzothiazoles is shown in Figure 7.

Table 4. Synthesis of 2-arylbenzothiazoles (**3a**–**3k**) using camphor sulfonic acid as catalyst at room temperature.

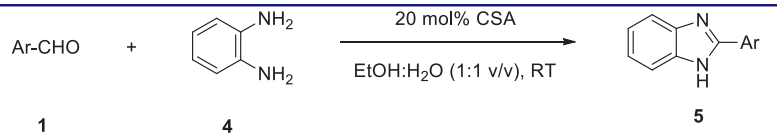


1 2 3

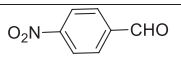
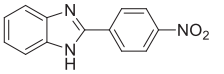
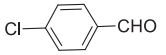
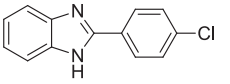
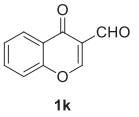
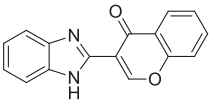
Entry	Ar-CHO	Product	Time (h)	Yield (%)[a,b]
1	 **1a**	 **3a**	1	93
2	 **1b**	 **3b**	1	89
3	 **1c**	 **3c**	1	94
4	 **1d**	 **3d**	1	88
5	 **1e**	 **3e**	1	91
6	 **1f**	 **3f**	1.5	83
7	 **1g**	 **3g**	1	88
8	 **1h**	 **3h**	1	86
9	 **1i**	 **3i**	1.5	82
10	 **1j**	 **3j**	1.5	79
11	 **1k**	 **3k**	1.5	74

[a]Reaction conditions: aldehydes (**1**; 1 mmol) and 2-aminothiophenol (**2**; 1 mmol) in the presence of 20 mol% camphor sulfonic acid as catalyst in aqueous ethanol at 28–32 °C. [b]Isolated yields.

Table 5. Synthesis of 2-arylbenzimidazoles (**5a**–**5c**) using camphor sulfonic acid as catalyst at room temperature.



1 **4** **5**

Entry	Ar-CHO	Product	Time (h)	Yield (%)[a,b]
1	 **1c**	 **5a**	1	91
2	 **1e**	 **5b**	1	87
3	 **1k**	 **5c**	1.5	79

[a]Reaction conditions: aldehydes (**1**; 1 mmol) and *o*-phenylenediamine (**4**; 1 mmol) in the presence of 20 mol% camphor sulfonic acid as catalyst in aqueous ethanol at 28–32 °C. [b]Isolated yields.

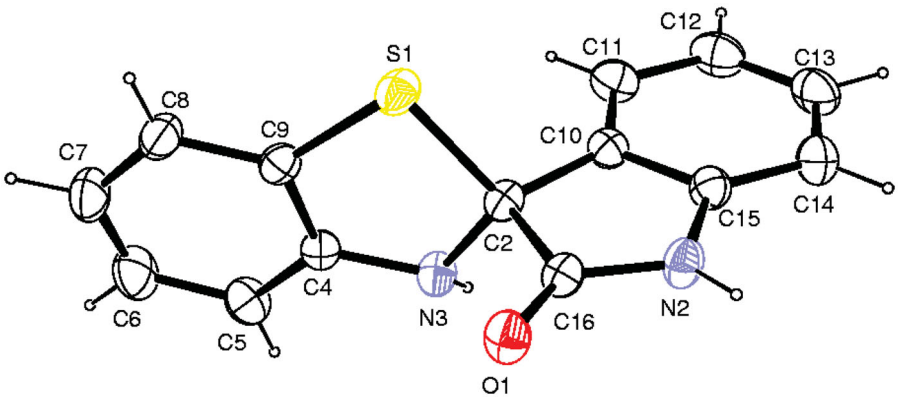


Figure 4. ORTEP view of the molecule **7a** with displacement ellipsoids drawn at 50% probability level (CCDC 2025015).

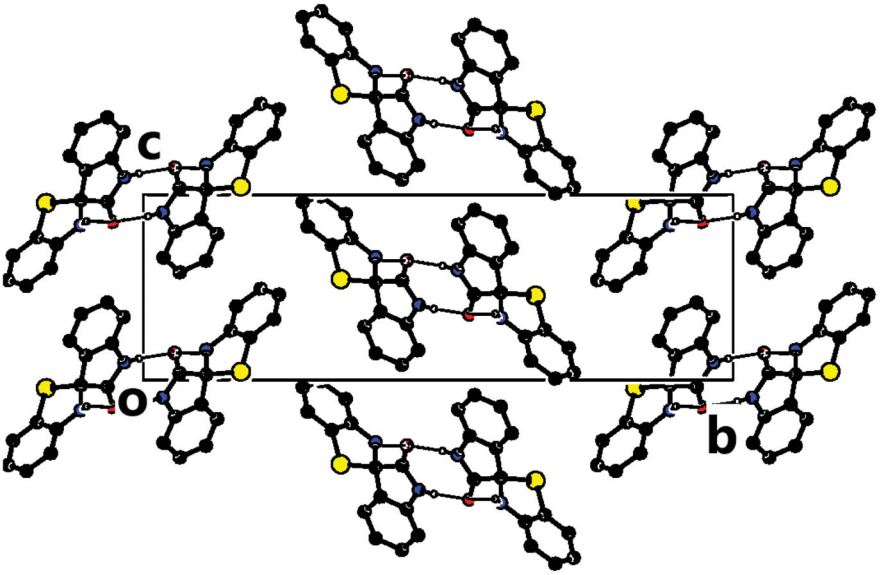


Figure 5. Packing view of the molecules in the unit cell viewed down the *a*-axis.

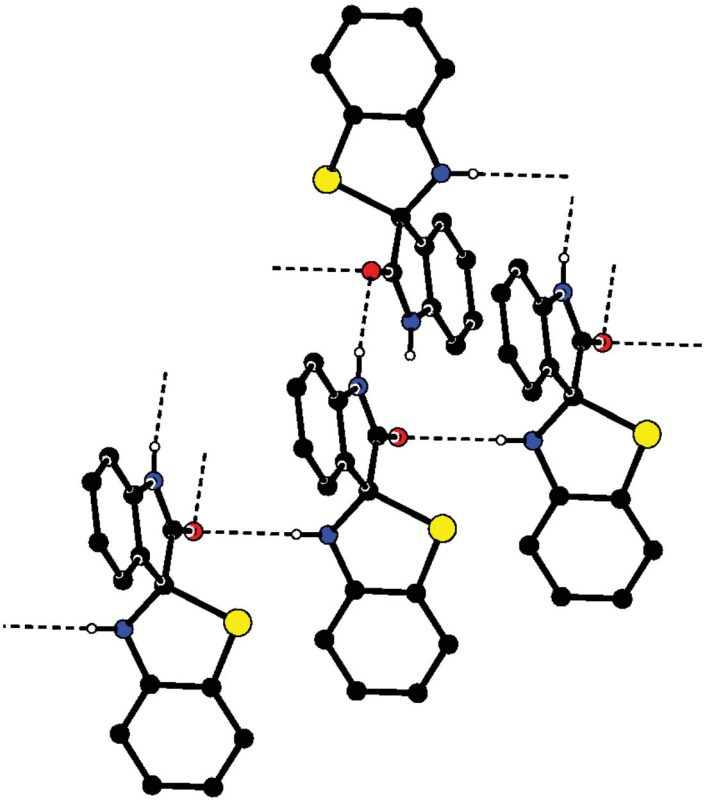


Figure 6. A plot of molecules of the compound **7a** showing the intermolecular N–H … O hydrogen bonds.

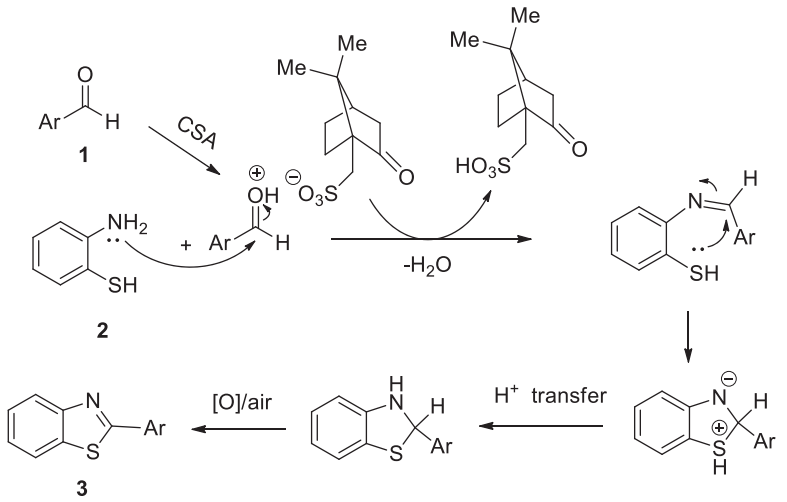


Figure 7. Plausible mechanism for the synthesis of 2-arylbenzothiazoles using CSA as catalyst.

Experimental section

General

Melting points were recorded on a Digital Melting Point Apparatus (Model No. MT-934) and are uncorrected. TLC was performed on silica gel 60 F254 (Merck) plates. Infrared spectra were recorded on Agilent (Cary 660) FT-IR spectrophotometer on KBr disks. ^{1}H and ^{13}C NMR spectra were obtained at 500 MHz Jeol (JNM ECX-500) NMR machines with $CDCl_3$ as the solvent. Mass spectra (TOF-MS ES^+) were measured on a Bruker Impact HD QTOF Micro mass spectrometer.

General procedure for the synthesis of 2-phenylbenzo[d]thiazole (3a)

In a dry screw-cap test tube a magnetic stir bar, benzaldehyde (**1a**; 1 mmol), 2-amino-thiophenol (**2**; 1 mmol), 4 mL aqueous ethanol and a catalytic amount of camphor sulfonic acid (20 mol%) were taken sequentially. On a magnetic stirrer, the reaction mixture was then stirred vigorously at room temperature and it was monitored by TLC. After completion of the reaction, the yellow product was isolated pure just by simple filtration and washing the crude products with aqueous ethanol (H_2O:EtOH = 1:2) subsequently. The structure of the synthesized compound was confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS analysis.

2-Phenylbenzo[d]thiazole (**3a**): Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.10-8.08 (1H, m, aromatic H), 8.07 (1H, s, aromatic H), 7.91 (1H, d, $J = 7.5$ Hz, aromatic H), 7.55–7.53 (1H, m, aromatic H), 7.51-7.48 (2H, m, aromatic H), 7.39 (1H, t, $J = 7.5$ Hz, aromatic H), 7.35-7.32 (2H, m, arpmatic H); ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 146.35, 131.09, 129.14, 128.88 (2 C), 127.66, 126.66, 126.432, 125.30, 123.32, 121.73, 120.81, 109.83; HRMS (ESI-TOF) m/z: For $C_{13}H_9NS$ Calcd. $[M+H]^+$ 212.0534; Found $[M+H]^+$ 212.0535.

General procedure for the synthesis of 2-(4-nitrophenyl)-1H-benzo[d]imidazole (5a)

By repeating the before mentioned procedure, 2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole (**5a**) was also synthesized from the reaction of *p*-nitrobenzaldehyde (**1c**; 1 mmol) and *o*-phenylenediamine (**4**; 1 mmol) in the presence of a catalytic amount of camphor sulfonic acid as catalyst under the same optimized conditions. The structure of the synthesized compound was confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS analysis.

2-(4-Nitrophenyl)-1*H*-benzo[*d*]imidazole (**5a**): Reddish solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.63 (1H, s), 8.31 (2H, d, $J = 8.25$ Hz, aromatic H), 8.06 (2H, dd, $J = 8.95$, 6.90, & 2.05 Hz, aromatic H), 7.14–7.12 (2H, m, aromatic H), 6.81–6.75 (2H, m, aromatic H), 4.25 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 153.73, 148.96, 143.09, 141.89, 135.58, 129.14, 129.08 (2 C), 123.99 (2 C), 118.43, 116.87, 115.80. HRMS (ESI-TOF) *m/z*: For $C_{13}H_9N_3O_2$ Calcd. $[M + H]^+$ 240.0773; Found $[M + H]^+$ 240.0546.

General procedure for the synthesis of 3H-spiro[benzo[d]thiazole-2,3′-indolin]-2′-one (7a)

Synthesis of 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-one **(7a)** was achieved from the reaction of 2-aminothiophenol (**2**; 1 mmol) and isatin (**6**; 1 mmol) using the same 20 mol% of camphor sulfonic acid as catalyst in aqueous ethanol at room temperature.

3*H*-Spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-one (**7a**): Off white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 11.01 (1H, s, NH), 7.63 (1H, d, $J = 7.5$ Hz, aromatic H), 7.42 (1H, s, NH), 7.29 (1H, t, $J = 7.5$ & 4.0 Hz, aromatic H), 7.10 (2H, t, $J = 10.5$ & 7.5 Hz, aromatic H), 7.00 (1H, t, $J = 7.5$ Hz, aromatic H), 6.85–6.81 (2H, m, aromatic H), 6.73 (1H, d, $J = 7.5$ Hz, aromatic H); ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 168.49, 146.32, 141.12, 139.49, 137.69, 130.89, 126.11, 125.79, 123.86, 121.79, 121.56, 110.84, 110.42, 73.35; HRMS (ESI-TOF) *m/z*: For $C_{14}H_{10}N_2OS$ Calcd. $[M + Na]^+$ 277.0412; Found $[M + Na]^+$ 277.0262.

Conclusions

In conclusion, we have developed a simple, facile, efficient, and general method for the synthesis of a series of structurally diverse 2-arylbenzothiazole derivatives via the condensation reactions of various aromatic aldehydes and 2-aminothiophenol using a catalytic amount of camphor sulfonic acid as catalyst in aqueous ethanol at room temperature. Reactions of aromatic aldehydes and *o*-phenylenediamine afforded the corresponding 2-arylbenzimidazole derivatives. Under the same optimized conditions, synthesis of 3*H*-spiro[benzo[*d*]thiazole-2,3′-indolin]-2′-ones was also achieved from the reactions of 2-aminothiophenol and isatins. Mild reaction conditions, use of metal-free commercially available low-cost organocatalyst, high yields, short reaction times, column chromatography-free purification procedure, and gram-scale production are some of the major advantages of this developed protocol.

Full experimental detail, scanned spectra including ^{1}H-NMR, ^{13}C-NMR, and HRMS of all the synthesized scaffolds are supplemented in supporting information. This material can be found via the "Supplementary Content" section of this article's webpage.'

Acknowledgments

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