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Article

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On Water: Metal-free Synthesis of Highly Functionalized Benzothiazolylidene from *ortho*-Haloanilines

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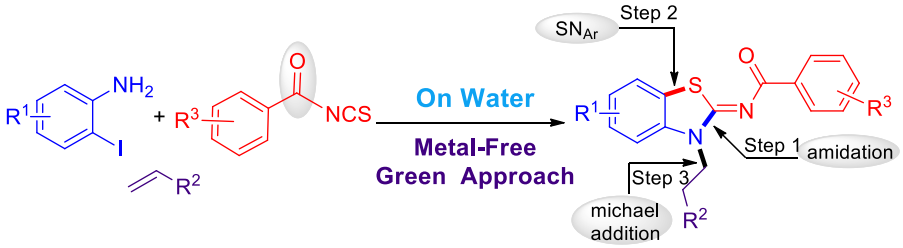


• **Metal-Free** • **Mild Condition** • **Green Solvent** • **Broad Substrate Scope**

ABSTRACT: An environmentally benign, transition-metal-free organic base promoted one-pot cascade synthesis of highly functionalized benzo[*d*]thiazol-2(3*H*)-ylidene benzamide in the presence of water has been accomplished by three-component reaction of *ortho*-iodoanilines, acrylates, and aroyl isothiocyanates. The protocol involves the *in situ* generation of thiourea intermediate followed by triethylamine induced intramolecular SN_{Ar} displacement reaction and subsequent Michael addition onto acrylate leads to the formation of benzo[*d*]thiazol-2(3H)-ylidene benzamide. Benzo[*b*]thiazole is also generated in good yields using amidation and intramolecular aromatic nucleophilic substitution chemistry. The control experiments support the proposed mechanistic pathway. Further X-ray crystallographic studies confirm the assigned structures of the fused benzamide.

INTRODUCTION

Heterocyclic processes in nature frequently inspire the organic chemist to discover new organic reactions for the synthesis of biologically active pharmacophores.[1] Among various efforts committed towards the development of bio-active compounds, cascade process [2] has appeared as a potent synthetic tool in modern organic chemistry. The evolution of unique five-membered heterocyclic framework is particularly important in drug discovery. In this perspective, the benzothiazolylidene and benzothiazole core reserve privileged structure in medicinal chemistry as antitumor agents, neuronal nicotinic receptor, anti-rotavirus infections, nuclear hormone receptor, anti-infective herbicidal, anti-inflammatory, anti-viral, anticonvulsant, and cardiovascular activity (Figure 1).[1-4]

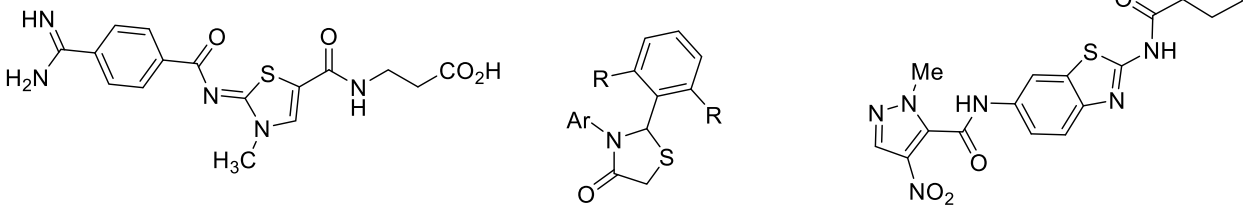
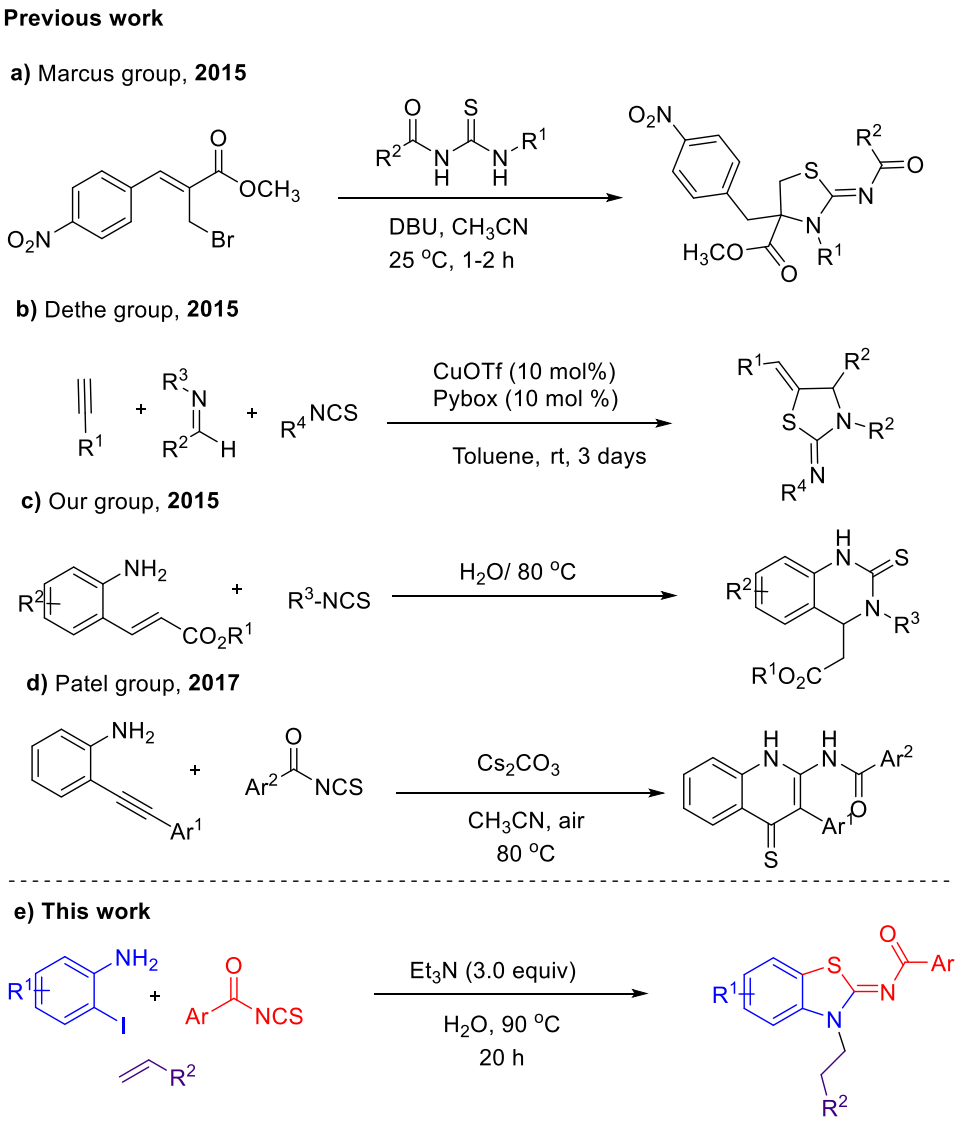


Figure 1. Medicinally important thiazolylidene and benzothiazole cores.

Industrial chemical processes mainly emphasis on the use of a metal-catalyst strategy. Recent years have validated great progress in the development of small ring heterocycles using tandem and cascade approaches.[5] In general, the transition metal catalyst is high- priced and often require a supporting ligand which invents the overall process eco-unfriendly. As a result, the sustainable development of metal-free catalysis is in high demand. Some improvements in the methodology

for the formation of benzothiazoles *via* amidation chemistry have been described by many research groups.[6] However, the synthesis of benzo[*d*]thiazol-2(3H)-ylidene in the absence of metal and ligand is quite rare.[7]

Scheme 1. Previous Strategies *vs* Present Work



In past decades Bao,[8] and Smith III[9] groups reported the synthesis of *N*-substituted-2-aminobenzothiazoles from 2-haloanilines and isothiocyanates using 15 mol% copper (I) in DMSO at 95-115 °C. In 2015, Marcus *et al.* demonstrated DBU promoted synthesis of 2-

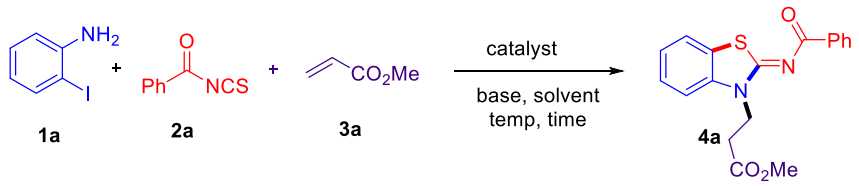
iminothiazolidines by employing substituted thioureas and allylic bromides (Scheme 1a).[10] Recently Dethe and co-workers[11a] developed a facile route for the synthesis of thiazolidine-2-imines and thiazolidine-2-ylideneamine using catalytic chiral copper–pybox complex under solvent-free conditions (Scheme 1b). In 2017, the same group reported an improved method for the synthesis of thiazolidine-2-ylideneamines by thiol-yne coupling of propargylamine under solvent-free condition by bond anion relay chemistry.[11b] In 2015, our group reported a green protocol, for the synthesis of functionalized tetrahydroquinazolines from 2-aminophenylacrylate with excellent chemoselectivity (Scheme 1c).[12] Recently, Patel and co-workers reported an interesting chemistry for the synthesis of quinoline-4(1*H*)-thiones from aroyl isothiocyanates and *o*-alkynylanilines by a *6-exo-dig S*-cyclization of the in situ generated thiourea followed by rearrangement (Scheme 1d).[13] Despite novelty and versatility of reported methods, metal-free, sustainable and operationally simple synthetic methods are still in demand. In continuation of our efforts on sustainable approaches for the synthesis of biologically useful molecules,[14] herein we have demonstrated the base-promoted one-pot synthesis of benzo[*d*]thiazol-2(3*H*)-ylidene benzamides *via* amidation followed by intramolecular SN_{Ar} displacement and Michael-addition reaction (Scheme 1e).

RESULTS AND DISCUSSION

A successful cascade synthesis of benzothiazolylidene required the catalytic system with high efficiency and cost-effective reagents. With this objective, we started our investigation using 2-iodoaniline **1a**, benzoyl isothiocyanate **2a**, and methyl acrylate **3a** as our model substrates (Table 1). The three component reaction of 2-iodoaniline **1a**, benzoyl isothiocyanate **2a** with **3a** using 10 mol% of bis(triphenylphosphine)palladium chloride and 2.5 equiv of triethylamine in water for 20 h at 100 ^{o}C, gave the benzothiazolylidene product **4a** in 70% yield

(entry 1). Switching, the water to polar organic solvents such as DMF and DMSO, did not provide the desired product **4a** (entries 2–3).

Table 1. Optimization of the Bio-active Benzothiazolylidene[a]

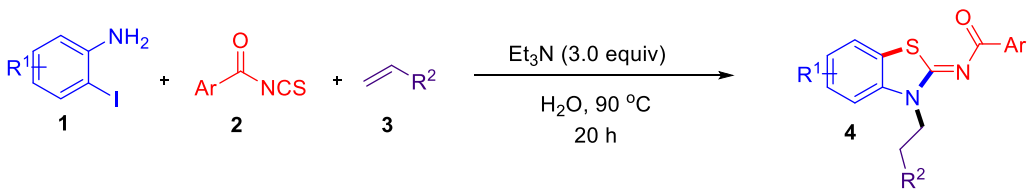


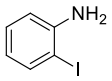
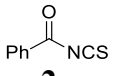
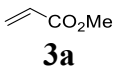
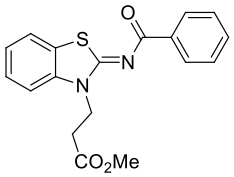
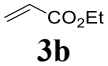
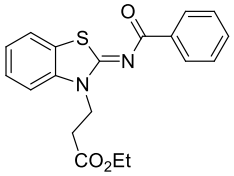
entry	catalyst (mol %)	base (equiv)	solvent	T (h) / t (°C)	yield (%)[b] **4a**
1	$Pd(PPh_3)_2Cl_2$/10	Et_3N / 2.5	H_2O	20/100	70
2	$Pd(PPh_3)_2Cl_2$/10	Et_3N / 2.5	DMF	20/100	00[c]
3	$Pd(PPh_3)_2Cl_2$/10	Et_3N / 2.5	DMSO	20/100	00[c]
4	-	Et_3N / 2.5	H_2O	20/90	75
5	-	Et_3N / 3.0	H_2O	20/90	85
6	-	Et_3N / 3.0	H_2O	24/90	85
7	-	Et_3N / 3.0	H_2O	24/70	50
8	-	Et_3N / 2.0	H_2O	20/90	60
9	-	Cs_2CO_3/ 2.0	H_2O	24/90	40
10	-	K_2CO_3/2.0	H_2O	24/90	35
11	-	Na_2CO_3/2.0	H_2O	24/90	28
12	-	KOH/2.0	H_2O	24/90	00[d]
13	-	-	H_2O	24/90	00
14	-	Et_3N / 3.0	EtOH	20/90	15[e]

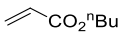
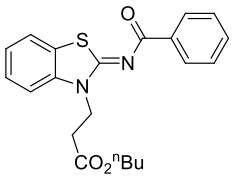
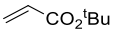
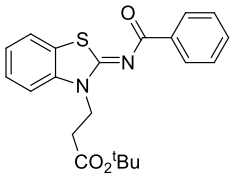
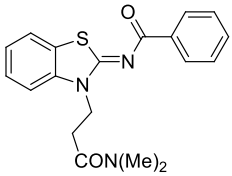
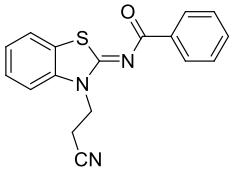
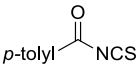
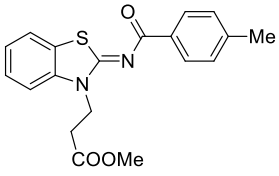
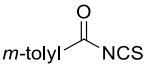
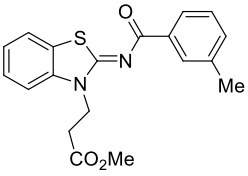
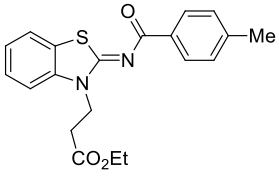
[a]Unless otherwise noted all reactions were carried out using 2-iodoaniline **1a** (0.50 mmol), benzoyl isothiocyanate **2a** (0.52 mmol), methyl acrylate **3a** (2.50 mmol), catalyst and base in 2 mL solvent, [b]Isolated yield. [c]Only urea intermediate was observed. [d]Benzo[*d*]thiazole product was observed. [e]Along with benzo[*d*]thiazole product.

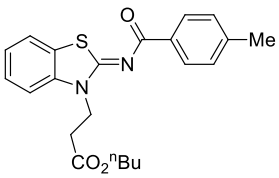
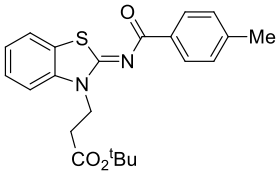
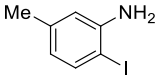
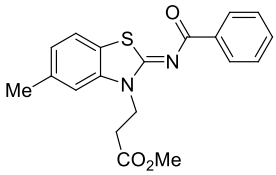
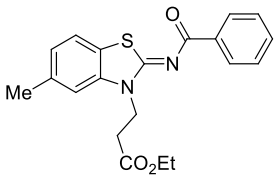
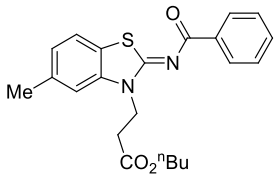
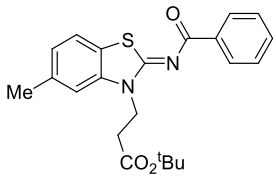
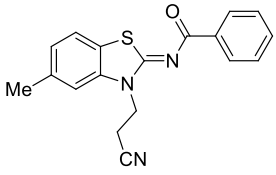
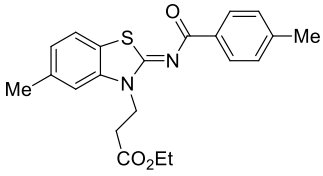
An interesting result was observed when the reaction was carried out in the absence of palladium catalyst; the product **4a** was obtained in 75% yield (entry 4). To our delight, the isolated yield was improved to 85% by decreasing the reaction temperature from 100 °C to 90 °C (entry 5). On running the reaction for 24 h, didn't affect the yield of the coupled product **4a** (entry 6). The further decrease in reaction temperature afforded the desired product **4a** in 50% yield (entry 7). Lowering the amount of Et_3N provided the cyclized product **4a** in 60% yield (entry 8). Use of Cs_2CO_3, K_2CO_3, and Na_2CO_3, instead of Et_3N furnished the product **4a** in lower yield (entries 9–11). KOH provided the Benzo[d]thiazole product in 40% yield (entry 12). It is noteworthy that no desired product **4a** was obtained in the absence of a base (entry 13). Ethanol gave product **4a** in 15% yield along with benzo[*d*]thiazole product (entry 14).

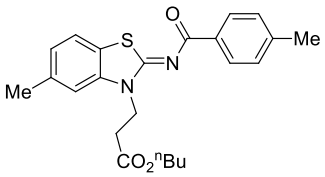
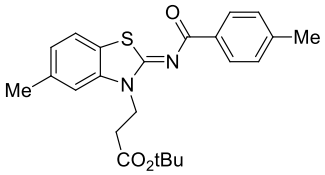
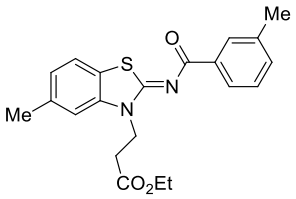
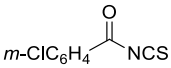
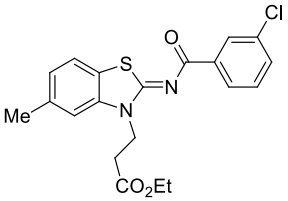
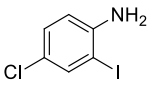
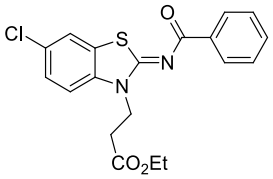
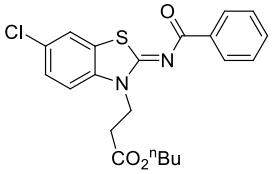
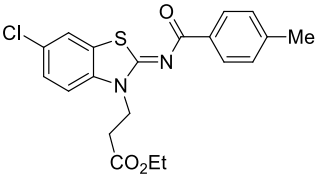
Table 2. Synthesis of Benzothiazolylidene Benzamide

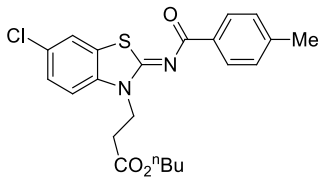
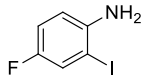
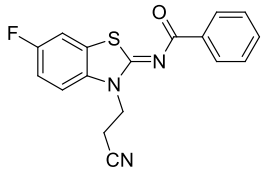


entry	anilines **1**	acyl iso-thiocyanate **2**	alkenes **3**	product **4**	yield (%)
1	 **1a**	 **2a**	 **3a**		**4a**	85
2	**1a**	**2a**	 **3b**		**4b**	84

3	**1a**	**2a**	 **3c**		**4c**	82
4	**1a**	**2a**	 **3d**		**4d**	78
5	**1a**	**2a**	 **3e**		**4e**	65 [b]
6	**1a**	**2a**	 **3f**		**4f**	68 [b]
7	**1a**	 **2b**	**3a**		**4g**	80
8	**1a**	 **2c**	**3a**		**4h**	77
9	**1a**	**2b**	**3b**		**4i**	78

10	**1a**	**2b**	**3c**		**4j**	78
11	**1a**	**2b**	**3d**		**4k**	76
12	 **1b**	**2a**	**3a**		**4l**	86
13	**1b**	**2a**	**3b**		**4m**	85
14	**1b**	**2a**	**3c**		**4n**	83
15	**1b**	**2a**	**3d**		**4o**	79
16	**1b**	**2a**	**3f**		**4p**	70 [b]
17	**1b**	**2b**	**3b**		**4q**	82

18	**1b**	**2b**	**3c**		**4r**	80
19	**1b**	**2b**	**3d**		**4s**	77
20	**1b**	**2c**	**3b**		**4t**	78
21	**1b**	 **2d**	**3b**		**4u**	79
22	 **1c**	**2a**	**3b**		**4v**	70[b]
23	**1c**	**2a**	**3d**		**4w**	65[b]
24	**1c**	**2b**	**3b**		**4x**	72[b]

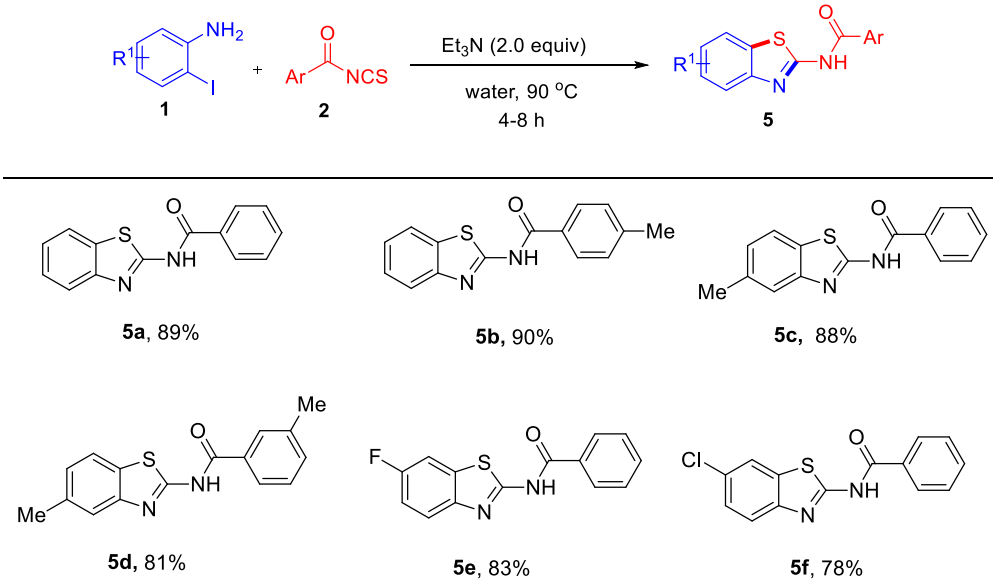
25	**1c**	**2b**	**3c**		**4y**	69 [b]
26	 **1d**	**2a**	**3f**		**4z**	68[b]

[a]All reactions were carried out using aniline **1** (0.50 mmol), benzoyl isothiocyanate **2** (0.52 mmol), acrylate **3** (2.50 mmol), Et_3N (3.0 equiv) in 2 mL H_2O, [b]Time 22 h

Having established the optimum reaction conditions, we next studied the substrate scope and generality of the reaction using an eco-friendly approach (Table 2). Reaction of 2-iodoaniline **1a**, benzoyl isothiocyanate **2a** and methyl acrylate **3a** proceeded with an inclusive conversion to gave the benzo[*d*]thiazol-2(3*H*)-ylidene benzamide **4a** in 85% yield (Table 2, entry 1). Ethyl (**3b**), *n*-butyl (**3c**) and *tert*-butyl (**3d**) acrylates with 2-iodoaniline **1a** and benzoyl isothiocyanate **2a** afforded the desired products **4b**–**d,** in 78–84% yields (entries 2–4). The structures of the desired products **4c** and **4d** were further confirmed by the X-ray crystallographic studies (See SI).[15] *N*, *N*-Dimethylacrylamide **3e** and acrylonitrile **3f** were well implemented in the reaction, providing the cyclized products **4e**–**f** in good yield (entries 5–6). Para and meta-substituted benzoyl isothiocyanate **2b**–**c** delivered the products **4g**–**k,** in good yield (entries 7–11). Our methodology was compatible with the combination of electron-rich 2-iodo-5-methylaniline **1b** and benzoyl isothiocyanate **2a** with Michael acceptor olefins **3a**–**f** fruitfully provided the desired products **4l**–**p,** in 70–86% yields (entries 12–16). Electron-donating aniline and isothiocyanate furnished the benzothiazolylidene products **4q**–**t** in 77–82% yield (entries 17–20). Electron-deficient 3-chlorobenzoyl isothiocyanate **2d** was well tolerated

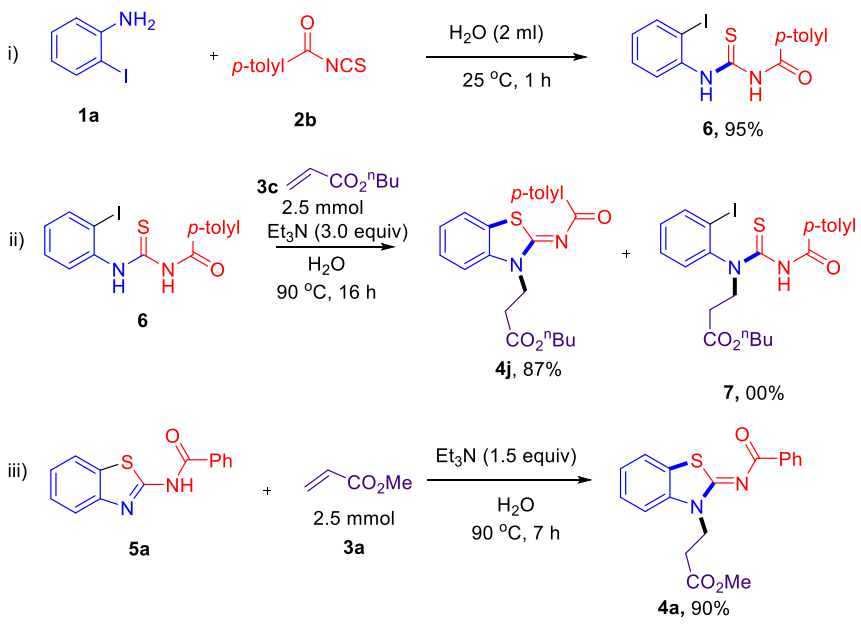
in the reaction to provide the cyclized product **4u** in good yield (entry 21). Functional groups such as 4-chloro and 4-fluoro substituted 2-iodoanilines afforded the desired product **4v**–**z,** in 65–72% yields (entries 22–26).

Scheme 2. Synthesis of Benzo[*d*]thiazole



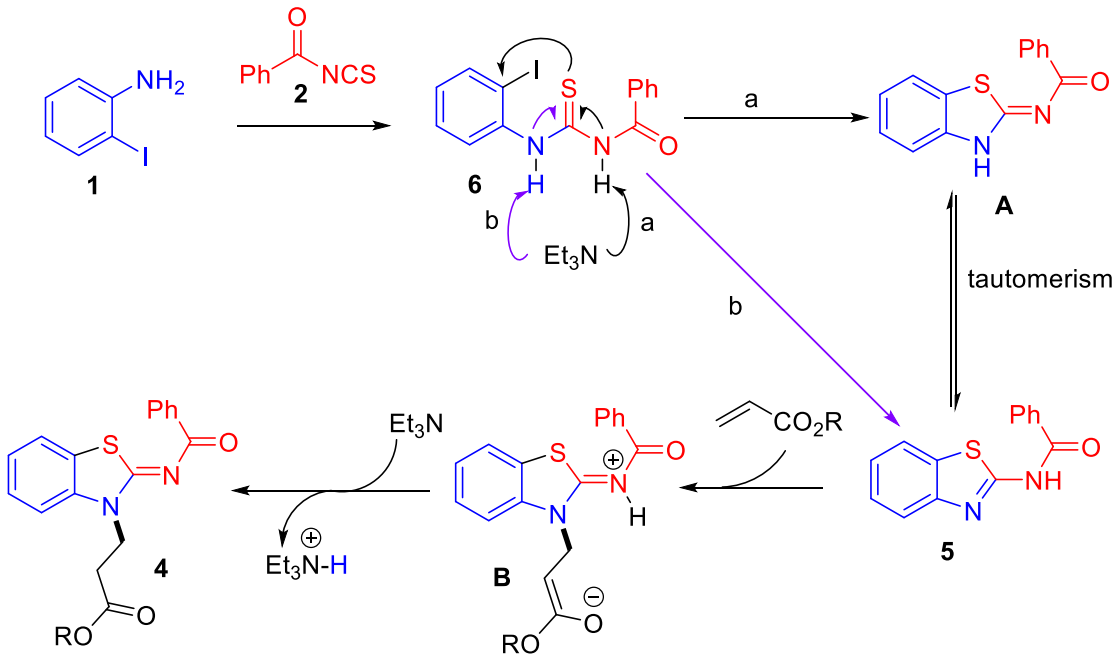
Additionally, we explored the synthesis of benzo[*d*]thiazolyl using green approach (Scheme 2). The reaction was initiated with 2-iodoaniline **1a**, benzoyl isothiocyanate **2a** using 2.0 equiv. of Et_3N and water as a green solvent at 90 °C for 4 h and the desired *N*-(benzo[*d*]thiazol-2-yl) benzamide **5a** was observed in 89% yield. As depicted in Scheme 2, 4-methylbenzoyl isothiocyanate was smoothly converted to product **5b** in 90% yield. It is worthy to note, electron-rich 2-iodoanilines provided the cyclized products **5c**–**d,** in 86–88% yields. It was found that the electron-withdrawing -F and -Cl substituted 2-iodoanilines were well tolerated in this reaction, yielded the benzothiazolyl products **5e**–**f** in good yield. X-ray crystal structure also confirmed the structure of product **5e** (See SI).[15]

Scheme 3. Mechanistic Control Experiments



Now, our next effort was directed towards the mechanistic studies of the reactions (Scheme 3). The reaction of 2-iodoanilines **1a** with **2b** in water at 90 °C, afforded the urea intermediate **6** (Scheme 3i). This urea adduct **6** was further employed with acrylate using 3.0 equiv of Et_3N in a green solvent, provided the benzothiazolylidene **4j;** however, the simple Michael adduct **7** was not formed (Scheme 3 ii). Benzo[*d*]thiazole **5a** participated well with acrylate **3a** to provide the desired product **4a** (Scheme 3 iii). All the above control experiments suggested that the reaction goes *via* a cascade process.

Scheme 4. Plausible Reaction Pathway



Based on the control experiments and literature studies,[16] we proposed a plausible mechanistic pathway in Scheme 4. The mechanism was initiated by the reaction of *o*-halo anilines **1** with isothiocyanates **2** which leads to the formation of urea intermediate **6**. With the support of the base (Et_3N), intramolecular nucleophilic attack of sulphur on the ipso position of iodobenzene occurs. The loss of iodine *via* an aromatic nucleophilic substitution reaction leads to the formation of benzothiazolyl product **5**. The regioselective olefin insertion at benzothiazolyl nitrogen then generates the product **4** *via* a 1, 4-addition step.

CONCLUSIONS

In conclusion, we have developed an environmentally benign; operationally simple, catalyst-free cascade approach for the synthesis of highly functionalized benzothiazolylidene benzamide derviatives using mild reaction conditions with excellent regioselectivity in good to excellent yields. *Ortho*-iodoanilines and aroyl isothiocyanates bearing electron-releasing and electron-withdrawing groups successfully provided the desired products in good yields. Water is non-

flammable and inexpensive solvent in contrast to other organic solvents, which show the remarkable effect on the yield and rate of the organic reaction *via* hydrophobic interactions. The developed chemistry can be used for the synthesis of benzo[*d*]thiazolyl derivatives from 2-iodoaniline, benzoyl isothiocyanate through *in situ* formations of *N*-(phenylcarbamothioyl) benzamide and concomitant intramolecular aromatic nucleophilic substitution reaction. We anticipate that this protocol is useful for the synthesis of highly substituted benzothiazole derivatives, which could find further application in the synthesis of the biologically active compound.

EXPERIMENTAL SECTION

General Information and Method. All the reactions were performed in an oven-dried Schlenk flask. Column chromatography was performed using silica gel (mesh 100-200). TLC analysis was performed on commercially prepared 60 F_{254} silica gel plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$.Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br s = broad singlet), coupling constants in Hertz, and integration. High-resolution mass spectra were recorded with q−TOF electrospray mass spectrometer. All purchased chemicals were used as received. All melting points are uncorrected.

General experimental procedure for green one-pot synthesis of benzo[*d*]thiazol-2(3*H*)-ylidene benzamides 4a-z: To a solution of *ortho*-haloanilines **1** (0.5 mmol), aroyl isothiocyanates **2** (0.52 mmol) in tap water (2.0 mL), acrylates **3** (2.5 mmol) and Et_3N (3.0

equiv) were added. The reaction was then stirred at 90 °C until TLC revealed complete conversion of the starting material. After the completion of the reactant, the reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3X10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100−200 mesh size silica gels (hexane) to afford the corresponding product.

Methyl (E)-3-(2-(benzoylimino)benzo[d]thiazol-3(2H)-yl) propanoate (**4a**). The product was obtained as a off white needles, mp: 140–142 ^{o}C (144.5 mg, 85%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26–8.24 (m, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.60–7.58 (m, 1H), 7.55–7.51 (m, 4H), 7.50–7.46 (m, 1H), 4.80 (t, J = 6.6 Hz, 2H), 3.49 (s, 3H), 2.92 (t, J = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 174.1, 170.9, 167.2, 136.7, 134.7, 133.7, 132.6, 129.8, 129.6, 129.1, 128.9, 126.2, 123.7, 123.2, 113.0, 52.1, 42.0, 32.1. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{18}H_{17}N_2O_3S]$ 341.0960, found 341.0941.

Ethyl (E)-3-(2-(benzoylimino)benzo[d]thiazol-3(2H)-yl)propanoate (**4b**). The product was obtained as a white needles, mp: 75–77 ^{o}C (148.7 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35–8.33 (m, 2H), 7.61 (d, J = 7.8 Hz, 1H), 7.50–7.47 (m, 1H), 7.45–7.38 (m, 4H), 7.25–7.21 (m, 1H), 4.72 (t, J = 7.3 Hz, 2H), 4.06 (q, J = 7.3 Hz, 2H), 2.94 (t, J = 7.3 Hz, 2H), 1.14 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 170.9, 167.0, 136.2, 136.0, 133.3, 131.9, 129.9, 129.4, 128.0, 126.8, 123.7, 122.8, 111.3, 60.9, 41.3, 32.2, 13.8. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{19}N_2O_3S]$ 355.1116, found 355.1104.

Butyl (E)-3-(2-(benzoylimino)benzo[d]thiazol-3(2H)-yl)propanoate (**4c**). The product was obtained as a white needles, mp: 69–71 ^{o}C (156.6 mg, 82%); ^{1}H NMR (400 MHz, DMSO–d_6) δ

8.22–8.20 (m, 2H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.55–7.44 (m, 4H), 7.32–7.29 (m, 1H), 4.75 (t, *J* = 6.4 Hz, 2H), 3.82 (t, *J* = 7.6 Hz, 2H), 2.87 (t, *J* = 8.2 Hz, 2H), 1.35–1.28 (m, 2H), 1.12–1.03 (m, 2H), 0.69 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 173.6, 170.7, 166.7, 136.2, 136.1, 132.1, 129.1, 128.3, 127.2, 125.7, 124.0, 123.1, 112.5, 64.1, 41.5, 32.1, 29.9, 18.5, 13.5. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{21}H_{23}N_2O_3S]$ 383.1429, found 383.1401.

tert-Butyl (E)-3-(2-(benzoylimino)benzo[d]thiazol-3(2H)-yl) propanoate (**4d**). The product was obtained as a white needles, mp: 133–135 ^{o}C (149.0 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.50–7.48 (m, 1H), 7.46–7.42 (m, 4H), 7.28–7.24 (m, 1H), 4.72 (t, *J* = 7.8 Hz, 2H), 2.87 (t, *J* = 8.7 Hz, 2H), 1.37 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 170.1, 167.0, 136.3, 132.0, 129.6, 128.1, 126.6, 123.6, 122.8, 111.3, 81.4, 41.5, 33.5, 27.9, 27.8. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{21}H_{23}N_2O_3S]$ 383.1429, found 383.1400.

(E)-N-(3-(3-(dimethylamino)-3-oxopropyl)benzo[d]thiazol-2(3H)-ylidene)benzamide (**4e**). The product was obtained as a white needles, mp: 119–121 ^{o}C (114.7 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34–8.32 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.51–7.47 (m, 2H), 7.45–7.41 (m, 3H), 7.28–7.25 (m, 1H), 4.81 (t, *J* = 7.8 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.91 (s, 3H), 2.87 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.1, 170.2, 167.3, 136.5, 136.46, 132.2, 129.6, 128.3, 127.2, 126.8, 124.0, 123.0, 111.8, 42.3, 37.3, 35.5, 31.0. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{20}N_3O_2S]$ 354.1276, found 354.1257.

(E)-N-(3-(2-cyanoethyl)benzo[d]thiazol-2(3H)-ylidene)benzamide (**4f**). The product was obtained as a white needles, mp: 208–210 ^{o}C (104.5 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.31

(m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.56–7.52 (m, 1H), 7.50–7.43 (m, 4H), 7.36–7.32 (m, 1H), 4.77 (t, *J* = 7.3 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.9, 167.3, 140.4, 135.9, 135.6, 132.3, 129.5, 128.2, 127.3, 126.6, 124.4, 123.3, 116.9, 110.8, 41.1, 16.1. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{17}H_{14}N_3OS]$ 308.0858, found 308.0856.

Methyl (E)-3-(2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4g**)**.** The product was obtained as a white needles, mp: 146–148 ^{o}C (141.6 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.39–7.38 (m, 2H), 7.24–7.18 (m, 3H), 4.70 (t, *J* = 7.3 Hz, 2H), 3.59 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.1, 171.6, 167.2, 142.7, 136.3, 133.8, 130.3, 129.7, 129.0, 127.0, 126.96, 123.9, 123.1, 111.4, 52.2, 41.5, 32.1, 21.8. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{19}N_2O_3S]$ 355.1116, found 355.1108.

Methyl (E)-3-(2-((3-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4h**). The product was obtained as a white needles, mp: 90–92 ^{o}C (136.3 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.14 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 4.1 Hz, 2H), 7.33–7.31 (m, 2H), 7.28–7.24 (m, 1H), 4.76 (t, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 171.3, 167.0, 137.6, 136.2, 136.1, 132.7, 130.0, 127.9, 127.2, 126.8, 126.7, 123.7, 122.9, 111.3, 52.0, 41.3, 31.9, 21.3. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{19}N_2O_3S]$ 355.1116, found 355.1118.

Ethyl (E)-3-(2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4i**)**.** The product was obtained as a white needles, mp: 117–119 ^{o}C (143.9 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.44–7.42 (m, 2H), 7.28–7.23(m, 3H), 4.74 (t,

J = 6.9 Hz, 2H), 4.08 (q, *J* = 7.3 Hz, 2H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.40 (s, 3H), 1.17 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 171.2, 167.1, 142.6, 136.3, 133.8, 129.7, 129.68, 129.0, 128.1, 127.0, 123.9, 123.0, 111.5, 61.2, 41.5, 32.4, 21.7, 14.1. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{20}H_{21}N_2O_3S]$ 369.1273, found 369.1273.

Butyl (E)-3-(2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4j**). The product was obtained as a white needles, mp: 166–168 ^{o}C (173.1 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.42–7.41 (m, 2H), 7.26–7.22 (m, 3H), 4.72 (t, *J* = 7.3 Hz, 2H), 4.02 (t, *J* = 6.9 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.38 (s, 3H), 1.53–1.46 (m, 2H), 1.30–1.21 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.8, 171.0, 166.8, 142.4, 136.1, 133.6, 129.5, 128.7, 126.8, 126.7, 123.6, 122.8, 111.3, 64.9, 41.4, 32.2, 30.3, 21.5, 18.9, 13.5. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{22}H_{25}N_2O_3S]$ 397.1586, found 397.1578.

tert-Butyl (E)-3-(2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4k**). The product was obtained as a white needles, mp: 139–141 ^{o}C (150.5 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.41–7.38 (m, 2H), 7.26–7.22 (m, 3H), 4.68 (t, *J* = 6.9 Hz, 2H), 2.85 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.37 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.7, 170.1, 166.6, 142.3, 136.1, 133.6, 129.4, 128.7, 126.7, 126.6, 123.5, 122.7, 111.3, 81.2, 41.4, 33.4, 27.8, 21.5. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{22}H_{25}N_2O_3S]$ 397.1586, found 397.1577.

Methyl (E)-3-(2-(benzoylimino)-5-methylbenzo[d]thiazol-3(2H)-yl)propanoate (**4l**). The product was obtained as a white needles, mp: 125–127 ^{o}C (152.2 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 2H), 7.55–7.44 (m, 4H), 7.24 (s, 1H), 7.11 (d, J = 7.8 Hz, 1H), 4.75 (t, J = 7.3 Hz, 2H), 3.67 (s, 3H), 2.97 (t, J = 7.8 Hz, 2H), 2.48 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 171.3, 167.5, 137.4, 136.3, 136.2, 133.3, 131.9, 130.0, 129.4, 128.0, 123.6, 122.6, 111.6, 52.0, 41.2, 31.9, 21.7. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{19}N_2O_3S]$ 355.1116, found 355.1112.

Ethyl (E)-3-(2-(benzoylimino)-5-methylbenzo[d]thiazol-3(2H)-yl)propanoate (**4m**). The product was obtained as a white needles, mp: 141–143 ^{o}C (156.4 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.34 (m, 2H), 7.54–7.51 (m, 2H), 7.49–7.44 (m, 2H), 7.24 (s, 1H), 7.10 (d, J = 7.8 Hz, 1H), 4.74 (t, J = 6.9 Hz, 2H), 4.11 (q, J = 7.3 Hz, 2H), 2.95 (t, J = 7.3 Hz, 2H), 2.47 (s, 3H), 1.19 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.7, 170.9, 167.4, 137.3, 136.3, 136.2, 131.8, 129.4, 128.7, 128.0, 125.0, 123.5, 122.5, 111.7, 61.0, 41.3, 32.2, 21.7, 13.9. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{20}H_{21}N_2O_3S]$ 369.1273, found 369.1256.

Butyl (E)-3-(2-(benzoylimino)-5-methylbenzo[d]thiazol-3(2H)-yl)propanoate (**4n**). The product was obtained as a white needles, mp: 86–88 ^{o}C (164.4 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36–8.34 (m, 2H), 7.55–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.24 (s, 1H), 7.10 (d, J = 7.3 Hz, 1H), 4.74 (t, J = 7.3 Hz, 2H), 4.06 (t, J = 6.4 Hz, 2H), 2.95 (t, J = 7.3 Hz, 2H), 2.48 (s, 3H), 1.57–1.50 (m, 2H), 1.34–1.24 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 171.1, 167.5, 137.4, 136.4, 136.3, 131.9, 129.5, 128.0, 125.1, 125.05, 123.6, 122.6, 111.7, 111.68, 65.0, 41.4, 32.3, 30.4, 21.7, 19.0, 13.6. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{22}H_{25}N_2O_3S]$ 397.1586, found 397.1570.

tert-Butyl(E)-3-(2-(benzoylimino)-5-methylbenzo[d]thiazol-3(2H)-yl)propanoate (**4o**). The product was obtained as a white needles, mp: 138–140 ^{o}C (156.5 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 2H), 7.54–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.24 (s, 1H), 7.09 (d, J = 8.2 Hz, 1H), 4.71 (t, J = 7.3 Hz, 2H), 2.86 (t, J = 7.3 Hz, 2H), 2.47 (s, 3H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 170.2, 167.4, 137.3, 136.4, 136.36, 131.8, 129.5, 128.0, 125.0, 124.9, 123.6, 122.5, 111.9, 111.8, 81.4, 41.5, 33.6, 27.9, 21.7.HRMS (ESI) $[M+H]^+$ Calcd for $[C_{22}H_{25}N_2O_3S]$ 397.1586, found 397.1565.

(E)-N-(3-(2-cyanoethyl)-5-methylbenzo[d]thiazol-2(3H)-ylidene)benzamide (**4p**). The product was obtained as a white needles, mp: 194–196 ^{o}C (112.3 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.27 (m, 2H), 7.54–7.48 (m, 2H), 7.46–7.42 (m, 2H), 7.19 (s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 4.71 (t, J = 7.3 Hz, 2H), 3.03 (t, J = 7.3 Hz, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.8, 167.5, 137.8, 135.7, 132.6, 129.9, 128.8, 128.6, 127.7, 126.0, 125.1, 123.3, 122.4, 116.9, 111.6, 40.9, 22.1, 16.0. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{18}H_{16}N_3OS]$ 322.1014, found 322.1000.

Ethyl (E)-3-(5-methyl-2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4q**). The product was obtained as a white needles, mp: 151–153 ^{o}C (156.6 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.24–7.19 (m, 3H), 7.06 (d, J = 8.2 Hz, 1H), 4.69 (t, J = 7.6 Hz, 2H), 4.09 (q, J = 7.3 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H), 1.17 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.6, 170.9, 167.1, 142.2, 137.2, 136.2, 133.7, 129.4, 128.7, 124.9, 123.5, 122.4, 111.6, 60.9, 41.2, 32.2, 21.6, 21.5, 13.9; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{21}H_{23}N_2O_3S]$ 383.1429, found 383.1400.

Butyl (E)-3-(5-methyl-2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4r**). The product was obtained as a white needles, mp: 166–168 ^{o}C (164.1 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.24–7.19 (m, 3H), 7.06 (d, J = 8.2 Hz, 1H), 4.70 (t, J = 7.3 Hz, 2H), 4.04 (t, J = 6.9 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H), 1.55–1.48 (m, 2H), 1.32–1.23 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.7, 171.0, 167.1, 142.3, 137.2, 136.3, 133.7, 129.5, 128.7, 124.9, 123.6, 122.5, 111.6, 64.9, 41.3, 32.2, 30.3, 21.7, 21.6, 18.9, 13.6; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{23}H_{27}N_2O_3S]$ 411.1742, found 411.1731.

tert-Butyl (E)-3-(5-methyl-2-((4-methylbenzoyl)imino)benzo[d] thiazol-3(2H)-yl)propanoate (**4s**). The product was obtained as a white needles, mp: 181–183 ^{o}C (157.9 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 9.2Hz, 1H), 7.26–7.25 (m, 3H), 7.11 (d, J = 9.2 Hz, 1H), 4.73 (t, J = 7.8 Hz, 2H), 2.87 (t, J = 7.8 Hz, 2H), 2.50 (s, 3H), 2.42 (s, 3H), 1.40 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.9, 170.3, 167.3, 142.4, 137.3, 136.5, 133.9, 129.7, 128.9, 128.8, 125.1, 123.8, 122.7, 111.9, 81.5, 41.5, 33.6, 28.0, 21.7, 21.69; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{23}H_{27}N_2O_3S]$ 411.1742, found 411.1736.

Ethyl (E)-3-(5-methyl-2-((3-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4t**). The product was obtained as a white needles, mp: 145–147 ^{o}C (149.0 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.02 (m, 2H), 7.38–7.35 (m, 1H), 7.23–7.18 (m, 2H), 7.08 (s, 1H), 6.95–6.93 (m, 1H), 4.58 (t, J = 6.9 Hz, 2H), 3.97 (q, J = 7.3 Hz, 2H), 2.81 (t, J = 7.8 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 1.06 (t, J = 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.6, 170.7, 167.1, 137.4, 137.0, 136.1, 136.0, 132.4, 129.8, 127.7, 126.4, 124.8, 123.4, 122.2, 111.5, 60.7, 41.1, 32.1, 21.5, 21.2, 13.8; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{21}H_{23}N_2O_3S]$ 383.1429, found 383.1419.

Ethyl (E)-3-(2-((3-chlorobenzoyl)imino)-5-methylbenzo[d]thiazol-3(2H)-yl)propanoate (**4u**). The product was obtained as a white needles, mp: 133–135 ^{o}C (158.8 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.22 (d, J = 6.2Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 7.49–7.47 (m, 1H), 7.41–7.37 (m, 1H), 7.27 (s, 1H), 7.14 (d, J = 8.3 Hz, 1H), 4.77 (t, J = 7.3 Hz, 2H), 4.13 (q, J = 7.3 Hz, 2H), 2.96 (t, J = 7.3 Hz, 2H), 2.50 (s, 3H), 1.21 (t, J = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 170.9, 167.9, 138.3, 137.6, 136.3, 134.2, 131.8, 129.6, 129.4, 127.6, 125.3, 123.6, 122.7, 111.9, 61.1, 41.5, 32.4, 21.8, 14.0; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{20}H_{20}ClN_2O_3S]$ 403.0883, found 403.0858.

Ethyl (E)-3-(2-(benzoylimino)-6-chlorobenzo[d]thiazol-3(2H)-yl)propanoate (**4v**). The product was obtained as a white needles, mp: 123–125^{o}C (136.1 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 7.8 Hz, 2H), 7.66 (s, 1H), 7.56–7.52 (m, 1H), 7.49–7.45 (m, 2H), 7.43–7.42 (m, 2H), 4.74 (t, J = 6.9 Hz, 2H), 4.10 (q, J = 7.3 Hz, 2H), 2.99 (t, J = 7.3 Hz, 2H), 1.19 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 171.1, 167.1, 136.1, 135.1, 132.3, 129.7, 129.5, 128.5, 128.3, 127.4, 122.8, 112.6, 61.3, 41.9, 32.3, 14.1; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{18}ClN_2O_3S]$ 389.0727, found 389.0723.

Butyl (E)-3-(2-(benzoylimino)-6-chlorobenzo[d]thiazol-3(2H)-yl)propanoate (**4w**)**.** The product was obtained as a white needles, mp: 78–80^{o}C (135.5 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.7 Hz, 2H), 7.65 (s, 1H), 7.56–7.52 (m, 1H), 7.48–7.45 (m, 2H), 7.42–7.41 (m, 2H), 4.73 (t, J = 6.6 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.99 (t, J = 6.6 Hz, 2H), 1.56–1.49 (m, 2H), 1.33–1.24 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 171.2, 167.1, 136.1, 135.1, 132.3, 129.7, 129.5, 128.5, 128.3, 127.4, 122.7, 112.6, 65.2, 41.9, 32.4, 30.5, 19.1, 13.7; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{21}H_{22}ClN_2O_3S]$ 417.1040, found 417.1048.

Ethyl (E)-3-(6-chloro-2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4x**)**.** The product was obtained as a white needles, mp: 135–137 ^{o}C (145.0 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 2H), 7.63 (s, 1H), 7.39 (s, 2H), 7.25 (d, J = 7.3 Hz, 2H), 4.71 (t, J = 6.9 Hz, 2H), 4.09 (q, J = 7.3 Hz, 2H), 2.97 (t, J = 6.9 Hz, 2H), 2.41 (s, 3H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 171.1, 166.8, 142.9, 135.1, 133.5, 129.7, 129.4, 129.0, 128.5, 127.3, 122.7, 112.5, 61.3, 41.8, 32.3, 21.8, 14.1; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{20}H_{20}ClN_2O_3S]$ 403.0883, found 403.0877.

Butyl (E)-3-(6-chloro-2-((4-methylbenzoyl)imino)benzo[d]thiazol-3(2H)-yl)propanoate (**4y**)**.** The product was obtained as a white needles, mp: 82–84 ^{o}C (148.6 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.8 Hz, 2H), 7.60 (s, 1H), 7.37–7.36(m, 2H), 7.22 (d, J = 8.2 Hz, 2H), 4.68 (t, J = 7.1 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.95 (t, J = 6.9 Hz, 2H), 2.39 (s, 3H), 1.53–1.46 (m, 2H), 1.28–1.23 (m, 2H), 0.85 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 171.3, 166.8, 142.9, 135.1, 133.5, 129.7, 129.4, 129.0, 128.5, 127.3, 122.7, 112.5, 65.2, 41.9, 32.3, 30.5, 21.8, 19.1, 13.8; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{22}H_{24}ClN_2O_3S]$ 431.1196, found 431.1205.

(E)-N-(3-(2-cyanoethyl)-6-fluorobenzo[d]thiazol-2(3H)-ylidene)benzamide (**4z**). The product was obtained as a white needles, mp: 170–172 ^{o}C (110.5 mg, 68%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27–8.25 (m, 2H), 7.90–7.86 (m, 2H), 7.60–7.56 (m, 1H), 7.52–7.49 (m, 3H), 7.44–7.39 (m, 1H), 4.83 (t, J = 6.9 Hz, 2H), 3.17 (t, J = 6.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 167.3, 159.7 (d, J = 245.6 Hz, 1C), 135.8, 132.6, 132.1, 129.6, 128.4, 116.9, 115.2 (d, J = 24.1

Hz, 1C), 111.8 (d, *J* = 9.6 Hz, 1C), 110.4 (d, *J* = 26.0 Hz, 1C), 41.6, 16.3. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{17}H_{13}FN_3OS]$ 326.0763, found 326.0762.

General experimental procedure for green one-pot synthesis of benzo[*d*]thiazolyl 5a-f: To a solution of *ortho*-haloanilines **1** (0.5 mmol), aroyl isothiocyanates **2** (0.52 mmol) in tap water (2.0 mL) Et_3N (2.0 equiv) was added. The reaction was then stirred at 90 °C until TLC revealed complete conversion of the starting material. After the completion of the reactant, the reaction mixture was then allowed to cool and diluted with H_2O and extracted with EtOAc (3X10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum, and purified by column chromatography using 100−200 mesh size silica gels (hexane) to afford the corresponding product.

N-(benzo[d]thiazol-2-yl)benzamide (**5a**). The product was obtained as a white needles, mp: 165–167 ^oC (113.1mg, 89%); ^1H NMR (400 MHz, $CDCl_3$) δ 12.10 (br s, 1H), 8.02–8.00 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.55–7.51 (m, 1H), 7.40–7.36 (m, 2H), 7.28–7.24 (m, 1H), 7.21–7.17 (m, 1H), 7.10–7.08 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 160.0, 147.6, 133.0, 132.0, 131.8, 128.9, 128.0, 126.0, 124.0, 121.3, 120.6. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{14}H_{11}N_2OS]$ 255.0592, found 255.0593.

N-(Benzo[d]thiazol-2-yl)-4-methylbenzamide (**5b**). The product was obtained as a white needles, mp: 180–182 ^oC (120.6 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ 11.73 (br s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.83–7.80 (m, 1H), 7.28–7.17 (m, 5H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 160.0, 147.9, 143.9, 132.0, 129.7, 129.3, 128.1, 126.0, 123.9, 121.4, 120.8, 21.7. HRMS (ESI) Calcd for $[M+H]^+$ Calcd for $[C_{15}H_{13}N_2OS]$ 269.0749, found 269.0750.

N-(5-methylbenzo[d]thiazol-2-yl)benzamide (**5c**).The product was obtained as a white needles, mp: 195–197 ^{o}C (117.9 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (br s, 1H), 8.00 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.52 (t, J = 6.8 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.05 (d, J = 7.7 Hz, 1H), 6.64 (s, 1H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 160.4, 147.7, 135.9, 132.8, 132.3, 128.9, 128.5, 128.2, 128.0, 127.3, 125.4, 120.7, 21.3. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{15}H_{13}N_2OS]$ 269.0749, found 269.0734.

3-Methyl-N-(5-methylbenzo[d]thiazol-2-yl)benzamide (**5d**).The product was obtained as a white needles, mp: 212–214 ^{o}C (114.3 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (br s, 1H), 7.74 (d, J= 7.8 Hz, 1H), 7.72–7.68 (m, 3H), 7.44–7.37 (m, 2H), 6.86–6.83 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.9, 159.9, 139.4, 139.1, 138.9, 138.86, 134.5, 131.3, 130.0, 129.0, 128.5, 128.2, 124.6, 21.3, 20.98. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{16}H_{15}N_2OS]$ 283.0905, found 283.0890.

N-(6-fluorobenzo[d]thiazol-2-yl)benzamide (**5e**).The product was obtained as a white needles, mp: 191–193 ^{o}C (112.8 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.04 (br s, 1H), 8.04 (d, J = 8.8 Hz, 2H), 7.62–7.56 (m, 1H), 7.53–7.49 (m, 1H), 7.46–7.42 (m, 2H), 7.18–7.14 (m, 1H), 7.01–6.96 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 159.8, 159.5 (d, J = 237.7 Hz, 1C), 143.9, 133.2, 132.7 (d, J = 10.5 Hz, 1C), 131.7, 130.0, 129.0, 128.0, 121.3, 114.5 (d, J = 24.9 Hz, 1C), 107.8 (d, J = 4.8 Hz, 1C), 107.5 (d, J = 3.8 Hz, 1C). HRMS (ESI) $[M+H]^+$ Calcd for $[C_{14}H_{10}FN_2OS]$ 273.0498, found 273.0500.

N-*(6-Chlorobenzo[d]thiazol-2-yl)benzamide* (**5f**).The product was obtained as a white needles, mp: 223–225 ^{o}C (112.3 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.99 (br s, 1H), 8.13 (s, 1H),

8.00 (d, J = 7.3 Hz, 2H), 7.64–7.61 (m, 1H), 7.57–7.55 (m, 1H), 7.52–7.48 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 161.4, 150.3, 133.5, 132.2, 131.5, 129.2, 127.8, 123.3, 120.9, 119.2. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{14}H_{10}ClN_2OS]$ 289.0202, found 289.0190.

N-((2-iodophenyl)carbamothioyl)-4-methylbenzamide (**6**). The product was obtained as an off white needles, mp: 160–162 ^oC (188.6 mg, 95%); ^1H NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H), 9.22 (s, 1H), 7.90–7.86 (m, 2H), 7.81–7.79 (m, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.31 (d, J = 7.3 Hz, 2H), 7.03–6.99 (m, 1H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.7, 166.6, 144.8, 139.7, 139.3, 129.7, 128.8, 128.4, 127.8, 127.6, 127.3, 95.5, 21.6; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{15}H_{14}IN_2OS]$ 396.9872, found 396.9880.

Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website at DOI: .

^{1} H, $^{13}C\{^1H\}$ and HRMS spectra of synthesized compounds and XRay data (PDF)

X-ray crystallographic data of compounds **4c**, **4d**, and **5e** (CIF)**.**

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Notes

The authors declare no competing financial interest.

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