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Catalyst-free reductive cyclization of bis(2-aminophenyl) disulfide with CO_2 in the presence of BH_3NH_3 to synthesize 2-unsubstituted benzothiazole derivatives†

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An efficient and catalyst-free methodology for the reductive cyclization of various disulfides using BH_3NH_3 as a reductant and CO_2 as a C1 resource was developed. The desired 2-unsubstituted benzothiazole derivatives were obtained in good to excellent yields. Moreover, mechanism investigation demonstrated that BH_3NH_3 played an important role in the formation of benzothiazole. As a reducing agent, BH_3NH_3 reduced CO_2 and cleaved the S–S bond of the disulfide efficiently. In addition, the N–H bond of the amino group was also activated by BH_3NH_3. To the best of our knowledge, this is an unprecedented catalyst-free protocol for the synthesis of 2-unsubstituted benzothiazole from bis(2-aminophenyl) disulfide and CO_2.

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1 Introduction

CO_2 is a low-cost, sustainable, and abundant C1 resource which has been widely employed in the synthesis of value-added chemicals.[1–3] Among the various reactions reported for the transformations of CO_2, reductive functionalization of amines with CO_2 in the presence of a reducing reagent has attracted extensive attention.[4–7] Significantly, new bonds such as C–N, C–O, C–C or C–S bonds were formed in the process of reductive functionalization by reducing CO_2 with different functionalization reagents.[8–12] Among these, formations of C–N and C–S bonds are important transformations in organic synthesis.

One of the common compounds containing both C–N and C–S bonds is benzothiazole, a bicyclic compound in which a thiazole ring is fused with a benzene ring. It is an important synthetic intermediate and an important privileged scaffold of many natural compounds and/or bioactive compounds.[13] Benzothiazole is used in the synthesis of pharmaceutical compounds such as ethoxzolamide, riluzole and florapronol (Fig. 1). In particular, 2-unsubstituted benzothiazole is the core structure that can be used to synthesize a variety of valuable 2-substituted benzothiazoles.

There are many methods to prepare 2-unsubstituted benzothiazole derivatives.[14] It is worth noting that various raw materials have been utilized *via* different reaction routes in the synthesis of 2-unsubstituted benzothiazole. Among these raw materials, 2-aminothiophenol has attracted extensive attention of researchers. The most commonly used method is the condensation reaction of 2-aminothiophenol with formic acid,[15] formamide,[16] or formaldehyde[17] in the presence of a catalyst. Recently, the synthesis of 2-unsubstituted benzothiazole using CO_2 as the carbon source has been reported, in the presence of various reductants and catalysts (Scheme 1, route a). With H_2 as the reductant, 2-unsubstituted benzothiazole could be obtained from the reaction of CO_2 and 2-aminothiophenol catalyzed by $CoF_2/PP_3/CsF$.[18] It should be noted that both H_2 and CO_2 need to be activated. Therefore, high temperatures and high pressures are needed in the reaction. With hydrosilanes as the reductant, 2-unsubstituted benzothiazole can be obtained from the reaction of CO_2 and 2-aminothiophenol catalyzed by 1,5-diazabicyclo [4.3.0] non-5-ene (DBN),[19] 1,5,7-triazabicyclo [4.4.0]

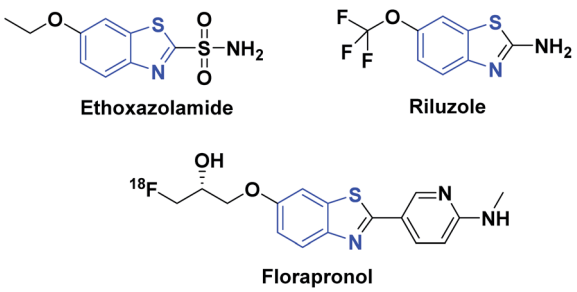

Fig. 1 Representative bioactive benzothiazoles.

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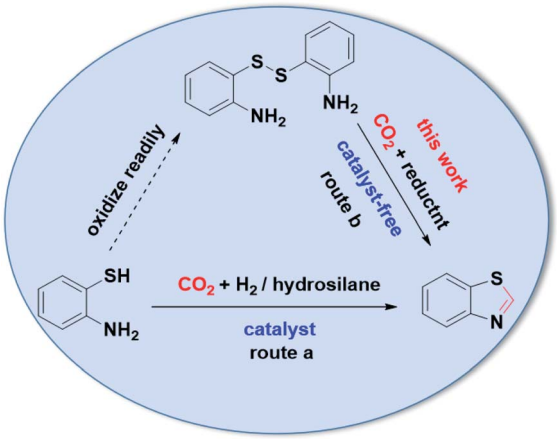
[d]Wu Hai Vocational &Technical College, Wu Hai, 010070, China

† Electronic supplementary information (ESI) available. See https://doi.org/10.1039/d2ra03134e



Scheme 1 The synthesis of 2-unsubstituted benzothiazole.

dec-5-ene (TBD),[20] acetate-based ionic liquids [Bmim][OAc][21] or biomass-derived γ-valerolactone.[22]

Although these synthetic routes for preparing 2-unsubstituted benzothiazole using efficient, non-toxic, and renewable catalysts have been reported, the exploration of catalyst-free and atom-economic methods under mild conditions is of great significance. Notably, 2-aminothiophenol is unstable and easily oxidized to form disulfide,[23,24] and 2-aminothiophenols containing various substituents are difficult to be prepared, which limits the application of 2-aminothiophenol as a substrate. Therefore, the method of synthesizing 2-unsubstituted benzothiazole compounds should be investigated using stable and readily available disulfides as raw materials. One of the key steps in the synthesis of benzothiazole from disulfide is the cleavage of S–S bond. It is found that the S–S bond can be cleaved by free radical reagents,[25,26] metal catalysts,[27,28] nucleophilic reagents,[23,29] reducing reagents,[30–32] thiol-disulfide exchange reaction[33–35] and the disulfide-metal sulfide dynamic interchange reaction.[36,37] Therefore, 2-unsubstituted benzothiazole is synthesized by reductive cyclization of disulfide and CO_2, a crucial reducing reagent which could reduce CO_2 and the S–S bond of disulfide is required (Scheme 1, route b).

Recently, BH_3NH_3, a high hydrogen storage reagent, has been reported to reduce CO_2 into formamides under mild conditions without any catalyst.[20,38] Subsequently, we have prepared 1*H*-benzimidazole by the cascade reaction of CO_2 and *o*-phenylenediamine under two-electron reduction process.[39] As part of our ongoing work, we investigated BH_3NH_3 as a reductant to synthesize 2-unsubstituted benzothiazole derivatives from bis(2-aminophenyl) disulfide and CO_2, in which C–N and C–S bonds were constructed simultaneously. This simple and effective method could be applicated in the synthesis of many 2-unsubstituted benzothiazole compounds.

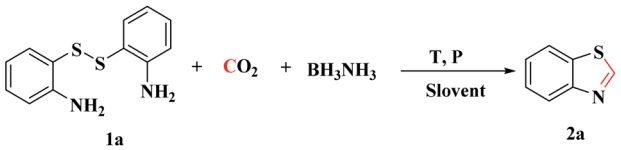
2 Results and discussion

The model reaction of bis(2-aminophenyl) disulfide (**1a**, 0.5 mmol) and CO_2 to synthesize benzothiazole (**2a**) was initially explored. First, the reaction was carried out in NMP at 1 MPa of CO_2 with 3 equiv. of BH_3NH_3 at 100 °C in 24 h, and the desired product **2a** was obtained in 32% yield (Table 1, entry 1). Notably, a large amount of disulfide was recovered, which demonstrated that the S–S bond of disulfide was not easily cleaved under this reaction condition and the raw material was not completely consumed. To improve the yield of target product, the reaction temperature was increased from 100 °C to 120 °C, which increased the yield of **2a** from 32% to 85% (Table 1, entries 1–3). These experimental results indicated that higher temperature is beneficial to the cleavage of S–S bond. However, as the reaction temperature was increased to 140 °C, the yield of target product decreased to 46% (Table 1, entries 4–5), possibly because the higher reaction temperature decreased the solubility of CO_2 and further reduced CO_2 into methylation by-products.[40] Consequently, the reaction temperature would be 120 °C in subsequent experiments.

To further improve the yield of **2a**, the amount of BH_3NH_3 and the pressure of CO_2 were optimized (Table 1, entries 3, 6–9). Increasing the amount of BH_3NH_3 reduced the yield of the target product, which demonstrated that the amount of BH_3NH_3 was critical to the reaction. The excessive BH_3NH_3 might further reduce CO_2 into methylated by-products.[41] When the amount of BH_3NH_3 was 2.5 equiv. of **1a**, the yield of **2a** reached 93% (Table 1, entry 6). However, when the amount of BH_3NH_3 was further reduced, the yield of **2a** was also reduced (Table 1, entries 7 and 8), suggesting that the amount of reducing agent is insufficient. Therefore, 2.5 equivalents of reducing agent were used in the subsequent reactions of **1a** and CO_2. Furthermore, the effect of CO_2 pressure on the reaction yield was also examined (Table 1, entries 6, 10–12). Only trace amount of **2a** was found at 0.1 MPa CO_2 (Table 1, entry 10), indicating that higher concentration of CO_2 was needed in the reaction of **1a** and CO_2. Increasing the pressure of CO_2 to 1 MPa led to a higher yield of **2a** (Table 1, entry 6). When the CO_2 pressure was further increased to 2 MPa, the yield of **2a** decreased significantly (Table 1, entry 12). These experimental results indicated that BH_3NH_3 is consumed by excess CO_2, resulting in insufficient amounts of BH_3NH_3 to break the S–S bond. Therefore, the balanced optimization of the reaction temperature, the amount of BH_3NH_3 and CO_2 pressure was critical for the high-yield formation of **2a** from **1a** and CO_2.

The effect of solvent on the reaction yield was also investigated. When weakly polar solvents such as 1,4-dioxane, CH_3CN and THF were used (Table 1, entries 13–15), **2a** was obtained in lower yields. When DMSO was used (Table 1, entry 16), a lower yield of **2a** was obtained, likely due to the oxidizing property of DMSO to convert thiol into disulfide.[42] When DMF was used (Table 1, entries 17 and 18), **2a** was obtained in 80% yield. However, **2a** could also be obtained in a yield of 75% in the absence of CO_2, because DMF can serve as the C1 source to produce the target product in the presence of BH_3NH_3.[16,43] Water was not suitable for the reaction system (Table 1, entry 19), because the formed carbonic acid promoted the hydrolysis of BH_3NH_3.[44] To our delight, an excellent yield of **2a** was obtained in NMP; therefore, NMP was chosen as the solvent in the following experiments. Finally, the reaction time was also

Table 1 Optimization of the reaction conditions[a]



1a 2a

Entry	BH_3NH_3 (mmol)	Solvent (mL)	P_{CO_2} (MPa)	T (°C)	t (h)	Yield[b] [%]
1	1.5	NMP	1	100	24	32
2	1.5	NMP	1	110	24	68
3	1.5	NMP	1	120	24	85
4	1.5	NMP	1	130	24	75
5	1.5	NMP	1	140	24	46
6	1.25	NMP	1	120	24	93
7	1	NMP	1	120	24	68
8	0.5	NMP	1	120	24	30
9	2	NMP	1	120	24	70
10	1.25	NMP	0.1	120	24	Trace
11	1.25	NMP	0.5	120	24	46
12	1.25	NMP	2	120	24	62
13	1.25	1,4-Dioxane	1	120	24	13%
14	1.25	CH_3CN	1	120	24	25%
15	1.25	THF	1	120	24	18%
16	1.25	DMSO	1	120	24	26%
17	1.25	DMF	1	120	24	80%
18[c]	1.25	DMF	0	120	24	75%
19	1.25	H_2O	1	120	24	Trace
20	1.25	NMP	1	120	18	83
21	1.25	NMP	1	120	12	60
22	1.25	NMP	1	120	6	25

[a] Reaction conditions: bis(2-aminophenyl) disulfide (0.1242 g, 0.5 mmol), solvent (1 mL). [b] Isolated yield. [c] No CO_2.

investigated (Table 1, entries 6, 20–22), and the highest yield was obtained in 24 h. Therefore, 1 equiv. of **1a** reacted with 1 MPa of CO_2 in the presence of 2.5 equiv. BH_3NH_3 in 120 °C for 24 h to give the highest yield of the target product.

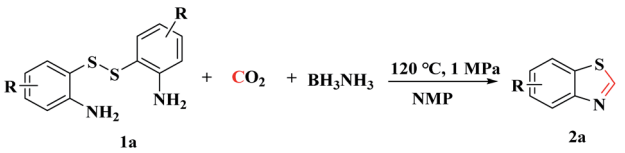
With the optimized reaction conditions in hand, the reaction scope was investigated with a range of differently substituted bis(2-aminophenyl) disulfide (Table 2). We found that all the substrates reacted with CO_2 and BH_3NH_3 to produce the corresponding target products in good to excellent yields. The reaction of **1a** with CO_2 and BH_3NH_3 provided **2a** in an isolated yield of 93% under the optimized reaction conditions (Table 2, entry 1). The substrates with electron-donating groups like methyl and methoxy displayed higher reactivity, and the corresponding products were obtained in excellent yields (86–95%, Table 2, entries 2–4). The substrates with electro-withdrawing groups including –F, –Cl, –Br and $-CF_3$ displayed good reactivity, and the corresponding products were obtained in good yields (63–85%, Table 2, entries 5–10). Furthermore, bis(2-aminophenyl) disulfides bearing functional groups at the C4 position showed higher reactivity than those at the C6 position, (Table 2, entries 2 *vs.* 3; entries 6 *vs.* 8) which presumably attributed to the steric effects of substituent groups. When the substituent group was $-SO_2CH_3$, a strong electron-withdrawing group, corresponding 6-(methylsulfonyl)-benzothiazole was obtained in a yield of 55% (Table 2, entry 11). In addition, naphtho[2,3]-thiazole could be obtained in 66% yield from the corresponding disulfide (Table 2, entry 12). To the best of our knowledge, this is the first example of successfully synthesizing 6-(methylsulfonyl)-benzothiazole and naphtho[2,3]-thiazole using CO_2 as the carbon source.

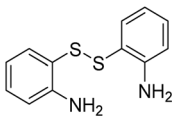
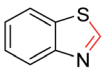
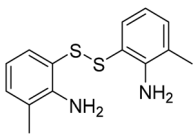
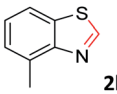
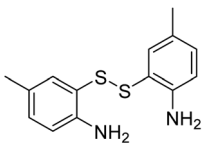
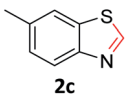
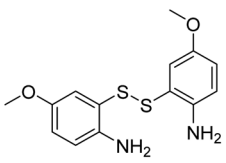
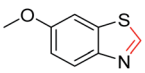
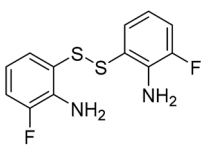
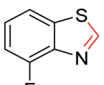
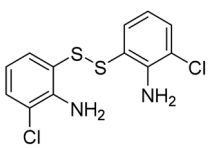
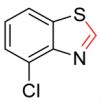
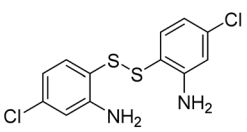
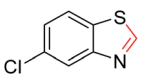
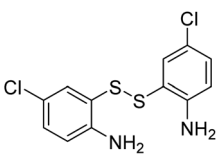
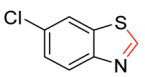
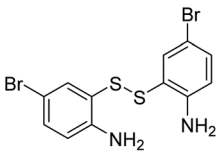
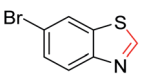
To verify the applicability of the developed methodology, the reductive cyclization of disulfide with CO_2 to synthesize benzothiazole was carried out on the gram scale (Scheme 2). The desired product was obtained in 80% isolated yield, demonstrating that this methodology can be used in gram-scale synthesis.

To explore the reaction mechanism, several control experiments were performed under the optimized conditions. As shown in Scheme 3, no desired product was detected in the absence of BH_3NH_3 or CO_2, which indicated that both BH_3NH_3 and CO_2 were indispensable (Scheme 3).

When BH_3NH_3 and CO_2 were mixed in NMP, it was interesting to find that the formate borohydride species $BH_{3-n}(OCOH)_nNH_3$ (**I**) was formed, which was confirmed by ^1H NMR (8.31 ppm, 8.04 ppm), ^{13}C NMR (166.38 ppm), and[11] B NMR (19.39 ppm) (Fig. S1†) analysis. The experimental results are similar with the data reported in the literature.[41,45–47] This

Table 2 Substrate scope of reductive cyclization to prepare benzothiazole derivatives[a]



Entry	Substrate	Product	Yield[b] (%)
1	 1a	 2a	93
2	 1b	 2b	86
3	 1c	 2c	95
4	 1d	 2d	90
5	 1e	 2e	63
6	 1f	 2f	70
7	 1g	 2g	77
8	 1h	 2h	80
9	 1i	 2i	85

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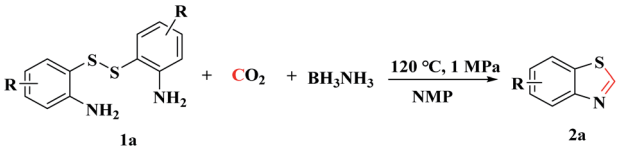

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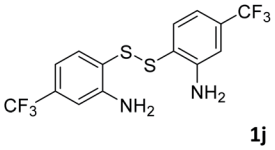
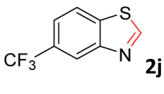
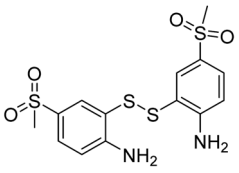
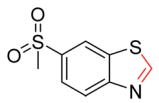
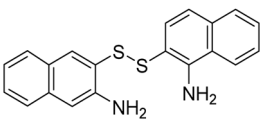
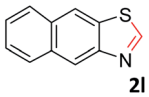
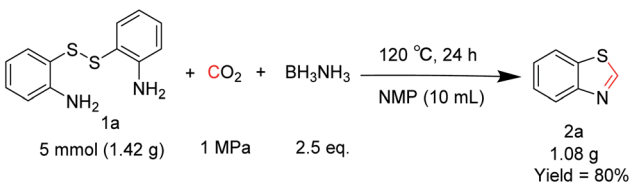
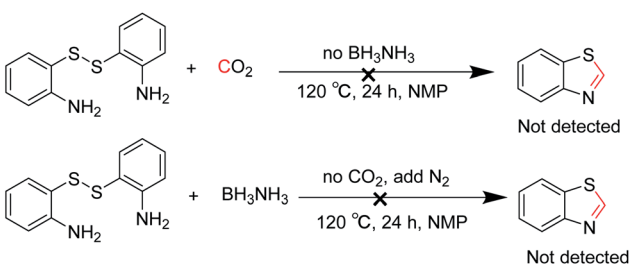
10	 1j	 2j	73
11	 1k	 2k	55
12	 1l	 2l	66

[a] Reaction conditions: substrate (0.5 mmol), BH_3NH_3(1.25 mmol), NMP (1 mL), reaction time: 24 h. [b] Isolated yield.



Scheme 2 The gram-scale reaction.



Scheme 3 Control experiments.

finding suggested that $BH_{3-n}(OCOH)_nNH_3$ (**I**) was an intermediate for the synthesis of benzothiazole.

Furthermore, ^1H NMR analysis was employed to identify the cleavage of S–S bond of disulfide by BH_3NH_3 during the reaction

process (Fig. 2). As illustrated in Fig. 2c, a peak pattern similar to that of 2-aminothiophenol appeared when disulfide reacted with BH_3NH_3 under an inert atmosphere at 120 °C in deuterated DMF (Fig. 2c red rectangle). However, the aromatic hydrogen shifted to upfield in 2-aminothiophenol after reduced by BH_3NH_3, which might be resulted from the coordination of boron atom of BH_3NH_3 with the nitrogen atom of 2-aminothiophenol.[48] In addition, the ^{1}H NMR spectra of reaction mixture (Fig. 2c) showed that the $-NH_2$ group hydrogen in 2-aminothiophenol formed from disulfide reduction shifted downfield from 4.87 to 5.19 (Fig. 2c blue rectangle), indicating that the N–H bond of 2-aminothiophenol was activated. These results demonstrated that BH_3NH_3 reduced disulfide to 2-aminothiophenol and activated the N–H bond of amino group, which increased the nucleophilicity of the amino group in 2-aminothiophenol.[49]

Based on our experimental results and previous reports,[18,21,50] a possible reductive cyclization reaction mechanism was proposed (Scheme 4). Firstly, BH_3NH_3 reacts with CO_2 to produce the intermediate $BH_{3-n}(OCOH)_nNH_3$ (**I**). Meanwhile, the S–S bond of the disulfide is cleaved by BH_3NH_3 to form complex (**II**) of 2-aminothiophenol with BH_3. Subsequently, the nucleophilic N atom of 2-aminothiophenol attacks the carbon atom of $BH_{3-n}(OCOH)_nNH_3$ (**I**) to form intermediate **III**. Finally, intermediate **IV** is formed through the intramolecular nucleophilic cyclization of intermediate **III**, followed by dehydration to yield the target product benzothiazole.

3 Experimental

3.1 General information

All reagents and solvents were purchased from commercial suppliers and used without further purification. All reactions were monitored by TLC with GF254 silica gel coated plates. Purification of reaction products were carried out by chromatography using silica gel (200–300 mesh). The ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on an Agilent 500 MHz DD2 spectrometer at 500 MHz (^{1}H), 126 MHz (^{13}C) and 160 MHz (^{11}B) in d_6-DMSO, or $CDCl_3$ or D_2O using tetramethylsilane (TMS) or solvent residue as internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Melting points were measured with SGC X-4 microscopic melting point meter and were uncorrected. Molecular weights were obtained using Shimadzu LCMS-2020 (ESI) instrument.

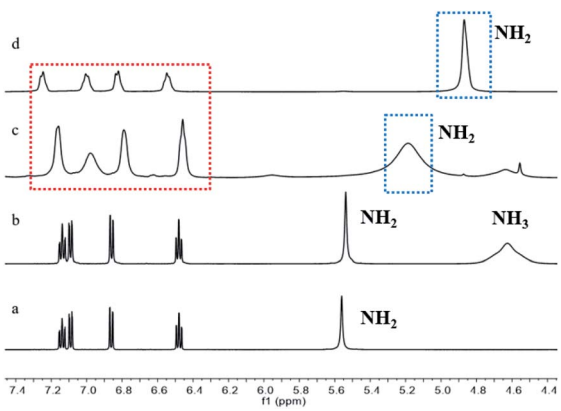


Fig. 2 The reaction of disulfide with BH_3NH_3 detected by ^{1}H NMR in deuterated DMF. (a) Disulfide **1a**, (b) the mixture of disulfide **1a** and BH_3NH_3, (c) the reaction of disulfide with BH_3NH_3 for 1 h, (d) 2-aminothiophenol.

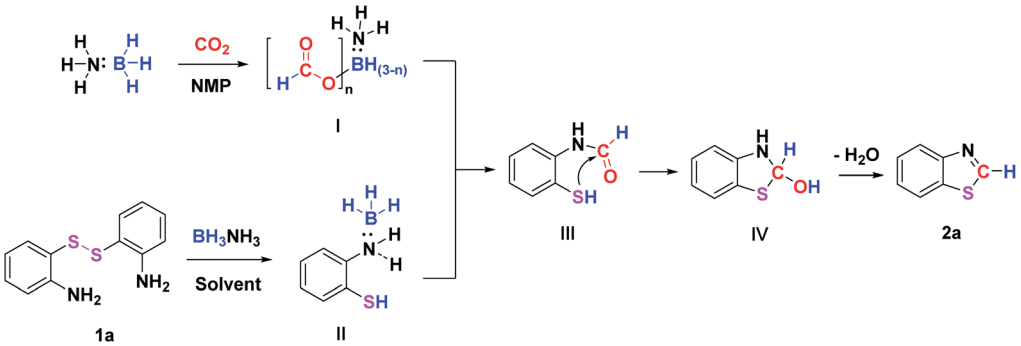
3.2 General procedure for the synthesis of benzothiazoles (2a–2l)

A stainless-steel autoclave reactor equipped with a magnetic stirrer was charged with bis(2-aminophenyl) disulfide (0.5 mmol), BH_3NH_3 (1.25 mmol) and NMP (1 mL). Then the stainless-steel autoclave was sealed and pressurized with 1 MPa of CO_2 after air was exchanged by CO_2 at ambient temperature. And then it was heated and stirred at 120 °C for 24 h. When the reaction was completed, it was cooled down to room temperature and the excessive CO_2 was released slowly. Subsequently, the reaction mixture solution was quenched by brine water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The desired products were obtained in good to excellent yields after purification by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. All the desired products were identified through comparisons with the corresponding ^{1}H NMR, ^{13}C NMR data reported in the literature.

3.3 Mechanistic study

3.3.1 Reaction of BH_3NH_3 and CO_2 in NMP. A stainless-steel autoclave reactor equipped with a magnetic stirrer was charged with BH_3NH_3 (1 mmol) and NMP (1 mL). The reactor was pressurized with 1 MPa of CO_2 at ambient temperature, and then was heated and stirred at 120 °C for 24 h. After the reaction was completed, the reactor was cooled to room temperature and excessive CO_2 was vented discreetly. Subsequently, 0.1 mL of the reaction mixture solution was dissolved in 0.4 mL of D_2O for NMR detection. The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra are measured at 298.15 K and shown in Fig. S1.†

3.3.2 Reaction of disulfide and BH_3NH_3 in deuterated DMF. The disulfide (0.05 mmol) was dissolved with 0.5 mL deuterated DMF in an NMR tube and detected by ^{1}H NMR. The ^{1}H NMR spectra of **1a** in deuterated DMF was obtained (Fig. S2.†). Then, the disulfide (0.05 mmol) and BH_3NH_3 (0.05 mmol) were dissolved with 0.5 mL deuterated DMF in an NMR tube under the inert atmosphere and detected by ^{1}H NMR. The ^{1}H NMR spectra of the mixture of **1a** and BH_3NH_3 in deuterated DMF were obtained (Fig. S3.†). Subsequently, the mixture solution was then heated to 120 °C for an indicated time, and then the reaction solution was detected by ^{1}H NMR at 0.5 h, 1 h, 2 h and 5 h. The corresponding ^{1}H NMR are measured and shown in Fig. S4.† Finally, the 2-aminothiophenol was dissolved with 0.5 mL deuterated DMF in an NMR tube and detected by ^{1}H NMR. The ^{1}H NMR spectra of 2-aminothiophenol was obtained (Fig. S5.†). Additionally, the stacked ^{1}H NMR spectra of Fig. S2–S5† were shown in Fig. S6.†



Scheme 4 The proposed mechanism of reductive cyclization of CO_2 with disulfide.

3.4 Characterization (NMR) of the products

3.4.1 Benzothiazole (2a). Isolated as a yellow oil (PE/EA = 3 : 1, 0.126 g, 93%); ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.00 (s, 1H), 8.14 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.54–7.49 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 153.91, 153.21, 133.70, 126.17, 125.54, 123.62, 121.87. MS (ESI): *m*/*z* calcd for C_7H_6SN $[M + H]^+$: 136.19, found 136.01.

3.4.2 4-Methyl-benzothiazole (2b). Isolated as a yellow oil (PE/EA = 6 : 1, 0.128 g, 86%); ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.98 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.36–7.31 (m, 2H), 2.80 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 152.70, 152.53, 133.56, 133.45, 126.66, 125.47, 119.29, 18.37. MS (ESI): *m*/*z* calcd for C_8H_8NS $[M + H]^+$: 150.21, found 150.05.

3.4.3 6-Methyl-benzothiazole (2c). Isolated as a yellow oil (PE/EA = 6 : 1, 0.141 g, 95%); ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.91 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.33 (d, J = 9.9 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 152.83, 151.35, 135.69, 133.86, 127.82, 123.03, 121.51, 21.50. MS (ESI): *m*/*z* calcd for C_8H_8NS $[M + H]^+$: 150.21, found 150.05.

3.4.4 6-Methoxy-benzothiazole (2d). Isolated as a yellow solid (PE/EA = 6 : 1, 0.149 g, 90%); mp: 71–73 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.84 (s, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.40 (s, 1H), 7.13 (dd, J = 9.0, 3.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 158.06, 151.44, 147.71, 135.12, 123.95, 115.89, 104.00, 55.80. MS (ESI): *m*/*z* calcd for C_8H_8NOS $[M + H]^+$: 166.21, found 166.00.

3.4.5 4-Fluoro-benzothiazole (2e). Isolated as a yellow oil (DCM/EA = 10 : 1, 0.096 g, 63%); ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.00 (s, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.42 (td, J = 2.01,1.13 Hz, 1H), 7.25–7.21 (m, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 156.30 (d, J = 257.79 Hz), 154.37, 142.26 (d, J = 13.73 Hz), 136.60 (d, J = 3.4 Hz), 126.45 (d, J = 7.18 Hz), 117.55 (d, J = 4.41 Hz), 111.81 (d, J = 17.77 Hz). MS (ESI): *m*/*z* calcd for C_7H_5FNS $[M + H]^+$: 154.17, found 154.00.

3.4.6 4-Chloro-benzothiazole (2f). Isolated as a yellow solid (DCM/EA = 10 : 1, 0.119 g, 70%); mp: 50–52 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.08 (s, 1H), 7.87 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 154.84, 150.25, 135.30, 128.67, 126.48, 126.21, 120.49. MS (ESI): *m*/*z* calcd for C_7H_5ClNS $[M + H]^+$: 170.63, found 169.95.

3.4.7 5-Chloro-benzothiazole (2g). Isolated as a yellow solid (DCM/EA = 40 : 1, 0.131 g, 77%); mp: 104–106 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.04 (s, 1H), 8.14 (s, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.44 (d, J = 10.2 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 155.72, 154.02, 132.41, 131.99, 126.22, 123.46, 122.58. MS (ESI): *m*/*z* calcd for C_7H_5ClNS $[M + H]^+$: 170.63, found 170.00.

3.4.8 6-Chloro-benzothiazole (2h). Isolated as a white solid (PE/EA = 6 : 1, 0.137 g, 80%); mp: 41–42 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.99 (s, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.95 (s, 1H), 7.49 (d, J = 9.4 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 154.34, 151.71, 134.95, 131.73, 127.12, 124.33, 121.49. MS (ESI): *m*/*z* calcd for C_7H_5ClNS $[M + H]^+$: 170.63, found 170.00.

3.4.9 6-Bromo-benzaothiazole (2i). Isolated as a yellow solid (PE/EA = 6 : 1, 0.182 g, 85%); mp: 53–55 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 8.98 (d, J = 2.5 Hz, 1H), 8.11 (t, J = 2.1 Hz, 1H), 8.00 (dd, J = 8.7, 2.3 Hz, 1H), 7.65–7.61 (m, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 154.32, 152.11, 135.44, 129.77, 124.72, 124.44, 119.37. MS (ESI): *m*/*z* calcd for C_7H_5BrNS $[M + H]^+$: 215.08, found 213.90.

3.4.10 5-(Trifluoromethyl)-benzothiazole (2j). Isolated as a yellow solid (PE/EA = 4 : 1, 0.148 g, 73%); mp: 63–65 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.13 (s, 1H), 8.43 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 155.87, 152.88, 137.23, 129.01 (q, J = 32.51 Hz), 124.11 (q, J = 272.79 Hz), 122.61, 121.99 (q, J = 3.53 Hz), 120.97 (q, J = 4.16 Hz). MS (ESI): *m*/*z* calcd for C_8H_5F3NS $[M + H]^+$: 204.18, found 204.00.

3.4.11 6-(Methylsulfonyl)-benzothiazole (2k). Isolated as a yellow solid (DCM/EA = 10 : 1, 0.117 g, 55%); mp: 99–102 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.26 (s, 1H), 8.64 (d, J = 1.8 Hz, 1H), 8.32 (d, J = 8.6 Hz, 1H), 8.07 (d, J = 6.8 Hz, 1H), 3.14 (s, 3H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 158.50, 156.19, 137.72, 134.45, 124.86, 124.67, 122.58, 44.88. MS (ESI): *m*/*z* calcd for $C_8H_8NO_2S_2$ $[M + H]^+$: 214.27, found 213.95.

3.4.12 Naphtho[2,3-*d*]-thiazole (2l). Isolated as a blackish green solid (PE/EA = 6 : 1, 0.122 g, 66%); mp: 48–51 °C; ^{1}H NMR (500 MHz, chloroform-*d*) δ 9.11 (s, 1H), 8.85 (d, J = 8.2 Hz, 1H), 7.99–7.95 (m, 2H), 7.86 (d, J = 8.7 Hz, 1H), 7.72 (d, J = 7.1 Hz, 1H), 7.60 (d, J = 7.0 Hz, 1H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 152.52, 149.77, 131.91, 130.65, 128.79, 128.05, 127.17, 126.40,

126.26, 123.66, 118.97. MS (ESI): *m*/*z* calcd for $C_{11}H_8NS\,[M+H]^+$: 186.24, found 186.00.

4 Conclusions

In conclusion, a green, catalyst-free and efficient approach to synthesize 2-unsubstituted benzothiazole derivatives by the reductive cyclization of bis(2-aminophenyl) disulfide with CO_2 was realized, which could be used to prepare a variety of 2-unsubstituted benzothiazole derivatives in good to excellent yields. The reaction mechanism investigation demonstrated that BH_3NH_3 plays an important role in the formation of benzothiazole, as an efficient reductant to reduce CO_2, to cleave the S–S bond of disulfide and to activate the N–H bond of amino group. This simple and green route provides a new method for the utilization of CO_2 in the synthesis of benzothiazole derivatives.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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