


 Cite this: *RSC Adv.*, 2022, 12, 18107

Catalyst-free reductive cyclization of bis(2-aminophenyl) disulfide with CO₂ in the presence of BH₃NH₃ to synthesize 2-unsubstituted benzothiazole derivatives†

 Xiao Li,^{abc} Zhenbao Liu,^{abc} Hailong Hong,^{abc} Limin Han^{*abcd} and Ning Zhu^{id *abc}

An efficient and catalyst-free methodology for the reductive cyclization of various disulfides using BH₃NH₃ as a reductant and CO₂ as a C1 resource was developed. The desired 2-unsubstituted benzothiazole derivatives were obtained in good to excellent yields. Moreover, mechanism investigation demonstrated that BH₃NH₃ played an important role in the formation of benzothiazole. As a reducing agent, BH₃NH₃ reduced CO₂ and cleaved the S–S bond of the disulfide efficiently. In addition, the N–H bond of the amino group was also activated by BH₃NH₃. 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 CO₂.

 Received 18th May 2022
Accepted 13th June 2022

DOI: 10.1039/d2ra03134e

rsc.li/rsc-advances

1 Introduction

CO₂ 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 CO₂, reductive functionalization of amines with CO₂ 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 CO₂ 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 floraspirone (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 formaldehyde¹⁷ in the presence of a catalyst. Recently, the synthesis of 2-unsubstituted benzothiazole using CO₂ as the carbon source has been reported, in the presence of various reductants and catalysts (Scheme 1, route a). With H₂ as the reductant, 2-unsubstituted benzothiazole could be obtained from the reaction of CO₂ and 2-aminothiophenol catalyzed by CoF₂/PP₃/CsF.¹⁸ It should be noted that both H₂ and CO₂ 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 CO₂ and 2-aminothiophenol catalyzed by 1,5-diazabicyclo [4.3.0] non-5-ene (DBN),¹⁹ 1,5,7-triazabicyclo [4.4.0]

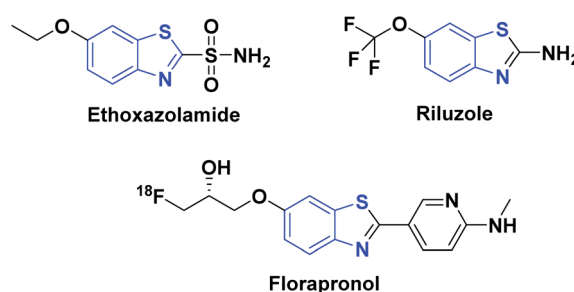


Fig. 1 Representative bioactive benzothiazoles.

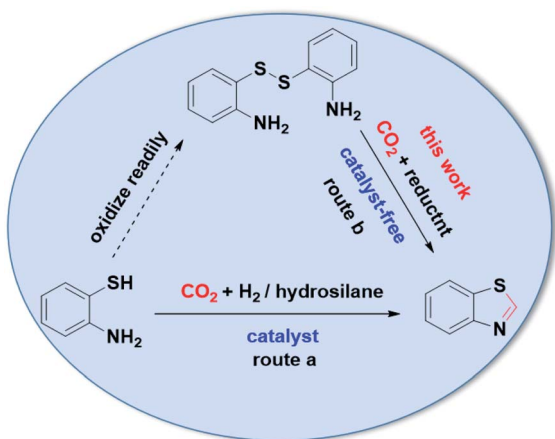
^aCollege of Chemical Engineering, Inner Mongolia University of Technology, Hohhot, 010051, China. E-mail: hanlimin_442@hotmail.com; zhuning@imut.edu.cn

^bKey Laboratory of CO₂ Resource Utilization at Universities of Inner Mongolia Autonomous Region, Hohhot, 010051, China

^cInner Mongolia Engineering Research Center for CO₂ Capture and Utilization, Hohhot, 010051, China

^dWu 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 CO₂, a crucial reducing reagent which could reduce CO₂ and the S–S bond of disulfide is required (Scheme 1, route b).

Recently, BH₃NH₃, a high hydrogen storage reagent, has been reported to reduce CO₂ into formamides under mild conditions without any catalyst.^{20,38} Subsequently, we have prepared 1*H*-benzimidazole by the cascade reaction of CO₂ and *o*-phenylenediamine under two-electron reduction process.³⁹ As part of our ongoing work, we investigated BH₃NH₃ as a reductant to synthesize 2-unsubstituted benzothiazole derivatives from bis(2-aminophenyl) disulfide and CO₂, in which C–N and C–S bonds were constructed simultaneously. This simple and effective method could be applied in the synthesis of many 2-unsubstituted benzothiazole compounds.

2 Results and discussion

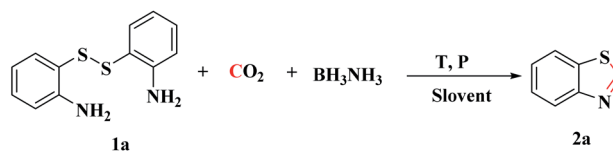
The model reaction of bis(2-aminophenyl) disulfide (**1a**, 0.5 mmol) and CO₂ to synthesize benzothiazole (**2a**) was initially

explored. First, the reaction was carried out in NMP at 1 MPa of CO₂ with 3 equiv. of BH₃NH₃ 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 CO₂ and further reduced CO₂ 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 BH₃NH₃ and the pressure of CO₂ were optimized (Table 1, entries 3, 6–9). Increasing the amount of BH₃NH₃ reduced the yield of the target product, which demonstrated that the amount of BH₃NH₃ was critical to the reaction. The excessive BH₃NH₃ might further reduce CO₂ into methylated by-products.⁴¹ When the amount of BH₃NH₃ was 2.5 equiv. of **1a**, the yield of **2a** reached 93% (Table 1, entry 6). However, when the amount of BH₃NH₃ 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 CO₂. Furthermore, the effect of CO₂ 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 CO₂ (Table 1, entry 10), indicating that higher concentration of CO₂ was needed in the reaction of **1a** and CO₂. Increasing the pressure of CO₂ to 1 MPa led to a higher yield of **2a** (Table 1, entry 6). When the CO₂ pressure was further increased to 2 MPa, the yield of **2a** decreased significantly (Table 1, entry 12). These experimental results indicated that BH₃NH₃ is consumed by excess CO₂, resulting in insufficient amounts of BH₃NH₃ to break the S–S bond. Therefore, the balanced optimization of the reaction temperature, the amount of BH₃NH₃ and CO₂ pressure was critical for the high-yield formation of **2a** from **1a** and CO₂.

The effect of solvent on the reaction yield was also investigated. When weakly polar solvents such as 1,4-dioxane, CH₃CN 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 CO₂, because DMF can serve as the C1 source to produce the target product in the presence of BH₃NH₃.^{16,43} Water was not suitable for the reaction system (Table 1, entry 19), because the formed carbonic acid promoted the hydrolysis of BH₃NH₃.⁴⁴ 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

Entry	BH ₃ NH ₃ (mmol)	Solvent (mL)	P _{CO₂} (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 ₃ CN	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 ₂ O	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 CO₂.

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 CO₂ in the presence of 2.5 equiv. BH₃NH₃ 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 CO₂ and BH₃NH₃ to produce the corresponding target products in good to excellent yields. The reaction of **1a** with CO₂ and BH₃NH₃ 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 –CF₃ 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 –SO₂CH₃, 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 CO₂ as the carbon source.

To verify the applicability of the developed methodology, the reductive cyclization of disulfide with CO₂ 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 BH₃NH₃ or CO₂, which indicated that both BH₃NH₃ and CO₂ were indispensable (Scheme 3).

When BH₃NH₃ and CO₂ were mixed in NMP, it was interesting to find that the formate borohydride species BH_{3–n}(–OCOH)_nNH₃ (**I**) was formed, which was confirmed by ¹H NMR (8.31 ppm, 8.04 ppm), ¹³C NMR (166.38 ppm), and ¹¹B NMR (19.39 ppm) (Fig. S1†) analysis. The experimental results are similar with the data reported in the literature.^{41,45–47} This



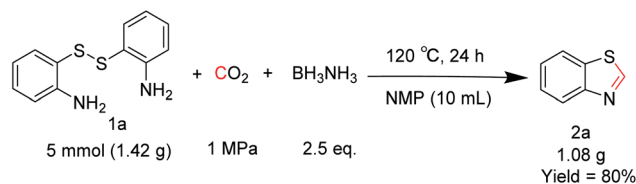
Table 2 Substrate scope of reductive cyclization to prepare benzo-thiazole derivatives^a

Entry	Substrate	Product	Yield ^b (%)
1			93
2			86
3			95
4			90
5			63
6			70
7			77
8			80
9			85

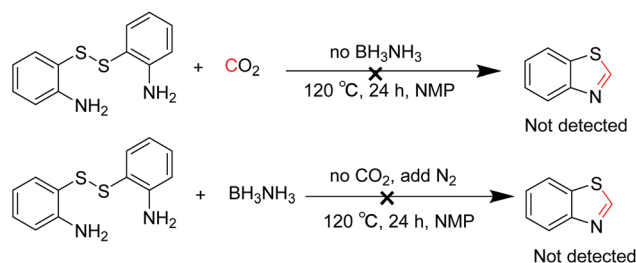
Table 2 (Contd.)

Entry	Substrate	Product	Yield ^b (%)
10			73
11			55
12			66

^a Reaction conditions: substrate (0.5 mmol), BH₃NH₃ (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 BH₃-*n*(COOH)*n*NH₃ (**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 BH₃NH₃ 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 ^1H NMR spectra of reaction mixture (Fig. 2c) showed that the $-\text{NH}_2$ 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 $\text{BH}_{3-n}(\text{COOH})_n\text{NH}_3$ (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 $\text{BH}_{3-n}(\text{COOH})_n\text{NH}_3$ (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 ^1H , ^{13}C and ^{11}B NMR spectra were recorded on an Agilent 500 MHz DD2 spectrometer at 500 MHz (^1H), 126 MHz (^{13}C) and 160 MHz (^{11}B) in

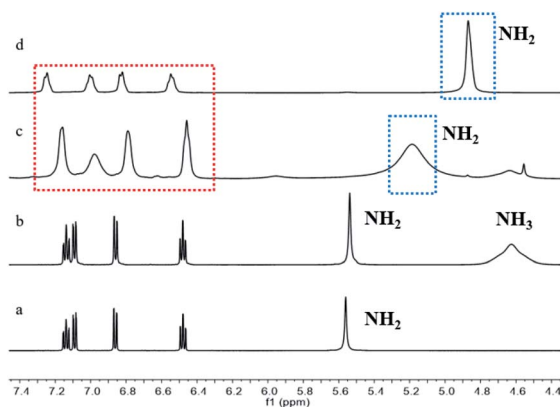


Fig. 2 The reaction of disulfide with BH_3NH_3 detected by ^1H NMR in deuterated DMF. (a) Disulfide **1a**, (b) the mixture of disulfide **1a** and BH_3NH_3 , (c) the reaction of disulfide with BH_3NH_3 for 1 h, (d) 2-aminothiophenol.

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.

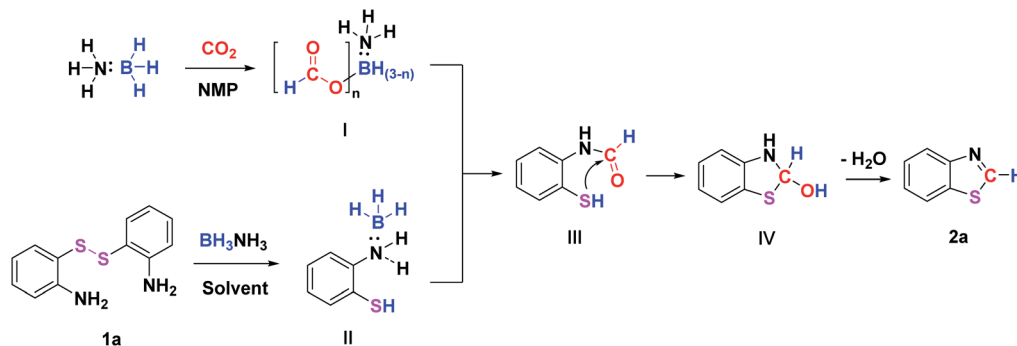
3.2 General procedure for the synthesis of benzothiazoles (2a–2l)

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 ^1H 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 ^1H 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 ^1H NMR. The ^1H 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 ^1H NMR. The ^1H 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 ^1H NMR at 0.5 h, 1 h, 2 h and 5 h. The corresponding ^1H 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 ^1H NMR. The ^1H NMR spectra of 2-aminothiophenol was obtained (Fig. S5.†). Additionally, the stacked ^1H NMR spectra of Fig. S2–S5† were shown in Fig. S6.†



Scheme 4 The proposed mechanism of reductive cyclization of CO₂ 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%); ¹H 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). ¹³C 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 C₇H₆SN [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%); ¹H 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). ¹³C 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 C₈H₈NS [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%); ¹H 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). ¹³C 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 C₈H₈NS [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; ¹H 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). ¹³C 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 C₈H₈NOS [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%); ¹H 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). ¹³C 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 C₇H₅FNS [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; ¹H 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). ¹³C 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 C₇H₅ClNS [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; ¹H 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). ¹³C 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 C₇H₅ClNS [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; ¹H 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). ¹³C 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 C₇H₅ClNS [M + H]⁺: 170.63, found 170.00.

3.4.9 6-Bromo-benzothiazole (2i). Isolated as a yellow solid (PE/EA = 6 : 1, 0.182 g, 85%); mp: 53–55 °C; ¹H 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). ¹³C 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 C₇H₅BrNS [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; ¹H 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). ¹³C 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 C₈H₅F₃NS [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; ¹H 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). ¹³C 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 C₈H₈NO₂S₂ [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; ¹H 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). ¹³C 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

This work was supported by the Program for Grassland Excellent Talents of Inner Mongolia Autonomous Region, the National Natural Science Foundation of China (21865020), the Natural Science Foundation of Inner Mongolia (No. 2019LH02009 and No. 2021ZD02), the Innovation Research Team of CO_2 Resource Utilization in Universities of Inner Mongolia Autonomous Region (NMGIRT2212), and the Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region (2019).

Notes and references

- A. H. Chowdhury, P. Bhanja, N. Salam, A. Bhaumik and S. M. Islam, *Mol. Catal.*, 2018, **450**, 46–54.
- X. F. Liu, X. Y. Li, C. Qiao, H. C. Fu and L. N. He, *Angew. Chem., Int. Ed.*, 2017, **56**, 7425–7429.
- C. K. Ran, L. L. Liao, T. Y. Gao, Y. Y. Gui and D. G. Yu, *Curr. Opin. Green Sustain. Chem.*, 2021, **32**, 100525.
- C. Das Neves Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190.
- A. I. Ojeda-Amador, J. Munarriz, P. Alamán-Valtierra, V. Polo, R. Puerta-Oteo, M. V. Jiménez, F. J. Fernández-Alvarez and J. J. Pérez-Torrente, *ChemCatChem*, 2019, **11**, 5524–5535.
- M. Hulla and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2020, **59**, 1002–1017.
- W. F. Zhao, H. Li, Y. Li, J. X. Long, Y. F. Xu and S. Yang, *Sustain. Chem. Pharm.*, 2020, **17**, 100276.
- Z. Q. Guo, B. Zhang, X. H. Wei and C. J. Xi, *ChemSusChem*, 2018, **11**, 2296–2299.
- Z. Q. Guo, B. Zhang, X. H. Wei and C. J. Xi, *Org. Lett.*, 2018, **20**, 6678–6681.
- G. H. Jin, C. G. Werncke, Y. Escudiee, S. Sabo-Etienne and S. Bontemps, *J. Am. Chem. Soc.*, 2015, **137**, 9563–9566.
- C. Shen, P. F. Zhang, Q. Sun, S. Q. Bai, T. S. Hor and X. G. Liu, *Chem. Soc. Rev.*, 2015, **44**, 291–314.
- G. Q. Yuan, C. R. Qi, W. Q. Wu and H. F. Jiang, *Curr. Opin. Green Sustain. Chem.*, 2017, **3**, 22–27.
- D. A. Horton, G. T. Bourne and M. L. Smythe, *Chem. Rev.*, 2003, **103**, 893–930.
- J. H. Zhu, Z. B. Zhang, C. X. Miao, W. Liu and W. Sun, *Tetrahedron*, 2017, **73**, 3458–3462.
- J. O. Rathi and G. S. Shankarling, *Sol. Energy*, 2019, **189**, 471–479.
- X. Gao, B. Yu, Q. Q. Mei, Z. Z. Yang, Y. F. Zhao, H. Y. Zhang, L. D. Hao and Z. M. Liu, *New J. Chem.*, 2016, **40**, 8282–8287.
- S. Dadwal, M. Kumar and V. Bhalla, *J. Org. Chem.*, 2020, **85**, 13906–13919.
- Z. G. Ke, B. Yu, H. Wang, J. F. Xiang, J. J. Han, Y. Y. Wu, Z. H. Liu, P. Yang and Z. M. Liu, *Green Chem.*, 2019, **21**, 1695–1701.
- X. Gao, B. Yu, Y. F. Zhao, L. D. Hao and Z. M. Liu, *RSC Adv.*, 2014, **4**, 56957–56960.
- B. Zhang, G. X. Du, W. Hang, S. Wang and C. J. Xi, *Eur. J. Org. Chem.*, 2018, **2018**, 1739–1743.
- X. Gao, B. Yu, Z. Z. Yang, Y. F. Zhao, H. Y. Zhang, L. D. Hao, B. X. Han and Z. M. Liu, *ACS Catal.*, 2015, **5**, 6648–6652.
- J. L. Song, B. W. Zhou, H. Z. Liu, C. Xie, Q. L. Meng, Z. R. Zhang and B. X. Han, *Green Chem.*, 2016, **18**, 3956–3961.
- D. B. Lima, F. Penteadó, M. M. Vieira, D. Alves, G. Perin, C. Santi and E. J. Lenardão, *Eur. J. Org. Chem.*, 2017, **2017**, 3830–3836.
- X. Liu and Z. B. Dong, *Eur. J. Org. Chem.*, 2020, **2020**, 408–419.
- R. Y. Tang, Y. X. Xie, Y. L. Xie, J. N. Xiang and J. H. Li, *Chem. Commun.*, 2011, **47**, 12867–12869.
- D. Asakawa, H. Takahashi, S. Iwamoto and K. Tanaka, *Phys. Chem. Chem. Phys.*, 2019, **21**, 26049–26057.
- M. Arisawa and M. Yamaguchi, *Molecules*, 2020, **25**, 3595–3630.
- N. Taniguchi, *J. Org. Chem.*, 2015, **80**, 1764–1770.
- Y. Liu, X. Sun, X. Zhang, J. Liu and Y. G. Du, *Org. Biomol. Chem.*, 2014, **12**, 8453–8461.
- W. Munbunjong, E. H. Lee, P. Ngermaneerat, S. J. Kim, G. Singh, W. Chavasiri and D. O. Jang, *Tetrahedron*, 2009, **65**, 2467–2471.
- J. McNulty, V. Krishnamoorthy, D. Amoroso and M. Moser, *Bioorg. Med. Chem. Lett.*, 2015, **25**, 4114–4117.
- F. Hofbauer and I. Frank, *Chem.–Eur. J.*, 2010, **16**, 5097–5101.
- R. Lu, S. Itabashi, N. Enjo and T. Miyakoshi, *Curr. Org. Synth.*, 2014, **11**, 295–300.
- N. Zhu, F. Zhang and G. Liu, *J. Comb. Chem.*, 2010, **12**, 531–540.
- B. H. Zhou, H. L. Hong, H. C. Wang, T. M. Zhang, L. M. Han and N. Zhu, *Eur. J. Org. Chem.*, 2018, **2018**, 6983–6990.
- C. Q. Lou, N. Zhu, R. H. Fan, H. L. Hong, L. M. Han, J. B. Zhang and Q. L. Suo, *Green Chem.*, 2017, **19**, 1102–1108.
- Y. Liu, Y. Jia, Q. Wu and J. S. Moore, *J. Am. Chem. Soc.*, 2019, **141**, 17075–17080.



- 38 T. X. Zhao, G. W. Zhai, J. Liang, P. Li, X. B. Hu and Y. T. Wu, *Chem. Commun.*, 2017, **53**, 8046–8049.
- 39 X. Li, J. H. Zhang, Y. Yang, H. L. Hong, L. M. Han and N. Zhu, *J. Organomet. Chem.*, 2021, **954–955**, 122079.
- 40 C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu and B. L. Lin, *ACS Catal.*, 2016, **6**, 7876–7881.
- 41 Q. Z. Zou, G. C. Long, T. X. Zhao and X. B. Hu, *Green Chem.*, 2020, **22**, 1134–1138.
- 42 K. S. Du and J. M. Huang, *Green Chem.*, 2018, **20**, 1405–1411.
- 43 B. Bhanage and D. Nale, *Synlett*, 2015, **26**, 2835–2842.
- 44 F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, *Angew. Chem., Int. Ed.*, 2007, **46**, 746–749.
- 45 I. Knopf and C. C. Cummins, *Organometallics*, 2015, **34**, 1601–1603.
- 46 B. Zhang, Z. N. Fan, Z. Q. Guo and C. J. Xi, *J. Org. Chem.*, 2019, **84**, 8661–8667.
- 47 Q. Z. Zou, Y. Yi, T. X. Zhao, F. Liu, C. Kang and X. B. Hu, *J. CO₂ Util.*, 2021, **50**, 101590.
- 48 Q. Y. Zhao, R. D. Dewhurst, H. Braunschweig and X. N. Chen, *Angew. Chem., Int. Ed.*, 2019, **58**, 3268–3278.
- 49 H. Lv, Q. Xing, C. T. Yue, Z. Q. Lei and F. W. Li, *Chem. Commun.*, 2016, **52**, 6545–6548.
- 50 S. Chun, S. Yang and Y. K. Chung, *Tetrahedron*, 2017, **73**, 3438–3442.

