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Organic Base-Catalyzed C–S Bond Construction from CO_2: A New Route for the Synthesis of Benzothiazolones

Xiang Gao [1], Yuehua Deng [1], Changyu Lu [1], Lei Zhang [1], Xintao Wang [1] and Bo Yu [2,*]

[1] College of Geology and Environment, Xi'an University of Science and Technology, Xi'an 710054, China; gaoxiang@iccas.ac.cn (X.G.); yhdeng2016@163.com (Y.D.); pzpzlxl@163.com (C.L.); leizh1981@sohu.com (L.Z.); xintaowang2015@163.com (X.W.)

[2] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

* Correspondence: boyu@iccas.ac.cn Tel.: +86-029-8558-3188

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Abstract: The synthesis of organosulfur compounds via the construction of C−S bonds using CO_2 as a C1 resource is very interesting. Herein, a novel method of synthesizing benzothiazolones via the cyclocarbonylation of 2-aminothiophenols with CO_2 was developed. A series of organic bases was investigated for the catalysis of cyclocarbonylation, and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) displayed the best catalytic activity. Then, various reaction parameters such as CO_2 pressure, temperature, amount of catalyst, and reaction time for the catalytic performance were studied. Finally, a series of benzothiazolones was synthesized under the optimal reaction conditions, and a possible catalytic mechanism was also proposed.

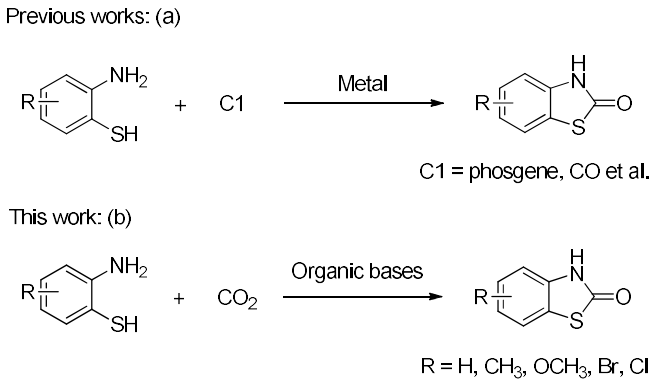
Keywords: organic bases; C–S bonds; carbon dioxide; benzothiazolones

1. Introduction

As a typical sulfur-containing organic compound, benzothiazolone and its derivatives are very important chemical and biological intermediates, and are widely used in the synthesis of agricultural chemicals, dyestuffs, pharmaceuticals, and achiral templates for asymmetric catalysis [1–5]. To date, numerous efforts focused on the development of improved methods for the synthesis of this heterocyclic compounds [6–10]. Among them, the direct cyclocarbonylation of 2-aminothiophenols in the presence of carbonylation agents, such as phosgene [11], CO [12], $ClCO_2Et$ [13], dimethyl carbonate [14], urea [15], and isocyanates [16] (Scheme 1a), is one of the most simple and versatile methods. However, phosgene is highly toxic and corrosive, the reactions involving CO are generally catalyzed by transition metals, and the use of super-stoichiometric amounts of carbonyl sources are all incompatible with green-chemistry principles. Therefore, the exploration of environmentally benign approaches using renewable carbonylation reagents to synthesize benzothiazolones is highly desirable.

In recent years, the chemical transformation of CO_2 drew much attention owing to its easily available, renewable, abundant, and nontoxic features. Various value-added chemicals were synthesized using CO_2 as a C1 building block via the construction of C–H, C–N, C–O, and C–C bonds [17–22]. The formation of the C–S bond is one of the important transformations in organic synthesis [23,24], and the construction of C–S bonds using CO_2 as a C1 source is an interesting topic. In our recent efforts, we discovered a new route for the synthesis of benzothiazoles via the reaction of 2-aminothiophenols with CO_2 and hydrosilanes, which was the first body of work describing the construction of C–S bonds from CO_2 [25,26]. It is worth mentioning that a byproduct, benzothiazolone, was detected in minute amounts along with benzothiazole, which was formed via

the reaction of 2-aminothiophenol with CO_2. Compared to traditional synthetic methods, the synthesis of benzothiazolones using CO_2 as a carbonyl source is more attractive (Scheme 1b). However, due to the inherent kinetic inertness and thermodynamic stability of CO_2, developing highly efficient catalysts is a key step for the cyclocarbonylation of 2-aminothiophenols with CO_2. In previous work from our group, Yu, and Zhao et al. found that ionic liquids could catalyze this reaction, providing only one example with a low yield [27,28]. The further exploration of highly efficient catalysts and the systematic study of the synthesis of benzothiazolone from CO_2 are of great importance.



Scheme 1. Cyclocarbonylation of 2-aminothiophenols with various carbonylation agents.

Recently, organic bases were widely applied to CO_2-joined reactions with highly efficient catalytic activity. The tertiary nitrogen of these compounds reacted with CO_2 to form the carbamate species, which resulted in the activation of CO_2, facilitating the reactions [29–36]. Moreover, from an organic synthesis point of view, base-promoted reactions also provide a very important complementary methodology for transition-metal catalyst systems [37–40]. In this work, a series of organic bases, including 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,1,3,3-tetramethylguanidine (TMG), 1,4-diazabicyclo [2.2.2]octane (DABCO), 1-methylimidazole (MIm), and hexamethylenetetramine (HMTA) (Figure 1), was investigated for the cyclocarbonylation of 2-aminothiophenols with CO_2. Then, various reaction parameters were studied, and a possible reaction mechanism was also discussed. This work presents an environmentally benign method for the synthesis of benzothiazolones directly from a renewable carbonylation source (CO_2).

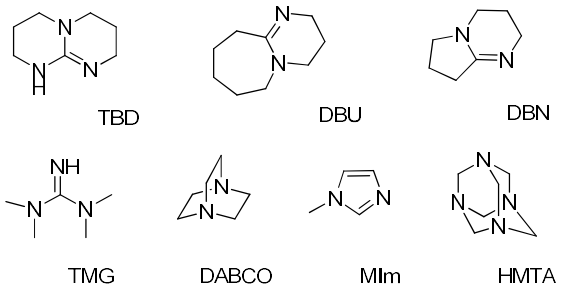


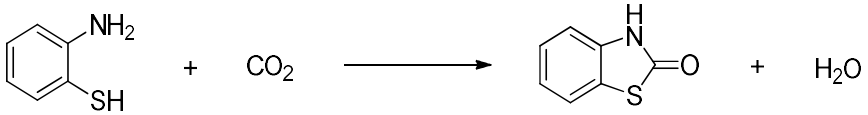
Figure 1. Structures of the organic bases used in this study: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,1,3,3-tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-methylimidazole (MIm), and hexamethylenetetramine (HMTA).

2. Results and Discussion

The reaction of 2-aminothiophenol with CO_2 was firstly carried out in various bases at 150 °C and 5 MPa, and the results are listed in Table 1. This reaction neither proceeded without a catalyst nor in the presence of inorganic bases (Table 1, entries 1 and 2). Interestingly, the organic bases were effective in catalyzing this reaction (Table 1, entries 3–8). In particular, DBN showed the best activity, affording benzothiazolone in a yield of 91% under the experimental conditions (Table 1, entry 5). Compared to DBN, both DBU and TBD afforded lower yields of the product, which may result from the joint effects of steric hindrance (DBN < TBD < DBU) and basicity (TBD > DBU > DBN) (Table 1, entry 5 vs. entries 3 and 4). Using TMG as the catalyst, the product yield decreased expectedly, due to its special structure (Table 1, entry 6). Other organic bases exhibiting weaker basicity, such as DABCO, MIm, and HMTA, had little catalytic activity for this reaction, and benzothiazolone was obtained in a yield of <10% (Table 1, entries 7–9). This is understandable, as their basicity and structure accounted for their catalytic activity.

The effect of solvents was also tested in the reaction of CO_2 with 2-aminothiophenol catalyzed by DBN at 150 °C and 5 MPa. The catalytic activity of DBN was greatly influenced by the nature of solvent. The product yield increased in the following order: dimethyl sulfoxide (DMSO) < CH_3CN < *N*,*N*-dimethylformamide (DMF) < 1-methyl-2-pyrrolidinone (NMP) (Table 1, entries 5, 10–12). This corresponded with the order of CO_2 solubility in these solvents (expressed as Henry's constant), DMSO (12.67) > CH_3CN (9.049) > DMF (7.966) > NMP (7.61) [41]. Based on the CO_2 solubility in various solvents being expressed as Henry's constants, it was concluded that the yield of benzothiazolone increased as Henry's constant decreased. As such, the lower the Henry's constant was, the higher the CO_2 solubility, and the higher the yield of benzothiazolone. It was demonstrated that the solvents with high CO_2 solubility were more favorable for the carbonylation reaction. Therefore, DBN was chosen as the catalyst and NMP was chosen as the solvent to investigate the synthesis of benzothiazolone under other various conditions.

Table 1. Carbonylation of 2-aminothiophenol with CO_2 under various conditions [a].



Entry	Catalyst	pKa of the Conjugated Acid [b]	Solvent	Yield [d] (%)
1	None	—	NMP	0
2	NaOH	15.7 [c]	NMP	0
3	TBD	26	NMP	87
4	DBU	24.3	NMP	84
5	DBN	23.8	NMP	91
6	TMG	23.3	NMP	30
7	DABCO	(8.7)	NMP	7
8	MIm	(7.1)	NMP	4
9	HMTA	6.2	NMP	0
10	DBN	23.8	DMF	57
11	DBN	23.8	CH_3CN	32
12	DBN	23.8	DMSO	16

Abbreviations: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo [4.3.0]non-5-ene (DBN), 1,1,3,3-tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-methylimidazole (MIm), hexamethylenetetramine (HMTA), 1-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). [a] Reaction conditions: 2-aminothiophenol, 2 mmol; base, 2 mmol; NMP, 2 mL; CO_2, 5 MPa; 150 °C; 24 h. [b] pKa values in acetonitrile, with values in water given in brackets. [c] pKa values in H_2O. [d] Yield was determined using HPLC analysis.

Firstly, the influence of CO_2 pressure on the reaction was investigated under identical reaction conditions (Table 2). As can be seen, pressure had a considerable effect on the yield of the product.

Initially, the product yield increased dramatically with an increase in pressure from 1 MPa to 5 MPa, and peaked at 5 MPa with a yield of 91%. However, further increasing CO_2 pressure to 9 MPa led to a relative decrease in the yield of benzothiazolone. This is understandable due to the reaction system's phase behavior. There were two phases in the reaction system in the pressure ranging from 1 MPa to 9 MPa; CO_2 not only acted as a reactant, but also as a reaction medium in the reaction process. On one hand, when the pressure was relatively low, an increase in pressure enhanced the reaction rate because the solubility of CO_2 in the liquid reaction phase increased with increasing pressure, which helped enhance the reaction rate, since CO_2 was a reactant. On the other hand, when the pressure was higher than 5 MPa, the concentration of CO_2 in the reaction phase was high enough. Thus, higher CO_2 pressure had almost no contribution to the reaction rate, while possibly decreasing the concentration of 2-aminothiophenol in the vicinity of the catalyst, which would retard the interaction, thus resulting in a low efficiency [42–44]. Therefore, 5 MPa was deemed a suitable CO_2 pressure.

Table 2. Effect of CO_2 pressure on the yield of benzothiazolone [a].

Entry	1	2	3	4	5
CO_2 pressure (MPa)	1	3	5	7	9
Yield [b] (%)	28	77	91	83	79

[a] Reaction conditions: 2-aminothiophenol, 2 mmol; DBN, 2 mmol; NMP, 2 mL; 150 °C; 24 h. [b] Yield was determined using HPLC analysis.

Table 3 shows the temperature dependence of the reaction. Obviously, the reaction was sensitive to the reaction temperature. The yield of benzothiazolone increased sharply as the temperature rose from 110 °C to 150 °C, and reached 91% at 150 °C. The product yield remained unchanged with a further increase in temperature to 160 °C. Accordingly, 150 °C was determined as an appropriate reaction temperature for the synthesis of benzothiazolone.

Table 3. Reaction temperature dependence of benzothiazolone yield [a].

Entry	1	2	3	4	5	6
Temperature (°C)	110	120	130	140	150	160
Yield [b] (%)	37	42	54	78	91	91

[a] Reaction conditions: 2-aminothiophenol, 2 mmol; DBN, 2 mmol; NMP, 2 mL; CO_2, 5 MPa; 24 h. [b] Yield was determined using HPLC analysis.

Table 4 shows the effect of catalyst amount on the yield of benzothiazolone. As can be seen, the product yield increased with an increase in the amount of catalyst, and the maximum yield was obtained with 2mmol of catalyst. A further increase in the amount of catalyst had no notable effect on the yield.

Table 4. Influence of catalyst amount on the reaction outcome [a].

Entry	1	2	3	4	5
Amount of catalyst (mmol)	0.5	1	1.5	2	2.5
Yield [b] (%)	41	71	78	91	92

[a] Reaction conditions: 2-aminothiophenol, 2 mmol; NMP, 2 mL; CO_2 , 5 MPa; 150 °C; 24 h. [b] Yield was determined using HPLC analysis.

The influence of reaction time on the synthesis of benzothiazolone is presented in Table 5. It was found that the yield noticeably increased with a variation in reaction time from 12 h to 24 h. Furthermore, a product yield of almost 99% was achieved when the reaction time was prolonged to 36 h.

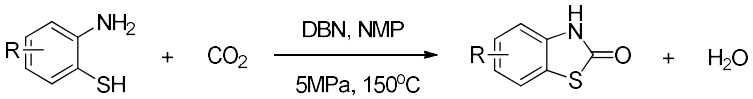
Table 5. Dependence of benzothiazolone yield on reaction time [a].

Entry	1	2	3	4	5
Time (h)	12	18	24	30	36
Yield [b] (%)	66	80	91	96	99

[a] Reaction conditions: 2-aminothiophenol, 2 mmol; DBN, 2 mmol; NMP, 2 mL; CO_2 , 5 MPa; 150 °C. [b] Yield was determined using HPLC analysis.

To explore the scope of the reaction, four substituted 2-aminothiophenols with electron-withdrawing groups or electron-donating groups were reacted with CO_2 using DBN as a catalyst, and the results are listed in Table 6. These substrates could be transformed to the corresponding benzothiazolones under the optimized reaction conditions. Methyl-substituted 2-aminothiophenol showed high activity when reacting with CO_2, producing the corresponding benzothiazolone in a yield of 70% (Table 6, entry 2). In contrast, methoxy-substituted 2-aminothiophenol was less active, producing the corresponding benzothiazolone in a yield of 45% (Table 6, entry 3). The substrates with electron-withdrawing groups (e.g., –Cl and –Br) showed poor activity, and yields of 36% with 2D, and 23% with 2E were obtained, even when the reaction time was prolonged to 40 h (Table 6, entries 4, 5). When using the strong electron-withdrawing group, NO_2, on the aromatic ring, the reaction did not take place. This was probably attributed to the electronic effect of 2-aminothiophenols. Substrates with electron-withdrawing groups showed lower reactivity, and the yields of the substituted substrates with neither electron-withdrawing groups nor electron-donating groups were also lower than the model reaction.

Table 6. Scope of the synthesis of benzothiazolones [a].



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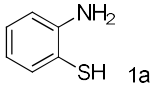
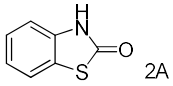
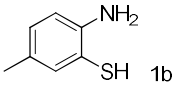
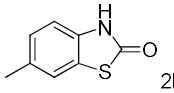
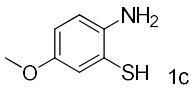
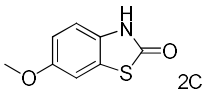
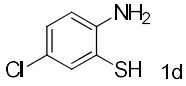
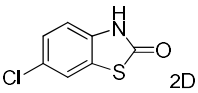
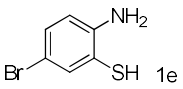
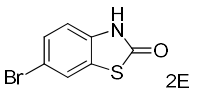
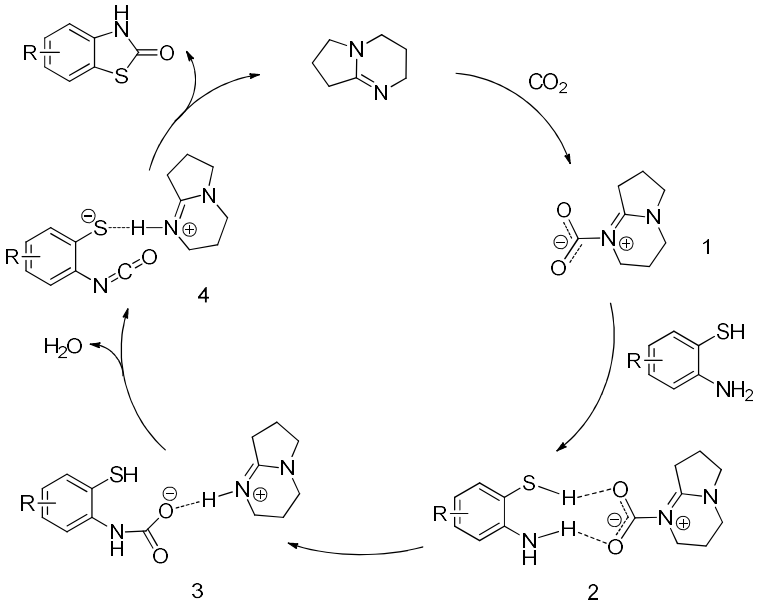
Entry	Substrate	Product	Yield [b](%)
1	 1a	 2A	91(88)
2	 1b	 2B	70(61)
3	 1c	 2C	45(36)
4	 1d	 2D	36 [c]
5	 1e	 2E	23 [c]

[a] Reaction conditions: reactant, 1 mmol; DBN, 1 mmol; NMP, 1 mL; CO_2, 5 MPa; 150 °C; 24 h. [b] Yield was determined using ^{1}H NMR with 4-nitroacetophenone as the internal standard; isolated yields are shown in brackets. [c] Reaction time: 40 h.

Based on previous reports and the experimental results [28,33,41,42,45], a probable catalytic cycle was proposed for the reaction of 2-aminothiophenols with CO_2 to benzothiazolones using DBN as a catalyst, as depicted in Scheme 2. Firstly, CO_2 could react with DBN to form the key carbamate

intermediate 1, leading to the activation of CO_2. The 2-aminothiophenols could be activated via a hydrogen bond between the carboxyl (COO) of intermediate 1, which could weaken the N–H bond of the NH_2 group in 2-aminothiophenols, making it more favorable for the insertion of CO_2. Then, the nucleophilic N atom would easily attack the carbon atom of the activated CO_2, and with the intervention of a new DBN molecule, would form intermediate 3. Subsequently, intermediate 4 could be obtained through a dehydration reaction of intermediate 3, and the release of a DBN molecule. Finally, the SH group of the substrates could be further activated via a hydrogen bond, and the intramolecular nucleophilic cyclization of intermediate 4 would take place, thus yielding the product benzothiazolones.



Scheme 2. The proposed mechanism.

3. Experimental Section

3.1. Materials

CO_2 was provided by the Beijing Analytical Instrument Company (Beijing, China) with a purity of 99.99%. Furthermore, 2-aminothiophenol (1a; 98%), 2-amino-6-methylbenzothiazole (98%), 2-amino-6-methoxybenzothiazole (99%), 2-amino-6-chlorobenzothiazole (99%), 2-amino-6-bromobenzothiazole (98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; 98%), 1,4-diazabicyclo [2.2.2]octane (DABCO; 97%), 1,1,3,3-tetramethylguanidine (TMG; 99%), 1-methylimidazole (MIm; 99%), hexamethylenetetramine (HMTA; 99%), 1-methyl-2-pyrrolidinone (NMP), and acetic acid (99%) were purchased from J&K Scientific Ltd (Beijing, China). On the other hand, 1,5-diazabicyclo [4.3.0]non-5-ene (DBN; 98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 98%), and 4-nitroacetophenone (98%) were purchased from Alfa Aesar (Shanghai, China). Acetonitrile, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) were analytical grade, and were provided by the Beijing Chemical Reagents Company (Beijing, China). NaOH was analytical grade, and was purchased from the Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China). Finally, 2-amino-5-methylbenzenethiol (1b), 2-amino-5-methoxybenzenethiol (1c), 2-amino-5-chlorobenzenethiol (1d), and 2-amino-5-bromobenzenethiol (1e) were synthesized according to the published procedures (Supplementary Materials, References [S1–S5]). The other chemicals were used without further purification.

3.2. General Procedure for the Synthesis of 2-Aminothiophenol Substrates

In a typical procedure for the preparation of 2-amino-5-methylbenzenethiol (1b), a mixture of 2-amino-6-methylbenzothiazole (5 mmol) and KOH (50 mmol) in H_2O (10 mL) was heated at 120 °C. The reaction mixture was kept on reflux for 24 h, and was then cooled to room temperature. Then, the mixture was filtered to remove the scraps, and the filtrate was neutralized with acetic acid (50% in water) to a pH of 6, before the precipitate was collected via filtration. Finally, the pure products were obtained via the column chromatography separation of the precipitate, and the target compound was obtained as a light yellow solid.

Similarly, 2-amino-5-methoxybenzenethiol (1c; reaction temperature, 120 °C; a yellow-green solid), 2-amino-5-chlorobenzenethiol (1d; reaction temperature, 140 °C; a bright-yellow solid), and 2-amino-5-bromobenzenethiol (1e; reaction temperature, 140 °C; a bright-yellow solid) were obtained via the same method using 2-amino-6-methoxybenzothiazole, 2-amino-6-chlorobenzothiazole, and 2-amino-6-bromobenzothiazole, respectively, as their corresponding raw materials.

The purified products were characterized via NMR (Bruker, Karlsruhe, Germany). The characterization data of the substrates are reported below, and the NMR spectra are given in the Supplementary Materials (Figures S1–S4).

3.3. Typical Procedure for the Synthesis of Benzothiazolones

The cyclocarbonylation of 2-aminothiophenol with CO_2 was conducted in a Teflon-lined stainless-steel 22-mL autoclave equipped with a magnetic stirrer. In one example, 2-aminothiophenol (2 mmol, 0.2504 g), DBN (2 mmol, 0.2483 g), and NMP (2 mL) were successively added into the reactor, and the reactor was placed into a water bath of 40 °C, before CO_2 was charged into the reactor until the desired pressure (e.g., 5 MPa) was achieved. Then, the reactor was placed into an oil bath of desired temperature (e.g., 150 °C), and the stirrer was started. After a certain time (e.g., 24 h), the reactor was moved into ice water, and CO_2 was slowly released. Finally, the reaction mixture was dissolved in methanol, and then transferred into a volumetric flask (100 mL). The quantity analysis of the products was conducted on an HPLC, using a Shimadzu LC-20AT pump, a Hypersil ODS2 5-μm column, and a Soma UV-Vis LC-830 detector at 282 nm. A methanol/water (50:50 v/v) solution was used as the mobile phase with a flow rate of 0.8 mL min^{-1}.

Similarly, the other benzothiazolone derivatives were obtained using the corresponding substituted 2-aminothiophenols as the substrates. The yields were determined via ^{1}H NMR using 4-nitroacetophenone as the internal standard. The pure benzothiazolones products were obtained via column chromatography separation. The characterization data of the products are reported below, and the NMR spectra are given in the Supplementary Materials (Figures S5–S9).

3.4. NMR Spectral Data of the Substrates and Products

Compound 1b, 2-amino-5-methylbenzenethiol: ^{1}H NMR (400 MHz, DMSO) δ 6.92 (d, J = 8.1 Hz, 1H), 6.81 (s, 1H), 6.65 (d, J = 8.1 Hz, 1H), 5.22 (s, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 147.84, 136.08, 132.35, 125.02, 117.12, 115.36, 20.13.

Compound 1c, 2-amino-5-methoxybenzenethiol: ^{1}H NMR (400 MHz, DMSO) δ 6.78 (dd, J = 8.8, 2.8 Hz, 1H), 6.72 (d, J = 8.8 Hz, 1H), 6.61 (d, J = 2.8 Hz, 1H), 5.05 (s, 2H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 150.60, 144.15, 119.12, 119.00, 117.56, 116.61, 55.74.

Compound 1d, 2-amino-5-chlorobenzenethiol: ^{1}H NMR (400 MHz, DMSO) δ 7.13 (dd, J = 8.7, 2.3 Hz, 1H), 6.90 (d, J = 2.2 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 5.71 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 149.18, 134.34, 131.39, 118.86, 117.60, 116.64.

Compound 1e, 2-amino-5-bromobenzenethiol: ^{1}H NMR (400 MHz, DMSO) δ 7.24 (dd, J = 8.7, 2.3 Hz, 1H), 6.99 (d, J = 2.2 Hz, 1H), 6.71 (d, J = 8.7 Hz, 1H), 5.75 (s, 2H); ^{13}C NMR (100 MHz, DMSO) δ 149.55, 137.25, 134.14, 118.13, 117.10, 105.84.

Compound 2A, benzothiazolone: ^{1}H NMR (400 MHz, DMSO) δ 11.87 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 4.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 170.47, 136.79, 126.85, 123.76, 123.14, 123.04, 111.94.

Compound 2B, 6-methylbenzothiazolone: ^{1}H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 7.36 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 170.40, 134.45, 132.28, 127.58, 123.73, 123.13, 111.69, 21.10.

Compound 2C, 6-methoxybenzothiazolone: ^{1}H NMR (400 MHz, DMSO) δ 11.67 (s, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.85 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 170.24, 155.70, 130.36, 124.82, 113.68, 112.57, 108.19, 56.04.

Compound 2D, 6-chlorobenzothiazolone: ^{1}H NMR (400 MHz, DMSO) δ 12.05 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 170.57, 137.94, 131.28, 124.75, 122.91, 122.68, 111.69.

Compound 2E, 6-bromobenzothiazolone: ^{1}H NMR (400 MHz, DMSO) δ 12.01 (s, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 170.14, 136.10, 129.65, 126.06, 125.48, 114.45, 113.61.

4. Conclusions

In conclusion, we displayed a novel method of synthesizing benzothiazolones via the cyclocarbonylation of 2-aminothiophenols with CO_2 as the C1 building block, catalyzed by DBN. A series of benzothiazolones was obtained. This work presents a green and environmentally benign method for the synthesis of benzothiazolones, and also opens a new way for the utilization of CO_2 in the construction of various chemical bonds, such as C–S bonds.

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Author Contributions: In this paper, X.G. and B.Y. designed the experiments; X.G., Y.D., C.L., L.Z. and X.W. conducted the experiments and analyzed the data; X.G. and B.Y. wrote the article.

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