Review Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Chemical Fixation of CO_2 with 2-Aminobenzenethiols into Benzothiazol(on)es: A Review of Recent Updates

Ahmed Kareem Obaid Aldulaimi[1, *], Ayat Hussein Adhab[2], Haider Radhi Saud[3], Mohammed Ubaid[4], Mustafa Humam Sami[5]

[1]*College of Food Sciences, Al-Qasim Green University, Babylon, Iraq*
[2]*Department of Pharmacy, Al-Zahrawi University College, Karbala, Iraq*
[3]*National University of Science and Technology, Dhi Qar, Iraq*
[4]*Medical technical college, Al-Farahidi University, Iraq*
[5]*Department of Pharmacy, Al-Noor University College, Nineveh, Iraq*

ARTICLE INFO

Article history:
Received 12 April 2023
Received in revised form 1 March 2024
Accepted 2 March 2024
Available online 2 March 2024

Keywords:
Carbon dioxide
2-Aminobenzenethiols,
Benzothiazoles
Benzothiazolones, Cyclocarbonylation

ABSTRACT

This paper presents an update review on recent advances and developments in chemical fixation of CO_2 with 2-aminobenzenethiols into benzothiazol(on)es. For clarity, the review is divided into two main sections. The first section is a discussion of the synthesis of benzothiazole derivatives *via* cyclization of 2-aminobenzenethiols with CO_2, while the second consists of an overview of cyclocarbonylation of 2-aminobenzenethiols utilizing CO_2 for the synthesis of benzothiazolone derivatives.

1.Introduction

The benzothiazole (1,3-benzothiazole) core is a privileged fused bicyclic heterocyclic scaffold in medicinal chemistry [1], agricultural chemistry [2], and material chemistry [3]. A number of benzothiazole-containing FDA-approved drugs are currently available on the market (Figure 1b) [4], and are used for the treatment of various types of diseases such as amyotrophic lateral sclerosis, glaucoma, duodenal ulcers, and epilepsy. In a similar way, benzothiazol-2-one is an important heterocyclic scaffold existing in various pharmaceuticals (Figure 1b) [5] and bioactive compounds [6]. In light of the wide importance of these heterocycles in various field, particularly in medicinal chemistry, there is continuing interest in the development of convenient and environmentally benign synthetic methods for their construction from simple, cheap, and easily accessible starting materials [7, 8].

Since carbon dioxide (CO_2) is a plentiful, non-toxic, non-flammable and renewable one-carbon (C1) feedstock, the conversion of CO_2 into high-added-value molecules by chemical reactions is of great significance both in academic and industrial fields [9-15]. By far, dozens of different reactions have been explored in which CO_2 is served as a raw material [16-20]. In this context, the cyclization of easily accessible 2-aminobenzenethiols with CO_2 has recently emerged as an efficient and sustainable method for constructing benzothiazole and benzothiazol-2-one derivatives. In 2017, Babazadeh and co-workers highlighted this novel page of benzothiazol(on)e synthesis in their interesting review paper entitled "chemical fixation of CO_2 with aniline derivatives: A new avenue to the synthesis of functionalized azole compounds" [21]. Since a number of important developments in this fast-growing research field have occurred during the past six years, an updated review in this hot topic seems to be timely. Therefore, in this review we will try to provide a comprehensive and updated overview of recent discoveries in the synthesis of benzothiazol(on)es through the reaction of respective

Corresponding author.; e-mail: ahmedaldulaimi1@gmail.com
https://doi.org/ 10.22034/crl.2024.443045.1296

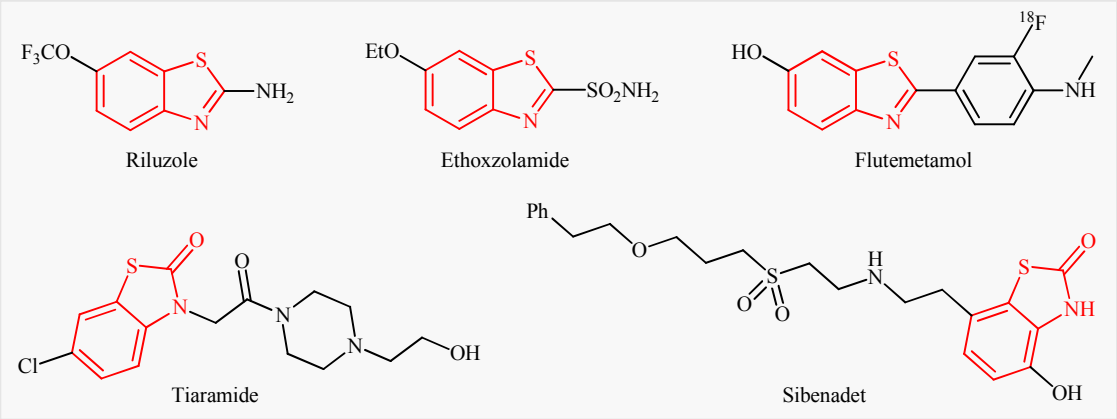


Fig. 1. Selected commercialized drugs containing benzothiazole and benzothiazol-2-one moieties.

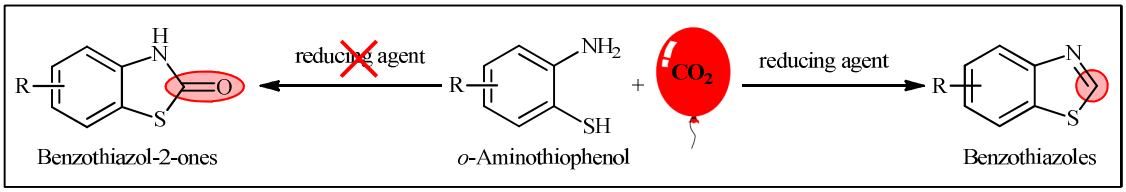
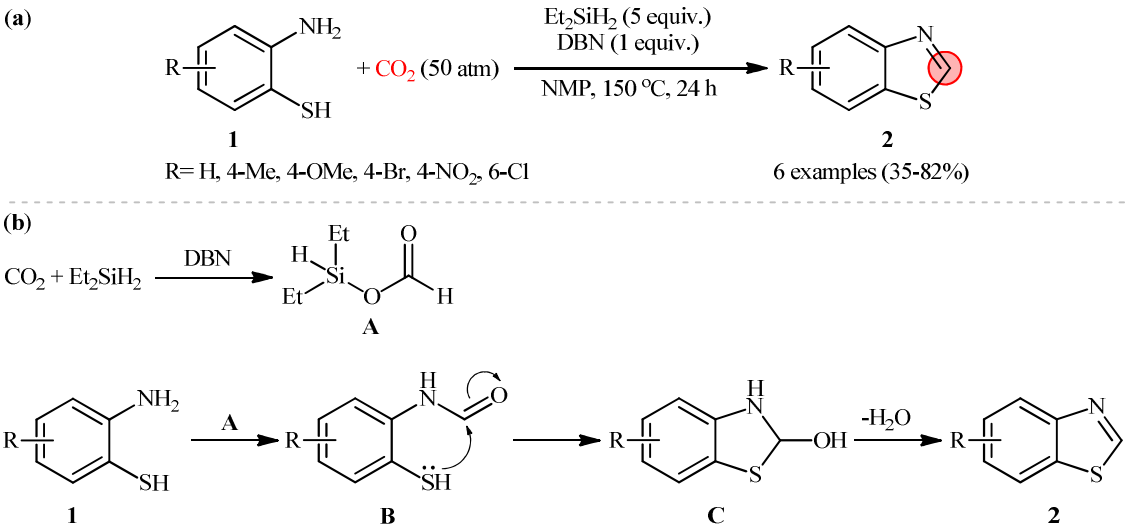


Fig. 2. Chemical fixation of CO_2 with *o*-aminobenzenethiols into benzothiazol(on)es.

o-aminobenzenethiols with CO_2 (Figure 2). The review is divided into two main sections. The first section is a discussion of the synthesis of benzothiazole derivatives through the cyclization of *o*-aminobenzenethiols with CO_2 in the presence of a reducing agent, while the second consists of an overview on the construction of benzothiazol-2-ones through the carbonyltive cyclization of *o*-aminobenzenethiols with CO_2.

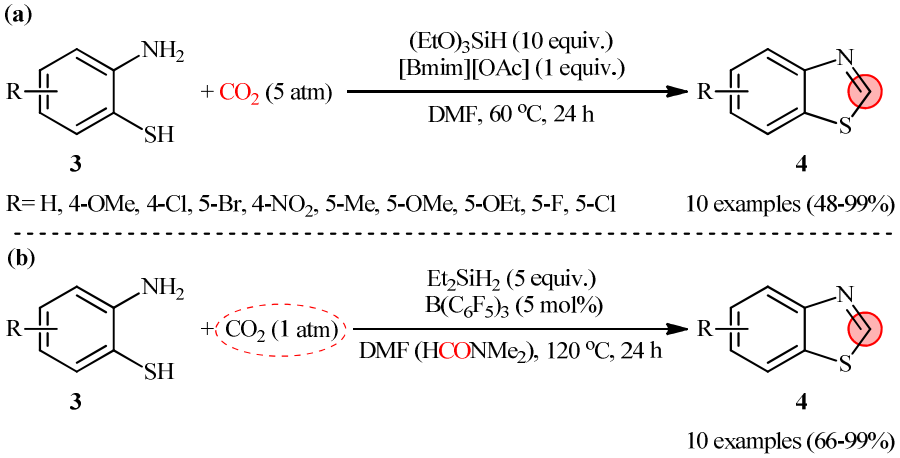
2. Synthesis of benzothiazoles

The story of benzothiazoles synthesis through the cyclization of *o*-aminobenzenethiols with CO_2 was began in 2014 by Liu and co-workers [22], who disclosed that the treatment of *o*-aminothiophenols **1** with 5 equiv. of Et_2SiH_2 in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as an organocatalyst under CO_2 atmosphere (50 atm) furnished the corresponding benzothiazoles **2** in fair to high yields (Scheme 1a). Although a series of functional groups (e.g., Me, OMe, Cl, Br) at different positions of phenyl rings of *o*-aminothiophenols were well tolerated under the reaction conditions, the nitro group was reduced to NH_2. Other organic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were also effective in this cyclization reaction but gave lower yield of product. The reaction was completely shut down in the absence of organocatalyst. It should be mentioned that small amounts of benzothiazolone by-products, formed by cyclocarbonylation of *o*-aminothiophenols, were also observed. It was found that that hydrosilane plays an important role in the formation of benzothiazoles and suppression of the production of benzothiazolones. According to the authors proposed mechanism (Scheme 1b), this CO_2-fixation reaction began with DBN-catalyzed reaction of Et_2SiH_2 with CO_2 to achieve silyl formate intermediate **A**. Then, the nitrogen of amino group in 2-aminothiophenol **1** was attached to the carbonyl group of the intermediate **A** to form the formamide intermediate **B**. Later, intramolecular nucleophilic attack of SH group to the carbon atom of intermediate **B** afforded to 2,3-dihydrobenzothiazol-2-ol intermediate **C**. Finally, dehydration reaction of intermediate **C** led to the target benzothiazoles **2**. Subsequently, with the aim of designing a milder procedure to benzothiazoles through the cyclization of *o*-aminothiophenols with CO_2, the same research group was able to demonstrate that a library of functionalized benzothiazoles **4** could be obtained in moderate to quantitative yields from the reaction of corresponding *o*-aminothiophenols **3** with CO_2 (5 atm) and hydrosilane [$(EtO)_3SiH$] at 60 °C using the ionic

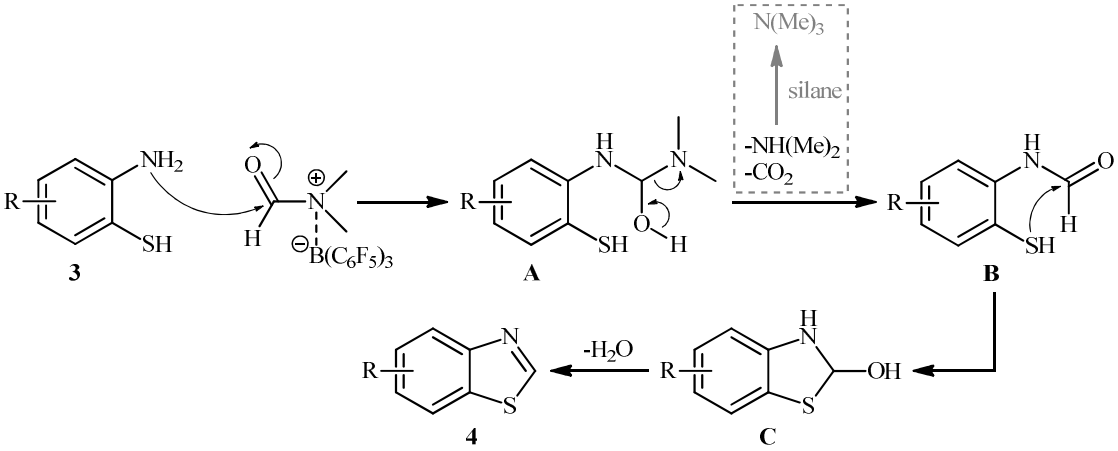


Scheme 1. (a) Liu's synthesis of benzothiazoles **2**; (b) a plausible mechanism for the formation of benzothiazoles **2**.

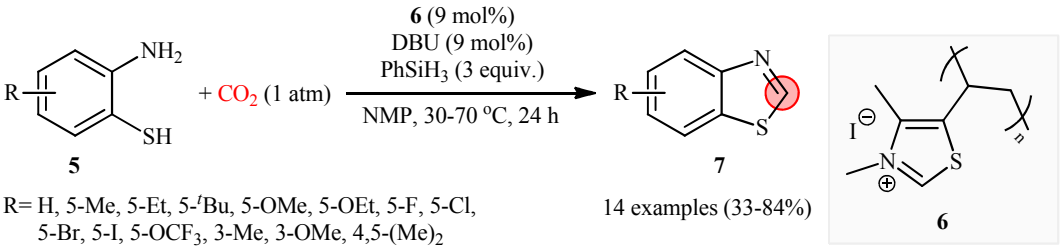
liquid 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) as catalyst in DMF (Scheme 2a) [23]. Gratifyingly, 2-amino-5-nitrobenzenethiol, a substrate bearing readily reducible nitro group, was also successfully applied under these conditions and the reducible group remained untouched. Next to benzothiazoles, benzimidazoles was also successfully achieved with use of *o*-phenylenediamines as substrates under the identical conditions. Shortly afterwards, this innovative research group developed an interesting CO_2-promoted cyclization of the same set of *o*-aminothiophenol derivatives **3** employing *N,N*-dimethylformamide (DMF) as an efficient source of carbon [24]. The reactions were performed in the presence of a catalytic amount of $B(C_6F5)_3$ under atmospheric pressure of CO_2, tolerated both electron-rich and electron-poor substrates, and provided the desired benzothiazoles **4** in good to quantitative yields (Scheme 2b). The mechanism of this cyclization reaction was proposed to initiate with the formation of formylated intermediate **A** through nucleophilic attack of the nitrogen of *o*-aminothiophenol **3** to the activated DMF which is followed by elimination of dimethylamine to form the formamide intermediate **B**. Next, this intermediate undergoes a sequential intramolecular nucleophilic cyclization and dehydration to afford observed products **4** (Scheme 3). In the same year, Yadav and co-workers disclosed that this reaction can also be successfully performed in the absence $B(C_6F5)_3$ by increasing temperature up to 150°C and CO_2 pressure up to 5 MPa [25]. Concurrently, Song's research group reported that biomass-derived γ-valerolactone (GVL) could act as an efficient catalyst for the cyclization of *o*-aminothiophenol derivatives with CO_2 [26]. In 2017, the group of Chung reported further examples of benzothiazoles **7** preparation through the cyclization of various *o*-aminothiophenols **5** with atmospheric CO_2 using poly(3,4-dimethyl-5-vinylthiazolium) iodide **6** as a precatalyst and DBU as a base under relatively mild condition (30-70 °C) [27]. As shown in Scheme 4, a relatively wide range of important functional groups such as F, Cl, Br, I, OCF_3, OMe, and OEt at different positions (C3, C4, and C5) of phenyl rings of substrates were well tolerated by this synthetic strategy, which might provide potential opportunities for further functionalization of products. However, the applicability of 6-substituted-2-aminobenzenethiols was not investigated in this study. Notably, recycling experiments indicated that the polymer precatalyst could be easily recovered from the reaction mixture as a salt by adding excess HI and reused up to seven times without any loss of activity. On the basis of experimental observations and literature reports, the authors proposed a plausible mechanism for this CO_2 conversion reaction as depicted in Scheme 5.



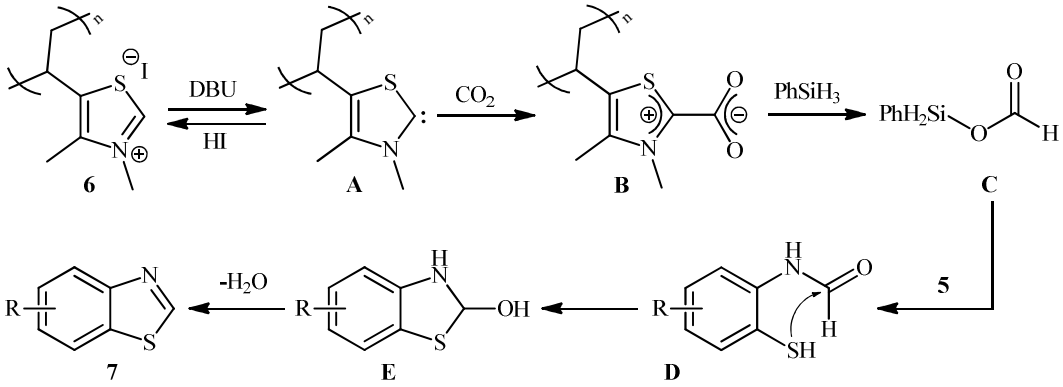
Scheme 2. (a) Ionic liquid-catalyzed cyclization of *o*-aminothiophenols **3** with CO_2; (b) CO_2-promoted cyclization of *o*-aminothiophenols **3** with DMF.



Scheme 3. The plausible mechanistic pathway for the reaction in Scheme 2b.



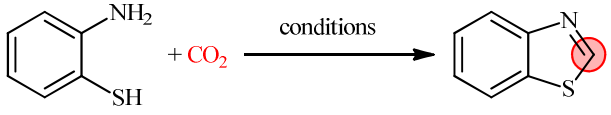
Scheme 4. Chung's synthesis of benzothiazoles **7**.



Scheme 5. Plausible mechanism for the formation of benzothiazoles **7**.

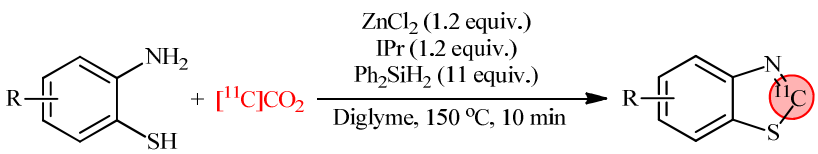
Two years later, Liu's research team reported a single example of metal-catalyzed version of the same reaction using commercially available low-cost but toxic cobalt(II) fluoride (CoF_2) as catalyst, tris 2-(diphenylphosphino)ethyl phosphine [$P(CH_2CH_2PPh_2)_3$] as a ligand and CsF as a base [28]. They showed that the treatment of unsubstituted *o*-aminothiophenol **8** with CO_2 (3 MPa) and H_2 (3 MPa) in the presence of aforementioned catalytic system furnished the desired benzothiazole **9** in an excellent isolated yield of 92% (Table 1, entry 1). The procedure was also successfully applied for the cyclization a diverse range of *o*-phenylenediaminest and *o*-aminothiophenols for the preparation of corresponding benzimidazoles and benzoxazoles, respectively. However, since both H_2 and CO_2 need to be activated, high temperatures were necessary for the success of this synthetic methodology. Later, the group of Li-Yang unraveled an interesting protocol for the reductive insertion of CO_2 into *o*-aminothiophenol **8** employing $PhSiH_3$ as a reductant and methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (DMO) as both reaction medium and promoter for the high yielding synthesis of benzothiazole **9** without using any catalyst or base (Table 1, entry 2) [29]. Following these works, Sun and Gao reported an attractive example of aminoguanidine-catalyzed cyclization of *o*-aminothiophenol **8** with CO_2 in the presence of triethoxysilane [30]. The reaction was performed using the merge of 10 mol% on non-toxic and inexpensive aminoguanidine hydrochloride salt and NaO^tBu under atmospheric pressure of CO_2 to obtain the target benzothiazole **9** in 94% yield (Table 1, entry 3). Notably, various 1,2-diamines displayed high reactivity under the identical conditions to afford the resoective imidazoles in excellent yields. Along this line, Parkin's research group developed a beautiful approach for the synthesis of benzothiazole **9** *via* catalyst-/additive-free reaction of *o*-aminothiophenol **8** with bis(silyl)acetal, $H_2C(OSiPh_3)_2$, which was easily prepared from atmospheric CO_2 and Ph_3SiH using the combination of $[Tism^{PriBenz}]MgX$ and $B(C_6F_5)_3$ as a catalytic system at room temperature [31]. In 2019, in an effort to develop a radiolabeling procedure for preparation of ^{11}C-labeled benzazoles, Liger *et al*. were able to demonstrate that a small series of ^{11}C-labeled benzothiazoles **11** could be synthesized in moderate radiochemical yields within minuts from the reaction of *o*-aminothiophenols **10** with cyclotron-produced $[^{11}C]CO_2$ in presence of zinc chloride, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), and phenylsilane (Scheme 6) [32]. This novel radiosynthesis was also successfully applied to the preparation of a relatively wide range of ^{11}C-labeled benzimidazoles from the corresponding 1,2-phenylenediamines.

Table 1. Single example reports for the cyclization of *o*-aminothiophenol **1** with CO_2.



8 **9**

Entry	Conditions	Yield (%)	Ref.
1.	CO_2 (3 MPa), H_2 (3 MPa), CoF_2 (10 mol %), $P(CH_2CH_2PPh_2)_3$ (5 mol %), CsF (1.5 equiv.), EtOH, 140 °C, 24 h	92	28
2.	CO_2 (1 MPa), $PhSiH_3$ (1.6 equiv.), DMO, 50 °C, 6 h	94	29
3.	CO_2 (0.1 MPa), aminoguanidine (10 mol%), NaOtBu (10 mol%), (EtO)3SiH (3 equiv.), DMO, 100 °C, 12 h	94	30



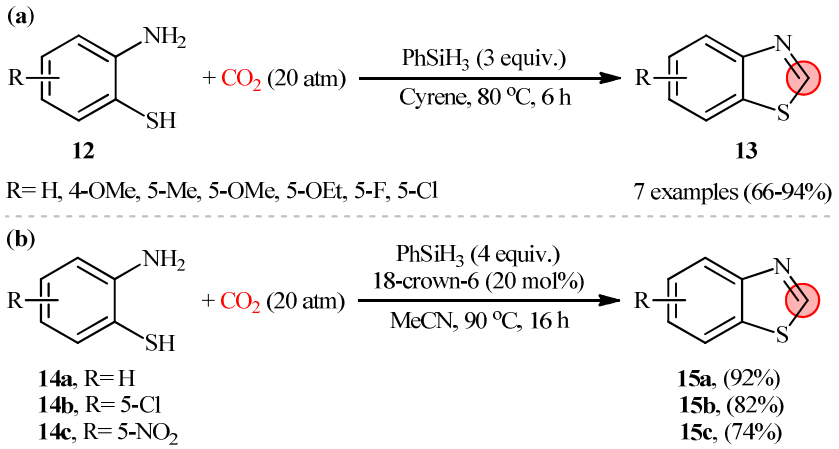
10a, R= H
10b, R= 4-Cl
10c, R= 4-CF_3

11a, (55%)
11b, (35%)
11c, (36%)

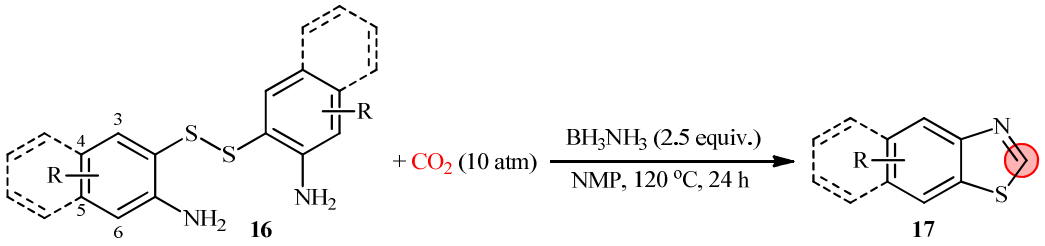
Scheme 6. Radiosynthesis ^{11}C-labeled benzothiazoles **11** reported by Liger *et al*.

Inspired by these works, in 2022, Xue and co-workers employed cellulose-derived dihydrolevoglucosenone (DLGO, Cyrene™) as a renewable catalytic solvent for the synthesis of a panel of seven benzothiazoles **13** from the reaction of *o*-aminothiophenols **12** and CO_2 using $PhSiH_3$ as the reductant (Scheme 7a) [33]. The obtained results from this study revealed that both electron-rich and electron-poor *o*-aminothiophenol derivatives were converted into the corresponding benzothiazoles in good to excellent yields without the use of any catalyst, base, or additive. After that, the research team of Xu described crown ether-catalyzed cyclization of a small series of *o*-aminothiophenols **14** with the same system (CO_2/$PhSiH_3$) [34]. The reaction proceeded smoothly using catalytic amounts of 18-crown-6 in refluxing MeCN and provided the target benzothiazoles **15** in high yields (Scheme 7b).

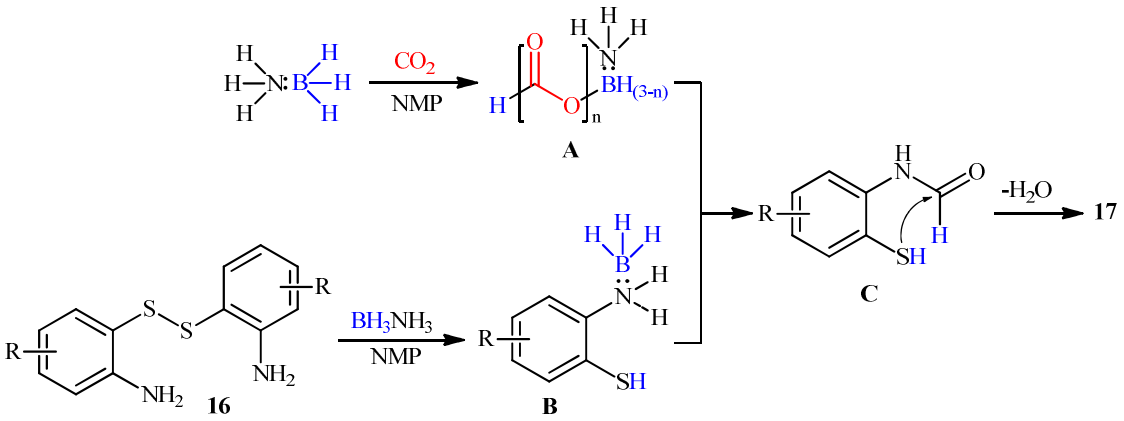
Recently, Han and Zhu along with their co-workers described an interesting route to benzothiazole derivatives **17** *via* catalyst-free reductive cyclization of bis(2-aminoaryl) disulfides **16** with CO_2 in the presence of ammonia borane (BH_3NH_3) as a reducing agent (Scheme 8) [35]. The presented methodology was shown to be relatively general (>12 examples) and exhibited a good tolerance to a range of differently substituted bis(2-aminophenyl) disulfide. The impact of substituents depended on their electronic character, and their position on the aromatic ring. The presence of electron-donating substituents (e.g., Me, OMe) tended to increase the reaction rate, and the electron-withdrawing groups (e.g., Cl, Br, CF_3, SO_2Me) slowed down the process. A possible mechanism that explains this transformation is shown in Scheme 9. Firstly, BH_3NH_3 reacted with CO_2 to form the intermediate $BH_{3-n}(OCOH)_nNH_3$ (**A**). Meanwhile, the S–S bond cleavage of disulfide **16** by BH_3NH_3 produced complex **B**. Subsequently, the nucleophilic attack of the nitrogen atom of intermediate **B** on the carbon atom of intermediate **A** formed the intermediate **C**. Finally, intramolecular nucleophilic cyclization of intermediate **C**, followed by dehydration afforded the observed benzothiazoles **17**.



Scheme 7. (a) Xue's synthesis of benzothiazoles **13**; (b) Xu's synthesis of benzothiazoles **15**.



Scheme 8. Catalyst-free reductive cyclization of bis(2-aminoaryl) disulfides **16** with CO_2 in the presence of ammonia borane.

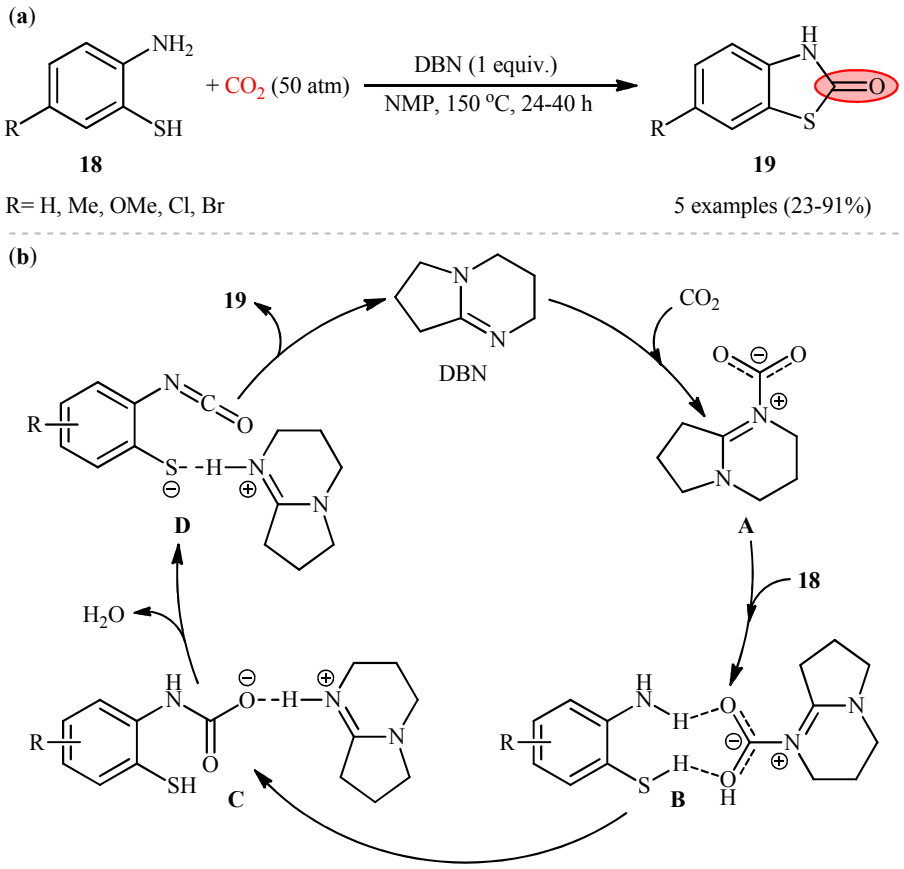


Scheme 9. Mechanistic proposal for the reactions in Scheme 8.

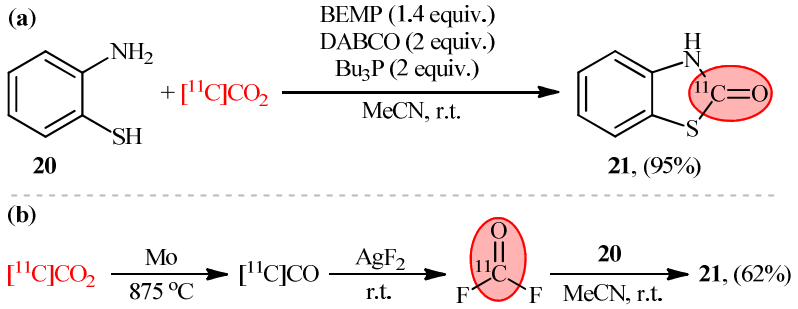
3. Synthesis of benzothiazolones

In 2018, Yu and co-workers communicated the first example of cyclocarbonylation of *o*-aminothiophenols utilizing CO_2 for the synthesis of benzothiazolone derivatives [36]. By employing unsubstituted *o*-aminothiophenol as the model substrate, various reaction parameters such as catalyst, solvent, CO_2 pressure, and temperature were carefully studied. The best conversion efficiency was obtained for the reaction performed in the presence of 1 equiv. of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in NMP at 150 °C. Under the optimized condition, a series of *o*-aminothiophenols **18** successfully underwent cyclocarbonylation and afforded the corresponding benzothiazolones **19** in poor to excellent yields (Scheme 10a). The results demonstrated that *o*-aminothiophenols possessing electron-donating groups afforded higher yields compared to the electron-poor *o*-aminothiophenols. It is important to note that this CO_2-fixation reaction was also strongly sensitive to the applied CO_2 pressure. The yield of the desired product increased sharply as the pressure rose from 1 MPa to 5 MPa, and then decreased by further increase in pressure. The mechanism shown in Scheme 10b was proposed for this amidine-catalyzed cyclocarbonylation reaction. It consists of the following key steps: (i) reaction of CO_2 with DBU to generate carbamate intermediate **A**; (ii) activation of the N–H bond of the NH_2 group in 2-aminothiophenols **18** by carbamate intermediate **A** *via* hydrogen bonding to form benzoyl amide intermediate **B**; (iii) nucleophilic attack of N atom of to the carbon atom of the activated CO_2 to afford intermediate **C**; (iv) dehydration of intermediate **C** to give 2-isocyanatobenzene-thiol **D**; and (v) intramolecular nucleophilic cyclization of 2-isocyanatobenzene-thiol **D** to form the desired benzothiazolones **19**. Subsequently, Krut'ko and co-workers found that tin(II) oxide could also effectively catalyze this reaction, albeit using supercritical CO_2 [37]. Later, it was found that cheaper alumina (Al_2O_3) could be employed for similar purpose [38]. Unfortunately, in both of these preliminary works, only one example was provided, without any substrate scope exploration. An important contribution to this field was reported by Zhang, Yu, and co-workers in 2021 [41], when various arylamines **22** were converted to the corresponding benzothiazolones **23** through the base-mediated reaction with elemental sulfur (S_8) and CO_2 (1 atm) *via* C–H bond functionalization. As shown in Scheme 12, this interesting three-component reaction tolerated various arylamines (anilines, naphthalen-2-amines and quinolin-6-amines) bearing both electron-donating and electron-withdrawing functional groups and gave the final products in synthetically useful yields. Notably, when naphthalen-1-amines were subjected to the reaction, biologically important quinolin-5-amines were obtained in moderate to good yields. Based on literature report and a series of control experiments, a plausible mechanism was suggested for the transformation, as depicted in Scheme 13. Firstly, arylamine **22** undergoes reaction with two molecules of CO_2 in the presence of base to produce the isocyanate **C** (through the intermediates **A** and **B**), that is in equilibrium with **D** and **E**. Meanwhile, nucleophilic attack to elemental sulfur might leads to the formation of intermediate **F** by a ring-opening process. Subsequently, nucleophilic attack of **F** to the isocyanate **C** forms intermediate **G** that, after intramolecular sulfuration produces intermediate **H**. Finally, deprotonation and re-aromatization of this intermediate affords the observed benzothiazolones **23** (Scheme 13, path a). In

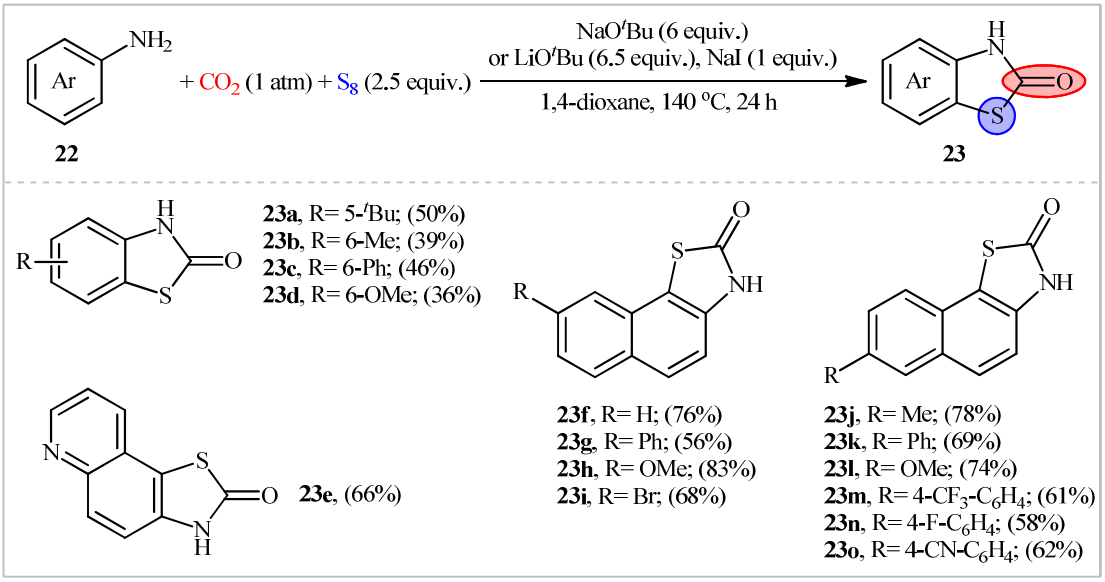
another possibility (Scheme 13, path b), the intermolecular sulfuration of intermediate **C** with S_8 affords aryl thiolate **J**, which after intramolecular cyclization gives the expected benzothiazolones **23**.



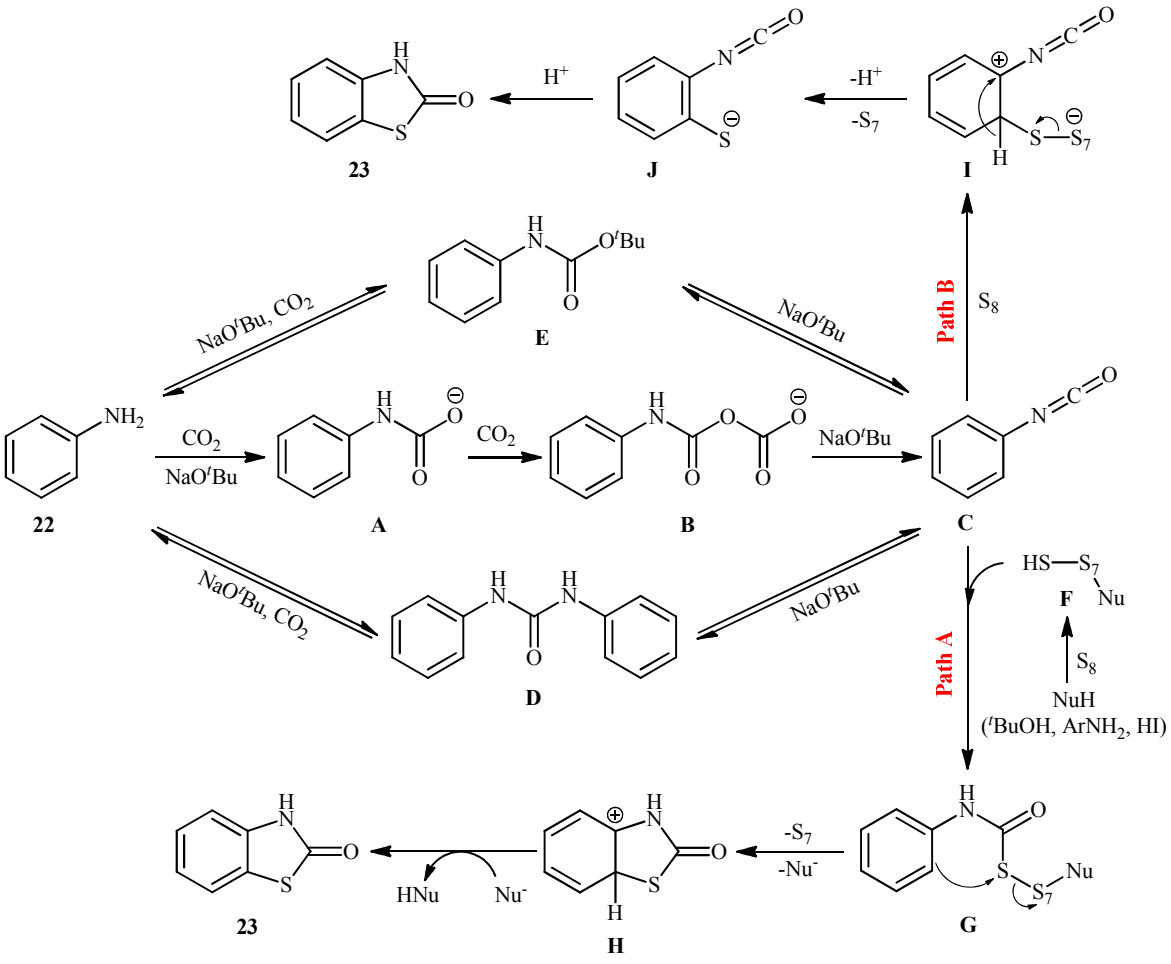
Scheme 10. (a) Yu's synthesis of benzothiazolones **19**; (b) plausible mechanism for DBN-catalyzed cyclocarbonylation of *o*-aminothiophenols **18** with CO_2.



Scheme 11. (a) Horkka's synthesis of ^{11}C-benzothiazolone **21**; (b) Jakobsson's synthesis of ^{11}C-benzothiazolone **21**.



Scheme 12. Synthesis of benzothiazolones **23** *via* three-component reaction between arylamines **22**, S_8, and CO_2.



Scheme 13. Plausible mechanistic pathways for the formation of benzothiazolones **23**.

4. Conclusion

Benzothiazoles and benzothiazol-2-ones are important targets in organic synthesis because of their recurrence as privileged structural scaffolds in medicinal chemistry, agricultural chemistry, and material chemistry. In light of the wide range of applications of titled compounds in different fields, there is continuing interest in the development of efficient and environmentally benign synthetic methods for their construction. In this regard, as shown in this review, the direct synthesis of various benzothiazol(2-one)s through the cyclization of easily accessible 2-aminobenzenethiols with CO_2 has attracted a lot of attention in recent years. Despite the significant developments over the past decade on this interesting field of research, many challenges still remain to be overcome. For example, the following can be mentioned: (i) further investigation of the substrate scope; (ii) development of milder protocols; and (iii) investigation of the applicability of this page of benzothiazol(2-one)s synthesis under non-conventional such as photo/electrochemical conditions.

References

[1] (a) R.S. Keri, M.R. Patil, S.A. Patil, S. Budagumpi, A comprehensive review in current developments of benzothiazole-based molecules in medicinal chemistry. Eur. J. Med. Chem., 89 (2015) 207-251; (b) M. Abdoli, A. Angeli, M. Bozdag, F. Carta, A. Kakanejadifard, H. Saeidian, C.T. Supuran, Synthesis and carbonic anhydrase I, II, VII, and IX inhibition studies with a series of benzo [d] thiazole-5-and 6-sulfonamides. J. Enzyme Inhib. Med. Chem., 32 (2017) 1071-1078; (c) M. Abdoli, C.T. Supuran, R. Žalubovskis, 2-((1H-Benzo [d] imidazol-2-yl) amino) benzo [d] thiazole-6-sulphonamides: a class of carbonic anhydrase II and VII-selective inhibitors. J. Enzyme Inhib. Med. Chem., 38 (2023) 2174981.

[2] Y. Zou, Y. Zhang, X. Liu, H. Song, Q. Cai, S. Wang, C. Yi, J. Chen, Research progress of benzothiazole and benzoxazole derivatives in the discovery of agricultural chemicals. Int. J. Mol. Sci., 24 (2023) 10807.

[3] S. Sulthana, P. Pandian, A review on indole and benzothiazole derivatives its importance. J. drug deliv. ther., 9 (2019) 505-509.

[4] K.A. Scott, J.T. Njardarson, Analysis of US FDA-approved drugs containing sulfur atoms. Top. Curr. Chem., 376 (2018) 5.

[5] J. Poupaert, P. Carato, E. Colacino, 2 (3*H*)-benzoxazolone and bioisosters as "privileged scaffold" in the design of pharmacological probes. Current medicinal chemistry, 12 (2005) 877-885.

[6] (a) Q. Jin, Z. Fu, L. Guan, H. Jiang, Syntheses of benzo [*d*] thiazol-2 (3*H*)-one derivatives and their antidepressant and anticonvulsant effects. Mar. Drugs, 17 (2019) 430; (b) F. Tok, N. Baltaş, G. Tatar, B. Koçyiğit-Kaymakçıoğlu, Synthesis, biological evaluation and in silico studies of new pyrazoline derivatives bearing benzo [*d*] thiazol-2 (3*H*)-one moiety as potential urease inhibitors. Chem. Biodivers., 19 (2022) 202100826; (c) N. Leleu-Chavain, D. Baudelet, V.M. Heloire, D.E. Rocha, N. Renault, A. Barczyk, M. Djouina, M. Body-Malapel, P. Carato, R. Millet, Benzo [*d*] thiazol-2 (3*H*)-ones as new potent selective CB2 agonists with anti-inflammatory properties. Eur. J. Med. Chem., 165 (2019) 347-362.

[7] X. Gao, J. Liu, X. Zuo, X. Feng, Y. Gao, Recent advances in synthesis of benzothiazole compounds related to green chemistry. Molecules, 25 (2020) 1675.

[8] (a) M.A. Waseem, A. Srivastava, A. Srivastava, I.R. Siddiqui, Water and ionic liquid synergy: A novel approach for the synthesis of benzothiazole-2 (3*H*)-one. J. Saudi Chem. Soc., 19 (2015) 334-339.; (b) X. Zhuo, L. Zheng, X. Zou, Y. Zhong, W. Guo, Metal-free temperature-controlled intermolecular [3+ 2] annulation to access benzo [d] thiazole-2 (3*H*)-thiones and benzo [d] thiazol-2 (3*H*)-ones. J. Org. Chem., 87 (2022) 10467-10475.; (c) E. Vessally, S. Mohammadi, M. Abdoli, A. Hosseinian, P. Ojaghloo, Convenient and robust metal-free synthesis of benzazole-2-ones through the reaction of aniline derivatives and sodium cyanate in aqueous medium. Iran. J. Chem. Chem. Eng., 39 (2020)11-19.

[9] A. Saravanan, D.V.N. Vo, S. Jeevanantham, V. Bhuvaneswari, V.A. Narayanan, P.R. Yaashikaa, S. Swetha, B. Reshma, A comprehensive review on different approaches for CO_2 utilization and conversion pathways. Chem. Eng. Sci., 236 (2021) 116515.

[10] T.A. Atsbha, T. Yoon, P. Seongho, C.J. Lee, A review on the catalytic conversion of CO_2 using H_2 for synthesis of CO, methanol, and hydrocarbons. J. CO_2 Util., 44 (2021) 101413.

[11] S. Dabral, T. Schaub, The use of carbon dioxide (CO_2) as a building block in organic synthesis from an industrial perspective. Adv. Synth. Catal., 361 (2019) 223-246.

[12] G. Yuan, C. Qi, W. Wu, H. Jiang, Recent advances in organic synthesis with CO_2 as C1 synthon. Curr. Opin. Green Sustain. Chem., 3 (2017) 22-27.

[13] G. Naik, N. Sarki, V. Goyal, A. Narani, K. Natte, Recent trends in upgrading of CO_2 as a C1 reactant in N-and C-methylation reactions. Asian J. Org. Chem., 11 (2022) 202200270.

[14] X.F. Liu, K. Zhang, L. Tao, X.B. Lu, W.Z. Zhang, Recent advances in electrochemical carboxylation reactions using carbon dioxide. Green Chem. Eng., 3 (2022) 125-137.

[15] Z. Fan, Y. Yi, C. Xi, Recent advances in light-induced carboxylation of organic (pseudo) halides with CO_2. Asian J. Org. Chem., 11 (2022) 202200207.

[16] W. Xu, D. Guo, A.G. Ebadi, M. Toughani, E. Vessally, Transition-metal catalyzed carboxylation of organoboron compounds with CO_2. J. CO_2 Util., 45 (2021) 101403.

[17] S. Arshadi, E. Vessally, M. Sobati, A. Hosseinian, A. Bekhradnia, Chemical fixation of CO_2 to N-propargylamines: A straightforward route to 2-oxazolidinones. J. CO_2 Util., 19 (2017) 120-129.

[18] E. Vessally, S. Soleimani-Amiri, A. Hosseinian, L. Edjlali, M. Babazadeh, Chemical fixation of CO_2 to 2-aminobenzonitriles: A straightforward route to quinazoline-2, 4 (1*H*, 3*H*)-diones with green and sustainable chemistry perspectives. J. CO_2 Util., 21 (2017) 342-352.

[19] K. Didehban, E. Vessally, M. Salary, L. Edjlali, M. Babazadeh, Synthesis of a variety of key medicinal heterocyclic compounds via chemical fixation of CO_2 onto o-alkynylaniline derivatives. J. CO_2 Util., 23 (2018) 42-50.

[20] F. Behmagham, S.M. Saied, M.D. Azeez, P.R. Abbass, A.H. Adhab, E. Vessally, Recent progress in reductive carboxylation of C–O bonds with CO_2. RSC Adv., 13 (2023) 32502-32517.

[21] E. Vessally, K. Didehban, M. Babazadeh, A. Hosseinian, L. Edjlali, Chemical fixation of CO2 with aniline derivatives: A new avenue to the synthesis of functionalized azole compounds (A review). J. CO_2 Util., 21 (2017) 480-490.

[22] X. Gao, B. Yu, Y. Zhao, L. Hao, Z. Liu, Hydrosilane-promoted cyclization of 2-aminothiophenols by CO_2 to benzothiazoles. RSC Adv., 4 (2014) 56957-56960.

[23] X. Gao, B. Yu, Z. Yang, Y. Zhao, H. Zhang, L. Hao, B. Han, Z. Liu, Ionic liquid-catalyzed C–S bond construction using CO_2 as a C1 building block under mild conditions: A metal-free route to synthesis of benzothiazoles. ACS Catal., 5 (2015) 6648-6652.

[24] X. Gao, B. Yu, Q. Mei, Z. Yang, Y. Zhao, H. Zhang, L. Hao, Z. Liu, Atmospheric CO_2 promoted synthesis of N-containing heterocycles over $B(C_6F_5)_3$ catalyst. New J. Chem., 40 (2016) 8282-8287.

[25] K.B. Rasal, G.D. Yadav, Carbon dioxide mediated novel synthesis of quinazoline-2, 4 (1 H, 3 H)-dione in water. Org. Process Res. Dev., 20 (2016) 2067-2073.

[26] J. Song, B. Zhou, H. Liu, C. Xie, Q. Meng, Z. Zhang, B. Han, Biomass-derived γ-valerolactone as an efficient solvent and catalyst for the transformation of CO_2 to formamides. Green Chem., 18 (2016) 3956-3961.

[27] S. Chun, S. Yang, Y.K. Chung, Synthesis of benzothiazoles from 2-aminobenzenethiols in the presence of a reusable polythiazolium precatalyst under atmospheric pressure of carbon dioxide. Tetrahedron, 73 (2017) 3438-3442.

[28] Z. Ke, B. Yu, H. Wang, J. Xiang, J. Han, Y. Wu, Z. Liu, P. Yang, Z. Liu, Cobalt-catalyzed synthesis of *N*-containing heterocycles *via* cyclization of ortho-substituted anilines with CO_2/H_2. Green Chem., 21 (2019) 1695-1701.

[29] H. Wu, W. Dai, S. Saravanamurugan, H. Li, S. Yang, Endogenous X–C [double bond, length as m-dash] O species enable catalyst-free formylation prerequisite for CO_2 reductive upgrading. Green Chem., 22 (2020) 5822-5832.

[30] Y. Sun, K. Gao, Aminoguanidine-catalyzed reductive cyclization of *o*-phenylenediamines with CO_2 in the presence of triethoxysilane. J. Org. Chem., 88 (2023) 7463-7468.

[31] M. Rauch, Z. Strater, G. Parkin, Selective conversion of carbon dioxide to formaldehyde *via* a bis (silyl) acetal: incorporation of isotopically labeled C1 moieties derived from carbon dioxide into organic molecules. J. Am. Chem. Soc, 141 (2019) 17754-17762.

[32] F. Liger, F. Cadarossanesaib, T. Iecker, C. Tourvieille, D. Le Bars, T. Billard, ^{11}C-Labeling: Intracyclic incorporation of carbon-11 into heterocycles. Eur. J. Org. Chem., (2019) 6968-6972.

[33] H. Yu, D. Yu, Z. Xue, B. Zhang, T. Mu, Dihydrolevoglucosenone as a bio-based catalytic solvent for efficient reductive-transformation of CO_2 with amines into formamides and benzothiazoles. J. Chem. Eng., 431 (2022) 133397.

[34] R. Yao, Y. Li, J. Wang, J. Chen, Y. Xu, Crown ether as organocatalyst for reductive upgrading of CO_2 to *N*-containing benzoheterocyclics and *N*-formamides. J. Catal., 418 (2023) 78-89.

[35] X. Li, Z. Liu, H. Hong, L. Han, N. Zhu, 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. RSC Adv., 12 (2023) 18107-18114.

[36] X. Gao, Y. Deng, C. Lu, L. Zhang, X. Wang, B. Yu, Organic base-catalyzed C–S bond construction from CO_2: A new route for the synthesis of benzothiazolones. Catalysts, 8 (2018) 271.

[37] Y.M. Panov, L.V. Erkhova, A.G. Balybin, D.P. Krut'ko, D.A. Lemenovskii, Cyclization of *o*-phenylenediamine and *o*-substituted anilines with supercritical carbon dioxide. Russ. J. Phys. Chem. B, 13 (2019) 1284-1289.

[38] H. Matsuo, J.C. Choi, T. Fujitani, K.I. Fujita, Carbonylation of o-phenylenediamines with CO_2 to 2-benzimidazolones catalyzed by alumina. Tetrahedron Lett., 96 (2022) 153772.

[39] K. Horkka, K. Dahl, J. Bergare, C.S. Elmore, C. Halldin, M. Schou, Rapid and efficient synthesis of ^{11}C-labeled benzimidazolones using [^{11}C] carbon dioxide. ChemistrySelect, 4 (2019) 1846-1849.

[40] J.E. Jakobsson, S. Lu, S. Telu, V.W. Pike, [^{11}C] Carbonyl difluoride—a new and highly efficient

[^{11}C] carbonyl group transfer agent. Angew Chem. Int. Ed. Engl., 132 (2020) 7323-7327.
[41] C.K. Ran, L. Song, Y.N. Niu, M.K. Wei, Z. Zhang, X.Y. Zhou, D.G. Yu, Transition-metal-free synthesis of thiazolidin-2-ones and 1, 3-thiazinan-2-ones from arylamines, elemental sulfur and CO_2. Green Chem., 23 (2021) 274-279.