

A review on the CO₂ Incorporation Reactions Using Arynes

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ABSTRACT

Arynes are highly reactive and kinetically unstable intermediates, which have been extensively utilized in various carbon-carbon and carbon-heteroatom bond formation reactions. Multi-component couplings of these intermediates are powerful transformations that allow for efficient synthesis of a wide range of carbocycles and heterocycles, as well as natural products. On the other hand, CO₂-fixation reactions are one of the safest and most inexpensive methods for the synthesis of various value-added chemicals. Along this line, recently, several elegant multi-component reactions involving arynes were designed for the incorporation of CO₂. This review provides a comprehensive overview of the CO₂ incorporation reactions using arynes, with the emphasis on the mechanistic aspects of the reactions.

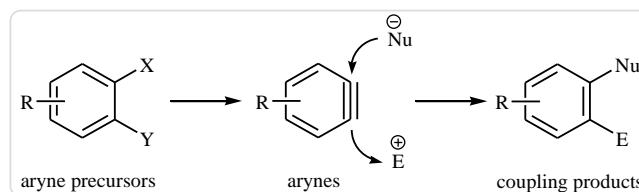
1. Introduction

The conversion of carbon dioxide (CO₂) as an abundant, safe, inexpensive, nontoxic, nonflammable, and renewable C1 synthon into value-added chemicals, such as carbonates, carbamates, esters, carboxylic acids and alcohols represents one of the hot topics in the fields of green and sustainable chemistry [1-10]. However, due to the inert nature of this greenhouse gas, the chemical fixation process with high efficiency is still a great challenge [11].

Arynes (benzynes) are highly strained, unstable, and reactive intermediates, which have been extensively utilized to the synthesis of a large number of valuable carbocyclic and heterocyclic compounds [12-16]. Over the past few years, this concept was further expanded by developing new multi-component reactions involving arynes [17]. Generally, arynes multi-component couplings involves the initial addition of nucleophiles to *in situ* generated arynes and subsequent trapping of the aryl anion intermediate with electrophiles (Scheme 1). Needless to say, the carbon atom of carbon dioxide is highly electrophilic due to the attached electronegative oxygen atoms and can undergo electrophilic attack by various nucleophiles [18]. According to the above

sentences, CO₂ could be utilized as a versatile electrophilic coupling partner in the multi-component reactions involving arynes.

Recently, several elegant multi-component coupling reactions involving arynes were designed that allow the incorporation of CO₂ to produce various multi-functionalized arenes and heteroarenes such as benzoxazin-4-ones, anthranilic acids, isocoumarins, phthalimides, 2-arylamino benzoates, 2-aminoaryl benzoates, and carbamates (Figure 1). To the best of our knowledge, a comprehensive review has not appeared on CO₂ incorporation reactions using arynes in literature thus far. In continuation of our recent reviews [11, 19-29], herein we will try to provide a concise overview of the recent advances and developments in this field with special emphasis on the mechanistic aspects of the reactions.



Scheme 1. Three-component coupling reactions involving arynes.

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2. Three-component reactions

The possibility of CO₂ incorporation reaction using arynes was first realized by Yoshida, Kunai and co-workers, who synthesized a series of highly substituted benzoxazin-4-ones **3** through a metal-free three-component reaction between 2-(trimethylsilyl)aryl triflates **1**, imines **2**, and CO₂ in the presence of 4 equiv. of KF/18-crown-6 in THF at 0 °C [30]. The presence of KF as a fluoride ion source is crucial to the success of the reaction, owing to the generation of required arynes by the fluoride induced 1,2-elimination of starting 2-(trimethylsilyl)aryl triflates under mild reaction conditions [31]. Under the optimal conditions, the desired six-membered heterocycles were obtained in fair to high yields (Scheme 2a). This three-component coupling reaction tolerated a range of substituents on the arynes and was efficient for the use of different primary and secondary alkyl imines. However, tertiary alkyl

imines and aryl imines failed to afford the expected products. According to the authors proposed mechanism, the reaction proceeds with nucleophilic addition of an imine **2** to *in situ* generated aryne **A** leading to a zwitterion intermediate **B**, which undergoes nucleophilic addition to CO₂ followed by intramolecular cyclization to give the target product **3** (Scheme 2b). The results showed that electronic and steric effects of the substituents on the arynes greatly affected the regioselectivity of reactions. For example, 3-methoxybenzyne, underwent nucleophilic attack by the imine at the *meta* position of the methoxy moiety to afford the 5-methoxybenzoxazin-4-one, exclusively. However, in the case of 3-methylbenzyne, the steric effect would be in conflict with an electron-donating inductive effect of the methyl moiety, leading to the production of a mixture of two possible products (Scheme 3).

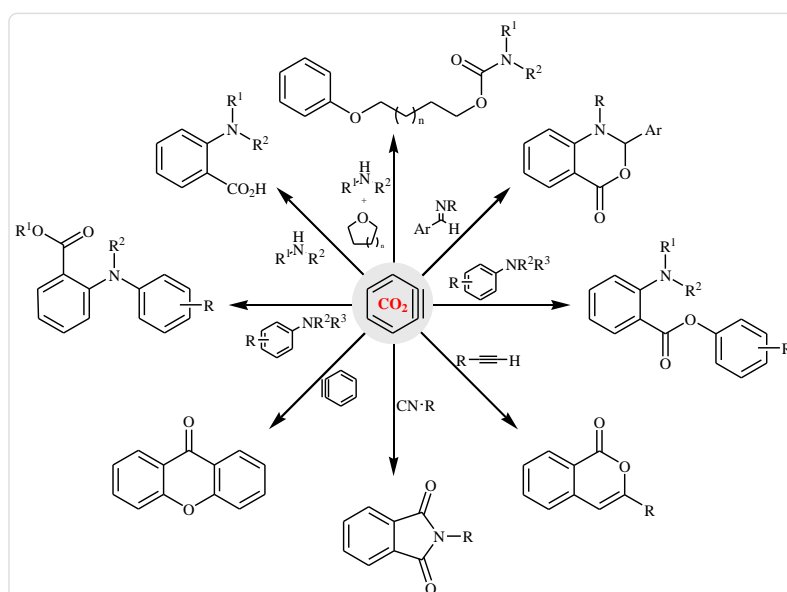
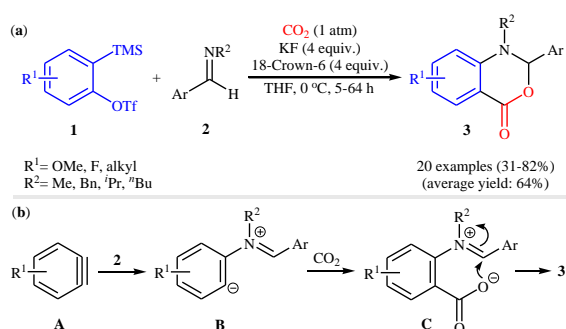


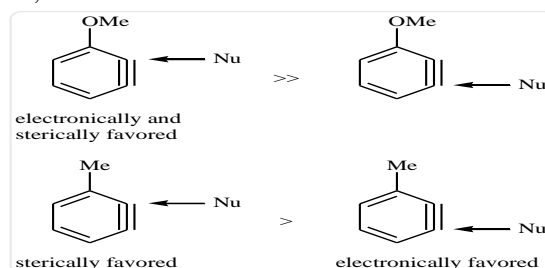
Fig. 1 CO₂ incorporation reactions using arynes.



Scheme 2. (a) Reaction of 2-(trimethylsilyl)aryl triflates **1** with imines **2** under a CO₂ atmosphere; (b) Mechanism that accounts for the formation of **3**.

Thus, under the above-mentioned standard conditions, three-component coupling reaction of CO₂, 2-(trimethylsilyl)aryl triflates **4**, and secondary amines **5**

furnished the desired anthranilic acids **6** in yields ranging from 7 to 90% (Scheme 4). The results demonstrated that acyclic secondary amines afforded better yields compared to the cyclic amines. For cyclic amines,

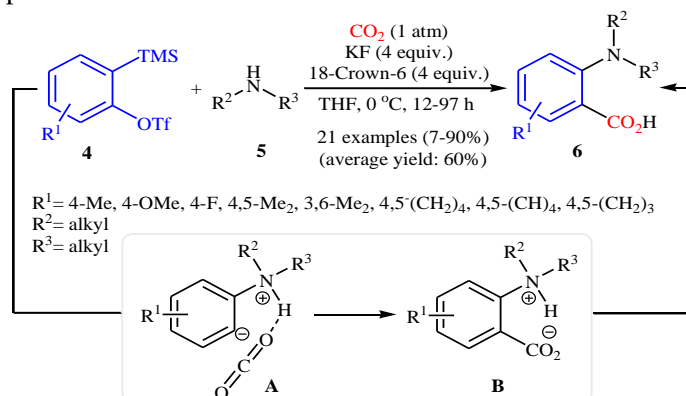


Scheme 3. Influence of the electronic and steric factors on the regioselectivity of the reaction.

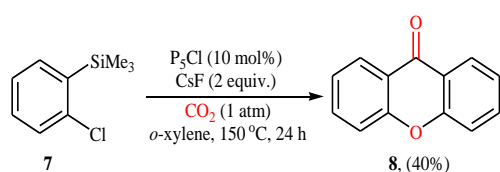
the decreasing order of reactivity is azepane > piperidine >> pyrrolidine. Just like previous work, the regioselectivity of reaction was heavily dependent to the

electronic and steric characteristics of the substituents on the arynes. The authors proposed that the reaction proceeds *via* the formation of a 1,3-zwitterionic species **A** between an aryne and an amine, which was quenched using CO₂ to afford the expected product.

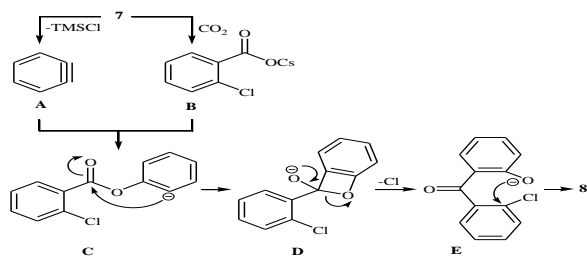
In 2014, Kondo's research team showed that the treatment of 2-chlorophenyltrimethylsilane **7** with CO₂ (1 atm) in the presence of a catalytic amount of P₅Cl and 2 equiv. of CsF as a fluoride ion source afforded 40% yield of unexpected xanthone **8** (Scheme 5) [33]. On the basis of the literature, the authors proposed a mechanism (Scheme 6) that involves the initial formation of benzyne **A** and carboxylate **B** intermediates through the 1,2-elimination and carboxylation of 2-chlorophenyltrimethylsilane **7**, respectively, which undergo combination reaction to form intermediate **C**. Subsequently, intramolecular addition of aryl anion of **C** to carbonyl group affords intermediate **D**. Next, rearrangement of this intermediate leads to the phenoxide intermediate **E**. Finally, intramolecular nucleophilic aromatic substitution of **E** gives the final product.



Scheme 4. Synthesis of anthranilic acids **6** through a three-component coupling using arynes, amines and CO₂.



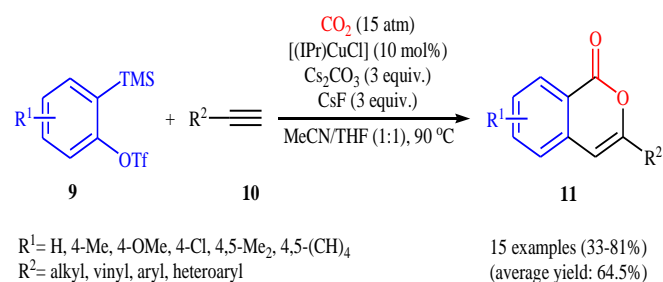
Scheme 5. Reaction of *o*-chlorophenyltrimethylsilane **7** with CO₂ in the presence of P₅Cl/CsF combination as a catalytic system.



Scheme 6. Mechanistic proposal for the reaction in Scheme 5.

Inspired by these works, the group of Kobayashi presented one of the most striking examples of the

synthesis of isocoumarins **11** *via* a copper-catalyzed three-component coupling reaction involving 2-(trimethylsilyl)aryl triflates **9**, terminal alkynes **10**, and carbon dioxide (Scheme 7) [34]. Various copper catalysts, bases, and solvents were carefully tested in order to optimize the reaction conditions and the combination of [(IPr)CuCl]/Cs₂CO₃/CsF as a catalytic system in binary solvent MeCN/THF with ratio 1:1 proved most effective. Various aryl/heteroaryl/vinyl/alkyl-substituted terminal alkynes and functionalized 2-(trimethylsilyl)aryl triflates were used to establish the general applicability of the method. Under optimized conditions, the corresponding isocoumarins were obtained in moderate to high yields. A gram-scale reaction was also successfully reported. However, when unsymmetrical aryne precursors were used, a mixture of two possible products were obtained demonstrating poor regioselectivity of the reaction. The authors proposed a mechanism in accordance with previous reports and their findings and this is represented in Scheme 8. The reaction starts with the deprotonation of terminal alkyne **10** by NHC-copper hydroxide, leading to the formation of copper acetylide **A**. Concurrently, the fluoride-induced silyl elimination of 2-(trimethylsilyl)aryl triflate **9** yields *ortho*-benzyne **B**. Its reaction with organometallic **A** forms the *ortho*-alkynyl copper complex **C**. Next, the nucleophilic attack of this intermediate to the carbon atom in CO₂ leads to copper carboxylate **D**, which undergoes a 6-*endo*-dig cyclization to form endocyclic copper heterocycle **E**. Finally, transmetalation between intermediate **E** and the cesium salt affords intermediate **F** that under the reaction condition converts to the expected product **11**.



Scheme 7. NHC-Cu-catalyzed three-component couplings of arynes **9**, terminal alkynes **10**, and CO₂.

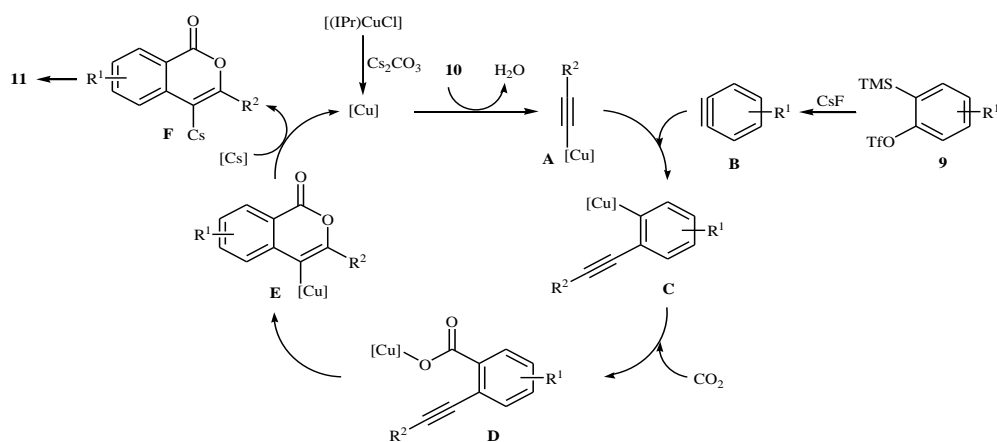
In 2014, Kaicharla, Thangaraj, and Biju showed that phthalimide derivatives **14** were formed *via* three-component reactions of 2-(trimethylsilyl)aryl triflates **12**, isocyanides **13**, and CO₂ employing CsF as a F⁻ source under transition-metal-free condition at 30 °C [35]. This methodology resulted in *N*-substituted phthalimides in moderate to good yields and tolerated a series of sensitive functional groups, such as fluoro and ether functionalities (Scheme 9). Interestingly, when CO₂ was replaced with H₂O, the corresponding benzamide derivatives **15** were obtained in yields ranging from 26 to 92%. The author proposed

mechanistic course for these reactions is depicted in Scheme 10 and involves the initial formation of 1,3-zwitterionic intermediate **B** via the nucleophile attack of the isocyanide **13** on the *in situ* generated aryne **A**, which undergoes a [3+2] cycloaddition with CO₂ to produce imino isobenzofuran **C**. Finally, a fluoride induced rearrangement of this intermediate leads to the observed phthalimide **14** through the acylfluoride intermediate **D**. However, in the presence of H₂O, the intermediate **B** gets protonated and the hydroxyl anion attacks the iminium leading to imine intermediate **E** that after a 1,3 hydrogen shift affords the benzamide product **15**.

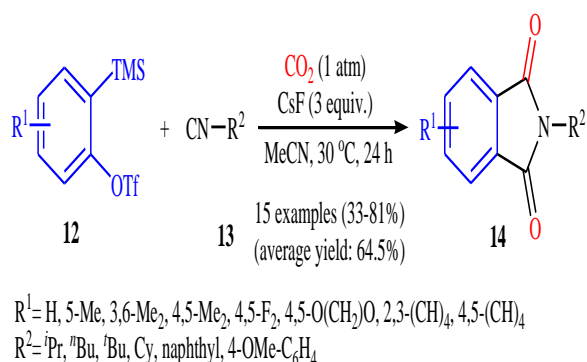
In a closely related investigation, the group of Wang-Ji found that treatment of functionalized 2-(trimethylsilyl)aryl triflates **16** with aromatic isocyanides **17** under the CO₂ atmosphere (1 atm) in the presence of 1.5 equiv. of KF/18-crown-6 in THF produced the corresponding phthalimides **18** in moderate yields (Scheme 11) [36]. In this study, the authors found some limitations in their methodology when they attempted to react aliphatic isocyanides. In these cases, no phthalimide product was observed. In addition, aromatic isocyanides a strongly electron-withdrawing substituent (e.g., NO₂) also failed to form the desired product.

Recently, Biju and co-workers developed an elegant and efficient substrate-controlled switchable three-

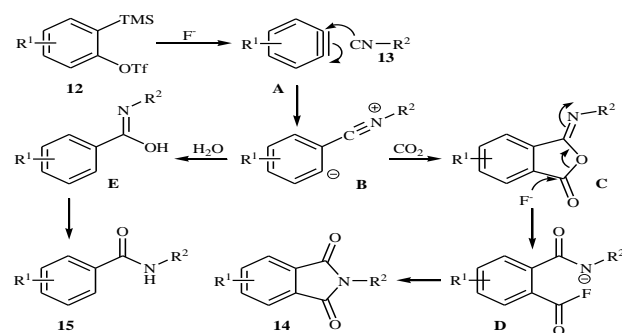
component reaction involving arynes, aromatic tertiary amines, and CO₂ [37]. This transition-metal-free coupling afforded 2-arylamino benzoates **21** in moderate to almost quantitative yields via the treatment of 2-(trimethylsilyl)aryl triflates **19** with electron-rich/neutral aromatic tertiary amines **20** under CO₂ atmosphere employing KF/18-crown-6 combination as a desilylation system. The reaction showed good functional group tolerance, including fluoro, bromo, ether and ester functionalities. This made possible the further elaboration of products. Interestingly, when the same reaction conditions were applied to the electron-deficient amines, the 2-aminoaryl benzoate products **22** were exclusively obtained (Scheme 12). The mechanistic course of this interesting reaction sequence is shown in Scheme 13, and involves the initial formation of 1,3-zwitterionic intermediate **B** from the addition of aromatic tertiary amines to arynes **A**. The reaction of this intermediate with CO₂ gives the key intermediate **C**, which with electron-rich/-neutral amines, undergoes an alkyl group transfer to produce 2-arylamino benzoates **21**. However, in the case of tertiary amines having an electron-poor group attached, the intermediate **C** undergoes an intramolecular nucleophilic aromatic substitution reaction to yield the expected 2-aminoaryl benzoates **22** via the σ -complex **D**.



Scheme 8. Mechanism that accounts for the formation of isocoumarins **11**.



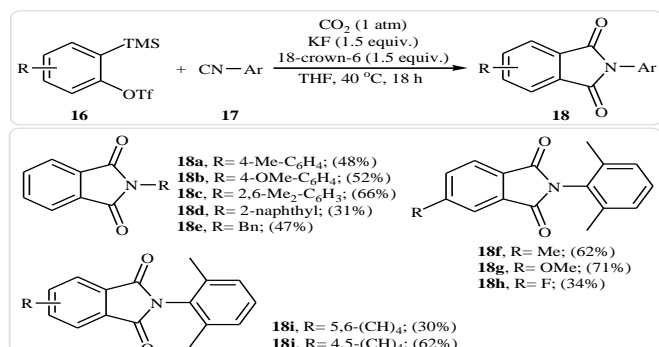
Scheme 9. Synthesis of phthalimides **14** by a multicomponent reaction involving arynes **12**, isocyanides **13**, and CO₂.



Scheme 10. Proposed mechanism for formation of phthalimides **14** and benzamides **15**.

3. Four-component reactions

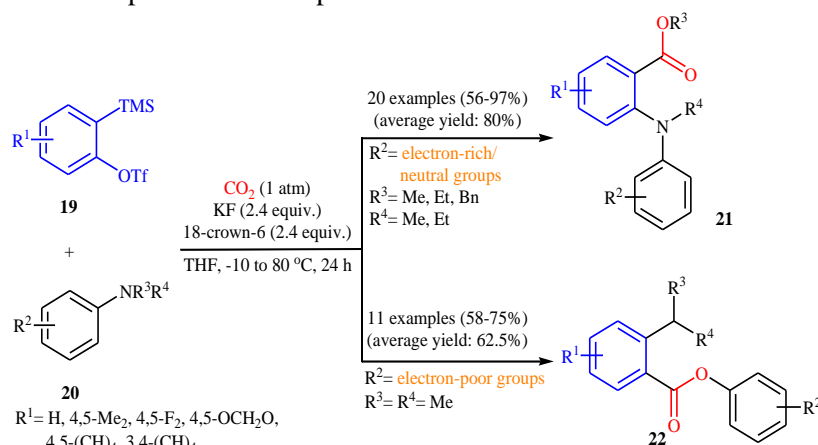
An interesting metal- and fluoride-free four-component coupling reaction for the synthesis of biologically and synthetically important carbamate derivatives **26** from 3-triflyloxybenzynes **23**, amines **24**, cyclic ethers **25** and CO₂ in which one new C–N bond, one new C–H bond and two C–O bonds are formed, was developed by Xiong *et al.* in 2018 (Scheme 14) [38].



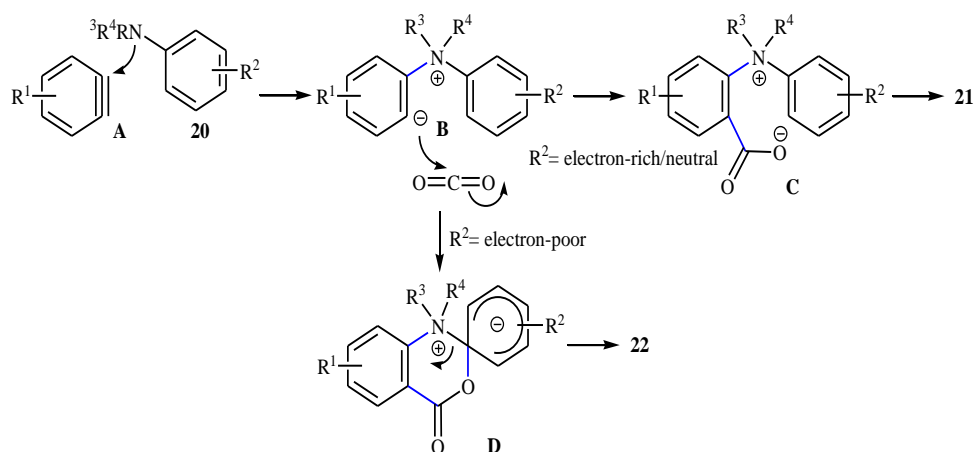
Scheme 11. Wang's synthesis of phthalimides **18**.

Among the various bases like Cs₂CO₃, K₂CO₃, CsF, KF, TBAI, TBAF, TBAC; TBAI was the most efficient for the transformation. The reaction was carried out under solvent-free conditions and atmospheric pressure of CO₂ at room temperature and provided the expected

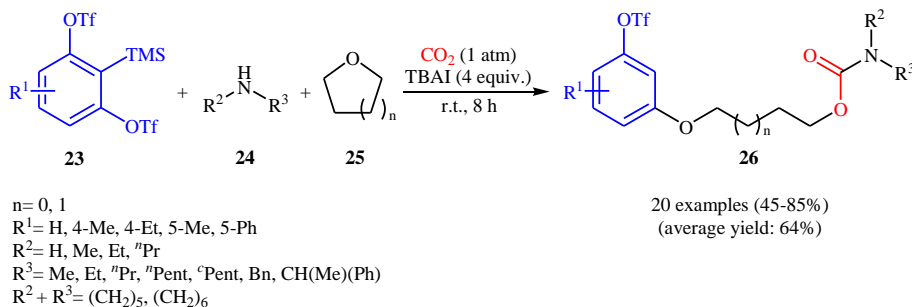
product in moderate to good yield. Interestingly, the reaction was equally effective for both the primary and secondary amines. However, in the cases of unsymmetrical cyclic ethers and 3-triflyloxybenzynes, regioisomeric mixture of two possible products were obtained. It is interesting to note that cyclic ether playing a dual role in this reaction; the reactant and the solvent. Beside moderate to high yields, mild reaction condition and easy available starting materials as well as scalability can be considered as the advantages of this atom economy synthetic approach. The mechanism proposed to explain this coupling reaction is shown in Scheme 15 and starts with the formation of 3-triflyloxybenzynes **A** from **23** with the assistance of TBAI, and then nucleophilic addition of cyclic ether **25** to the triple bond of **A** to give zwitterion intermediate **B**, which undergoes protonation by the ammonium cation of carbamate **C**, which is generated *in situ* from amine **24** and CO₂, to produce oxonium intermediate **D**. Finally, the nucleophilic attack of the carbamate anion **C** on intermediate **D** affords the observed products **26**. To the best of our knowledge, this is the only example of four-component reactions involving arenes and CO₂ reported so far.



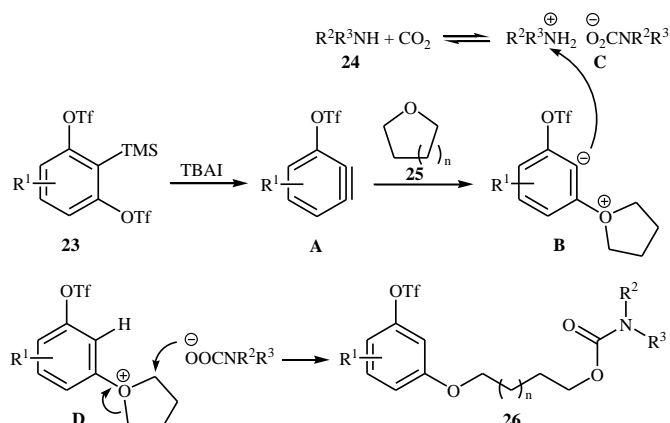
Scheme 12. Transition-metal-free three-component coupling of arynes, aromatic tertiary amines, and CO₂ developed by Biju.



Scheme 13. Mechanistic proposal for the reaction in Scheme 12.



Scheme 14. Synthesis of functionalized carbamates **26** through a four-component coupling reaction of 3-triflyloxybenzynes **23**, amines **24**, cyclic ethers **25** and CO_2 .



Scheme 15. Mechanism that accounts for the formation of carbamates **26**.

4. Conclusions

The efficient utilization of CO_2 as an abundant, inexpensive, nontoxic, nonflammable, and renewable C1-building block in organic synthesis has attracted significant attention in view of sustainable chemistry and green chemistry concepts. However, this is a great challenge, owing to its inert nature and low reactivity. Arynes are a kind of highly unstable and reactive intermediates, which have been widely used in various carbon-carbon formation and carbon-heteroatom bond formation reactions. As illustrated, over the last 12 years, several interesting multi-component coupling reactions involving arynes were designed that allow the efficient incorporation of CO_2 to produce various value-added chemicals (e.g. benzoxazin-4-ones, anthranilic acids, isocoumarins, phthalimides, 2-aryl amino benzoates, 2-aminoaryl benzoates, and carbamates). Interestingly almost all of the conversion of CO_2 covered in this focus-review could be achieved under very mild (atmospheric pressure of CO_2 and room temperature) and metal-free conditions demonstrating the greener feature of the present protocol. However, the number of reported examples in this interesting research arena is limited and there is still further need to study the scope and limitations of this novel protocol for the synthesis of arenes and heteroarenes. It is our hope that this review will stimulate researchers to further research and study in this really interesting research field.

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