

## Review

# Research Progress on the Reaction of Carbon Dioxide with Hydrazones and Their Derivatives

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**Abstract:** CO<sub>2</sub>, an abundant and renewable C1 source, presents significant potential for applications in organic synthesis. Hydrazones, recognized for their distinctive properties, exhibit high versatility in synthetic chemistry, facilitating numerous chemical transformations. Given their crucial roles in organic synthesis, the combination of CO<sub>2</sub> with hydrazones has garnered increasing research interest. This review provides a comprehensive summary of recent progress in reactions involving CO<sub>2</sub> and hydrazones or their derivatives. These include the coupling of amines and N-tosylhydrazones with CO<sub>2</sub>, the umpolung-mediated carboxylation of hydrazones/N-tosylhydrazones with CO<sub>2</sub>, the cyclization of hydrazones with CO<sub>2</sub>, and lactamization reactions incorporating N-tosylhydrazones and CO<sub>2</sub>. These transformations utilize the diverse reactivity of hydrazones and their derivatives to capture and convert CO<sub>2</sub>, generating valuable organic compounds with both academic and practical relevance. Additionally, the review examines the mechanisms underlying these reactions, offering critical insights for advancing research in this area.

**Keywords:** carbon dioxide (CO<sub>2</sub>); hydrazones; carbamates; umpolung strategy; cyclization; lactamization



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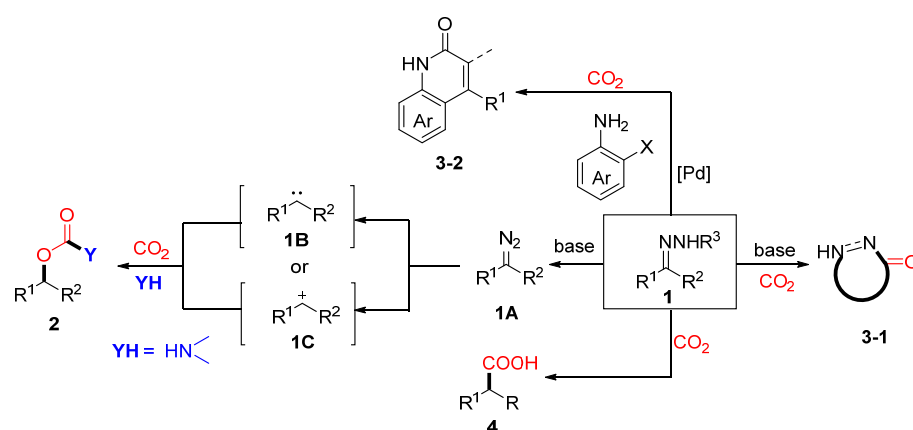
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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>), a major greenhouse gas associated with global warming, has attracted widespread attention for its capture and utilization. As an abundant and renewable C1 feedstock, CO<sub>2</sub> offers significant potential for applications in organic synthesis [1–5]. Its low cost, wide availability, and environmentally sustainable nature make it an appealing option for green chemistry. However, the activation and efficient utilization of CO<sub>2</sub> in organic reactions present substantial challenges due to its intrinsic thermodynamic stability and kinetic inertness, which impede its involvement in conventional chemical processes. Despite these obstacles, significant advancements have been made in developing strategies for CO<sub>2</sub> activation and conversion [6–26].

Hydrazone derivatives are formed through the condensation of aldehydes or ketones with hydrazine or its derivatives, possessing the general structure  $RR'C=N-NHR''$ . Their distinctive properties are highly useful in synthetic chemistry, facilitating participation in diverse chemical transformations. For example, they act as intermediates in the Wolff–Kishner reduction and play a crucial role in the synthesis of Barton vinyl iodides, among other synthetically valuable reactions [27]. Recent studies by Li and other researchers have led to significant progress, highlighting the importance of hydrazone-based compounds in organic synthesis [28–31]. Among various hydrazone derivatives, N-tosylhydrazones have gained prominence due to their role as operationally safe carbene precursors. Considerable advancements have been reported in transition metal-catalyzed reactions, metal-free conditions, and photocatalytic processes under light irradiation [32–35]. Furthermore, hydrazones have been extensively utilized in cyclization reactions, facilitating the synthesis of heterocyclic compounds containing N–N moieties, which hold significant value in organic chemistry [36].

Given the essential roles of hydrazones (1) in coupling, cyclization, and polarity-reversal reactions, along with the significance and challenges associated with  $CO_2$  conversion, research efforts have increasingly focused on integrating hydrazone chemistry with  $CO_2$  utilization and fixation. By exploiting the distinctive reactivity of hydrazones, a variety of  $CO_2$ -involved transformations have been developed, facilitating the synthesis of valuable compounds such as carbamates (2), carbonyl compounds (3-1, 3-2), and organic carboxylic acids (4) (Figure 1).



**Figure 1.** Overview of  $CO_2$ -involved transformations of hydrazones and their derivatives.

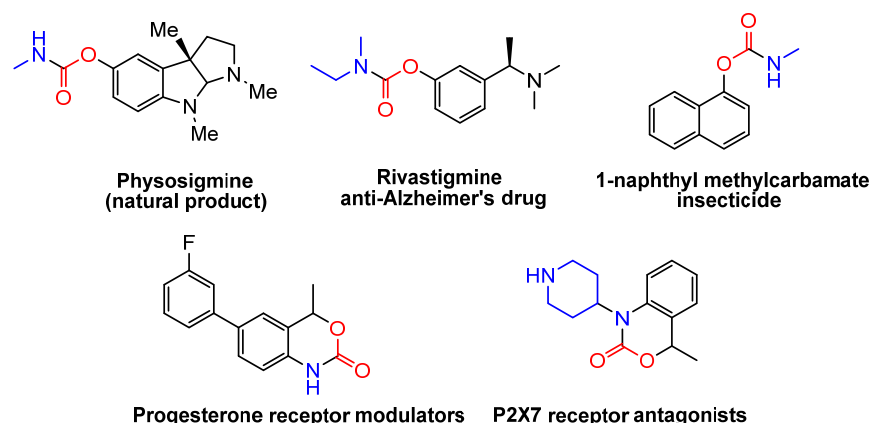
This review highlights recent progress in reactions involving  $CO_2$  and hydrazones or their derivatives, with an emphasis on how the diverse chemical properties of hydrazones contribute to different modes of  $CO_2$  fixation. Additionally, the scope and mechanisms of these reactions are analyzed to provide a deeper understanding of their underlying principles. Through this comprehensive examination, valuable perspectives and potential directions for the future advancement of  $CO_2$  utilization are proposed.

## 2. Reaction of Carbon Dioxide with Hydrazones and Their Derivatives

### 2.1. Coupling of Amines and N-tosylhydrazones with $CO_2$ to Generate Carbamates

Organic carbamates are an important class of compounds with significant biological and pharmaceutical properties, frequently found in natural products [37–47] (Figure 2). Their synthesis has been extensively investigated. Conventionally, carbon monoxide (CO), phosgene, triphosgene, and isocyanates have been commonly utilized as carbonyl sources for their construction [40–44]. Additionally,  $CO_2$  has been explored as a starting material for carbamate synthesis [45–53]. This approach primarily involves the nucleophilic

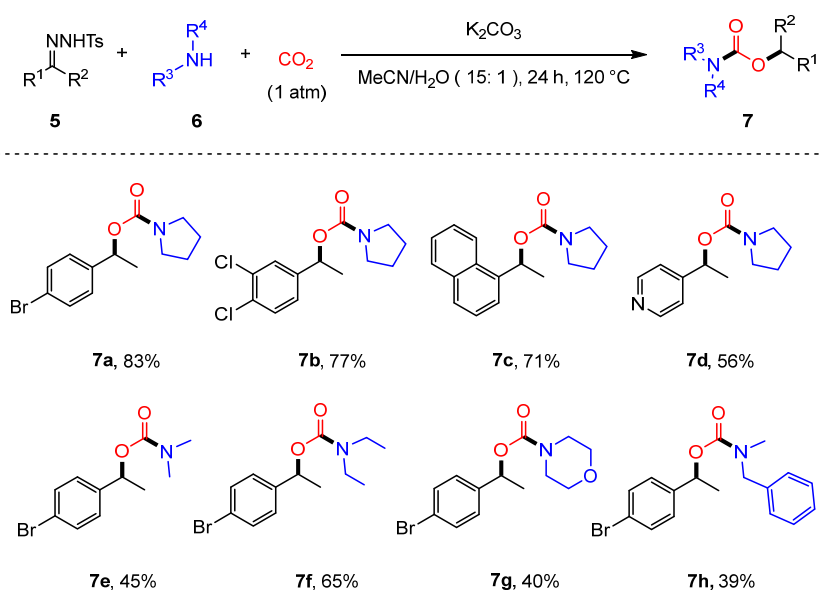
attack of amines on CO<sub>2</sub>, leading to the formation of carbamic acids (or their salts), which subsequently undergo coupling to afford the target products.



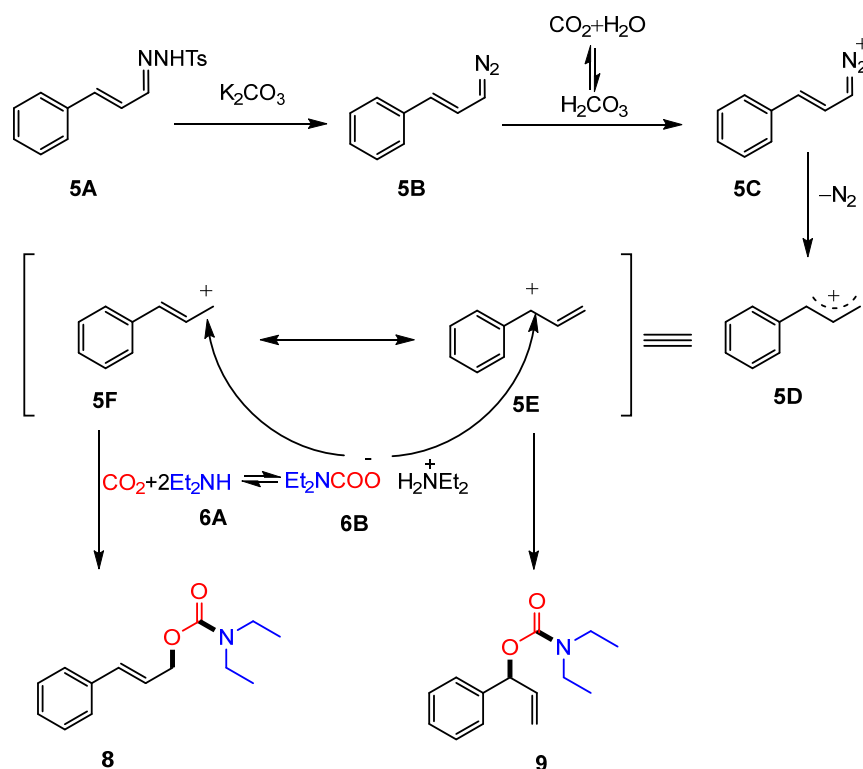
**Figure 2.** Representative pharmaceuticals containing the carbamate motif.

N-tosylhydrazones are widely recognized as synthetic intermediates in the formation of carbon–carbon or carbon–heteroatom bonds through both transition metal-catalyzed and metal-free cross-coupling reactions [37,54,55]. Under protonic conditions, diazo compounds generated in situ from N-tosylhydrazones undergo decomposition, yielding carbocation intermediates [56].

In 2015, JIANG and co-workers reported a base-promoted coupling reaction involving CO<sub>2</sub>, amines (6), and N-tosylhydrazones (5) [57]. Under basic conditions, amines—particularly secondary amines with strong nucleophilicity—interact with CO<sub>2</sub> to generate carbamate salts. These salts are then captured by carbocation intermediates generated in situ from N-tosylhydrazones, enabling an efficient synthesis of diverse carbamate esters (7). This reaction system also accommodates primary amines, although the yields are comparatively lower (Figure 3). However, N-tosylhydrazones derived from aliphatic ketones or aldehydes and aromatic amines did not yield the desired products. Mechanistic investigations and control experiments confirmed the presence of a carbocation intermediate (5D) and demonstrated that both H<sub>2</sub>O and CO<sub>2</sub> facilitate the protonation process through forming carbonic acid, promoting carbocation intermediate formation from the diazo compound (Figure 4).

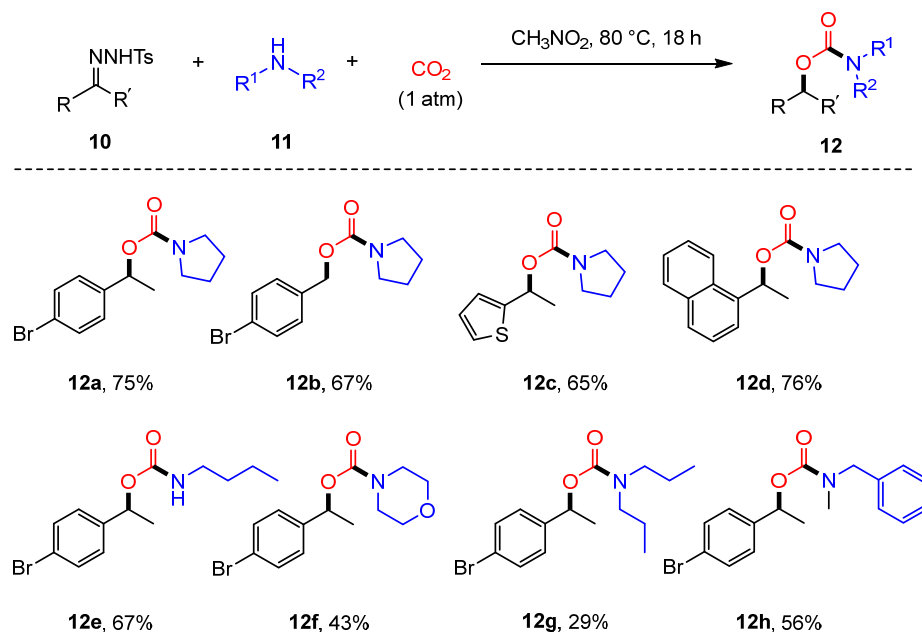


**Figure 3.** Base-promoted coupling of CO<sub>2</sub>, amines, and N-tosylhydrazones for carbamate synthesis.



**Figure 4.** Mechanism of carbamate formation through a carbocation intermediate.

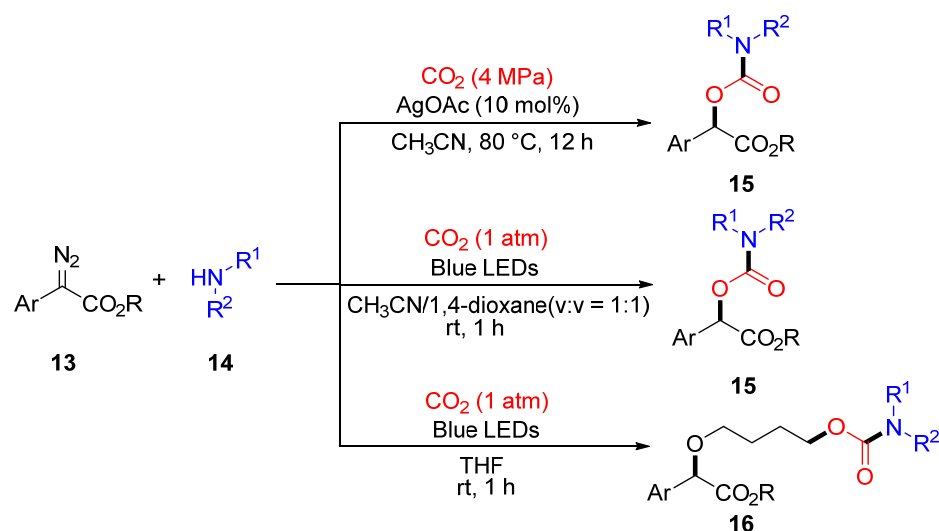
Owing to the intrinsic basicity of amine compounds, they can function as bases, enabling the formation of carbamate salts without requiring additional bases. In 2016, Chung et al. successfully carried out this reaction under 1 atm of  $CO_2$  without an external base, employing nitromethane as the solvent [58]. Notably, the reaction conditions allowed for scalability, enabling synthesis on a gram scale. This study also included several examples of reactions involving primary amines, with most yields observed within the moderate range (Figure 5).



**Figure 5.** Synthesis of carbamates under 1 atm  $CO_2$  without an external base.

The authors propose that the reaction proceeds via a mechanism in which the amine (**11**) reacts with CO<sub>2</sub> in situ to generate a carbamate species (**12**), which acts as a nucleophile to couple with the N-tosylhydrazone (**10**), ultimately yielding the carbamate product. This mechanistic pathway eliminates the need for high-pressure conditions and external bases, offering a milder and more efficient synthetic approach compared to conventional methods (Figure 5).

Here, it is worth noting that diazo compounds are recognized as pivotal intermediates in the aforementioned reaction and have attracted considerable attention due to their versatile reactivity in diverse chemical transformations. The Jiang and Qi successfully developed a silver-catalyzed or photocatalytic three-component coupling reaction involving  $\alpha$ -diazooesters (**13**), CO<sub>2</sub>, and amines (**14**), which enabled the efficient synthesis of  $\alpha$ -carbamoyloxy esters (**15**, **16**) [59,60]. Notably, under photocatalytic conditions using tetrahydrofuran (THF) as the reaction medium, an exclusive four-component coupling reaction was observed between  $\alpha$ -aryldiazooesters, amines, CO<sub>2</sub>, and THF. This process resulted in the formation of a wide range of structurally diverse carbamate products (Figure 6).

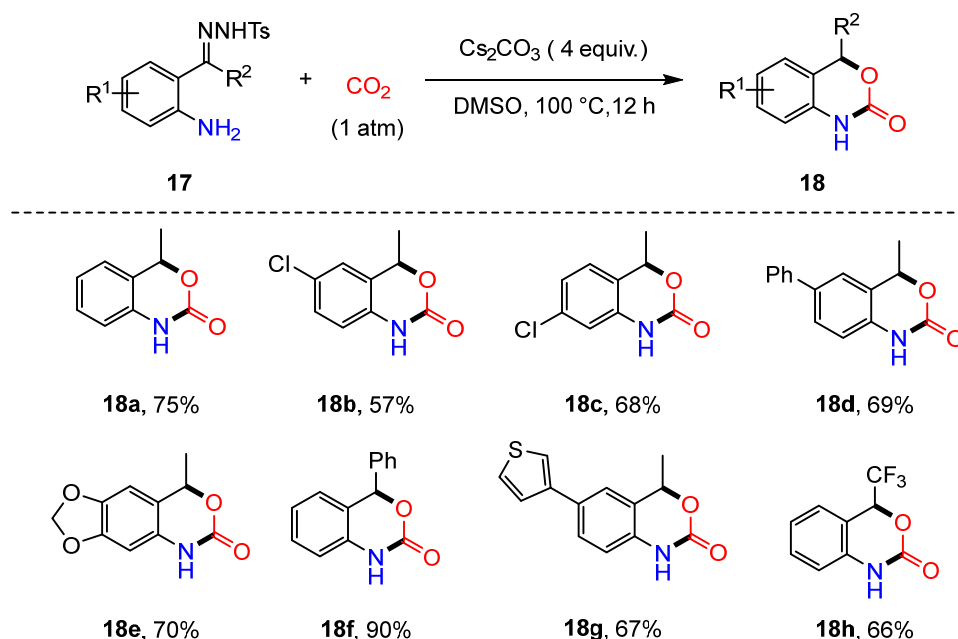


**Figure 6.** The reaction of diazonium and CO<sub>2</sub> under different conditions.

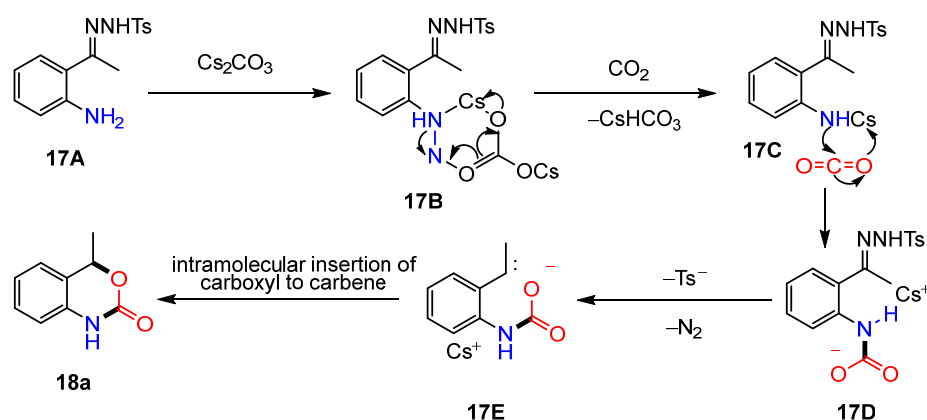
The above reactions, due to the use of different catalytic systems, exhibit slightly different reaction paths. Under AgOAc catalysis,  $\alpha$ -diazooesters decompose to generate silver carbene intermediates, which then undergo multi-step coupling with CO<sub>2</sub> and amines to form  $\alpha$ -carbamates. The mechanism involves carbene insertion into CO<sub>2</sub> and nucleophilic attack by amines, followed by protonation to afford the product [59]. In contrast to the silver-catalyzed system, blue light excitation of  $\alpha$ -diazooesters generates carbene intermediates, with the solvent (THF or 1,4-dioxane/MeCN) dictating the reaction pathway: in THF, the carbene forms an oxonium ylide with the solvent, which then combines with the carbamate anion generated from amines and CO<sub>2</sub>; in the mixed solvent, the carbene directly couples with the carbamate anion without metalcatalysis [60].

The previous discussion primarily addressed intermolecular reactions; however, intramolecular processes had not been reported until 2019, when Cheng et al. introduced a novel strategy for incorporating CO<sub>2</sub> into *o*-aminoacetophenone N-tosylhydrazone derivatives (**17**). This approach enabled the synthesis of a series of 1,4-dihydro-2H-3,1-benzoxazin-2-one compounds (**18**) using Cs<sub>2</sub>CO<sub>3</sub> [61] (Figure 7). The proposed reaction mechanism is illustrated in Figure 8. Initially, Cs<sub>2</sub>CO<sub>3</sub> interacts with aniline, promoting proton abstraction and generating intermediate **17C**. This is followed by the carboxylation of the amine with CO<sub>2</sub>, leading to the formation of intermediate **17D**. Subsequently, intermediate **17D** under-

goes a stepwise elimination of Ts and N<sub>2</sub>, facilitated by the base, resulting in the formation of a carbene intermediate (17E). Finally, the carboxyl group undergoes an intramolecular insertion into the carbene intermediate, yielding the 1,4-dihydro-2H-3,1-benzoxazin-2-one products (Figure 8).



**Figure 7.** Intramolecular cyclization of *o*-aminoacetophenone N-tosylhydrazone with CO<sub>2</sub>.



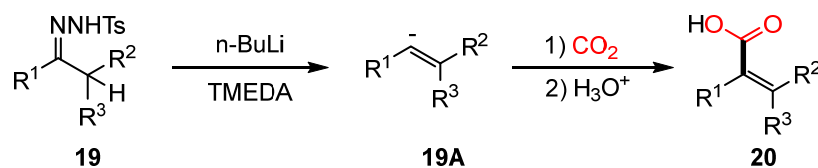
**Figure 8.** Mechanism of intramolecular cyclization with CO<sub>2</sub>.

In summary, this method presents several advantages, including the use of readily available starting materials, broad substrate scope, mild reaction conditions, and operational simplicity. It offers an efficient and practical approach for synthesizing a diverse range of organic alkyl carbamate esters.

## 2.2. Carboxylation of Hydrazones/N-Tosylhydrazones with CO<sub>2</sub> Through Umpolung

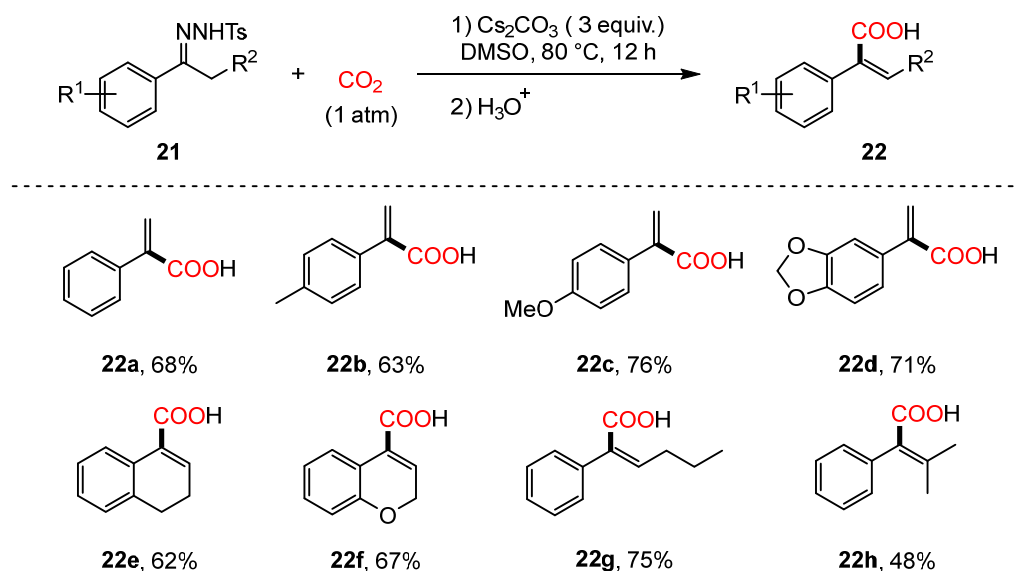
The Umpolung strategy modifies the inherent electronic characteristics of functional groups, effectively reversing their typical polarity. This polarity shift enables the emergence of novel reactivity patterns, allowing the formation of new chemical bonds [62–65]. A well-known example is the Shapiro reaction, in which an N-tosylhydrazone (19) undergoes deprotonation by a base, generating a vinyl lithium intermediate. This intermediate subsequently reacts with electrophiles, leading to the formation of alkene-based products (20). When CO<sub>2</sub> is employed as the electrophile, α-arylacrylic acids can be synthesized [66–73].

Conventionally, these reactions require the use of a strong base (e.g., *n*-BuLi) and extremely low temperatures, which has restricted their practical applicability (Figure 9).



**Figure 9.** Traditional Shapiro reaction for  $\alpha$ -arylacrylic acid synthesis.

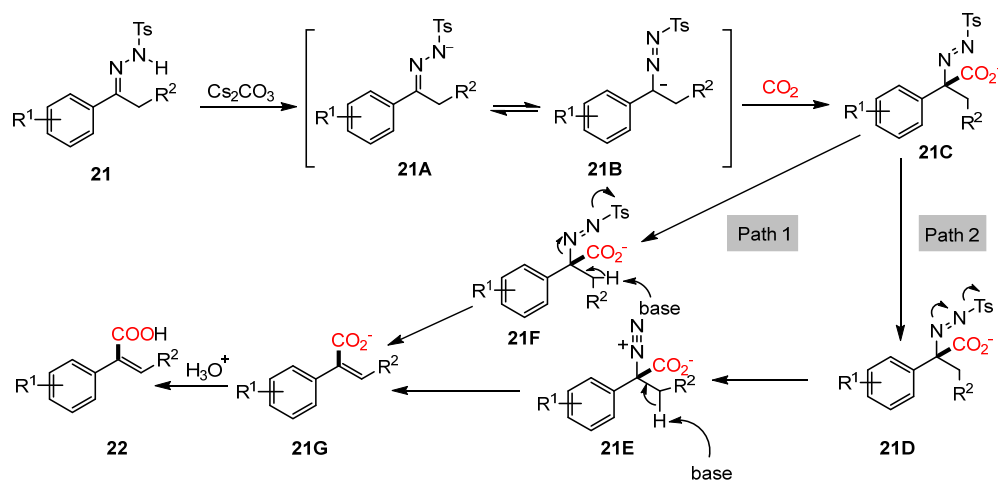
In 2015, Cheng and colleagues developed a  $\text{Cs}_2\text{CO}_3$ -mediated carboxylation reaction between N-tosylhydrazones (21) and  $\text{CO}_2$ , providing an efficient approach for synthesizing  $\alpha$ -arylacrylic acids (22) [74]. This method serves as a practical and elegant alternative to the conventional Shapiro reaction. Through systematic optimization and control experiments, it was demonstrated that  $\text{CO}_2$  functions as the carbonyl source in this transformation. The reaction exhibits compatibility with a range of aromatic ring substitution patterns; however, substrates bearing strong electron-withdrawing groups did not afford the desired products, indicating possible interference with the reaction mechanism (Figure 10).



**Figure 10.**  $\text{Cs}_2\text{CO}_3$ -promoted carboxylation of N-tosylhydrazones using  $\text{CO}_2$ .

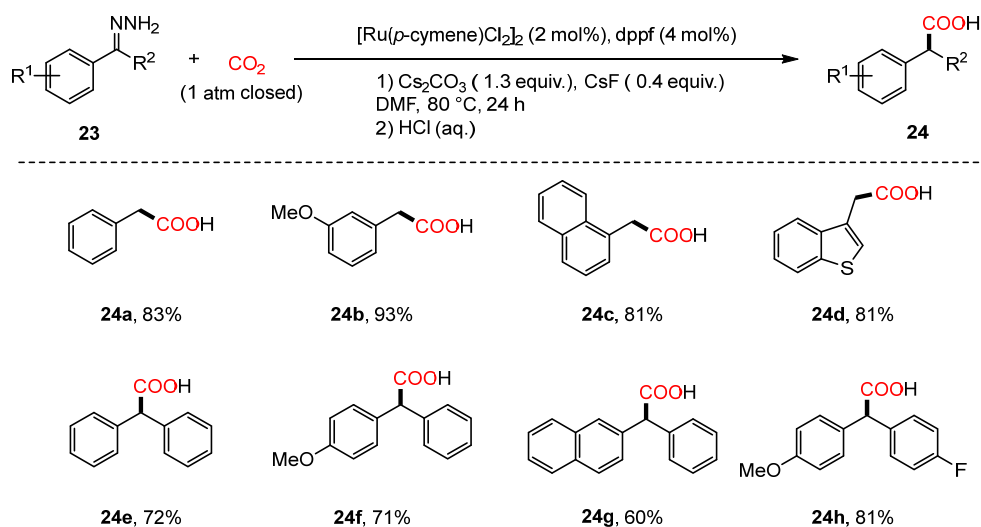
The reaction mechanism involves the in situ formation of a diazo intermediate from N-tosylhydrazones, catalyzed by  $\text{Cs}_2\text{CO}_3$  under mild conditions. Initially,  $\text{Cs}_2\text{CO}_3$  promotes deprotonation of the hydrazone substrate, generating a nitrogen-centered anion, which subsequently undergoes isomerization to form a carbanion. This carbanion then captures  $\text{CO}_2$ , forming an intermediate that undergoes desulfonylation, leading to the generation of a diazo intermediate. Under basic conditions, the diazo species undergoes nitrogen extrusion, followed by protonation, ultimately yielding the  $\alpha$ -arylacrylic acid product (Figure 11).

The key parts of the mechanism of this reaction are as follows: (i) deprotonation by  $\text{Cs}_2\text{CO}_3$  generating a nitrogen-centered anion; (ii) isomerization to carbanion enabling  $\text{CO}_2$  capture; and (iii) desulfonylation and  $\text{N}_2$  extrusion yielding  $\alpha$ -arylacrylic acids.



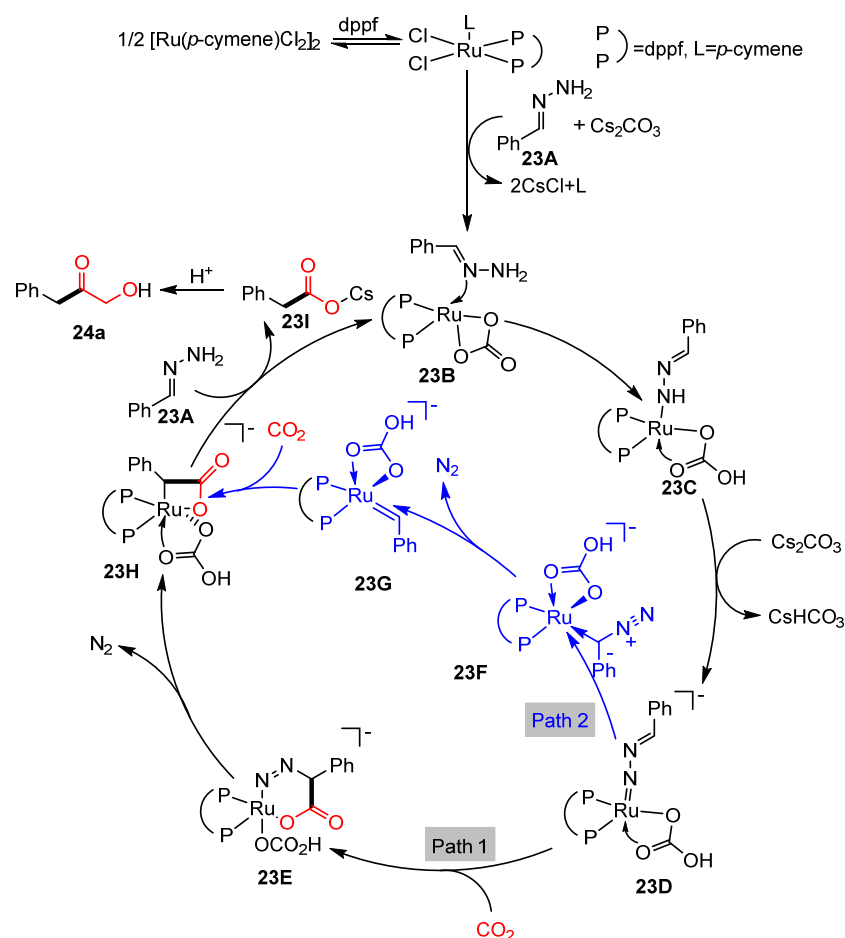
**Figure 11.** Mechanism of  $\text{Cs}_2\text{CO}_3$ -promoted carboxylation of N-tosylhydrazones.

The described process operates as a base-promoted reaction. Expanding upon Li's work on Ru-catalyzed umpolung reactions that utilize carbonyls as carbanion equivalents [28], Yu, Lan, and Li introduced a novel strategy in 2018 for synthesizing aryl acetic acids (**24**). This approach involves the cleavage of C=N double bonds in hydrazones through Ru-catalyzed umpolung reactions [75] (Figure 12). In these transformations, the air-stable ligand dppf (1,1'-Bis(diphenylphosphino)ferrocene) was identified as optimal for efficient aryl acetic acid synthesis. Furthermore, reaction conditions were refined to accommodate less reactive hydrazones derived from ketones. A proposed mechanism, supported by experimental findings and Density Functional Theory (DFT) calculations, suggests that the reaction initiates with ligand exchange between the ruthenium catalyst and phenylhydrazone in the presence of  $\text{Cs}_2\text{CO}_3$ , forming a ruthenium–hydrazone complex (**23B**). This complex subsequently undergoes a sequence of protonation steps, generating a Ru-nitrenoid intermediate (**23D**). A [4 + 2] cycloaddition between this intermediate and  $\text{CO}_2$  then forms a six-membered Ru complex (**23E**), which, upon nitrogen extrusion and protonation, regenerates the catalyst and releases the target aryl acetic acid. Additionally, an alternative mechanistic pathway has been proposed, wherein isomerization, carbene formation, and  $\text{CO}_2$  insertion result in the formation of an alternative intermediate complex (Figure 13).



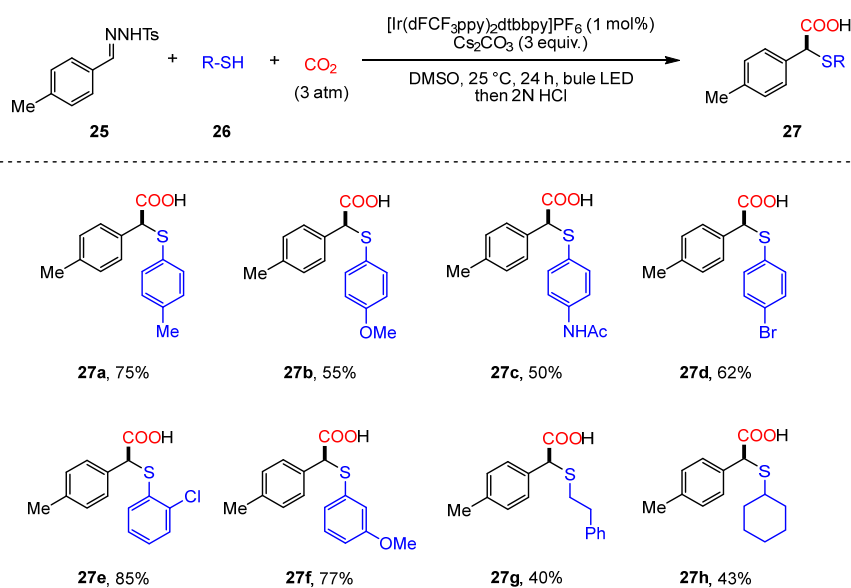
**Figure 12.** Ru-catalyzed umpolung carboxylation of hydrazones involving  $\text{CO}_2$ .





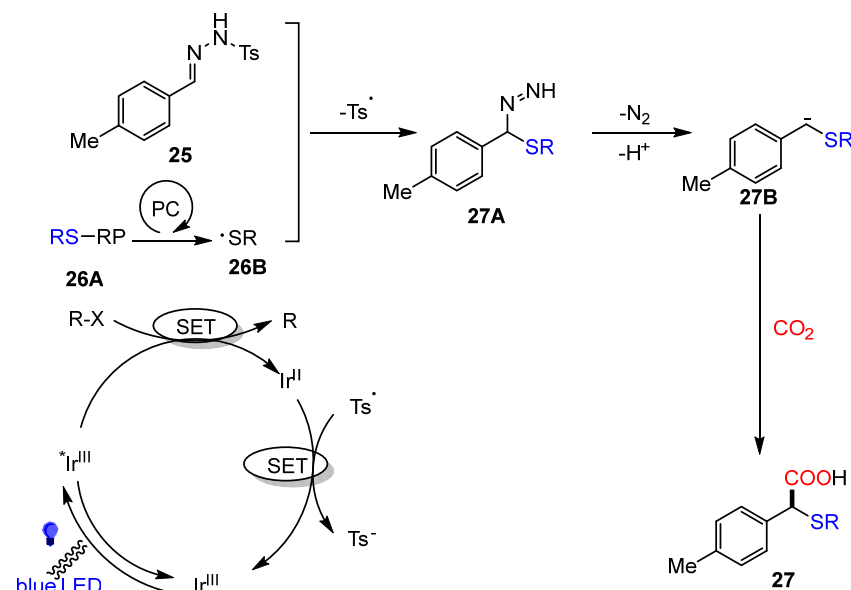
**Figure 13.** Mechanism of Ru-catalyzed umpolung carboxylation reaction.

In 2020, König and colleagues introduced a significant advancement by integrating photoredox catalysis with the Wolff–Kishner reaction to achieve the difunctionalization of N-tosylhydrazones (**27**) using CO<sub>2</sub> [76] (Figure 14). This reaction follows a three-component mechanism involving preformed N-tosylhydrazones, thiols, and CO<sub>2</sub>.



**Figure 14.** Photoredox-catalyzed difunctionalization of tosylhydrazones with CO<sub>2</sub>.

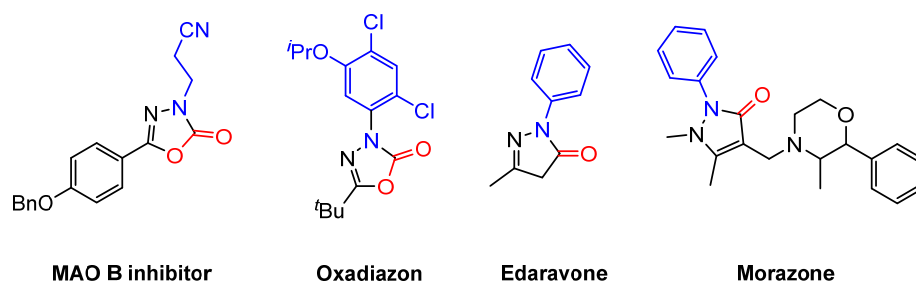
The proposed mechanism involves: (i) Photoredox-generated thiyl-radical addition to N-tosylhydrazone; (ii) Base-assisted formation of diazene intermediate; (iii) Carbanion trapping by CO<sub>2</sub> to afford  $\alpha$ -thioether carboxylic acids. A key aspect of the mechanism is the photoredox-mediated generation of a thiyl radical (**26B**), which subsequently adds to the N-tosylhydrazone substrate (**25**). This step is followed by the formation of a diazene intermediate (**27A**), which undergoes base-promoted nitrogen extrusion to generate a carbanion (**27B**). CO<sub>2</sub> then functions as the electrophile, capturing the carbanion and completing the difunctionalization process (Figure 15). Through this method, a variety of  $\alpha$ -thioether-functionalized carboxylic acids were synthesized under relatively mild conditions, highlighting the potential for practical applications.



**Figure 15.** Mechanism of photoredox-catalyzed difunctionalization reaction.

### 2.3. Cyclization of Hydrazones with CO<sub>2</sub>

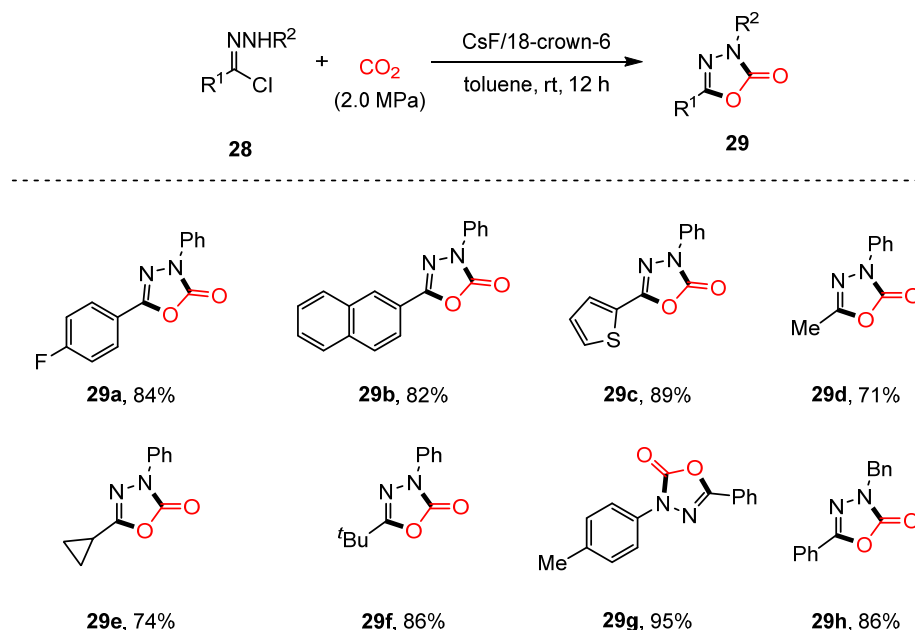
The significance of nitrogen-containing heterocyclic compounds is well recognized. Carbonylation reactions utilizing carbon dioxide offer a greener and safer alternative to highly toxic reagents such as carbon monoxide and phosgene, contributing to the synthesis of carbonyl-containing heterocyclic compounds [11]. The nucleophilic nitrogen atom in hydrazones and their derivatives enables reactions with carbon dioxide, facilitating the formation of carbonyl-containing azole compounds (Figure 16).



**Figure 16.** Representative structures containing the carbonyl-containing azole motif.

In 2017, Lv and colleagues developed an efficient methodology for synthesizing 1,3,4-oxadiazol-2(3H)-ones (**29**) through the 1,3-dipolar cycloaddition of nitrilimines (**28**) with carbon dioxide, catalyzed by CsF/18-crown-6 [77] (Figure 17). This strategy demonstrates broad substrate compatibility, enabling hydrazinyl chlorides with various substituents

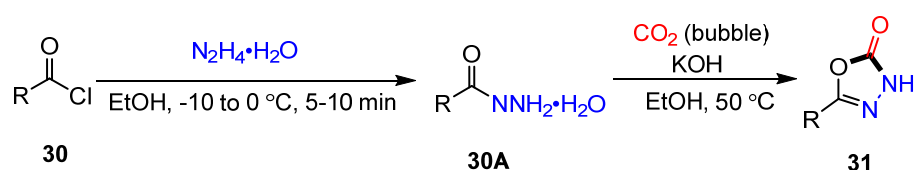
to participate in the reaction. The successful synthesis of a reversible MAO-B inhibitor and the commercial herbicide Oxadiazon further underscores the practical applicability of this approach.



**Figure 17.** 1,3-Dipolar cycloaddition of nitrilimines with CO<sub>2</sub>.

Control experiments and NMR analysis revealed that 18-crown-6 plays a critical role in facilitating the formation of the nitrilimine intermediate, while the CsF/18-crown-6 system significantly enhances the reactivity of CO<sub>2</sub>.

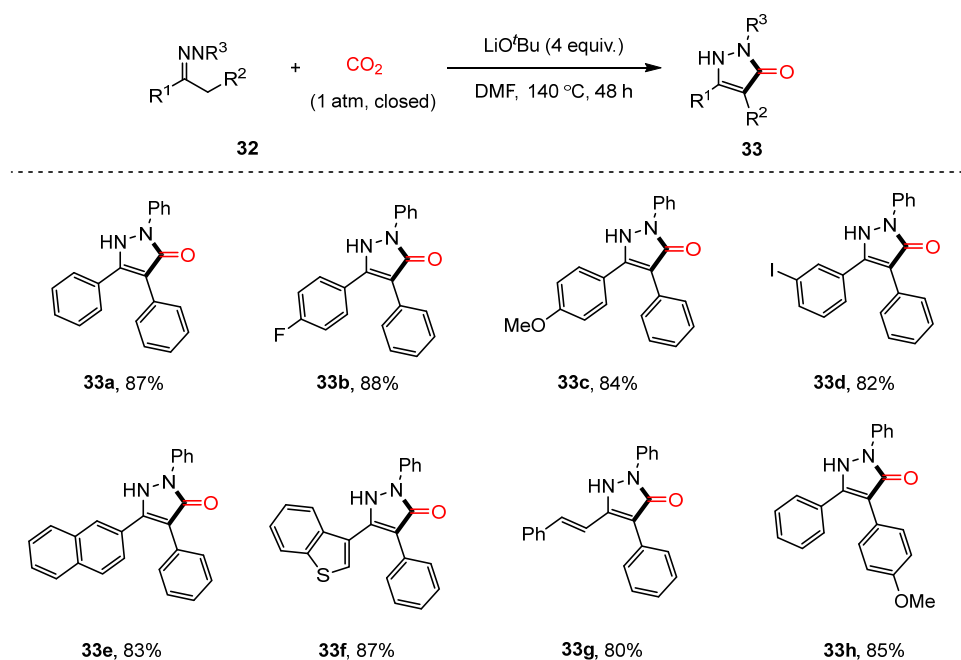
Interestingly, these structures can also be synthesized via the carbonylation of hydrazides using CO<sub>2</sub> as a reactant. A notable example is the work by Suen and colleagues in 2015, who demonstrated a KOH-mediated carbonylation reaction of hydrazides (30A) with CO<sub>2</sub> [78]. The hydrazide precursors were readily obtained through the reaction of acid chlorides (30) with hydrazine monohydrate, offering a highly efficient synthetic route (Figure 18).



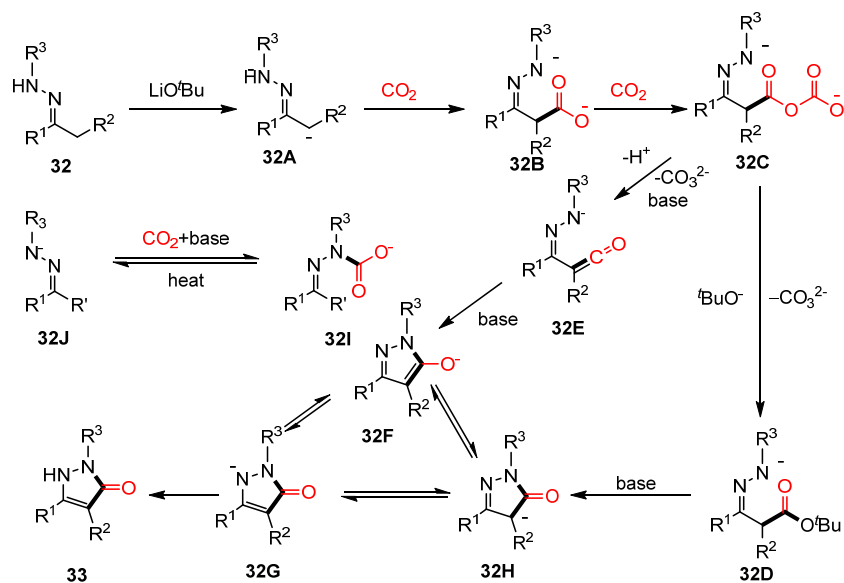
**Figure 18.** CO<sub>2</sub>-involved transformations involving diazo compounds.

The carbonylation of C(sp<sup>3</sup>)-H bonds using carbon dioxide has attracted considerable interest; however, due to its inherent challenges, only a limited number of studies have been reported in this area [11]. Recently, Hu's team successfully developed a method for the cyclization of hydrazones with CO<sub>2</sub>, enabling the synthesis of various pyrazolone derivatives via 1°, 2°, or 3° C(sp<sup>3</sup>)-H carbonylative cyclization reactions [79] (Figure 19). To evaluate the practical applicability of this reaction, synthesis was achieved on a gram scale, and several functional transformations were performed on the resulting pyrazolone derivatives (33). Notably, the successful synthesis of a PKC inhibitor with anti-cancer activity demonstrated the potential biomedical relevance of this approach. Experimental findings and previous literature suggested that mixed acid anhydride compounds 32C serve as crucial intermediates. Under basic conditions, these intermediates can undergo

transformations leading to the formation of either **32D** or **32E**, ultimately yielding the target cyclic products (Figure 20).



**Figure 19.** C(sp<sup>3</sup>)-H carbonylative cyclization reaction of hydrazones using CO<sub>2</sub>.

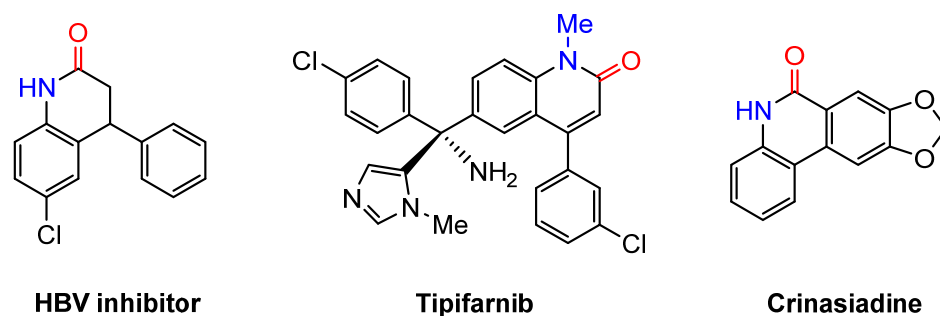


**Figure 20.** Mechanism of C(sp<sup>3</sup>)-H carbonylative cyclization reaction.

Overall, carbonylation reactions utilizing carbon dioxide have become a crucial approach for synthesizing carbonyl-containing heterocyclic compounds. The interaction of carbon dioxide with hydrazones and their derivatives frequently results in the formation of valuable carbonyl-containing azole compounds, which hold significant promise for broad applications in pharmaceuticals and materials science.

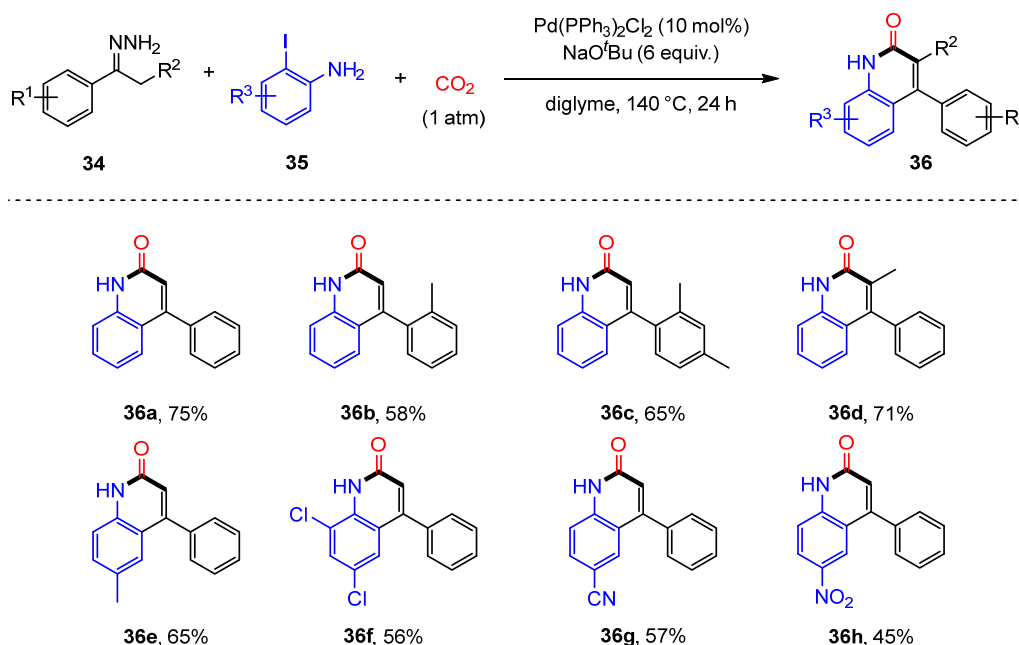
#### 2.4. Lactamization Reaction of *N*-Tosylhydrazones, 2-Iodoanilines, and CO<sub>2</sub>

Quinolinones are an important class of organic compounds with broad applications in pharmaceuticals and materials science (Figure 21).



**Figure 21.** Representative structures containing the quinolinone motif.

In 2016, Yu's group developed a method for synthesizing quinolinone derivatives via the lactamization of C(sp<sup>2</sup>)-H bonds with CO<sub>2</sub> [80]. However, this approach requires the use of pre-synthesized *o*-alkenyl- or *o*-(hetero)arylanilines as substrates. Later that year, Cheng's group introduced a palladium-catalyzed three-component reaction involving N-tosylhydrazones (34), 2-iodoanilines (35), and atmospheric CO<sub>2</sub>, enabling the efficient synthesis of a variety of 4-aryl-2-quinolinones (36) (Figure 22) [81]. This methodology allows the formation of two C-C bonds, one C=C bond, and one C-N bond within a single reaction vessel, providing a highly effective strategy for incorporating CO<sub>2</sub> into heterocyclic frameworks.



**Figure 22.** Pd-catalyzed synthesis route for 4-aryl-2-quinolinones.

The proposed reaction mechanism begins with the palladium-catalyzed coupling of aryl halides and N-tosylhydrazones, leading to the formation of an *o*-vinyl aniline intermediate (36E). This intermediate subsequently undergoes C(sp<sup>2</sup>)-H lactamization with CO<sub>2</sub>, yielding the target quinolinone. Additionally, an alternative reaction pathway involving the formation of *o*-iodoisocyanatobenzene before the generation of *o*-vinyl aniline remains a possibility (Figure 23).

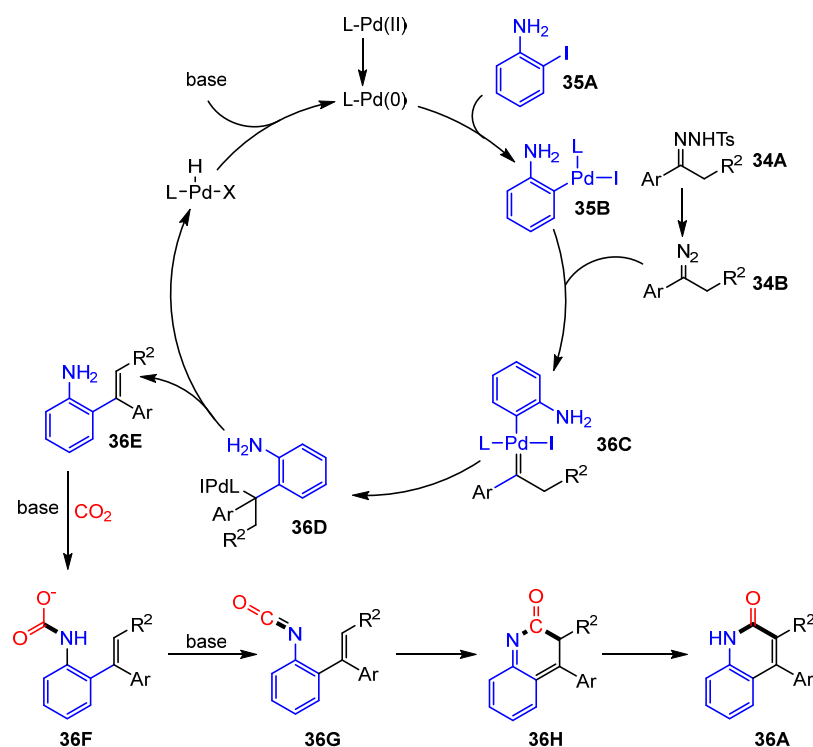


Figure 23. Mechanism of palladium-catalyzed three-component coupling reaction.

### 3. Conclusions

As research on carbon dioxide fixation and utilization continues to gain attention, the conversion of  $CO_2$  into high-value-added chemicals has emerged as a key focus. Hydrazone compounds and their derivatives, which serve as essential raw materials or intermediates in organic synthesis, represent a promising avenue for  $CO_2$  utilization when integrated with  $CO_2$  conversion strategies. Based on the reactions discussed in this paper, the primary products currently obtained include carbamates, organic carboxylic acid derivatives, and certain nitrogen-containing heterocycles. These compounds are widely utilized in pharmaceuticals, materials science, and as intermediates in organic synthesis, underscoring the relevance of combining  $CO_2$  utilization with hydrazone chemistry. The major reaction types involved include coupling, polarity inversion, and cyclization.

However, the development of this integration has not yet matched the progress in  $CO_2$  chemistry or hydrazone chemistry, and the range of reactions and products remains relatively limited. For instance, in Section 2.1, the predominant reaction described involves the coupling of nitrogen as a nucleophile with  $CO_2$  and phenylhydrazine to form carbamate compounds. Reactions involving other nucleophiles such as oxygen, sulfur, and carbon, which could potentially yield asymmetric carbonates or carboxylates, have not been explored, despite their significance in related fields. In Section 2.2, among the reaction types discussed, only ruthenium-catalyzed polarity inversion has been reported for the synthesis of organic carboxylic acids. The use of alternative metal catalysts, such as nickel and palladium, remains unexplored, with the primary products being aryl acetic acids and acrylic acids. Expanding the use of more cost-effective metals in this field could significantly enhance the applicability of these reactions. Furthermore, this section highlights photocatalytic transformations that successfully facilitate the formation of thioacids. The application of rational design strategies to achieve carboxylation reactions involving other heteroatoms, such as nitrogen, could further expand potential applications. Based on the current state of development, there remains substantial room for growth in the integration of  $CO_2$  chemistry with hydrazone chemistry.

Additionally, with the rapid advancements in photocatalysis and electrocatalysis as sustainable chemical methods, numerous transformations previously unattainable through traditional organic or transition metal catalysis have been realized, significantly advancing organic chemistry. The feasibility of applying photocatalysis and electrocatalysis to the CO<sub>2</sub>-involved conversion of hydrazone compounds presents an important avenue for further investigation.

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