CHEMICAL REVIEWS

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Review

Visible Light-Induced Reactions of Diazo Compounds and Their Precursors

Ziyan Zhang and Vladimir Gevorgyan*

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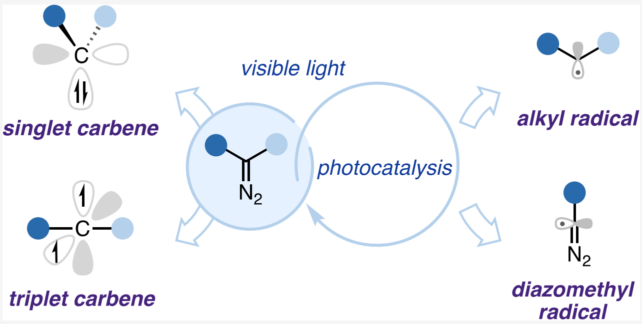

ABSTRACT: In recent years, visible light-induced reactions of diazo compounds have attracted increasing attention in organic synthesis, leading to improvement of existing reactions, as well as to the discovery of unprecedented transformations. Thus, photochemical or photocatalytic generation of both carbenes and radicals provide milder tools toward these key intermediates for many valuable transformations. However, the vast majority of the transformations represent new reactivity modes of diazo compounds, which are achieved by the photochemical decomposition of diazo compounds and photoredox catalysis. In particular, the use of a redox-active photocatalysts opens the avenue to a plethora of radical reactions. The application of these methods to diazo compounds led to discovery of transformations inaccessible by the classical reactivity associated with carbenes and metal carbenes. In most cases, diazo compounds act as radical sources but can also serve as radical acceptors. Importantly, the described processes operate under mild, practical conditions. This Review describes this subfield of diazo compound chemistry, particularly focusing on recent advancements.

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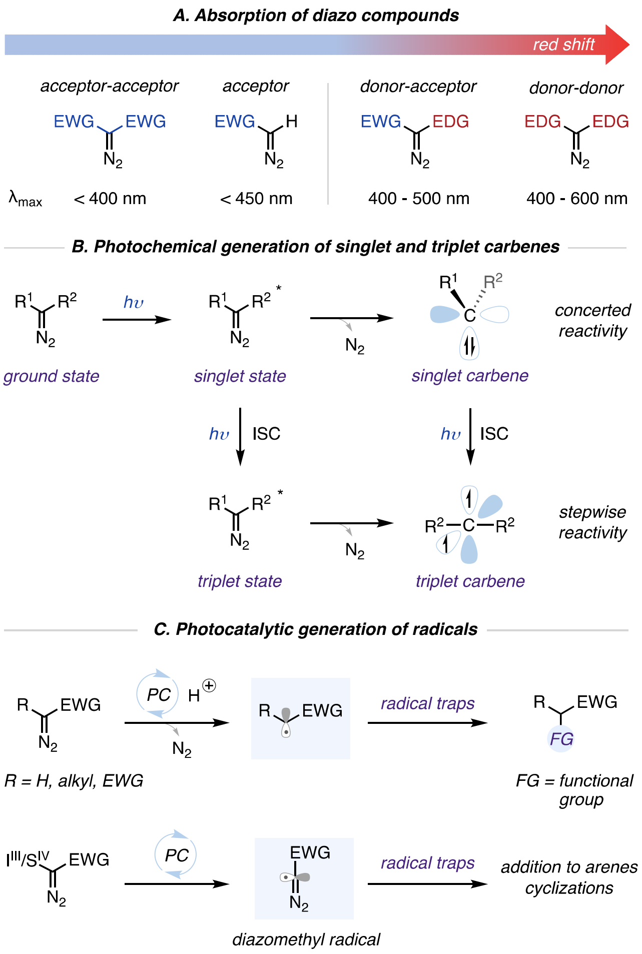
1. INTRODUCTION

Diazo compounds are versatile reagents in organic synthesis. In particular, they are extensively utilized as precursors for generating free carbene or metal carbenoid intermediates. These reactive species can undergo a variety of potent synthetic transformations, including cyclopropanations, X−H insertions, and ylide formations. The earliest developed techniques employ thermal conditions, although their applicability is limited due to the harsh reaction conditions and low selectivity.[1] Consequently, transition metal catalysis has emerged as a powerful tool, providing access to metal carbenes whose electronic properties and stabilities can be easily tuned. In this scenario, transformations frequently occur at room temperature. Importantly, the careful design of catalysts and ligands enables exceptional control over selectivity and reactivity, offering opportunities for asymmetric reactions. The topic of transition metal-catalyzed reactions of diazo compounds has been extensively reviewed.[2]

In contrast to the numerous protocols reported on thermal processes throughout the years, photochemical studies with diazo compounds have been performed mostly several decades ago.[3,4] Contemporary applications were relatively scarce until recently. Photolysis is a critical tool in investigating denitrogenative reactions of diazo compounds within the realm of physical organic chemistry. Thus, it has played an important role in establishing the basis for contemporary carbene chemistry. Matrix isolation techniques[5] and ultrafast spectroscopy studies significantly contributed to the experimental determination of the structural and electronic properties of carbene intermediates. Platz and co-workers conducted a series of studies[6−10] on ultrafast photolysis of diazo compounds to carbenes and their subsequent reactions, such as cyclopropenation.[9] They observed a singlet carbene produced directly from the excited state of a diazo precursor. Additionally, they studied dynamics of solvation of the singlet carbene.[10] The initial absorbance of the carbene is solvent dependent and is red-shifted in coordinating solvents, such as alcohols, indicating the formation of hydrogen bonds. However, it is important to note that these approaches produced carbene species from diazo compounds using high-energy UV irradiation. This typically required special medium- and high-pressure xenon and mercury lamps in combination with monochromators or filters. Given that the majority of organic molecules are capable of absorbing UV light, exposing a reaction to UV radiation can induce simultaneous and competitive excitation of multiple compounds, such as reagents, intermediates, products, and even solvents. These harsh reaction conditions led to numerous side reactions, thus limiting the synthetic applications of the methods.

Scheme 1. Diazo Compounds under Visible Light Irradiation



Recently, the application of visible light in organic synthesis has garnered tremendous attention and evolved into a powerful tool for developing a wide range of transformations. Consequently, interests in the chemistry of diazo compounds under visible light-induced conditions have been reignited, as evidenced by several review articles.[11] Diazo compounds are often colored molecules with their absorption strongly dependent on the substituents of the carbon bearing the diazo functional group. Notably, the presence of a donor group, often an aryl ring, induces a bathochromic shift in the absorption band. Thus, donor−acceptor diazo compounds, such as aryl diazoacetates, exhibit strong absorption in the visible light region (Scheme 1A). Furthermore, the donor−acceptor carbenes are capable of very efficient reactions without the need for stabilization by a transition metal, as was seen in thermal studies conducted a few years earlier.[12−15] In 2018, Jurberg and Davies pioneered a photochemical method to generate carbenes from aryl diazoacetates using blue light.[16] Since then, various transformations of aryl diazoacetates have been developed under mild conditions, utilizing visible light as the sole energy source at ambient temperature, and frequently without the need for a catalyst. Theoretical studies indicate that the preferred electronic configuration of carbenes originating from aryldiazoacetates varies based on the aryl substituent. For instance, a singlet ground state is preferred in the presence of a donor substituent like a *para*-methoxy group, whereas a triplet ground state is favored with an acceptor substituent such as a *para*-nitro group.[17] While earlier reports

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primarily focused on aryl diazoacetate substrates, recent developments in the field have demonstrated the possibilities of using donor−donor and acceptor diazo compounds for carbene generation.

Generally, when exposed to light, diazo compounds in the ground state undergo photoexcitation to singlet state (Scheme 1B).[6,7,9] Subsequently, they could follow different decomposition pathways, leading to the formation of carbenes in either the singlet or triplet states, which exhibit orthogonal reactivity. In the former case, the singlet diazo compound undergoes denitrogenation, producing a singlet carbene with two nonbonding electrons at the divalent carbon. The two electrons have antiparallel spins, occupying a single hybridized orbital while leaving a p orbital vacant. Thus, determined by the electronic properties of nearby substituents, singlet carbenes exhibit ambiphilic behavior, acting as both electrophiles and nucleophiles. On the other hand, triplet carbenes can be formed through two mechanisms: one involves the singlet carbene converting into a triplet carbene via intersystem crossing (ISC), while the other entails the singlet diazo compound to its triplet form through intersystem crossing, followed by decomposing into the triplet carbene. These pathways to triplet carbenes are typically facilitated by energy transfer from a photosensitizer. Unlike the singlet state, triplet carbenes have unpaired electrons with parallel spins distributed across two different orbitals. As a result, they are commonly classified as diradicals and typically participate in stepwise reactions, including hydrogen atom abstraction or non-stereospecific addition to olefins.

Importantly, in combination with photoredox catalysis,[18−20] diazo compounds can serve as precursors for various radical species under visible light irradiation (Scheme 1C). This has led to the discovery of transformations that were previously inaccessible through classical free carbene and metal carbene reactivity. Thus, diazo compounds undergo efficient single-electron reduction by a photocatalyst to produce *C*-centered radicals with the extrusion of dinitrogen, even in cases where diazo compounds are transparent in the visible light region. Furthermore, specifically designed diazoalkanes that possess a redox-active leaving group, such as a hypervalent iodine or sulfonium functionalities, yield diazomethyl radicals under visible light irradiation, thus preserving the valuable diazo functionality. Additionally, other photocatalytic transformations, in which diazo compounds can act as radical acceptors or nucleophiles have also attracted increasing attention in recent years.

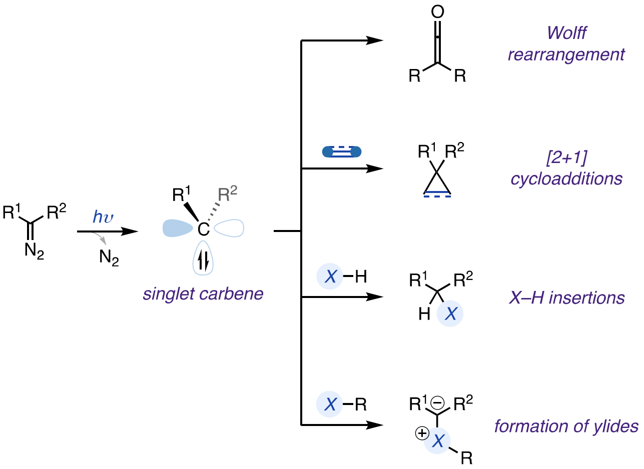
This review intends to offer readers an overview of this emerging field, spanning from its early development to recent advances. As each reactive intermediate produced from diazo compounds exhibits unique reactivity, we have organized this review based on these reactive intermediates. Photoinduced reactions of diazo compound precursors are also covered. We have restricted our discussion to photochemical or photocatalytic methods that utilize visible light or near-visible light (>390 nm). Therefore, UV-induced transformations, which requires the use of specialized glassware, are not included in this discussion. It is worth noting that, given the typical focus of newly developed synthetic methodologies on expanding the scope of reactions, certain mechanistic aspects of these protocols may remain unclear. Therefore, the reaction mechanisms presented herein represent reasonable proposals by the authors and may include speculative steps.

2. DIAZO COMPOUNDS AS SINGLET CARBENE PRECURSORS

2.1. Introduction

The majority of the reactions covered in this review utilize diazo compounds as precursors for singlet carbenes, which serve as crucial intermediates in various transformations. These transformations include the Wolff rearrangement, [2 + 1] cycloadditions, insertions into C−H and X−H bonds, and the formation of ylides (Scheme 2). While many of these reactions are well-established in classical metal carbene chemistry, the photochemical method for generating free carbenes has proven to be a valuable alternative, at times demonstrating complementary reactivities.

Scheme 2. Diverse Transformations of Singlet Carbenes



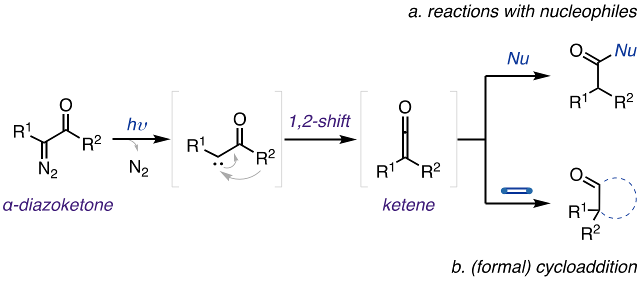
2.2. The Wolff Rearrangement

The Wolff rearrangement is one of the most extensively studied reactions of α-diazoketones.[21] Initially, this rearrangement was primarily employed to prepare homologues of carboxylic acids, serving as a key step in Arndt−Eistert reaction. The process starts with the extrusion of dinitrogen, followed by a 1,2-shift to afford highly reactive ketenes,[22] which can occur either through a concerted mechanism or in a stepwise manner involving a carbene intermediate. Many mechanistic investigations have been conducted by aiming at determining whether migration occurs in a concerted fashion with the loss of dinitrogen.[21] The conclusion that has emerged is that a carbene is formed in photochemical reactions,[23] whereas the reaction is concerted under thermal conditions.

Traditionally, the Wolff rearrangement of α-diazoketones is promoted by thermolysis, photolysis, or metal ions, with the latter two methods being more widely employed.[21] However, these approaches often require high-energy UV lights or metal salts. Recent advances have shown that Wolff rearrangements can be efficiently conducted under visible light irradiation. The resulting ketene then reacts with various nucleophiles to yield carboxylic acid derivatives in both intermolecular and intramolecular fashion (Scheme 3). Additionally, they can participate in (formal) cycloaddition reactions with various unsaturated systems. These new protocols offer milder and more sustainable reaction conditions, enabling practical operations in the laboratory setting.

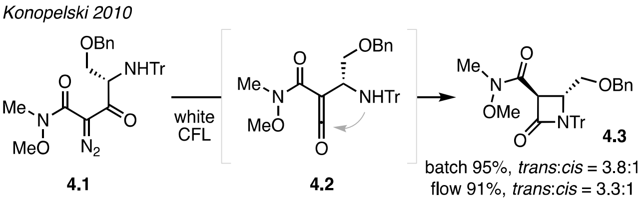
2.2.1. Reactions with Nucleophiles. Early reports in this field involved intramolecular reactions with nitrogen nucleo-

Scheme 3. Wolff Rearrangement and Its Applications



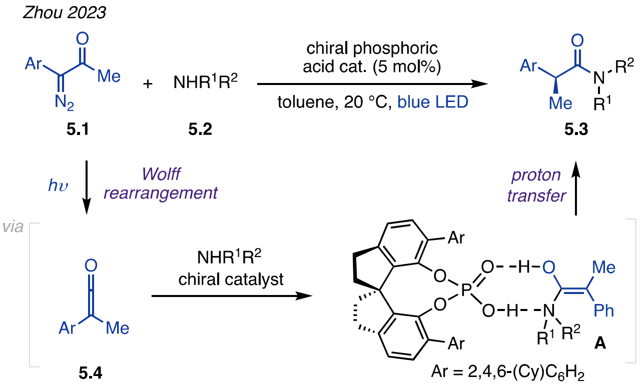
philes. In 2010, Konopelski and co-workers reported synthesis of β-lactams **4.3** from α-diazo-β-ketoamide **4.1**. This transformation proceeds through a sequence of photochemical Wolff rearrangement and intramolecular nucleophilic attack of ketene **4.2** by amine (Scheme 4).[24] White compact fluorescent lamps (CFLs) were utilized as the light source, proving to be equally efficient as the commonly employed high-energy UV lamps in these processes. Additionally, flow conditions were implemented to accommodate the reaction at larger scales.

Scheme 4. Synthesis of β-Lactams via Wolff Rearrangement



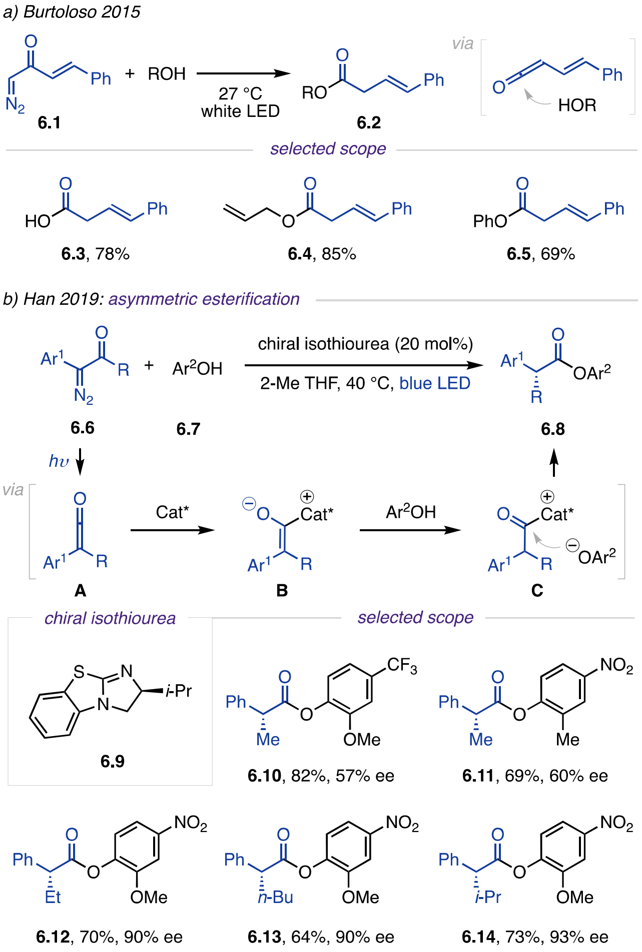
Very recently, Zhou's group achieved an asymmetric synthesis of chiral amides **5.3** using α-diazoketones **5.1** and amines **5.2** (Scheme 5).[25] This transformation is catalyzed by a chiral phosphoric acid, which not only accelerates the reaction between ketene **5.4** and amines to form an *E*-configurated amino enol species **A** but also enables the enantioselective proton transfer process to yield chiral amides.

Scheme 5. Chiral Phosphoric Acid-Catalyzed Enantioselective Synthesis of Chiral Amides via Wolff Rearrangement



Furthermore, it was found that oxygen nucleophiles can participate in reactions with ketenes. In 2015, Burtoloso's group efficiently synthesized allylic esters and carboxylic acids **6.2** using alcohols, phenols, and water as nucleophiles under white LEDs (Scheme 6a).[26] Later, Han's group achieved asymmetric esterification toward α,α-disubstituted carboxylic esters **6.8** (Scheme 6b).[27] They employed a chiral isothiourea catalyst **6.9** to facilitate the formation of an ammonium enolate intermediate **B** from ketene **A**. The enolate then underwent an asymmetric proton-transfer process with phenol, followed by nucleophilic attack by a phenoxide anion (**C**) to yield the products. A wide range of chiral esters (**6.10**−**6.14**) were efficiently prepared with high enantioselectivity.

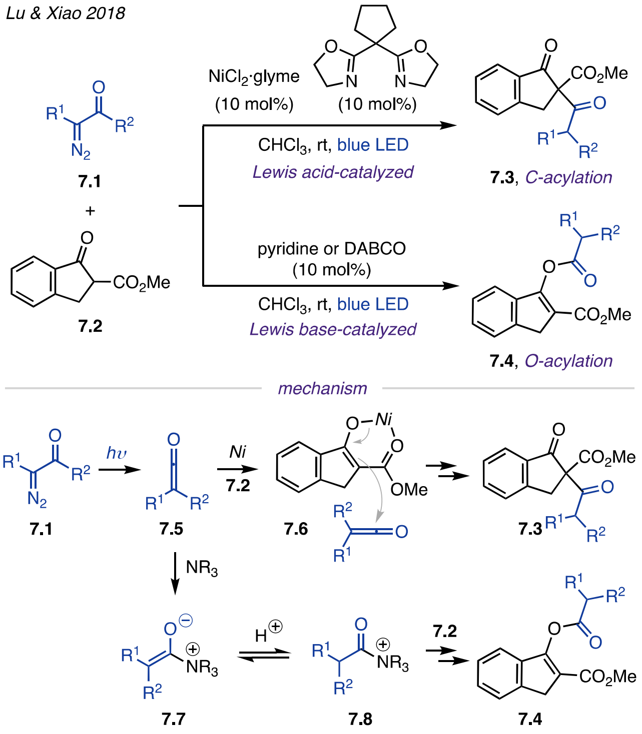
Scheme 6. Esterification via Wolff Rearrangement



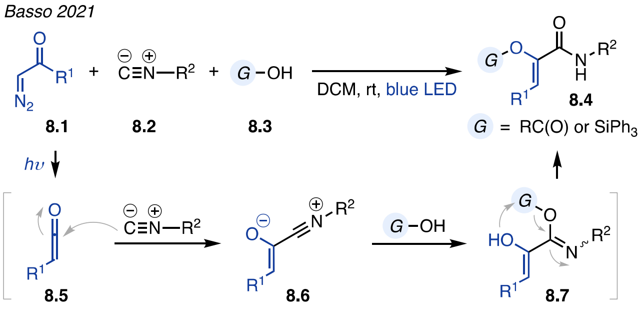
Carbon nucleophiles have also been employed in reactions with ketene. However, in certain cases, the addition of a suitable catalyst may be necessary. In 2018, Lu's and Xiao's group documented a regioselective acylation method for β-ketoesters **7.1**. The selectivity was controlled by the use of either a Lewis acid or base catalyst (Scheme 7).[28] The presence of the Lewis acidic $NiCl_2$·glyme facilitated the generation of an LA-chelated enolate intermediate **7.6**, which subsequently reacted with ketene **7.5** to form the *C*-acylation product **7.3**. In contrast, the use of a Lewis base catalyst resulted in *O*-acylation of the carbonyl group at the β-ketoester. Nucleophilic addition of the Lewis base to ketene produced a zwitterionic intermediate **7.7** capable of abstracting a proton from the β-ketoester. The resulting transient acylated species **7.8** then reacted with enolates, furnishing enol esters **7.4**.

In 2021, Basso's group employed isocyanides **8.2** as *C*-nucleophiles in a three-component reaction with α-diazoketones **8.1** (Scheme 8).[29] The reaction is proposed to proceed through the nucleophilic addition of isocyanides to ketenes,

Scheme 7. Regioselective Acylation of β-Ketoesters with α-Diazo Ketones



Scheme 8. Isocyanides as *C*-Nucleophiles



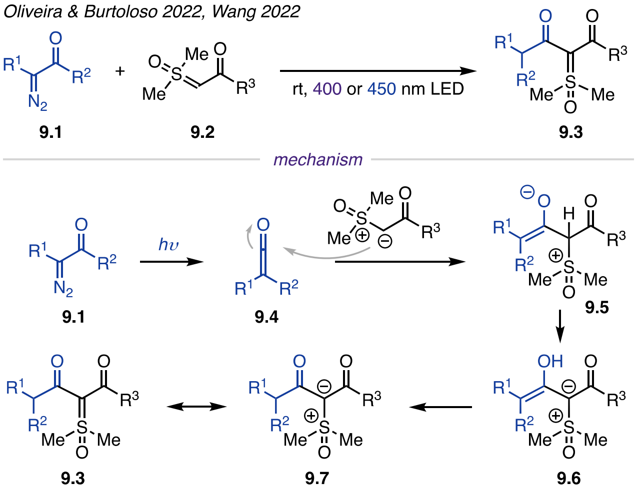
producing a nitrilium ion **8.6**. The latter was captured by either a carboxylic acid or a silanol. Finally, an intramolecular rearrangement of intermediate **8.7** occurs to afford the corresponding α-acyloxy- or α-silyloxyacrylamides **8.4**.

Sulfoxonium ylides have been shown to engage in nucleophilic addition to ketenes, as evidenced by two simultaneous reports. The groups of Oliveira and Burtoloso disclosed an acylation reaction of monocarbonyl sulfoxonium ylides **9.2** and α-diazo ketones **9.1** (Scheme 9).[30] This method enables the synthesis of dicarbonylated products **9.3** under 400 nm irradiation. Notably, the transformation can be carried out using a continuous flow setup, leading to improved yields and shorter reaction times. Independently, Wang's group reported a similar approach using 450 nm LEDs.[31] The proposed mechanism involves the nucleophilic addition of sulfoxonium ylides **9.2** to ketenes **9.4** and a subsequent proton transfer event, delivering 1,3-dicarbonyl sulfur ylides **9.3**.

2.2.2. Formal Cycloadditions.

Apart from directly coupling with nucleophiles, ketenes, which are formed through the visible light-induced Wolff rearrangement of α-diazo ketones, can also participate in formal cycloadditions with different unsaturated π-systems. These cyclization reactions often follow a stepwise mechanism and demonstrate excellent stereocontrol when chiral ligand or organocatalyst is present.

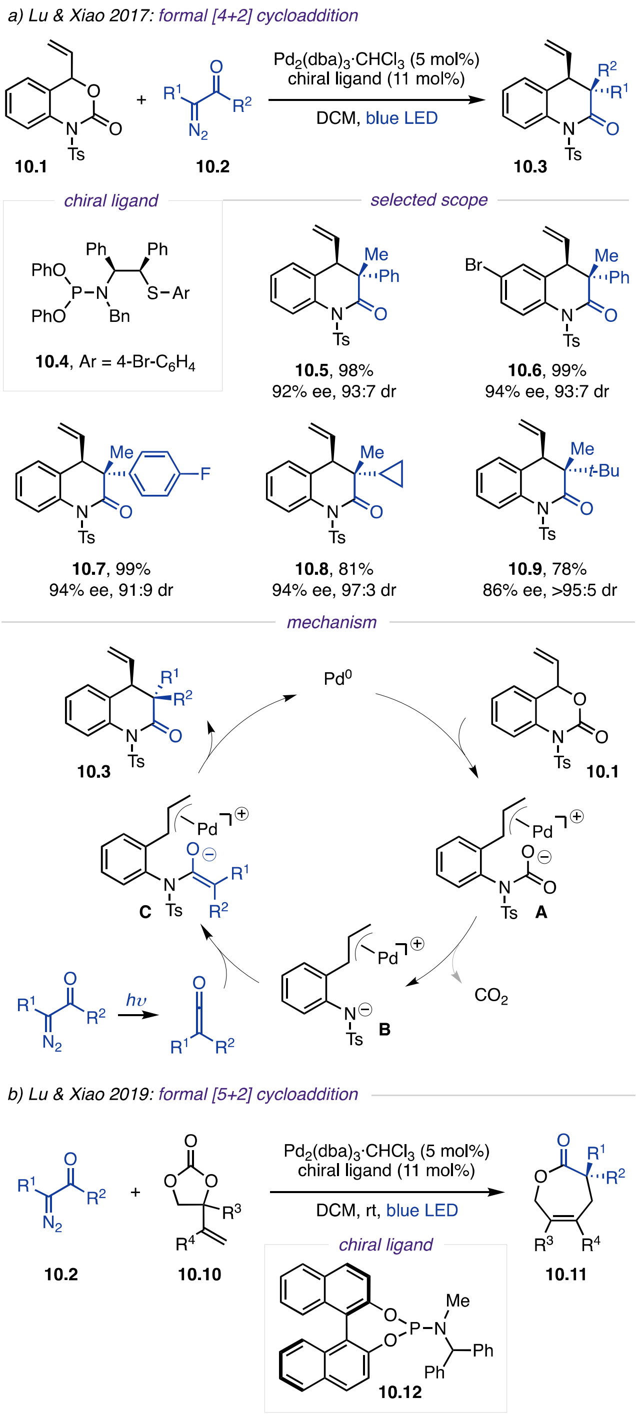
Scheme 9. Synthesis of Dicarbonyl Sulfoxonium Ylides



In 2017, Lu and Xiao's groups achieved Pd-catalyzed asymmetric formal [4 + 2] cycloadditions between vinyl benzoxazinanones **10.1** and α-diazo ketones **10.2**, utilizing a chiral P,S ligand **10.4** (Scheme 10a).[32] Various aryl α-diazoketones proved to be suitable substrates, providing the corresponding quinolinones **10.5**−**10.9** in excellent yields with high degrees of enantioselectivity and diastereoselectivity. The reaction mechanism begins with the oxidative addition of Pd^0 to the allyl ester, affording a π-allyl palladium complex **A**. A subsequent decarboxylation of the latter yields tosyl amide anion **B**, which can undergo nucleophilic addition to ketene, producing a zwitterionic intermediate **C**. Finally, an intramolecular asymmetric allylic alkylation generates quinolinones. Following this, the same groups employed vinylethylene carbonates **10.10** in a formal [5 + 2] asymmetric cycloaddition reaction, enabling the efficient synthesis of 7-membered chiral lactones **10.11** via a similar mechanism (Scheme 10b).[33] Furthermore, it was found that vinyl cyclopropane **11.1** acts as an efficient reaction partner for a formal [3 + 2] cycloaddition with ketenes, as reported by Lu's group in 2019 (Scheme 11).[34] This approach allows access to a wide range of highly functionalized tetrahydrofurans **11.5**−**11.9**. Under similar Pd-catalyzed reaction conditions, vinyl cyclopropanes undergo a ring-opening process in the presence of Pd(0), producing a 1,3-dipolar intermediate **A**. The nucleophilic addition of the latter to ketene and a subsequent intramolecular allylic alkylation event **B** furnished tetrahydrofurans **11.3**.

In addition to Pd catalysis, the asymmetric formal cycloaddition of ketenes can also be achieved through organocatalysis. Chiral organocatalysts efficiently react with photochemically generated ketenes to form chiral enolates **A**, enabling precise control over the stereoselectivity of the subsequent cyclization processes with unsaturated π-systems (Scheme 12a). Thus, in 2019, Song and co-workers reported a chiral isothiourea-catalyzed approach for the formal [4 + 2] cycloaddition of azadienes **12.1** with ketenes (Scheme 12b).[35] This method allows for a highly enantioselective synthesis of benzofuran-fused heterocycles **12.5**−**12.9** with all-carbon quaternary stereocenters. Similarly, Hui's group employed a chiral *N*-heterocyclic carbene (NHC) catalyst **12.12** for

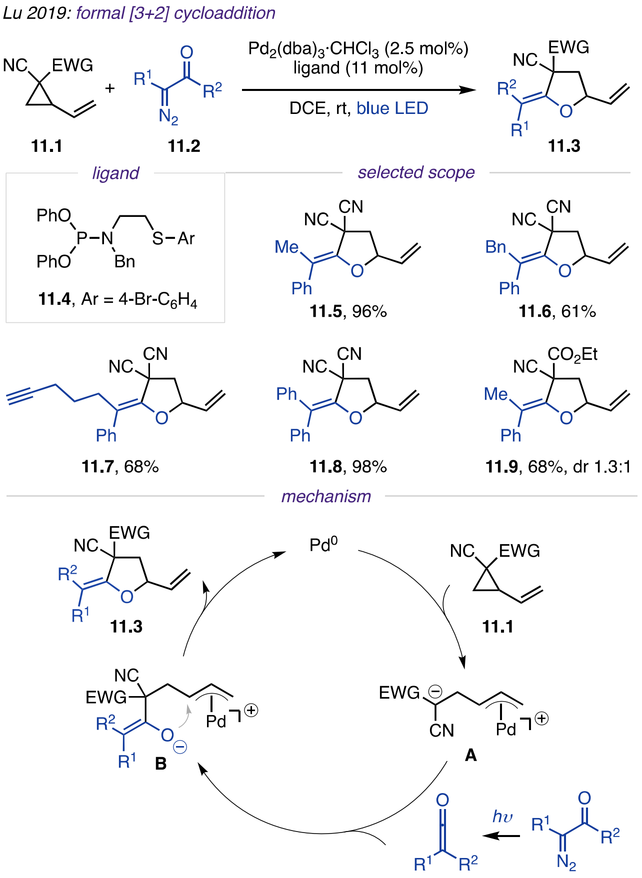
Scheme 10. Pd-Catalyzed Asymmetric Formal [4 + 2] and [5 + 2] Cycloadditions



preparation of tetrahydropyranoindoles **12.11** from enamides **12.10** and α-diazoketones **12.2** (Scheme 12c).[36] This visible light-induced protocol yielded the formal [4 + 2] cycloaddition products **12.13−12.17** in high yields and good stereoselectivities.

Imines (**13.1**) represent a class of substrates suitable for efficient cycloaddition reactions with ketenes. In 2021, Jurberg's group introduced a photochemical method for the formal [2 + 2] cycloaddition to synthesize β-lactams **13.3** (Scheme 13a).[37] They also reported a formal [3 + 2] cycloaddition reaction employing sulfoxonium ylides **13.5** for synthesis of furanones **13.6** (Scheme 13b).[37] The proposed mechanism involves the nucleophilic attack by the sulfoxonium ylide onto the ketene intermediate. Subsequently, the elimination of dimethyl sulfoxide (DMSO) takes place, followed by a Nazarov-type cyclization to give the desired product.

Scheme 11. Pd-Catalyzed Formal [3 + 2] Cycloaddition Employing Vinyl Cyclopropanes

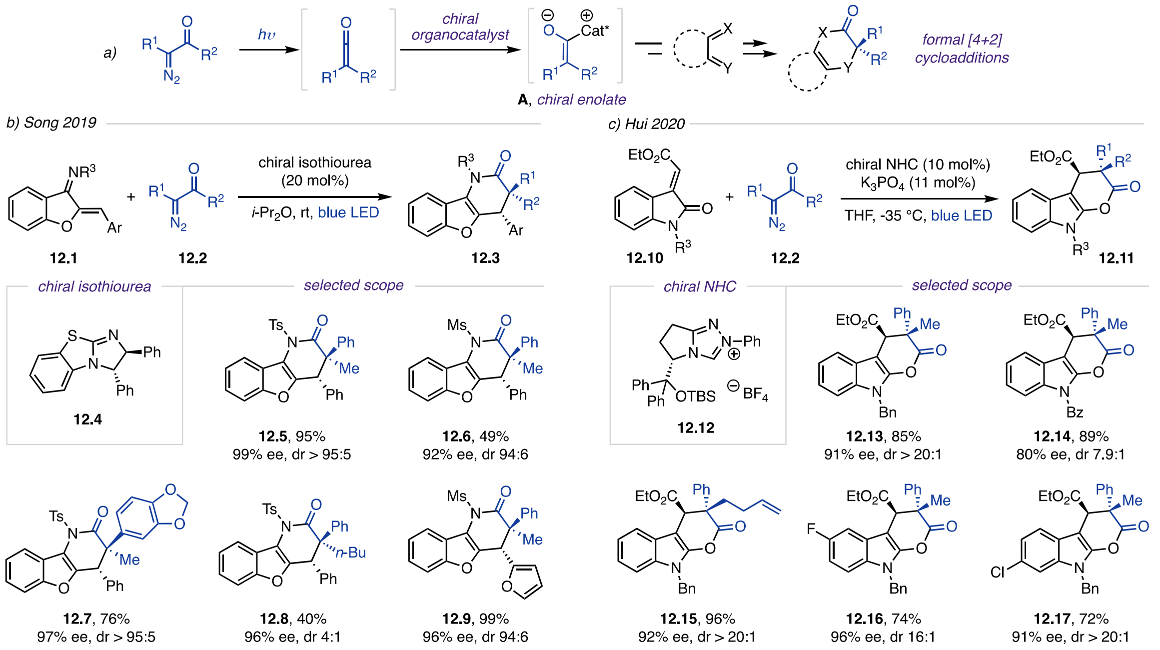


2.3. [2 + 1] Cycloadditions

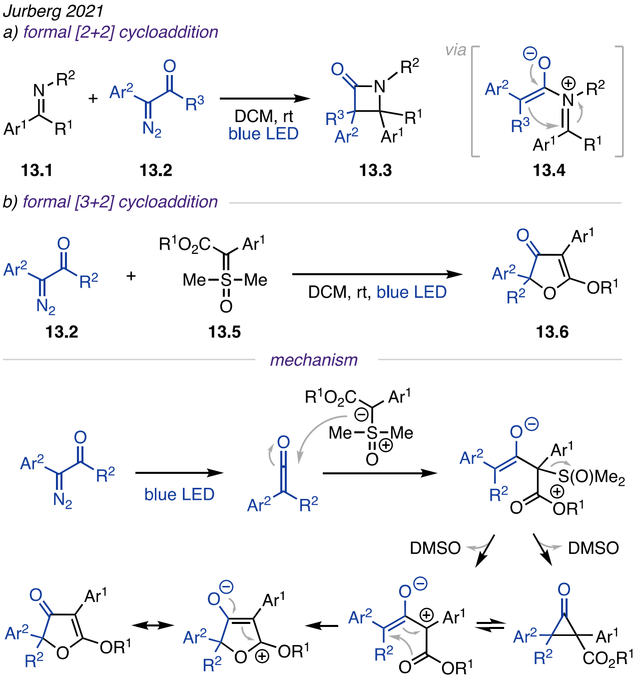
2.3.1. Cyclopropanation. Cyclopropanation of C−C double bonds is one of the most well-developed, valuable, and characteristic transformations of diazo compounds.[38,39] The cyclopropane ring itself is widely present in various natural products[40,41] and serves as a versatile building block in organic synthesis.[42,43] Although approaches involving various transition metals are well-established for cyclopropanation reactions, visible light-induced metal-free photolysis of aryl diazoacetates has recently emerged as a more straightforward and milder method for accessing the corresponding cyclopropanes.[44] In recent years, significant progress has been made in the field of metal-free photochemical cyclopropanation reactions. Scheme 14 summarizes the contributions made by various research groups in employing different alkenes or arenes for these transformations. Many of the cyclopropanes were formed with high diastereocontrol. However, enantioselective cyclopropanation has not been achieved, as typically no catalysts or ligands were employed in these photochemical reactions.

In 2018, the pioneering work by the groups of Jurberg and Davies revealed that aryldiazoacetates absorb in the blue light region (460−490 nm) to undergo photolysis at room

Scheme 12. Asymmetric Formal [4 + 2] Cycloaddition via Organocatalysis



Scheme 13. Photochemical Formal [2 + 2] and [3 + 2] Cycloaddition



temperature toward carbenes.[16] In the presence of styrenes **14.4**, arenes **14.10**, and heteroarenes **14.7**, the formed carbene species efficiently participated in cycloaddition reactions to produce the corresponding cyclopropanes in good yields with high diastereoselectivity (Scheme 14a−c). Following this work, Niu and Song's groups reported cyclopropanation of aryl diazoacetates with *N*-protected indoles and pyrroles (Scheme 14b).[45] However, it was observed that unprotected indoles did not display any reactivity under these conditions. Later, the groups of Reiser and Barham adapted the cyclopropanation reaction to be carried out in continuous flow with various heteroarenes, further improving the safety, sustainability, and scalability of this transformation.[46]

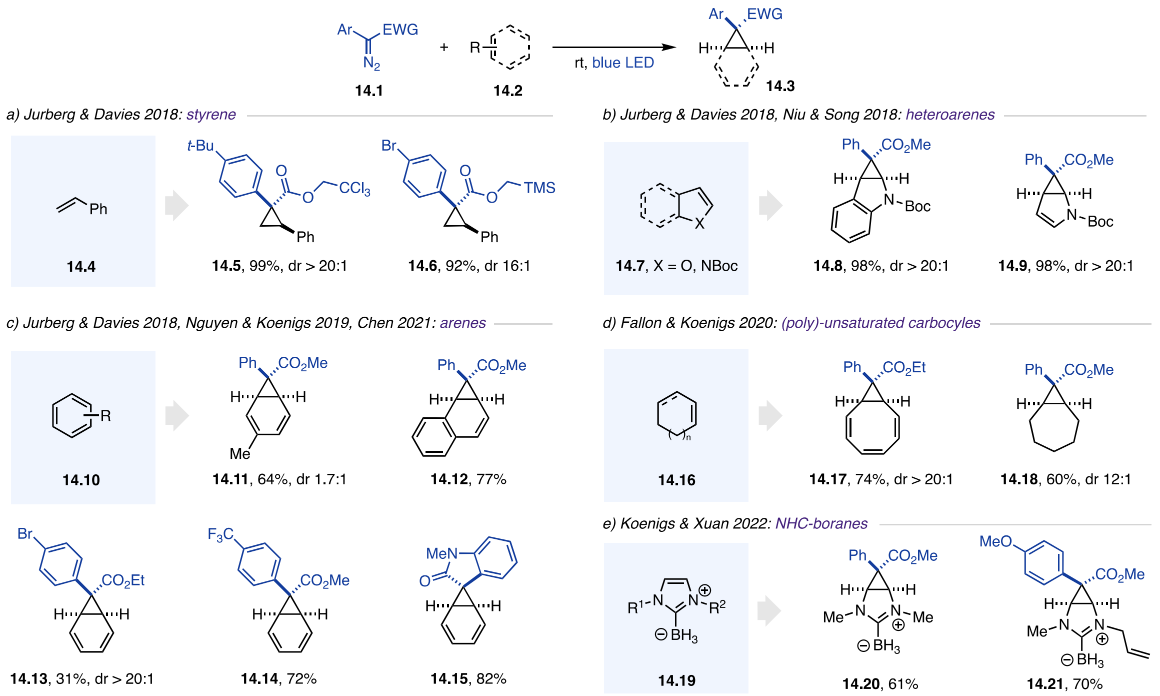
In 2019, the groups of Nguyen and Koenigs made further advancements by expanding the scope of arenes to include different types of methyl-substituted arenes, such as toluene **14.11**, xylenes, and *p*-cymene (Scheme 14c).[47] These arenes were used in excess as solvents to achieve efficient cyclopropanation with diazo compounds. Furthermore, for polycyclic aromatic compounds, such as naphthalenes **14.12**, anthracene and triphenylene, reactions can be conducted in DCM using 10 equiv of these reagents. Additionally, Chen and co-workers contributed to extending this reaction to novel carbene precursors, 3-diazooxindoles, enabling synthesis of spiro-fused norcaradiene indolinones **14.15**.[48]

In 2020, the groups of Fallon and Koenigs revealed that (poly-)unsaturated carbocycles **14.16** can also serve as suitable reaction partners for cyclopropanation with diazo compounds (Scheme 14d).[49] Despite the presence of multiple double bonds in the substrates, the exclusive formation of monocyclopropanated products **14.17** and **14.18** was observed. This selectivity was achieved by employing large excess of alkenes.

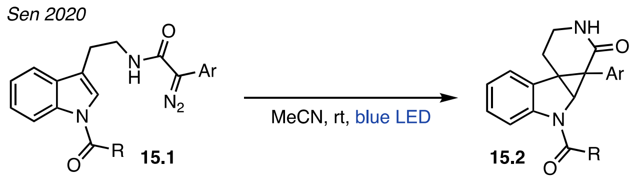
In 2022, Koenigs and Xuan's groups employed NHC boranes **14.19** in cyclopropanation reactions under photochemical conditions (Scheme 14e).[50] This unusual cyclopropanation reaction chemoselectively occurred at the imidazolium backbone of the NHC boranes (**14.20** and **14.21**).

Photochemical intramolecular cyclopropanation of diazo compounds with *N*-protected indoles **15.1** was achieved by Sen and co-workers (Scheme 15).[51] By modifying the substitution pattern at the nitrogen atom of the indole, they were able to access different products. When employing *N*-acetyl and *N*-Boc protected indoles, cyclopropane-fused polycyclic products **15.2** were obtained, whereas *N*-methyl and *N*-H substrates delivered cyclopropyl ring expansion products. Subsequently, the same research group further expanded this photochemical methodology to an intermolecular cyclopropanation/ring expansion cascade.[52]

Scheme 14. Intermolecular Cyclopropanation of Diazo Compounds with Alkenes and Arenes

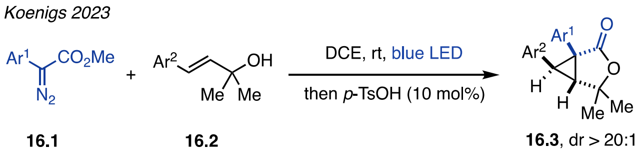


Scheme 15. Intramolecular Cyclopropanation of Diazo Compounds with *N*-Protected Indoles



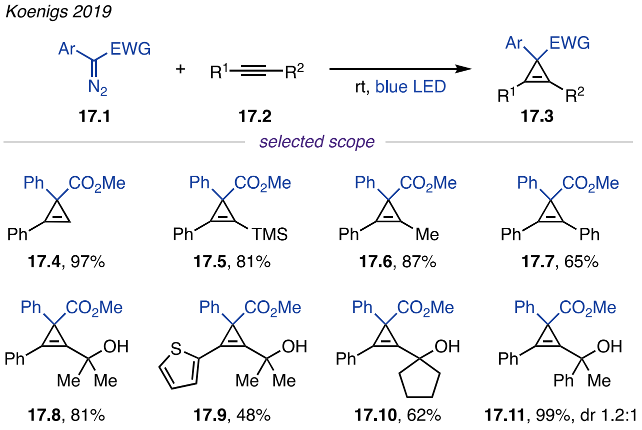
Very recently, Koenigs and co-workers introduced a one-pot procedure that combines cyclopropanation of diazo compounds **16.1** with transesterification using allylic alcohols **16.2** (Scheme 16). This method allows for synthesis of various cyclopropane-fused bicyclic lactones **16.3** with high diastereoselectivity.[53] Notably, this photochemical approach demonstrates excellent chemoselectivity toward cyclopropanation of allylic alcohols, without the formation of O−H insertion or ylide rearrangement products.

Scheme 16. One-Pot Cyclopropanation and Transesterification Approach Toward Cyclopropane-Fused Lactones



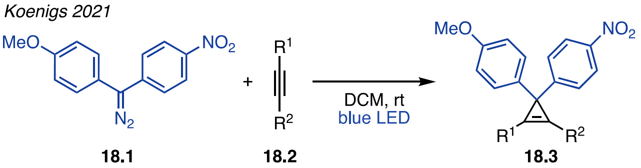
2.3.2. Cyclopropenation. In 2019, Koenigs and co-workers developed a photochemical catalyst-free approach for cyclopropenation of aryl diazoacetate **17.1** and alkyne **17.2** (Scheme 17).[54] Various phenylacetylene derivatives, as well as internal alkynes, efficiently participated in this transformation. The protocol was further examined in a continuous-flow setup, which increased productivity by 36-fold compared to the conventional batch cyclopropenation reactions. Following this success, the same research group extended this photochemical cyclopropenation method to propargylic alcohols.[55] Important differences in reactivity were observed between photochemical and metal-catalyzed reaction of carbenes. In the metal-free transformation, a highly chemoselective cyclopropenation reaction (**17.8**−**17.11**) of the tertiary alcohol occurred. This is in a contrast with the reactions involving transition metals, where rearrangements of an ylide intermediate are more common due to the increased reactivity of more electrophilic metal carbene complexes toward nucleophilic alcohols.[56,57] However, when switching to primary alcohols, exclusive formation of the O−H insertion products, propargylic ethers, were observed, without the generation of cyclopropene or rearrangement products.

Scheme 17. Cyclopropenation of Diazo Compounds with Alkynes



In 2021, they further investigated this photochemical cyclopropenation reaction by employing diaryl diazo compounds **18.1** with alkynes **18.2** (Scheme 18).[58] Upon

Scheme 18. Cyclopropenation of Diaryl Diazo Compounds with Alkynes



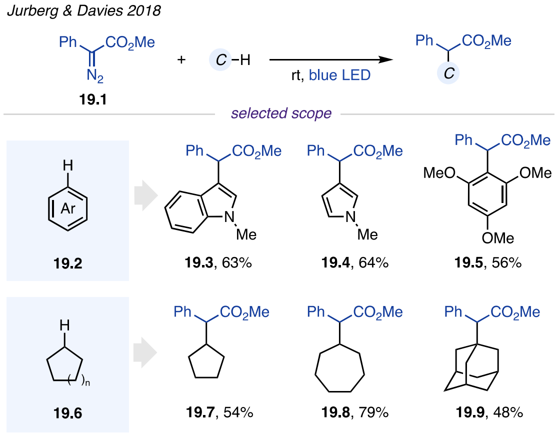
photolysis, the formed singlet diaryl carbenes are stabilized by the introduction of electron-withdrawing nitro group at the aryl rings. Consequently, these carbenes exhibit similar characteristics to the ones substituted with an ester group. Thus, these can engage in reactions that are common for singlet carbenes, such as cyclopropenation of alkynes. Unlike the reactions involving aryl diazoacetates, the photolysis of diaryl diazo compounds, in order to achieve high yields, requires an anaerobic and anhydrous atmosphere.

2.4. C−H Insertions

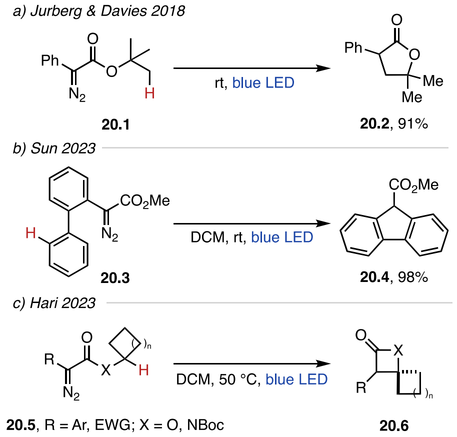
Given the ubiquitous presence of C−H bonds in organic molecules, C−H insertion reactions of diazo compounds represent a powerful strategy for forging new carbon−carbon bonds.[2b] Over the last few decades, this field has undergone substantial development, notably in the realm of enantioselective intermolecular reactions catalyzed by transition metals.[2a] Recently, visible light offered new opportunities for C−H functionalizations under milder and metal-free conditions.

Pioneering investigations by Jurberg and Davies demonstrated the use of cyclic alkanes **19.2** and electron-rich arenes **19.6** in photochemical intermolecular C−H insertion reactions with diazo compounds (Scheme 19).[16] Various electron-rich arenes, such as *N*-methylindole (**19.3**), *N*-methyl pyrrole (**19.4**), or 1,3,5-trimethoxybenzene (**19.5**), efficiently participated in this transformation. However, reactions of cyclic alkanes need to be conducted in neat or with a large excess of the substrate to compensate their lower reactivity. In the same report, the authors also found that this reaction can be performed intramolecularly with C(sp^3)−H to afford 5-membered lactone **20.2** (Scheme 20a). Later, Sun and co-workers extended this intramolecular strategy to C(sp^2)−H bonds, which allowed for preparation of fluorene derivatives **20.4** (Scheme 20b).[59] Very recently, Hari's group demonstrated the efficient synthesis of various spiro-*β*-lactones and lactams **20.6** using this photochemical approach (Scheme 20c).[60]

Scheme 19. Intermolecular C−H Insertions of Diazo Compounds

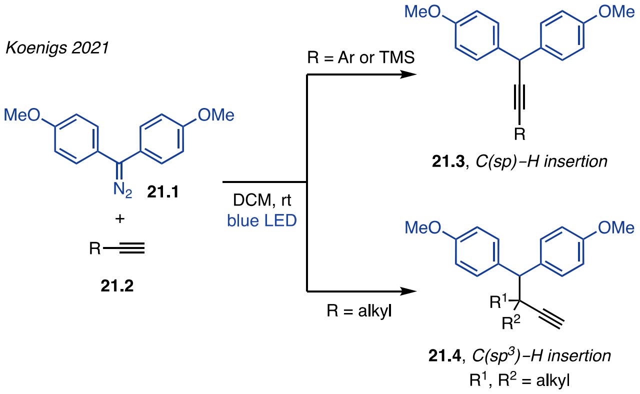


Scheme 20. Intramolecular C−H Insertions of Diazo Compounds



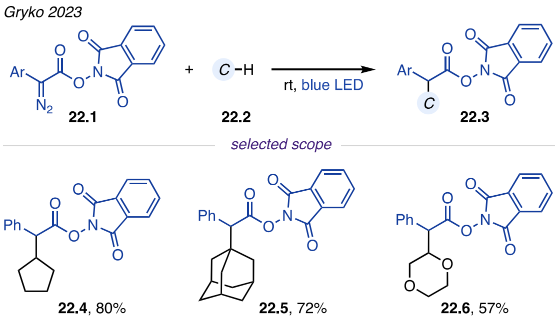
In 2021, Koenigs and co-workers employed diaryl diazo compounds **21.1** in photochemical intermolecular C−H insertion reactions with alkynes **21.2** (Scheme 21).[58] In a combined experimental and computational study, the authors proposed that incorporating two electron-donating methoxy groups onto aryl rings leads to the nearly degenerated singlet−triplet carbene intermediates. Therefore, the reaction outcome strongly depends on substrates. For instance, terminal aromatic alkynes or TMS-acetylene reacted exclusively at the C(*sp*)−H site (**21.3**) via a low-lying transition state involving a singlet carbene, whereas aliphatic alkynes produced C−H insertion products **21.4** at the propargylic C(sp^3)−H site via the triplet carbene intermediates.

Scheme 21. Intermolecular C−H Insertions of Diaryl Diazo Compounds with Terminal Alkynes



Diazo compounds containing an *N*-(acyloxy)phthalimide (NHPI) ester moiety are attractive reagents in organic synthesis. They have previously been employed by Mendoza's group in Rh-catalyzed reactions with alkenes for the enantioselective synthesis of highly substituted cyclopropanes.[61,62] On the other hand, because redox-active esters can produce *C*-centered radicals through the photoexcitation of electron donor−acceptor (EDA) complexes,[63] such diazo compounds hold the potential for orthogonal functionalizations. Very recently, Gryko and co-workers investigated the photochemical behavior of these two functionalities coexisting within a single molecule, a diazo compound containing a redox-active ester group **22.1**.[64] UV/vis spectra analysis of the diazo compounds with the NHPI moiety indicates that they absorb in the visible light region, albeit with a hypsochromic shift of their λ_{max}. Nevertheless, further investigation demonstrated that the reactions exclusively occur at the diazo group, leaving the NHPI ester functionality intact. For example, it was found that under photochemical conditions, the diazo compounds undergo efficient C−H insertions with both linear and cyclic alkanes (**22.4**−**22.6**) (Scheme 22).

Scheme 22. C−H Insertions of Aryl Redox-Active Diazo Compounds



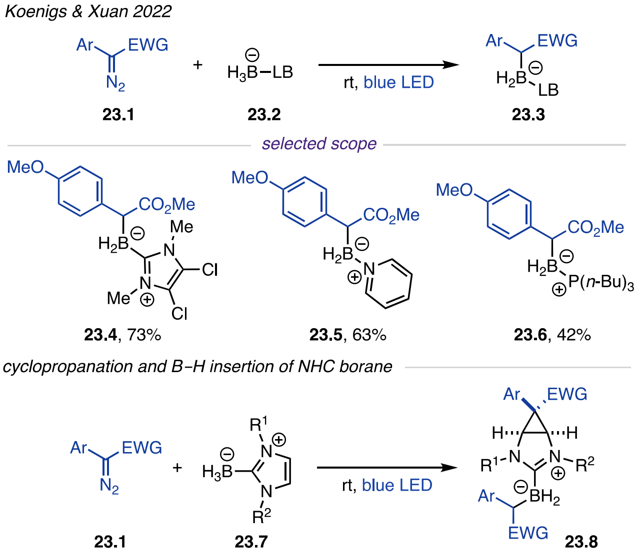
2.5. X−H Insertions

X−H (X = B, N, O, Si, S) insertion by carbenes is a potent strategy for constructing diverse C−heteroatom bonds. This field is primarily dominated by transition metal-catalyzed reactions,[65,66] with only a few instances of metal-free transformations at elevated temperatures.[13,15] Recent advancements in the direct photolysis of diazo compounds demonstrate that visible light-induced approaches offer a valuable alternative and, in some cases, are highly complementary to the traditional transition metal-catalyzed pathways. While the product resulting from X−H insertion can be formally considered as the outcome of a carbene inserting into the X−H bond, the actual mechanistic processes involved may vary widely. Under photolytic conditions, free carbenes are generated from diazo compounds, which can either undergo nucleophilic attack by various heteroatoms, followed by protonation, or proceed via a concerted process.[67,68]

2.5.1. B−H Insertions. In the previously mentioned study on the cyclopropanation of NHC-boranes using aryl diazoacetates conducted by Koenigs and Xuan,[50] it was observed that when substitutions blocked the cyclopropanation site on imidazole, B−H insertion products **23.4** were formed (Scheme 23). Other Lewis base borane complexes, such as pyridine borane (**23.5**) and phosphine borane (**23.6**), also efficiently participate in this reaction. Furthermore, cyclopropanation and B−H insertion can occur simultaneously on NHC-boranes when both reaction sites are available.

2.5.2. N−H Insertions. In the previously referenced report by Jurberg and Davies, they demonstrated N−H insertion of aryl diazoacetates into amines and anilines **24.4** under blue light irradiation (Scheme 24a).[16] Various *N*-alkylated products **24.5** and **24.6** were obtained in great efficiency. Following this report, several research groups have further advanced and expanded upon this photochemical strategy for constructing C−N bonds. The scope of this transformation is summarized in Scheme 24.

Scheme 23. B−H Insertions of Diazo Compounds with NHC Boranes

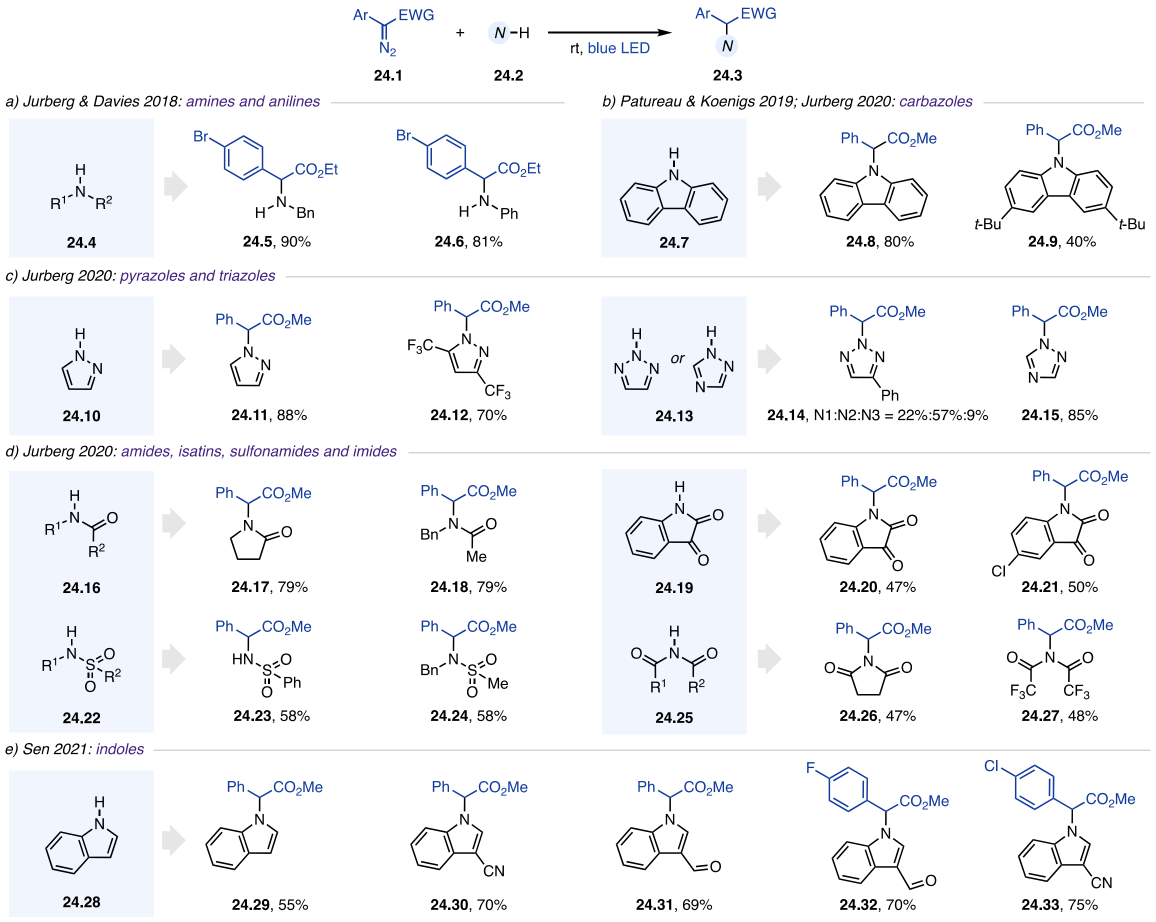


Aza-arenes are capable reaction partners in photochemical N−H insertion protocols with aryl diazoacetates. In 2019, the groups of Patureau and Koenigs employed carbazoles **24.7** to construct *N*-alkylated products (Scheme 24b).[69] Later, Jurberg and co-workers also reported the N−H insertion of aryl diazoacetates into carbazoles, as well as pyrazoles **24.10** and triazoles **24.13** (Scheme 24b,c).[70] However, nonsymmetrical pyrazoles and 1,2,3-triazoles produced different *N*-alkylated regioisomers **24.14**. In 2021, Sen's group further expanded the scope of *N*-heterocycles to include indoles **24.28**, under both batch and flow conditions (Scheme 24e).[71] Notably, other competing reactions of carbenes, such as cyclopropanation and C−H insertion at the C3 position, were not observed in this case.

Apart from *N*-heterocycles, Jurberg and co-worker demonstrated that amides **24.16**, isatins **24.19**, sulfonamides **24.22**, and imides **24.25** can effectively engage in N−H insertion reactions with aryldiazoacetates (Scheme 24d).[72] It was observed that substrates with less acidic N−H bonds, such as amides **24.16** and isatins **24.19**, required the addition of a catalytic amount of DBU to improve yields.

As summarized above, while racemic photochemical N−H insertion of free carbenes has been extensively studied, there are limited examples of its enantioselective counterparts. A recent development in this area involves the use of a chiral phosphoric acid catalyst, as reported by the groups of Guo and Sun. (Scheme 25).[73] They accomplished asymmetric N−H insertion reactions of aryl diazoacetates **25.1** for the synthesis of enantioenriched α-amino esters **25.3**. Various anilines were found to be efficient reaction partners (**25.5**−**25.8**). However, it was observed that aliphatic amines lead to racemic products. This was attributed to the increased basicity of aliphatic amines, which may deactivate the catalyst. The proposed mechanism begins with the rapid capture of free carbene **A** by DMSO to produce a sulfoxonium ylide **B**. A subsequent protonation of the latter by a chiral acid catalyst affords sulfoxonium ions **C** and **D**. These chiral anions then guide the amine to preferentially react with one of the two diastereomers, delivering the enantioenriched product **25.3** through dynamic kinetic resolution.

Scheme 24. N−H Insertions of Diazo Compounds

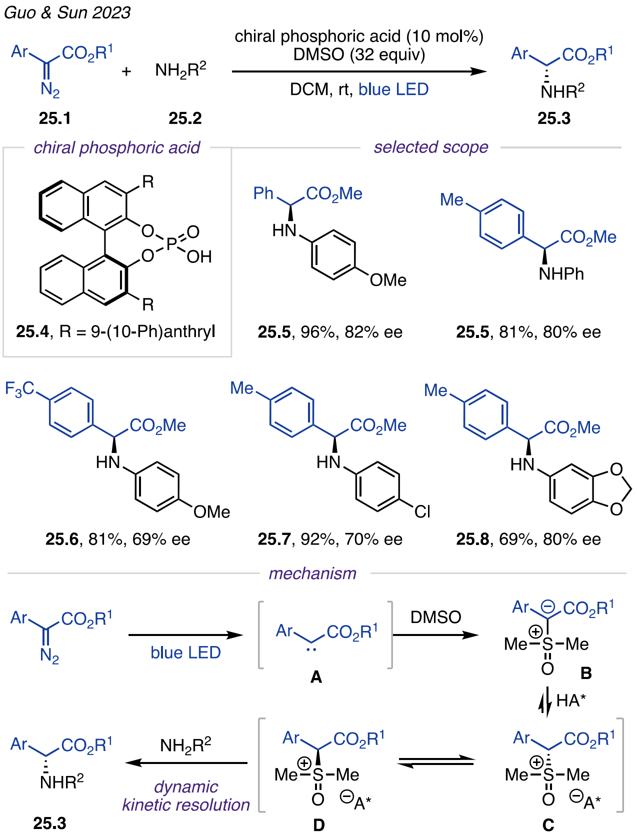


Thereafter, the groups of Li and Zhou designed spiro phosphamide catalysts **26.4** to achieve enantioselective N−H insertion reactions (Scheme 26).[74] Differently from the previous case, photochemically generated free carbene species were directly captured by amine substrates **26.2** through a nucleophilic attack. The resulting ammonium ylide intermediate then engaged in an enantioselective proton transfer process with the chiral phosphamide catalyst, affording the enantioenriched product **26.3**. Various aromatic amines proved to be suitable reaction partners (**26.5**−**26.7**). Moreover, challenging substrates, such as benzylamine (**26.8**) and ammonia (**26.9**), also participated in the reaction, albeit with lower enantioselectivities. Soon after, Guo's group reported a similar N−H insertion approach for the asymmetric synthesis of α-amino esters, enabled by an enantioselective proton transfer process using a chiral phosphoric acid catalyst.[75]

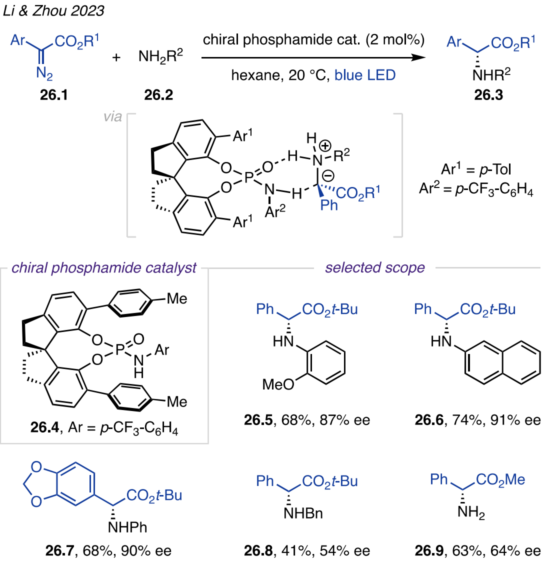
2.5.3. O−H Insertions. In 2018, Jurberg and Davies reported that carboxylic acids **27.4** and alcohols **27.7** efficiently undergo O−H insertions with aryl diazoacetates under blue light irradiation (Scheme 27a,b).[16] Additionally, control experiments revealed that reactions involving stronger carboxylic acids can proceed in dark, which presumably involved protonation of the diazo compound followed by S_N2 displacement of N_2. Later, Rostovskii and co-workers employed carboxylic acids containing an azirine moiety to synthesize the corresponding esters **27.6**.[76] They observed that photochemically generated free carbenes chemoselectively reacted at the carboxyl group rather than at the azirine ring. In contrast, the metal carbene underwent nucleophilic attack by the azirine nitrogen in the presence of a gold catalyst. In 2022, the groups of Yang and Xia further extended the scope of alcohols (Scheme 27b).[77] In the same report, the authors also utilized water for O−H insertions targeting α-hydroxy esters **27.11** and **27.12** (Scheme 27c). The use of oximes **27.13** in photochemical O−H insertion reactions with aryl diazoacetates was independently developed by the groups of Xuan,[78] Wang,[79] and Jurberg[80] (Scheme 27d). Various oxime esters were obtained in good yields from both ketoximes **27.14** and aldoximes **27.15**. It was also shown that donor−donor type diazo compound, such as diphenyl diazomethane, can be utilized in this reaction.[78] Furthermore, the groups of Zhang, Li, and Xia demonstrated the O−H insertion of hydroxylamies **27.16** formed *in situ* through nitroso aldol reaction using β-keto esters and nitrosopyridines (Scheme 27e).[81] This approach provided an efficient pathway toward trisubstituted hydroxylamines **27.17** and **27.18**. Moreover, Yang, Zhou, Huo, and co-workers demonstrated that 2-hydroxypyridines **27.19**, formed *in situ* from 2-pyridones, also participated in O−H insertion reactions (Scheme 27f).[82] The proposed mechanism suggests the initial formation of free carbenes from diazo compounds, which then engage in radical pathways.

2.5.4. Si−H Insertions. Si−H insertions are convenient and effective methods for constructing C−Si bonds. In 2020, Koenigs and co-workers reported a photochemical insertion reaction of silanes **28.2** with aryl diazoacetates **28.1** (Scheme 28).[83] This approach enabled synthesis of a wide range of silanes with moderate to good yields (**28.4**−**28.7**), including sterically hindered substrates such as triphenyl silane (**28.6**).

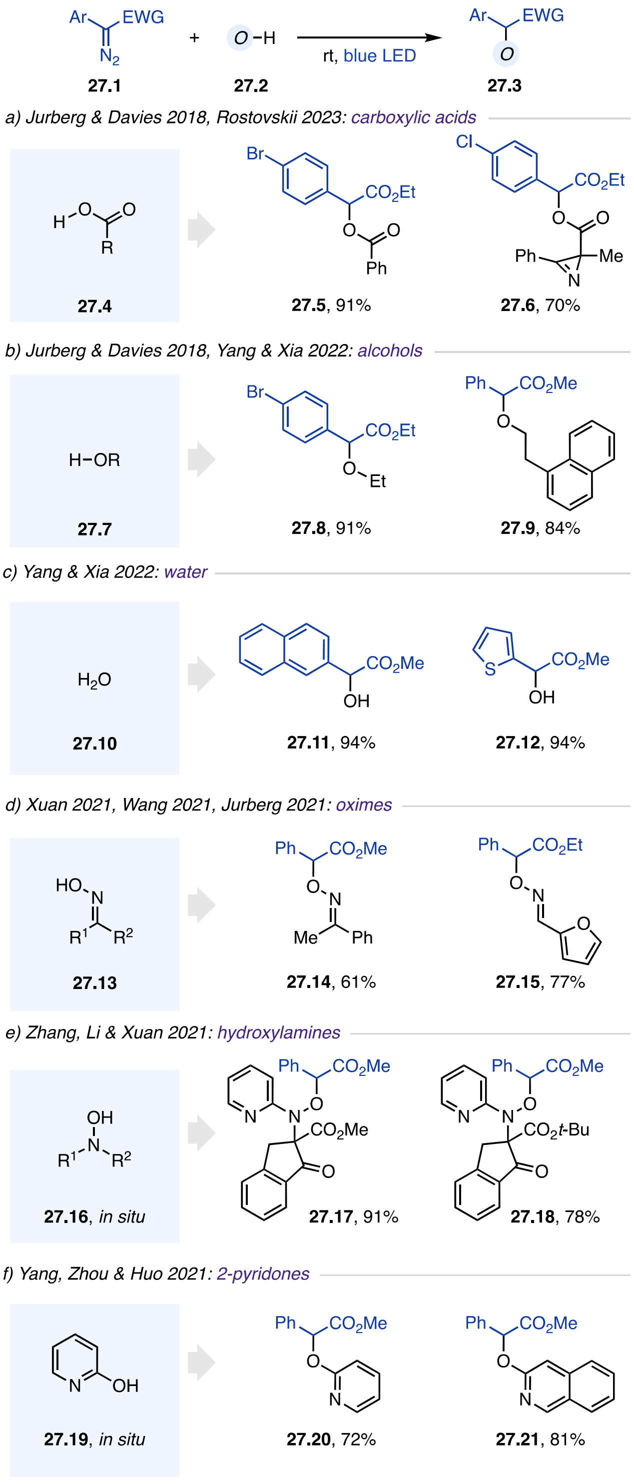
Scheme 25. Enantioselective N−H Insertion Catalyzed by Chiral Phosphoric Acid



Scheme 26. Enantioselective N−H Insertion Catalyzed by Chiral Phosphamide



Scheme 27. O−H Insertions of Diazo Compounds

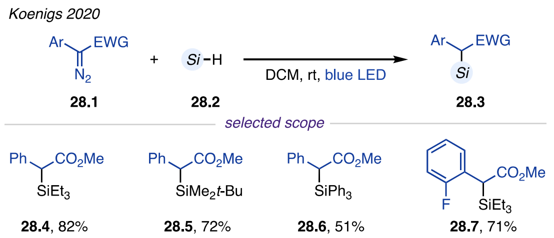


2.5.5. S−H Insertions. In 2020, Qiu and Guo's groups reported a photochemical S−H insertion reaction of aryl diazoacetates **29.1** with cysteine residues **29.4** (Scheme 29a).[84] This reaction was also found to be applicable to common thiols (**29.8**) and thiophenol (**29.9**), resulting in various *S*-alkylated products. Additionally, during the same year, the groups of Yang, Ma, and Huo also disclosed a S−H insertion reaction of thiols **29.10** and **29.13** (Scheme 29b).[85] Both donor−acceptor and acceptor-type diazo compounds were found to be suitable reagents. However, it was observed that ethyl diazoacetate failed reacted with alkyl thiols. The proposed mechanism suggests the formation of thiyl radicals from thiols, followed by their subsequent addition to carbenes.

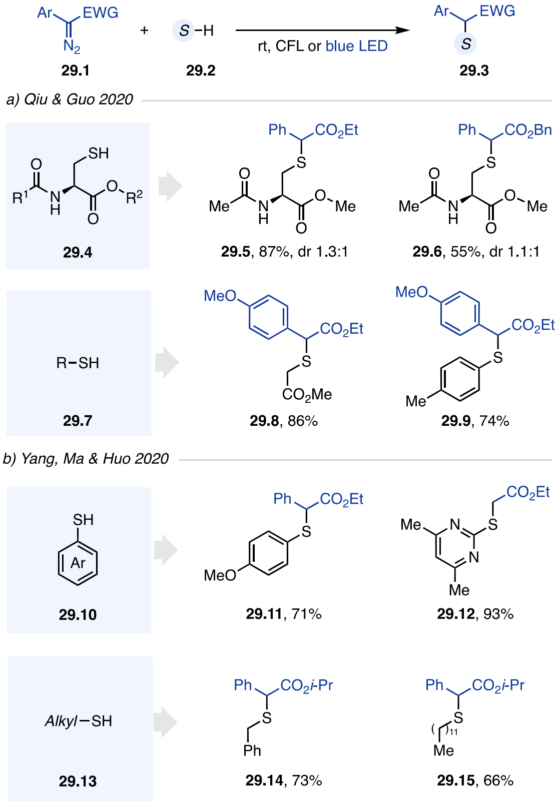
2.6. Ylides Formation

Free singlet carbenes derived from *α*-diazocarbonyl compounds are highly reactive electrophiles and thus can readily react with various heteroatoms possessing lone pairs such as

Scheme 28. Si−H Insertions of Diazo Compounds

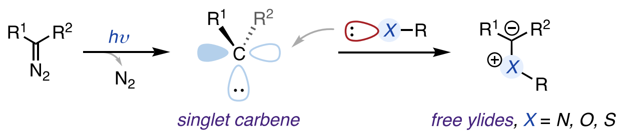


Scheme 29. S−H Insertions of Diazo Compounds



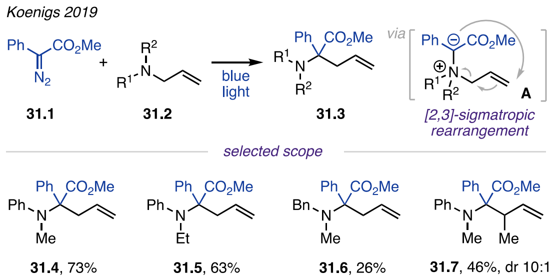
ethers, sulfides, and amines (Scheme 30).[86] These reactions lead to the formation of "free ylides," which are versatile intermediates capable of undergoing various reactions, including [2,3]-sigmatropic rearrangements of allyl-substituted species, [1,2]-rearrangements, and cycloadditions.

Scheme 30. Formation of Ylides



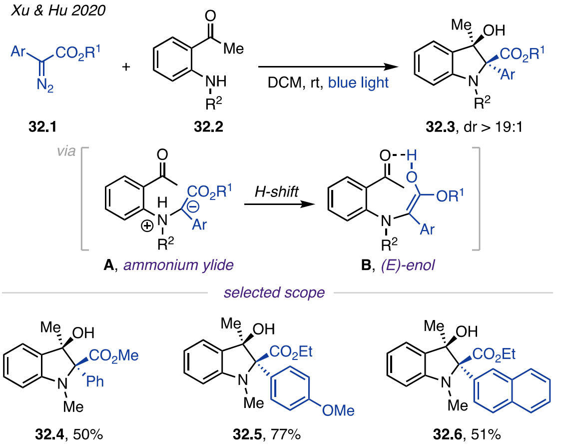
2.6.1. Nitrogen Ylides. In 2019, Koenigs and co-workers reported a photochemical [2,3]-sigmatropic rearrangement reaction of ammonium ylides **A** (Scheme 31).[87] Different allylic amines **31.2** participate in reactions with aryl diazoacetates **31.1**, delivering various homoallylic products **31.4**−**31.7**.

Scheme 31. [2,3]-Sigmatropic Rearrangement of Ammonium Ylides



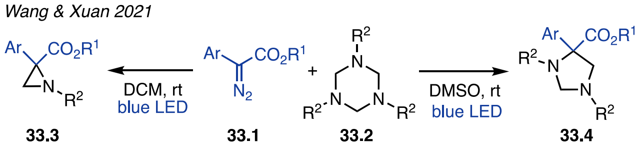
Subsequently, Xu and Hu's groups developed a photochemical annulation reaction of ammonium ylides **A** for synthesis of polysubstituted indolines **32.3** from aryl diazoacetates **32.1** and *o*-aminoacetophenones **32.2** (Scheme 32).[88] Various aryl diazoacetates smoothly reacted in this transformation, affording the corresponding products **32.4**−**32.6** with high diastereoselectivity. DFT calculations suggested the formation of (*E*)-enol intermediates **B** through the H-shift of ylide **A**. The high diastereoselectivity observed in the subsequent intramolecular Aldol-type addition is facilitated by H-bonding interactions between the enol species and the tethered carbonyl group.

Scheme 32. Formal [4 + 1]-Annulation of Diazoacetates with *o*-Aminoacetophenones



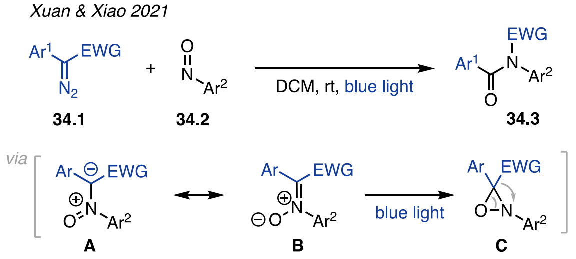
In 2021, Wang and Xuan's groups reported a photochemical protocol for the chemodivergent synthesis of aziridine **33.3** and imidazolidine **33.4** frameworks using diazo compounds **33.1** and 1,3,5-triazines **33.2** (Scheme 33).[89] Interestingly, they were able to access different products by altering the solvents used. Mechanistic studies and DFT calculations indicated the involvement of key ammonium ylide intermediates, which formed through the trapping of free carbenes by 1,3,5-triazines.

Scheme 33. Divergent Synthesis of Aziridines and Imidazolidines



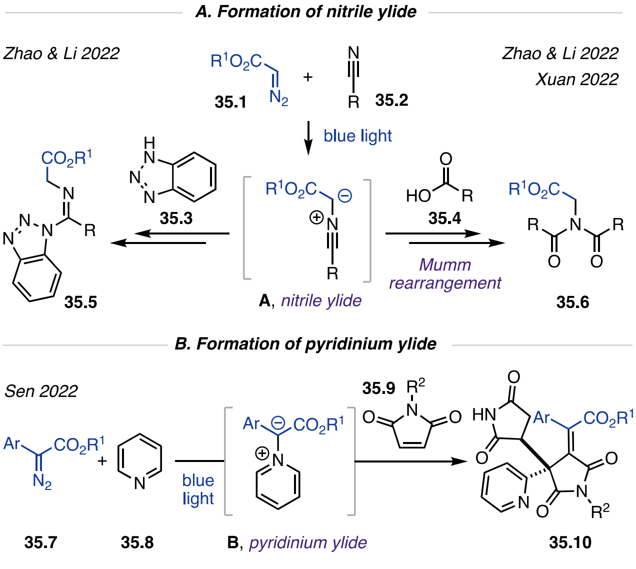
In the same year, Xuan and Xiao's groups described a highly efficient photochemical method for constructing amides **34.3** from aryl diazoacetates **34.1** and nitrosoarenes **34.2** (Scheme 34).[90] Mechanistically, free carbenes were trapped by the nucleophilic *N*-center of nitrosoarenes, producing ylides **A** that predominantly exist in their resonance form as nitrones (**B**). Under blue light irradiation, the latter gets converted to an oxaziridine **C**, which subsequently is rearranged into an amide product.

Scheme 34. Synthesis of Amide from Diazo Compounds and Nitrosoarenes



Unlike the generation of ammonium ylides using donor–acceptor aryl diazoacetates, nitrile ylides were formed using acceptor-only diazo compounds. In 2022, Zhao and Li reported a three-component photochemical approach for constructing diacylglycine esters **35.6** and *N*-imidoylbenzotriazoles **35.5** from *α*-diazo esters **35.1** and nitriles **35.2**.[91] Carboxylic acids **35.4** and benzotriazoles **35.3** were used as nucleophiles, respectively (Scheme 35A). The reaction mechanism involves the capture of free carbenes by nitriles to generate nitrile ylides **A**, followed by protonation to afford a nitrilium ion. A nucleophilic attack of the latter by carboxylate, followed by the Mumm rearrangement, delivered imides **35.6**. Alternatively, the nitrilium ion can undergo nucleophilic attack by benzotriazole to produce various *N*-imidoylbenzotriazoles **35.5**. Independently, Xuan's group later reported a similar approach using carboxylic acids.[92] Pyridinium ylides can be formed through reactions of free carbenes and pyridines. Thus, in 2021, Beeler and co-workers demonstrated the dearomatized ring expansion of pyridinium ylides to produce azepines.[93] However, this reaction has a low yield of 25% due to competitive carbene side reactions. Subsequently, Sen's group utilized pyridinium ylides **B** in a [3 + 2] cycloaddition with maleimides **35.9** (Scheme 35B).[94] The targeted itaconimide derivatives **35.10** were obtained through the sequential oxidation and ring-opening of the adducts, followed by the addition of another equivalent of maleimide.

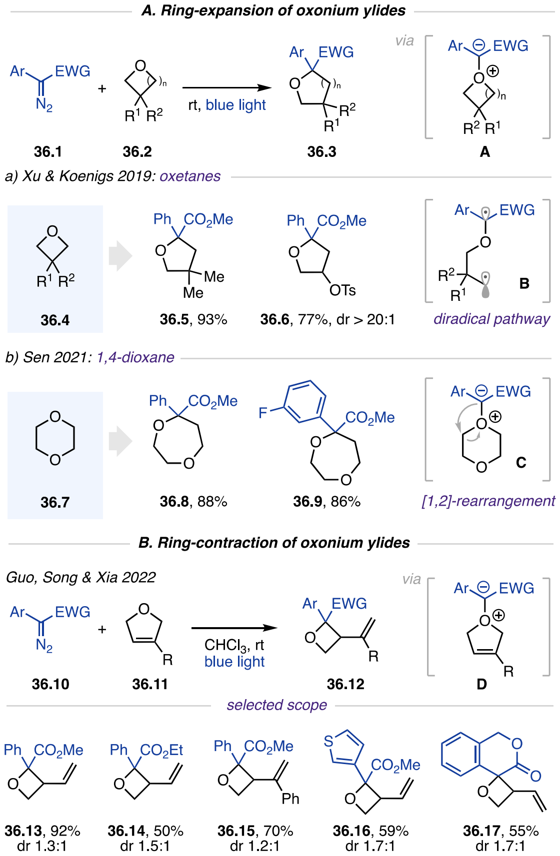
Scheme 35. Formation of Nitrile and Pyridinium Ylides



2.6.2. Oxygen Ylides.

In 2019, the groups of Xu and Koenigs reported photochemical ring expansion of oxonium ylides **A**, allowing for synthesis of various tetrahydrofurans **36.3** from oxetanes **36.2** and aryl diazoacetates **36.1** under mild and operationally simple reaction conditions (Scheme 36A).[95] DFT calculations suggested a diradical pathway (**B**) for the ring expansion of oxonium ylides. Later, Sen's group reported similar ring expansion of dioxanes **36.7** to afford a wide range of dioxepanes **36.8** and **36.9**.[96] However, unlike the previous report, the proposed mechanism involved a [1,2]-rearrangement of oxonium ylides **C**.

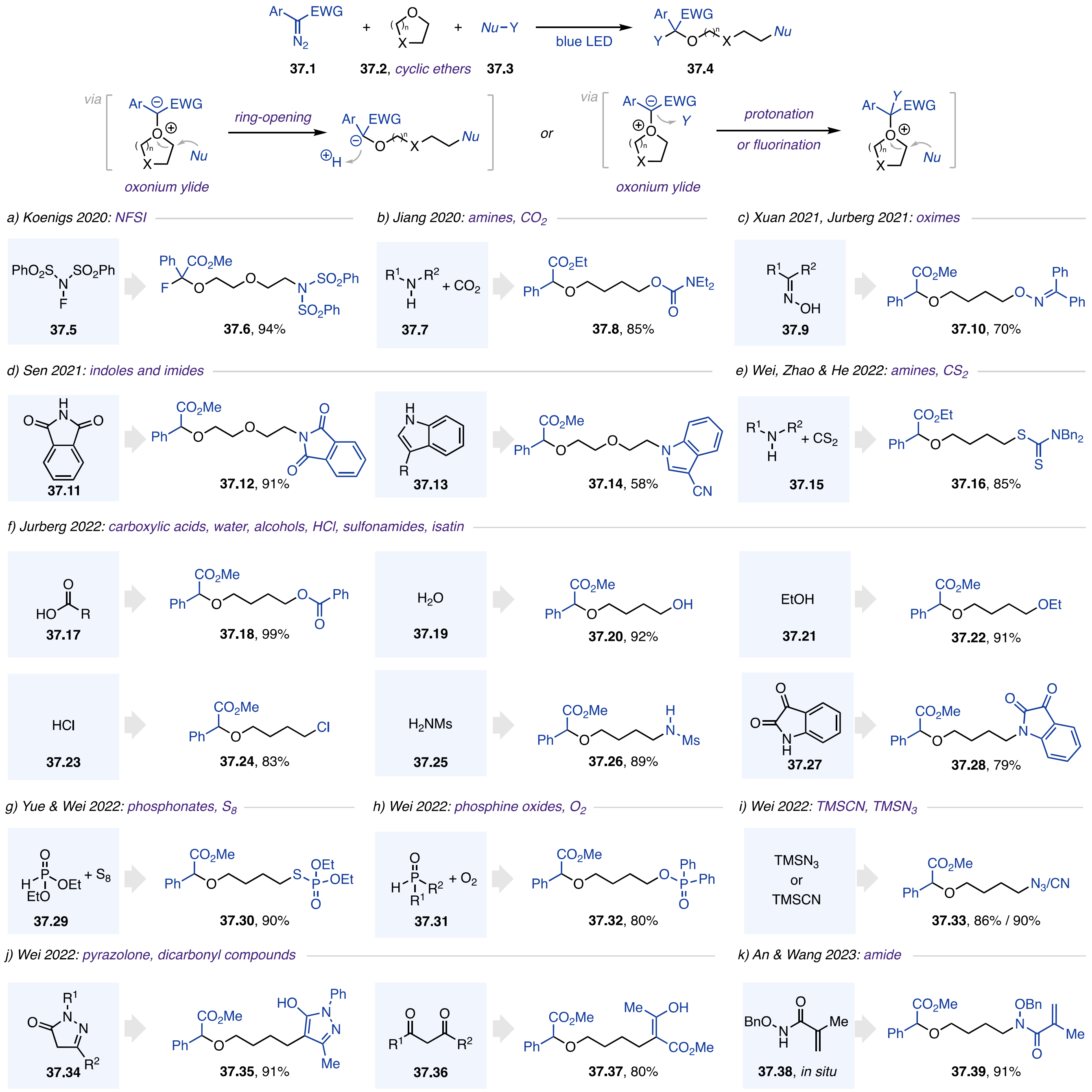
Scheme 36. Ring Expansion and Contraction of Oxonium Ylides



Apart from the ring expansion reactions, oxonium ylides can also participate in ring contraction processes. In 2022, the research groups of Guo, Song, and Xia reported a photochemical approach for synthesis of vinyl oxetanes **36.12** from 2,5-dihydrofurans **36.11** and diazo compounds **36.10** (Scheme 36B).[97] The DFT calculations indicated a mechanistic sequence similar to that proposed in the work of Xu and Koenigs, suggesting the formation of an oxonium ylide intermediate **D**, followed by a diradical rearrangement pathway.

In recent years, significant progress has been made in the development of photochemical cascade ring-opening reactions

Scheme 37. Photochemical Cascade Ring-Opening Reactions of Oxonium Ylides



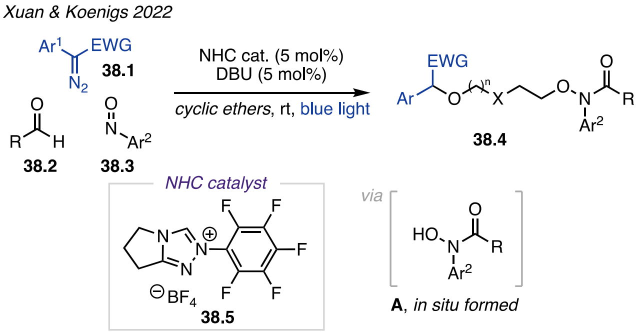
of oxonium ylides. The mechanism of these multicomponent transformations begins with the nucleophilic addition of cyclic ethereal solvents **37.2**, such as THF or dioxane, to free carbenes producing the key oxonium ylides. A subsequent ring-opening of the ylides in the presence of various nucleophiles **37.3** furnishes products **37.4** with a short polyether side chain. Scheme 37 summarizes the contributions from different research groups regarding the employment of a diverse range of nucleophiles.

The initial discovery was made by Koenig's group in 2020. They reported a photochemical fluoro-amino etherification reaction of aryl diazoacetates **37.1** with *N*-fluorbenzolsulfonimide (NFSI) **37.5** in 1,4-dioxane (Scheme 37a).[98] In this reaction, the formed oxonium ylide undergoes electrophilic fluorination with NFSI, followed by ring-opening reaction of resulting oxonium ion to afford the final products **37.6** with newly constructed C−O, C−F, and C−N bonds.

Other groups have adopted this photochemical platform to install polyether side chains with diverse functional groups. In the same year, Jiang and co-workers reported synthesis of carbamates **37.8** by employing carbamate ions formed *in situ* from CO_2 and amines as nucleophiles. (Scheme 37b).[99] Later, the groups of Wei, Zhao, and He developed an analogous reaction using CS_2 to prepare dithiocarbamates **37.16** (Scheme 37e).[100] A further advance was achieved by Xuan's group, using oximes **37.9** to produce various oxime ethers **37.10** (Scheme 37c).[78] In this process, the ylide intermediate was protonated by oximes, followed by a ring-opening reaction to yield the desired products. Independently, Jurberg and co-workers reported a similar approach using oximes.[80] Sen and co-workers further explored this cascade ring opening approach of oxonium ylides, incorporating various *N*-heterocycles such as phthalimides **37.11** and indoles **37.13** (Scheme 37d).[96] In 2022, Jurberg systematically tested a variety of nucleophiles, expanding the scope to include carboxylic acids, water, alcohols, HCl, sulfonamides **37.25**, and isatins **37.27** (Scheme 37f).[101] During the same year, the groups of Yue and Wei disclosed a four-component photochemical reactions of aryl diazoesters, cyclic ethers, S_8, and *H*-phosphonates **37.29** (Scheme 37g).[102] In this reaction, a nucleophilic phosphorothioic anion was formed *in situ*, which subsequently participated in the ring-opening process of oxonium ylides, affording a broad range of *S*-alkyl phosphorothioates **37.30**. Later, Wei's group reported an analogous approach employing O_2 from the air for the synthesis of various phosphonates **37.32** and phosphinates (Scheme 37h).[103] Moreover, the same group demonstrated the utilization of $TMSN_3$, TMSCN, pyrazolones, and dicarbonyl compounds as nucleophiles in three-component cascade reactions involving diazo compounds and cyclic ethers (Scheme 37i,j).[104,105] More recently, An and Wang's groups employed the *in situ* formed *O*-substituted hydroxamic acids **37.38** toward various *N*-alkylated acrylamides **37.39** (Scheme 37k).[106]

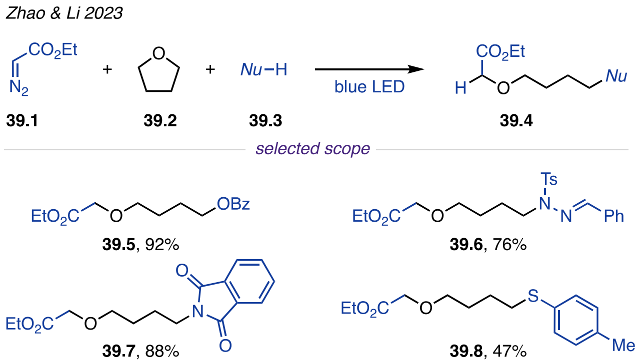
The photochemical cascade ring-opening reaction of oxonium ylides can be synergistically combined with NHC catalysis, thus further expanding the range of suitable substrates for this transformation. In 2022, Xuan and Koenigs introduced a four-component approach for efficient synthesis of a wide range of *O*-protected hydroxylamines **38.4** using aryl diazoacetaes **38.1**, aldehydes **38.2**, and nitroso arenes **38.3** (Scheme 38).[107] The NHC catalyst was used to promote the *in situ* formation of hydroxamic acids **A** from aldehydes and nitroso arenes, which then acted as nucleophiles in ring-opening reactions of oxonium ylides.

Scheme 38. NHC-Catalyzed Approach for Synthesis of *O*-Protected Hydroxylamines



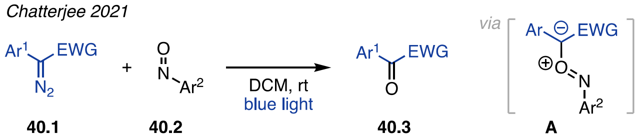
The vast majority of published studies of cascade ring-opening reactions of oxonium ylides employ donor−acceptor diazo compounds, particularly aryl diazoacetaes. Much less attention has been given to other diazo substrates, such as acceptor diazo compounds, mainly due to their limited absorption in visible light region. However, a recent report by Zhao and Li demonstrate the successful employment of acceptor-type diazo compounds **39.1** in cascade ring-opening reactions of oxonium ylides under blue light (Scheme 39).[108] A variety of *N*-, *O*-, and *S*-based nucleophiles (**39.5**−**39.8**) efficiently participated in this transformation. Competition experiments indicated that, although *α*-diazoesters are viable substrates, aryl diazoacetates still more readily generate free carbenes, owing to their relatively strong absorption in the visible light region.

Scheme 39. Cascade Ring-Opening Reactions of Oxonium Ylides Using Acceptor-Type Diazo Compounds



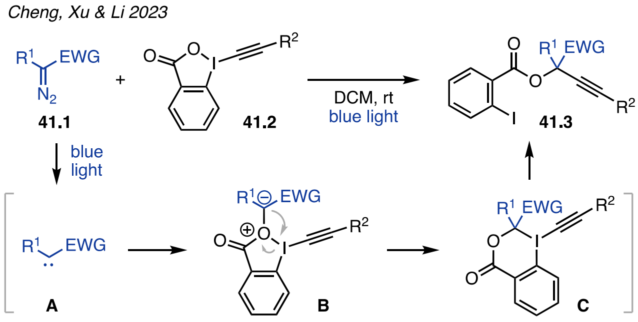
In addition to cyclic ethers, Chatterjee and co-workers have demonstrated that nitroso arenes **40.2** can also react with free carbenes to form oxygen ylides **A** (Scheme 40).[109] They developed a photochemical oxygenation process for the preparation of a series of ketones **40.3**.

Scheme 40. Synthesis of Ketones from Nitroso Arenes



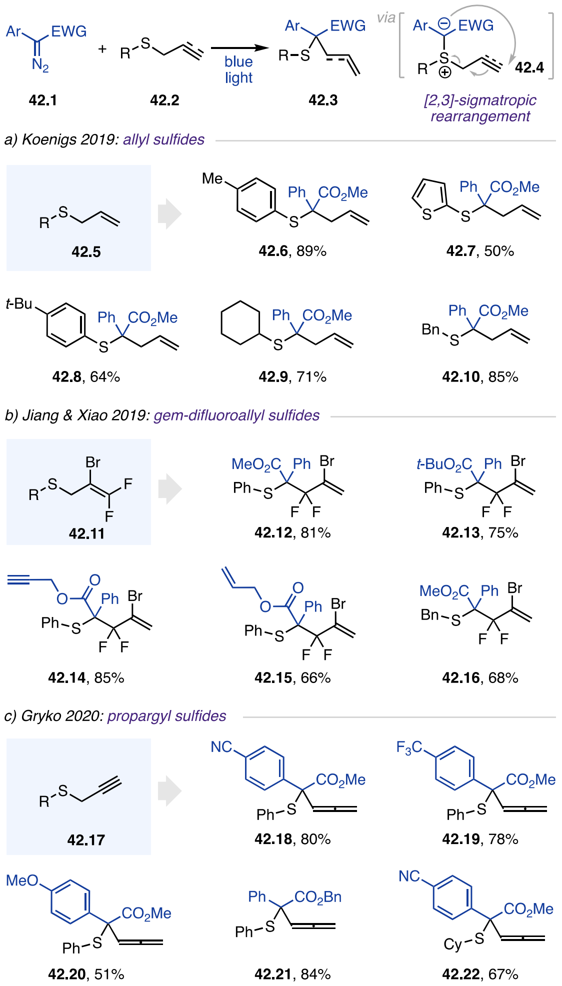
Very recently, the groups of Cheng, Xu, and Li reported a photochemical oxy-alkynylation reaction of diazo compounds **41.1** with ethynylbenziodoxolones **41.2** (Scheme 41).[110] This method efficiently delivers a wide range of propargylic esters **41.3** under metal-free conditions. In comparison to the previously developed Cu-catalyzed version of this transformation by Waser and co-workers,[111] this reaction proceeds via an oxonium ylide **B**. Subsequently, a 1,2-rearrangement occurs, followed by a reductive elimination process of intermediate **C**, yielding a propargylic ester. Both acceptor− and donor−acceptor-type diazo compounds are suitable substrates in this reaction.

Scheme 41. Synthesis of Propargylic Esters via Oxonium Ylide Intermediates



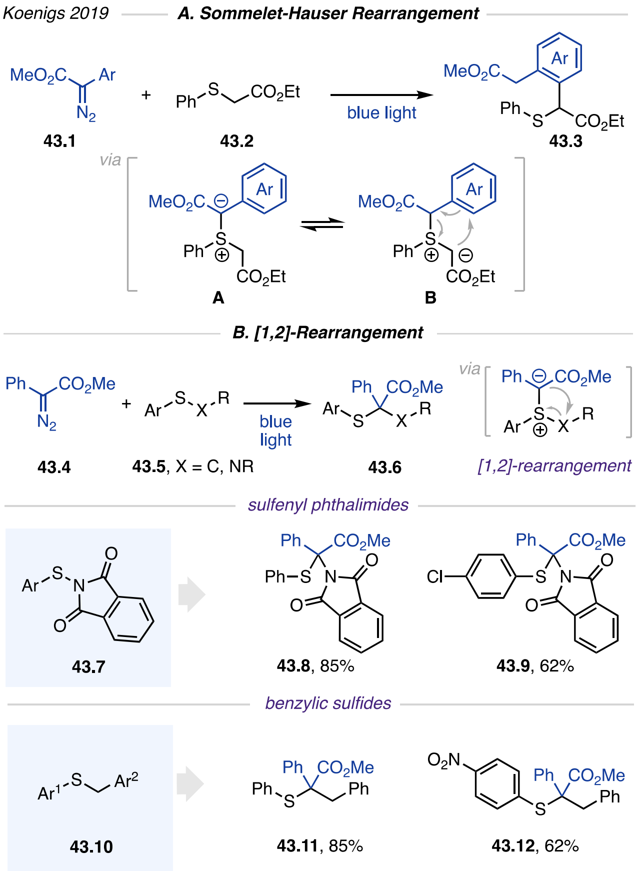
2.6.3. Sulfur Ylides. The [2,3]-sigmatropic rearrangement of sulfonium ylides in the presence of a transition metal, known as the Doyle–Kirmse reaction, was first reported by Kirmse in 1968[112] and later modified by Doyle in 1981.[113] However, the metal-free, photochemical process was only recently reported by Koenigs and co-workers in 2019 (Scheme 42a).[54] Under blue light irradiation, various allylic sulfides **42.5** smoothly reacted with aryl diazo acetates **42.1** in a Doyle–Kirmse reaction. This method provides access to a wide range of homoallylic sulfides **42.6**–**42.10**, including both aliphatic and heteroaromatic thioethers, in high yields. Later, the groups of Jiang and Xiao employed *gem*-difluoroallyl sulfides **42.11** in Doyle–Kirmse reaction for synthesis of corresponding homoallylic sulfides **42.12**–**42.16** (Scheme 42b).[114] The obtained products possess a vinyl bromide moiety that can be further functionalized. The scope of the photochemical [2,3]-sigmatropic rearrangement reaction extends beyond allyl compounds. In 2020, Gryko's group demonstrated the use of propargyl sulfides **42.17** for synthesis of allenes **42.18**–**42.22** (Scheme 42c).[115] While these studies mainly focus on employing aryl diazoacetates, in 2021, Lu and Wang expanded the scope of diazo compounds to 4-diazo-1,4-dihydroisoquinolin-3-ones, which participate in reactions with both allyl and propargyl sulfides.[116]

Scheme 42. [2,3]-Sigmatropic Rearrangement of Sulfonium Ylides



The Sommelet–Hauser rearrangement was observed in sulfonium ylides obtained from the reaction of α-mercapto esters and free carbenes. In 2019, Koenigs and co-workers revealed the photochemical synthesis of various alkylated arenes **43.3** from aryl diazoacetates **43.1** and α-mercapto esters **43.2** (Scheme 43A).[117] Thus, the initially formed sulfur ylide **A** tautomerizes to generate the more reactive ylide **B**, which subsequently engages in consecutive [2,3]-sigmatropic dearomatization and [1,3]-shift rearomatization to yield the *ortho*-alkylated arenes. In the same report, the authors also explored the reactivity of aryl diazoacetates in the presence of sulfenyl phthalimides **43.7** and benzylic sulfides **43.10** (Scheme 43B).[117] Thus, it was found that the resulting sulfonium ylides underwent [1,2]-rearrangement. The scope mainly involved aryl diazoesters and sulfides with different substitution patterns at the aromatic rings.

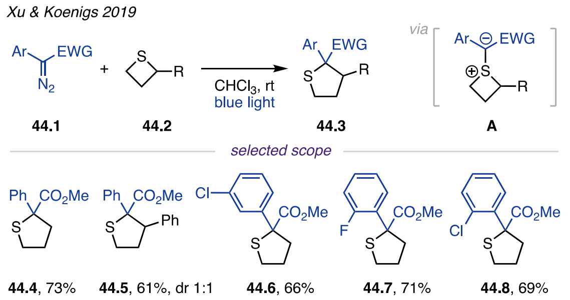
Scheme 43. Sommelet–Hauser and [1,2]-Rearrangement of Sulfonium Ylides



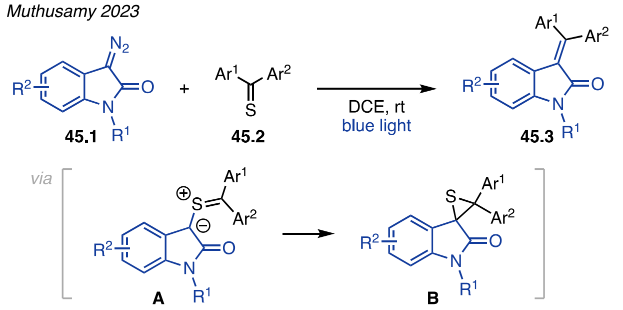
Sulfonium ylides can participate in ring expansion reactions. Thus, in 2019, the groups of Xu and Koenigs disclosed a ring expansion reaction of thietanes **44.2** with donor–acceptor diazo compounds **44.1** toward thiolanes **44.3** (Scheme 44).[95] The DFT calculations revealed that, similarly to the aforementioned mechanism of oxygen ylides, the subsequent ring expansion of sulfonium ylides likely proceeds through a diradical pathway.

Very recently, Muthusamy's group introduced a photochemical protocol for synthesis of arylidene oxindoles **45.3** from diazoindolones **45.1** and thioketones **45.2** (Scheme 45).[118] The proposed mechanism suggests the formation of sulfonium ylide **A**, followed by an electrocyclization reaction to produce episulfide **B**. Subsequently, elemental sulfur is eliminated, furnishing various tetrasubstituted alkenes **45.3**.

Scheme 44. Ring Expansion of Sulfonium Ylides

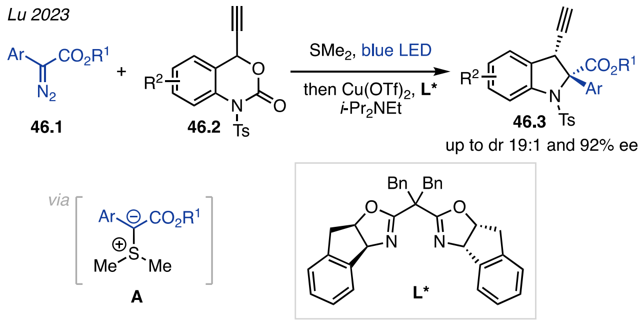


Scheme 45. Synthesis of 3-Arylidene Oxindoles



In an effort to achieve high levels of enantiocontrol for formal [4 + 1] cycloadditions of sulfonium ylides **A** and ethynylbenzoxazinones **46.2**, Lu and co-workers examined a copper-catalyzed approach employing chiral bisoxazoline ligand **L*** (Scheme 46).[119] Sulfur ylides were generated from diazo compounds and dimethyl sulfide under blue light irradiation. This method allowed for preparation of a wide range of chiral indolines **46.3**, bearing C2-quaternary stereocenters with good degrees of enantio- and diastereoselectivity.

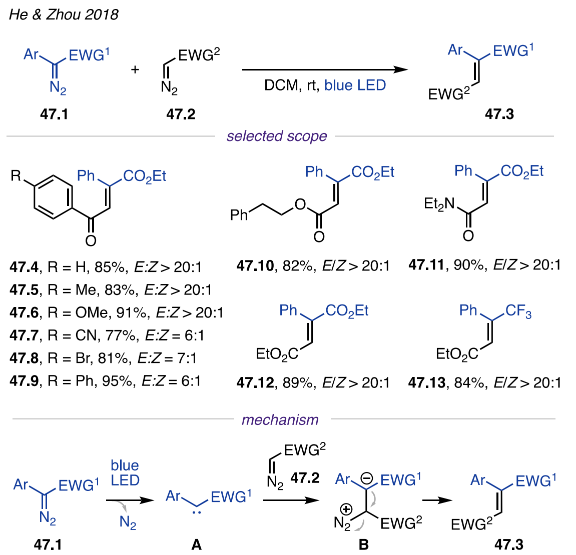
Scheme 46. Copper-Catalyzed Asymmetric Formal [4 + 1] Cycloadditions



2.7. Miscellaneous Reactions

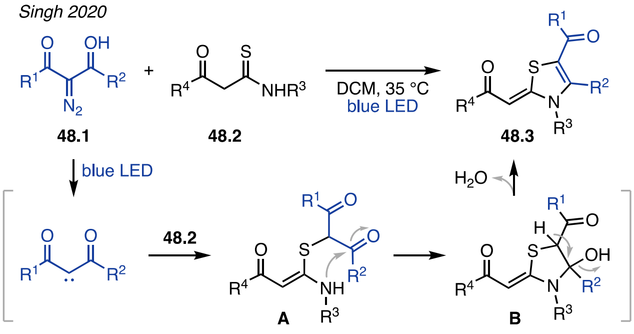
Shortly after the work by Jurberg and Davies,[16] in 2018, another seminal publication on photochemical reactions of diazo compounds was reported by He and Zhou (Scheme 47).[120] In this study, a mixture of donor−acceptor **47.1** and acceptor diazoalkane **47.2** was subjected to a reaction under blue light irradiation. Only the latter absorbed a sufficient amount of visible light for photolysis to generate singlet carbenes. The acceptor-type diazoalkanes, however, remained untouched during this photochemical process. As a result, it can subsequently attack the electrophilic singlet carbene to afford trisubstituted alkenes **47.3** as the final products. Various α-diazo ketones, amides, and esters successfully participated in the reaction, producing a series of α,β-unsaturated *E*-alkenes (**47.4**−**47.13**). This report highlighted the difference in reactivity between the two types of diazo compounds when subjected to visible light irradiation.

Scheme 47. Selective Visible Light Photolysis of Donor−Acceptor Diazoalkanes in the Presence of Acceptor-Type Diazo Compound



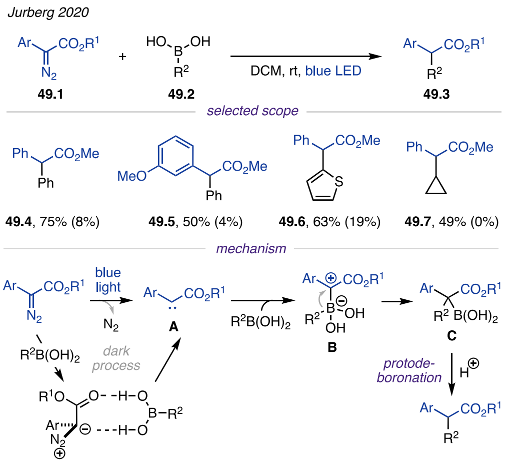
In 2020, Singh and co-workers disclosed a photochemical heterocyclization reaction between α-diazo 1,3-diketones **48.1** and β-ketothiamides **48.2** toward highly functionalized thiazolines **48.3** (Scheme 48).[121] The reaction mechanism involves a nucleophilic attack by the sulfur atom of the β-ketothiamides at carbene to afford intermediate **A**. An intramolecular cyclization of the latter led to intermediate **B**, which upon elimination of water produced thiazolines. It should be noted that Wolff rearrangements of α-diazo 1,3-diketones were not observed in this case.

Scheme 48. Synthesis of Thiazolines from α-Diazo 1,3-Diketones and β-Ketothiamides



In the same year, Jurberg's group reported a photochemical arylation/alkylation protocol using aryl diazoacetates **49.1** and boronic acids **49.2** (Scheme 49). This method enables preparation of various α-branched esters **49.3** in moderate to good yields.[122] The proposed mechanism suggests that free singlet carbenes **A** can react with boronic acids to form ylide intermediates **B**. The ylides then undergo a [1,2]-sigmatropic shift, which upon protodeboration leads to the formation of

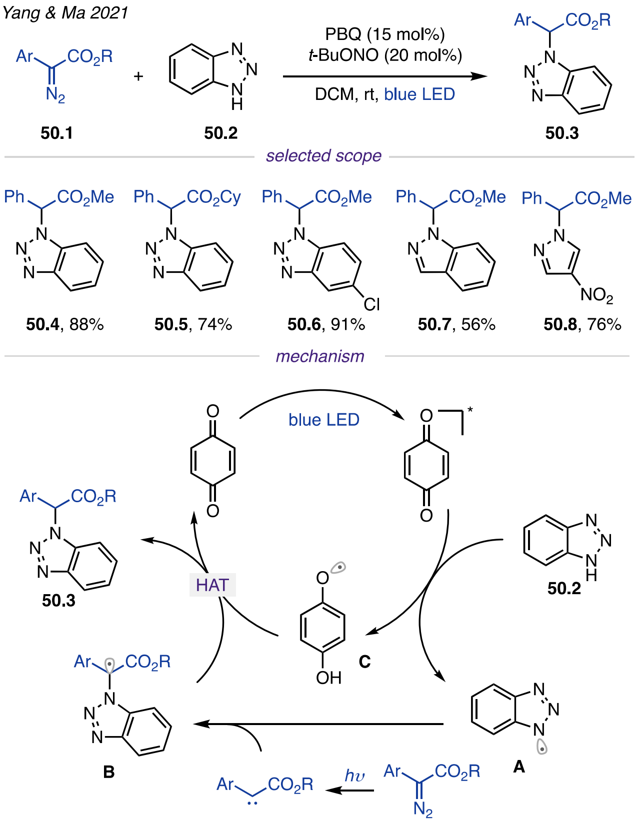
Scheme 49. Arylation and Alkylation of Diazo Compounds with Boronic Acids



C−C coupled products **49.3**. Furthermore, it was also found that the reaction could proceed in the dark under thermal conditions, albeit with much more limited scope. The reaction presumably proceeded through the coordination of the aryldiazoacetate with boronic acid in the absence of light, which can stabilize the resulting carbene intermediate through hydrogen bonding, thus following the elimination of N_2.

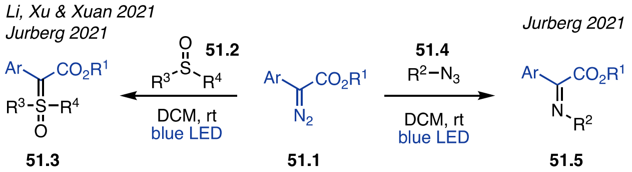
In 2021, the groups of Yang and Ma demonstrated a photocatalytic strategy for the site-selective N^1-alkylation of benzotriazoles **50.2** with α-diazoacetates **50.1** (Scheme 50).[123] The *N*-alkylation of benzotriazoles usually results in a mixture of N^1- and N^2-substituted products, given that benzotriazole exists in equilibrium between its 1*H* and 2*H* tautomers.[124,125] In this work, the authors addressed this synthetic problem by generating a N^1-centered radical from benzotriazole. The reaction mechanism commences with the photoexcitation of 1,4-benzoquinone (PBQ) catalyst, which produces radical intermediate **A** from benzotriazole via either HAT or PCET. A subsequent capture of radical species **A** by a carbene leads to the formation of carbon-centered radical **B**, which upon a HAT event with intermediate **C** affords N^1-alkylated product **50.3**. Various aryl diazo esters worked well in this reaction (**50.4**−**50.8**). It was also found that other *N*-heterocycles, such as indazole (**50.7**) and pyrazole (**50.8**), are also capable substrates. This work demonstrated complementary selectivity compared to that by previously reported Rh-catalyzed N^2-selective N−H insertion of diazo compounds into benzotriazoles[126] and visible light-induced methods involving 1,2,3-triazoles.[70]

Scheme 50. Site-Selective N^1-Alkylation of *N*-heterocycles with α-Diazoacetates



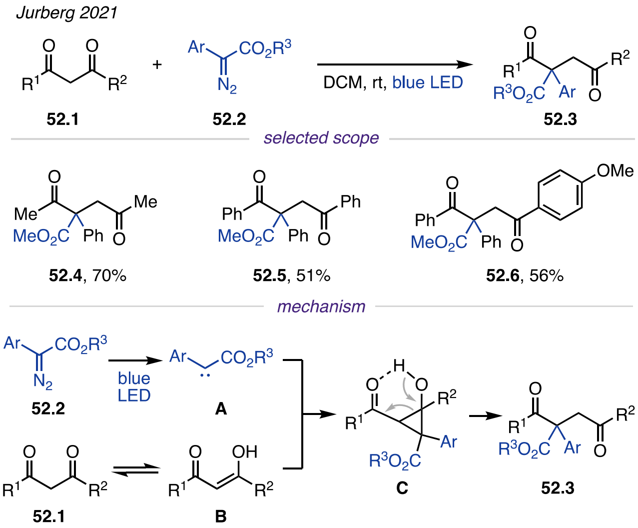
In the same year, the groups of Li, Xu, and Xuan reported a photochemical protocol for preparation of sulfoxonium ylides **51.3** using diazo compounds **51.1** in combination with sulfoxides **51.2** (Scheme 51).[127] Shortly after, similar approaches toward sulfoxonium ylides were independently disclosed by Bhat[128] and Jurberg.[37] Furthermore, in Jurberg's report, they also explored the reactivity of aryl diazoacetates in the presence of azides **51.4**, which, upon light irradiation, produced a diverse array of imines **51.5**.[37]

Scheme 51. Synthesis of Imines and Sulfoxonium Ylides Using Diazo Compounds



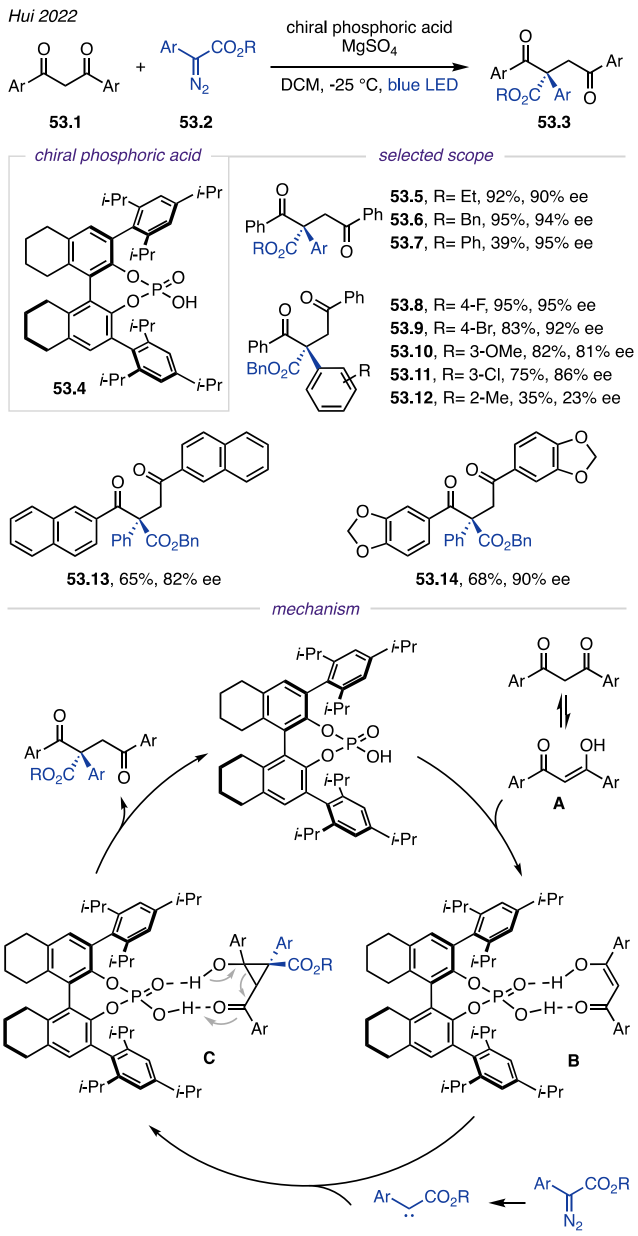
A year later, Jurberg's group developed a formal C−C bond insertion protocol of aryl diazoacetates **52.2** with 1,3-diketones **52.1** (Scheme 52).[129] This method allowed for efficient

Scheme 52. Racemic Approach for Formal C−C Bond Insertion

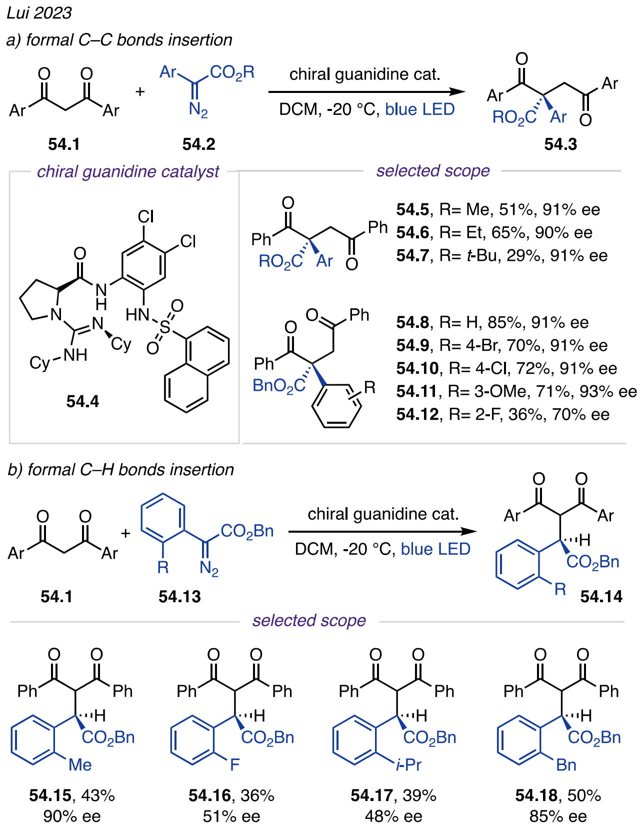


synthesis of various 1,4-dicarbonyl compounds **52.3**. The proposed mechanism begins with the formation of a free carbene **A** under blue light irradiation, which then undergoes cyclopropanation with the enol form **B** of 1,3-diketone. The resulting cyclopropanol intermediates then rearrange into formal C–C bond insertion products **52.3**. Later, a similar racemic approach using enaminones was demonstrated by the groups of Lin and Jin.[130] Furthermore, an analogous asymmetric version of this formal C–C bond insertion reaction of aryl diazoacetates was achieved by Hui's group (Scheme 53).[131] A wide range of enantioenriched 1,4-dicarbonyl compounds **53.5**–**53.14** bearing a quaternary carbon center were efficiently prepared. Asymmetric induction was accomplished by employing a chiral phosphoric acid catalyst **53.4**. Dual hydrogen-bonding interactions between the catalyst and the enol tautomer of 1,3-diketone ensured the stereoselectivity of the following cyclopropanation step. In 2023, Lui and co-workers employed chiral guanidine amide catalysts **54.4** in the asymmetric formal C–C bond insertion reaction (Scheme 54).[132] Interestingly, in the cases of *ortho*-substituted aryl diazo esters **54.13**, formal C–H bond insertion products, 1,3-diketones **54.14**, were obtained in moderate yields. This chemoselectivity was not observed in the previous catalyst-free racemic approach and chiral phosphoric acid-catalyzed process. Control experiments and DFT calculations indicated a stepwise reaction mechanism rather than a direct cyclopropanation process, which could explain the influence of substitution at the aryl group of α-diazoesters and the hydrogen-bonding ability of the catalyst on both the chemoselectivity and enantioselectivity observed in the reaction.

Scheme 53. Asymmetric Formal C–C Bond Insertion Using Chiral Phosphoric Acid Catalysts

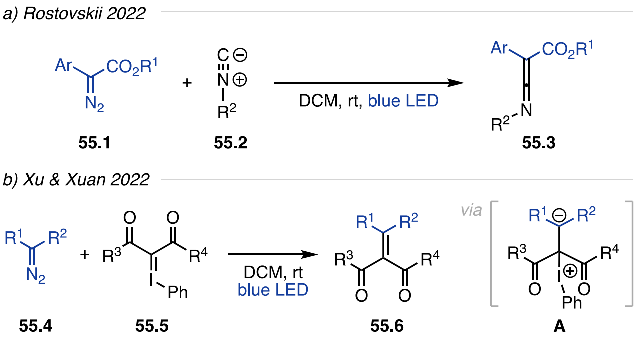


Scheme 54. Asymmetric Formal C–C and C–H Bond Insertion Using Chiral Guanidine Amide Catalysts



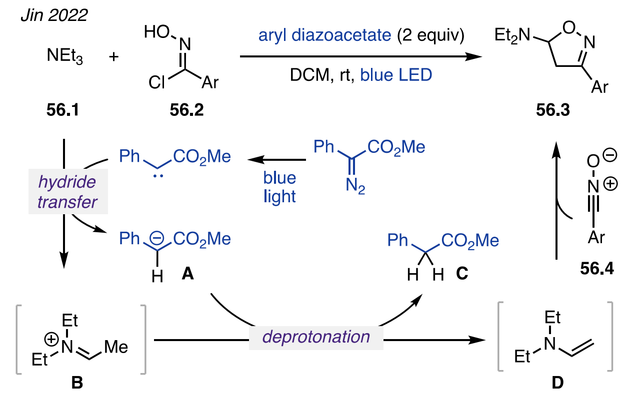
In 2022, Rostovskii and co-workers reported a photochemical approach for construction of various ketenimines **55.3** from donor–acceptor type diazo compounds **55.1** and alkyl isocyanides **55.2** (Scheme 55a).[133] The DFT calculations and mechanistic studies showed that carbenes in both singlet and triplet states can react with isocyanides; however, only the reaction of the former leads to the smooth formation of ketenimines. In the same year, the groups of Xu and Xuan reported preparation of tetrasubstituted alkenes **55.6** from diazo compounds **55.4** and iodonium ylides **55.5** (Scheme 55b).[134] Mechanistically, the nucleophilic attack of carbenes by iodonium ylide afforded intermediate **A**. A subsequent elimination of iodobenzene provided the final all-carbon tetrasubstituted olefins. However, it should be mentioned that an alternative mechanism involving the photolysis of

Scheme 55. Synthesis of Ketenimines and Tetrasubstituted Alkenes



iodonium ylide to generate diradical species cannot be ruled out.[135]

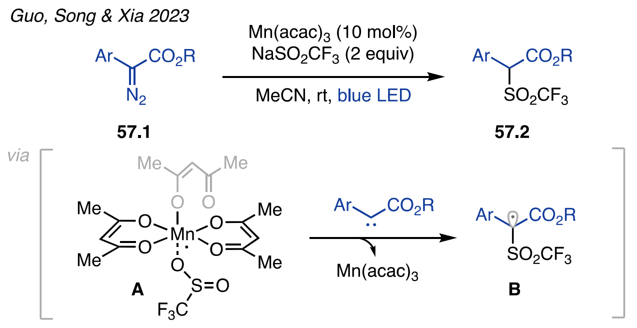
Scheme 56. Free Carbenes as Hydride Acceptor



An example of free singlet carbenes functioning as hydride acceptors came from Jin's group, who reported the synthesis of functionalized isoxazolidines **56.3** using tertiary amines **56.1** and *N*-hydroximoyl chloride **56.2** (Scheme 56). In this work, the highly reactive electrophilic carbene species were observed to abstract hydrides adjacent to the nitrogen in tertiary amines, resulting in the formation of ion pairs **A** and **B**. The deprotonation occurring at the β-position of the iminium ion afforded the reduced product **C**, along with an enamine intermediate **D**. A subsequent 1,3-dipolar cycloaddition of the latter with the *in situ* formed nitrile oxide **56.4** delivered isoxazoline derivatives **56.3**.

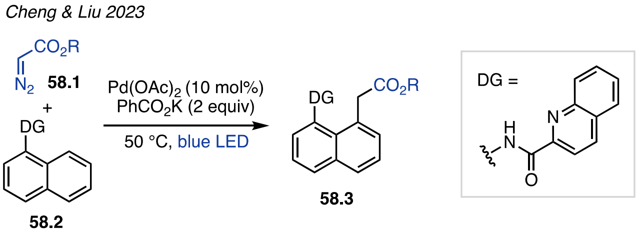
In 2023, the groups of Guo, Song, and Xia reported a Mn-catalyzed trifluoromethylsulfonylation reaction of aryl diazoesters **57.1** to prepare α-trifluoromethyl sulfone esters **57.2** (Scheme 57).[136] This transformation features the generation of trifluoromethyl sulfone radicals **A** through coordination to the $Mn(acac)_3$ catalyst, followed by their combination with a carbene, producing a stable radical intermediate **B**.

Scheme 57. Trifluoromethylsulfonylation Reaction of Aryl Diazoesters Enabled by Manganese Catalysis



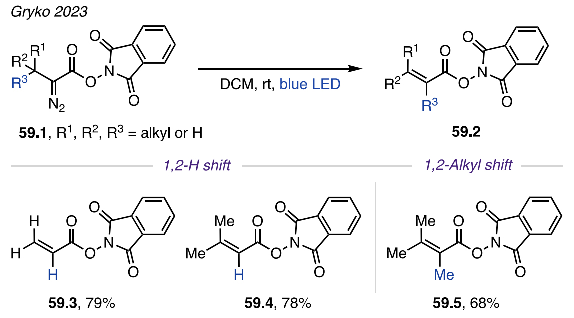
Very recently, the groups of Cheng and Liu disclosed a Pd-catalyzed strategy for the directed C−H alkylation of 1-naphthylamines **58.2** with α-diazoesters **58.1** (Scheme 58).[137] The proposed mechanism suggests the formation of carbene species under blue light irradiation, which undergo addition to Pd^{II} complexes. However, the reactions required a considerable excess of diazo substrates, which served as the solvent.

Scheme 58. Pd-Catalyzed C−H Alkylation of 1-Naphthylamines with α-Diazoester



As previously discussed, aryl-substituted NHPI diazoacetates were involved in C−H insertions with alkanes. In the same report, Gryko and co-workers observed that NHPI diazoacetates with alkyl substitutions **59.1** can also undergo photolysis to produce singlet carbenes (Scheme 59).[64] However, in this scenario, either a 1,2-H shift (**59.3** and **59.4**) or an alkyl shift (**59.5**) occurs, producing vinyl NHPI esters **59.2**.

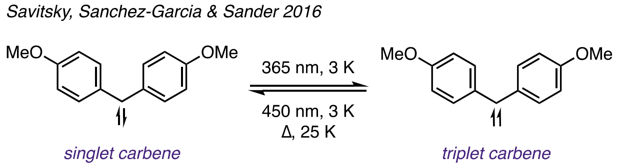
Scheme 59. 1,2-Rearrangement of Alkyl Redox-Active Diazo Compounds



3. DIAZO COMPOUNDS AS TRIPLET CARBENE PRECURSORS

Compared with extensive studies on transformations via singlet carbenes, reactions involving triplet carbenes are relatively underdeveloped.[138] A direct photolysis of diazo compounds can lead to triplet carbenes, although singlet carbenes are typically formed through this process, as the nitrogen dissociation of the excited diazoalkene is usually faster than intersystem crossing to the triplet state. The electronic properties of substituents attached to carbenes greatly affect the spin state and the energy difference between their singlet and triplet states. Thus, it is possible to switch the spin state by modifying substitutions on them, for example, by employing donor−donor type diazo compounds with tunable aryl rings. Diphenyl carbene favors the triplet state over the singlet state by 4 kcal/mol,[139] while the energy difference between the singlet and triplet states of the electron-rich bis(4-methoxyphenyl)carbene is nearly negligible, with the singlet state being only 0.3 kcal/mol energetically favored, as was reported by Sander and co-workers.[140] They reported that the spin state of bis(4-methoxyphenyl)carbene can be reversibly switched between the singlet and triplet states by utilizing different wavelengths (Scheme 60).[140] Furthermore, Sander reported the switching of the spin ground state of diphenylcarbene from triplet to singlet when the carbene interacts with methanol.[141] The singlet carbene becomes more stable compared to its triplet state by forming hydrogen bonds with an alcohol, which represents a unique way to control chemical reactivity. This effect was further analyzed in-depth by Sanchez-Garcia and Nuernberger, using broadband femtosecond transient absorption and quantum mechanics/molecular mechanics simulations.[142]

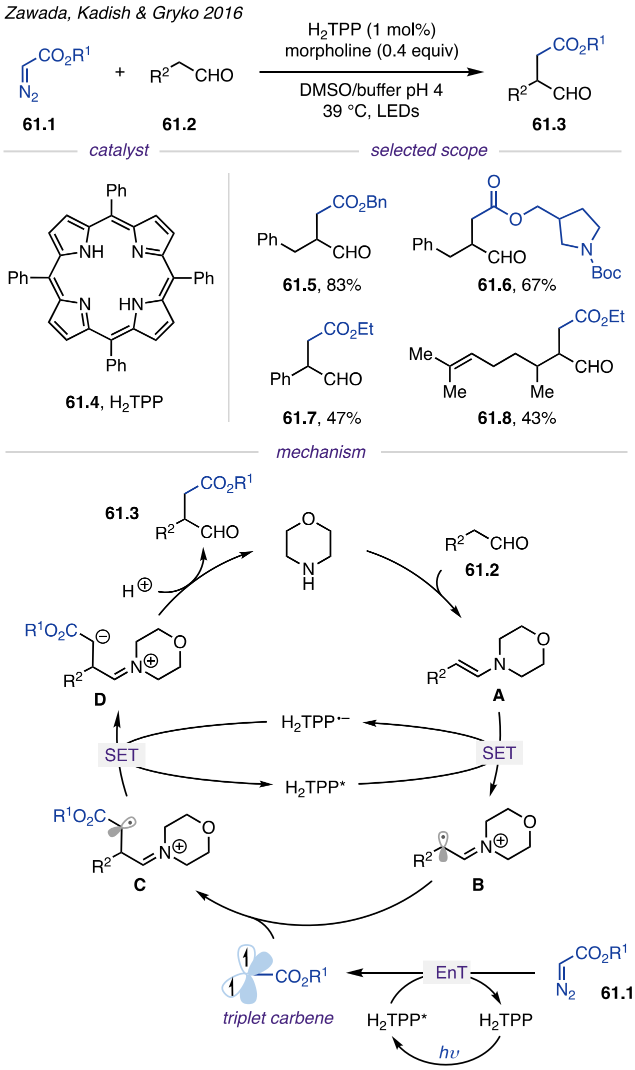
Scheme 60. Spin State of Bis(4-methoxyphenyl)carbene



Another important method to access triplet carbenes is the denitrogenative decomposition of diazo compounds through energy transfer with a photosensitizer. The employment of a photosensitizer allows for mild, efficient activation of diazo compounds that may not have sufficient absorption in the visible light region.

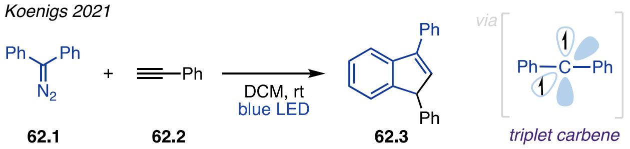
In 2016, the groups of Zawada, Kadish, and Gryko reported a photosensitized approach for α-alkylation of aldehydes **61.2** using diazo compounds **61.1** (Scheme 61). In this transformation, acceptor-type diazo compounds underwent energy transfer with a free base tetraphenylporphyrin (H_2TPP) catalyst **61.4**, leading to the formation of triplet carbenes.[143] Various diazoacetates were found to be competent substrates (**61.5**−**61.7**). Notably, aldehydes bearing an alkene moiety furnished C−H alkylated compound **61.8** exclusively, without the formation of cyclopropane. The reaction mechanism begins with the photoexcitation of H_2TPP from the singlet ground state to the excited state. The energy transfer from the catalyst to diazoacetates produced triplet carbene with simultaneous loss of dinitrogen. In organocatalytic cycle, enamines **A** were formed from aldehyde substrate **61.2** in the presence of an amine catalyst. Subsequently, the photoexcited H_2TPP oxidizes enamine **A** to form a porphyrin radical anion and an active cation radical **B**. The latter reacts with triplet carbene, furnishing a radical intermediate **C**. A following single electron transfer from the porphyrin radical anion and a subsequent protonation led to the final alkylated products **61.3**. Notably, the porphyrin serves both as a photoredox catalyst and as a photosensitizer in this transformation. However, it should be noted that chain propagation processes may also be involved.[144]

Scheme 61. Generation of Triplet Carbene via Energy Transfer



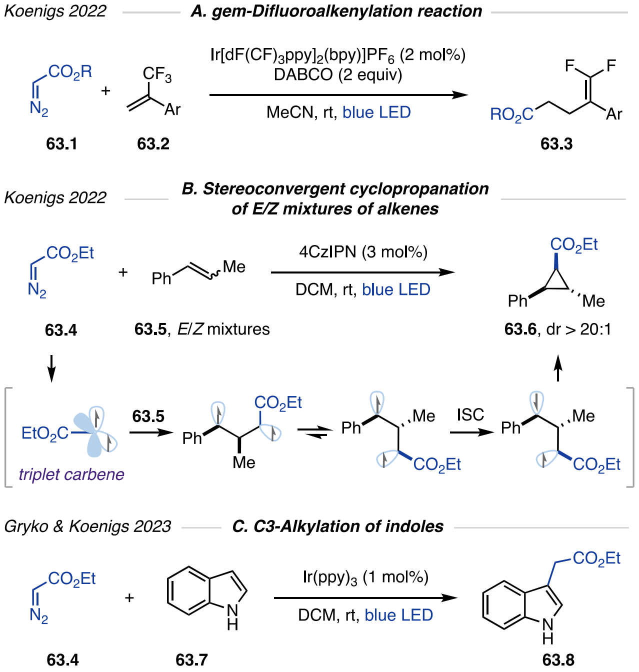
In 2021, Koenigs and co-workers conducted a systematic study on the photochemical generation of free carbenes from diaryl diazo compounds **62.1**, along with their subsequent chemoselective reactions with terminal alkynes **62.2** (Scheme 62).[58] The introduction of electronically diverse substituents at the aryl rings effectively controlled the reactivity of free diaryl carbenes. This led to a significant perturbation of the singlet−triplet energy splitting of the diaryl carbene intermediates, as well as the activation energies of their subsequent reactions. For instance, the reaction of an electron-neutral diazo compound with terminal alkynes afforded indenes **62.3**, following a stepwise process involving a triplet carbene intermediate formed through intersystem crossing from a singlet carbene state.

Scheme 62. Reaction of Aryl−Aryl Diazo Compounds with Terminal Alkynes via Triplet Carbene Intermediates



A year later, the same research group developed a photosensitized method for generating triplet carbenes from acceptor-type diazo compounds **63.1** using an Ir complex as a photosensitizer (Scheme 63A).[145] This approach allows for efficient *gem*-difluoroalkenylation reactions of α-trifluorome-

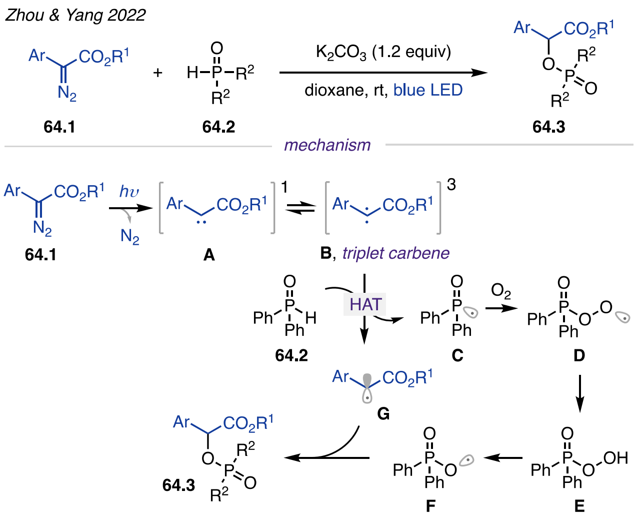
Scheme 63. Photocatalytic *gem*-Difluoroalkenylation, Stereoconvergent Cyclopropanation Reactions and C3-Alkylation of Indoles by Diazo Acetates via Triplet Carbene Intermediates



thylstyrenes **63.2**. The produced triplet carbene undergoes efficient addition to α-trifluoromethylstyrenes, followed by the β-F elimination to furnish the products **63.3**. It was also found that the use of a tertiary amine is crucial for preventing the formation of cyclopropanes. Building on this success, the authors reported a photocatalytic strategy that allows the employment of a mixture of *E*- and *Z*-isomers of olefins **63.5** to give access to a single isomer of cyclopropane products **63.6** in a stereoconvergent reaction (Scheme 63B).[146] Both experimental and theoretical evidence indicate the presence of a triplet carbene intermediate, which readily reacts with either isomer of the olefin. The intersystem crossing from triplet to singlet state proceeds in a diastereoselective fashion, offering an explanation for this highly stereoselective reaction. Additionally, the authors adapted this photosensitization strategy for synthesis of multisubstituted furans.[147] Very recently, Gryko and Koenigs further investigated reactivity of triplet carbenes in a photosensitized alkylation reaction of indoles **63.7** using diazo acetates **63.4** (Scheme 63C).[148] While the C2-alkylation occurs in protic solvent, the employment of aprotic solvents leads to exclusive C3-functionalization (**63.8**). Mechanistic investigations and DFT calculations revealed that the unusual selectivity arises from the generation of triplet carbenes in aprotic solvents. Although the triplet carbene initially adds to the C2 position of indoles, a subsequent 1,2-alkyl radical shift and 1,2-hydrogen shift led to the observed C3-alkylated products in aprotic solvents.

In 2022, the groups of Zhou and Yang reported a visible light-induced aerobic oxyphosphorylation reaction of α-diazoesters **64.1** and H-phosphine oxides **64.2** (Scheme 64).[149] In this transformation, the authors proposed that the triplet carbene **B** serves as a HAT reagent, which upon reaction with phosphine oxides produce phosphinoyl radicals **C**. The latter is then promptly intercepted by molecular oxygen to deliver a peroxy radical intermediate **D**, which then abstracts a hydrogen atom to furnish phosphoryl hydroperoxide **E**. A subsequent homolysis and radical−radical coupling afforded the desired product **64.3**.

Scheme 64. Triplet Carbene as an HAT Reagent



4. DIAZO COMPOUNDS AS ALKYL OR VINYL RADICAL PRECURSORS

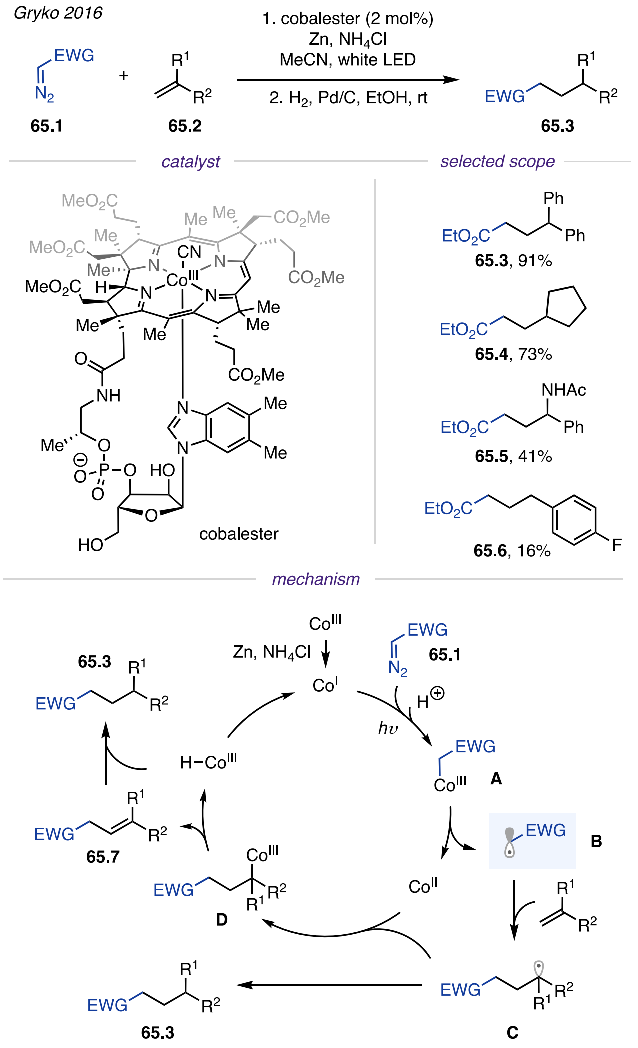
4.1. Introduction

Diazo compounds have traditionally served as precursors for carbenes, and significant advancements have been made in this field. In contrast, radical reactions involving diazo compounds have received less attention. Nevertheless, with the recent emergence of photocatalysis[18−20] and visible-light induced transition metal catalysis,[150,151] new possibilities have arisen. The combination of these photocatalytic methods with diazo compounds has led to the discovery of novel radical reactivities that differ from classical carbene transformations. Typically, a photocatalyst reduces diazo compounds through a single electron transfer process. After extrusion of dinitrogen and protonation by an acid or a protic solvent, radical intermediates are formed. Acceptor-type diazo compounds, such as α-diazo esters, are more commonly used in these processes, possibly due to their limited absorption in visible light region, thus making them less prone to decomposition or side reactions. The resulting radicals can then participate in various transformations, such as addition to alkenes or heteroarenes, as well as recombination with other radical species. These breakthroughs have significantly expanded synthetic applications of diazo compounds, offering new opportunities in organic synthesis.

4.2. Radical Addition to Alkenes

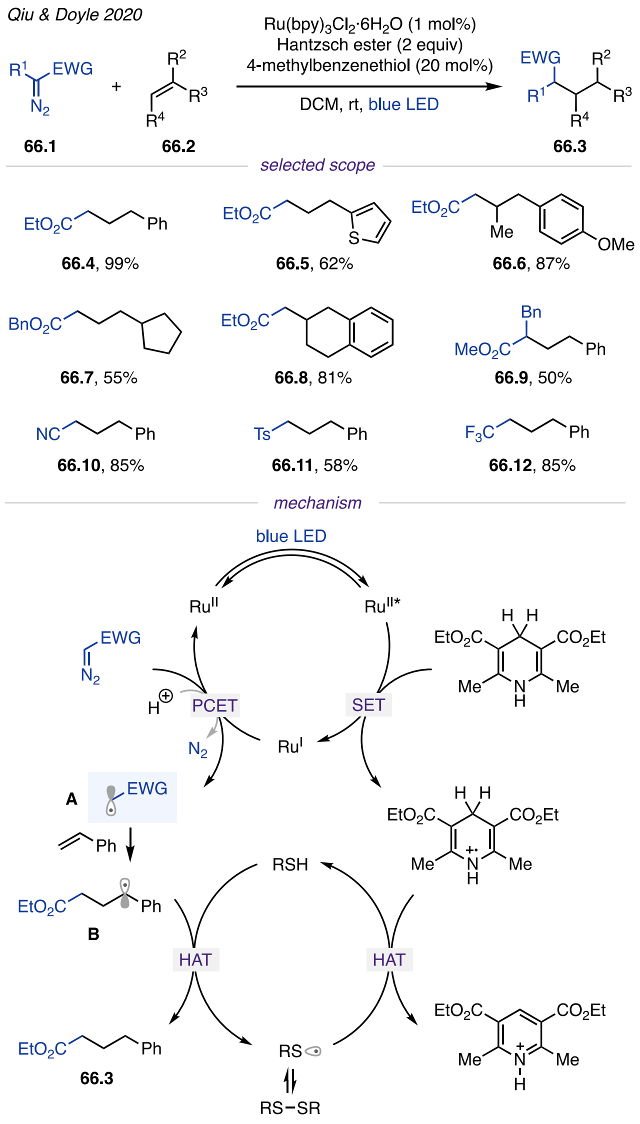
4.2.1. Giese- or Heck-Type Reactions. In 2016, Gryko and co-workers reported cobaltester-catalyzed method for the generation of alkyl radicals from diazoacetates **65.1** under white LEDs, allowing for alkylation reaction of alkenes **65.2** (Scheme 65).[152] The resulting alkyl radicals undergo an intermolecular Heck-type reaction. However, the authors observed a mixture of Heck-type (oxidative) and Giese-type (reductive) products. Thus, a subsequent hydrogenation step was performed to obtain reduced products **65.3**. α-Diazo esters reacted well with aliphatic or disubstituted olefins (**65.3**−**65.5**). However, transformations with styrene derivatives

Scheme 65. Generation of Alkyl Radicals from Diazo Compounds via Cobalt Catalysis



(**65.6**) were found to be less efficient. The proposed mechanism begins with the reduction of cobalester to form the catalytically active Co(I) species. Upon reaction with diazo compounds, alkyl-Co(III) intermediates **A** are formed. A subsequent homolytic cleavage of the Co–C bonds produces electrophilic radical **B**, which upon addition to the electron-rich alkene affords radical **C**, that can either recombine with Co(II) species or abstract a proton, leading to reduced products. Dehydrocobaltation of intermediate **D** yields the Heck-type product. Alternatively, the Giese-type products can be formed through reduction by hydridocobaltester. It is important to note that, in all cases, the typical cobalt-catalyzed cyclopropanation process[153,154] was not observed, highlighting the crucial role of visible light irradiation in this reaction.

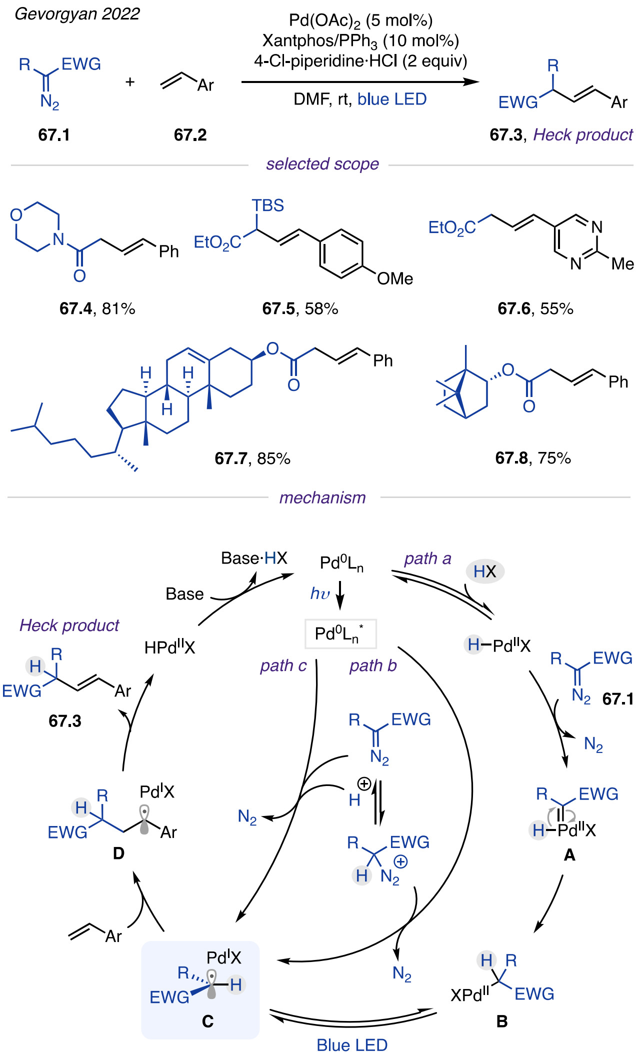
Scheme 66. Generation of Alkyl Radicals from Diazo Compounds via PCET



In 2020, the groups of Qiu and Doyle employed diazo compounds **66.1** to access primary and secondary alkyl radicals via reductive proton coupled electron transfer (PCET) with a Ru^{II} photocatalyst (Scheme 66).[155] The formed *C*-centered radicals efficiently added across both aliphatic alkenes and styrene derivatives, allowing for synthesis of various *anti*-Markovnikov hydroalkylated products (**66.4–66.12**). The proposed mechanism begins with photoexcitation of the ruthenium complex $Ru(bpy)_3Cl_2·6H_2O$ to form $Ru^{II}*$, which is able to oxidize Hantzsch ester to generate a radical cation and Ru^{I} species. The newly formed Ru^{I} species participates in an SET process with the diazo compound, while regenerating Ru^{II} catalyst. A sequential extrusion of N_2 with protonation delivers *C*-centered radical **A**, which upon radical addition to alkene **B**, followed by HAT, delivers Giese-type product **66.3**. A thiol catalyst was added for promoting the HAT process. This methodology also marks a distinct difference from the traditional reactivity of diazo compounds in the presence of alkenes, where cyclopropanation via the intermediary of carbenes are dominant. Inspired by this work, many other groups have adapted this photocatalytic PCET strategy for the generation of alkyl radicals from diazo compounds to develop many other transformations. For example, Qiu and Hu's groups successfully developed a hydroalkylation reaction of DNA-tagged alkenes using diazo compounds toward the construction of DNA-encoded libraries using this platform.[156]

In 2022, Gevorgyan's group reported a photoinduced alkyl-Heck reaction of diazo compounds **67.1** via hybrid alkyl-Pd radical species (Scheme 67).[157] A diverse range of acceptor and donor–acceptor type diazo compounds were found to efficiently participate in reactions with styrene derivatives,

Scheme 67. Heck Reaction of Diazo Compounds via Photoinduced Palladium Catalysis



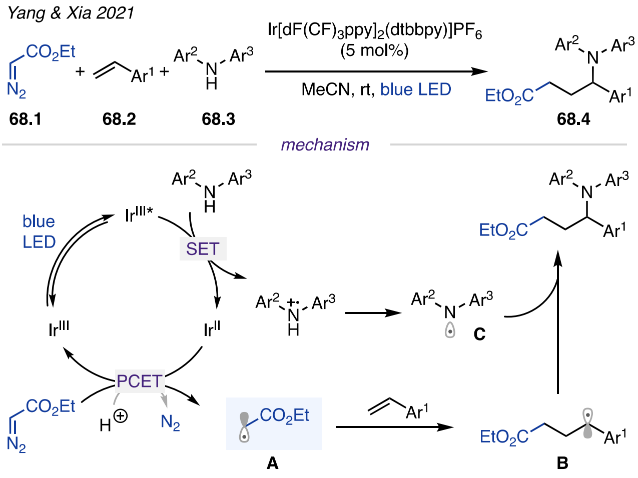
leading to the exclusive formation of allylic compounds **67.4**−**67.8**. Three possible mechanistic pathways were proposed for this reaction. Path **a** begins with oxidative addition of Pd(0) into HX to afford an active palladium hydride species. A denitrogenative reaction between H−PdXL$_2$ with diazo compound takes place, producing a Pd-carbene intermediate **A**. A subsequent hydride shift leads to the formation of palladium species **B**. Upon blue light irradiation, the C−Pd bond undergoes homolysis, producing a hybrid alkyl Pd-radical species **C**. Alternatively, the formation of the latter can occur through two additional pathways. In path **b**, it is generated by a single electron transfer (SET) to diazonium ion, which is the protonated form of the diazo compound. In path **c**, a PCET takes place directly from the diazo compounds, furnishing species **C**. Subsequently, the hybrid alkyl Pd-radical species **C** undergoes an addition reaction with styrene to deliver a hybrid benzylic radical **D**. The rest of the catalytic cycle follows the classical Heck reaction mechanism, which includes a β-H-elimination step to afford the desired Heck products **67.3**.

4.2.2. 1,2-Difunctionalization of Alkenes.

Upon the addition of radicals to alkenes, the newly formed radical species can be effectively captured by various radical traps. Two C−C or C−heteroatom bonds are formed efficiently in these multicomponent photocatalytic reactions of diazo compounds to deliver a wide range of 1,2-difunctionalized products under mild conditions.

In 2021, the groups of Yang and Xia employed the photocatalytic PCET strategy to generate radicals from ethyl diazoacetate and to engage **68.1** in a 1,2-carboamination reaction of alkenes **68.2** with diarylamines **68.3** (Scheme 68).[158] In this transformation, alkyl radicals **A** efficiently added to various styrene derivatives, affording relatively persistent benzylic radical intermediates **B**. The final products were formed through a radical recombination between the latter and transient *N*-centered radicals **C** derived from diarylamines.

Scheme 68. Photocatalytic 1,2-Amino-alkylation of Styrenes with Diazoacetates and Diarylamines

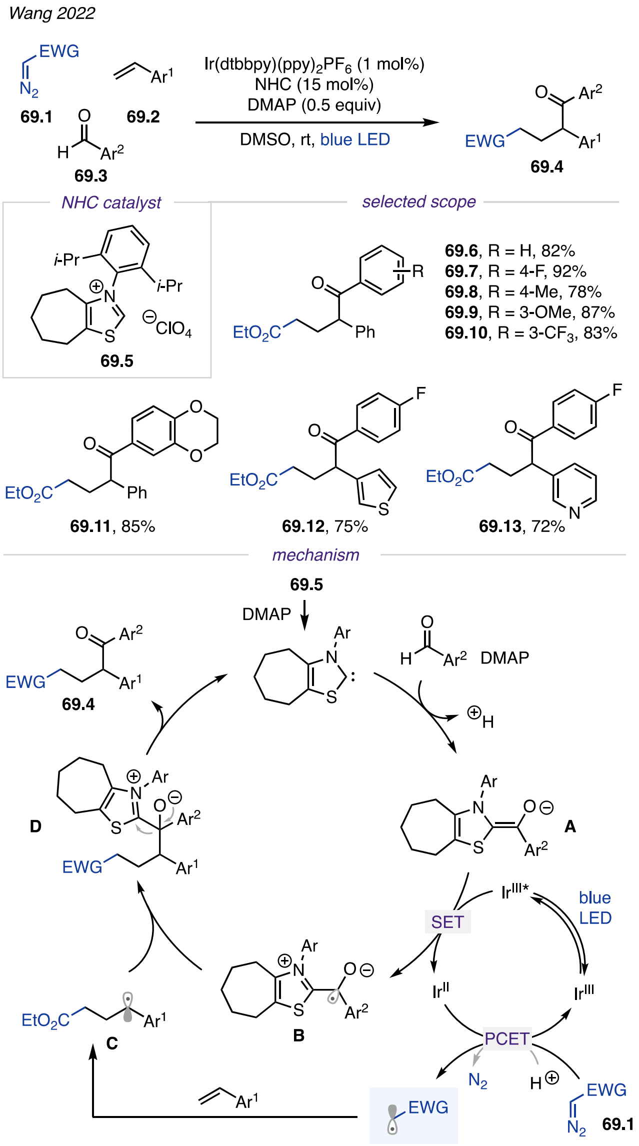


In 2022, Wang and co-workers disclosed a method for 1,2-alkyl-acylation of alkenes **69.2** by employing diazo esters **69.1** and aldehydes **69.3**, featuring cooperative photoredox and NHC catalysis (Scheme 69).[159] A wide range of functionalities on benzaldehydes were well tolerated (**69.6**−**69.11**). Vinyl heteroarenes also proven to be competent substrates (**69.12** and **69.13**). The proposed mechanism commences with the generation of an active NHC catalyst from thiazolium in the presence of a base. The produced NHC catalyst then reacts with aldehydes to deliver Breslow intermediate **A**, which undergoes a single electron oxidation by excited photocatalyst to produce ketyl radical **B**. Similarly to the previous approaches, alkyl radicals are produced from diazo compounds through a PCET process. Radical addition to alkenes and a subsequent radical recombination with the ketyl radical **B** afford tetrahedral intermediates **D**. Finally, ketones were formed with the release of the NHC catalyst.

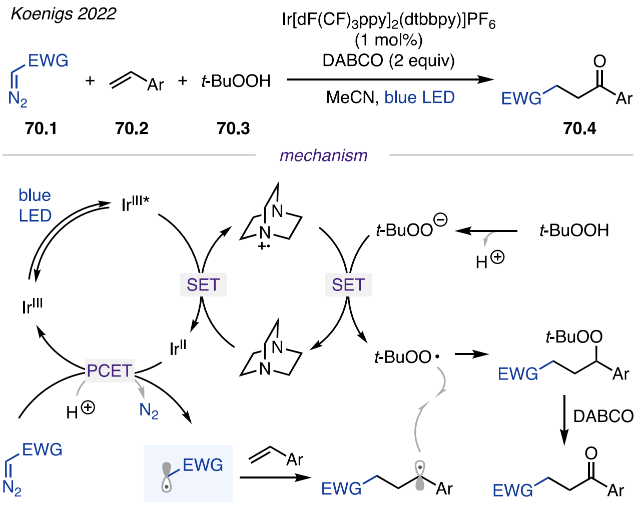
In the same year, Koenigs and co-workers developed a photocatalytic approach to achieve 1,2-oxo-alkylation of vinyl arenes **70.2** employing diazoacetates **70.1** and hydroperoxide **70.3** (Scheme 70).[160] Alkyl radicals efficiently added to alkenes, followed by the capture of the resulting benzylic radical by peroxyl radical, resulting in the formation of peroxyl ethers. Under basic conditions, Kornblum−DeLaMare rearrangement of peroxyl ethers occurred, affording 1,2-difunctionalized products **70.4**.

The groups of Qiu and Doyle reported a three-component photocatalytic Minisci reactions of *N*-heterocycles **71.3**, diazo compounds **71.1**, and alkenes **71.2** (Scheme 71).[161] Various aliphatic alkenes and acceptor-type diazo compounds under-

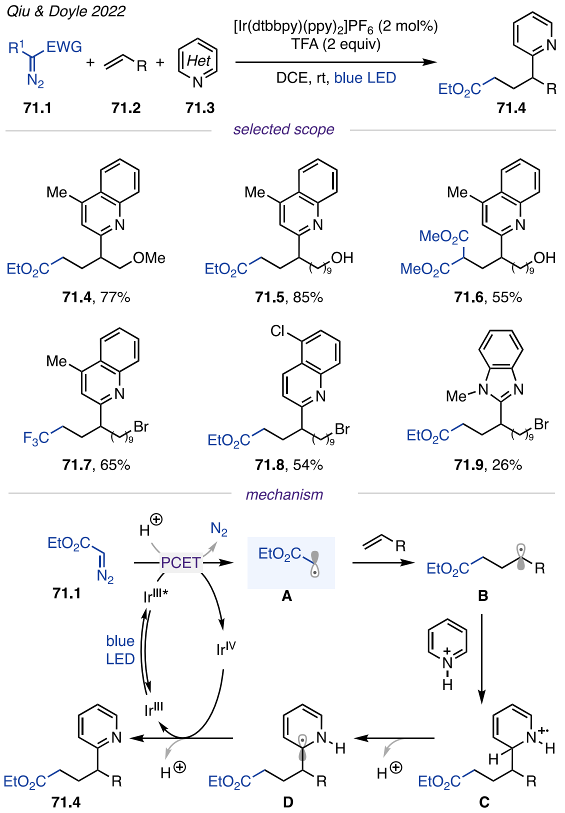
Scheme 69. Difunctionalization of Alkenes via Cooperative Photoredox and NHC Catalysis



Scheme 70. Photocatalytic 1,2-Oxo-Alkylation of Styrenes with Diazoacetates and Hydroperoxides



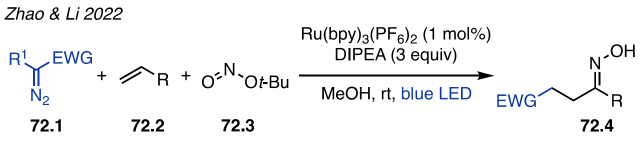
Scheme 71. Photocatalytic Minisci Reactions



went smooth transformation with electron-deficient *N*-heteroarenes in good yields (**71.4**–**71.8**). An example of benzimidazole was also demonstrated, albeit with diminished efficiency (**71.9**). In this transformation, electrophilic *C*-centered radicals **A** generated from acceptor diazo compounds **71.1** undergo selective addition to alkenes, affording nucleophilic radicals, which readily react with various electron-deficient *N*-heteroarenes. Trifluoroacetic acid (TFA) was employed to protonate both the heteroarene and the diazo compound in this reaction.

Zhao, Li, and co-workers reported a photocatalytic difunctionalization reaction of alkenes **72.2** with diazo compounds **72.1** and *tert*-butyl nitrites **72.3** (Scheme 72).[162] In this case, *tert*-butyl nitrites were used as radical traps, which allowed for synthesis of various γ-oximino esters **72.4**.

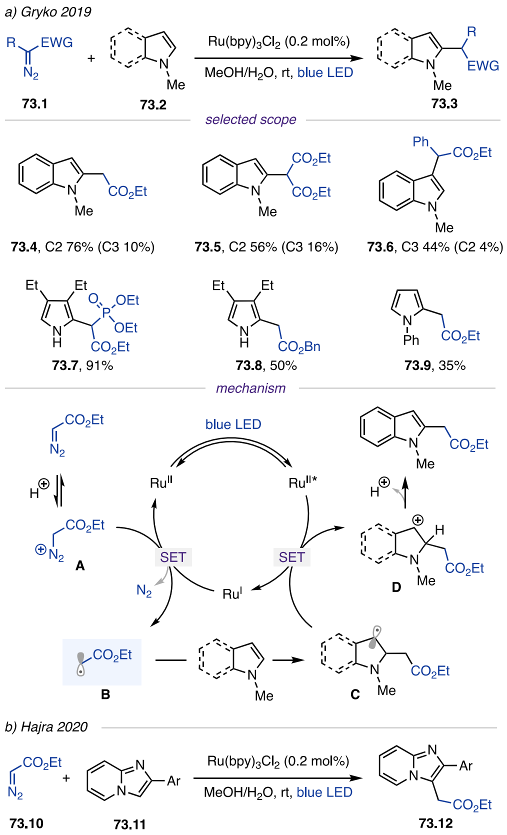
Scheme 72. Photocatalytic Difunctionalization of Alkenes with Diazo Compounds and *tert*-Butyl Nitrite



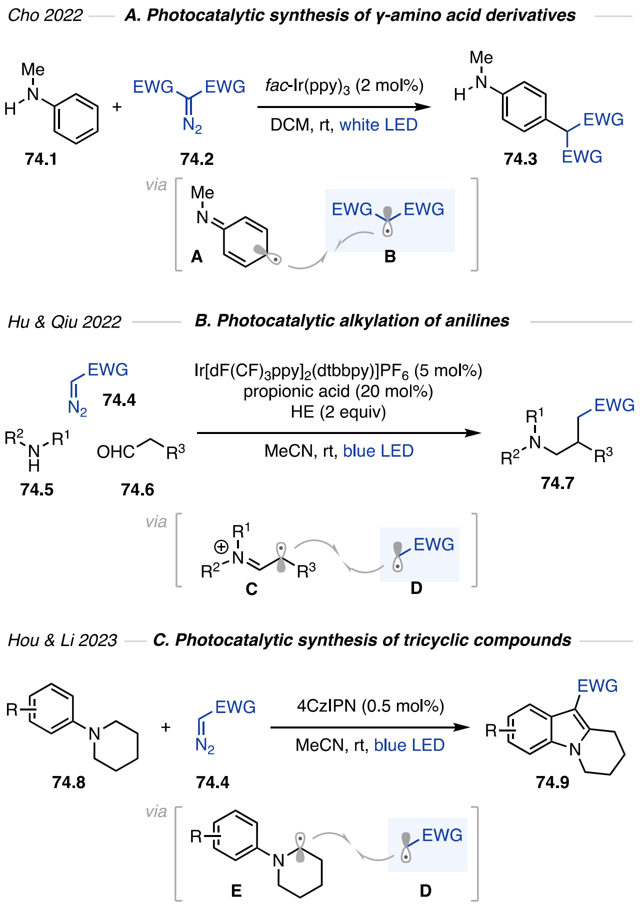
4.3. Radical Addition to Heteroarenes

Apart from alkenes, the electrophilic radicals produced from acceptor type diazo compounds undergo efficient addition to electron-rich heteroarenes. In 2019, Gryko and co-workers reported a photocatalytic method for alkylation of pyrroles and indoles **73.2** using α-diazo esters **73.1** (Scheme 73a).[163] This approach allows for synthesis of diverse C2-alkylated indole and pyrrole derivatives **73.3**. In the case of **73.6**, C3-alkylation

Scheme 73. Photocatalytic Alkylation of Pyrroles and Indoles with α-Diazo Esters



Scheme 74. Photocatalytic Transformations Involving Radical–Radical Recombinations



product prevails, possibly as a result of a parallel carbene C−H insertion pathway.[16] *N*-methyl protected and unprotected indoles, as well as pyrroles, delivered the respective products in good yields (**73.4**−**73.9**). When electron-deficient substrates are used, the addition of a sacrificial reductant, such as amine, is required. In protic solvent, diazo compounds undergo protonation to form diazonium ions **A**, which can be reduced to alkyl radicals **B** via a SET by excited Ru photocatalyst. Subsequently, the alkyl radicals undergo addition to *N*-heterocycle to give radical **C**. After oxidation and deprotonation, the desired alkylated product is formed. A year later, Hajra and co-workers reported a similar radical approach using diazo compounds for C3-alkylation of imidazopyridines under the same reaction conditions (Scheme 73b).[164] In addition to aforementioned Ru complex, graphitic carbon nitride (g-C_3N_4) also could serve as a photocatalyst in alkylation of indoles with diazo compounds, as shown by Zhou and Guo.[165]

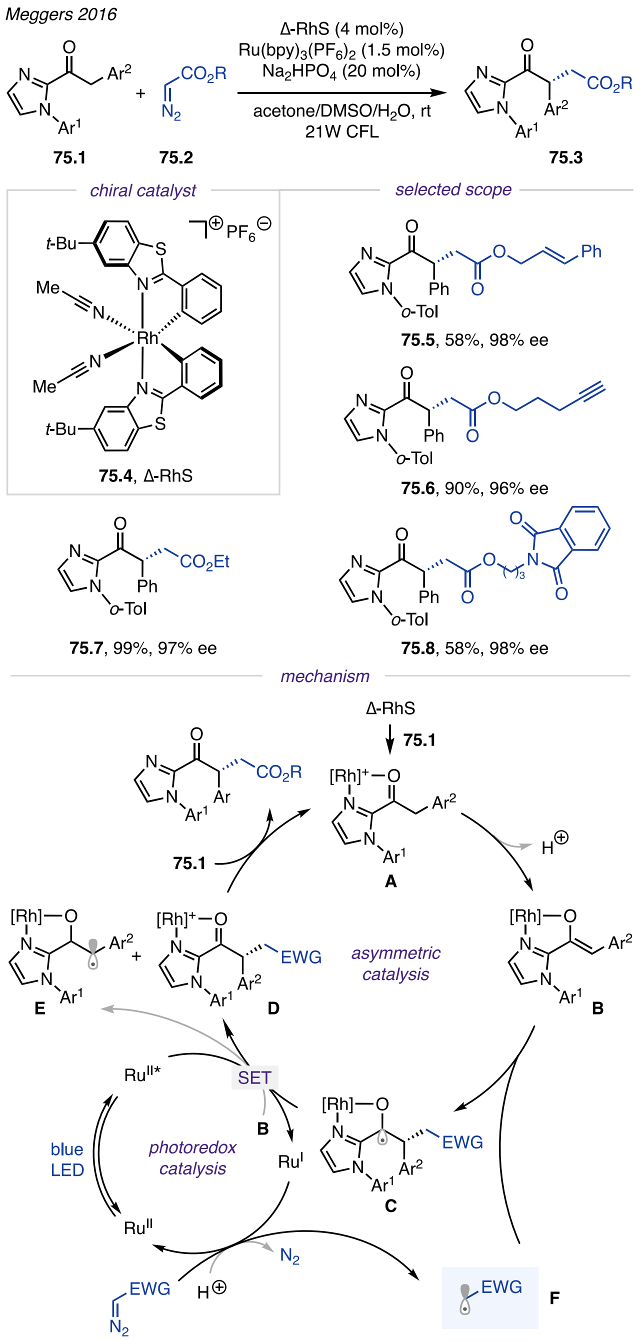
4.4. Radical−Radical Recombinations

Besides radical additions to alkenes and heteroarenes, as mentioned above, alkyl radicals derived from diazo compounds can also participate in radical−radical couplings. In 2022, Cho and co-workers successfully developed a photocatalytic alkylation reaction of anilines **74.1** with acceptor−acceptor type diazo compounds **74.2** (Scheme 74A).[166] This protocol showed no sensitivity to electronics, as both electron-deficient and electron-rich anilines performed equally well. The proposed mechanism involves radical recombination between persistent radical **A** and transient radical **B**, followed by rearomatization, affording *para*-C−C coupled aniline derivatives. In the same year, the groups of Hu and Qiu developed a photocatalytic, three-component reaction of secondary amines, aldehydes, and diazo compounds (Scheme 74B).[126] This protocol afforded various γ-amino acid derivatives in good yields. In this reaction, enamines were formed *in situ* via condensation between aldehyde **74.6** and secondary amine **74.5**, which can be oxidized to radical intermediate **C** by an excited photocatalyst. Radical recombination between intermediate **C** and a transient α-ester radical **D** occurs, followed by reduction using a Hantzsch ester, delivering the desired γ-amino acid derivatives. Very recently, the groups of Hou and Li reported a photocatalytic approach for synthesis of various indole-fused tricyclic compounds **74.9** using diazo compounds **74.4** and *N*-phenylpiperidines **74.8** (Scheme 74C).[167] The mechanism of this protocol features the recombination between nucleophilic radical **E** and electrophilic radical **D**.

4.5. Other Radical Reactions

In 2016, Meggers and co-workers pioneered a photocatalytic approach employing α-diazo esters **75.2** for asymmetric alkylation of 2-acyl imidazoles **75.1** (Scheme 75).[168] This method was enabled by the combination of a chiral Lewis acidic Δ-RhS complex with a Ru photocatalyst. A variety of acceptor-type diazo compounds were compatible with this transformation, delivering the alkylated products in good yields and high enantioselectivities (**75.5**−**75.8**). The mechanism of this reaction features dual photoredox and asymmetric catalytic cycles. Upon coordination of the substrate with the chiral rhodium complex **A** and deprotonation, rhodium enolate **B** is formed. This electron-rich enolate acts as a single electron

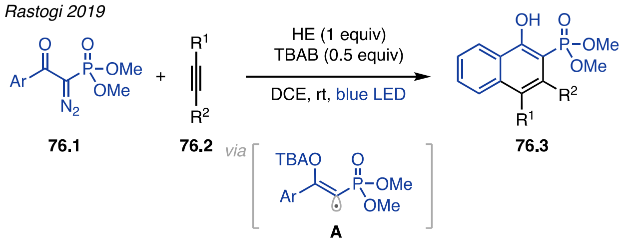
Scheme 75. Asymmetric Alkylation with Diazo Compounds



donor to the photoexcited ruthenium complex, leading to the formation of strongly reducing $[Ru(bpy)_3]^+$, which subsequently transfers a single electron to the diazo esters. Extrusion of N_2 and protonation produces alkyl radicals, which stereoselectively add to the rhodium enolate to form the Rh-coordinated ketyl radical **C**. This highly reducing agent can either directly reduce the diazo reagent for chain propagation or quench the photoexcited $[Ru(bpy)_3]^{2+}$. Ultimately, the alkylated products are obtained through the oxidation of radical **D** and the recoordination of the substrate with Δ-RhS.

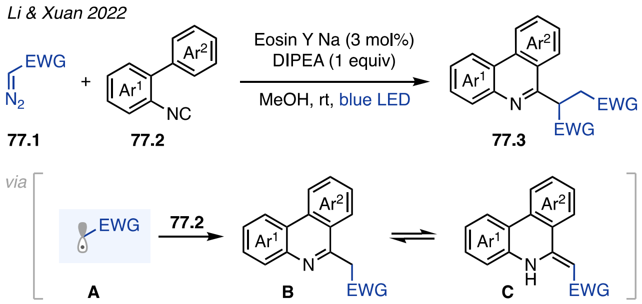
In 2019, Rastogi and co-workers reported a visible light-induced benzannulation reaction of diazo ketones **76.1** and alkynes **76.2** (Scheme 76).[169] This reaction proceeds through single-electron reduction of the diazo enolate by Hantzsch ester to form vinyl radical **A**. Then, this radical is subsequently trapped by alkyne, delivering functionalized naphthalenol **76.3** in good efficiency.

Scheme 76. Visible Light-Induced Benzannulation Reaction of Diazo Ketones and Alkynes



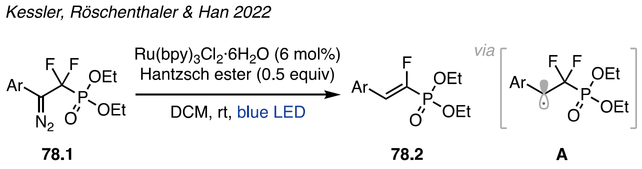
In 2022, Li, Xuan and co-workers disclosed an organophotocatalytic protocol for synthesis of phenanthridines **77.3** using acceptor-type diazo compounds **77.1** and biphenyl isocyanides **77.2** (Scheme 77).[170] Similarly to the previous report, alkyl radical **A** is generated via PCET mechanism. The formed C-centered radical **A** then engages in a radical addition/intramolecular radical cyclization cascade with biphenyl isocyanates. The resulting 2-alkylated phenanthridine **B** exists in equilibrium with its tautomer **C**, which can capture another equivalent of an alkyl radical to afford phenanthridine product bearing a succinate moiety.

Scheme 77. Organophotocatalytic Approach for Synthesis of Phenanthridines



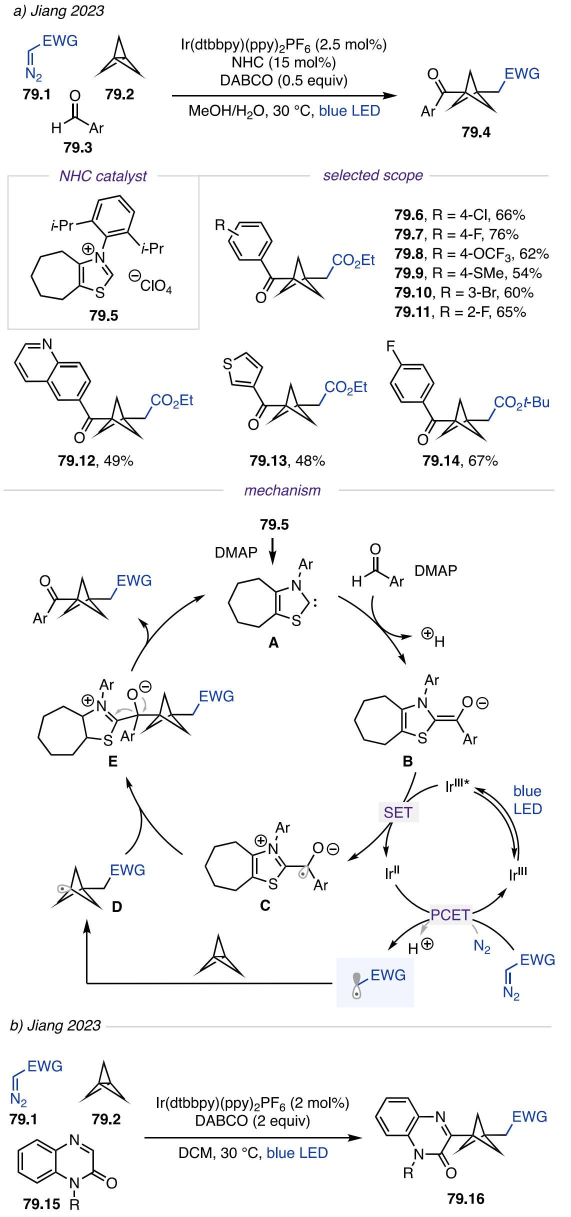
In the same year, the groups of Kessler, Röschenthaler, and Han introduced a photocatalytic approach for synthesizing α-fluorovinylphosphonates **78.2** from difluoroalkyl diazo compounds **78.1** (Scheme 78).[171] Differently from the previously reported PCET mechanism, the authors proposed that the alkyl radical **A** is produced through a Hantzsch ester-assisted HAT process, as supported by mechanistic experiments and DFT calculations.

Scheme 78. Synthesis of α-Fluorovinylphosphonates



More recently, Jiang and co-workers reported a cooperative photoredox and NHC-catalyzed protocol for 1,3-difunctionalization of [1.1.1]propellane **79.2** using α-diazo esters **79.1** and benzaldehydes **79.3** (Scheme 79a).[172] Benzaldehydes bearing various functional groups efficiently participated in this transformation, producing various bicyclo[1.1.1]pentanes

Scheme 79. Synthesis of Disubstituted Bicyclo[1.1.1]pentanes



79.6–79.14. Heteroaryl aldehydes (**79.12** and **79.13**) were also capable substrates. The proposed mechanism begins with the generation of NHC **A** in the presence of a base, which then reacts with aldehydes to form the Breslow intermediates **B**. Subsequently, the photoexcited Ir^{III} complex oxidizes the intermediate **B**, leading to the formation of radical species **C**. The resulting Ir^{II} catalyst then reduces diazo ester, generating an alkyl radical through a PCET process. This transient radical rapidly adds to [1.1.1]propellane to afford the radical species **D**. The recombination of two radical intermediates eventually leads to the formation of difunctionalized product **79.4**, along with the regeneration of the NHC catalyst. Next, the same group expanded the scope of radical acceptors to quinoxalinones **79.15** in analogous difunctionalization of [1.1.1]-propellanes (Scheme 79b).[173]

5. DIAZO COMPOUNDS AS DIAZOMETHYL RADICAL PRECURSORS

5.1. Introduction

In above-mentioned reports, the generation of reactive intermediates require the release of dinitrogen from diazo compounds. However, by utilizing specifically designed substrates, such as α-diazo onium salts, the valuable diazo functional group can be retained.[174] These diazo species possess a redox-active leaving group, such as a hypervalent iodine[175,176] or sulfonium[177] group. These substrates could be converted into diazomethyl radicals, thus unlocking new reactivities that can be accessed from diazo compounds using visible light. Initial reports focused on the employment of a photocatalyst, which produces the key diazomethyl radical species through a single-electron reduction event. However, later studies demonstrated the possibilities of visible light-induced homolytic cleavage of the weak C−I bond in hypervalent iodine reagents, without the need of a catalyst, to arrive at the same reactive intermediates. The produced diazomethyl radical is highly electrophilic, which undergoes efficient addition to arenes, delivering C−H functionalized products, or participates in a stepwise cyclization with other unsaturated systems, affording various heterocycles.

5.2. Radical Addition to Arenes

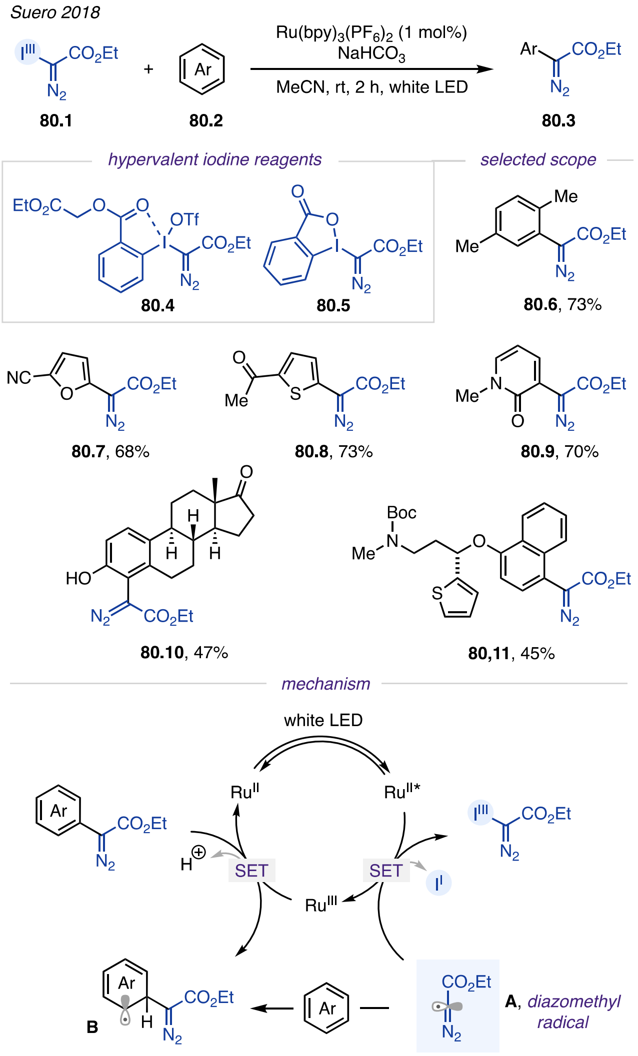
In 2018, Suero and co-workers pioneered a photocatalytic approach for the generation of diazomethyl radicals from α-diazo iodonium triflates **80.1** (Scheme 80).[178] This mild protocol allowed for efficient C−H diazomethylation of arenes **80.2**, affording various aryl diazo esters **80.3**. This method is also amenable to the functionalization of complex molecules **80.10** and **80.11**. Under white light irradiation, hypervalent iodine reagents undergo single-electron reduction by a photoexcited Ru complex, leading to the formation of key diazomethyl radical intermediates **A**. This electrophilic radical undergoes efficient addition to arenes, affording cyclohexadienyl radical **B**. Subsequently, oxidation with Ru^{III} complex and proton elimination deliver the desired diazomethylation product. Furthermore, it was demonstrated that the obtained products can undergo various carbene transformations, enabling the efficient synthesis of complex chiral molecules from readily available chemical feedstocks.

In 2023, Li and co-workers developed a photocatalytic cascade reaction for the preparation of acridines **81.3** via double sp^2 C−H bond activation of diarylamines **81.2** by using hypervalent iodine reagents **81.1** (Scheme 81).[179] Similarly to the Suero's method, the mechanism commences with an SET from the photoexcited Ru complex to hypervalent iodine substrate, producing the key diazomethyl radical intermediate **A**. A subsequent radical addition of the latter to the aryl ring of diphenylamine affords radical intermediate **B**. Upon oxidation and proton loss, diazo compound **C** is formed, which produces free carbene species **D** under blue light irradiation with the extrusion of dinitrogen. Finally, the intramolecular cyclization of **D** and oxidation leads to the formation of acridine **81.3**. Notably, this reaction highlights the dual reactivity of hypervalent iodine diazo reagents, producing both radical and carbene species.

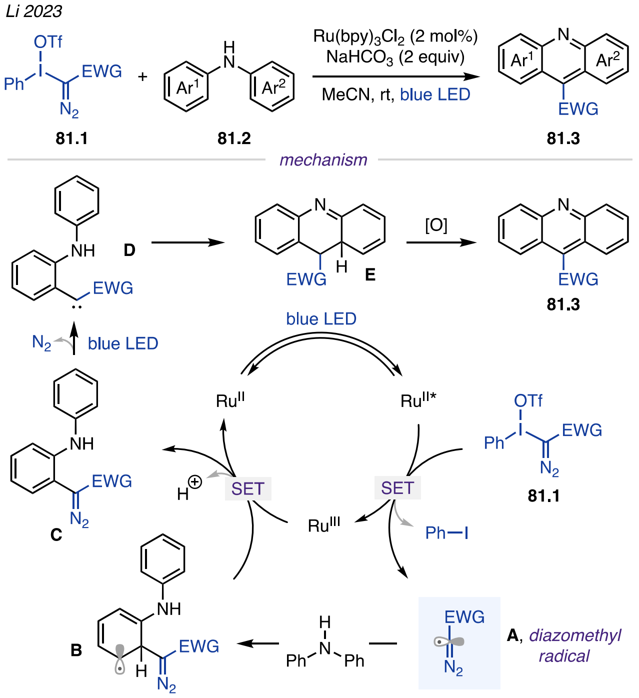
5.3. Heterocyclization

Besides radical addition to arenes, diazomethyl radicals can also undergo cyclization reactions with different unsaturated π-systems toward various *N*-heterocycles. In 2020, the groups of

Scheme 80. Generating Diazomethyl Radicals via Photoredox Catalysis



Scheme 81. Photocatalytic Synthesis of Acridines

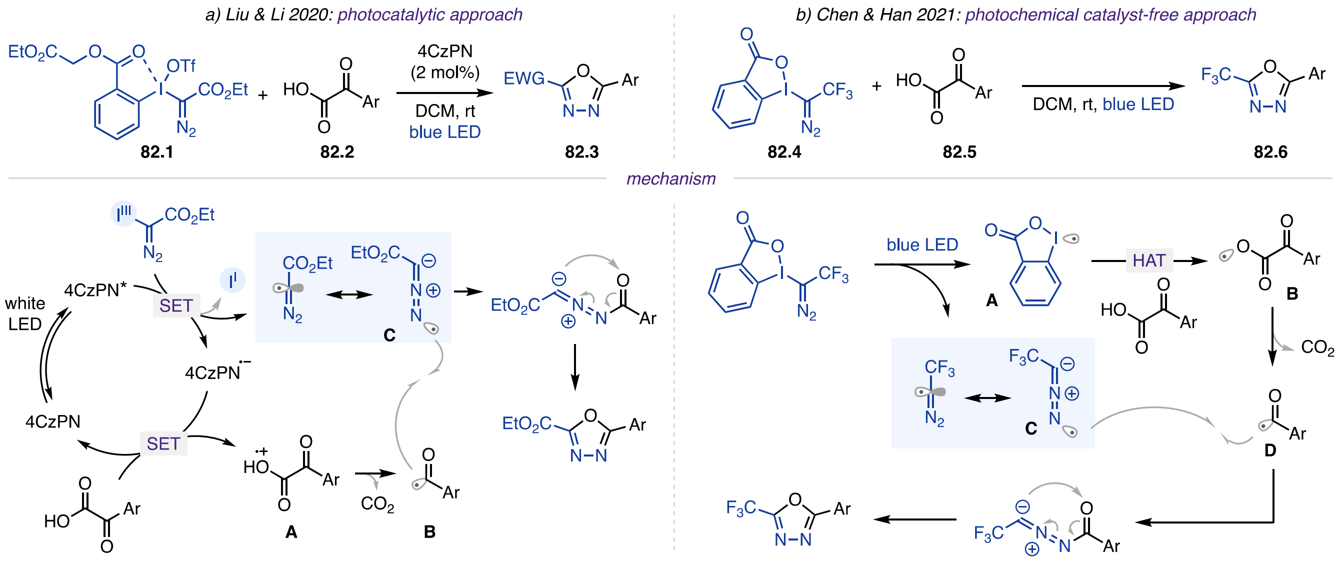


Liu and Li reported a photocatalytic approach for synthesizing oxadiazoles **82.3** from hypervalent iodine reagents **82.1** and benzoyl formic acids **82.2** (Scheme 82a).[180] The proposed mechanism begins with the photoexcitation of 4CzPN catalyst, followed by its reductive quenching by benzoyl formic acid, producing a benzoyl cation radical **A** and 4CzPN$^{\bullet-}$. Subsequent deprotonation and decarboxylation afford benzoyl radical **B**. Upon single electron reduction by 4CzPN$^{\bullet-}$, a diazomethyl radical is formed, which is a resonance form of intermediate **C**. The recombination of **C** with benzoyl radical **B**, followed by cyclization, furnish the targeted oxadiazole. A year later, the groups of Chen and Han revealed an analogous catalyst-free method toward oxadiazoles **82.6** (Scheme 82b).[181] In this case, the proposed mechanism suggests that diazotrifluoroethyl radical is formed through visible-light-induced homolysis of the C−I bond in hypervalent iodine reagent with the concurrent generation of iodanyl radical **A**. Subsequently, a HAT process between iodanyl radical **A** and *α*-ketoacid **82.5**, followed by decarboxylation, affords the benzoyl radical **D**. Similarly to the previous method, radical−radical coupling and ring-closure furnished the heterocyclic product. In the same year, the groups of Li and Li reported a similar approach employing benzaldehydes and hypervalent iodine reagents for synthesizing oxadiazoles under catalyst-free conditions.[182]

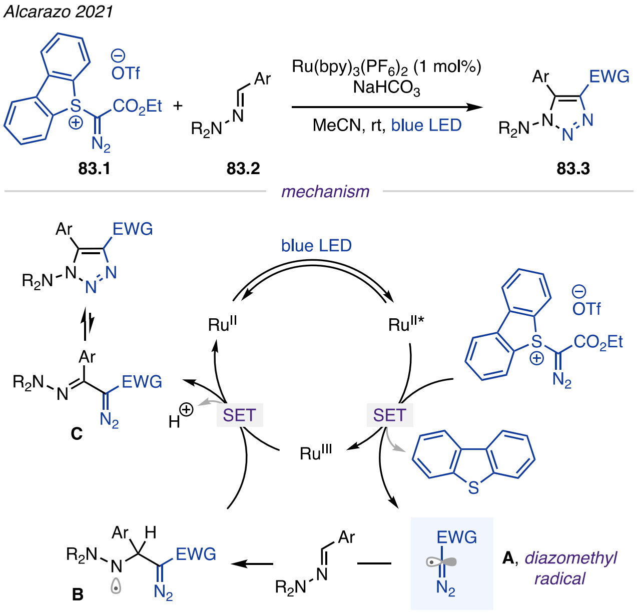
In 2021, Alcarazo and co-workers employed *α*-diazo sulfonium triflates **83.1** for the generation of diazomethyl radicals under photocatalytic conditions, allowing for efficient synthesis of *N*-amino triazoles **83.3** with hydrazones **83.2** (Scheme 83).[183] Mechanistically, the photoexcited Ru complex is capable of reducing *α*-diazo sulfonium triflates via a single-electron transfer process, producing the key diazomethyl radical **A**. Addition of the latter to the azomethine carbon of *N*,*N*-dialkyl hydrazones affords an aminyl radical species **B**, which is subsequently oxidized by Ru^{III} complex. Upon deprotonation, intermediate **C** is formed, which cyclizes into triazoles. Simultaneously, Li's group reported a similar photocatalytic method employing hypervalent iodine reagents **84.1** for synthesis of triazoles **84.3** (Scheme 84a).[184] In 2022, the groups of Liu and Li disclosed a related photocatalytic strategy for synthesizing triazoloquinoxalinones **84.5** from hypervalent iodine reagents **84.1** and quinoxalinones **84.4** (Scheme 84b).[185] This reaction proceeds via a similar mechanism involving diazomethyl radical intermediates. Subsequently, Pla-Quintana, Poater, and co-workers conducted DFT calculations of this transformation, unveiling that the rate-determining step is the C−C bond formation step through the attack of diazomethyl radicals onto the C−N double bond of the quinoxalinone.[186]

In 2022, the group of Yuan and Zhao reported a photochemical catalyst-free annulation reaction of *α*-diazo sulfonium triflates **85.1** with *α*-oxocarboxylic acids **85.2** and alkynes, producing oxadiazoles **85.3** and pyrazoles **85.4**, respectively (Scheme 85).[187] In this catalyst-free reaction, the authors proposed that diazomethyl radicals were formed through the homolytic cleavage of S−C bond in *α*-diazosulfonium triflates upon exposure to blue light irradiation.

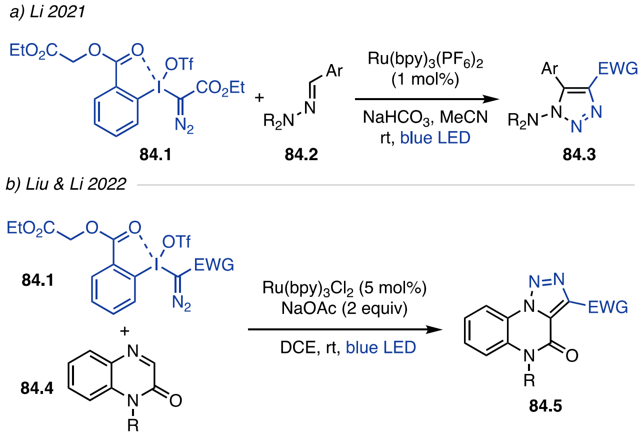
Scheme 82. Synthesis of Oxadiazoles via Diazomethyl Radical Intermediates



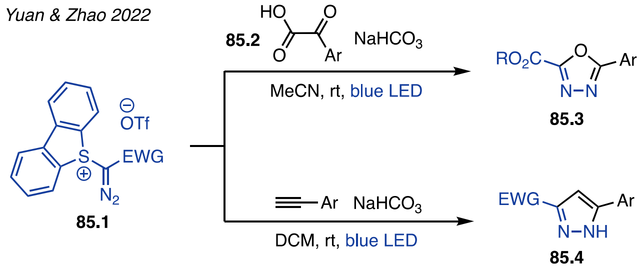
Scheme 83. Synthesis of *N*-Amino Triazoles from *α*-Diazo Sulfonium Triflates



Scheme 84. Synthesis of Triazole Derivatives from Hypervalent Iodine Reagents



Scheme 85. Synthesis of Oxadiazoles and Pyrazoles from *α*-Diazo Sulfonium Triflates

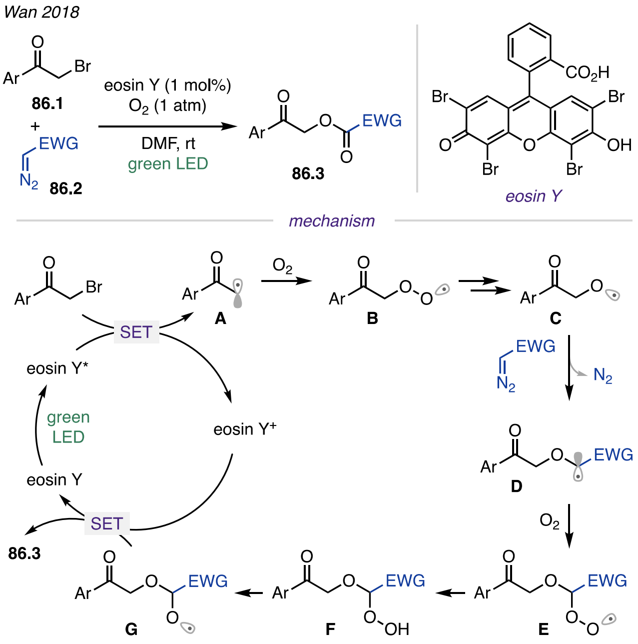


6. DIAZO COMPOUNDS AS RADICAL ACCEPTORS

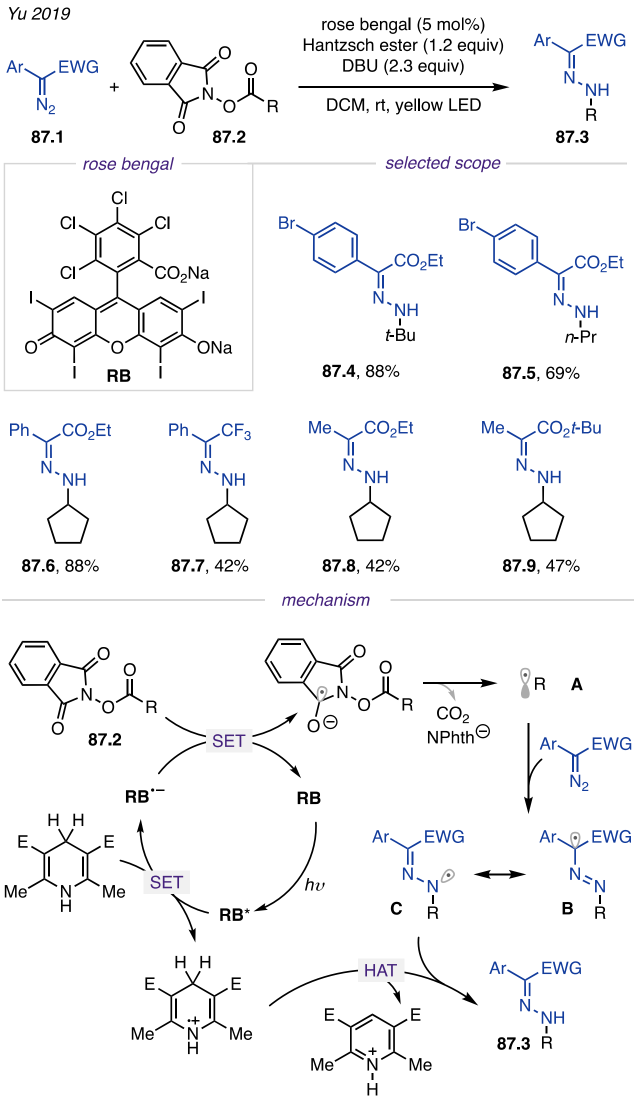
Diazo compounds can act as acceptors for radicals, generating an additional free radical by releasing dinitrogen, enabling cascade transformations. In 2018, Wan and co-workers reported a photocatalytic approach to access oxalate esters **86.3** from diazo compounds **86.2** and *α*-bromo-ketones **86.1** in the presence of molecular oxygen (Scheme 86).[188] The mechanism of this reaction begins with the single-electron reduction of *α*-bromo-ketones by photoexcited eosin Y to generate alkyl radical species **A**, which is then trapped by molecular oxygen, producing superoxide radical **B**. Upon HAT and a subsequent homolysis of the weak O−O bond, the oxygen-centered radical **C** is formed. Radical addition to diazo compound and a subsequent extrusion of dinitrogen produces radical intermediate **D**. Similarly, successive reactions of radical **D** with molecular oxygen produce oxygen-centered radical **G**, which is then oxidized to furnish oxalate ester.

One year later, Yu and co-workers disclosed a photocatalytic method for synthesizing *N*-alkyl hydrazones **87.3** from alkyl *N*-hydroxyphthalimide esters (NHPI esters) **87.2** and diazo compounds **87.1** (Scheme 87).[189] Donor−acceptor type diazo compounds were found to be suitable substrates. Additionally, primary, secondary, and tertiary alkyl radicals all effectively participated in this transformation **87.4**−**87.9**. A plausible mechanism for this reaction begins with the single-electron

Scheme 86. Photocatalytic Method for Accessing Oxalate Esters from Diazo Compounds and α-Bromo-ketones



Scheme 87. Synthesis of *N*-Alkyl Hydrazones



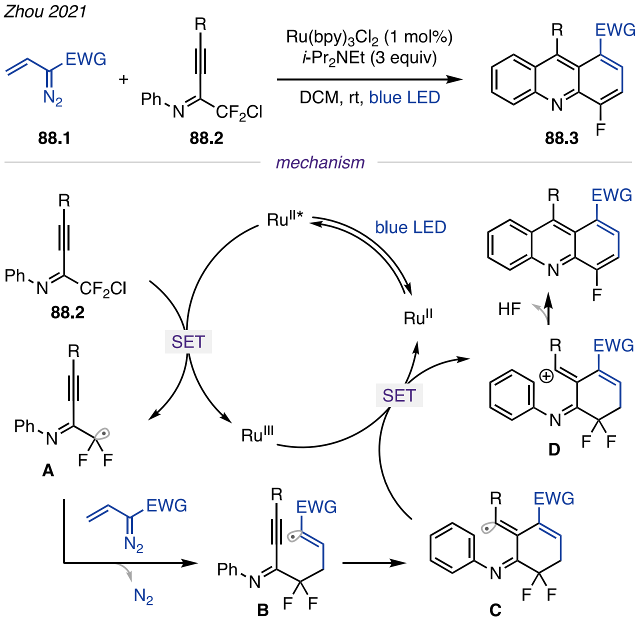
reduction of the redox-active ester **87.2** by a photoexcited rose bengal catalyst. A subsequent decarboxylation leads to alkyl radical **A**, which undergoes addition to the terminal nitrogen of the diazo compound. The resulting radical species **B** is a resonance form of intermediate **C**, which, upon HAT from the Hantzsch radical cation, produces *N*-alkyl hydrazone as the final product.

In 2021, Zhou and co-workers utilized vinyl diazo compounds **88.1** as radical acceptors to construct fluorinated acridines **88.3** in a cascade radical cyclization reaction (Scheme 88).[190] In this transformation, chlorodifluoromethyl alkynyl ketoimine **88.2** serves as a radical precursor, which upon single-electron reduction by a photoexcited Ru complex produces difluoromethyl radical **A**. A subsequent trapping of the latter by vinyl diazo compounds generates a vinyl radical **B**, which intramolecularly adds to C−C triplet bond of ketoimine to deliver vinyl radical **C**. Then, intramolecular homolytic aromatic substitution (HAS) and oxidation provides vinyl cation **D**, which upon elimination of HF furnishes 4-fluoroacridine as the final product. In addition to chlorides, perfluoroalkyl iodides were also employed as radical sources in this denitrogenative reaction with vinyl diazo compounds. Thus, the groups of Ke and Zhou documented an atom transfer radical addition (ATRA) reaction targeting fluorinated vinyl iodides.[191] It was found that the reaction does not require external photocatalysts or additives.

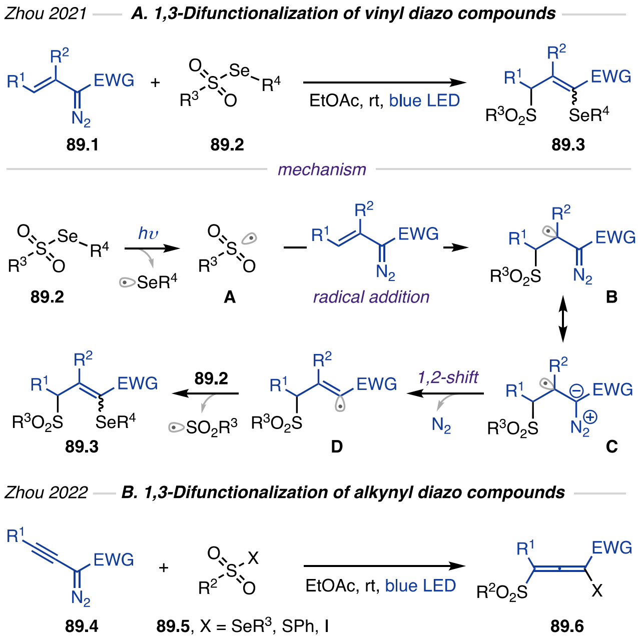
In the following studies, the same group developed a photochemical 1,3-selenosulfonylation reaction that also employs vinyl diazo compounds **89.1** (Scheme 89A).[192] In this transformation, selenosulfonates **89.2** serve as radical precursors, which allows for the efficient preparation of various γ-seleno allylic sulfones **89.3**. A plausible mechanism was proposed that begins with the visible light-induced homolysis of Se−S bonds, producing sulfonyl **A** and selenyl radicals. The addition of an electrophilic tosyl radical **A** to the C−C double bond of vinyl diazo compounds results in the formation of radical **B**, which has a resonance structure represented by intermediate **C**. Following a 1,2-radical shift and the extrusion of N_2, vinyl radical **D** is formed, which affords 1,3-selenosulfonylation product upon reaction with selenosulfonates **89.2**. A year later, they expanded this photochemical strategy to include alkynyl diazo compounds **89.4**, thus enabling synthesis of tetrasubstituted allenes **89.6** (Scheme 89B).[193] The reaction mechanism closely resembles the one described earlier. Moreover, apart from selenosulfonates, it was observed that this method can be applied to thiosulfonates and sulfonyl iodides, delivering 1,3-thiosulfonylation and iodosulfonylation products, respectively.

In the same year, the groups of Koenigs and Xuan reported a photochemical reaction between diazo compounds **90.1**, azodicarboxylates **90.2**, and nitriles **90.3** for preparation of dihydrotriazole **90.4** (Scheme 90).[194] Control experiments and computational studies suggested the formation of a triplet species **A** from azodicarboxylates upon light irradiation. A subsequent radical-type addition to diazo compound produces diradical intermediate **B**. Upon extrusion of dinitrogen, azomethine ylide intermediate **C** is formed, which has a resonance form of intermediate **D**. Finally, dipolar cycloaddition of the latter with acetonitrile **90.3** delivered the desired dihydrotriazole **90.4**.

Scheme 88. Synthesis of 4-Fluoroacridines via Cascade Radical Cyclization

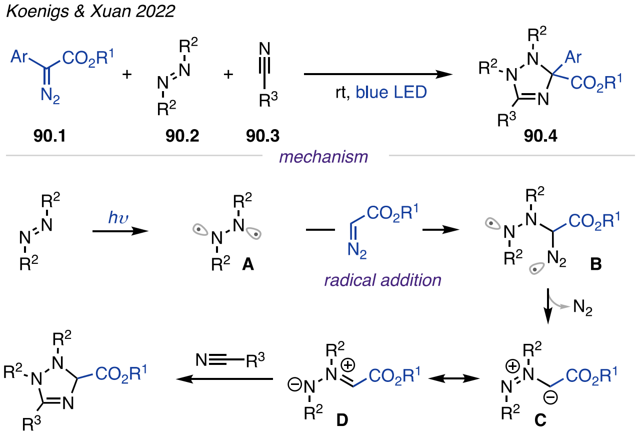


Scheme 89. 1,3-Functionalization of Vinyl and Alkynyl Diazo Compounds

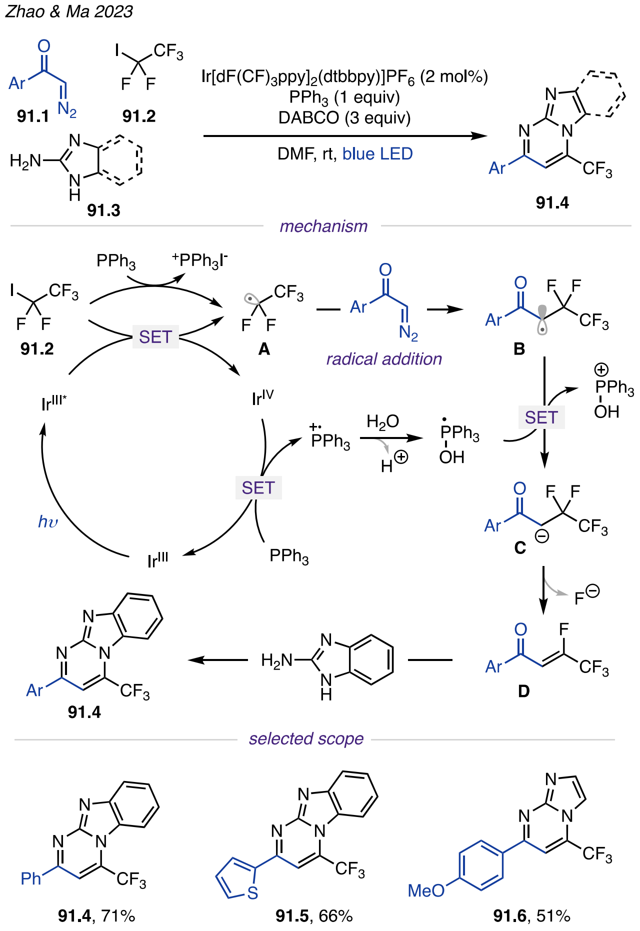


Very recently, Zhao, Ma, and co-workers reported a photocatalytic three-component reaction between α-diazoketones **91.1**, perfluoroalkyl iodides **91.2** and amino *N*-heterocycles **91.3** (Scheme 91).[195] This method allows for efficient synthesis of *N*-heterocycles containing valuable CF_3 and perfluoroalkyl groups. Mechanistically, the produced perfluoroalkyl radical **A** undergoes efficient addition to the diazo compound, resulting in the formation of radical intermediate **B**. A subsequent single-electron reduction with a phosphoranyl radical delivers anion **C**. Upon β-F elimination, alkenyl fluoride **D** is formed, which cyclizes with amino benzoimidazole, delivering fluorinated tricyclic heterocycle **91.4**.

Scheme 90. Photochemical Synthesis of Dihydrotriazole from Diazo Compounds, Azodicarboxylates, and Nitriles



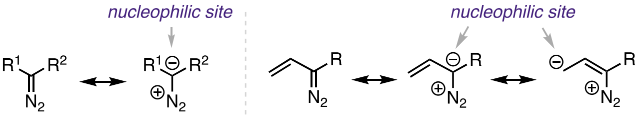
Scheme 91. Synthesis of Fluorinated *N*-Heterocycles via Multicomponent Cyclization Reactions



7. DIAZO COMPOUNDS AS NUCLEOPHILES

Diazo compounds exhibit ambiphilic reactivity. This property is evident from the resonance structure of the diazo group, which indicates a pronounced negative charge at the carbon to which the diazo group is attached, thus rendering it nucleophilic (Scheme 92).[196] Conversely, the terminal nitrogen of the diazo group serves as a preferred electrophilic site. Among various diazo reagents, vinyl diazo compounds have garnered attention as versatile and valuable substrates in recent

Scheme 92. Nucleophilic Sites in Diazo Compounds

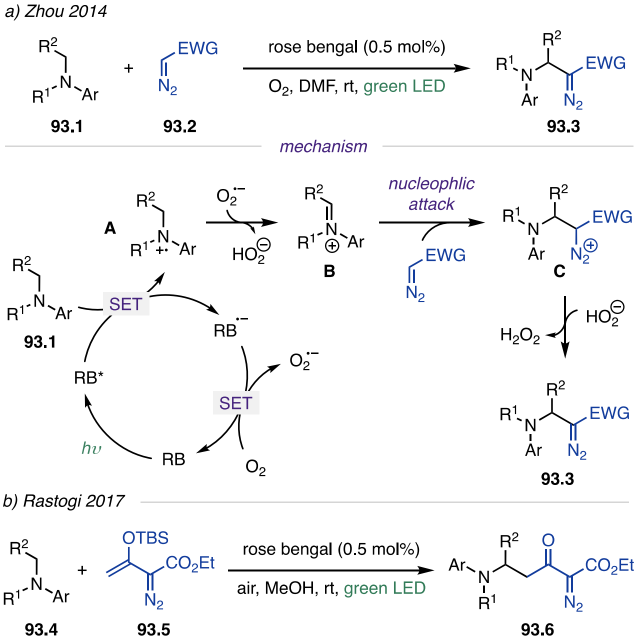


years.[197] Apart from the above-mentioned nucleophilic carbon to which the diazo group is attached, vinyl diazo compounds possess an extra nucleophilic site at the terminal alkene carbon. Furthermore, the vinylic moiety can be considered an activated olefin capable of engaging in cyclization reactions.

Many transformations featuring diazo compounds as nucleophiles have been documented in the past.[198] More recently, photoredox catalysis has allowed for mild generation of diverse radical species from a wide range of radical precursors. The process of single-electron oxidation produces various radical cations, which can either function as electrophiles themselves or undergo transformations into electrophilic species before reacting with diazo compounds. In certain instances, the valuable diazo functionality remains intact during the nucleophilic addition, thus enabling subsequent functionalizations.

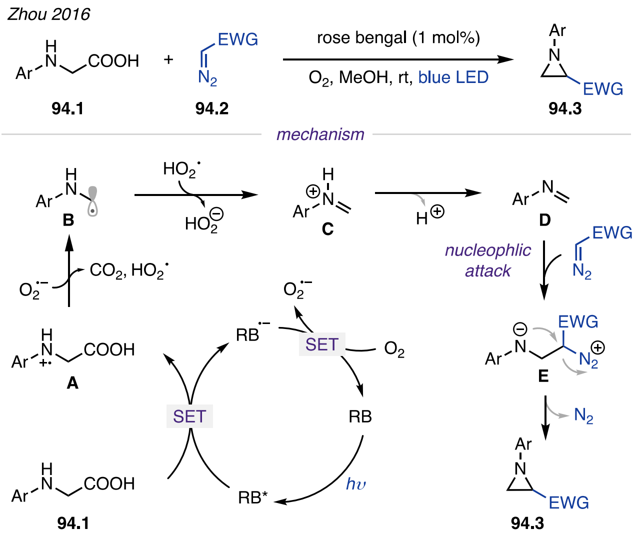
In 2014, Zhou's group reported an organic dye-catalyzed coupling reaction involving tertiary amines **93.1** and α-diazocarbonyl compounds **93.2** (Scheme 93a).[199] In this transformation, the diazo functionality is preserved, affording donor–acceptor-type diazo compounds **93.3** as final products. The mechanism begins with the oxidation of the tertiary amine by the photoexcited rose bengal catalyst, yielding radical cation **A** and the reduced form of the catalyst $RB^{\bullet-}$. A subsequent oxidation of the latter by oxygen regenerates the catalyst and produces a superoxide radical anion capable of HAT from radical cation **A**, delivering iminium ion **B**. A nucleophilic attack of the latter by a diazo compound generates intermediate **C**, which is then deprotonated by a hydroperoxide anion to furnish the final product **93.3**. It is important to note that photolysis of diazo compounds was not observed under the given conditions, likely due to the relatively low energy of the green light utilized in this reaction. Later, Rastogi and co-workers published a follow-up work employing silyl diazoenolate **93.5** as a nucleophile under similar reaction conditions (Scheme 93b).[200]

Scheme 93. Organic Dye-Catalyzed Coupling Reaction Between Tertiary Amines and Diazo Compounds



Building on the efficient nucleophilic addition of diazo compounds to the *in situ* formed iminium ions, in 2016, Zhou's group introduced an additional photocatalytic approach that enables the efficient synthesis of aziridines **94.3** from *N*-aryl glycines **94.1** (Scheme 94).[201] Mechanistically, the decarboxylation of the radical cation **A** derived from *N*-aryl glycine produces an α-amino radical **B**, which, following oxidation yields an iminium cation **C**. Subsequently, the nucleophilic addition of a diazo compound to imine **D**, followed by a denitrogenative 3-*exo-tet* cyclization, furnishes aziridine.

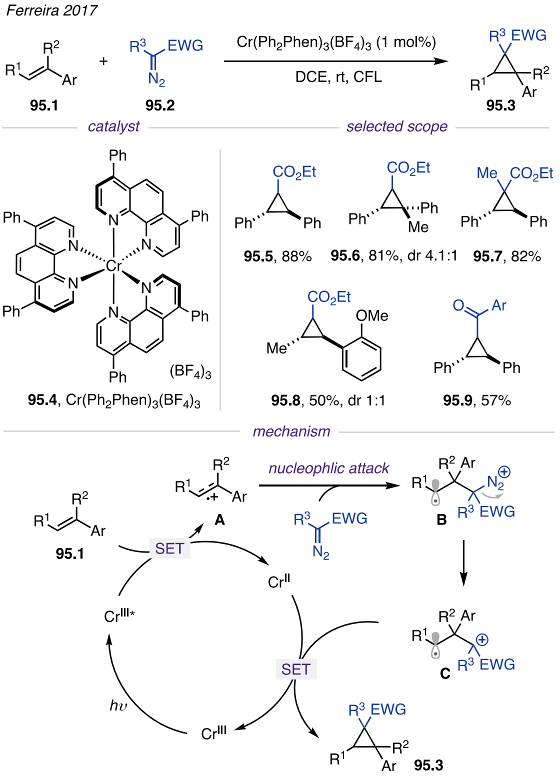
Scheme 94. Synthesis of Aziridines via Organophotoredox Catalysis



In 2017, Ferreira and co-workers reported a Cr-catalyzed cyclopropanation reaction of diazo compounds **95.2** and alkenes **95.1** by using CFL as a light source (Scheme 95).[202] It was found that this reaction does not involve a carbene intermediate. Instead, the diazo reagent serves as a nucleophile. The mechanism commences with the single-electron oxidation of electron-rich alkene by a photoexcited Cr(III) catalyst. The resulting radical cation **A** undergoes nucleophilic attack by the diazo compound, which, upon loss of dinitrogen, delivers a radical cation intermediate **C**. A subsequent reduction and intramolecular cyclization furnish the cyclopropane. The reaction proceeds well for alkenes whose reduction potentials fall within the range of +1.11 V to +1.80 V (vs SCE). Different diazo compounds also underwent this transformation smoothly **95.5**–**95.9**.

Following the successful development of radical cyclopropanation, the same research group has further achieved a formal [3 + 2] cycloaddition reaction of alkenes **96.1** using vinyl diazo compounds **96.2** (Scheme 96a).[203] It was discovered that both chromium and ruthenium complexes are capable of catalyzing this transformation. Although similar yields were obtained for both catalysts, the reaction time was significantly shorter for the Ru catalyst. Mechanistically, the nucleophilic attack of vinyl diazo compound at radical cation **A**

Scheme 95. Radical Cation Cyclopropanations via Chromium Photooxidative Catalysis

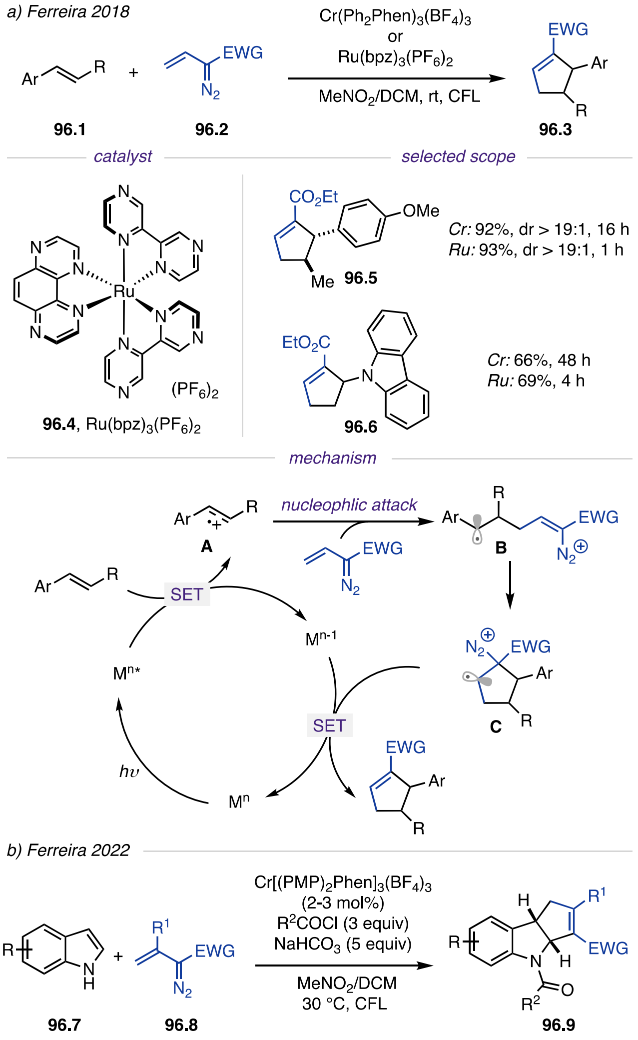


produces a stabilized benzylic radical **B**. This offers an explanation for the observed high regioselectivity. A rare 5-*endo-trig* radical cyclization generates radical species **C**, which upon reduction and loss of N_2, forms cyclopentene **96.3**. The authors also proposed an alternative route that involves 4-*exo-trig* cyclization of **B**, followed by the ring expansion. Mechanistic studies supported the radical cyclization pathway instead of a cyclopropanation and isomerization process. Later, the authors expanded this formal [3 + 2] cycloaddition protocol to include indoles **96.7**, which allowed for synthesis of a wide variety of indoline-fused tricyclic compounds **96.9** (Scheme 96b).[204]

In 2020, Nicewicz and co-workers reported an organo-photocatalytic approach for C−H alkylation of arenes **97.2** (Scheme 97).[205] It was shown that acceptor-type diazo compounds **97.1** are capable substrates for this transformation. Simple aromatics and electron-rich anisole-derived substrates also reacted well (**97.4**−**97.7**); however, regioisomers were obtained in some cases **97.4**. Generally, functionalization at *ortho*-position to electron-donating groups is observed, while the *para*-selectivity is favored in more sterically hindered cases. The reaction mechanism begins with the single-electron oxidation of the arene by the photoexcited acridinium catalyst, producing a radical cation **A**. A subsequent nucleophilic addition by diazo compounds leads to the formation of distonic cation radical **B**, which is then reduced by an acridine radical (Mes-Acr•) to form a norcaradiene intermediate **C**. Following a second SET process, intermediate **C** undergoes a ring-opening process to afford distonic benzylic radical cation **D**, which upon reduction and deprotonation, produces alkylated arenes.

Very recently, Koenigs, Zhou, and co-workers developed a photocatalytic method for the self-cyclization of vinyldiazo compounds **98.1** (Scheme 98).[206] This transformation preserves the valuable diazo functional group, allowing for the efficient synthesis of cyclopentenyl α-diazo compounds **98.2**. The reaction mechanism commences with the single-electron oxidation of the vinyldiazo substrate by the photo-excited Ir^{III} complex, yielding a radical cation intermediate. A subsequent nucleophilic attack of radical cation **A** by another vinyldiazo molecule generates radical intermediate **B**. Following this addition step, a 5-*endo* radical cyclization of **B**, with the extrusion of dinitrogen, produces intermediate **C**. Finally, single-electron reduction of **C** by Ir^{II} provides the cyclo-pentenyl α-diazo compounds **98.2**.

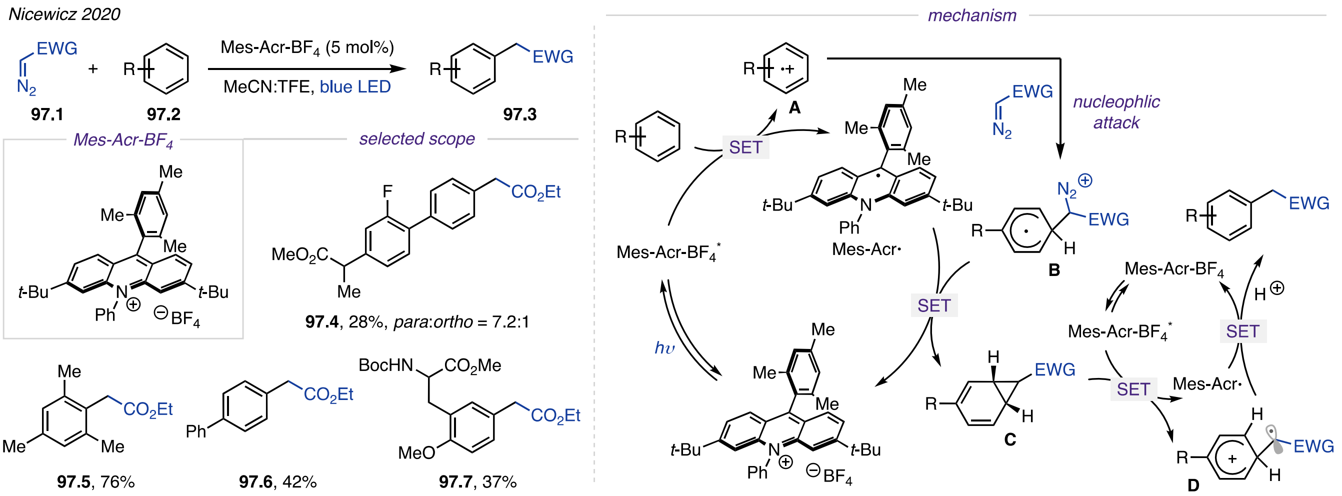
Scheme 96. Formal [3 + 2] Cycloadditions of Vinyl Diazo Compounds with Alkenes or Indoles



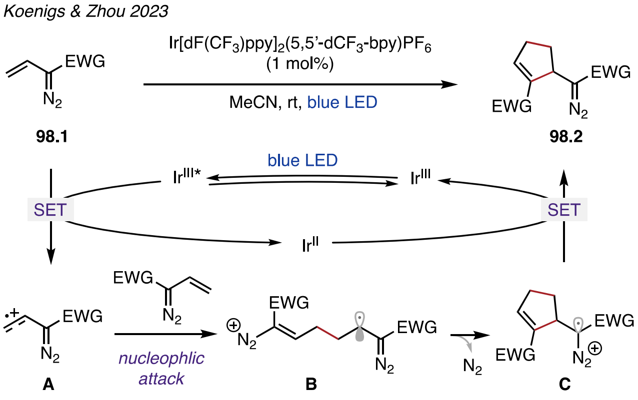
8. MISCELLANEOUS REACTIONS OF DIAZO COMPOUNDS

In 2018, the groups of Shi and Li introduced an iodine-catalyzed approach for activating ethyl diazoacetate **99.1** to access radical intermediates (Scheme 99a).[207] This photo-catalytic protocol allows for synthesis of a wide variety of cyclopropanes **99.3**. Upon reaction of diazo compounds with iodine, a diiodoalkyl intermediate **A** is generated, which is reduced by a photoexcited Ru^{II} complex to produce the carbon-centered radical **B**. A subsequent radical addition to an alkene gives a radical intermediate **C**. Intramolecular

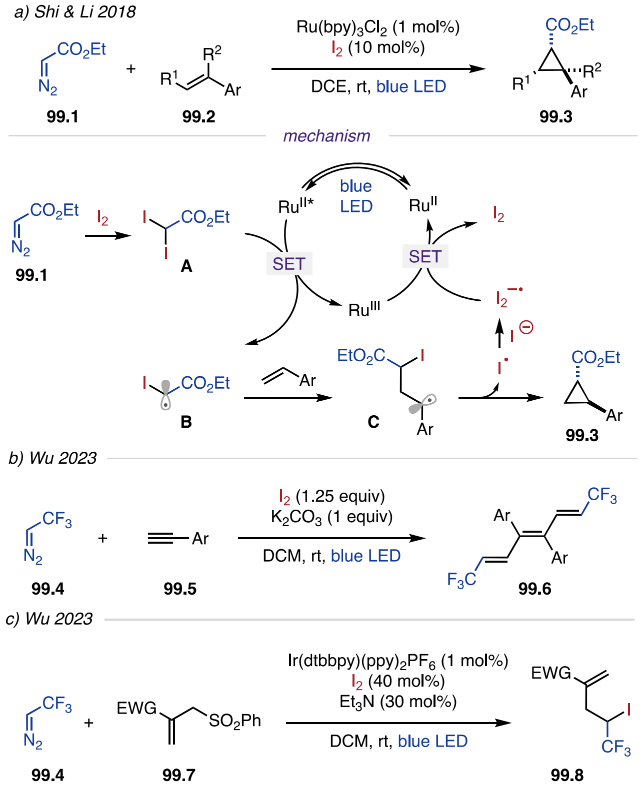
Scheme 97. Regioselective C−H Alkylation of Arenes Enabled by Organic Photoredox Catalysis



Scheme 98. Photocatalytic Self-Cyclization of Vinyldiazo Compounds



Scheme 99. Iodine-Enabled Diazo Activation to Access Radical Reactivity

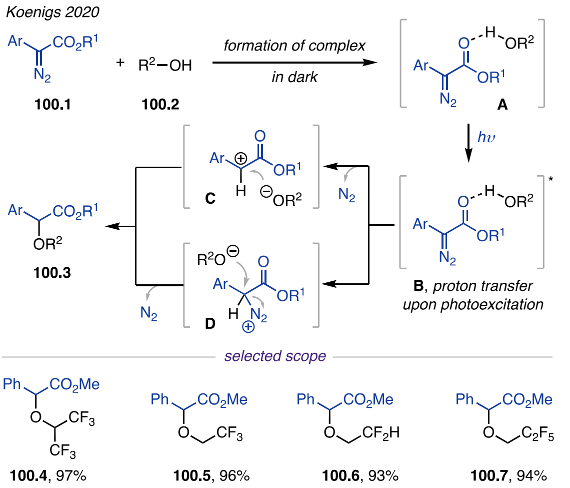


cyclization of the latter affords a cyclopropane **99.3** with the release of an iodine radical. Following this, the produced iodine radical reacts with iodide, forming an anionic radical $I_2^{-\bullet}$, which is further oxidized to regenerate iodine and the photocatalyst. Inspired by this work, Chen and co-workers later reported a photochemical iodine-mediated method for homocoupling of diazo substrates, enabling synthesis of tetrasubstituted alkenes.[208] In 2023, Wu's group developed an iodine-mediated multicomponent coupling between trifluorodiazoethane **99.4** and aryl alkynes **99.5** (Scheme 99b).[209] This reaction involves two diazo and two alkyne components, providing a convenient access to bistrifluoromethylated conjugated trienes **99.6**. Shortly after, the same research group expanded this strategy to allyl sulfones **99.7** as radical acceptors under photocatalytic conditions (Scheme 99c).[210] This transformation features a β-sulfonyl elimination process, leading to the formation of α-CF_3-substituted homoallylic iodides **99.8**.

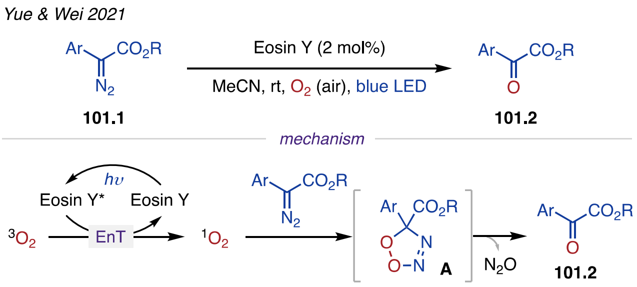
In 2020, Koenigs and co-workers reported a photoexcited proton transfer strategy for O−H functionalization of weakly acidic alcohols **100.2** using diazo compounds **100.1** (Scheme 100).[211] The reaction initiates with the formation of a hydrogen bonding complex **A**. Upon photoirradiation, the photoexcited complex readily deprotonates the mildly acidic substrates. The resulting ion pair undergoes rapid nucleophilic substitution, extruding dinitrogen in a concerted or stepwise manner, leading to O−H functionalized products **100.3**. It was found that various fluorinated alcohols efficiently participated in this reaction **100.4**−**100.7**. In same year, the authors expanded the scope of the developed photochemical platform to include cyclic diazo amides[212] and phenols.[213] Later on, both the same research group[214,215] and Petit's group[216] conducted computational studies, which suggested a different mechanism: the O−H insertion mechanism in several acidic alcohols includes free carbenes as essential reactive intermediates.

In 2021, Yue, Wei, and co-workers established a photocatalytic method for synthesis of α-ketoesters **101.2** through aerobic oxidation of α-diazoesters **101.1** (Scheme 101).[217] The

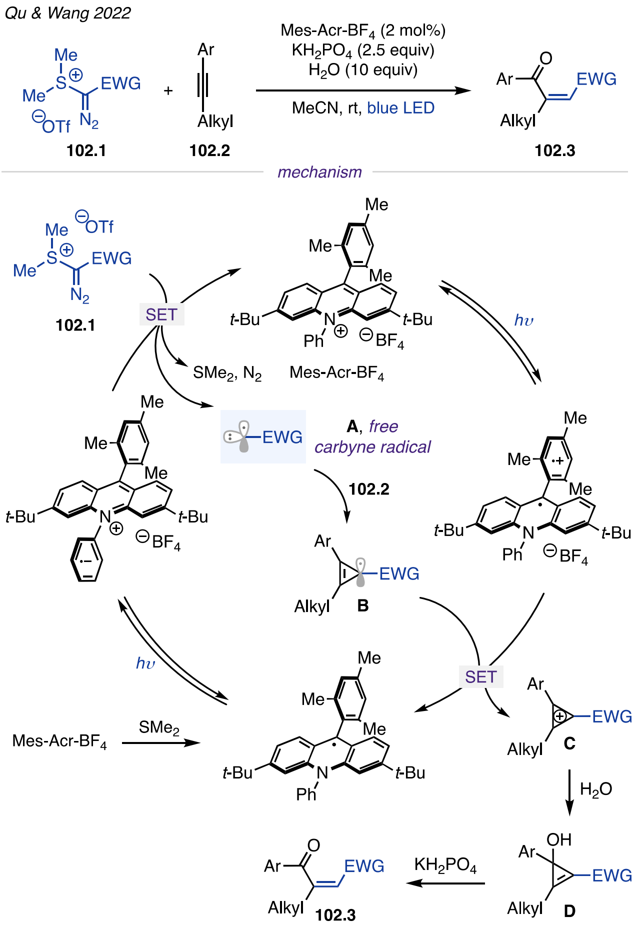
Scheme 100. Photoexcited Proton Transfer Reaction



Scheme 101. Synthesis of α-Ketoesters via Aerobic Oxidation of α-Diazoesters



Scheme 102. Generation of Free Carbyne Radical Intermediates from α-Diazo Sulfonium Triflates

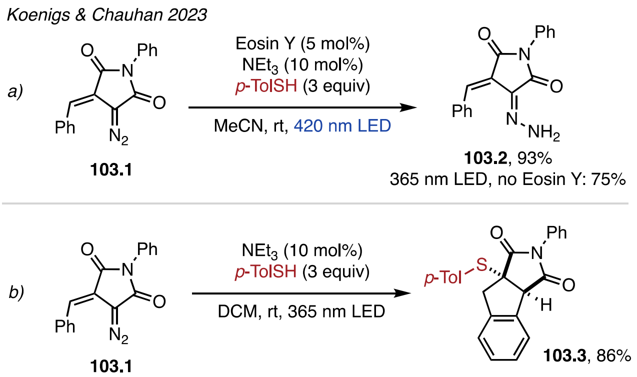


proposed mechanism entails the formation of singlet oxygen via an energy transfer process with the photoexcited eosin Y catalyst. Following this, a concerted 1,3-dipolar cycloaddition of α-diazoesters **101.1** with $^1O_2$ generates the dioxadiazole intermediate, which swiftly decomposes to yield the desired product **101.2** while releasing N_2O.

A year later, the groups of Qu and Wang reported a rare example of photocatalytic generation of free carbyne radical intermediates **A** from α-diazo sulfonium triflates **102.1** (Scheme 102).[218] This three-component coupling reaction between internal alkyne **102.2**, α-diazo sulfonium triflate **102.1**, and water allows for synthesis of various 1,4-dicarbonyl *Z*-alkenes **102.3**. The isotope labeling experiments indicated that both the oxygen and hydrogen atoms in the product originated from water. Furthermore, it was discovered that dibenzothiophene-substituted α-diazo sulfonium salts failed to react. However, the addition of SMe_2 promoted the reaction, albeit with low efficiency. This observation, coupled with cyclic voltammetry analysis and fluorescent quenching experiments, suggests that the *in situ* formed Me_2S is necessary for the initial single-electron reduction of the photocatalyst, which initiates the catalytic cycle. The reduced photocatalyst is excited once more and undergoes single-electron transfer with α-diazo sulfonium triflate, which leads to the formation of a radical carbyne intermediate. Addition of the latter to alkyne produces radical intermediate **B**, which is oxidized by the excited photocatalyst to the corresponding cyclopropenium cation **C**. A subsequent capture of the latter by water delivers cyclopropeneol **D**, followed by a KH_2PO_4-assisted ring-opening process that furnishes the dicarbonyl alkenes with *Z*-configuration.

Very recently, the groups of Koenigs and Chauhan observed that cyclic diazo imides **103.1** are capable of engaging in two different reaction pathways in the presence of thiols under light-induced conditions (Scheme 103).[219] In acetonitrile solvent, an unusual reduction of the diazo compound to a hydrazone **103.2** was observed, with no carbene intermediate formed (Scheme 103a). However, in dichloromethane, a triplet carbene is generated under 365 nm light irradiation, which then participates in a cascade cyclization/thiolation reaction,

Scheme 103. Solvent-Dependent Selectivity of Cyclic Diazo Imides



ultimately yielding indane-fused pyrrolidines **103.3** (Scheme 103b).

9. PRECURSORS OF DIAZO COMPOUNDS

9.1. Diazirines

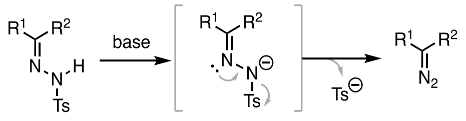
Diazirines are three-membered cyclic isomers of diazo compounds. These carbene precursors are more stable compared to diazo compounds, without the need for an electron-withdrawing group to ensure their safe handling. However, harsh conditions, such as elevated temperatures or UV photolysis, are required for their activation.[220]

The photochemical transformations of diazirines are well-documented.[220] Moreover, exciting biological applications have been extensively reported, wherein they serve as probes in photoaffinity labeling[221−223] and chemical proteomics.[224] However, these reactions utilize high energy UV light, as diazirines exhibit little to no direct absorption of blue light (410−490 nm).[225] Recently, Fadeyi, Oslund, and MacMillan introduced a microenvironment-mapping (μMap) platform that exploits photocatalytic carbene generation from diazirines to selectively identify protein−protein interactions on cell membranes.[226] Iridium (Ir) photocatalysts facilitate the conversion of nearby diazirines into carbenes through Dexter energy transfer and biotinylate proteins within a ~4 nm radius, allowing for high spatial and temporal control over labeling. Importantly, this technology has been employed to rapidly profile immunological synapse interactions,[226] identify small molecule targets,[227] and track chromatin reorganization events,[228] and map small molecule binding site mapping.[229]

9.2. *N*-Tosylhydrazones

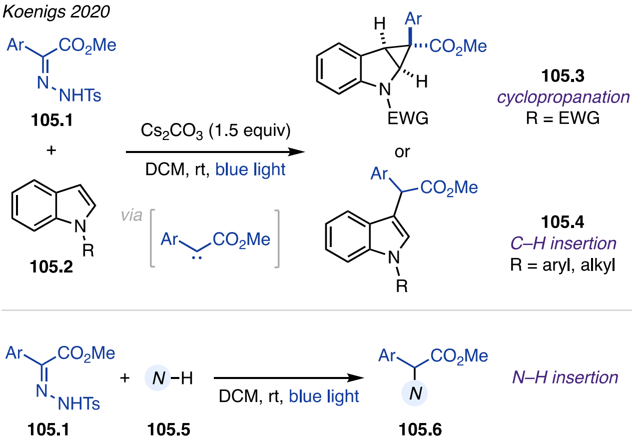
N-Tosylhydrazones are useful synthons in organic synthesis,[230,231] notably via the *in situ* generation of diazo compounds through the Bamford−Stevens reaction (Scheme 104).[232] In turn, *N*-tosylhydrazones can easily be synthesized through the condensation of ketones or aldehydes with $TsNHNH_2$. They are generally stable compounds, often crystalline solids that are easy to purify. Particularly, *N*-tosylhydrazones serve as safe precursors for diazo compounds without electron-withdrawing groups at the diazo carbon, such as alkyl- and aryl-substituted diazomethane derivatives, which are typically unstable and challenging to handle.

Scheme 104. *In Situ* Formation of Diazo Compounds from *N*-Tosylhydrazones



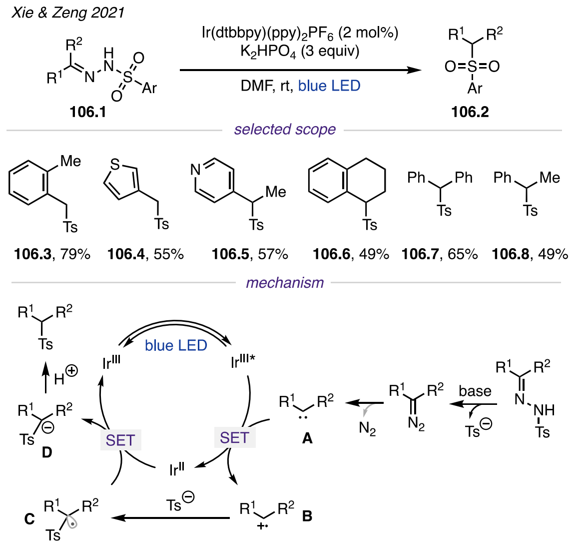
In 2020, Koenigs and co-workers achieved the photochemical generation of carbenes from *N*-tosylhydrazones **105.1** (Scheme 105).[233] Under basic conditions, *N*-tosylhydrazones readily participated in reactions with indoles **105.2**, yielding either cyclopropanation **105.3** or C−H insertion products **105.4**, depending on the electronic properties of the substrates. Additionally, the authors tested unprotected *N*-heterocycles **105.5**, including indoles, carbazoles, and piperidine derivatives. In this scenario, N−H insertion products **105.6** were observed. Moreover, the employment of *N*-tosylhydrazones under photochemical conditions for X−H (X = C, N, O, S) insertions,[234] [2 + 1] cycloadditions,[235] Doyle−Kirmse and Sommelet−Hauser reactions,[236] was also reported.

Scheme 105. Photochemical Generation of Carbenes from *N*-Tosylhydrazones



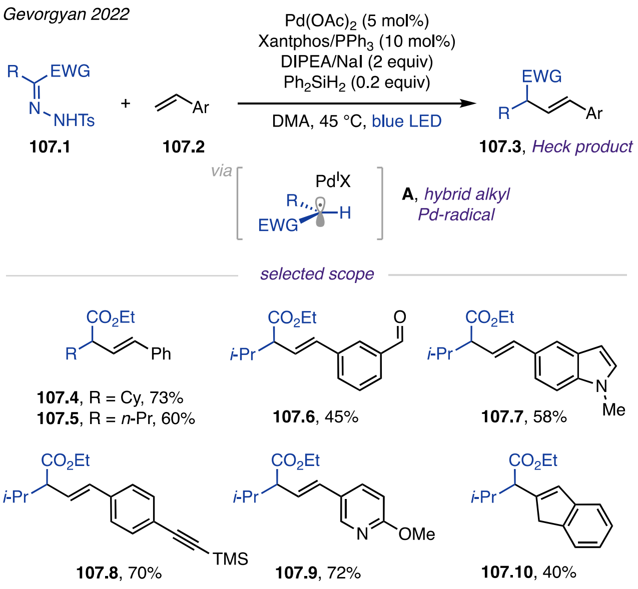
N-Sulfonylhydrazones can be applied in denitrogenative sulfonylation reactions. In 2021, Xie, Zeng, and co-workers introduced a photocatalytic method for synthesizing aryl or alkyl sulfones **106.2** (Scheme 106).[237] It was found that aryl or heteroaryl-substituted sulfonylhydrazones **106.1** worked well in this transformation. Similarly, sulfonylhydrazones derived from acetophenone, benzophenone, and benzocycloketone were also proven to be capable substrates (**106.3**−**106.8**). The reaction mechanism begins with the formation of a diazo compound from *N*-sulfonylhydrazones, accompanied by desulfonylation. A subsequent denitrogenation generates a carbene intermediate **A**, which is oxidized by the photoexcited Ir^{II} complex, yielding radical cation **B**. The nucleophilic attack of the latter by tosylate results in the formation of radicals **C**, followed by reduction and protonation to give the desired sulfone product.

Scheme 106. Denitrogenative Sulfonylation of *N*-Sulfonylhydrazones



In 2022, Gevorgyan's group reported an alkyl-Heck reaction of *N*-tosylhydrazones **107.1** with vinyl arenes **107.2** (Scheme 107).[157] Similarly to the previously mentioned method for

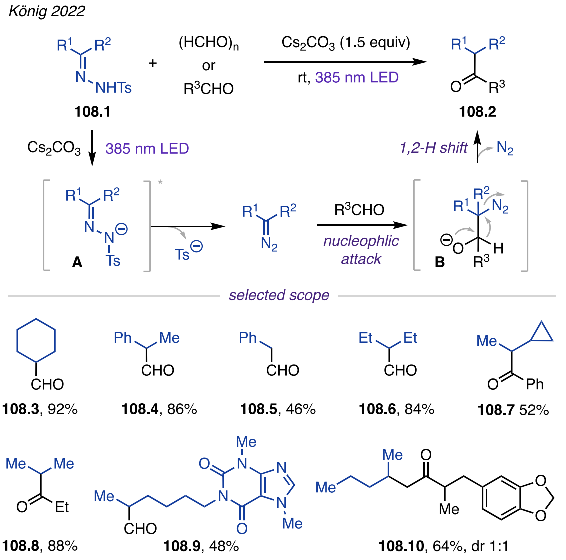
Scheme 107. Heck Reaction of *N*-Tosylhydrazones via Photoinduced Palladium Catalysis



Heck reaction of diazo compounds by the same group, this reaction proceeds via a hybrid alkyl palladium radical intermediate **A**. *N*-Tosylhydrazones bearing different primary and secondary alkyl chains are capable substrates for this transformation (**107.4**−**107.6**). Various vinyl arenes and heteroarenes also reacted well (**107.6**−**107.10**).

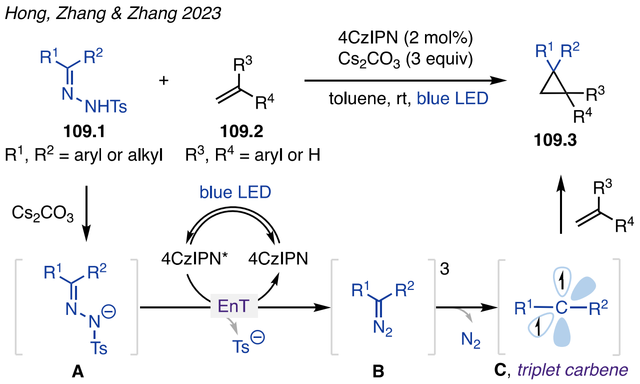
In the same year, König and co-workers developed a photochemical method for the *in situ* formation of highly reactive alkyl diazo compounds (Scheme 108).[238] This approach proceeds via the photoexcitation of *N*-tosylhydrazone anions **A**, enabling the efficient preparation of complex carbonyl compounds **108.2** from the corresponding aldehydes. The UV−vis absorption spectra demonstrate that *N*-tosylhydrazone derived from cyclohexanone absorbs exclusively in the UV region (<340 nm). However, upon the addition of one equivalent of Cs_2CO_3, a notable bathochromic shift of 50 nm occurs, extending the absorption band into the near-visible light region (390 nm). Thus, upon the deprotonation of *N*-tosylhydrazone, anion **A** undergoes photoexcitation under 385 nm light irradiation. Subsequently, the extrusion of a tosylate delivers the diazo intermediate, which participates in nucleophilic attack on the aldehyde, producing a diazonium alkoxide **B**. Finally, a 1,2-hydride shift of intermediate **B** occurs, which, upon extrusion of dinitrogen, furnishes the product.

Scheme 108. Synthesis of Ketones and Aldehydes Enabled by Photoexcitation of *N*-Tosylhydrazone Anions



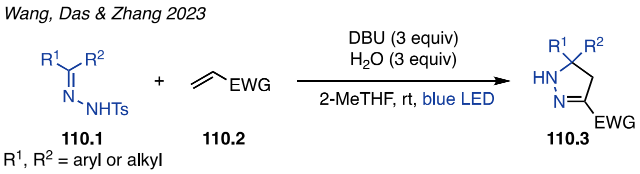
In contrast to König's method, which relies on UVA light, the groups of Hong, Zhan,g and Zhang recently introduced a visible light-mediated energy transfer approach by using a photosensitizer for the *in situ* formation of donor−donor-type diazo compounds from *N*-tosylhydrazones **109.1** (Scheme 109).[239] Notably, this method enables access to tetrasubstituted cyclopropanes **109.3** featuring two all-carbon quaternary centers. In terms of the reaction mechanism, the process begins with the deprotonation of *N*-tosylhydrazone by a base, resulting in the formation of the *N*-tosylhydrazone anion **A**. This anion then engages in an energy transfer process with the photoexcited 4CzIPN, affording intermediate in triplet state **B**. Subsequently, the triplet intermediates readily undergo desulfonylation to generate diazo compounds in a triplet state. After the release of dinitrogen, a triplet carbene species **C** is formed, which can then add to alkenes, ultimately yielding the desired cyclopropanes.

Scheme 109. Synthesis of Tetrasubstituted Cyclopropanes Enabled by Energy Transfer



Recently, Wang, Das, and Zhang's groups have introduced a photochemical method for the [3 + 2] cycloaddition of alkenes **110.2** and *in situ* formed donor−donor-type diazo compounds from *N*-tosylhydrazones **110.1** (Scheme 110). This method proves highly effective in synthesizing a diverse range of pyrazolines **110.3**. Moreover, by applying modified reaction conditions with additional bases or oxidants, the obtained pyrazolines can be easily transformed into pyrazoles.

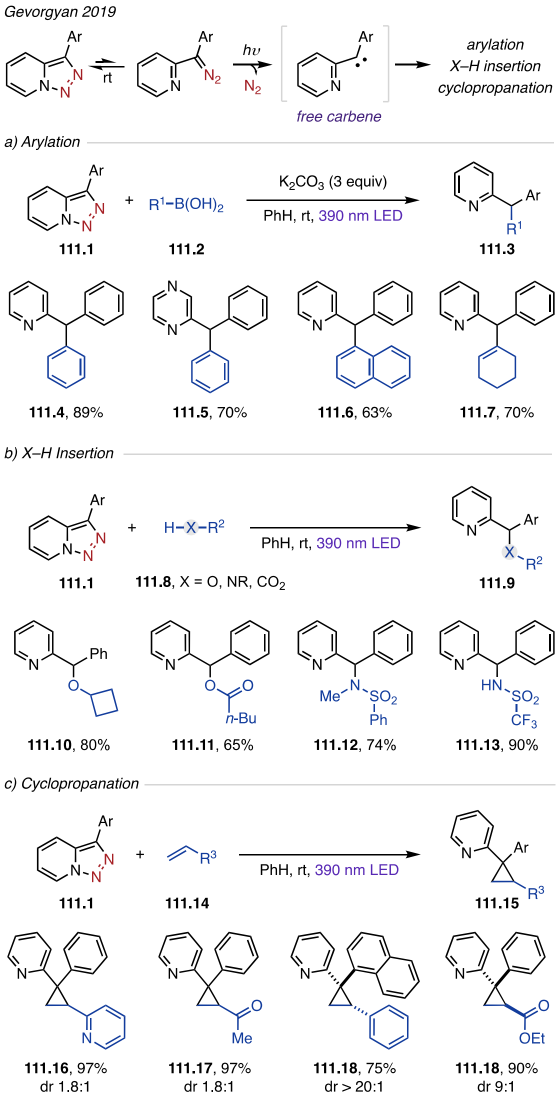
Scheme 110. [3 + 2] Cycloaddition of *in Situ* Formed Diazo Compounds and Alkenes



9.3. Pyridotriazoles

1,2,3-Triazoles can serve as viable precursors for diazo compounds. These heterocyclic compounds are robust, stable, and easily available.[240] Recently, transition metal-catalyzed denitrogenative transformations of pyridotriazoles have emerged as a powerful tool for synthesis of diverse *N*-heterocyclic scaffolds.[241,242] These transformations take advantage of the ring−chain tautomerization of pyridotriazoles in solution into the corresponding diazo tautomer. Although the generation of carbene species from pyridotriazoles under photochemical conditions has been reported, it is important to note that these photolysis approaches involved the use of harmful, high-energy UVC irradiation, leading to many side reactions, thus limiting the synthetic applications of these methods.[243] In 2019, Gevorgyan group observed that pyridotriazoles **111.1** bearing aromatic substitutions at C3 position exhibited good absorption around 390 nm region.[244] This observation inspired the authors to develop light-induced metal-free approach for arylation, X−H insertion, and cyclopropanation reactions of pyridotriazoles (Scheme 111). Under 390 nm light irradiation, the C−C bond forming reaction of pyridotriazoles with boronic acids **111.2** proceeded efficiently in the presence of K_2CO_3, producing a series of triarylmethanes **111.4**−**111.7**. Moreover, 3-aryl pyridotriazoles underwent X−H insertion reactions with alcohols, amines, and carboxylic acids delivering benzylpyridine derivatives without any additives or catalysts. In addition, it was also found that upon photoirradiation, the pyridotriazoles participated in efficient [2 + 1] cyclopropanation with a variety of alkenes. However, this approach, is limited to pyridotriazoles with aryl substituents at C3 position. Other derivatives, which are transparent in that area, such as 3-methyl and ester pyridotriazoles, remained intact and did not show reactivity under these conditions.

Scheme 111. Light-Induced and Metal-Free Transformations of Pyridotriazoles



9.4. 1,3,4-Oxadiazolines

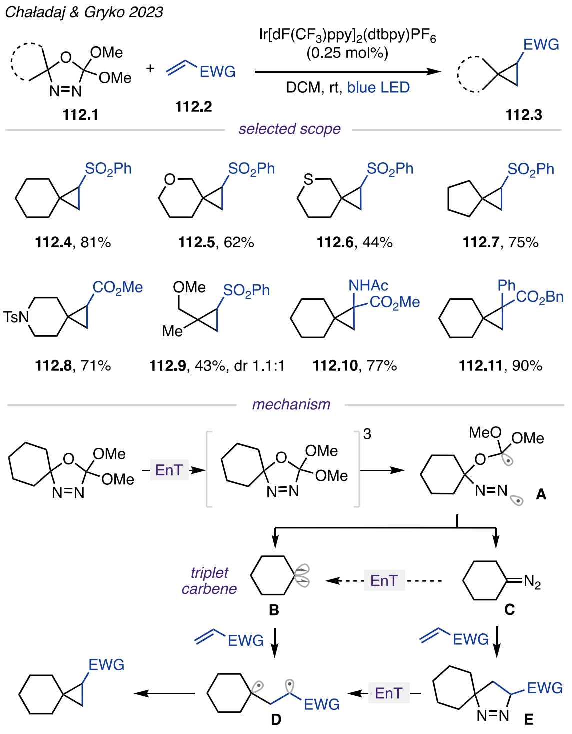
1,3,4-Oxadiazolines are reasonably stable compounds that can be easily prepared, making them valuable substrates for organic synthesis. Depending on the reaction conditions used, these heterocyclic compounds can undergo decomposition to produce various reactive intermediates. When subjected to thermolysis, bis(heteroatom)carbenes can be generated via ylide intermediates.[245] Extensive research by Warkentin and co-workers has demonstrated their utility as dimethoxycarbene precursors in synthesis of structurally diverse heterocycles.[246] Conversely, exposure to UV light leads to the formation of nonstabilized alkyl diazo compounds from these substrates. Notably, although the initial report on photolysis dates to 1968,[247] it was only recently demonstrated by Ley's group that 1,3,4-oxadiazolines efficiently serve as diazo precursors under UV light irradiation. Utilizing this strategy, they accomplished aryl−alkyl cross-coupling reactions of *in situ*-formed non-stabilized diazo compounds with boronic acids via a flow method.[248] Additionally, they showcased the synthesis of various unsymmetrical ketones by adding the *in situ*-formed diazo compound to an aldehyde, followed by a subsequent 1,2-hydride shift.[249]

Very recently, Chaładaj, Gryko, and co-workers developed a visible light-mediated strategy for activating oxadiazolines **112.1** through triplet energy transfer (Scheme 112).[250] This method enables the efficient generation of dialkyl-substituted carbenes, which, upon reacting with Michael acceptors, produce a wide range of spirocyclopropanes **112.3**. Mechanistically, oxadiazolines engage in energy transfer with a photosensitizer, leading to their triplet state. Subsequently, the cleavage of the C−N bond in oxadiazoline produces a diazenyl radical, which decomposes into triplet carbene **A** and diazoalkane **B**. In the presence of an alkene, triplet carbene **A** delivers cyclopropanes in a stepwise manner through a diradical intermediate. Simultaneously, diazoalkane participates in 1,3-dipolar cycloaddition with the alkene, producing pyrazoline **C**, which upon photosensitization, delivers spirocyclopropane via a diradical intermediate **D** with the extrusion of dinitrogen. Mechanistic experiments support both carbene and diazoalkane-mediated pathways. However, at this point, there is insufficient evidence to determine which of these pathways predominates.

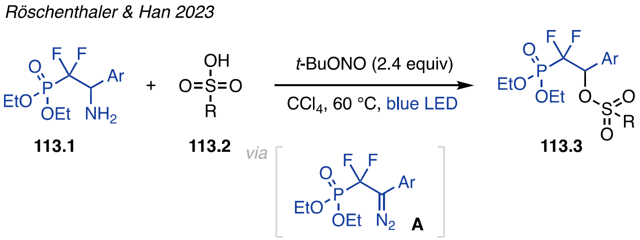
9.5. (*β*-Amino-*α*,*α*-difluoroethyl)phosphonates

In 2021, Röschenthaler and Han's groups disclosed the *in situ* formation of (2-diazo-1,1-difluoroethyl)phosphonates **113.1** from corresponding amine precursors by using *tert*-butyl nitrite (Scheme 113).[251] Upon photoirradiation, a wide range of sulfonate esters **113.3** were efficiently synthesized from sulfonic acid. The proposed reaction mechanism involves a

Scheme 112. Cyclopropanation of Oxadiazolines



Scheme 113. *In Situ* Formation of Diazo Species from (*β*-Amino-*α*,*α*-difluoroethyl)phosphonates



nucleophilic substitution of diazonium by sulfonate. It is worth noting that the transformation also proceeded in the absence of blue light, albeit with lower efficiency.

10. CONCLUSIONS

Visible light-induced reactions of diazo compounds are a rapidly emerging area in organic synthesis. Despite being a relatively recent field of study, these methods have provided access to a variety of reactive intermediates from diazo compounds, as demonstrated by the wide array of transformations discussed in this review. It is anticipated that this subfield will continue to grow in the future.

Many of the photochemical, metal-free reactions of diazo compounds were performed at room temperature, frequently in air, and without requisite removal of moisture from the solvent. The ability to conduct transformations under such mild conditions enhances selectivity and prevents side reactions commonly found in thermal reactions or those induced by higher-energy UV radiation. Importantly, the reactivity or selectivity of these photochemical reactions can vary significantly from that of metal-catalyzed reactions. In the case of photocatalytic reactions, utilizing a photoredox catalyst enables the generation of radical intermediates from diazo compounds. This offers new reactivity modes for diazo compounds, which were previously regarded as carbene precursors only.

Although a substantial progress has been made in the field of visible light-induced transformations of diazo compounds, this area is still in its infancy. Furthermore, certain limitations are yet to be overcome. Within the context of photochemical reactions, a majority of transformations presented herein employ donor−acceptor or donor−donor type diazo compounds that have good absorption in the visible light region. Thus, one of the remaining challenges is to engage diazo compounds that are transparent in this region, such as acceptor types. Moreover, although several enantioselective methods have been reported by employing chiral catalyst or ligand, achieving stereoselective transformations in photochemical reactions remains majorly underexplored. Additionally, many of the reactions require the excess of one of the reacting partners. Besides these limitations, in-depth mechanistic investigations are essential to provide a more comprehensive understanding of the reaction mechanisms. Thus, it is expected that development toward asymmetric transformations and the engagement of novel diazo substrates or precursors will constitute an important future direction in this field.

We anticipated that visible light-induced reactions of diazo compounds will become a versatile strategy with broad applications in organic synthesis, pharmaceutical chemistry, and material science.

AUTHOR INFORMATION

Corresponding Author

Vladimir Gevorgyan − *Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas 75080-3021, United States;* orcid.org/0000-0002-7836-7596; Email: vlad@utdallas.edu

Author

Ziyan Zhang − *Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas 75080-3021, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.chemrev.3c00869

Notes

The authors declare no competing financial interest.

Biographies

Ziyan Zhang received her B.Sc. from Beijing Technology and Business University. In 2017, she joined the Gevorgyan group at the University of Illinois at Chicago as a Ph.D. student and later moved to the University of Texas at Dallas. Her research interests are focused on the development of novel photoinduced methodologies.

Vladimir Gevorgyan received his Ph.D. from the Latvian Institute of Organic Synthesis. After two years of postdoctoral research (1992−1994, JSPS- and CibaGeigy International Postdoctoral Fellowships) at Tohoku University, Japan, and a visiting professorship (1995) at CNR, Bologna, Italy, he joined the faculty at Tohoku University (Assistant Professor, 1996; Associate Professor, 1997−1999). In 1999, Vladimir Gevorgyan moved to USA to join UIC (Associate Professor, 1999; Professor, 2003; LAS Distinguished Professor, 2012). In 2019, he joined the University of Texas at Dallas to become a Robert. A. Welch Distinguished Chair in Chemistry. Vladimir also holds a Professor position at the University of Texas Southwestern

Medical Center. His group is interested in the development of novel synthetic methodology, particularly toward biologically relevant molecules.

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