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Blue light-induced diazo cross-coupling: synthesis of allyldiazo compounds through reshuffling of functionalities†

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In this paper, we describe a new type of cross-coupling between simple diazo and vinyldiazo compounds that gives access to unusual allyldiazo products. Blue light discriminates two diazo compounds towards free carbene formation, triggering sequential cyclopropenation, (3+2) cycloaddition and ring opening rearrangement processes. This strategy involves an overall reshuffle of diazo functionality and olefinic carbons of vinyldiazo compounds with an extrusion of nitrogen. Mechanistic studies including a ^{15}N-labelling experiment demonstrate that the diazo functionality of allyldiazo products derives from simple diazo compounds, while vinyldiazo reagents are selectively decomposed *via* energy transfer with thioxanthone photocatalyst. The obtained allyldiazo compounds can be efficiently converted into synthetically useful structures such as 1,3-dienes, *gem*-difluoro-1,4-diene, hydrazine, dihydropyrazole, pyridazine, and bicyclobutane.

Introduction

The chemistry of diazo compounds has been intensively studied since the first synthesis of ethyl diazoacetate by Curtius in 1883.[1,2] The coupling of diazo compounds by complete decomposition of two diazo moieties is an alternative method for the synthesis of unsymmetrically substituted alkenes.[3,4] However, this transformation has not found widespread applications due to the inevitable competition between homo- and cross-coupling processes.[5] The challenge for the selective cross-coupling lies in the discrimination of diazo compounds toward carbenoids because most of them are readily decomposed by transition metals or under thermal and photochemical conditions. Diazo compounds are often coloured molecules, and their absorption is significantly affected by the substituents of the diazo carbon.[6] In 2018, Jurberg and Davies pioneered the photolysis of aryldiazoacetates under blue light irradiation.[7] Soon after this work, we reported a blue light-promoted selective diazo cross-coupling for the synthesis of trisubstituted alkenes by distinguishing aryldiazoacetates from other diazo compounds.[8] Since then, various classical transition metal-catalyzed transformations of diazo compounds have been re-examined using visible light as the sole energy source, unlocking novel reaction pathways *via* free carbene intermediates.[9]

As a result of its high reactivity, the diazo group is usually introduced onto a targeted product at the end of synthesis.[2e] Additional functionalization of an existing diazo compound without affecting the diazo functionality is also a promising method to prepare complex or even unconventional diazo compounds.[10] Such manipulation usually employs relatively stable diazo compounds and relies on the transformations of molecular skeleton remote to the diazo functionality. Regarding the reactions of two diazo compounds, it is difficult to decompose one diazo compound while conserving the diazo functionality of another. In this context, our group developed a photoredox-enabled self-(3+2) cyclization of two vinyldiazo reagents, which provides cyclopentene derivatives with retention of one diazo functional group in the products.[11]

At this point, we became intrigued in the photochemical reaction of vinyldiazo with simple diazo compounds. Previous works by Davies and Sun disclosed the selective cross-coupling of vinyldiazoacetates and aryldiazoacetates for the generation of conjugated 1,3-dienes catalyzed by Rh(II) and Au(I) respectively (Scheme 1a-1).[4] Switching the ligands, the Au(I)-catalyzed cross-coupling of these two diazo compounds can produce *N*-substituted pyrazoles.[12] The selective diazo cross-coupling towards pyrazoles was also reported by Melen using a borane catalyst (Scheme 1a-2).[13] Barluenga demonstrated the discrimination of simple and vinyldiazo systems towards carbenoids by a Cu(I) catalyst, allowing the formation of cyclobutenes *via* a sequential cyclopropanation/ring expansion process (Scheme 1a-3).[14] Nevertheless, these transformations always result in the complete decomposition or functional loss of diazo groups. Herein, we report the use of blue light to discriminate vinyldiazo and simple diazo compounds, leading to the formation of

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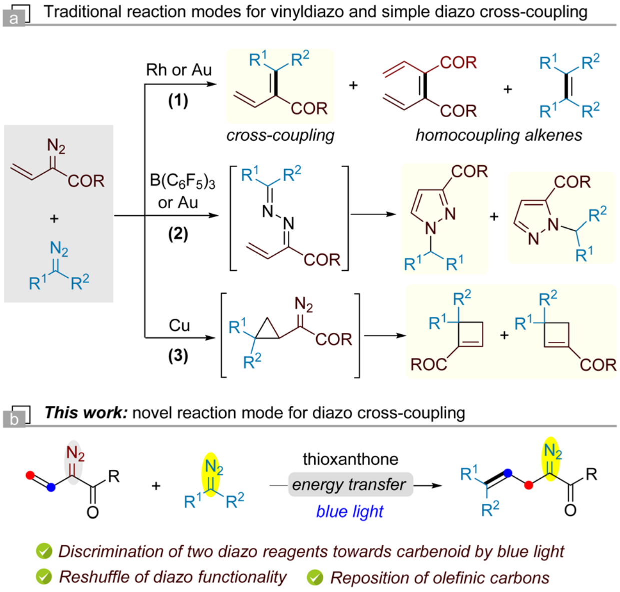
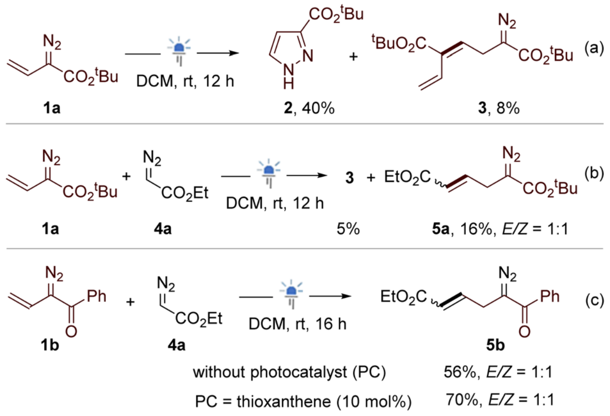


Scheme 1 The reactions of simple diazo and vinyldiazo compounds.



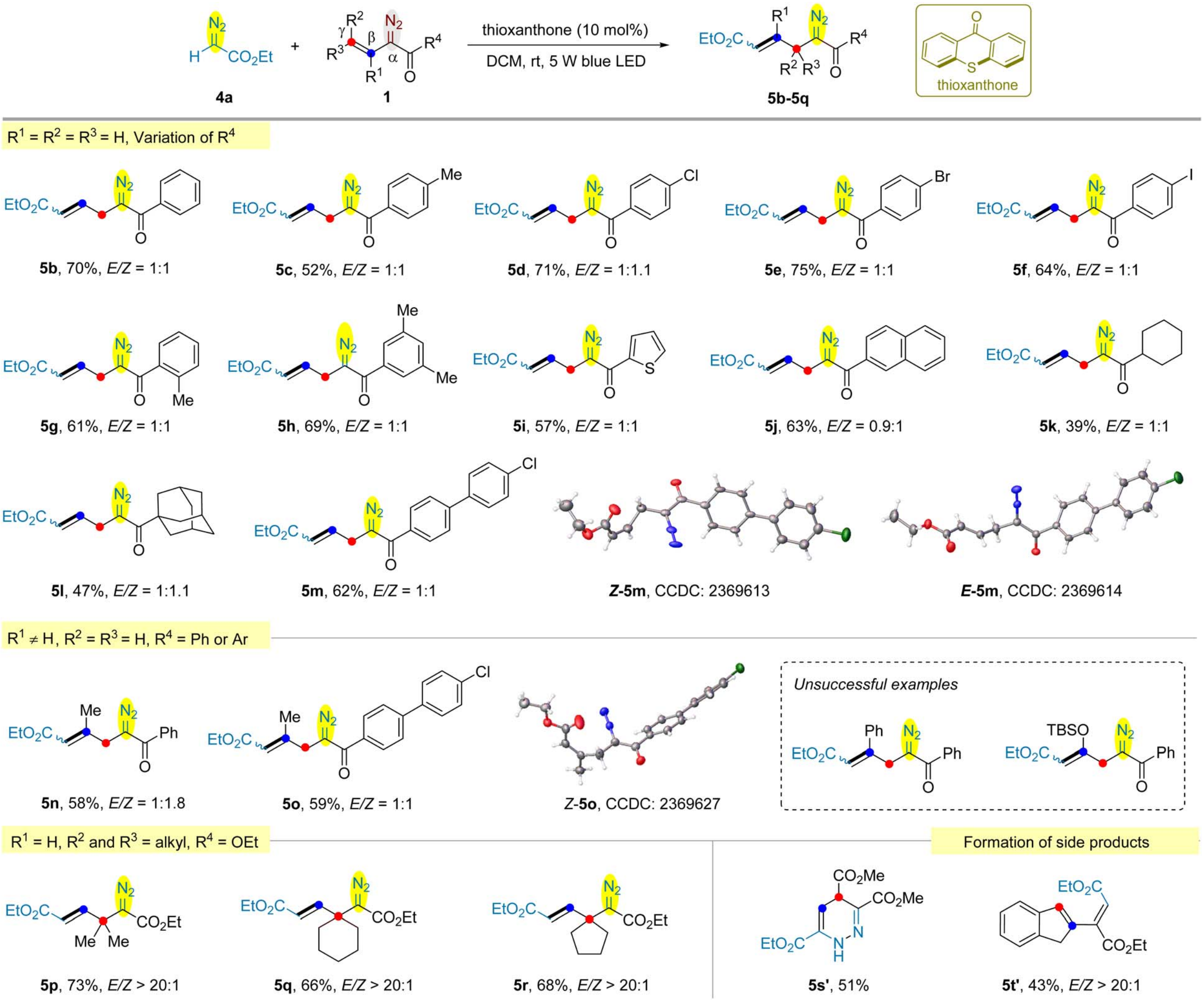
Scheme 2 Selective diazo cross-coupling toward allyldiazo compounds.

allyldiazo compounds *via* a distinct diazo cross-coupling reaction. Both vinyldiazo and simple diazo compounds undergo structural reorganization in which the diazo functionality and olefinic carbons have been reshuffled with an extrusion of nitrogen. Due to the low energy of blue light, such allyldiazo products can be isolated and were used for further derivatization on the basis of the rich chemistry of the diazo functional group.

Results and discussion

During our studies of photochemical reactions of vinyldiazo compounds,[15] we need to examine the stability of typical substrates under light irradiation conditions in the presence or absence of photocatalysts. Irradiating the DCM solution of *tert*-butyl vinyldiazoacete **1a** for 2 h without photocatalyst provided minor amount of pyrazole *via* 1,5-electrocyclization.[16] After prolonging the irradiation time to 12 h, despite the yield of pyrazole **2** increased to 40%, an unexpected homo-coupling diazo product **3** was isolated in 8% yield (Scheme 2a). However, efforts to further improve the yield of **3** failed. We envisioned that the vinyl group of another molecule of **1a** might only act as a substituent. To validate the hypothesis, the reaction of ethyl diazoacetate **4a** with **1a** was examined. Except for the homo-coupling product **3** (5% yield), the cross-coupling product **5a** was obtained in 16% yield (Scheme 2b). We were delight to find that the irradiation of vinyldiazoketone **1b** and **4a** afforded allyldiazo **5b** in 56% yield and the homo-coupling of **1b** was not observed (Scheme 2c). This interesting result encouraged us to optimize the reaction conditions using **1b** and **4a**. It was found that the yields of **5b** were not significantly affected by the solvents (see Table S1 in the ESI†). The addition of thioxanthone as the photocatalyst can increase the yield to 70%, while other photocatalysts such as benzophenone, riboflavin, Ru(bpy)$_3$Cl$_2$, fac-Ir(ppy)$_3$ disfavoured the reactions. The best reaction time is 16 h because further prolonging the irradiation time led to the gradual decomposition of allyldiazo product.

Under the above optimized reaction conditions, we explored the scope of the reaction. As shown in Scheme 3, the cross-coupling of ethyl diazoacete **4a** with vinyldiazo bearing distinct aryl ketones gave the desired allyldiazoketones **5c**–**5h** in 52–75% yields. Many substituents, including methyl and halogen (Cl, Br, and I) at the *ortho*- (**5g**), *meta*- (**5h**) and *para*- (**5c**–**5f**) are well tolerated. The reaction was also compatible with 2-thienyl ketone (**5i**) and 2-naphthyl ketone (**5j**). We prepared vinyldiazo alkyl ketones (R^4 = cyclohexyl and adamantyl), and their reactions with **4a** afforded allyldiazo compounds **5k** and **5l** in moderate yields. Allyldiazoketone **5m** is a solid and both structures of its *Z*- and *E*-isomers were confirmed by X-ray diffraction. Subsequently, the cross-coupling of β-methyl substituted vinyldiazoketone **1n** with ethyl diazoacetate **4a** was examined. Surprisingly, the β-methyl group of **1n** relocated at γ-position in the product **5n**, indicating a rearrangement occurred in this reaction. The X-ray diffraction of *Z*-isomer of allyldiazoketone **5o** confirmed our proposed structure. Switching the methyl on the β-position to phenyl or OTBS led to complex mixtures. Although we detected the formation of allyldiazoketones by GC-MS, the attempt to obtain pure products failed. To further verify the reposition, γ,γ-dimethyl substituted vinyldiazoacetate **1p** was employed to react with **4a**, providing **5p** in 73% yield with >20 : 1 *E*/*Z* selectivity. It was found that both methyl groups were presented on the β-position of product **5p**. Using exocyclic vinyldiazoacetates **1q** and **1r** as the substrates, no ring expansion was observed and the corresponding allyldiazoacetates **5q** and **5r** were obtained in 66% and 68%, respectively.[17] However, 1,4-dihydropyridazine **5s′** was isolated as the major product in the reaction of **4a** with vinyldiazoacete **1s** bearing an ester motif at the γ-position. We speculate that the additional electron-withdrawing ester group further destabilized the cyclopropane of 2,3-diazabicyclo[3.1.0]hex-2-ene intermediate, thus facilitating the direct cleavage of weakened fused [*c*] bond to form 1,4-dihydropyridazine.[18] The cross-coupling of 2-indenyldiazoacetate **1t** with **4a** provided

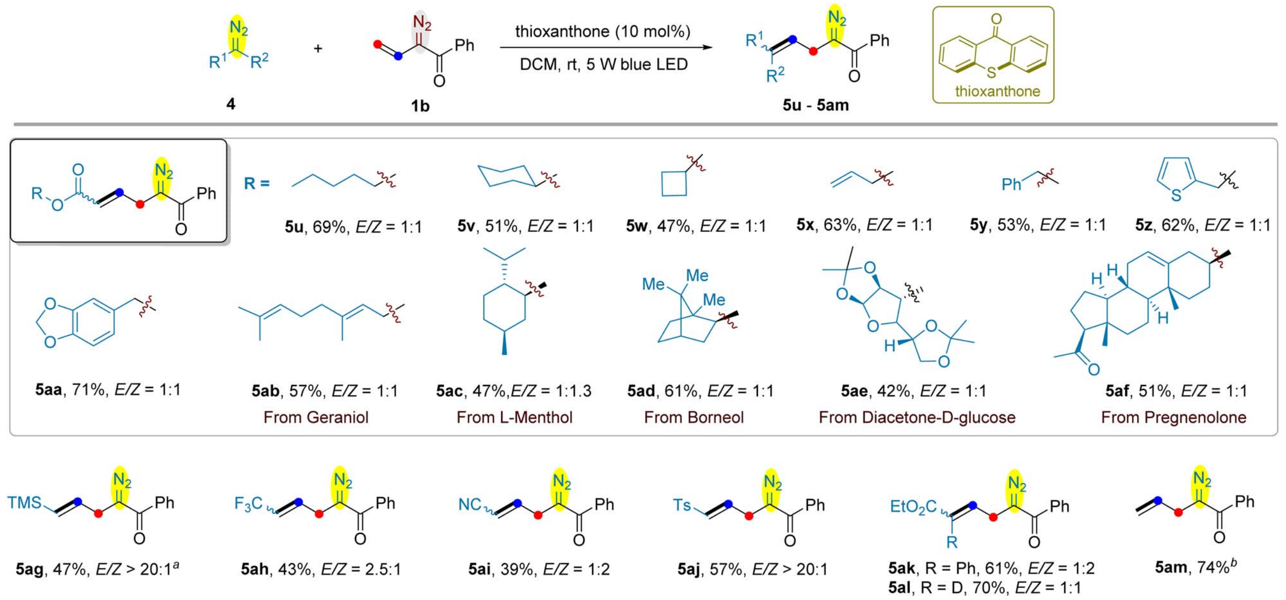


Scheme 3 Visible light-promoted cross-coupling of ethyl diazoacetate **4a** with various vinyldiazo compounds. Reaction conditions: vinyldiazo compound **1** (0.4 mmol, 2 equiv.), ethyl diazoacetate **4a** (0.2 mmol, 1 equiv.), thioxanthone (10 mol%), DCM (2 mL), rt, 5 W blue LED, 16 h. Isolated yields of the products.

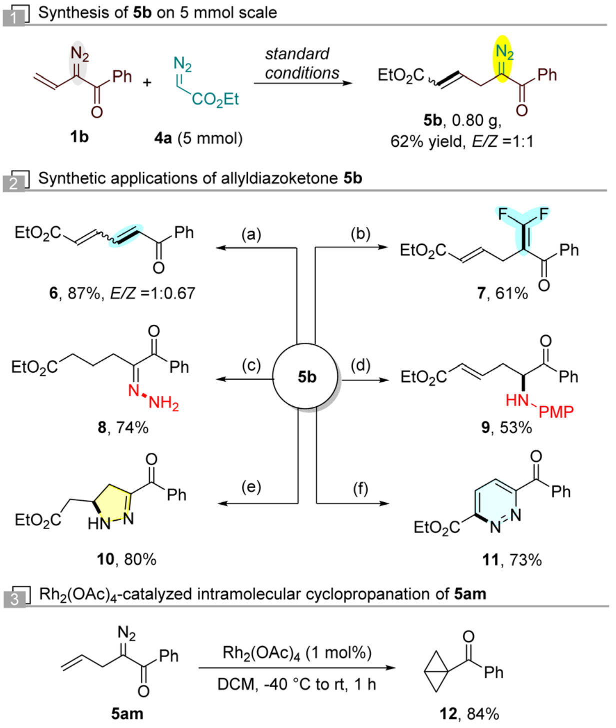
carbene dimerization product **5t′** presumably due to the difficulty in generating indene-fused cyclopropene.

Next, we used vinyldiazoketone **1b** to examine its cross-coupling with a series of acceptor-type diazo compounds (Scheme 4). Alkyl diazoacetates, such as *n*-pentyl (**5u**), cyclohexyl (**5v**) and cyclobutyl (**5w**) were found to react with **1b** smoothly to give the anticipated coupling products **5u–5w** in 47–69% yields. The C–C double of allyl diazoacetate remained intact, providing **5x** in 63% yield. Benyzl (**5y**) and its analogues such as thiophenylmethyl (**5z**) and benzodioxolylmethyl (**5aa**) in the ester motif of diazoacetates were compatible. Encouraged by these results, diazoacetates deriving from naturally occurring alcohols, including geraniol (**5ab**), L-menthol (**5ac**), borneol (**5ad**), diacetone-D-glucose (**5ae**), and pregnenolone (**5af**) were employed for the cross-coupling with vinyldiazoketone **1b**; and they were all converted into the corresponding allyldiazoketones in satisfactory yields. The electron-withdrawing group of acceptor-type diazo compounds is not limited to ester, as exemplified by the use of trimethylsilyl (**5ag**), trifluoromethyl (**5ah**), cyano (**5ai**), and tosyl (**5aj**) substituteddiazomethanes as the substrates. The reaction of donor–acceptor aryldiazoacetate with **1b** afforded the product **5ak** in 61% yield. However, acceptor–acceptor diethyl diazomalonate was not suitable substrate for this reaction. Replacing the terminal hydrogen of ethyl diazoacetate **4a** by deuterium led to allyldiazoketone **5al** bearing a vinyl C–D bond in identical yield as compared to **5b**. Finally, we were delighted to find that the cross-coupling of **1b** with unstable diazomethane proceeded smoothly, providing allyldiazoketone **5am** in 74% yield. In most of cases, the *E*- and *Z*-isomers were separable, except for **5ah**, **5ai** and **5ak**.

To demonstrate the synthetic applications of allyldiazo compounds, the cross-coupling of vinyldiazoketone **1b** and ethyl diazoacetate **4a** was performed on 5 mmol scale (Scheme 5-1). Both *E*- and *Z*-isomers of **5b** were isolated in 62% total yield in a ratio of 1 : 1. Typical transformations of allyldiazoketone **5b** were shown in Scheme 5-2. Using $Cu(MeCN)_4PF_6$ as the catalyst, *E*-**5b** underwent selective 1,2-*H* migration to give conjugated 1,3-diene **6** in 87% yield. *gem*-Difluoroalkene **7** was obtained in 61%



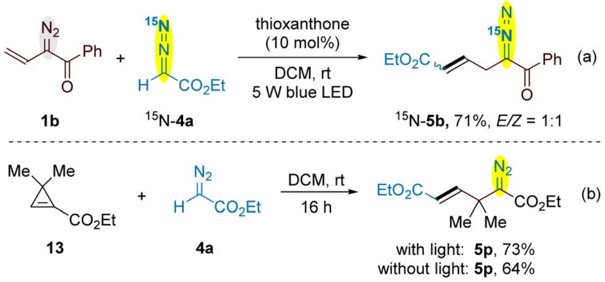
Scheme 4 Visible light-promoted cross-coupling of vinyldiazoketone **1b** and simple diazo compounds. Reaction conditions: vinyldiazo ketone **1b** (0.4 mmol, 2 equiv.), simple diazo compound **4** (0.2 mmol, 1 equiv.), thioxanthone (10 mol%), DCM (2 mL), rt, 5 W blue LED, 16 h. Isolated yields of the products. [a] The ratio of $TMSCHN_2$ and vinyldiazoketone **1b** is 2 : 1. [b] The reaction was carried out using 20 equiv. of CH_2N_2 in 3 mL of DCM/Et_2O ($v:v = 1:2$).



Scheme 5 Synthesis of **5b** on 5 mmol scale and synthetic applications of the products. (a) *E*-**5b** (0.1 mmol), $Cu(MeCN)_4PF_6$ (10 mol%), DCM, rt; (b) *E*-**5b** (0.1 mmol), $TMSCF_3$ (1.2 equiv.), NaI (2 equiv.), THF, 65 °C; (c) **5b** ($E/Z = 1:1$, 0.1 mmol), PtO_2 (10 mol%), H_2 (1 atm), HOAc (1 equiv.), EtOAc, rt; (d) *E*-**5b** (0.1 mmol), $Cu(MeCN)_4PF_6$ (5 mol%), *p*-anisidine (1 equiv.), DCM, rt; (e) **5b** ($E/Z = 1:1$, 0.1 mmol), P^nBu_3 (3 equiv.), $^iPr_2O$, rt; (f) **5b** ($E/Z = 1:1$, 0.1 mmol), DABCO (1 equiv.), DCM, rt.

yield *via gem*-difluoroolefination of the diazo group of *E*-**5b**. Both the diazo group and C–C double were reduced by hydrogen gas (1 atm), affording hydrazine **8** in 74% yield. Cu-catalyzed N–H insertion of *E*-**5b** onto *p*-anisidine produced the corresponding product **9** in 53% yield. In the presence of P^nBu_3, the reduced **5b** (1 : 1 *E*/*Z* mixture) further underwent intramolecular Michael addition to form dihydropyrazole **10** in 80% yield. Treatment of **5b** (1 : 1 *E*/*Z* mixture) with DABCO led to pyridazine **11** in the air. Although intermolecular cyclopropanation of **5b** with styrene was unsuccessful due to the competitive 1,2-*H* migration, we were delighted to find that $Rh_2(OAc)_4$-catalyzed intramolecular cyclopropanation of allyldiazoketone **5am** produced bicyclo[1.1.0]butane **12** in 84% yield (Scheme 5-3).[19]

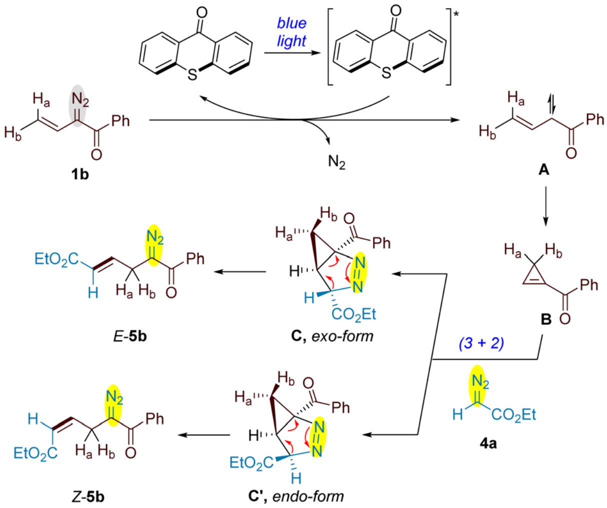
In this cross-coupling reaction of vinyldiazo and simple diazo system, only one diazo group is decomposed while another is preserved in the products. To figure out the origin of diazo functionality of the products, we prepared ^{15}N-labeling ethyl diazoacetate **4a** and its cross-coupling with vinyldiazoketone **1b** provided ^{15}N-**5b** in 71% yield (Scheme 6a). This result indicated that the reaction was initiated by the decomposition of vinyldiazo compounds. Very recently, the conversion of vinyldiazo compounds to unstable cyclopropenes under blue light irradiation has been reported by several groups.[20] To verify cyclopropene is involved as an intermeidate in this reaction, a stable cyclopropene **13** was prepared and its reactions with ethyl diazoacetate **4a** provided allyldiazo compound **5p** with or without the irradiation of blue light (Scheme 6b).[21] Indeed, such a 1,3-dipolar addition of stable cyclopropenes with diazo compounds to give 2,3-diazabicyclo[3.1.0]hex-2-enes has been reported, which usually underwent rapid rearrangement to form 1,4-dihydropyridazines under the reaction conditions or



Scheme 6 (a) The cross-coupling of **1b** with ^{15}N-**4a**; (b) the reaction of stable cyclopropene **13** with ethyl diazoacetate **4a**.

on treatment with a trace of acid or base.[22] The thermal or photolytic rearrangement of 2,3-diazabicyclo[3.1.0]hex-2-enes to form diazo compounds is also viable, but in most cases bicyclo[1.1.0]butanes or complex mixture were obtained due to the decomposition of diazo compound under reaction conditions.[23] The luminescence quenching experiments demonstrated that vinyldiazoketone **1b** displayed luminescence quenching of the excited state of thioxantone*, while a decrease was not observed by adding ethyl diazoacetate **4a** (Fig. S1–S3 in the ESI†). Vinyldiazoketone **1b** has a slightly higher oxidation potential ($E_{1/2}$ = + 1.35 V *vs.* SCE) than thioxantone ($E_{1/2}^{\mathrm{PC*/PC-}}$ = + 1.18 V *vs.* SCE),[24] suggesting the single electron transfer between **1b** and the excited thioxantone is less likely (Fig. S4 in the ESI†). As shown in Scheme 2c, moderate yield of **5b** was obtained without photocatalyst, while the use of thioxanthone of high triplet energy (E_{T} = 63.4 kcal mol^{-1}) increased the yield.[24] Therefore, the current reaction process may go through an energy-transfer mechanism. The conjugated vinyldiazoketones are better quenching reagents than other diazo compounds. Using slightly excess amounts of vinyldiazo starting materials can suppress the further decomposition of allyldiazo products (for the reaction time profile, see Fig. S5 in the ESI†).

A plausible mechanism for this new type of diazo cross-coupling reaction has been depicted in Scheme 7. Under the irradiation of blue light, the energy transfer between photoexcited thioxanthone* and vinyldiazoketone **1b** generates free vinyl carbene **A** with a nitrogen extrusion. Intramolecular cyclization of **A** produces unstable cyclopropene **B**, which undergoes (3+2) cycloaddition with ethyl diazo acetate **4b** to give a mixture of *exo*- and *endo*- 2,3-diazabicyclo[3.1.0]hex-2- ene **C** and **C′** respectively. The rearrangement of *exo*-**C** by opening both cyclopropane and pyrazoline rings forms the allyldiazo product *E*-**5b**, while *Z*-**5b** is generated *via* ring-opening of *endo*-form **C′**. In the cases of γ,γ-disubstituted vinyldiazoacetates **1p–1r**, the replacement of H$_a$ and H$_b$ by alkyl groups significantly increases the steric hindrance of cyclopropane motif in 2,3-diazabicyclo[3.1.0]hex-2-enes, thus favours the formation of *exo*-intermediate **C**. The current results indicated that the bulky groups attached to carbonyl group of vinyldiazoketones or in the ester motif have little effect on the diastereoselectivity of (3+2) cycloaddition.



Scheme 7 A plausible reaction pathway.

Conclusions

In summary, we have developed a new type of cross-coupling reaction between simple diazo and vinyldiazo systems, affording allyldiazo products through sequential cyclopropenation, (3+2) cycloaddition and ring opening rearrangement processes. Unlike classical transition metal-catalyzed diazo coupling reactions, which often lead to the complete decomposition of two diazo moieties, the present photochemical protocol discriminates two diazo compounds towards free carbene formation. The reaction reshuffles another diazo functionality into the products and repositions olefinic carbons as well as substituents on them. The method depicted herein provides a distinct route to access complex or even unconventional allyldiazo compounds, which themselves are ideal precursors for advanced carbene transfer reactions.

Data availability

The data underlying this study are available within the article and in the ESI.†

Author contributions

JT, JL and YW performed the experiments and analysed the data. LZ conceived and directed the project. LZ prepared the manuscript while JT prepared the ESI.† All authors discussed the experimental results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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