

Photosensitizer-Free Photoinduced Ground-State Triplet Carbene-Assisted Aryloxy Radical Generation via HAT

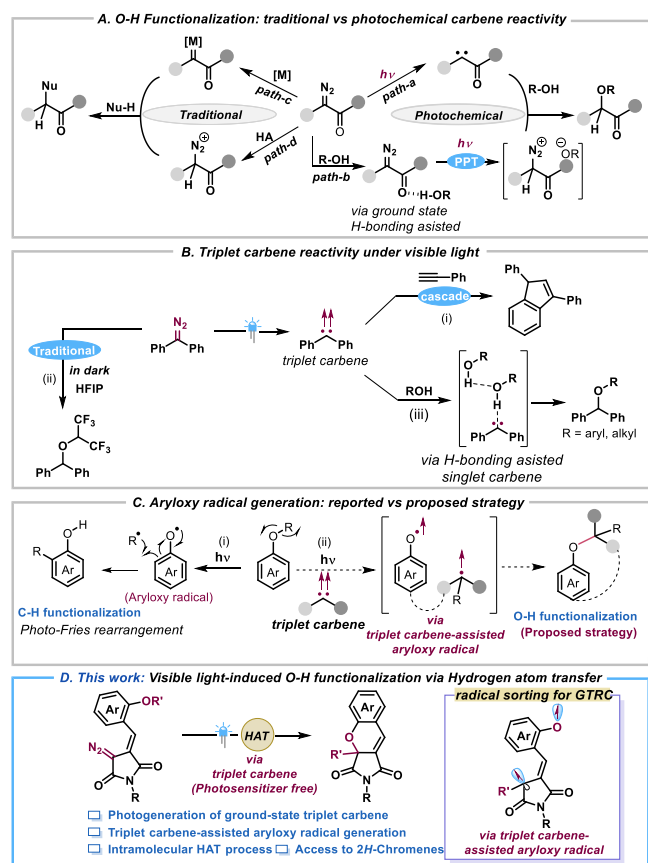
Debasish Laha,^a Onkar S. Bankar,^a Balu S. Navale,^{a,b} Supriyo Santra,^c Debashree Ghosh^c and Ramakrishna G. Bhat^{*a}

Carbene is the pivotal reactive intermediate and its reactivity potential has been extensively explored in a variety of synthetic transformations ranging from cycloaddition to site-selective C–H functionalizations. However, controlling the reactivity of carbene is a key parameter for achieving the selective carbene transfer reactions. Usually, strategies rely on the combined effect of metal catalysts and ligands to accomplish the selective transformations *via* the generation of singlet carbene intermediate. Contrarily, the triplet carbene has gained a very little attention from the researchers as its generation and reactivity relies on the use of specific metal complexes thus limiting its wider utility. Nevertheless, the organic transformations involving a triplet spin state carbene have been explored with diazo compounds under visible light utilizing photosensitizer. However, the development of the visible light induced sensitizer-free strategy for the generation of triplet carbene is highly challenging and is seldom reported. Herein, we have demonstrated vinyl diazosuccinimide as a new class of diazo compound which upon exposure to blue LEDs (456 nm) generates ground-state triplet carbene (without ISC) in the absence of any photosensitizer. We have successfully explored this strategy and utilized to construct the biologically relevant scaffold such as 2*H*-chromenes. A series of control experiments, EPR studies as well as DFT calculations have supported the existence of ground-state triplet carbene followed by the aryloxy radical during the course of the reaction.

Introduction

Visible light-induced diazo decomposition has emerged as a viable and practical technique for the generation of free carbene under metal-free and mild reaction conditions.¹ The spin state and the reactivity of carbene, and its singlet-triplet splitting are dependent on the electronic as well as steric properties of the substituents that are directly attached to the carbene carbon center.² While some of the recent studies have demonstrated the free singlet carbene reactivity and that can be selectively achieved *via* the photolysis of mainly donor/acceptor-type diazo compounds (Scheme 1A_Path-a).¹ Very recently a few reports have gained significant attention on the free triplet carbene reactivity/radical reactivity and these are typically based on the use of photosensitizers/energy transfer catalysts utilizing acceptor-type diazoacetates.³ In this context, Meggers,^{3a} Gryko,^{3b} Doyle,^{3c,e} Koenigs,^{3d,f} and their co-workers have reported the reactivity of diazo compounds in presence of sensitizers that are usually inaccessible in the ground state.⁴ Some of these strategies have successfully trapped the photoexcited state reactivity *via* photoinduced electron transfer (PET),^{3a,b} proton-coupled electron transfer (PCET)^{3c,e} and/or photoinduced proton transfer (PPT) processes.^{4a,b,5} Very recently, Koenigs and co-workers have elegantly explored the photobase-reactivity pattern of unreactive diazoacetates with mild acids such as phenols/alcohols for the O–H functionalization by exploring the PPT strategy under low energy visible light irradiation for the very first time (Scheme 1A_Path-b).⁵ This strategy was triggered by the photoexcitation of a ground state unreactive hydrogen-bonded complex unlike the traditional carbene transfer reactions which usually proceed either *via* metallo-carbene O–H insertion (Scheme 1A_Path-c)^{6a-c} or through protonation-substitution reactions with strong

acids (Scheme 1A_Path-d).^{6d} Despite the ground-breaking progress on the photoexcited state triplet carbene reactivity utilizing photosensitizers, it will be even more challenging to develop the photoinduced sensitizer-free triplet carbene generation for the organic transformations. Moreover, the direct generation of ground-state triplet carbene⁷ and their useful synthetic applications have scarcely been reported.⁸ Usually, sensitizer-free generation of ground-state triplet carbene is tedious and above all the rapid singlet vs triplet spin state equilibrium restricts its synthetic applications.^{8c} It's also interesting to note that ground-state triplet carbenes have numerous applications in material science for their paramagnetism.⁹ Very recently, the Koenigs research group has elegantly demonstrated the protocol for tuning the reactivity of carbene precursors (diazo compounds) to carry out the transformations either *via* singlet carbene or triplet carbene in a controlled manner by varying the electronic properties of substituents over the diazo compounds [e.g.; see Scheme 1B(i)].^{8a} In 2022, the same research group has further illustrated the direct alkylation of hydroxyl group with diphenyl diazoalkanes in absence of light which followed the traditional route [Scheme 1B(ii)].¹⁰ While interestingly, the diphenyl diazoalkanes under the photochemical conditions led to the triplet carbene that undergoes intersystem crossing (ISC) to singlet carbene *via* the alcohol assisted hydrogen-bonding subsequently leading to rapid protonation and C–O bond formation [Scheme 1B(iii)].¹⁰ However, to the best of our knowledge there are no reports on the use of diazo compounds for the direct alkylation of hydroxyl group *via* visible light induced hydrogen atom transfer (HAT) process. This formidable challenge could be addressed by the successful and selective generation of triplet state carbene or diradical intermediate in



Scheme 1 (A) O–H functionalization: traditional vs photochemical condition, (B) Direct photoinduced triplet carbene-based organic applications, (C) Aryloxy radical generation strategies, and (D) O–H functionalization via HAT.

a controlled manner so as to react with hydroxyl group in its triplet state. Unlike the previous report¹⁰ wherein the triplet carbene undergoes ISC to form singlet carbene through hydrogen bonding, the proposed photoinduced HAT process is expected to through hydrogen atom transfer retaining its triplet state and subsequently to form a radical (via intermolecular approach) or a diradical species (via intramolecular approach) or even through aryloxy radical. Whereas the well-known photo-Fries rearrangement¹¹ is the resultant of traditional photoinduced cleavage to generate phenoxy radical leading to C–H bond functionalization [Scheme 1C(i)]. However, it is very important to note that the catalyst-free triplet carbene-assisted aryloxy radical formation directly from arenols to achieve direct O–H bond functionalization remains as a challenging task till date [Scheme 1C(ii)].

Vinyl diazosuccinimide is emerging as a versatile reagent in recent years for its distinct structural features^{12a} with diverse metallo-carbene reactivity explored in a variety of transformations ranging from cycloaddition to site-selective C–H bond functionalization.¹² Despite the progress, its reactivity under visible light has not been investigated so far. Based on our continuous interest and experience in dealing with diazosuccinimide under metal catalysis, we sought to explore its photochemical reactivity to achieve the convenient and

sustainable approach under metal-free conditions to construct the molecules of industrial relevance with potent bioactivity.

Herein, in this article vinyl diazo succinimide has been utilized for the direct intramolecular O–H functionalization to access biologically important chromeno[2,3-*c*]pyrrole-1,3(2*H*,3*aH*)-diones under visible light conditions. Also, we have successfully demonstrated the protocol by tuning the reactivity of vinyl diazosuccinimide for generating singlet or triplet carbene selectively. Furthermore, as a proof of concept we have also demonstrated the photoinduced intramolecular group-transfer radical cyclization (GTRC) under catalyst-free visible light conditions that has further validated the HAT process (Scheme 1D).

Results and Discussion

Initial spectroscopic studies: In order to develop the visible light photochemical carbene reactivity of donor-/acceptor-type vinyl diazosuccinimides under milder reaction conditions, we designed and synthesized a few diazosuccinimides **2aa–2ac** (see ESI for details optimization). Further these diazo succinimides have been analysed by UV-visible absorption spectra and compared that with the absorption properties of donor-/acceptor-type phenyl diazoacetate **1**.

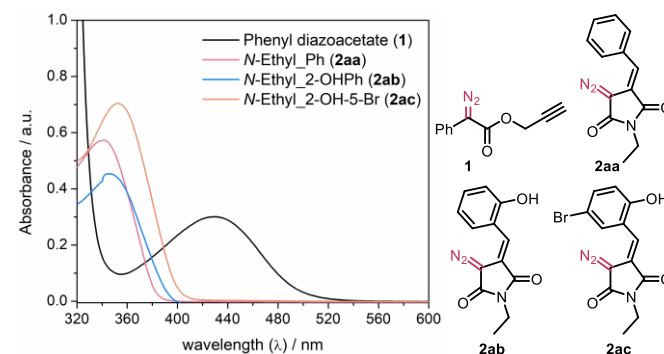


Figure 1 Photochemical properties (UV-visible absorbance spectra) of diazo compounds (**1–2ac**) in DCM (*c* = 0.2 mM).

While the phenyl diazoacetate **1** has a distinct absorption spectrum at the visible region ($\lambda_{\text{max}} = 432 \text{ nm}$), while the vinyl diazosuccinimide **2aa** exhibits a strong absorption near UV region (335 nm - 380 nm) in DCM, whereas others (**2ab–2ac**) display bathochromic shift which presumably attributes to the enhancement of electronic delocalization into the system. As blue LED has a maximum emission at 470 nm, hence they also emit radiation in 470 nm \pm 50 nm range. In this regard, we surmised that the excitation of diazo surrogates or direct photolysis of diazo surrogates (**2ab–2ac**) may happen under the irradiation of blue LEDs.

Synthetic Application:

Synthesis of chromenopyrroledione under photochemical condition

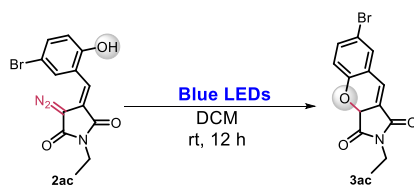
2*H*-Chromene is a privileged scaffold that is core to many pharmaceutical ingredients and is known to elicit potent bioactivities. Molecules having this scaffold as a core are known for their interesting optical properties and they are utilized as fluorescence probes and photochromic compounds.¹³ Chromeno[2,3-*c*]pyrrole-1,3(2*H*,3*aH*)-dione is a prime sub-family of 2*H*-chromenes having diverse biological properties such as

antiproliferative activity,^{14a} antitumor,^{14b-c} antiulcer,^{14d} antibacterial,^{14e} TNF- α -inhibitory activity.^{14f} Thus, the synthesis of this important subclass of 2*H*-chromene derivatives under metal-free conditions is highly desirable. We envisioned that this subunit of 2*H*-chromenes could be directly synthesized from the *ortho*-OH modified diazosuccinimides **2** in one-step under visible light conditions. It is also very important to highlight that some of the substituents like halogens, long-chain alkyl etc. at the C-6 position in 2*H*-chromenes are known to enhance the biological activities significantly.^{15a} Owing to importance of the 2*H*-chromenes as well as for exploring of the reactivity of diazosuccinimides under visible light conditions, we hypothesized a metal-free carbene-promoted strategy that would facilitate the photoinduced intramolecular O–H functionalization to construct the 2*H*-chromene scaffold.

Optimization studies of the intramolecular O–H functionalization:

Having obtained the UV-vis absorbance spectral data, in order to validate the hypothesis, we explored the initial optimization of the intramolecular O–H functionalization with 5-bromo-2-hydroxyphenyl vinyl diazosuccinimide **2ac** as a model substrate. Gratifyingly, the compound **2ac** in DCM upon exposure to the visible light irradiation (5 W Blue LEDs) at room temperature furnished the desired product **3ac** in modest yield (32%, Table 1, Entry 1). The control experiments unambiguously proved that the light is an essential energy source for the key transformation to afford the desired product **3ac**, which otherwise is inaccessible *via* thermal process (Table 1, Entries 2-3). Further optimization studies clearly revealed that the reaction is neither sensitive to air and nor to the moisture (Table 1, Entries 4-6). Also, we have observed that the reaction undergoes smoothly under low as well as high intensity blue LEDs (see ESI, section 3.3 for details). Gratifyingly, the low energy monochromatic light source (456 nm, Blue LEDs) significantly enhanced the yield of **3ac** in polar solvent such as 1,4-dioxane (65%, Table 1, Entry 7). Intriguingly, the low concentrated solution of **2ac**

Table 1 Background and Optimization Studies of the Visible Light-Induced Intramolecular O–H functionalization^a



Entry	Deviations from tested conditions ^a	Yield ^b (%) of 3ac
1	None	32 (28) ^c
2	No light	N.R.
3 ^d	No light, CH ₃ CN, at 60 °C	N.R.
4	under N ₂ atmosphere	28
5	under N ₂ atmosphere (degassed)	30
6	dry DCM	30
7 ^e	456 nm, 1,4-Dioxane, 12 h, 27 °C	65
8 ^{e,f}	456 nm, 1,4-Dioxane, 12 h, 27 °C	73
9	UV light (370 nm) instead of blue LEDs	0

^aTested reaction conditions: Diazo succinimide **2ac** (0.1 mmol), a. r. grade DCM (c = 0.066 M), blue LEDs (5 W), 25 °C, 18 h. ^bYields of **2ac** were determined by ¹H NMR spectroscopic analyses of the reaction mixture using 1,3,5-trimethoxybenzene as the internal standard. ^cIsolated yield in the parenthesis. ^dA. R. grade CH₃CN was used. ^eA. R. grade 1,4-Dioxane was used. ^fSubstrate concentration (c = 0.04 M) was used.

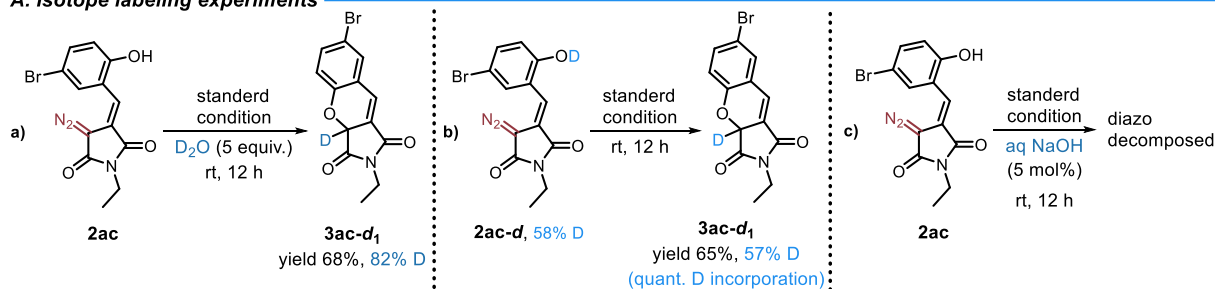
(c = 0.04 M in 0.1 mmol scale) in 1,4-dioxane under 456 nm blue light irradiation for 12 h proved to be highly efficient to afford the

corresponding desired product **3ac** in very good yield (73%, Table 1, Entry 8). On contrary, upon exposure to the UV light (370 nm), we did not observe even trace of desired product **3ac** though **2ac** was completely consumed (Table 1, Entry 9).

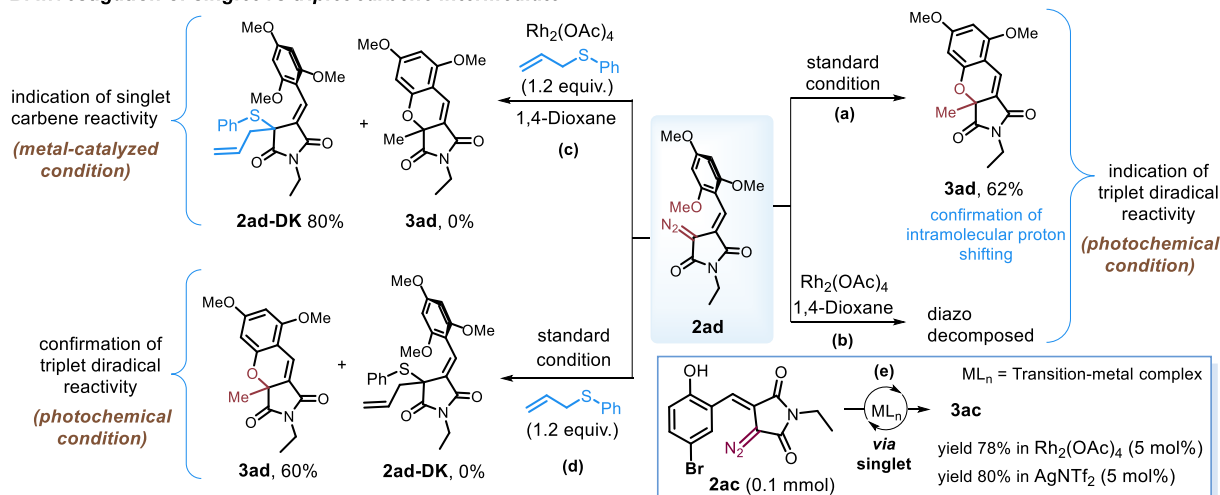
Mechanistic investigations: In order to investigate whether the intramolecular O–H functionalization is undergoing either *via* the photoinduced proton transfer process (PPT) or *via* the traditional photolysis of diazo succinimide, we performed various control experiments (Scheme 2). To begin with we carried out the labelling experiments in order to have evidence for the source of proton in the overall reaction. The diazo succinimide **2ac** upon illumination with blue LEDs (456 nm) under standard reaction condition but in presence of D₂O (5 equiv.) afforded the deuterium incorporated desired product **3ac-d₁** [82%, Scheme 2A(a)]. This result indicated that the proton source is either the moisture in the solvent or due to the deuterium exchange with phenolic -OH followed by intramolecular deuterium transfer. Further, lightening the pre-installed *ortho*-OD substituted diazo succinimide **2ac-d₁** furnished the exclusively deuterium incorporated desired product **3ac-d₁** [Scheme 2A(b)]. From this result it is evident that the hydroxyl group of **2ac** is the source of hydrogen for the intramolecular 1,6-hydrogen transfer and not the moisture. Later the addition of NaOH (5 mol%) while maintaining the standard reaction conditions completely prevented the formation of the desired product **3ac** while the **2ac** was decomposed [Scheme 2A(c)]. Probably, this may be due to the *in-situ* formation of sodium phenolate as it has been confirmed by the UV absorbance spectrum (see ESI for details, section 4.4). This result indicated the possible intramolecular O–H functionalization *via* hydrogen transfer during the course of the reaction. However, there could also be the possibility of PPT reaction pathway. In order to prove whether or not it proceeds through PPT pathway and to gain further mechanistic insight, we carried out the transformation using *ortho*-methoxy diazo arylidene succinimide **2ad** (hydroxy protected) at the standard reaction condition under illumination of blue LEDs (456 nm) in 1,4-dioxane at room temperature [Scheme 2B(a)]. Interestingly, the reaction afforded a new product **3ad** *via* the intramolecular 1,6-methyl shift [Scheme 2B(a)]. The molecular structure of this compound **3ad** was further confirmed by the single-crystal X-ray diffraction analysis.¹⁶ This interesting observation unambiguously supported the 1,6-hydrogen shift and not the proton shift from the solvent moisture (Scheme 2B(a) and (b)). Also the formation of 3a-methylchromeno[2,3-c]pyrrole-1,3(2*H*,3*aH*)-dione **3ad** very interesting and indeed ruled out the possibility of PPT pathway during the course of the titled transformation. However, this unusual yet interesting product **3ad** is likely to be formed either from the singlet carbene intermediate *via* the ylide formation or it could also be through the possible triplet diradical intermediate (see ESI, Section 4.6, Scheme S3). In order to obtain the deeper understanding about the spin state of carbene intermediate, we performed the reaction of **2ad** in presence of Rh₂(OAc)₄ [Scheme 2B(b)]. The reaction led to the decomposition of diazo succinimide **2ad** and proved to be unproductive reaction [Scheme 2B(b)]. This result indicated that the reaction of **2ad** under visible light condition might be undergoing *via* a triplet carbene intermediate [Scheme 2B(a)] as Rh₂(OAc)₄ catalyzed reaction is known to undergo *via* traditional singlet carbene intermediate through the formation of reactive rhodium carbenoid species that is well established in the literature.¹⁵

In order to have deeper insight and to examine whether or not **2ad** has capability to undergo singlet carbene reactivity under transition-metal catalysis, we carried out the reactions in presence of allyl sulfide. Interestingly, allyl phenyl sulfide, a well-known

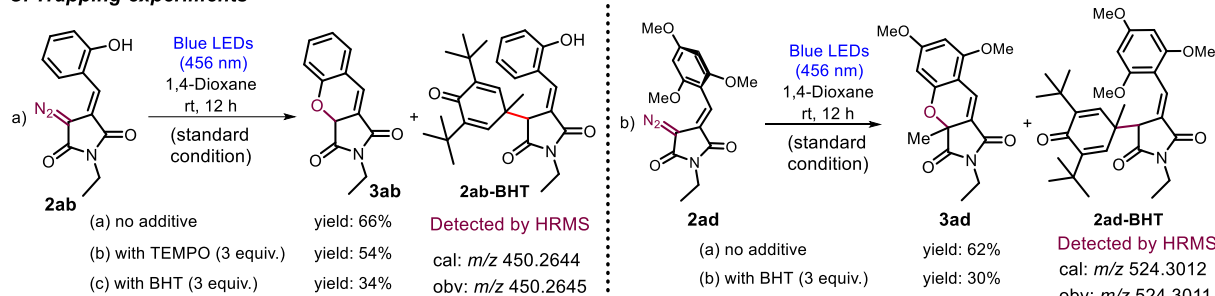
A. Isotope labeling experiments



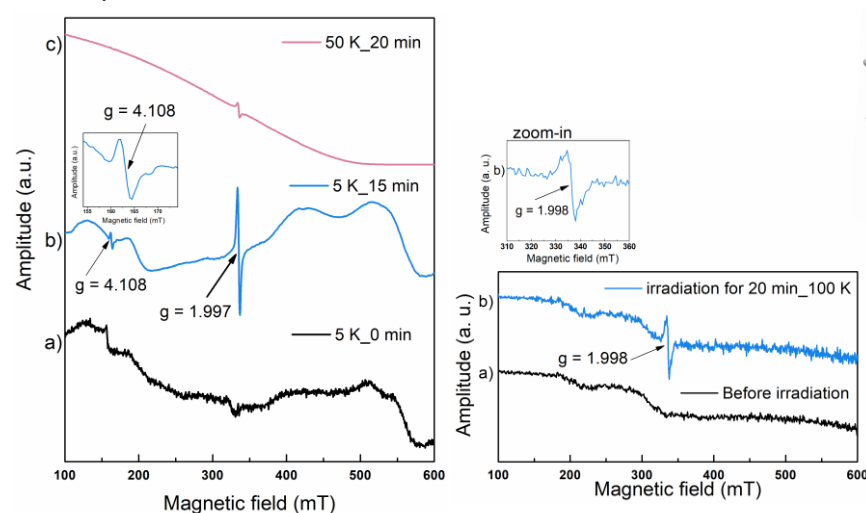
B. Investigation of singlet vs triplet carbene intermediate



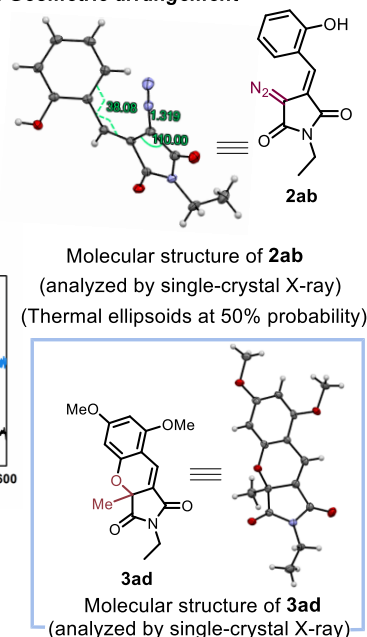
C. Trapping experiments



D. EPR experiments



E. Geometric arrangement



Scheme 2 Control experiments

reagent for the Doyle–Kirmse reaction under metal catalysis¹⁷ as well as photochemical condition *via* singlet carbene,¹⁸ upon treatment with **2ad** in presence of dirhodium acetate furnished the corresponding Doyle–Kirmse reaction product **2ad-DK** [Scheme 2B(c)] via singlet carbene and we did not observe even trace of 1,6-methyl-shifted product 3a-methylchromeno[2,3-c]pyrrole-1,3(2*H*,3*aH*)-dione **3ad** [Scheme 2B(c)]. This distinct reactivity pattern of **2ad** under the photochemical as well as metal-catalyzed reaction conditions further demonstrated the ability of diazosuccinimides to undergo a tunable carbene reactivity (singlet vs triplet) thus leading two different reaction modes. While the reaction of **2ad** with allyl phenyl sulfide under standard photochemical conditions (instead of dirhodium catalysis) gratifyingly afforded the 1,6-methyl shifted product 3a-methylchromeno[2,3-c]pyrrole-1,3(2*H*,3*aH*)-dione **3ad** (60% yield) exclusively instead of any trace of the Doyle–Kirmse reaction product **2ad-DK** [Scheme 2B(d)]. This reaction also indicates that there is a sufficient energy gap between two spin states of photochemically generated carbene species. While the reaction of **2ac** under metal catalysis (Rh, Ag) furnished the corresponding product **3ac** via singlet carbene pathway [see Scheme 2B(e)]. The product **3ad** formation via the intramolecular 1,6-methyl shift [Scheme 2B(a) and (b)] is quite remarkable. The analogous atom-transfer radical addition (ATRA) reaction was illustrated by Kharasch over 70 years ago.¹⁹ However, this kind of reaction has been achieved to some extent involving diazo compounds.²⁰ The GTRA²¹ is a very interesting concept developed recently where in the photoexcited state reactivity has been explored. Our result on intramolecular 1,6-methyl shift to obtain **3ad** is a proof of concept of GTRC.

Later we have proved the formation of diradical intermediate during course of the reaction by the carrying out the radical trapping experiments by the addition of TEMPO/BHT before the blue light irradiation to afford the corresponding products **3ab** and **3ad** in diminished yields [Scheme C(a)-(b)]. Moreover, we have also observed BHT trapped intermediates (**2ab-BHT** and **2ad-BHT**) thus supporting the formation radical species during the course of the reaction pathway. Possibly, due to the much faster intramolecular reactivity than the intermolecular one, the reaction might not have been completely quenched by the radical trapping agents.

In order to confirm the ability of diazo succinimide **2ab** to self-generate the triplet carbene (**TC**), we measured the electron paramagnetic resonance (EPR) spectrum of the **TC** precursor in a frozen matrix of 1,4-dioxane (1.0 × 10⁻³ mM) at 5 K [Scheme 2D]. After the irradiation with blue LEDs (λ = 456 nm) for 15 min, new peaks appeared at 163 mT and 335 mT that are associated with the **TC**. The decay of these peaks at 5 K was remained same for prolonged time (checked up to 2 h). With the increase in the temperature (to 50 K), the intensity of the EPR peaks gradually decreased after 30 minutes. Notably, it has been observed that diazo succinimide **2ad** is proved to be a **TC** precursor as it is confirmed by the peak appeared at 336 mT in frozen 1,4-dioxane matrix of **2ad** under irradiation of visible light (456 nm Blue LEDs) at 100 K.

The molecular structure and geometric arrangements of the diazosuccinimide (**2ab**) was unambiguously determined using single-crystal X-ray analysis.²¹ The bond angle of ∠C–C(N₂)–C is determined as 110° with a dihedral angle θ ~ 38° at the *s-cis* conformation occurring from the orientation of benzylidene ring.

Computational DFT calculations: The plausible reaction pathway and the existence of triplet carbene as well as radical species has been further evaluated on the basis of density functional calculations [B3LYP/6-31G(d)] of the starting vinyl diazo succinimide **2ac** using Q-Chem quantum chemistry software^[22] and Gaussian09.^[23] The

excitation energies of the lowest excited states of the diazo compound **2ac** are given in Table S1 (see also ESI, Section 4.10). It has been observed that the singlet state (S2) is optically bright and there are two triplet states (T3 and T4) that are in the vicinity of the bright state S2. The spin orbit couplings between S2–T3 and S2–T4 are 8.11 and 11.57 cm⁻¹ respectively. This results clearly supports the favourable transition from singlet to triplet state carbene.

In order to validate the mechanism of rearrangement, further calculations have been performed on the structure **Int-I** formed after N₂ gas extrusion upon photoexcitation (Figure 2, **Int-I**). Here it is confirmed that the triplet carbene is more stable than the singlet carbene for **2ac** (Shown in Table 3). It has been observed that the potential energy surface along the rearrangement reaction and the activation energy is found to be extremely low (~1 kcal/mol, Energy) for the forward reaction (Figure 2) which further leads to the formation of stable triplet diradical intermediate **Int-II** (Figure 2). Subsequently, the conversion to open-shell singlet **Int-II'** (by 8.7 kcal/mol, Energy) allows the formation of the C–O bond which is a downhill process and therefore very facile as shown the potential energy surface (Figure 2).

Looking at practicability and based on the computational calculation of O–H functionalization of the *ortho*-OH substituted derivative, we expect qualitatively similar pathway to be feasible and favorable for that of the 1,6-methyl shift in case of **2ad** as an analogy. The reason for this low activation energy barrier can be attributed to the singly occupied molecular orbitals (SOMOs) of the reactant (**Int-I**) and **TS** which are similar in energy and nature (Figure 3).

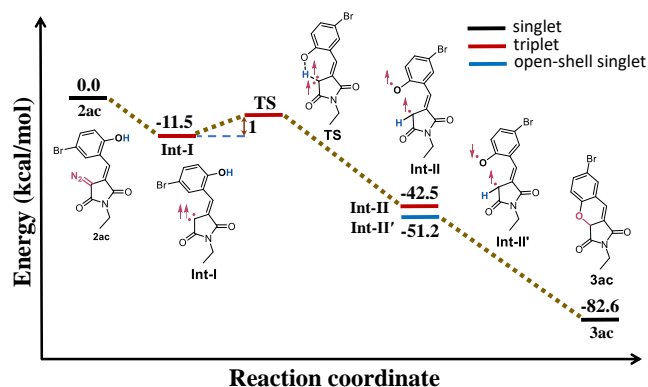


Figure 2 Potential energy surface of the proposed reaction mechanism; calculated at the [B3LYP/6-31G(d)] level of theory.

Table 3 The energies of the triplet and singlet states of **2ac**

Spin state	Energy (in Hartree)
Singlet	-3355.5633
Triplet	-3355.6120

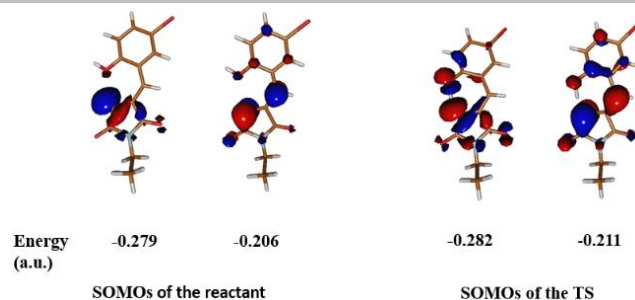


Figure 3 Molecular orbitals of the reactant and the **TS** along with their energies.

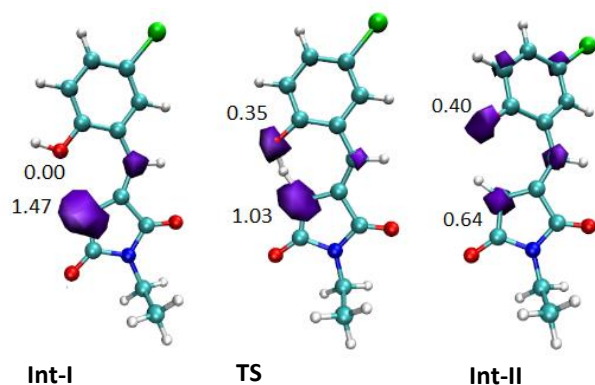
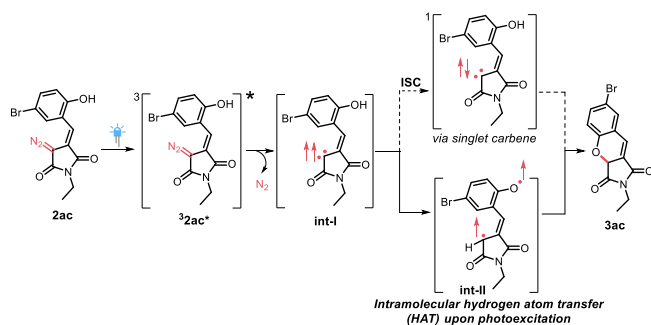


Figure 4 Plot of spin density mapping.

In the Figure 4, it can be seen that for the **Int-I** there is a large accumulation of spin (the purple color blobs) on the carbene C ($\rho = 1.47$) on the triplet state, but as we go forward to the **TS**, the spin density gets distributed in between C ($\rho = 1.03$) and O ($\rho = 0.35$) centers and forms a diradical species. In **Int-II** the spin gets delocalized on the whole molecule (spin densities $\rho = 0.64$ and 0.40 over C and O centers respectively). This shows that the reaction proceeds from the triplet carbene to the final product via a diradical transition state.

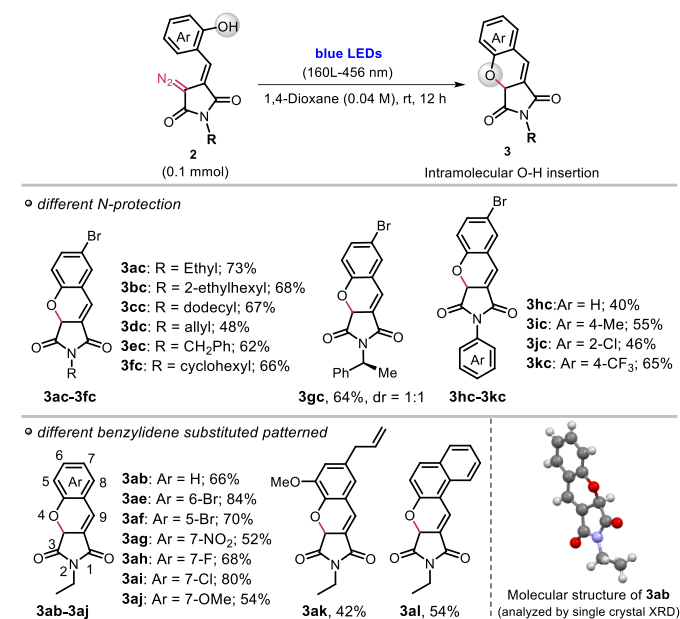


Scheme 3 Plausible mechanism for the O-H functionalization.

On the basis of the several control experimental findings and DFT calculations, a plausible mechanistic pathway for the intramolecular O-H functionalization has been depicted (Scheme 3). The diazo succinimide **2ac** upon irradiation with blue light (465 nm) gets excited directly to form the photoinduced ground-state triplet carbene $^3\mathbf{2ac}^*$ (without ISC) which subsequently leads to the intermediate **Int-I** by the extrusion of dinitrogen. Regardless of undergoing to singlet carbene via ISC, this intermediate **Int-I** further undergoes the intramolecular 1,6-hydrogen atom transfer at the expense of cleavage of the O-H bond and formation of a new C-H bond leading to the formation of triplet intermediate **Int-II** via **TS**. **Int-II** upon spin-flipping converted to barrierless open-shell diradical intermediate **Int-II'** which subsequently furnishes the desired product **3ac**.

Substrate Scope studies: Having optimized the reaction condition and systematically looked into the mechanistic pathway, we turned our attention to expand the substrate scope looking at the diverse biological properties of the chromeno[2,3-c]pyrrole-1,3(2*H*,3*aH*)-dione. In this regard, in order to evaluate the practicability and generality of the developed methodology, we synthesized a diverse range of aryl-substituted as well *N*-protected 2-hydroxyphenyl vinyl diazosuccinimides (**2bc–2kc**). Different *N*-protected 5-bromo-2-

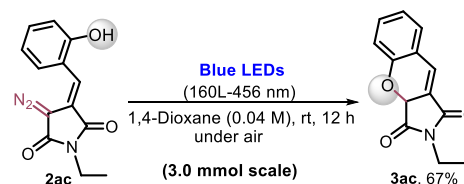
hydroxybenzylidene diazosuccinimides (**2bc–2kc**) under optimized reaction conditions afforded the corresponding desired products (**3bc–3kc**) in moderate to good yields (up to 68%, see Scheme 4). While the *N*-aryl substituted diazosuccinimides (**2hc–2jc**) having electron-donating, -withdrawing and -deactivating groups under the



Scheme 4 Substrate scope studies of intramolecular O-H functionalization.

optimized reaction condition afforded the corresponding desired products (**3bc–3jc**) in modest to moderate yields (up to 65%, Scheme 4). Interestingly, the chiral auxiliary derived *N*-(*S*)-1-phenylethyl 2-hydroxyphenyl vinyl diazosuccinimide **2gc** afforded the desired O-H functionalization product **3gc** in moderate yield (64%) albeit in low diastereoselectivity (dr 1:1, Scheme 4). Later, we explored the reactivity of few *N*-ethyl 2-hydroxyaryl vinyl diazosuccinimides having different substituents at the phenyl group (**2ab–2ak**) under the optimized reaction conditions. Gratifyingly, all the derivatives tolerated the reaction conditions to afford the corresponding desired products (**3ab–3ak**) in moderate to very good yield (up to 80%, Scheme 4). The 2-hydroxynaphthalene substituted diazosuccinimide **2al** also furnished the corresponding desired product **3al** in 54% yield. The molecular structure and geometric arrangements of the 2*H*-chromene **3ac** has been unambiguously determined by the single-crystal X-ray diffraction analysis.¹⁶

In order to have wider practicability of this visible light mediated protocol, the reaction of 5-bromo-2-hydroxyphenyl vinyl diazosuccinimide **2ac** has been carried out on a gram scale quantity to afford corresponding desired product **3ac** in moderate yield (0.93 g, 67% yield, Scheme 5).



Scheme 5 Gram-scale synthesis of chromenopyrroledione

Conclusions

In summary we have demonstrated the vinyl diazosuccinimide as a new class of bench-stable diazo compound that is susceptible to undergo direct photo-generation to ground-state triplet carbene without any photosensitizer when exposed to visible light irradiation. The distinct electronic structure, as well as geometrical arrangement of diazosuccinimides, make them unique from other diazoalkanes which have been reported to be unstable. We have successfully demonstrated the novel reactivity of hydroxyl substituted bezylidene succinimides to access biologically important chromeno[2,3-*c*]pyrrole-1,3(2*H*,3*aH*)-dione by directly exploring the potential of ground-state triplet carbene through the HAT pathway. For the first time a protocol has been developed that relied on the triplet carbene-assisted aryloxy radical to access useful scaffold. This class of diazo compounds having interesting photoreactivity and capability to have tunable reactivity under both photochemical and transition metal reaction conditions have been explored. A series of systematic control experiments, computational calculations (excited state DFT) supported the photoinduced hydrogen atom transfer (HAT) process occurring throughout the reaction pathway. Also, we have demonstrated group-transfer radical cyclization (GTRC) process as a proof concept. The high spin ground state species possess huge applications in magnetic materials and these new class of diazo succinimides may prove to be efficient platform to access useful compounds.

Data availability

General information, detailed experimental procedures, characterization data for all new compounds, and NMR spectra are in the ESI. EPR data has been included. Data for the crystal structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under the deposition number CCDC 2267622 (compound **2ab**), 2289687 (compound **3ac**), and 2289689 (compound **3ad**).

AUTHOR INFORMATION

Corresponding Author

***Ramakrishna G. Bhat** – Department of Chemistry, Indian Institute of Science Education and Research (IISER)-Pune, 411008 Pune, Maharashtra, India; orcid.org/0000-0002-7739-9553; Email: rgb@iiserpune.ac.in

Authors

Debasish Laha^a, Onkar S. Bankar^a

^aDepartment of Chemistry, Indian Institute of Science Education and Research (IISER)-Pune, 411008 Pune, Maharashtra, India; orcid.org/0000-0002-2479-6467

Balu S. Navale^{a,b} - ^aDepartment of Chemistry, Indian Institute of Science Education and Research (IISER)-Pune, 411008 Pune, Maharashtra, India; ^bDepartment of Chemistry, Institute of Science, Nagpur, Maharashtra 440001, India

Supriyo Santra,^c Prof. Debashree Ghosh^c - ^cSchool of Chemical Sciences, Indian Association for the Cultivation of Sciences, Jadavpur, Kolkata 700032, India

Author Contributions

D. L. conceived the project, optimized the reaction, performed the investigation on the control experiments, other spectroscopic techniques, the scope of the reaction, the purification of final compounds, and the first draft of the manuscript and prepared ESI. O. S. B. and B. S. N purified the starting materials. S. S. performed the computational DFT calculation and the first draft of the corresponding part. D. G. supervised the DFT part. R. G. B. supervised the project, edited the manuscript and proofread the experimental part.

Conflicts of interest

“There are no conflicts to declare”.

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