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Electron donor–acceptor complex-driven photocatalyst-free synthesis of nitrocyclopropanes†

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Herein, a visible light-promoted metal-free protocol for the synthesis of nitrocyclopropanes under mild conditions is reported. Specifically, the process is driven by the photochemical activity of ternary EDA complexes formed upon complexation of α-bromonitrostyrenes and DIPEA in the presence of benzaldehyde. This reaction provides a variety of densely functionalized cyclopropanes with good selectivity under mild reaction conditions. Mechanistic investigations on the aspects of the process also demonstrate formation of the hypothesized EDA complex.

Introduction

Cyclopropanes, with their high strain energy and unique structure, have been fascinating organic chemists for decades. The cyclopropane motif is present in a broad range of natural products and bioactive compounds[1] and has widespread application in modern drug discovery owing to its ability to influence the physico-chemical and pharmacological properties of small molecules.[2] Moreover, owing to their strained ring, cyclopropanes possess higher reactivity than other alkanes, making them important precursors or key intermediates in synthetic chemistry.[3] Therefore, the preparation of cyclopropanes has attracted much attention over the past decades.[4]

Traditional strategies for the construction of the cyclopropane ring involve the reaction of alkenes with carbenoids. These carbenoids are usually generated from organozinc, samarium or chromium reagents and halomethanes[5] or by the transition-metal-catalyzed decomposition of diazo compounds.[6] Another common cyclopropanation strategy relies on the Michael-initiated ring closure (MIRC) reaction of electron-deficient alkenes.[7] A relevant example is the Corey–Chaykovsky reaction, initiated by the reaction of sulfur ylides with enones.[8]

As with every other field in organic synthesis, the chemistry of cyclopropanes is evolving, with a greater concern on the environmental impact caused by the hazardous chemical wastes generated by industries and laboratories.[9] In this regard, visible light-mediated cyclopropanation recently emerged as a promising alternative strategy to build cyclopropane backbones in a more sustainable fashion.[10] The vast majority of these cyclopropanation strategies typically involve the generation of carbenes from diazo precursors and their reaction with olefins.[11] As an alternative strategy, Suero's group developed an alkene cyclopropanation reaction of olefins based on the photocatalytic generation of radical carbenoid species.[12] Using this concept, several cyclopropane derivatives were prepared from diverse Michael acceptors *via* photocatalytic cascade radical carbenoid addition/cyclopropanation reactions (Scheme 1a).[13]

Although the direct intermolecular construction of cyclopropanes *via* photocatalysis was a remarkable development, the synthesis of nitrocyclopropanes remained unattainable, as nitroolefins were not suitable Michael acceptors for carbenoid radicals.[13a] In fact, to the best of our knowledge, the photocatalytic synthesis of nitrocyclopropanes is still unknown and has never been the focus of systematic investigation. Nitrocyclopropanes are a unique class of cycloalkanes that combine the conformational rigidity of the cyclopropane ring and the reactivity associated with the presence of a nitro group.[14] Therefore, there have been significant efforts toward the synthesis of nitro-functionalized cyclopropanes.[15]

Inspired by the work of Suero's group on the photocatalytic cyclopropanation of Michael acceptors, we herein report a photocatalyst-free strategy for the synthesis of nitrocyclopropanes from highly versatile α-bromonitrostyrenes,[16] in which the initiating radical is generated within the Michael acceptor *via* the formation of a ternary electron donor–acceptor (EDA) complex between α-bromonitrostyrenes and DIPEA in the presence of benzaldehyde (Scheme 1b).

In the past few years, EDA complex photochemistry has emerged as a powerful strategy for expanding the potential of visible-light-promoted radical chemistry.[17] The strategy differs from catalysis in that no external photocatalyst is added, but rather an advantage is taken of the formation of an electron

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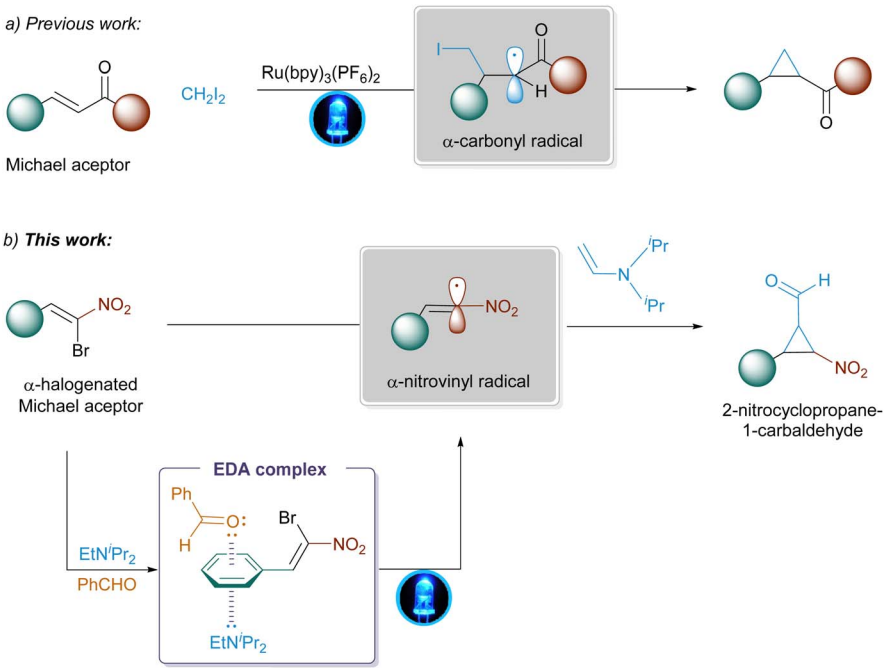


Scheme 1 Methods for the photocatalytic construction of cyclopropanes from Michael acceptors.

donor–acceptor (EDA) complex that absorbs visible light from two or more compounds that do not.[18] Visible light irradiation then triggers an intramolecular single-electron-transfer (SET) event, able to generate radical intermediates under mild conditions.[19] The most common synthetic application of the EDA complex activation strategy involves the light-driven coupling of two substrates, which are also involved in the EDA complex formation, the donor and the acceptor.[20] In this regard, the chemical diversity of the reaction products is limited by the required donor and acceptor properties on the two molecular scaffolds that finally end up in the products. A recent strategy developed to overcome this limitation is to introduce sacrificial donor compounds that aggregates with the electron donor and electron acceptor partners and increase productive light absorption without directly participating in the process.[21] This approach improved the synthetic versatility of the photochemistry of EDA complexes, since the electronic properties of the reactants can be tuned by the addition of a suitable additive.

Results and discussion

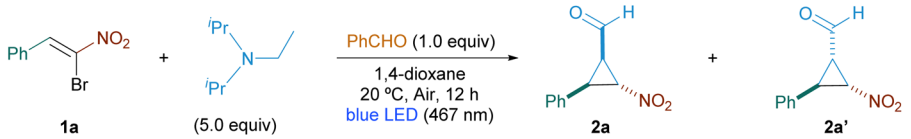
Initially, we evaluated the cyclopropanation of α-bromonitrostyrene **1a** as model substrate in the presence of DIPEA and stoichiometric benzaldehyde as a sacrificial electron donor, in 1,4-dioxane as solvent at 20 °C, under irradiation with 465 nm blue LED, and an air atmosphere. We were delighted to find that the reaction led to the expected 2-nitrocyclopropane-1-carbaldehydes **2a**/**2a′** in good yield and moderate diastereoselection (74%, *d. r.* 68 : 32). The relative stereochemistry of the obtained products was confirmed by NOE experiments on **2a**/**2a′** and from the coupling constants of the ring protons.

We evaluated other solvents, donors and visible-light sources and the results are depicted in Table 1. 1,4-Dioxane was the most effective solvent for promoting the reaction, while other commonly used solvents gave less favorable results (entries 2–6). Poorer efficiency was also observed when reactions were irradiated at other blue LED wavelengths (entries 8, 9). Under irradiation with either purple or green LED (entries 7, 10) the reaction failed, as both light sources are unable to activate the EDA complex. We further identified benzaldehyde as the most effective sacrificial donor.

Electron-donating and electron-withdrawing substituents in the benzylic ring alter the electron donor properties, affecting the formation of the EDA complex and deactivating the desired radical process (entries 11, 12). In addition, aromatic ketones were not suitable for efficiently forming the required EDA complex (entry 13).

One particularly relevant parameter in photoredox chemistry is the reaction temperature. Although this parameter has often been neglected, recent studies highlight that efficient control of the temperature is crucial to achieve reproducible results.[22] In fact, an increased number of photoredox reactions have been described as requiring a defined temperature range to obtain optimal results.[23] To avoid reproducibility issues and ensure optimal temperature control, we developed a simple and cost-effective set-up that can overcome the limitations of the configurations in current use for controlling the temperature in photoredox reactions. Moreover, as a thermostatic fluid from a recirculating chiller/heater unit is used, the arrangement permits temperature control over a wide range of temperatures. This possibility encouraged us to explore the effect that temperature has on the yield and selectivity of the cyclopropanation process. Surprisingly, when the cyclopropanation

Table 1 Optimization studies



Entry	Deviation from the standard conditions[a]	Yield[b] (%)	d.r[c]
1	None	74	68/32
2	DMF as solvent	25	n.d[d]
3	CH_3CN as solvent	34	59/41
4	CH_2Cl_2 as solvent	37	52/48
5	Toluene as solvent	42	57/43
6	DME as solvent	58	61/39
7	390 nm purple LED	0	n.d
8	440 nm blue LED	16	n.d
9	456 nm blue LED	29	n.d
10	525 nm green LED	0	n.d
11	*p*-$MeOC_6H_4CHO$ as donor	10	n.d
12	*p*-ClC_6H_4CHO as donor	34	n.d
13	PhCOPh as donor	26	n.d
14	0 °C	44	42/58
15	40 °C	68	70/30
16	60 °C	0	n.d
17	6 h reaction time	49	59/41
18	24 h reaction time	71	66/34
19	Without PhCHO	0	n.d
20	2 equiv. PhCHO	73	68/32
21	In the dark	0	n.d
22	Under N_2	Traces	n.d

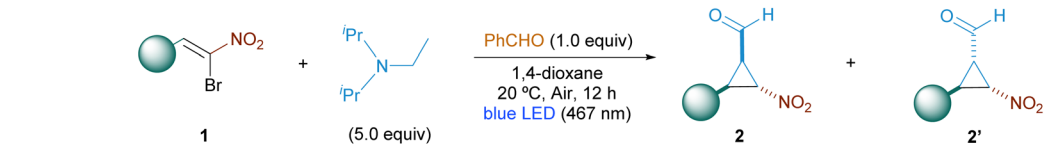
[a] Standard reaction conditions: α-bromonitrostyrene **1a** (0.3 mmol), benzaldehyde (0.3 mmol) and DIPEA (1.5 mmol) in 2 mL of 1,4-dioxane under air, irradiation with a 465 nm lamp (52 W) at 20 °C for 12 hours. [b] Isolated yield after column chromatography. [c] Diastereomeric ratio **2a**/**2a′** determined using ^{1}H NMR (300 MHz) analysis. [d] Not determined.

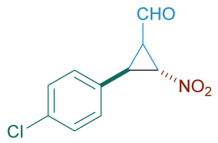
of α-bromonitrostyrene **1a** was performed at 0 °C, the selectivity was reversed and 2-nitro-cyclopropane-1-carbaldehyde **2a′** was the major isomer isolated from the reaction mixture. However, the process was less efficient both in terms of yield and selectivity (entry 14). On the contrary, when the temperature of the process was raised to 40 °C, the diastereoisomeric ratio of the cyclopropanation products **2a**/**2a′** was similar to that of the reaction performed at 20 °C, whereas the yield slightly decreased (entry 15). Attempts to further increase the temperature of the process resulted in a complex reaction mixture in which the desired cyclopropanes could not be detected (entry 16). Shorter times led to lower product yields (entry 17) and no significant differences were observed, in terms of yield, when the reaction was carried out at longer reaction times (entry 18).

Control experiments further confirmed that benzaldehyde (entry 19) and light (entry 21) are essential components for this process. The reaction is not significantly affected by a higher concentration of benzaldehyde (entry 20). Furthermore, when the reaction mixture was degassed and irradiated under nitrogen atmosphere, only traces of the cyclopropanation were detected by ^{1}H NMR (entry 22). This result underscores the essential role of oxygen in this transformation.

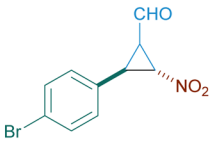
To investigate the substrate scope of this cyclopropanation strategy, α-bromonitroalkenes **1** containing various substitutions were reacted under the optimal conditions (Table 2). The substituent group on the aryl moiety of the bromonitrostyrene had a significant effect on the reactivity and efficiency of the cyclopropanation reaction. Specifically, bromonitroalkenes bearing halogenated electron-withdrawing groups on the aromatic ring (fluoro, trifluoromethyl, chloro, and bromo) were well tolerated, leading to cyclopropanation products with moderate to good yields. In contrast, the cyclopropanation of bromonitrostyrenes bearing electron-donating groups (methyl and methoxy) required longer reaction times and gave rise to the cyclization product in comparatively lower yields. The cyclopropanation process was also sensitive to steric bulk, and the position of the substituents on the phenyl moiety markedly affected the reaction efficiency. Furanyl bromonitroalkene was also amenable for this photo-transformation, affording the target cyclopropanes **2k**/**2k′** in moderate yields. However, these latter products are unstable and significantly degrade upon purification, even in neutral alumina. In all cases, except for **2k**/**k′**, the remaining mass balance comprised mainly unreacted starting material, along with other minor non-identified byproducts. 4-(Methoxycarbonyl)-substituted bromonitrostyrene was

Table 2 Scope of α-bromonitroalkene cyclopropanation

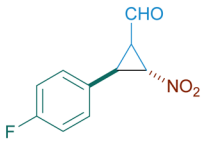




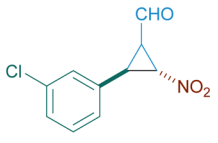
2b/2b': 48% yield[a]
d.r.[b] 71/29



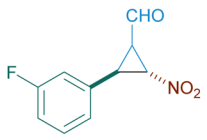
2c/2c': 52% yield
d.r. 64/38



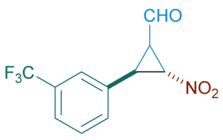
2d/2d': 50% yield
d.r. 70/30



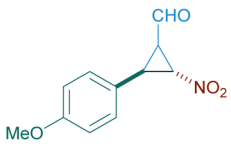
2e/2e': 38% yield
d.r. 64/38



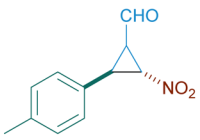
2f/2f': 42% yield[c]
d.r. 63/37



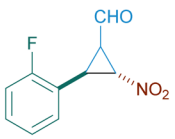
2g/2g': 45% yield[c]
d.r. 74/26



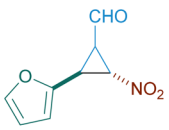
2h/2h': 28% yield[d]
d.r. 74/26



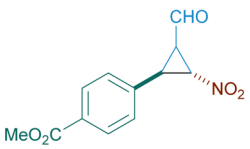
2i/2i': 32% yield[d]
d.r. 67/33



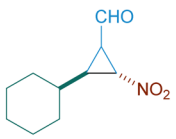
2j/2j': 39% yield[d]
d.r. 59/41



2k/2k': 40% yield[e]
d.r. 64/26



n.r.



n.r.

[a] Isolated yield after column chromatography. [b] Diastereomeric ratio 2/2′ determined using ^{1}H NMR (300 MHz) analysis. [c] Reaction time 24 h. [d] Reaction time 48 h. [e] Purification over neutral alumina.

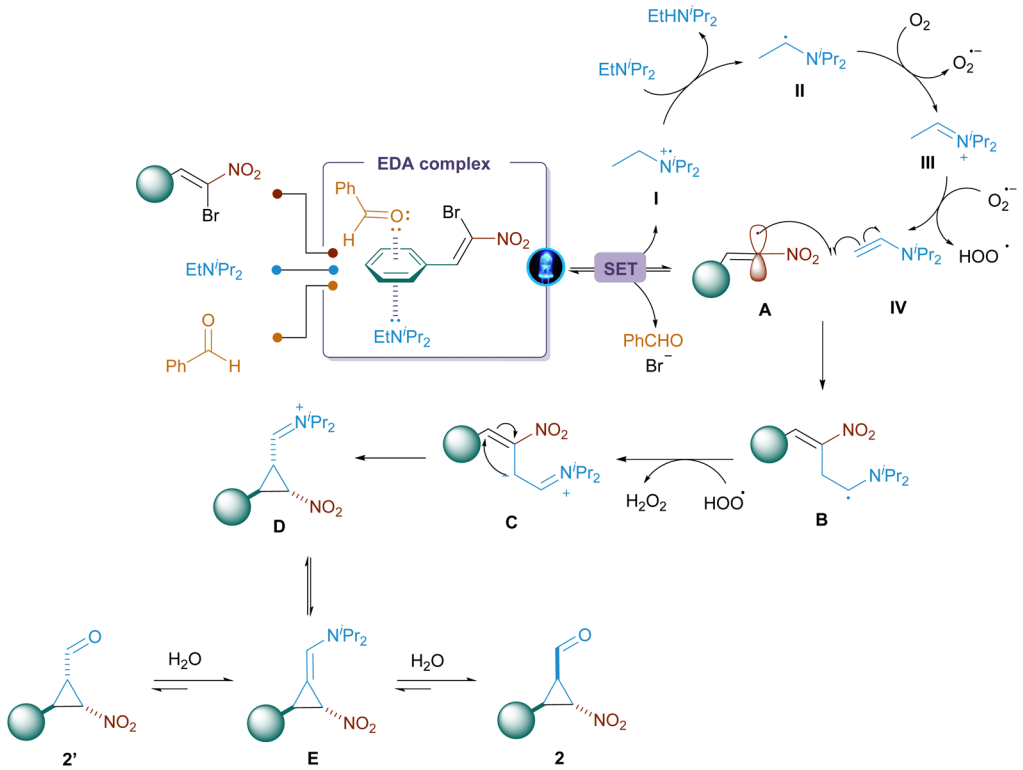
inapplicable to the cyclopropanation protocol, probably due to destabilizing interactions of the carbonyl group. Aliphatic 2-bromo-2-nitrovinyl cyclohexane also failed to produce the desired cyclopropanes, pointing to the need of a conjugated π-system to obtain satisfactory results.

We considered that alternative Michael acceptors could be cyclopropanated by using the process developed for α-bromonitrostyrenes. However, α-bromo-α,β-unsaturated esters and amides and α-bromocyanostryrene were not suitable for this radical cyclopropanation reaction. Furthermore, the use of α-iodonitrostyrene as a starting material also failed to produce the desired nitrocyclopropanes **2a**/**2a**′.

To gain further insight into the mechanism underlying this visible light-promoted cyclopropanation, a series of control experiments and spectroscopy assays were carried out. First, the addition of the radical scavenger TEMPO under the standard reaction conditions completely inhibited the formation of the desired product, confirming the intermediacy of the radical species. To investigate the possibility of a propagative mechanism occurring within this system, we conducted a ''light on/light off'' experiment, which showed that no radical chain propagation events took place (see the ESI† for details). In order to confirm the formation of a ground EDA complex between α-bromonitroalkene, DIPEA and benzaldehyde, the system was examined by UV-Vis spectroscopy. Specifically, upon mixing bromonitrostyrene and DIPEA in 1,4-dioxane, a weak but detectable bathochromic shift was observed in the UV-Vis spectrum. Subsequent addition of benzaldehyde to the mixture and further measurement of the UV-Vis spectrum indicated a significant red shift and increased absorption of visible light, corresponding to the charge-transfer absorption of a ternary EDA complex.

This observation is consistent with the expected charge redistribution among these three components to form a ternary EDA complex, which enables more productive light absorption (see the ESI† for details).

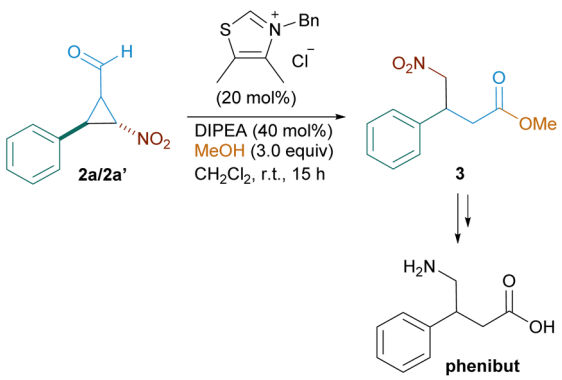
Based on the above experiments, a plausible mechanism for this new cyclopropanation reaction is proposed in Scheme 2.



Scheme 2 Proposed mechanism for the EDA complex-driven cyclopropanation strategy.

Initially, the molecular interactions of α-bromonitrostyrene, DIPEA and benzaldehyde lead to the formation of a ternary EDA complex. Under excitation by visible light, a single electron transfer (SET) process takes place. The electron-accepting intermediate, the α-bromonitrostyrene radical anion, loses the bromine leaving group, leading to the intermediate nitrovinyl radical **A**. On the other hand, the electron-donor DIPEA forms the corresponding amine cation radical **I**, while benzaldehyde is recovered without any changes.

The amine radical cation **I** in the presence of DIPEA as H atom acceptor affords α-amino radical **II**.[24] Subsequently, a dioxygen molecule captures the electron, generating a superoxide radical, which undergoes hydrogen atom transfer (HAT) with the generated imine **III** to form enamine **IV**.[25] Formation of enamines from trialkylamines in visible light photoredox processes has been widely reported, as the competitive alkylation of enamines has been one of the major problems facing successful implementation of intermolecular radical coupling reactions.[26] The addition of the α-nitro vinyl radical to the enamine forms a C–C bond and generates the strongly reducing α-amino radical **B**, which can be rapidly oxidized with the [HOO$^\bullet$] radical species to the corresponding iminium cation **C**.[27] Subsequent abstraction of a hydrogen atom α to the iminium ion, followed by intramolecular nucleophilic Michael-addition affords cyclopropane **D**, which tautomerizes into enamine **E**. Upon hydrolysis, nitrocyclopropane **2′** is formed, which can be epimerized through the enolate intermediate **E** to provide **2**. Due to the electrostatic repulsion between the nitro group and the carbonyl group, **2′** is less stable, and the balance favors the formation of **2**.[28] The observed dependence of the diastereoselectivity on the temperature is in agreement with the proposed mechanism. Thus, at lower temperatures, the reaction proceeds under kinetic control, where a faster-forming isomer **2′** is favoured. When the temperature is increased, this reaction shifts to thermodynamic control, where the stereoisomeric ratio is enriched in the more stable isomer **2**.



Scheme 3 Organocatalytic ring-opening reaction of nitrocyclopropanes **2a/2a′**.

In order to investigate the synthetic utility of the photoinduced nitrocyclopropanation reaction and based on the pharmacological importance of GABA (γ-amino butyric acid) derivatives, the chemoselective ring-opening of the 1-formyl-2-nitrocyclopropane ring was carried out under heterocyclic carbene catalysis.[29] As depicted in Scheme 3, reaction of

nitrocyclopropanes **2a**/**2a′** and methanol in the presence of both DIPEA and catalytic 3-benzyl-4,5-dimethylthiazol-3-ium chloride, afforded in good yield the corresponding methyl 3-nitro-3-phenylpropanoate **3**, precursor of anxiolytic drug phenibut (3-amino-3-phenylpropanoic acid).[30]

Conclusions

In summary, this study describes a simple and effective metal-free, visible light-mediated method for the direct formation of nitrocyclopropanes from α-bromonitrostyrenes. This approach exploits the photochemical activity of electron donor–acceptor (EDA) complexes formed between α-bromonitrostyrenes, DIPEA and benzaldehyde, which acts as a sacrificial donor.

Selective photolysis to the EDA complex leads to the generation of the nitrovinyl radicals, which are suitably trapped by an enamine radical trap *in situ* generated from DIPEA. The subsequent intramolecular Michael reaction, followed by hydrolysis, provides a potent and versatile synthetic method for the effective formation of 2-nitrocyclopropane-1-carbaldehydes. Mechanistic studies support the proposed formation and photolysis of an EDA complex.

The synthetic utility of the 1-formyl-2-nitrocyclopropane products was demonstrated by conversion of cyclopropane **2a** to the corresponding γ-nitromethylester **3**, precursor of the GABA analogue phenibut.

Experimental section

General methods

All the bromonitrostyrenes **1** were prepared following previously reported methodologies.[31] The different reagents employed during the development of this work are commercially available, and were purchased from Chemosapiens S.L. Dry 1,4-dioxane stored over molecular sieves commercially available from Sigma Aldrich Chemical Co. was used for the photochemical reactions. NMR spectra were recorded in $CDCl_3$ at 300 MHz for ^1H and 75 MHz for ^{13}C, with tetramethylsilane as an internal standard for ^1H and the residual solvent signals as the standard for ^{13}C. The data are reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, p = quintuplet and m = multiplet or unresolved, with chemical shifts in ppm and coupling constant(s) in Hz. The values of the chemical shift of the signals in the NMR reports are in ppm. HRMS were measured in APCI negative mode, and the mass analyzer of the HRMS was TOF (Bruker model Impact II).

Photochemical reactions setup

A Kessil® PR160 Rig equipped with different lamps (PR160-366 nm, PR160-390 nm, PR160-427 nm, PR160-440 nm and PR160-456 nm) fan was used for the photochemistry setup. A glassware reactor developed in our group was used to run the photochemical reactions under controlled temperature (see the ESI† for details). The reactor was placed at a distance of approximately 5 cm away from the lamp prior to irradiation at maximum intensity (100% power) of the Kessil lamp (see the ESI† for details).

General procedure for the cyclopropanation reaction

To a solution of α-bromonitrostyrene (0.3 mmol) in 1,4-dioxane (2 mL), DIPEA (1.5 mmol) and benzaldehyde (0.3 mmol) were added. The mixture was stirred at 20 °C for 12 hours under irradiation with a blue LED light (467 nm). After completion of the reaction, the solvent was removed under vacuum and the crude products were purified by column chromatography.

2-Nitro-3-phenylcyclopropane-1-carbaldehyde 2a/2a′. Orange oil. 74% yield (43 mg). R_f = 0.29 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_9NO_3$, 191.0588; found: 191.0581. ^1H NMR (300 MHz, $CDCl_3$): δ 9.71 (d, J = 5.0 Hz, 1H, CHO-**2a′**), 9.30 (d, J = 3.5 Hz, 1H, CHO-**2a**), 7.45–7.13 (m, 10H, ArH), 5.33 (dd, J = 4.9, 3.5 Hz, 1H, H2-**2a**), 4.83 (dd, J = 8.2, 4.7 Hz, 1H, H2-**2a′**), 4.03 (dd, J = 7.8, 4.7 Hz, 1H, H3-**2a′**), 3.88 (dd, J = 11.1, 4.8 Hz, 1H, H3-**2a**), 3.44 (dt, J = 11.1, 3.5 Hz, 1H, H1-**2a**), 2.73 (dt, J = 8.0, 5.0 Hz, 1H, H1-**2a′**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 193.1, 130.2, 129.2, 128.97, 129.03, 128.8, 128.6, 128.7, 66.6, 62.4, 39.3, 38.6, 36.3, 32.6.

2-Nitro-3-(*p*-chlorophenyl)cyclopropane-1-carbaldehyde 2b/2b′. Orange oil. 48% yield (33 mg). R_f = 0.14 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8{}^{35}ClNO_3$: 225.0198; found: 225.0197; calcd for $C_{10}H_8{}^{37}ClNO_3$: 227.0172; found: 227.0167. ^1H NMR (300 MHz, $CDCl_3$): δ 9.69 (d, J = 4.8 Hz, 1H, CHO-**2b′**), 9.39 (d, J = 3.5 Hz, 1H, CHO-**2b**), 7.44–7.06 (m, 8H, ArH), 5.30 (dd, J = 4.9, 3.5 Hz, 1H, H2-**2b**), 4.81 (dd, J = 4.8, 3.7 Hz, 1H, H2-**2b′**), 3.99 (dd, J = 8.0, 4.8 Hz, 1H, H3-**2b′**), 3.83 (dd, J = 11.1, 4.8 Hz, 1H, H3-**2b**), 3.49 (dt, J = 11.1, 3.5 Hz, 1H, H1-**2b**), 2.70 (dt, J = 8.0, 4.8 Hz, 1H, H1-**2b′**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9, 192.7, 134.6, 130.2, 129.0, 129.4, 129.2, 128.6, 128.2, 127.1, 66.3, 62.5, 39.1, 38.4, 35.8, 31.8.

2-Nitro-3-(*p*-bromophenyl)cyclopropane-1-carbaldehyde 2c/2c′. Orange oil. 52% yield (33 mg). R_f = 0.30 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8{}^{79}BrNO_3$, 268.9693; found: 268.9700; calcd for $C_{10}H_8{}^{81}BrNO_3$, 270.9673; found: 270.9671. ^1H NMR (300 MHz, $CDCl_3$): δ 9.69 (d, J = 4.8 Hz, 1H, CHO-**2c′**), 9.39 (d, J = 3.0 Hz, 1H, CHO-**2c**), 7.61–7.48 (m, 4H, ArH), 7.17–7.00 (m, 4H, ArH), 5.29 (dd, J = 4.9, 3.6 Hz, 1H, H2-**2c**), 4.80 (dd, J = 4.8, 3.7 Hz, 1H, H2-**2c′**), 3.98 (dd, J = 8.0, 4.8 Hz, 1H, H3-**2c′**), 3.80 (dd, J = 11.1, 4.8 Hz, 1H, H3-**2c**), 3.49 (dt, J = 11.1, 3.0 Hz, 1H, H1-**2c**), 2.69 (dt, J = 8.0, 4.8 Hz, 1H, H1-**2c′**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9, 192.7, 132.4, 132.2, 131.8, 130.5, 129.2, 128.5, 127.5, 122.7, 66.2, 62.4, 39.0, 38.3, 35.8, 31.9.

2-Nitro-3-(*p*-fluororophenyl)cyclopropane-1-carbaldehyde 2d/2d′. Orange oil. 50% yield (31 mg). R_f = 0.24 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8FNO_3$, 209.0494; found: 209.0504. ^1H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, J = 4.8 Hz, 1H, CHO-**2d′**), 9.38 (d, J = 3.0 Hz, 1H, CHO-**2d**), 7.30–7.01 (m, 8H, ArH), 5.34–5.25 (m, 1H, H2-**2d**), 4.79 (dd, J = 8.0, 4.8 Hz, 1H, H2-**2d′**), 3.98 (dd, J = 8.0, 4.8 Hz, 1H, H3-**2d′**), 3.83 (dd, J = 11.1, 4.8 Hz, 1H, H3-**2d**), 3.48 (dt, J = 11.1, 3.1 Hz, 1H, H1-**2d**), 2.69 (dt, J = 8.0, 4.8 Hz, 1H, H1-**2d′**); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-**2d**): δ 189.8, 162.7 (d, J = 248.4 Hz), 130.7 (d, J = 8.3 Hz), 126.1, 116.2 (d, J = 21.9 Hz), 62.0, 38.6, 35.8.

2-Nitro-3-(*m*-chlorophenyl)cyclopropane-1-carbaldehyde 2e/2e′. Yellow oil. 31% yield (26 mg). R_f = 0.21 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8{}^{35}ClNO_3$: 225.0198; found: 225.0198. calcd for $C_{10}H_8{}^{37}ClNO_3$: 227.0172; found: 227.0170. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (d, J = 4.8 Hz, 1H, CHO-2e′), 9.37 (d, J = 2.8 Hz, 1H, CHO-2e), 7.22–7.01 (m, 8H, ArH), 5.29 (dd, J = 4.9, 3.6 Hz, 1H, H2-2e), 4.80 (dd, J = 8.0, 4.6 Hz, 1H, H2-2e′), 3.97 (dd, J = 8.0, 4.6 Hz, 1H, H3-2e′), 3.85–3.79 (m, 1H, H3-2e), 3.50–3.47 (m, 1H, H1-2e), 2.70 (td, J = 8.0, 4.8 Hz, 1H, H1-2e′); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2e): δ 192.5, 134.3, 132.2, 130.2, 129.1, 128.2, 127.0, 62.5, 38.2, 35.6.

2-Nitro-3-(*m*-fluorophenyl)cyclopropane-1-carbaldehyde 2f/2f′. Bright yellow oil. 42% yield (27 mg). R_f = 0.30 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8FNO_3$, 209.0494; found: 209.0484. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (d, J = 4.8 Hz, 1H, CHO-2f′), 9.36 (d, J = 2.9 Hz, 1H, CHO-2f), 7.42–7.29 (m, 6H, ArH), 7.06–6.95 (m, 2H, ArH), 5.28 (dd, J = 4.9, 3.5 Hz, 1H, H2-2f), 4.79 (dd, J = 8.3, 4.7 Hz, 1H, H2-2f′), 3.98 (dd, J = 7.7, 4.7 Hz, 1H, H3-2f′), 3.82 (dd, J = 11.1, 4.9 Hz, 1H, H3-2f), 3.46 (dt, J = 11.1, 3.5 Hz, 1H, H1-2f), 2.69 (dt, J = 8.0, 4.7 Hz, 1H, H1-2f′); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2f): δ 192.6, 162.8 (d, J = 247.2 Hz), 132.5 (d, J = 8.3 Hz), 130.6 (d, J = 8.5 Hz), 124.5, 116.1 (d, J = 22.5 Hz), 115.8 (d, J = 20.9 Hz), 62.3, 38.3, 29.7.

2-Nitro-3-(*m*-trifluoromethyphenyl)cyclopropane-1-carbaldehyde 2g/2g′. Bright yellow oil. 45% yield (34 mg). R_f = 0.32 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{11}H_8F_3NO_3$, 259.0458; found: 259.0469. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (d, J = 4.7 Hz, 1H, CHO-2g′), 9.44 (d, J = 2.5 Hz, 1H, CHO-2g), 7.65–7.36 (m, 8H, ArH), 5.33 (dd, J = 4.8, 3.8 Hz, 1H, H2-2g), 4.84 (dd, J = 8.3, 4.8 Hz, 1H, H2-2g′), 4.05 (dd, J = 7.8, 4.7 Hz, 1H, H3-2g′), 3.88 (dd, J = 11.1, 5.0 Hz, 1H, H3-2g), 3.54 (dt, J = 11.1, 5.0 Hz, 1H, H1-2g), 2.74 (dt, J = 8.0, 4.8 Hz, 1H, H1-2g′); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2g): δ 192.4, 134.3, 132.1, 131.5 (d, J = 32.6 Hz), 129.5, 129.2 (q, J = 232.6 Hz), 128.8 (d, J = 3.7 Hz), 125.4 (d, J = 3.7 Hz), 62.3, 38.2, 35.9.

2-Nitro-3-(*p*-methoxyphenyl)cyclopropane-1-carbaldehyde 2h/2h′. Yellow oil. 28% yield (18 mg). R_f = 0.33 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{11}H_{11}NO_4$, 221.0694; found: 221.0697. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, J = 5.0 Hz, 1H, CHO-2h′), 9.31 (d, J = 3.5 Hz, 1H, CHO-2h), 7.24–7.11 (m, 4H, ArH), 6.93–6.81 (m, 2H, ArH), 5.29 (dd, J = 4.8, 3.5 Hz, 1H, H2-2h), 4.77 (dd, J = 8.1, 4.8 Hz, 1H, H2-2h′), 3.98 (dd, J = 8.0, 4.6 Hz, 1H, H3-2h′), 3.89 (q, J = 11.1, 4.8 Hz, 1H, H3-2h), 3.83 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 3.41 (dt, J = 11.0, 3.5 Hz, 1H, H1-2h), 2.67 (td, J = 8.0, 5.0 Hz, 1H, H1-2h′); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2h): δ 192.9, 157.6, 136.9, 130.4, 114.4, 114.2, 62.7, 55.3, 38.3, 34.9.

2-Nitro-3-(*p*-methylphenyl)cyclopropane-1-carbaldehyde 2i/2i′. Orange oil. 32% yield (19 mg). R_f = 0.36 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{11}H_{11}NO_3$, 205.0744; found: 205.0740. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83 (d, J = 5.0 Hz, 1H, CHO-2i′), 9.42 (d, J = 3.6 Hz, 1H, CHO-2i), 7.26–7.15 (m, 8H, ArH), 5.28 (dd, J = 4.8, 3.6 Hz, 1H, H2-2i), 4.92 (dd, J = 8.0, 4.5 Hz, 1H, H2-2i′), 3.77–3.70 (m, 1H, H3-2i′), 3.81 (dd, J = 11.1, 4.8 Hz, 1H, H3-2i), 3.39 (dt, J = 11.1, 3.6 Hz, 1H, H1-2i), 2.85–2.78 (m, 1H, H1-2i′), 2.50 (s, 3H, CH_3), 2.48 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2i): δ 190.0, 138.3, 129.69, 129.67, 128.7, 62.6, 36.1, 29.7, 21.1.

2-Nitro-3-(*o*-fluorophenyl)cyclopropane-1-carbaldehyde 2j/2j′. Yellow oil. 39% yield (25 mg). R_f = 0.29 (Hex/EtOAc 5 : 1); HRMS (APCI$^-$) [M]$^-$ calcd for $C_{10}H_8FNO_3$, 209.0494; found: 209.0486. ^{1}H NMR (300 MHz, $CDCl_3$) (data for the major isomer-2j): δ 9.49 (d, J = 2.5 Hz, 1H, CHO), 7.42–7.02 (m, 4H, ArH), 5.25 (dd, J = 4.9, 3.6 Hz, 1H2), 3.77 (dd, J = 11.0, 4.9 Hz, 1H, H3), 3.56 (dd, J = 11.0, 4.9, 2.5 Hz, 1H, H1); ^{13}C NMR (75 MHz, $CDCl_3$) (data for the major isomer-2j): δ 192.6, 163.7 (d, J = 276.4 Hz), 130.6 (d, J = 8.3 Hz), 130.4 (d, J = 2.5 Hz), 124.5 (d, J = 2.9 Hz), 115.9 (d, J = 21.2 Hz), 62.1, 37.2, 30.5 (d, J = 3.6 Hz).

2-(Furan-2-yl)-3-nitrocyclopropane-1-carbaldehyde 2k/2k′. Yellow oil. 40% yield (21 mg). R_f = 0.29 (Hex/EtOAc 5 : 1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.67 (d, J = 4.8 Hz, 1H, CHO-2k′), 9.43 (d, J = 4.0 Hz, 1H, CHO-2k), 7.36 (bs, 2H), 6.38–6.36 (m, 4H), 5.29 (dd, J = 4.3, 4.0 Hz, 1H, H2-2k), 4.92 (dd, J = 8.3, 4.5 Hz, 1H, H2-2k′), 3.99 (dd, J = 7.6, 4.5 Hz, 1H, H3-2k′), 3.70 (dd, J = 10.8, 4.7 Hz, 1H, H3-2k), 3.35 (dt, J = 10.8, 4.0 Hz, 1H, H1-2k), 2.82 (td, J = 7.9, 4.8 Hz, 1H, H1-2k′).

Ring opening of nitrocyclopropane 2a

To a solution of nitrocyclopropane **2a** (0.13 mmol) in dichloromethane (0.5 mL) was added 3-benzyl-4,5-dimethylthiazol-3-ium (6 mg, 20 mol%). To this solution, DIPEA (20 μL, 40 mol%) and MeOH (20 μL, 0.26 mmol, 3 equiv.) were added. The mixture was stirred at r. t. for 15 hours, and then treated with sat. aq. NH_4Cl (1 mL) and extracted with EtOAc (2 × 5 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (Hex/EtOAc 6 : 1) to afford nitroester **3** (24 mg, 86%).

Methyl 4-nitro-3-phenylbutanoate 3 (ref. 32)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38–7.18 (m, 5H, C7–C9), 4.74 (dd, J = 12.6, 7.0 Hz, 1H, C5), 4.64 (dd, J = 12.6, 7.9 Hz, 1H, C5), 3.99 (*p*, J = 7.4 Hz, 1H, C4), 3.63 (s, 3H, C1), 2.78 (d, J = 7.4 Hz, 2H, C3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 138.4, 129.2, 128.2, 127.4, 79.5, 52.0, 40.3, 37.6.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Conceptualization, R. G. S. and H. R. S.; investigation, P. P. R. and P. I. C. G; writing—original draft preparation, R. G. S.; writing—review and editing, H. R. S.; supervision, R. G. S. and H. R. S.; funding acquisition, R. G. S. and H. R. S.

Conflicts of interest

There are no conflicts to declare.

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