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# Visible Light Photocatalytic Intramolecular Cyclopropane Ring Expansion<sup>†‡</sup>

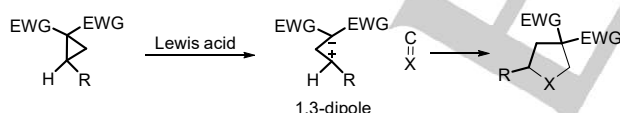
Javier Luis-Barrera, Víctor Laina-Martín, Thomas Rigotti, Francesca Peccati, Xavier Solans-Monfort, Mariona Sodupe, Rubén Mas-Ballesté, Marta Liras, José Alemán\*

*Dedicated to Professor Carmen Navarro Ranninger on the occasion of her retirement*

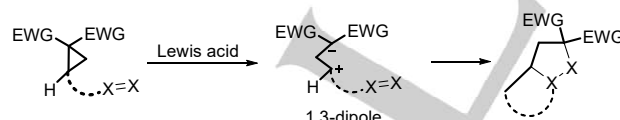
**Abstract:** In this communication, a new visible light photocatalytic strategy for the synthesis of enantioenriched dihydrofuranes and cyclopentenones via an intramolecular nitro-cyclopropane ring expansion reaction is presented. Mechanistic studies and DFT calculations are used to elucidate the key factors in this new expansion and the need for the nitro group in the cyclopropane.

[3+2] Cycloaddition reactions of 'donor-acceptor' cyclopropanes (DACs) with double bonds under Lewis acid catalysis are one of the most commonly used methods for the construction of different cycles through ring expansion reactions.<sup>[1]</sup> Therefore, in the presence of a Lewis acid, 1,3-zwitterions can be generated and trapped by different double C=C, C=N, C=O bonds. Brilliant examples of intermolecular cycloadditions (Scheme 1a) from Maulide's,<sup>[2a]</sup> Trushkov's,<sup>[2b]</sup> Tang's,<sup>[2c]</sup> Doyle's,<sup>[2d]</sup> Tomilov's,<sup>[2e]</sup> and Werz's<sup>[2f-h]</sup> groups have been reported recently, while Wang's group and others have developed related intramolecular cross-cycloadditions (IMCC) (Scheme 1b).<sup>[3]</sup>

**[a] Intermolecular DACs: Known cycloaddition**



**[b] Intramolecular cross-cycloadditions (IMCC): Known cycloaddition**



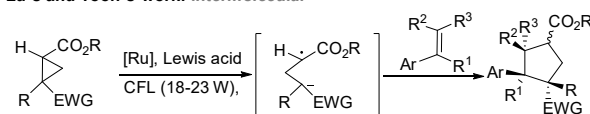
**Scheme 1.** DAC and IMCC type reactions.

Visible light photocatalysis has received significant attention during the last few years due to its ability to achieve bond constructions that are not possible using other procedures.<sup>[4]</sup> However, although thermal DAC reactions have been studied in the literature, only two examples of intermolecular ring

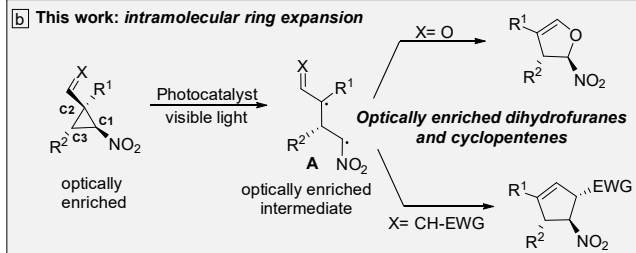
cyclopropane expansion using photocatalysis have been reported.<sup>[5]</sup> Lu's group has published the cyclopropane opening under visible light photocatalysis, and its intermolecular addition to a double bond, generating racemic cyclopentanes with a moderate diastereomeric ratio (Scheme 2a).<sup>[5a]</sup> More recently, Yoon and co-workers published a very elegant investigation in which photocatalysis is used in combination with a chiral Lewis acid, to get cyclopentanes through an intermolecular process (Scheme 2a).<sup>[5b]</sup>

Based on these investigations, we hypothesized that enantiomerically enriched cyclopropanes could be used as starting materials for the intramolecular visible light photocatalytic ring-expansion, a process that has remained elusive up to now. Very recently, the synthesis of chiral cyclopropanes that contain a chiral center flanked by an aldehyde and a nitro group was reported by our group.<sup>[6]</sup> We thought that the formation of a chiral intermediate **A**, which could preserve the chiral information to the final product, would be an appropriate strategy for its intramolecular expansion reaction (Scheme 2b). This is a challenging approach, because two other plausible C-C bond ruptures might take place (C2-C3 and C3-C1), but only the C1-C2 should be broken in order to obtain the adequate precursor (**A**) for the expansion reaction. This ring-enlargement (C1-C2 cleavage) stands in contrast to the common expansion of DACs (C2-C3 cleavage).<sup>[3e-f]</sup> Therefore, in this communication, the first visible light photocatalytic strategy for the synthesis of enantioenriched dihydrofuranes and cyclopentenones,<sup>[7]</sup> via an intramolecular cyclopropane expansion reaction is presented.

**[a] Lu's and Yoon's work: intermolecular**



**[b] This work: intramolecular ring expansion**



**Scheme 2.** Different strategies for the intermolecular reaction of cyclopropanes with double bonds and the expansion shown in this work.

First, we studied the expansion of the aldehyde **1a** to **2a** using different photocatalysts such as acridinium salts, eosin Y and different iridium and ruthenium complexes. Only two iridium complexes were active, and **3b** (Ir(dFppy)<sub>3</sub>) allowed higher

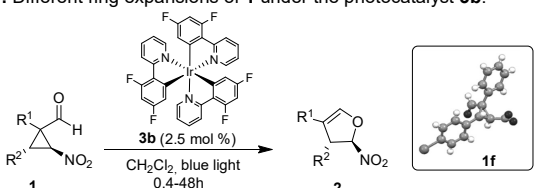
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conversion than **3a** ( $\text{Ir}(\text{ppy})_3$ ), being  $\text{CH}_2\text{Cl}_2$  the best solvent, and irradiating blue light into the reaction media through a glass bar, achieving full conversion of **2a** after 4h (see S.I. for full optimization). The scope of the reaction was studied with different cyclopropanes **1**<sup>[8]</sup> (Table 1). Regarding  $\text{R}^2$ , different aromatic groups with substitutions at the *para* position and alkyl groups were studied. Excellent yields for compounds **2a**, **2b** and **2c** were achieved (Table 1). In addition, different  $\text{R}^1$  groups were studied, showing that the reaction takes place with primary alkyl groups (**2d**), aromatics (**2e** and **2f**) and hydrogen (**2g** and **2h**).<sup>[9]</sup> In all cases, we observed similar final enantioselectivities in the

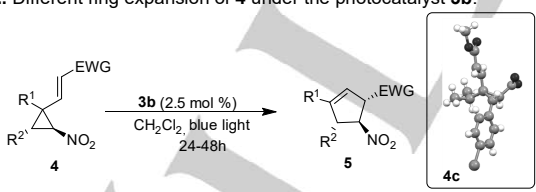
**Table 1.** Different ring expansions of **1** under the photocatalyst **3b**.<sup>[a]</sup>



Compound	Yield	ee	ee <sub>1a</sub>	ee <sub>1b</sub>	ee <sub>1c</sub>	ee <sub>1d</sub>	dr
<b>2a</b>	86%	97%	(ee <sub>1a</sub> = 97%)				>98:2
<b>2b</b>	82%	90%	(ee <sub>1b</sub> = 92%)				>98:2
<b>2c</b>	84%	94%	(ee <sub>1c</sub> = 96%)				>98:2
<b>2d</b>	98%	95%	(ee <sub>1d</sub> = 98%)				>98:2
<b>2e</b>	51% <sup>[b]</sup>	92%	(ee <sub>1e</sub> = 94%)				>98:2
<b>2f</b>	57% <sup>[b]</sup>	88%	(ee <sub>1f</sub> = 91%)				>98:2
<b>2g</b>	78%	75%	(ee <sub>1g</sub> = 76%)				>98:2
<b>2h</b>	86%	n.d. <sup>[c]</sup>	(ee <sub>1h</sub> = 76%)				>98:2

[a] All the reactions were performed at 0.1 mmol scale of **1** in 1.0 mL  $\text{CH}_2\text{Cl}_2$ . E.e. of the starting material cyclopropane **1** (in brackets) and final dihydrofuranes **2** were determined by SFC. Yield isolated after flash chromatography. [b] Yield based on conversion by  $^1\text{H}$ -NMR. [c] E.e. could not be determined by SFC, although possess optical rotation activity.

**Table 2.** Different ring expansion of **4** under the photocatalyst **3b**.<sup>[a]</sup>



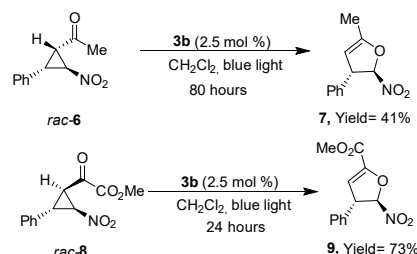
Compound	Yield	ee	ee <sub>1a</sub>	ee <sub>1b</sub>	ee <sub>1c</sub>	ee <sub>1d</sub>	dr
<b>5a</b>	57%	87%	(ee <sub>1a</sub> = 97%)				>98:2
<b>5b</b>	75%	99%	(ee <sub>1b</sub> = 99%)				>98:2
<b>5c</b>	50%	96%	(ee <sub>1c</sub> = 96%)				>98:2
<b>5d</b>	45% <sup>[b]</sup>	94%	(ee <sub>1d</sub> = 98%)				>98:2
<b>5e</b>	c.m. <sup>[c]</sup>						
<b>5f</b>	90%	97%	(ee <sub>1f</sub> = 97%)				dr = 70:30
<b>5g</b>	33%	97%	(ee <sub>1g</sub> = 97%)				>98:2
<b>5h</b>	55%	97%	(ee <sub>1h</sub> = 97%)				>98:2

[a] All the reactions were performed at 0.1 mmol scale of **4** in 1.0 mL  $\text{CH}_2\text{Cl}_2$ . E.e. of the starting material cyclopropane **4** (in brackets) and final cyclopentenones **5** were determined by SFC. Yield isolated after flash chromatography. [b] Yield based on conversion by  $^1\text{H}$ -NMR. [c] Complex mixture.

products **2** than in the reactants **1** (ee between parenthesis), indicating that no loss of stereochemical information at C3 was observed. The absolute configuration of starting material **1f** was unequivocally determined by its X-ray diffraction structure (see right-top, Table 1).<sup>[10]</sup>

In order to expand the scope of the reaction, we studied cyclopropanes with a double bond instead of an aldehydic group (Table 2). Firstly, the aldehydes **1** were treated with different commercially available Wittig's reagents to give cyclopropanes starting materials **4** (see S.I.). The reaction worked with the cyclopropane **4a** to give **5a** in good ee under the same reaction conditions for the expansion of aldehydes **1**, but with slightly longer reaction times compared to the aldehyde expansion. Other aromatic residues such as  $\text{R}^2$  (**4b** and **4c**) also allowed the ring expansion reaction from moderate to good yields, as well as other groups at  $\text{R}^1$  such as *n*-Pr (**4d**). Unexpectedly, the aromatic group at  $\text{R}^1$  (**4e**) did not yield the desired product **5e**. Other double bonds containing benzyl-esters (**4f**), ketones (**4g**) or nitriles (**4h**) also worked giving moderate to good yields and without any erosion in the final enantioselectivity. The absolute configuration of the starting material **4c** was unequivocally determined by its X-ray diffraction structure (see right-top, Table 2).<sup>[10]</sup>

Furthermore, the photocatalytic cyclopropanation expansion reaction also worked with other functional groups (Scheme 3). When the reaction was performed with the ketone **6**, the reaction was much slower (3 days) in comparison with aldehyde derivatives **1**, obtaining **7** in moderate yield. However, the  $\alpha$ -keto-ester **8** was more reactive (24h), giving the trisubstitute dihydrofuran **9** in good yield.



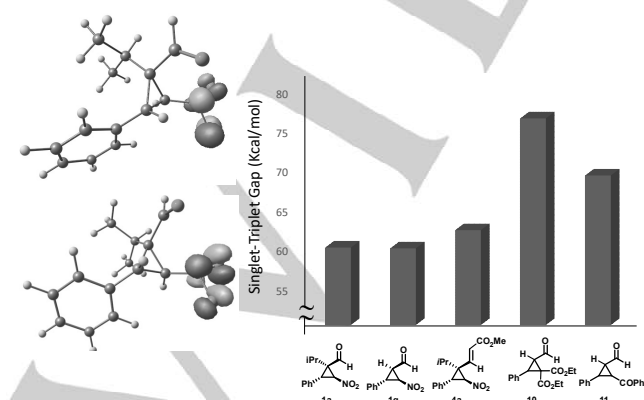
**Scheme 3.** Reaction with ketone and  $\alpha$ -ketoester cyclopropanes derivatives.

In order to understand this process, we carried out additional experiments and DFT(M06/6-31+G(d,p)) calculations,<sup>[11a]</sup> including the SMD implicit model<sup>[11b]</sup> (see S.I. for details). The process starts with the excitation of photocatalyst **3b** to **3b\*** with visible light irradiation. In order to evaluate the possibility of a photo-redox mechanism, cyclic voltammetry measurements were carried out for substrate **1a** and compared with the reported redox potentials in excited state of **3b**<sup>[12]</sup> (see S.I.). Electrochemical characterization rules out photocatalytic oxidation as a mechanism of activation since no oxidation features below +1.5 V (vs Ag/AgCl) were observable in the cyclic voltammogram of **1a**. However, one irreversible reduction of **1a** at half-wave potential of -1.06 V (vs Ag/AgCl) was observed. Although photoreduction of **1a** by **3b\*** ( $\text{Ir}^{4+}/\text{Ir}^{3+*} = -1.39$  V vs Ag/AgCl) would be possible, we found that the use of Eosyn Y as photo reductor catalyst ( $E^\circ(\text{EY}^+/\text{EY}^*) = -1.11$  V vs Ag/AgCl<sup>[4d]</sup>) did not result in any conversion (see S.I.). Furthermore, despite the higher reducing power of  $[\text{Ir}(\text{ppy})_3]$  (**3a**) in its excited state ( $E^\circ(\text{Ir}^{4+}/\text{Ir}^{3+*}) = -1.67$  V vs Ag/AgCl), the conversion of observed product using **3a** is very poor in comparison with the results obtained with **3b** (27% vs >98%, see S.I.). Therefore, an energy

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transfer process should be considered as an alternative mechanism.<sup>[13]</sup> Considering that we did not observe any overlap in the emission of the photocatalysts **3b** ( $\lambda_{\text{max}} = 453 \text{ nm}$ ) and the absorption of the nitrocyclopropane **1a** ( $\lambda_{\text{max}} = 229 \text{ nm}$ ) (see S.I.), the energy transfer process from **3b**\* to the substrate should proceed through a Dexter type mechanism (instead of a Forster pathway). Such mechanism implies that triplet spin state in substrate is induced by short distance interaction with triplet excited state of photocatalyst. Indeed, the calculated values of singlet-triplet gap in **1a** and the emission energy of photocatalyst **3a** are in good agreement (see below). In a quest for evidence of an energy transfer mechanism, the cyclopropane **8** was irradiated with UV light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ), observing the expansion reaction with a moderate conversion (23%) in 24h. Although a value of the quantum yield lower than one does not exclude a possible radical chain mechanism, we have measured the  $\Phi$  of the reaction of **1a** in the presence of the photocatalyst **3b** (see S.I.). The observed value ( $\Phi = 0.05$ ) could suggest that a radical chain propagation is not taking place.

Considering that changes in  $R^1$ ,  $R^2$  and CHO/CH=EWG did not suppress the observed reactivity, we hypothesized that the nitro group must play a key role in the photocatalytic activation of cyclopropane. Indeed, when the nitro group is substituted by an ester or a ketone (**10** and **11**, see Figure 1), the reaction under visible light photocatalytic conditions did not take place, indicating that the presence of the nitro group is essential for the ring-expansion process. With the aim of gaining a deeper insight into this point, the singlet-triplet Gibbs energy gap was calculated for **1a** and other related structures where nitro group was substituted by different functional groups (Figure 1). Interestingly, the lowest singlet-triplet gaps are computed for molecules enclosing the nitro group. In fact, such energetic difference between the spin states of the organic reagent, reasonably matches the reported emission energy for photocatalyst **3b** (~60 kcal/mol).<sup>[12]</sup> Certainly, when the nitro group is substituted by CPh or two esters, the gap substantially increases (>70 kcal/mol), hindering the photocatalytic process, which is in agreement with the absence of reactivity of **10** and **11**. The two SOMO orbitals of the triplet state are localized on the  $\text{NO}_2$  group, in agreement with the role of such a fragment on lowering the excitation energy of the reagent.



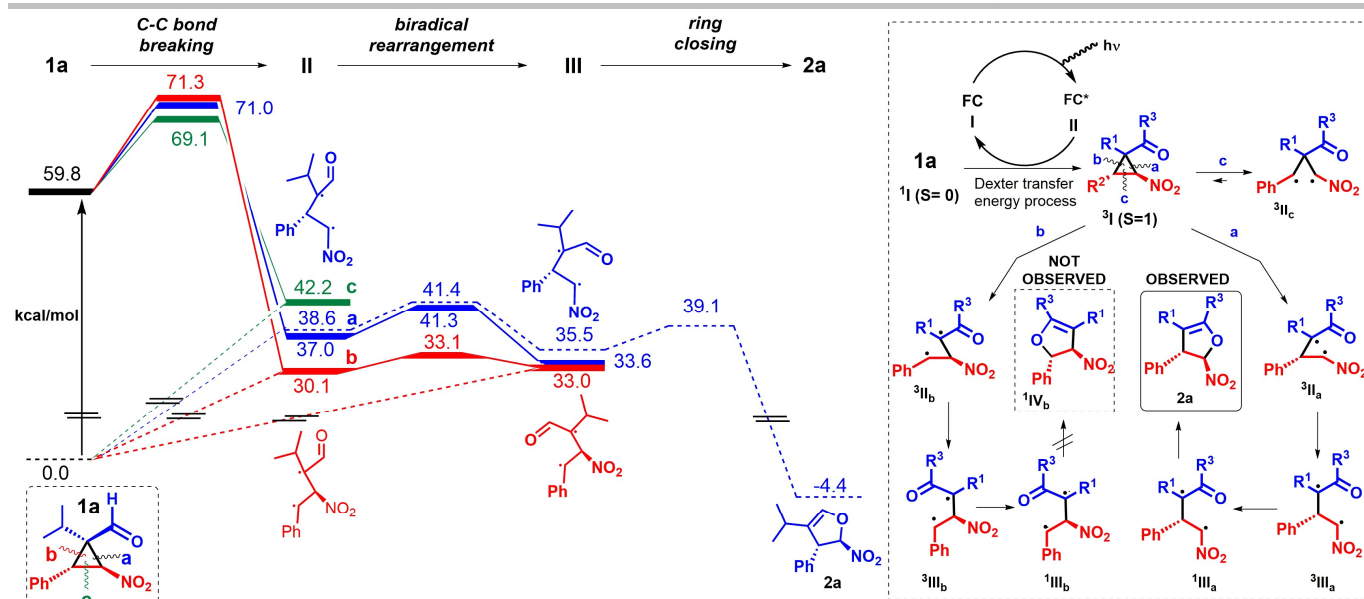
**Figure 1.** SOMO orbitals calculated for triplet state of **1a** (left) and singlet-triplet energy gap in a range of cyclopropane reagents (right).

The first step is the opening of the cyclopropane ring that leads to the formation of a first biradical **<sup>3</sup>Ila** (right-Figure 2). Three C-C bond breaks are possible (paths **a**, **b** or **c**), which give three different isomers (**<sup>3</sup>Ila**, **<sup>3</sup>Ilb** and **<sup>3</sup>Ilc**). Ring expansion from **<sup>3</sup>Ila**

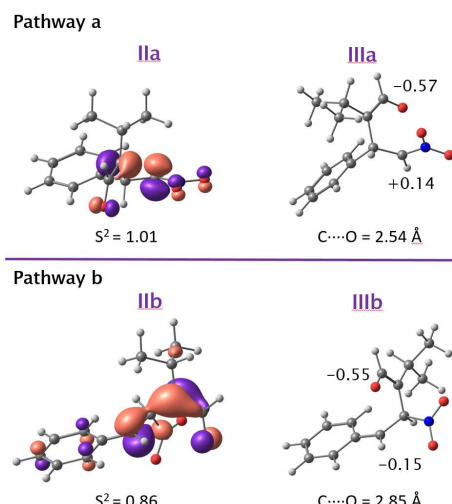
enables the final observed 5-membered ring isomer (**2a**) whereas that from **<sup>3</sup>Ilb** would lead to the 5-membered ring **<sup>1</sup>Ivb** that is not observed experimentally. Finally, **<sup>3</sup>Ilc** is an unproductive pathway due to the disposition of the aldehyde group. Product formation through pathways **a** and **b** requires the conformational change from **<sup>3</sup>II** to another biradical **<sup>3</sup>III** in order to properly orient the reacting groups before ring closure occurs. This ring closure implies a spin crossing from the triplet to the singlet state that can occur either before or after **<sup>3</sup>II**  $\rightarrow$  **<sup>3</sup>III** interconversion. In order to understand the reaction mechanism, we explored the reactivity of **1a** as a representative example (for cyclopentene **5a**, see S.I.), considering both the triplet and open shell singlet states for all biradical intermediates.

Figure 2 shows the Gibbs energy profiles for pathways **a**, **b** and **c** of **1a**. The three possible C-C cleavages are kinetically and thermodynamically favored. Energy barriers are low (9.3-11.5 kcal mol<sup>-1</sup>) and the reaction  $\Delta G$  ranges from -15 to -30 kcal mol<sup>-1</sup>. Noteworthy, the most stable biradical corresponds to **<sup>3</sup>Ilb**. In these species, the radical character lies at the two carbons that are able to better stabilize the unpaired electrons: the tertiary carbon presenting the stabilizing CHO group and the benzyl carbon (See S.I. for details). However, this cleavage pathway would lead to a ring expansion product **<sup>1</sup>Ivb** that is not experimentally observed (right-Figure 2), thereby indicating that other factors determine the observed reactivity. In particular, the evolution of intermediates **<sup>3</sup>Ila** and **<sup>3</sup>Ilb** differ significantly. That is, although for both intermediates the Gibbs energy barrier for the biradical rearrangement (**<sup>3</sup>II**  $\rightarrow$  **<sup>3</sup>III**) is low, this process is exergonic for path **a** and endergonic for path **b**. This suggests that the intermediate **<sup>3</sup>Ila** would be a more long-lived species than **<sup>3</sup>Ila** while the opposite is expected for pathway **b**. Moreover, open-shell singlet state optimizations of intermediates **<sup>1</sup>Ila** and **<sup>1</sup>Ila** yield to two minima with very similar geometries and energetics to those of the triplet states. **<sup>1</sup>Ila** evolves to reactants in an essentially barrierless process, whereas **<sup>1</sup>Ila** leads to the final product observed, after overcoming a low energy barrier of 3.6 kcal mol<sup>-1</sup>. This suggests that spin crossing probably occurs after biradical rearrangement; that is, at geometries close to **<sup>3</sup>Ila**. On the other hand, all attempts to locate open-shell singlet state structures for **<sup>1</sup>Ilb** and **<sup>1</sup>Ilb** collapsed to reactants, suggesting that spin crossing always leads to the initial reactants.<sup>[14]</sup> Thus, spin crossing in pathway **b** appears to be unproductive, which is in agreement with the non-observation of **<sup>1</sup>Ivb** as resulting product<sup>[15]</sup> and the low value of the quantum yield.

The calculations suggest that the key point is that the biradical intermediates of pathway **a** can evolve to products, whereas those of pathway **b** can only return to reactants. This seems to originate from three key points: i) The biradical rearrangement is only exergonic for pathway **a**. This favors the species that leads to the final product and suggests that it is more likely that spin crossing occurs after biradical rearrangement. ii) There is almost no overlap between the carbon p orbitals in both species (**<sup>1</sup>Ila** and **<sup>1</sup>Ila**) involved in the formation of dihydrofurane in pathway **a**, in contrast to the overlap observed in **<sup>1</sup>Ilb**. Furthermore, the  $S^2$  expectation value obtained for open shell singlets is around 1. Indeed, this is observed for **<sup>1</sup>Ila** and **<sup>1</sup>Ila**, whereas in the case of **<sup>1</sup>Ilb** the calculated value is 0.86 (Figure 3). Consequently, the latter intermediate exhibits a smaller biradical character. Therefore, after spin-crossing in pathway **b** the reactant is easily recovered



**Figure 2.** Gibbs Energy profile calculated for reaction pathway from **1a** to **2a** (left). Solid lines correspond to species in the triplet state, whereas dashed lines refer to the energies of the spin-corrected singlet state.<sup>[11d]</sup> Possible reaction pathways of triplet excited state of **1a** (right).



**Figure 3.** a) Lowest energy singly occupied orbital of the unrestricted broken shell singlet at the **3IIa** and **3IIb** geometries. b) Partial charges of the oxygen and carbon atoms involved in the formation of the 5-membered ring in the **3IIa** and **3IIb** structures.

but not the product, which requires a larger electronic reorganization. iii) The partial charges of the atoms involved in the new C-O bond formation in the ring closure step are both negative for **IIIb**, while they present opposite signs in **IIIa** (Figure 3). That is, the NO<sub>2</sub> electron-withdrawing character induces a positive charge on the carbon directly bonded to it, resulting in a Coulombic attraction in **IIIa** with the negatively charged oxygen fragment. Therefore, this could favour the orientation of the reacting fragments and overall facilitate the reaction along pathway **a**.

In conclusion, a new visible light photocatalytic strategy for the synthesis of enantioenriched dihydrofuranes and cyclopentenones via an intramolecular cyclopropane ring expansion reaction has been developed. This process proceeds under mild conditions, achieving good to excellent yields with excellent enantioselectivities in the final products. Moreover, DFT calculations have been carried out in order to show the role of the nitro group and the origin of product selectivity.

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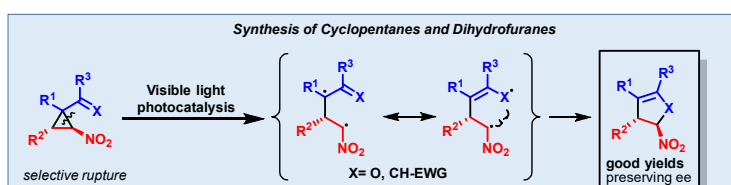
**Keywords:** ring-expansion • cyclopropanes • photocatalysis • cyclopentenones

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- [8] The absolute configuration at C-2 with aromatic groups of the starting material **1** possess opposite configuration to those with hydrogen or alkyls groups. See reference 6 and S.I. for more details.
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- [10] CCDC 1404743 (**1f**) and 1529711 (**4c**) contain the crystallographic data. These data can be obtained free of charge at [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk). Because the chiral center configuration supporting R<sup>2</sup> did not change during the ring expansion process, we assumed the same configuration at this carbon in the final product **2** or **5**, whereas the configuration of the  $\alpha$ -nitro carbon (C1) and  $\alpha$ -EWG carbon in products **5** were confirmed by <sup>1</sup>H-NMR experiments (See S.I.).
- [11] [a] Y. Zhao, D.G. Truhlar *Theor. Chem. Account* **2006**, *120*, 215; [b] A.V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B*, **2009**, *113*, 6378; [c] K. Yamagushi, F. Jensen, A. Dorigo, K. N. Houk, *Chem. Phys. Lett.* **1988**, *149*, 537.
- [12] T.B. Demissie, K. Ruud, J. H. Hansen, *Organometallics* **2015**, *34*, 4218.
- [13] For a related study, see: T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei, T. P. Yoon, *Science*, **2016**, *354*, 1391.
- [14] The unique transition state leading to **1IVb** that we have been able to locate is a close shell singlet that connects **1a** with **1IVb** and can be associated with a high energy barrier ( $\Delta G^\ddagger = 34.2 \text{ kcal mol}^{-1}$ ) via a thermal process.
- [15] In order to understand why racemization processes are not taking place with pathways b and c, we also calculated the unproductive racemization pathways (see S.I.). Interestingly, all intermediates that would be involved a loss of enantioselectivity are higher in energy than the most stable bi-radical **3II** of each pathway by between 2.9 and 8.5 kcal mol<sup>-1</sup>.

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In this communication, we present a new visible light photocatalytic strategy for the synthesis of enantioenriched dihydrofuranes and cyclopentenes via ring expansion.

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