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From prediction to reality: Harnessing strain energy to achieve a photodriven retro-Diels–Alder reactions

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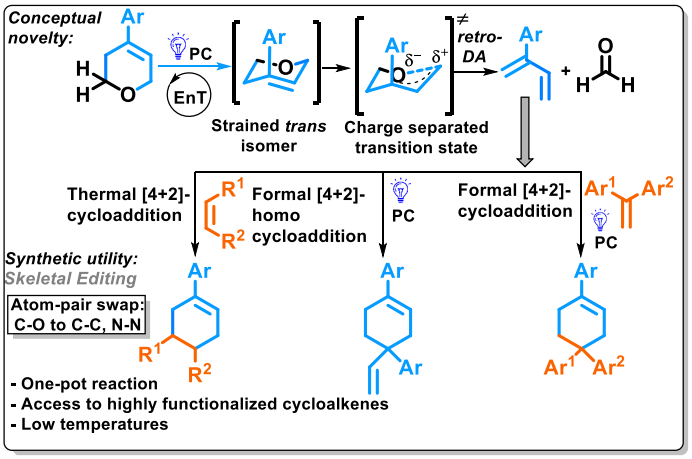
Abstract

The retro-Diels-Alder (rDA) reaction followed by a Diels-Alder reaction is a potentially powerful sequence for molecular remodeling and skeletal editing, yet its synthetic utility has been limited by the high activation barriers and unfavorable thermodynamics associated with cycloreversion. Here, we report the first experimental realization of a long-standing theoretical prediction that strain-loaded trans-cyclohexene analogs can undergo efficient retro-Diels-Alder fragmentation. Building on computational studies and our work on visible-light-driven trans-cycloalkene formation, we demonstrate that energy-transfer photocatalysis converts aryl dihydropyrans into highly strained trans-dihydropyran intermediates whose stored strain energy drives cycloreversion under mild conditions. Mechanistic investigations, including trapping experiments, Stern–Volmer analysis, Hammett studies, and computational calculations, support an asynchronous but concerted cycloreversion pathway involving a polarized transition state, providing insight into the lack of retro-Diels-Alder reactivity in the parent cyclohexene. The resulting dienes can be generated on demand and intercepted in one-pot cycloaddition sequences, enabling atom-pair exchange and skeletal-editing transformations.



Keywords: Visible-light photocatalysis, retro-Diels–Alder reaction, strain-release chemistry, skeletal editing

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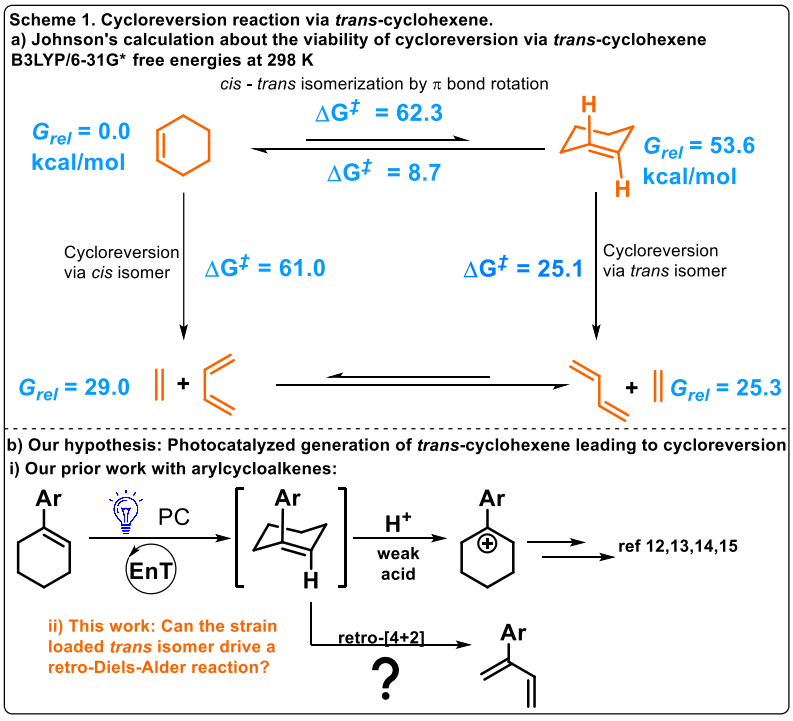
1. Introduction

The Diels-Alder (DA) reaction is among the most influential transformations in organic chemistry, providing a powerful means to construct six-membered rings with exceptional regio- and stereocontrol.[1] Its synthetic impact extends from natural product synthesis to medicinal chemistry and materials science.[2,3] In contrast, the reverse process, the retro-Diels-Alder (rDA) reaction, has played a far more limited role despite its enormous potential for skeletal editing and molecular remodeling.[28,29] This is generally due to both the endothermic nature of the rDA and the associated large energy barrier. So, the ability to selectively deconstruct cyclic frameworks would provide a valuable strategy for ring contraction and expansion,[4,5] atom insertion and deletion,[6] and atom exchange processes.[7,8] Practical applications of rDA chemistry have historically been constrained by both the substantial activation barriers associated with cycloreversion, which typically necessitate extreme thermal conditions that limit functional-group compatibility and synthetic utility, and the thermodynamic preference for the DA product.



Scheme 1. Cycloreversion reaction *via trans*-cyclohexene

Herein, we report a striking solution to this long-standing challenge by harnessing the strain energy of transient *trans*-cycloalkene intermediates to drive rDA fragmentation under exceptionally mild conditions.[9] Our work provides the first experimental realization of a mechanistic hypothesis proposed more than two decades ago by Johnson and co-workers, who computationally predicted that the barrier for cycloreversion of a strained *trans*-cyclohexene should be dramatically lower than that of its *cis* counterpart (**Scheme 1a**).[10]

Photoinduced *cis*–*trans* isomerization of cycloalkenes has long been recognized as a route to highly strained *trans*-cycloalkenes. In particular, *trans*-cyclohexene is significantly less stable than its *cis*-isomer due to the substantial strain associated with incorporating a *trans* double bond into a six-membered ring. This stored strain energy prompted Johnson and DiRico to investigate its potential impact on rDA reactivity through computational studies.[11] Their calculations predicted that the activation barrier for concerted cycloreversion of *trans*-cyclohexene would be dramatically reduced relative to *cis*-cyclohexene (ca. 25 vs. 61 kcal/mol)(**Scheme 1a**) as a result of strain release during fragmentation. However, the same study also predicted a rapid (8.7 kcal/mol) thermal isomerization of *trans*-cyclohexene back to the thermodynamically favored *cis*-isomer, which would outcompete cycloreversion and prevent experimental observation. Consequently, this strain-assisted fragmentation pathway remained a compelling but unverified theoretical prediction.

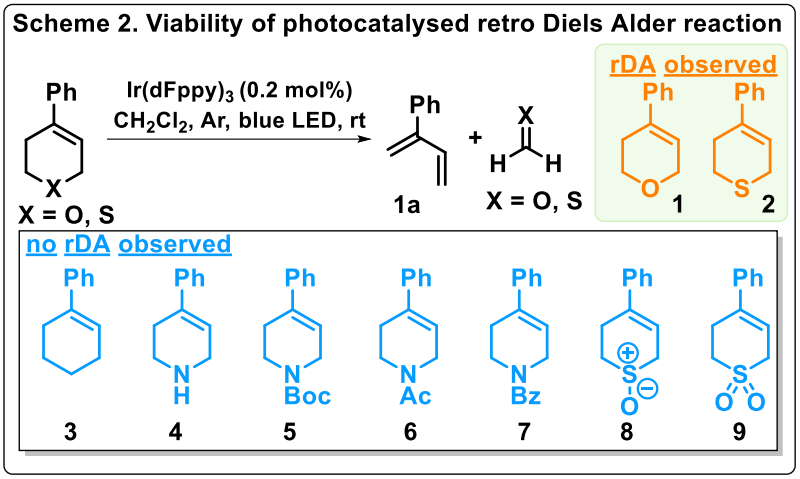
Our group has previously investigated the visible light photosensitized generation of *trans*-cycloalkenes[12–17] and their protonation by weak acids to form carbenium ion species, which can drive further chemical transformations (**Scheme 1b**).[12,13,15,16] Using an appropriate photosensitizer and blue light, we have demonstrated the synthetic utility of the previously reported photoisomerization of *cis*-arylcyclohexenes to the strained *trans*-isomers. Despite the short lifetime of *trans*-phenylcyclohexene (9 µs at rt),[18] its high strain energy (ca. 46 kcal/mol)[18–21] enables unique and extreme reactivity. Thus, our group proposed designing substrates to investigate whether structural modification could enable retro-Diels–Alder fragmentation to compete successfully with the rapid double bond isomerization of trans-cycloalkenes (**Scheme 1b**).

Hinting at this possibility of rDA, we occasionally observed diene formation during studies of the photochemistry of some cyclohexene derivatives. Motivated by these observations, we systematically investigated the reactivity of *trans*-arylcyclohexenes and related heteroatomic analogs. Herein, we reported the experimental demonstration of photo-driven, strain-mediated retro-Diels–Alder reactions of heteroatomic analogs of *trans*-phenylcyclohexene, providing direct access to substituted 1,3-dienes and ultimately enabling a one-pot conversion into valuable cyclohexene frameworks through a net atom-pair exchange strategy.[9]

2. Searching for the ideal platform

A systematic study of 2-phenylcyclohexene derivatives bearing structural modifications at the C4-position under visible-light energy-transfer conditions was conducted (**Scheme 2**). The study began by subjecting the small library of analogs to blue LED irradiation in the presence of $Ir(dFppy)_3$ in CH_2Cl_2 at room temperature. Product formation was monitored by ^1H NMR spectroscopy. These conditions closely resembled those previously employed in the studies of *trans*-cyclohexene-mediated carbon capture[22] and ether formation,[12] with the key difference being the absence of the weak acid typically used to protonate the transient *trans*-cyclohexene intermediate (**Scheme 2**).[9]

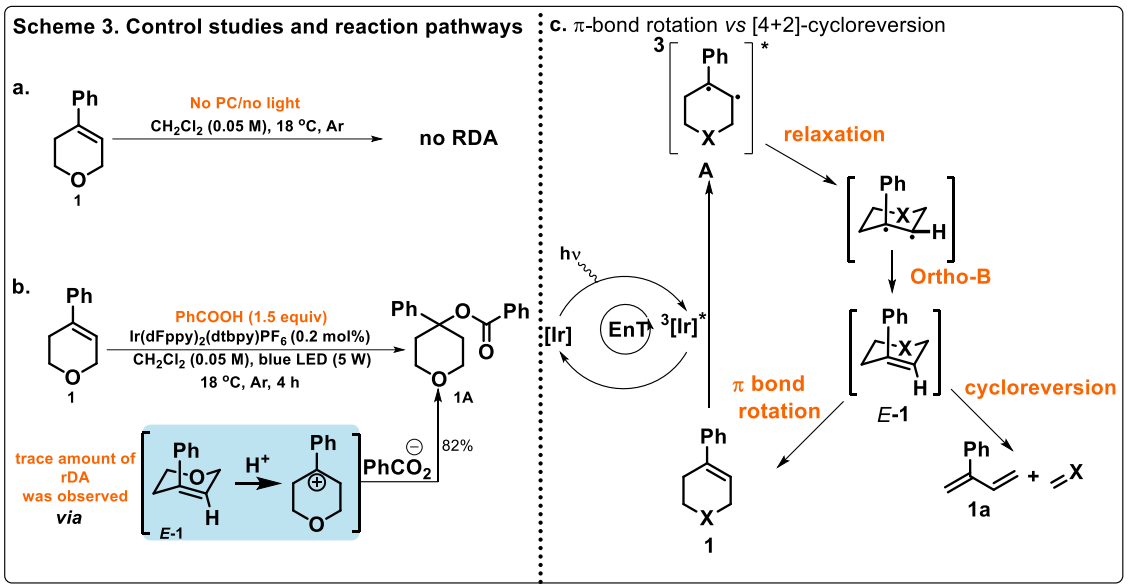
At first glance, the results appeared discouraging. Most carbocyclic and heterocyclic analogs either remained unchanged or decomposed without productive rDA fragmentation. While substrates bearing CH_2, NH, NBoc, NAc, NBz, SO, and SO_2 groups respectively (**3, 5, 6, 7, 8, 9**) failed to deliver the desired diene,[9] two substrates behaved differently. The oxygen- and sulfur-containing analogs (**1** and **2**) underwent visible-light-driven rDA fragmentation, producing 2-phenyl-1,3-butadiene together with formaldehyde or thioformaldehyde, respectively (**Scheme 2**). Among these, 4-phenyl-3,6-dihydro-2-pyran emerged as the most promising platform, affording the corresponding diene in approximately 75% conversion, whereas the thiopyran analog gave only 26% conversion (**Scheme 2**). These observations prompted us to revisit Johnson and DiRico's[11] prediction that strain in *trans*-cyclohexene could facilitate rDA fragmentation, and suggested that suitably designed analogs might enable experimental realization of this long-standing prediction. Additionally, it begged the question of why is it possible in certain cases but not others.



Scheme 2. Viability of photocatalysed retro Diels-Alder reaction

3. Mechanistic validation

The strength of this study lies not only in the discovery of a visible-light-driven rDA but also in the careful mechanistic validation that explains how it occurs. Control experiments established that both visible light and the photocatalyst are required; in their absence, no rDA products were observed (**Scheme 3a**).[9] It is possible that this could also occur in the absence of a sensitizer by direct irradiation at a lower wavelength.[27]

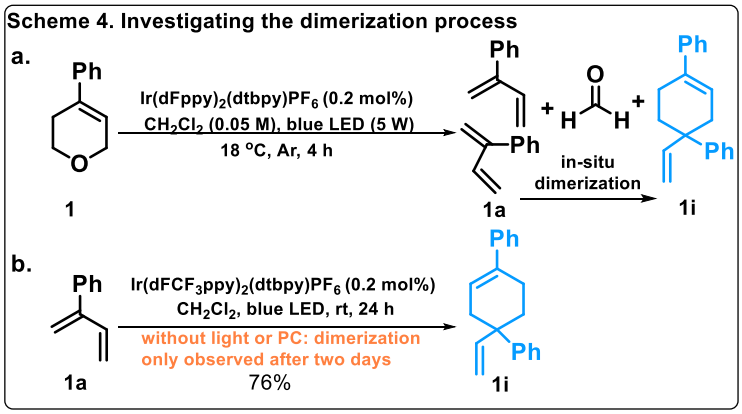


Scheme 3. Control studies and reaction pathways

This confirms that the transformation is initiated by photocatalytic energy transfer rather than by conventional thermal activation or from a photochemically excited state.

Evidence for a strained *trans*-cycloalkene intermediate was obtained through acid-trapping experiments. When benzoic acid was added to the reaction mixture, the corresponding ester was isolated in 82% yield, with only trace rDA products observed (**Scheme 3b**).[9] This experiment is important because previous studies by Weaver showed that strained ground-state *trans*-arylcyclohexenes undergo rapid protonation by weak acids, whereas the corresponding *cis*-isomers do not.[23] The formation of the ester therefore supports the formation of an intermediate ground-state trans-dihydropyran rather than a direct reaction from the triplet excited state.

Although we observed full conversion of **1** under the reaction conditions, a byproduct was formed (**Scheme 4a**). The Isolation and characterization of the byproduct revealed that it was cyclohexene derivative **1i**, which is a dimer of diene **1a**. To investigate the dimerization process, freshly prepared diene **1a** was subjected to the reaction conditions, affording dimer **1i** in 76% yield. In control experiments without light or a photocatalyst, the dimerization took place slowly, only appearing after two days; this supports the conclusion that the dimer formation was also a photoinitiated process (**Scheme 4b**).



Scheme 4. Investigating the dimerization process

Stern–Volmer quenching studies further clarified the photochemical landscape (**Figure 1**).[9] The excited photocatalyst was quenched by the starting pyran **1**, the diene product **1a**, and the dimer **1i**. However, diene **1a** quenched the photocatalyst nearly four times more efficiently than either the starting material or the dimer. The significantly higher quenching efficiency of diene **1a** explains why it was necessary that the reactions not be driven to complete conversion. As the diene forms, it increasingly competes with the starting pyran for triplet energy transfer, leading to the secondary photochemical reaction, dimerization. These data rationalize the optimized conditions: lower substrate concentration, reduced light intensity, low photocatalyst loading, and careful monitoring of reaction time all help suppress diene dimer **1i** formation. More broadly, the Stern–Volmer results reveal an important challenge for "diene-on-demand" chemistry: the product diene is not merely a passive intermediate but a photoactive species that must be generated and trapped before it undergoes secondary reactions.

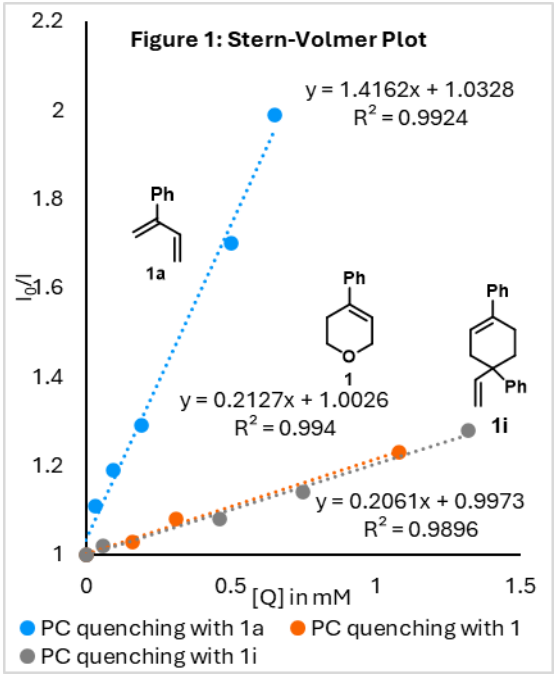
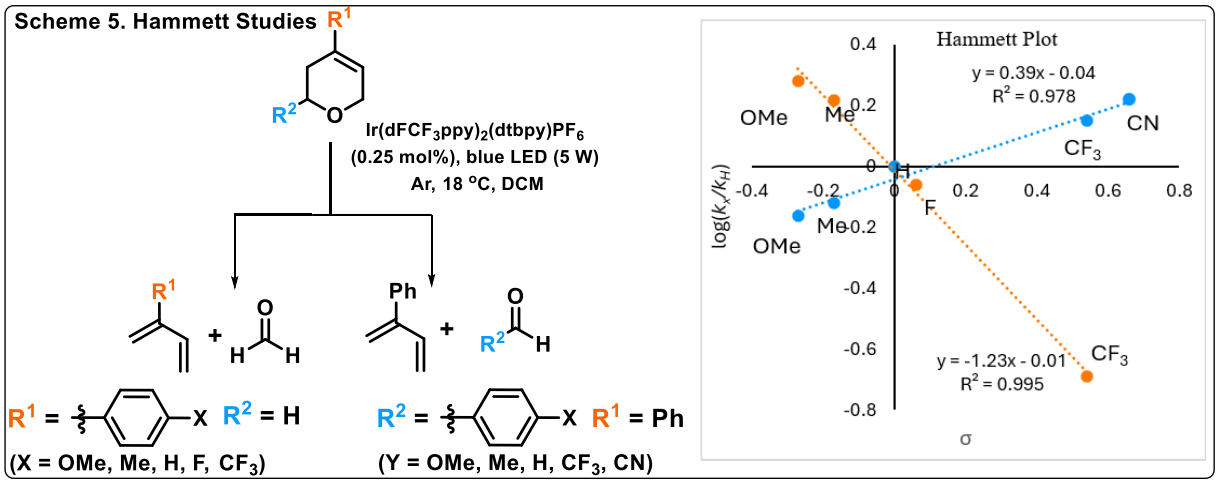


Figure 1. Stern-Volmer plot

Based on these experiments and the literature studies[18–21], the following mechanism was proposed for this novel reaction (**Scheme 3c**). The photocatalyst is excited by the absorption of a blue photon, which ultimately promotes it to a long-lived triplet state. This excited photocatalyst then acts as a photosensitizer, transferring its energy to substrate **1** *via* Dexter energy transfer (EnT), generating the corresponding triplet-state biradical intermediate **A**. On the triplet energy surface, biradical **A** relaxes by undergoing rotation about the former alkene bond to generate the orthogonal biradical intermediate **Ortho-B**. This species then undergoes intersystem crossing (ISC) to return to the ground-state surface, likely from a geometry and energy closely resembling the transition state for bond rotation. A substantial fraction of these high-energy species relax to give strained *E*-**1**.[13,22]

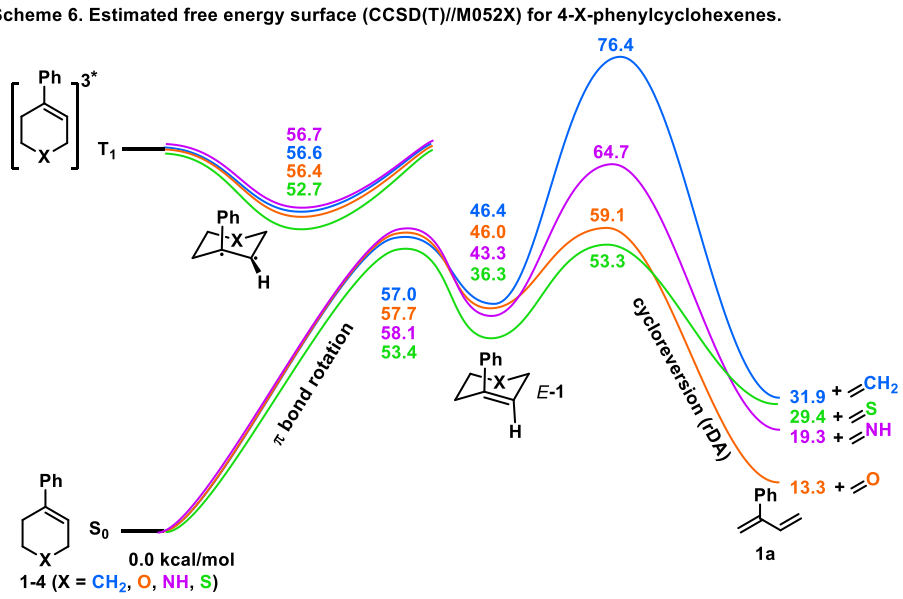


Scheme 5. Hammett studies

The substantial energy stored in this highly strained intermediate *E*-**1** can be released either by π-bond rotation and return to **1**, or by [4+2]-cycloreversion to give **1a** and dienophile. As implied in **Scheme 3c**, the relative energy barriers of π-bond rotation *vs* rDA will determine the net reaction outcome of a single pass. Stated differently, *E*-**1** serves as a bifurcation point, with the amounts of rDA and π-bond rotation reflecting the relative energy barriers from the strained *E*-**1**- though with continued irradiation, more passes occur. The question of why rDA was favored for the pyran and the thio-pyran remained.

Two Hammett studies on different parts of the pyran to probe the electronic nature of the rDA transition state were performed (**Scheme 5**). In one series, substituents were introduced onto the aromatic ring that becomes part of the liberated diene fragment. Here, electron-donating groups accelerated the reaction, yielding a negative Hammett slope (ρ = –1.2). In the second series, substituents were placed on the aryl group associated with the dienophile fragment. In this case, electron-withdrawing groups increased the reaction rate, yielding a positive Hammett slope (ρ = +0.39).[9] Together, these opposing electronic effects provide a coherent picture. The rDA reaction is accelerated when the diene component is more electron-rich, and the dienophile component is more electron-poor. This trend mirrors the electronic requirements of a normal-electron-demand Diels-Alder reaction. Based on the principal of microscopic reversibility, the same orbital interactions that favor cycloaddition should also influence the reverse cycloreversion process.[24]

The Hammett data therefore supports an asynchronous but concerted rDA pathway with significant polarization in the transition state. The linear free-energy relationships do not suggest discrete ionic intermediates; rather, they indicate uneven bond cleavage within an overall pericyclic framework.



Scheme 6. Estimated free energy surface (CCSD(T)//M052X) for 4-X-phenylcyclohexenes

A central mechanistic question is why the oxygen-containing pyran and thiopyran succeeds while most related analogs fail. The answer emerges from the combination of experimental observations and high-level computational analysis (**Scheme 6** and **Table 1**). Computational analysis provides the energetic basis for the observed reactivity trends (**Scheme 6** and **Table 1**). Using DFT geometries followed by higher-level CCSD(T) single-point calculations, the authors compared phenylcyclohexene with oxygen-, nitrogen-, and sulfur-containing analogs. The computational protocol benchmarked the energies against known experimental values for *trans*-phenylcyclohexene, including triplet energies and *cis-trans* energy differences, giving confidence in the calculated energy surfaces.[25,26]

Computational analysis of the 4-X-phenylcyclohexene series provides a clear explanation for the experimentally observed differences in reactivity (**Scheme 6** and **Table 1**). Calculations revealed that replacing the methylene at the C4-position with oxygen does not significantly alter the strain energy of the *trans*-isomer. In the parent carbocyclic system, the calculated barrier for rDA fragmentation from the *trans*-isomer is approximately 30 kcal/mol, which is far too high to compete with the lower barrier for *trans*-to-*cis* rotation. As a result, phenylcyclohexene simply relaxes back to the *cis*-alkene before rDA can occur. The calculated *cis-trans* energy differences show that the *trans* isomers of the carbocyclic, oxo-, and aza- analogs are all similarly highly strained, with values of 46.4, 46.0, and 43.3 kcal/mol, respectively. In contrast, the thia- analog has a smaller *cis-trans* energy difference of 36.3 kcal/mol, likely a result of the longer C–S bonds, which allow the ring to better accommodate the *trans*-alkene geometry, thereby reducing strain. A comparative analysis of the key exit barriers for each *trans*-isomer, i.e. π-bond rotation and rDA fragmentation provides insight.

Table 1. Relative Energies (kcal/mol) from Computations on 4-X-Phenylcyclohexenes

CCSD(T) corr Results (a)	3 (X=CH_2)	1 (X=O)	4(X=NH)	2 (X=S)
Cis-trans energy difference	46.4	46.0	43.3	36.3

Barrier to π bond rotation from *trans* isomer	10.6	11.7	14.8	17.1
Barrier to retro Diels-Alder (rDA) from *trans*	30.0	13.1	21.4	17.0
rDA energetics from *trans* isomer	-14.5	-32.7	-24.0	-6.9
(a) CCSD(T) corr = CCSD(T)/cc-pvdz//M052X + DFT thermal correction (298 K)				

For the parent carbocycle, the barrier for π-bond rotation is only 10.6 kcal/mol, whereas the rDA barrier is much higher at 30.0 kcal/mol. Therefore, the *trans*-carbocycle preferentially relaxes back to the *cis*- alkene rather than undergoing fragmentation. Oxygen substitution dramatically changes the energetic landscape. While the oxo analog retains nearly the same *cis*-*trans* energy difference as the parent system, 46.0 kcal/mol, its rDA barrier is lowered to 13.1 kcal/mol, which is relatively close to the π-bond rotation barrier of 11.7 kcal/mol. As a result, rDA becomes competitive with relaxation, allowing productive formation of diene **1a**. Note that while it still has a slightly larger barrier and is expected to occur less frequently than thermal relaxation, the *cis*-isomer is expected to be re-excited. The aza- analog shows an intermediate case. Its rDA barrier is reduced compared to cyclohexene to 21.4 kcal/mol, but is still substantially higher than the π-bond rotation barrier of 14.8 kcal/mol. Thus, the aza-analog is predicted to favor relaxation over productive cycloreversion. The thia-analog is distinct. Its *trans*-isomer is less strained, with a *cis*-*trans* energy difference of only 36.3 kcal/mol, and its rDA is only modestly exergonic at −6.9 kcal/mol. However, the barriers for π-bond rotation and rDA, while raised relative to cyclohexene, are nearly identical to each other, 17.1 and 17.0 kcal/mol, respectively, making the two pathways competitive. Overall, oxygen occupies the optimal energetic sweet spot: it preserves the high strain energy of the *trans*-isomer while selectively lowering the rDA barrier enough to compete with *trans*-to-*cis* relaxation.[9] This study was consistent with the Hammett studies, which suggested that the barrier is lowered for rDA when the C4-position better supports negative charge.

4. Substrate scope

With the mechanistic foundation established, the transformation's synthetic value was demonstrated. Stable dihydropyrans can serve as masked diene precursors that release reactive dienes only upon visible-light activation. The generated dienes can then be intercepted in a one-pot rDA, DA sequence of reactions using suitable dienophiles (**Table 2**).[9] This “diene-on-demand” strategy proved broadly useful. *N*-Butylmaleimide, maleic anhydride, dimethyl fumarate, dimethyl acetylenedicarboxylate, methyl vinyl ketone, acrylonitrile, benzoquinone, and disopropyl azodicarboxylate all served as effective trapping partners. In all cases, very good isolated yields were obtained and excellent yields based on recovered starting material.[9] Since the diene outcompetes the pyran for quenching and can undergo dimerization, it was important not to allow its concentration to get too high, preventing full conversion.

Table 2. Synthetic scope of the photocatalyzed retro Diels-Alder reaction

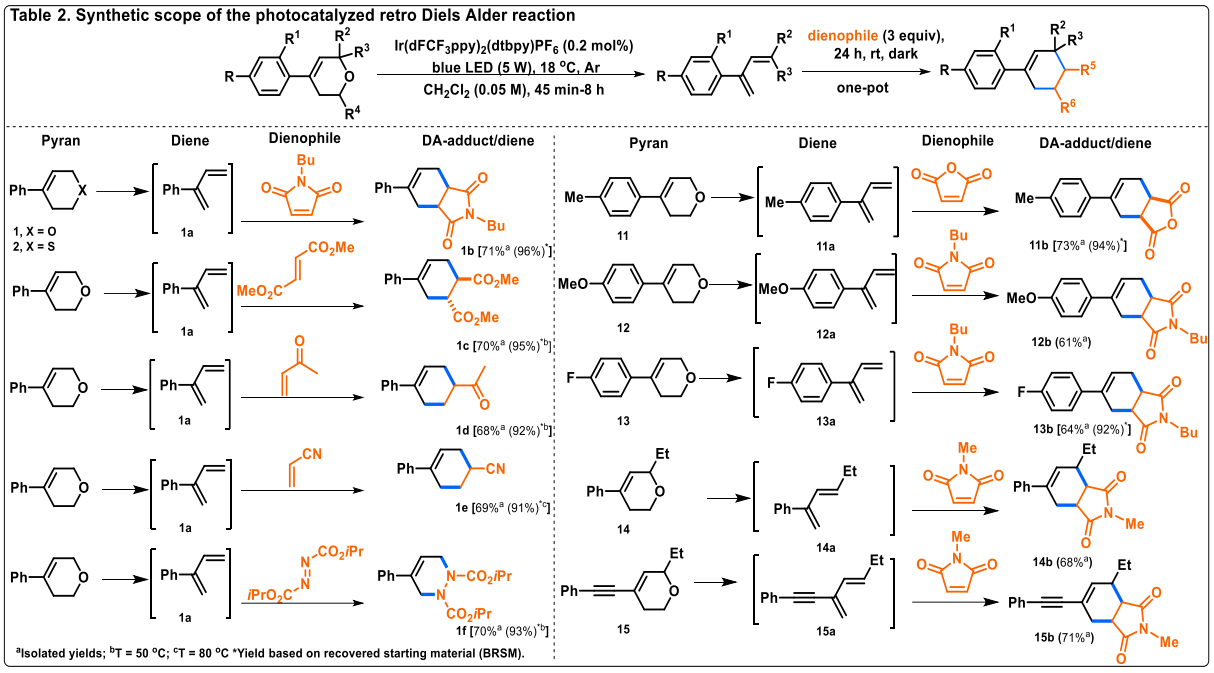
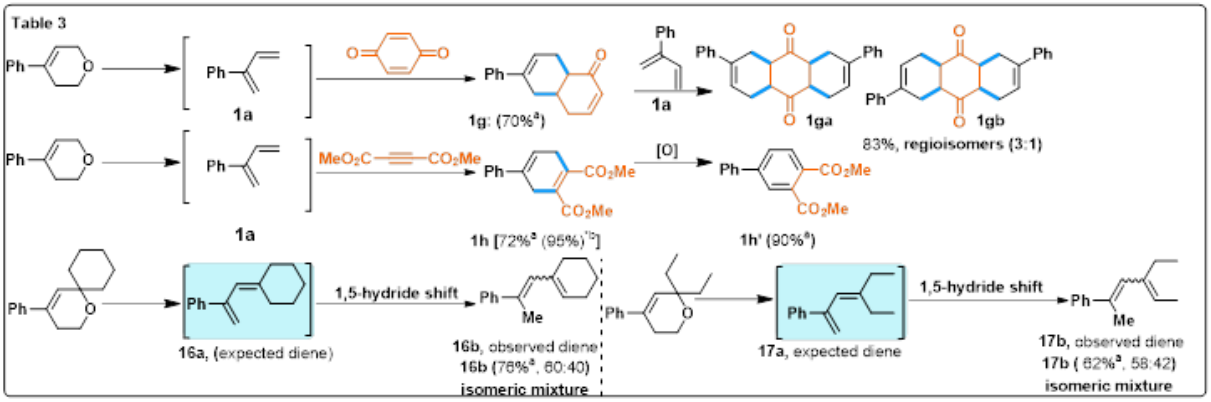
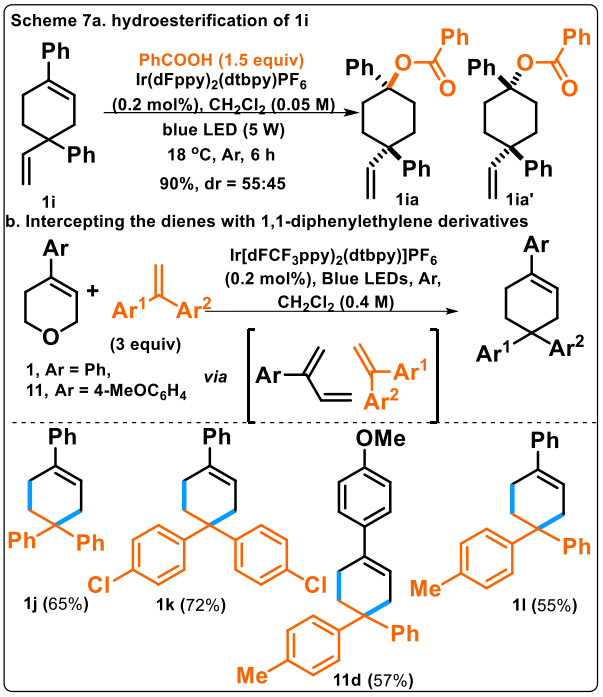


Table 3.



Particularly notable is the reaction with disopropyl azodicarboxylate, which enables a net C–O to N–N atom-pair exchange and provides rapid access to substituted tetrahydropyridazines (**1ga, 1gb) (Table 3**). Similarly, trapping with dimethyl acetylenedicarboxylate (**1h**), followed by oxidation, furnishes biphenyl products **1h'** (**Table 3**), while reactions with benzoquinone provide access to anthraquinone-like frameworks. The scope studies also revealed important limitations. Ortho-substituted aryl pyrans were poorly reactive, likely because allylic strain prevents effective conjugation between the arene and alkene, which is required for visible-light sensitization. Highly arylated dienes were prone to secondary photochemistry, whereas 6,6-disubstituted substrates **16a** and **17a** underwent unexpected 1,5-hydrogen-atom (**16b, 17b**) migration rather than clean diene isolation (**Table 3**). These results underscore both the power and the sensitivity of the platform; productive reactivity depends on balancing substrate excitation, *trans*-isomer formation, cycloreversion, and the photostability of the diene product.



Scheme 7. a) Hydroesterification of **1i** ;

b) Intercepting the dienes with 1,1-diphenylethylene derivatives

The study further shows that the diene products can participate in additional photochemical and cycloaddition pathways. By extending reaction time, increasing concentration, and using higher light intensity, the dimerization pathway could be intentionally favored, providing axially chiral vinylcyclohexene dimers in high yields (**1i**). These dimers themselves remain photoactive. Upon irradiation in the presence of benzoic acid, they undergo further sensitization and protonation, yielding ester products in high yield (**Scheme 7a**), suggesting that these structures also undergo energy transfer and isomerization, implying that they may function as molecular transducers. The authors also demonstrated that the diene can be intercepted by 1,1-diarylethylenes present from the start of the reaction, thereby generating new cyclohexene derivatives with diaryl quaternary centers *via* a photochemical coupling pathway (**Scheme 7b**). This expansion highlights the versatility of the diene-on-demand approach and suggests that visible-light-triggered rDA chemistry can be merged with multiple downstream reaction manifolds.

5. Conclusion

A conceptually important feature of this work is its contribution to skeletal editing. Rather than modifying peripheral functional groups, the method enables deconstruction and reconstruction of the molecular framework itself. A C–O-containing dihydropyran can be converted into new C–C- or N–N-containing ring systems through a visible-light-driven rDA/Diels-Alder sequence. In this sense, the reaction functions as a photochemical atom-pair swap. By experimentally validating Johnson's decades-old computational prediction, a new strategy for using photochemically generated strain as a driving force for molecular remodeling once

stabilized. The study demonstrates a facile approach to convert photochemical energy into strain energy within a molecule, and that this stored energy can undergo controlled release and be used to overcome otherwise prohibitive reaction barriers. This work therefore provides a compelling blueprint for future reaction design, in which visible-light energy transfer catalysis and strain-enabled intermediates are combined to achieve selective skeletal editing under mild conditions.

Declaration of interests

The authors declare no competing interests.

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