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Using Restricted Bond Rotations to Enforce Excited-State Behavior of Organic Molecules

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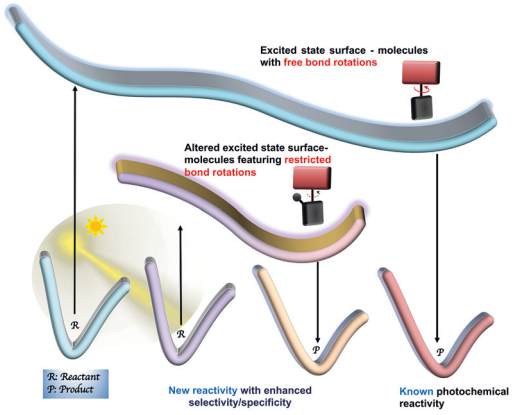

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This account highlights the role of restricted bond rotations in influencing the excited-state reactivity of organic molecules. It highlights the photochemical reactivity of various organic molecules and the design strategies that could be exploited by chemists to utilize restricted bond rotations to uncover new excited-state reactivity and to achieve selectivity.

Key words photocycloaddition, axial chiral transfer, excited-state reactivity, photocatalysis, energy transfer catalysis

1 Introduction

Molecular restrictions play a critical role in controlling the outcome of chemical transformations.[2–6] Molecules featuring restricted bond rotations can be tailored to be optically active, which could be exploited to influence stereochemical features in molecules and materials.[7–10] These structural features of compounds, known as atropisomers, are found in many natural products and lifesaving drugs.[11] Due to their significance and effectiveness in propagating chiral information, atropisomers are often employed as chiral perturbers[7–10] (e.g., as ligands) and as chiral catalysts[12–16] to influence the stereochemical outcome of chemical reactions. Atropisomers are also utilized as reaction templates to transfer chirality from the reactant to products.[7–10] While the impact of atropisomers in influencing the stereochemistry of thermal reactions have garnered widespread attention, their impact on excited-state processes has been an emerging area of interest.[7–10] This review highlights the systematic studies undertaken in our research group on employing restricted bond rotations, how to utilize them for chiral transfer during excited-state transformations, and how to tailor their properties to uncover new photochemical pathways.[9]

Unlike thermal reactions, synthesis of chiral molecules by photochemical methods has faced obstacles due to the nature of the excited-state processes (see below).[17] Stereoselectivity in a thermal reaction is governed by the differential activation energy of diastereomeric transition states formed during the reaction. However, photochemical reactions involve high-energy species in the excited state(s), often without any significant barriers. Hence, the reactivity of photoexcited molecules are often dictated by the excited-state lifetimes in which dynamics of the system plays a crucial role.[17] An added complication to the excited-state reactivity involves spin multiplicity (singlet vs. triplet), which dictates the mode of reactivity as well as selectivity.[18,19] Regardless of these challenges, light-mediated reactions are considered to be an excellent strategy for the synthesis of chemical compounds that are difficult to synthesize by thermal methods due to complementary nature of excited-state reactions vs. ground-state reactions.[20–22] Strained ring systems, which are difficult to synthesize by thermal reactions (such as four-membered rings), can be easily synthesized in the presence of light – a benign, green reagent.[23–24]

Several research groups in the past explored the challenge associated with photochemical asymmetric synthesis. Some of the earliest reports were by Le Bell (1874)[25] and van't Hoff (1894),[26] who proposed the idea of using circularly polarized light (CPL) for the synthesis of optically active compounds. This method depended on differential ab-

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Biographical Sketches

Dr. Sunil Kumar Kandappa received his M.Sc in Applied Chemistry from Mangalore University, India (2009). After working as a project assistant at JNCASR, India, he joined the research group of Prof. Jayaraman Sivaguru in 2014 and received his doctoral degree in 2019. For his doctoral work, Sunil was awarded the McMaster Fellowship. His thesis work is titled 'Light as a Reagent for Chemical Reactions-Uncovering the New Reactions from the Excited State'. He is currently pursuing his post-doctoral work with Prof. Mark E. Thompson at the University of Southern California.

Dr. Sapna Ahuja received her B.Sc. (Hons.) and M.Sc. (Hons.) in Chemistry from Panjab University, India (2015). She joined the research group of Prof. Jayaraman Sivaguru in 2015 and received her doctoral degree in 2020. For her doctoral work, Sapna received the McMaster Fellowship. Her thesis work is titled 'Uncovering New Excited State Reactivity through Molecular Restrictions'. She is currently pursuing her post-doctoral studies at the University of Pennsylvania under the guidance of Prof. Sergei Vinogradov.

Dr. Ravichandranath (Ravi) Singathi did his Bachelor's in Science (Chemistry) at Osmania University (2009) and Master's (Industrial Chemistry) from the National Institute of Technology Warangal, India (2011). Before moving to USA in 2014, he worked at Asian Paints Pvt. Ltd India, as a quality control officer for a couple of years. Ravi received his doctoral degree under the guidance of Prof. Jayaraman Sivaguru at Bowling Green State University, Ohio. After his graduation, Ravi joined the HEROES (Harnessing Emerging Research Opportunities to Empower Soldiers) program at the University of Massachusetts, Lowell as Postdoctoral Research associate and worked for a year. Currently, he is working as Sr. Research Chemist at LANXESS corporation, Connecticut, USA.

Ms. Lakshmy Kannadi Valloli received her BS-MS in Chemistry from the Indian Institute of Science Education and research, Thiruvananthapuram, India (2018). She joined the group of Prof. Jayaraman Sivaguru at BGSU in 2018 and is working towards her doctoral degree. Her research focuses on developing new excited-state photochemical transformations and evaluation of photophysical characteristics of compounds to understand their chemical reactivity.

Ms. Sruthy Baburaj received her BS-MS in Chemistry from Indian Institute of Science Education and Research, Kolkata, India (2018). She joined the group of Prof. Jayaraman Sivaguru at BGSU in 2018 and is working towards her doctoral degree. Her research focuses on developing novel excited-state phototransformations, light-responsive materials, and developing strategies to understand photodegradation in materials.

Mr. Jayachandran Parthiban received his M.Sc in Chemistry from Madras Christian college, India (2011). He spent two years in Academia Sinica, Taiwan. He joined the research group of Prof. Jayaraman Sivaguru at BGSU in 2019 and is working towards his doctoral degree. His research is focused on developing new catalytic methods for photochemical transformations and developing new materials for optical applications and eye protection, as well as understanding excited-state phenomenon using photophysical methods.

Prof. Dr. Jayaraman Sivaguru (Siva) is the Distinguished University Professor and the Antonia and Marshall Wilson Professor at the Department of Chemistry at Bowling Green State University (BGSU), Bowling Green, Ohio. He serves as the Associate Director for the Center for Photochemical Sciences at BGSU. He completed his bachelor's (1996) and master's (1998) degrees from St. Joseph's College, Trichy, Tamil Nadu, India, and Indian Institute of Technology, Madras, Tamil Nadu, India, respectively. He came to the United States in 1998 to pursue his doctoral degree with Prof. V. Ramamurthy at Tulane University, New Orleans, LA, USA. For his doctoral work, he was recognized by the Inter-American Photochemical society with the Closs award in 2003. After receiving his Ph.D. in 2003, he did his postdoctoral studies with Prof. Nicholas J. Turro at Columbia University, NY, USA, from 2003 to 2006. Siva began his independent career as an assistant professor at North Dakota State University (NDSU) in 2006, promoted to an associate professor in 2011 and to a full professor in 2014. His recognitions include 2008 NSF CAREER award, 2010 Grammaticakis-Neumann Prize from the Swiss Chemical Society for outstanding independent research by a young faculty below 40 years in the areas of photochemistry and photobiology, 2011 young-investigator award from the Inter-American Photochemical Society (I-APS), and 2012-young investigator award from Sigma-Xi. At NDSU, Siva was honored with the 2010 Excellence in Research award and 2011 Excellence in Teaching awards, both from the College of Science and Mathematics, and the 2012 Peltier Award for Innovation in Teaching. He was a visiting young professor for Global Centre for Excellence at Osaka University, Japan. In 2018 he was a visiting fellow of the Chinese Academy of Sciences under the President's International Fellowship Initiative. From 2013, he has served as the American editor for the *Journal of Photochemistry and Photobiology A: Chemistry*, published by Elsevier. From 2020, he has served as the co-editor-in-chief of *Journal of Photochemistry and Photobiology*. He is also an international advisory board member of the photochemistry IUPAC symposium. In 2021, Prof. Sivaguru was named Honda-Fujishima Lectureship awardee by the Japanese photochemical association for extremely outstanding achievement in the study of photochemistry. In Fall 2017, he moved his research program to Bowling Green State University and the Center for Photochemical Sciences. Currently his research program works on both basic and applied aspects of photochemical sciences. His group's research interest span the areas of (a) developing new excited-state transformations, (b) light-induced axial to central chiral transfer in atropisomeric systems, (c) asymmetric organophotocatalysis, (d) supramolecular photocatalysis (e) light-responsive materials and coatings, and (f) visible-light photoinitiators.

sorption of left- and right-circularly polarized light (CPL) by enantiomers.[27] Several decades later, Kuhn and Braun (1929)[28] experientially demonstrated the feasibility of this approach by irradiating a racemic mixture of α-bromopropionic ester in the presence of circularly polarized light. Preferential absorption of circularly polarized light by one of the isomers resulted in photodecomposition, leaving the other enantiomer in an excess amount. They observed an optical rotation of $[\alpha]_D$ +0.5 after 50% conversion. Kagan and co-workers (1974) achieved 20% enantiomeric excess by photodecomposition of a racemic mixture of camphor with circularly polarized light after 99% conversion.[29] However, due to low stereoselectivity and product yields, these methods did not attract the attention of chemists for traditional synthetic purposes. Nonetheless, the interest in achieving high enantiomeric excess by the application of circularly polarized light in earlier days were directed towards the origin of homochirality of biomolecules in nature.[30–31]

Solution-phase photochemical asymmetric synthesis, which was developed in the later decades, showed significant increase in the optical yield.[27,32,33] Scharf and co-workers reported chiral-auxiliary-mediated Paternò–Büchi reaction with high diastereomeric excess (*de* >96%).[34,35] Pioneering work of Inoue and co-workers showcased the enantio-differentiating photoisomerization of (*Z*)-cycloheptene to (*E*)-cycloheptene in the presence of chiral sensitizers, leading to high enantioselectivity.[36–38] High enantiomeric excess was also achieved by using a chiral complexing agent that interacted with the ground-state reacting partner to induce chirality in the photoproduct.[39] Extensive investigation of supramolecular systems as confined media has shown promising outcomes in achieving high stereoselectivity during excited-state transformations.[40] For example, photoreactions in crystalline media has showed excellent diastereo-/enantioselectivity.[41,42] Readers are encouraged to refer to other reviews related to supramolecular photochemistry for approaches to controlling excited-state phenomenon in organized assemblies.[40,43]

While organized assemblies have provided immense knowledge about controlling excited-state reactivity, a general strategy for achieving high optical yields during photoreaction in solution was lacking. For example, photoreaction in crystalline media showed stereoselectivity close to 100%.[41,42] But, this strategy cannot be employed for substrates that are not crystalline in nature.[44,45]

2 NEER – Principle and Restricted Bond Rotations in the Excited State

In an attempt to develop a generalized strategy for inducing chirality in a photochemical reaction, our research group utilized atropisomeric molecules with an inbuilt photoactive chromophore that were geared towards a specific photoreaction of interest. Atropisomers that are stable at room temperature have energy barriers in excess of 27 kcal/mol.[7–10] The rationale for utilizing such stable atropisomeric molecules, or molecules featuring restricted bond rotations, is to translate the different dynamics that are prevalent in the ground- and excited-state towards efficient reactivity and stereo-enrichment in the photoproduct. This strategy was termed as 'axial to point chiral transfer strategy'[9] and was developed by merging Havinga's 'non-equilibrating excited rotamers' (NEER) principle[46–48] and Curran's 'prochiral auxiliary approach'[8] for non-biaryl atropisomeric substrates. Figure 1 illustrates the NEER principle[46–48] and the different dynamics present in ground and excited states, by showcasing diene as a model system. The diene *s-cis* and *s-trans* rotamers that are in equilibrium in the ground state do not equilibrate in the excited state (Figure 1, top). This difference in dynamics affects the reactivity of the diene in the excited state. The same phenomenon was envisioned for chiral rotamers that feature restricted bond rotations in the ground state; namely, atropisomeric compounds that slowly racemize in the ground state that, upon photoexcitation, will not equilibrate in the excited state, leading to effective chirality transfer as the photoreaction occurs at a faster rate than racemization. This effective transfer of axial chirality was labeled as 'axial-to-point chirality transfer in photochemical reactions'.[49–52]

Based on the above NEER-principle-inspired strategy, our group has established a general strategy for employing axially chiral compounds for asymmetric photochemical

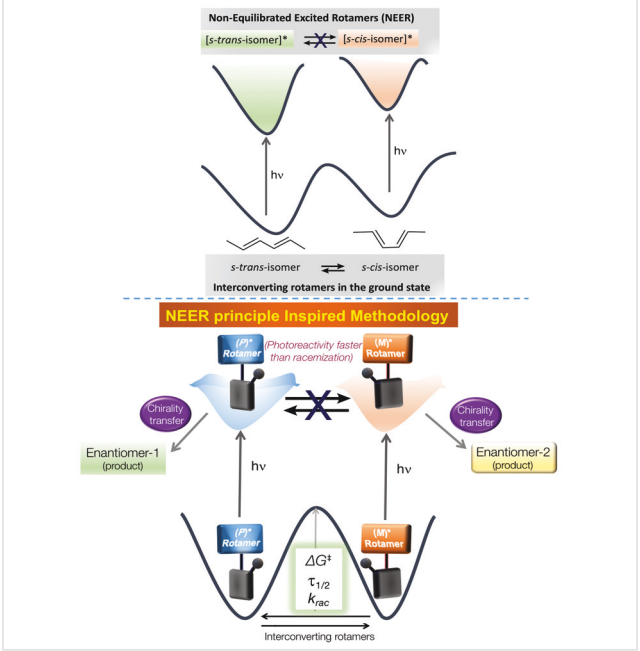
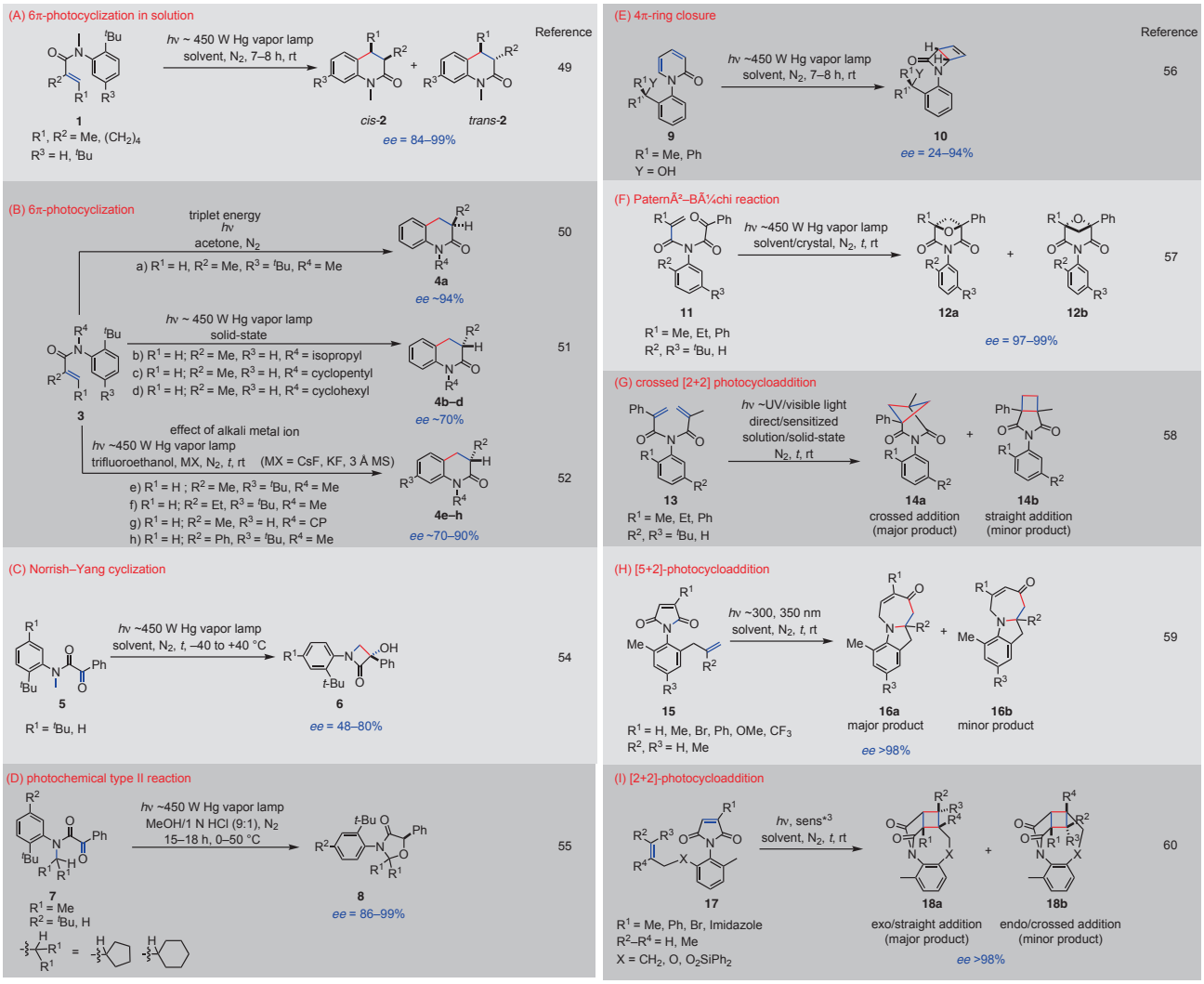


Figure 1 Translating restricted bond rotations in the excited state for atropselective phototransformations – A NEER-principle-inspired methodology[46–48]



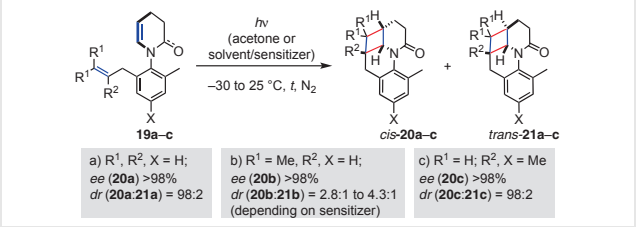
Scheme 1 Photochemical axial to point chirality transfer strategy/atropselective photoreactions developed by Sivaguru and co-workers.

transformations.[9] The strategy was shown to work for various excited-state transformations. One of the first reports by our group to illustrate the above axial chirality to point chirality transfer strategy from the excited state involved 6π-photocyclization of atropisomeric acrylanilides **1** and **3** in solution (Scheme 1; entries A, B)[49–52] to form the corresponding 3,4-dihydroquinolinone products **2** and **4** with high atropselectivity (atropselectivity is selective transformation of a single atropisomer) in the photoproduct (84–99% *ee*). This reaction was also investigated under triplet energy transfer conditions[50] as well as under the influence of alkali metal ions[52] (Scheme 1) leading to highly enantioenriched photoproducts (Scheme 1; entry B). The atropselective strategy was also successfully evaluated in crystalline media[51] (Scheme 1; entry B) and under elevated pressure.[53] Some of the other successful approaches from our group include Norrish–Yang type II reaction of atropisomeric α-oxoamides **5** to form the corresponding cyclobutanol derivatives **6** (Scheme 1; entry C),[54] Norrish–Yang type II reaction of atropisomeric α-benzoylformamides **7** to oxazolidine-4-ones **8** (Scheme 1; entry D),[55] 4π-ring closure of atropisomeric 2-pyridones **9** (Scheme 1; entry E),[56] Paternò–Büchi reaction of atropisomeric imides **11** in solution and in the solid state (Scheme 1; entry F) leading to oxetanes **12**,[57] crossed-[2+2]-photocycloaddition of atropisomeric imides **13** (Scheme 1; entry G),[58] [5+2]-photocycloaddition of atropisomeric maleimides **15** (Scheme 1; entry H) leading to azidipines **16**,[59] and [2+2]-photocycloaddition of atropisomeric alkenyl-maleimides **17** (Scheme 1; entry I) leading to the corresponding photoproduct **18**.[60] The reactions related to the systems listed in Scheme 1 were highlighted as an *Accounts* article.[9] The present review highlights divergent reactivity observed in various excited chromophores *viz.*, (a) enamide chromo-

phores that undergo [2+2]-photocycloaddition, Paternò–Büchi reaction vs. [3+2]-photocycloaddition,[23,61,62] (b) atropisomeric enone chromophores that can be manipulated for photoreactivity towards Norrish–Yang vs. 6π-photocyclization,[63] and (c) maleimide chromophores that undergo [2+2]-photocycloaddition vs. photoene reaction (see below).[64,65]

3 [2+2]-Photocycloaddition of Enamides

Acyclic enamides featuring *N*-acyl substituent typically undergo acyl migration under photochemical conditions. Ninomiya, Mori and co-workers[66] reported 6π-cyclization of *N*-benzoyl enamides to form the corresponding cyclic adducts. However, reports on the photocycloaddition of cyclic enamides are scarce. Sivaguru and co-workers explored photocycloaddition reactions involving atropisomeric enamides **19a–c** (Scheme 2) with a suitably tethered double bond. Triplet sensitized [2+2]-photocycloaddition of C=C double bond of 3,4-dehydro-2-pyridone derivative[61] tethered with an allylic C=C double bond at the *ortho*-position of phenyl ring **19a–c** resulted in the formation of the corresponding cycloadduct **20a–c** and **21a–c** with high atropselectivity (>98%, Scheme 2). The photoproduct **20a–c** featured a *cis*-fusion of the hydrogens between the cyclobutyl and lactam rings, while photoproduct **21a–c** featured a *trans*-fusion of the hydrogens between the cyclobutyl and lactam rings. Atropisomeric enamides **19a–c** had a fairly high racemization barrier that dictated the atropselectivity in the photoproduct. Diastereoselectivity in the *cis*-**20a–c** and *trans*-**21a–c** photoproducts was dictated by the nature of allylic substitution (Scheme 2) with *gem*-dialkyl substituted alkenyl enamide **19b** giving low diastereoselectivity compared to high diastereoselectivity with unsubstituted terminal alkenyl enamides **19a**,**c**.



Scheme 2 [2+2]-Photocycloaddition of atropisomeric six-membered enamides **19a–c**[61]

Photophysical experiments established that enamides **19** had triplet energy of 73 kcal/mol (Figure 2). In the absence of triplet sensitizer, no reaction was observed, whereas [2+2]-photocycloaddition was observed with triplet sensitizer acetone (which was used as solvent and sensitizer E_T = 79 kcal/mol), xanthone (E_T = 74 kcal/mol), and acetophenone (E_T = 73 kcal/mol) in methanol. Based on this observation it was proposed (Scheme 3) that the reaction proceeded through energy transfer, leading to the triplet state of **19** (^{3}[**19**]*). This triplet species underwent cyclization to form triplet biradical t-BR**19**. Enamide **19b**, featuring a *gem*-dimethyl substituent at the terminal alkene (R^1 = CH_3 in **19b**), proceeded via a tertiary radical that was long-lived, leading to pyramidal inversion at the β-carbon of the lactam ring, producing triplet radical t-BR**19'b**. This triplet biradical intersystem crossed to form the corresponding singlet biradical s-BR**19'b**, which subsequently ring closed to the photoproduct with moderate diastereoselectivity (Scheme 3). On the other hand, triplet

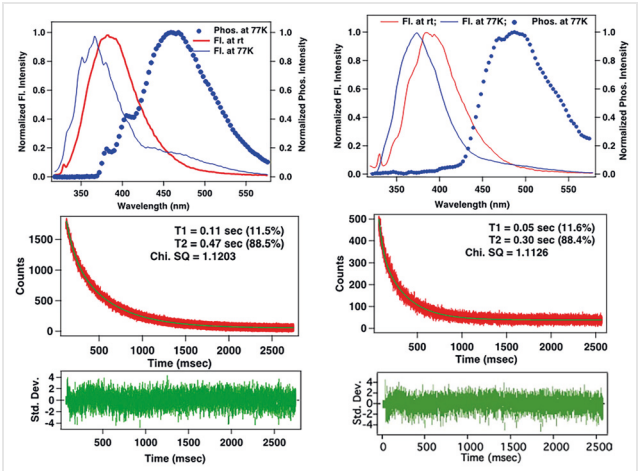
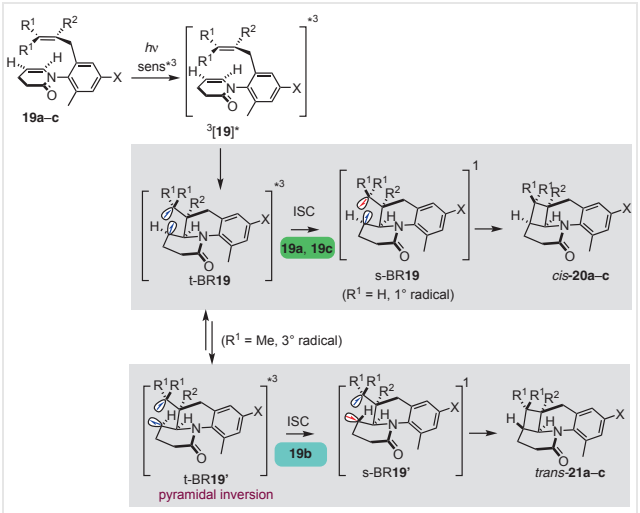


Figure 2 (Top) Fluorescence at 298 K and 77 K (red and blue) and phosphorescence at 77 K (blue dotted) of **19a** in methylcyclohexane (right) and ethanol (left). (Bottom) Phosphorescence decay kinetics at 77 K in MCH glass (right) and ethanol glass (left). Reproduced from reference[61] with permission from the Royal Society of Chemistry.



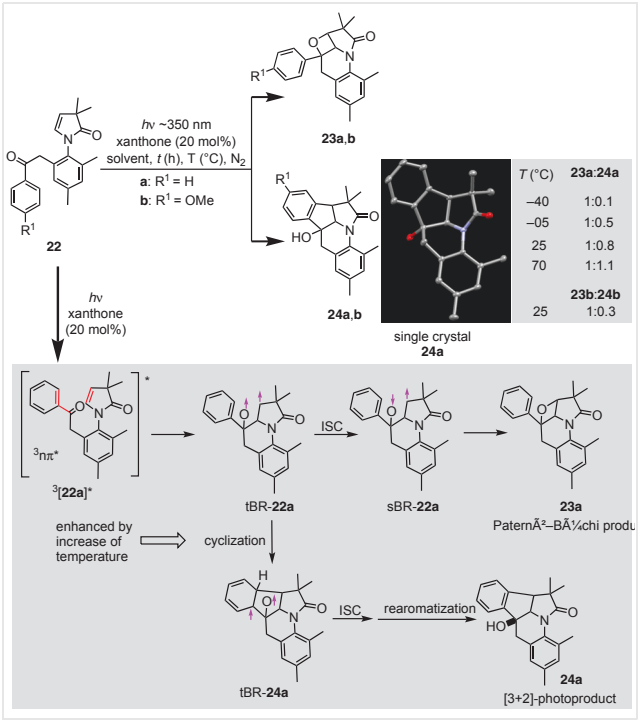
Scheme 3 Mechanistic rationale for intramolecular [2+2]-photocycloaddition of **19a–c**

energy transfer to enamides **19a** and **19c** led to the corresponding triplet biradical t-BR**19a/c**, featuring a primary radical centre at the carbon bearing R^1 substituent (as R^1 = H, Scheme 3). This short-lived primary triplet-biradical underwent intersystem crossing at a faster rate than the biradical generated from **19b** to form the singlet biradical s-BR**19a/c**. The singlet biradical s-BR**19a/c** subsequently cyclized to form the cycloadduct with high diastereoselectivity (Scheme 2 and Scheme 3).

4 [3+2]-Photocycloaddition vs. Paternò–Büchi Reaction of Enamides

Divergent photochemical reactivity of enamides **22**, featuring a phenyl ketone tether, was investigated towards [3+2]-photocycloaddition vs. Paternò–Büchi reaction.[23,61,62] While the staple photochemical reactivity of phenyl ketones towards Paternò–Büchi reaction was well established,[67–69] altering the course of reactivity to a different photochemical pathway is quite challenging due to the short time span of the reactive species involved in the phototransformations.[18] Research from our group showed that higher temperatures can be employed to alter the chemical reactivity of **22**. Moreover, the effect of entropic factors influencing enantioselectivity/diastereoselectivity in photoreactions have been elegantly demonstrated by Inoue, Mori and co-workers.[70,71] Results from our group demonstrated that the chemoselectivity from the same excited state can be controlled by varying the reaction temperature. This is different from photoreactions in which chemoselectivity can be achieved by altering the nature of the excited state.[72,73] We showed that enamides **22**, featuring benzoyl substituents, react in a divergent fashion preferring the expected Paternò–Büchi product **23** at low temperature (as well as at room temperature), whereas the [3+2]-photoproduct **24** was preferred at higher temperatures (Scheme 4).[23,61,62]

Photoreactivity of **22a** in acetonitrile under energy transfer from xanthone as the triplet sensitizer gave Paternò–Büchi product **23a** as the major product (Scheme 4). Upon increasing the temperature to 70 °C, an unusual product **24a** was observed and its structure was unequivocally established by single-crystal XRD analysis to be a [3+2]-photocycloaddition product (Scheme 4). Based on photophysical studies, it was established that the enamide with a benzoyl substituent featured an nπ* excited state (Figure 3, top) with a triplet energy (E_T) of ca. 73 kcal/mol above the ground state, with a lifetime of 8 ms in EtOH at 77 K.[23] Conversely, time-resolved phosphorescence of **22b** in EtOH at 77 K showed a multiexponential decay (due to distinctive chromophores viz., enamide and the carbonyl functionalities) with phosphorescence lifetimes ranging from 62 to 438 ms (Figure 3, bottom).[62] The lowest triplet excited state of **22b** was assigned as ππ* characteristic due to the similarities with *para*-methoxy acetophenone chromophores (compare the spectra in Figure 3B). Based on photophysical studies, temperature-dependent chemoselective behavior from the same excited state (e.g., nπ* excited state in **22a**) was mechanistically rationalized to proceed via a triplet excited **22a** (i.e., ^{3}[**22a**]*) centered around the benzoyl chro-



Scheme 4 [2+2]-Photocycloaddition of atropisomeric six-membered enamides **22a,b**

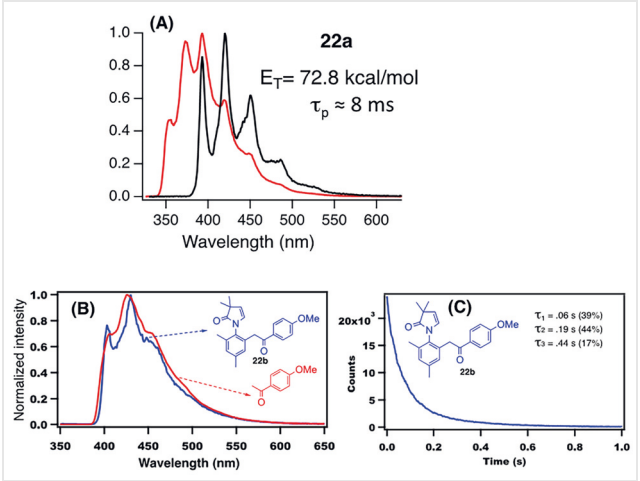


Figure 3 (A) Phosphorescence spectra at 77 K of benzoyl substituted enamides **22a** and (B and C) **22b**. Top figure reproduced from references[23] with permission from the American Chemical Society. Bottom figure reproduced from references[62] with permission from John Wiley & Sons.

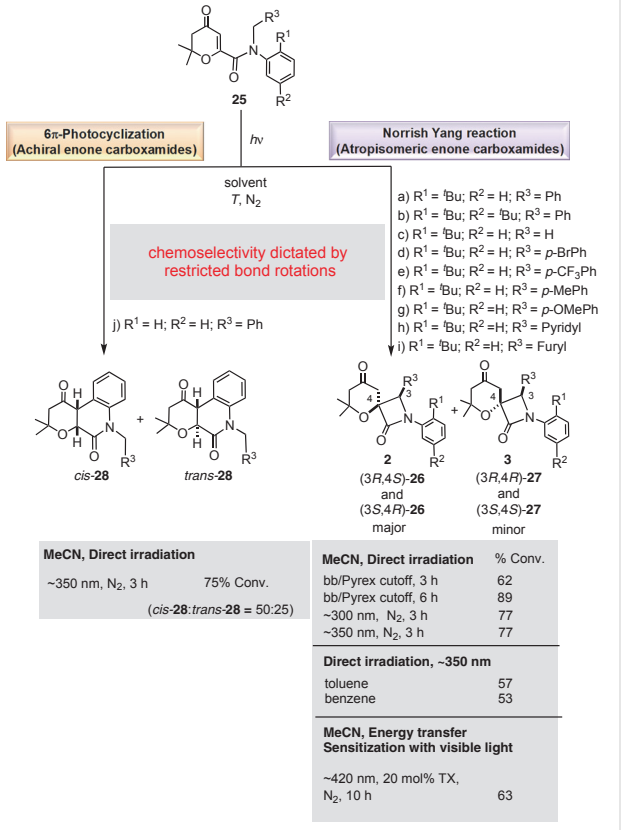
mophore (Scheme 4, bottom). This benzoyl-based triplet in **22a** reacted with the enamide alkene unit to produce a 1,4-triplet biradical tBR-**22a**. At low temperatures, tBR-**22a** intersystem crossed to singlet biradical sBR-**22a** en route to the formation of the Paternò–Büchi product **23a**. Carrying out the reaction at elevated temperature enabled the 1,4-triplet biradical tBR-**22a** to undergo cyclization and led to the formation of 1,3-triplet biradical tBR-**24a**, which underwent intersystem crossing followed by re-aromatization to from the [3+2]-photoproduct **24a**. As the [3+2]-photoproduct **24a** was observed at elevated temperatures, it revealed an energy barrier for the conversion of tBR-**22a** to tBR-**24a′**. This energy barrier was insurmountable at low temperatures, leading to the Paternò–Büchi product **23a**. At high temperatures, the triplet 1,4-biradical tBR-**22a** had divergent pathways; namely, Paternò–Büchi pathway through intersystem crossing or overcoming the energy barrier to form tBR-**24a**. The different reactivity of the tBR-**22a** was dictated by temperature, which was reflected in the **23**/**24** product ratio. The study showcased that the established Paternò–Büchi reactivity towards [3+2]-photocycloaddition pathway can be altered by manipulating factors that control reaction coordinates such as the orientation of the orbitals, trajectory, and accessibility of the radical center.

5 Divergent Photoreactivity of Enones Dictated by Restricted Bond Rotations: Norrish–Yang Reactions vs. 6π-Photocyclization

Photochemical reactivity of enones **25** under both visible-light-mediated energy transfer catalytic conditions and under directed irradiations displayed divergent behavior depending on restricted bond rotations around the amide bond (Scheme 5).[63] Photochemical reactivity of atropisomeric enone carboxamides **25a–i** featured hydrogen abstraction, leading to the corresponding spiro-β-lactams **26/27** (Scheme 5, right), whereas the corresponding achiral/planar enone carboxamide **25j** underwent 6π-photocyclization, leading to 3,4-dihydroquinolin-2-one photoproduct **28** (Scheme 5, left). For example, photoexcitation of enone **25a** under direct irradiation (ca. 300 or 350 nm) or through energy-transfer sensitization with visible light led to efficient reactivity (Scheme 5) with the formation of spiro-β-lactams **26a/27a**. The conversion varied based on the reaction conditions from 53 to 77% (Scheme 5). The diastereomeric ratio (*d.r.*) in the spiro-β-lactam photoproduct **26**/**27** was 95:5. The enantioselectivities in the diastereomeric photoproducts were >95%. A critical point of note is that the restricted C–N_{Ar} bond rotation in the reactant enone **25** was not prevalent in the photoproduct due to the reduced C–N–C bond angle in the β-lactam ring.

The facile C–N_{Ar} bond rotation in the spiro-β-lactam was confirmed through opposite optical rotation values in the corresponding enantiomeric photoproducts. This feature was exploited for transferring axial chirality in the reactant to point chirality in the photoproduct(s) with high enantiomeric excess. While atropisomeric enones **25a–h** underwent hydrogen abstraction to form spiro-β-lactam type **26**/**27**, the corresponding non-atropisomeric enones **25j** underwent 6π-photocyclization (Scheme 5) leading to *cis*- and *trans*-product (*cis*-**28**/*trans*-**28**) with *cis*-product being the major product.

Detailed photophysical studies (Figure 4) were performed to understand the reactive dichotomy in atropisomeric and non-atropisomeric enones leading to chemoselective reactivity from the excited state by utilizing atropisomeric enones **25b–c**, and the achiral enone **25j**. As no noticeable room temperature fluorescence was observed in either methylcyclohexane (MCH) or ethanol (EtOH), the emission studies were performed at 77 K in EtOH glass, which showed observable phosphorescence in **25b** and **25j** (Figure 4A,B) with triplet energies of 62 and 61 kcal/mol, respectively. A bi-exponential decay was observed for this phosphorescence with lifetimes of around 0.15 ms and 0.1s

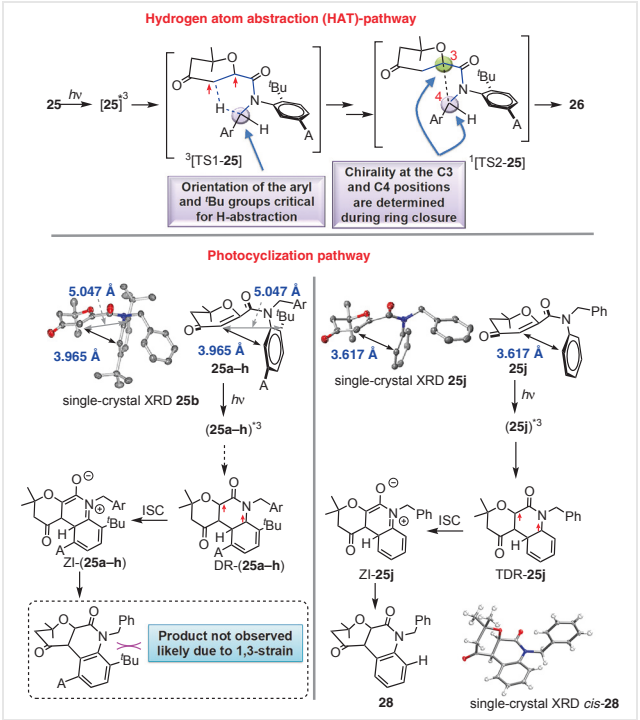


Scheme 5 Chemoselective photoreaction of enones carboxamides **25a–i**: Norrish–Yang reaction vs. 6π-photocyclization[63]

for both **25b** and **25j** (Figure 4A,B). Based on this, it was postulated that **25** featured a mixture of both nπ* and ππ* triplet excited states (Figure 4), and that the observed reactivity (Scheme 5) originated from triplet excited states of both atropisomeric and achiral enones.

Transient absorption spectra (Figure 4C) centered around 330 nm were generated using pulsed laser excitation of an argon-saturated solution of atropisomeric substrates **25b** and **25c** in acetonitrile with lifetimes of 1.7 ms and 1.9 ms, respectively (Figure 4C, inset). The transients were assigned to triplet states because they were efficiently quenched by oxygen. In the case of achiral enone **25j** (Figure 4, bottom), the triplet transient generated in acetonitrile was centered around 380 nm with a lifetime of ca. 15 ns (Figure 4D–E). This transient gave rise to a new transient centered around 330 nm as well as a broad absorbance at 750 nm (Figure 4F) with a lifetime of ca. 6 µs (Figure 4G–H) and was not quenched by molecular oxygen. Based on literature precedence[74] and on the characteristic features, this transient was assigned to zwitterion (ZI-**25j**) involved in the reaction pathway.

Computational analysis provided insight into the divergent reactivity of achiral and atropisomeric enones. Utilizing **25a** as model for computational studies, two key transition states, the triplet ^{3}[TS1-**25a**]‡and the singlet ^{1}[TS2-**25a**]‡, were identified as playing seminal roles in determining the stereochemistry of the spirolactam product



Scheme 6 Proposed mechanistic rationale for the observed photochemical dichotomy in atropisomeric and achiral enones leading to Norrish–Yang reaction vs. 6π-photocyclization

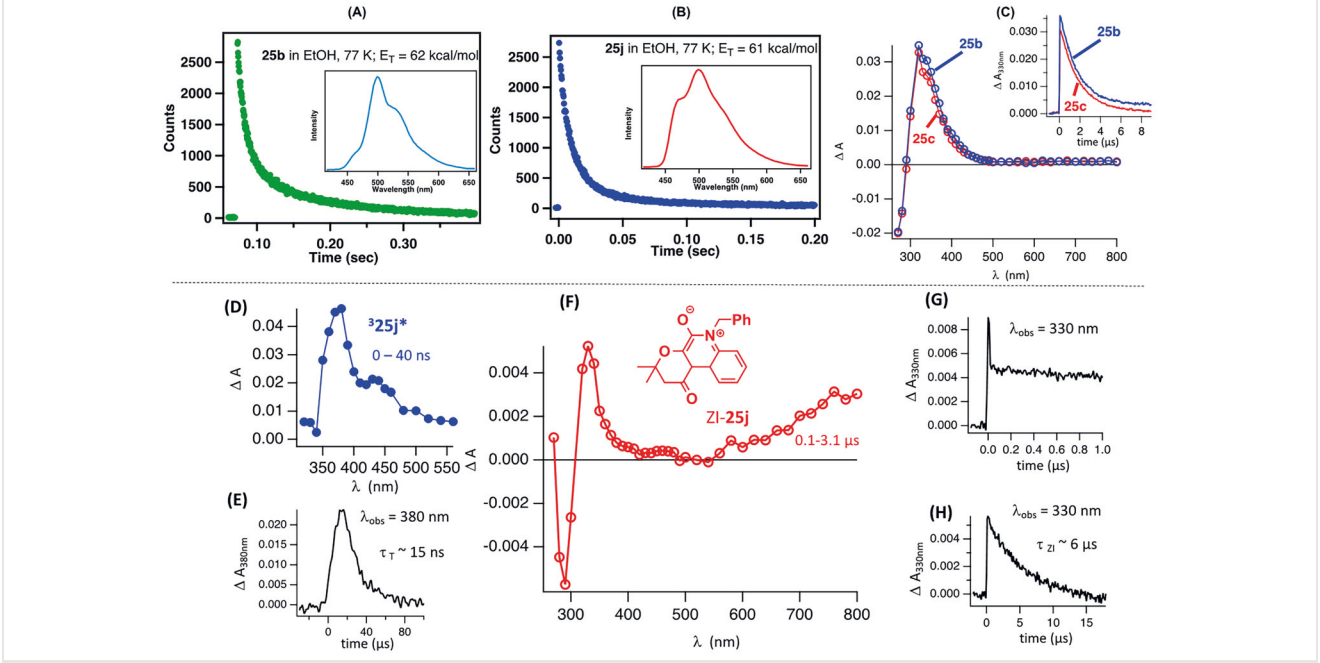


Figure 4 (Top) Phosphorescence decay kinetics of atropisomeric enone **25b** (A) and achiral enone **25j** (B) at 77 K in EtOH glass. The respective phosphorescence spectra are given in the insets. (C) Transient absorption spectra after pulsed laser excitation (λ_{ex} = 308 nm, 15 ns pulse width) of argon-saturated solutions of atropisomeric enones **25b** and **25c** in acetonitrile. Absorbance kinetic traces monitored at 330 nm (inset). (Bottom) Transient absorption spectra of **25j** monitored at 0–40 ns (D) and 0.1–3.1 ms (F) after pulsed laser excitation (λ_{ex} = 308 nm, 15 ns pulse width) of an argon-saturated solution of **25j** in acetonitrile. Absorbance kinetic traces monitored at different wavelengths and timescales are shown in (E), (G), and (H). Reproduced from references[63] with permission from John Wiley & Sons

(Scheme 6, top). For abstraction of the benzylic hydrogen atom through triplet ^{3}[TS1-**25a**]‡, the orientation of the benzylic phenyl ring away from the *ortho*-*tert*-butyl substituent, was found to be lower in energy. In the next key transition state, singlet ^{1}[TS2-**25a**]‡ was found to be crucial in determining the stereochemistry of the spirolactam photoproduct. In the case of **25a**, the relative energy of the transition state for the formation of (3*S*,4*R*)-**26a** was lower in energy by 2.6 kcal/mol than that for the formation of (3*S*,4*S*)-**26a** (Scheme 5 and Scheme 6). This computed energy difference reflected a diastereoselectivity of 97%, which was in line with the observed experimental selectivity.

Single-crystal XRD analysis provided further insights into the different reactivity in atropisomeric enones **25a–h** and achiral enone **25j**. In the case of enone **25j**, the distance from the α-enone-carbon to the N-phenyl *ortho*-carbon was found to be optimal (ca. 3.6 Å) for photocyclization from a triplet excited-state **25j** (Scheme 6, bottom right). This triplet excited-state **25j** underwent cyclization through a triplet diradical **TDR-25j** followed by intersystem crossing to a zwitterion ZI-**25j**, which was observed as a transient in laser flash photolysis (Figure 4) en route to the cyclized photoproduct **28**. Single-crystal X-ray structure of atropisomeric enone **25b** divulged that due to steric factors, the N-aryl substituent was orthogonal to the plane formed by CH_2-N-C=O substituents, which was reflected in a higher distance of 5.047 Å between the α-enone-carbon and the N-phenyl *ortho*-carbon featuring the butyl group (Scheme 6, bottom left). The developing 1,3-strain (A-strain) between the N-(CH_2-aryl) substituent and the *ortho*-*tert*-butyl group in the photoproduct hindered formation of the 6π-photocyclization product (Scheme 6, left) in spite of the distance (ca. 3.9 Å) from the α-enone-carbon to the N-phenyl *ortho*-carbon without a *tert*-butyl group. Thus, a comprehensive investigation of photochemical, photophysical, computational, and structural features of achiral and atropisomeric enones showcased the factors responsible for the divergent reactivity.

6 Divergent Photoreactivity of Imides with Alkenes: [2+2]-Photocycloaddition vs. Photoene Reaction

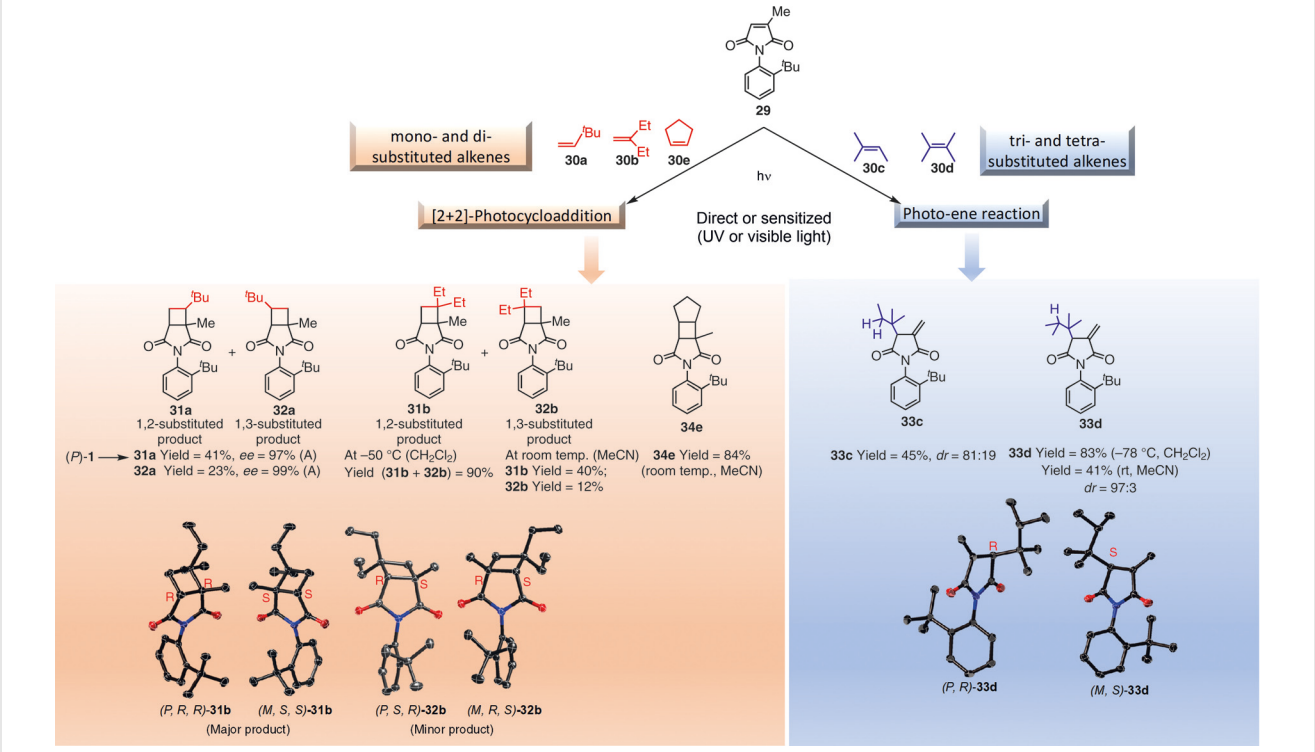
The [2+2]-photocycloaddition is a textbook example for photoreactivity of two alkene double bonds and it is an allowed process in the excited state.[75,76] The ene-reaction on the other hand is a thermally allowed process that requires elevated temperatures or can be performed under catalytic conditions.[77,78] There are exceptions to the mode of reactivity of an excited molecule towards [2+2]-photocycloaddition vs. an ene-reaction. The well-studied system is singlet oxygen that can either undergo a [2+2]-photocycloaddition or an ene-reaction depending on the alkene reactant and conditions employed.[64,65] Based on this, Sivaguru and coworkers altered the reactivity of triplet excited alkenes towards photoene reaction[79] rather than a conventional [2+2]-photocycloaddition.

Intermolecular photochemical reaction between citraconicimide derivative **29** was evaluated with differently substituted alkenes **30a–e** under visible-light irradiation with thioxanthone acting as a photosensitizer/photocatalyst (Scheme 7). Irradiation of citraconicimide **29** with mono- or di-substituted alkenes **30a–b** led to the corresponding regioisomeric-[2+2] photocycloaddition products, with 1,2-substituted cyclobutane **31a–b** as the major-isomer and 1,3-substituted cyclobutane **32a–b** as the minor isomer (Scheme 7, left). For example, photoreaction of mono-substituted alkene **30a** with **29** afforded photoproducts **31a** and **32a** with isolated yields of 41 and 23%, respectively (total isolated yield 64%). The stereochemistry of substituent in the cyclobutane products **31** and **32** were unambiguously confirmed by single-crystal XRD analysis (Scheme 7, left).

Conversely, photoreaction of citraconicimide **29** with trisubstituted alkenes **30c** and tetrasubstituted alkenes **30d** gave the corresponding photoene product **33c** (45% isolated yield) and **33d** (41% isolated yield), respectively (Scheme 7, right). The isolated yield of the photoproduct increased to 83% when the photoreaction was carried out at –78 °C in dichloromethane. The formation of the photoene adduct was unambiguously established by single-crystal XRD (Scheme 7, right). Both the [2+2]-photocycloaddition (with mono- and di-substituted alkenes) and photoene reaction (with tri- and tetra-substituted alkenes) were atropselective when optically pure atropisomers were employed as the reactants, leading to highly stereoenriched photoproducts. The reaction was less effective under direct irradiation conditions (16–38% conversion) compared to sensitized photoirradiation with thioxanthone (isolated yields as high as 83%).

Detailed photophysical studies were carried out to understand the reactive dichotomy leading to [2+2]-photocycloaddition vs. photoene reaction. As the reaction was efficient with thioxanthone, laser flash photolysis experiments were carried out with citraconicimide **29** as the quencher (Figure 5). Efficient quenching of the thioxanthone (and xanthone) triplets were observed (Figure 5A) with bimolecular quenching rate constant k_q of 4.6±0.1 × 10^9 $M^{-1}s^{-1}$ (k_q = 6.6±0.1 × 10^9 $M^{-1}s^{-1}$ for xanthone). The quenching study revealed that the lowest triplet state energy (E_T) of citraconicimide **29** is well below 63 kcal/mol (E_T thioxanthone) and that the triplet energy transfer was feasible in this system. As the photoene product was dependent on the substitution pattern of alkenes, bimolecular quenching rate constants were determined for quenching of triplet excited citraconicimide **29**; i.e., ^{3}[**29**]* by alkenes **30a–d** (Figure 5C). Laser pulse excitation of **29** at 308 nm (20 ns pulse width) generated a weak transient absorption spectrum that decayed with a lifetime of 8.7 μs. This transient was assigned

(Figure 5B) as the triplet excited citraconicimide **29**, i.e., ^{3}[**29**]*, that was quenched by alkenes **30a–d** with rate constant k_q ranging from 1 × 10^8 $M^{-1}s^{-1}$ to 11 × 10^8 $M^{-1}s^{-1}$ (Figure 5C). Based on the experimental details and on the photophysical investigation, a mechanistic rationale for the photoene reaction was proposed (Scheme 8) in which the triplet excited **29** (formed by sensitization or by direct irradiation) reacted with alkene to form a triplet 1,4-biradical t-1,4-BR-**30d**. The stability of this diradical (3° radical in both the radical centers), which was relatively long-lived, led to the abstraction of the allylic hydrogen of citraconicimide through a cyclic six-membered transition state to form triplet 1,2-biradical t-1,2-BR-**30d**. This diradical subsequently intersystem crossed to a singlet 1,2-birad-



Scheme 7 Divergent photoreactivity of imides with alkenes: [2+2]-photocycloaddition vs. photoene reaction. The yields indicated are from reaction performed with 30 mol% TX and 10 equiv of **30** using a 420 nm Rayonet reactor. The *ee* values are based on chiral stationary phase HPLC analysis with A and B representing the order of eluting enantiomers; dr values were obtained from ^{1}H NMR spectroscopy.

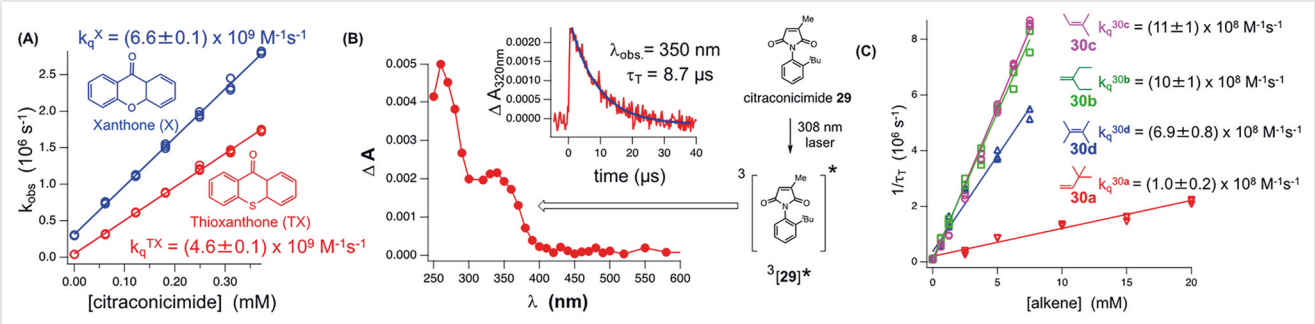
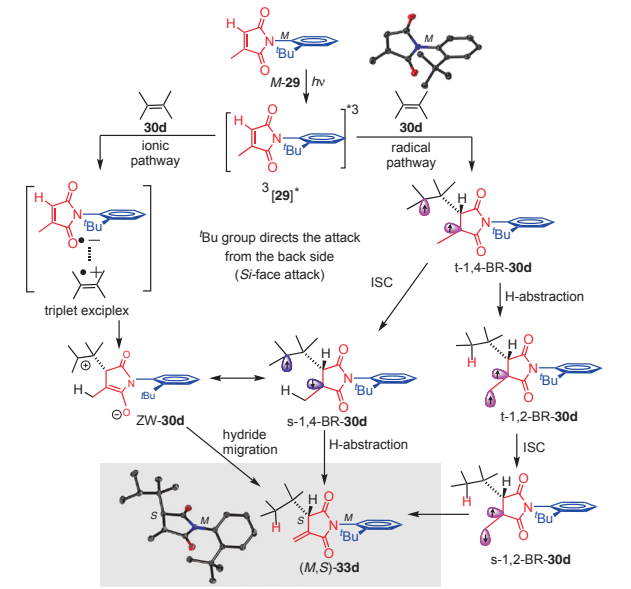


Figure 5 Photophysical studies for determining the divergent reactivity of **29** with alkenes. (A) Bimolecular rate constant (k_q) for quenching of xanthone and thioxanthone triplet states by **29** using laser flash photolysis (λ_{ex} = 355 nm, 7 ns pulse width). Inverse xanthone and thioxanthone triplet lifetimes determined from triplet absorption decay traces monitored at 620 nm vs. varying concentration of **29** in argon saturated MeCN solutions. (B) Transient absorption spectrum of **29** monitored at the end of the laser pulse (λ_{ex} = 308 nm, 20 ns pulse width) of argon-saturated MeCN solutions. Inset: decay trace monitored at 350 nm. (C) Bimolecular rate constant (k_q) for quenching of ^{3}[**29**]* by alkenes **30a–d** using LFP (λ_{ex} = 308 nm, 20 ns pulse width). Inverse triplet lifetime of **29** determined from triplet absorption decay traces monitored at 350 nm vs. varying concentration of **30a–d** in argon-saturated MeCN solutions. Reproduced from references[64] with permission from the American Chemical Society.



Scheme 8 Mechanistic rationale for the divergent photoreactivity of imides with alkenes

ical s-1,2-BR-**30d**, leading to the observed photoene product **33d**. An ionic pathway involving electron transfer was ruled out due to its endergonic nature of electron transfer from excited **29**. When the alkene employed was mono- or di-substituted, the diradical formed is relatively short-lived due to the high reactivity of secondary/primary radical centers, leading to the observed [2+2] photocycloaddition product.

7 Summary and Outlook

This review has showcased how restricted bond rotations in molecules can be exploited to uncover new and exciting photochemical reactivity. The photochemistry and photophysics of achiral and atropisomeric molecules diverge significantly. One of the main bottlenecks for this strategy is to access pure atropisomers. Emerging synthetic methods to access atropisomers foretell a bright future for this strategy, which could be exploited not only for asymmetric photochemical transformations but also to uncover new photochemical pathways and to develop new photocatalytic methods to build molecules with complex chemical features.[80,82]

Conflict of Interest

The authors declare no conflict of interest.

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