

Synergistic Excited State Photocatalysis: Divergent Energy Transfer vs Lewis Acid Mediated Phototransformations

Jayachandran Parthiban, Dipti Garg, Sapna Ahuja, Steffen Jockusch, Angel Ugrinov, and Jayaraman Sivaguru*



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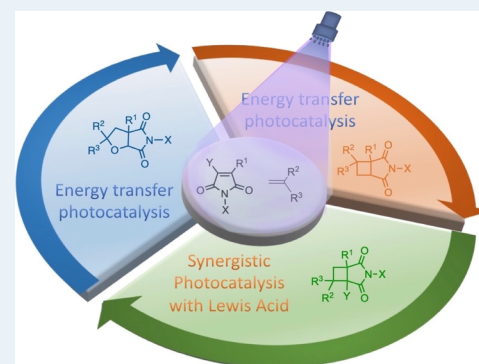


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ABSTRACT: Energy transfer vs Lewis acid photocatalysis dependent product selectivity is reported for the photochemical reaction of maleimides with alkenes. The photoproduct selectivity depends on the mode of photocatalysis that was deciphered using photochemical and photophysical studies. Under energy transfer conditions, hydroxy maleimides undergo a [3+2]-photocycloaddition, while in the presence of Lewis acids [2+2]-photocycloaddition was observed. Synergistic interactions between the Lewis acid, triplet sensitizer, and the substrate dictate both the outcome and efficiency of [2+2]-photocycloaddition.



KEYWORDS: synergistic photocatalysis, Lewis acid, chemoselectivity, regioselectivity, photocycloaddition reaction

Synergistic interactions between substrates and catalysts are hallmarks of enzymatic biocatalysis that often features unparalleled rate acceleration in addition to providing access to unique molecular architectures.^{1,2} Translating such phenomena to chemical processes is challenging due to the difficulty in altering the reaction trajectories to dictate product outcome with high efficiency.³ This problem is even more pronounced for excited state transformations where reaction pathways often involve short-lived transient(s) and/or intermediate(s). In spite of this challenge, altering photochemical pathways offer a unique opportunity to modulate excited state reactivities with control over product chemo-, regio-, and stereoselectivities.^{4,5} This requires manipulation of excited state dynamics to channel photoreactivity toward a specified reaction trajectory.^{6–9} Recent developments in photocatalytic approaches have centered around the development of visible light mediated reactions.^{10–15} The prospect of affecting excited state transformation with visible light is both challenging and stimulating due to the energetics and the multiplicity of reactive intermediate(s) involved in the reaction, when compared to ground state thermal/photoredox transformations. Accessing excited states of organic molecules often requires direct excitation in the UVA region that places limitations on the manipulation of their photochemistry.^{8,9}

The seminal work of Lewis and co-workers in the early 1980s showed that complexation of reactive substrates with Lewis acids led to a bathochromic shift in absorption profiles of reactive substrates, indicating the lowering of the excited state energies.^{16,17} In recent years,^{18,19} this has been exploited

by the groups of Bach,^{20,21} Yoon,^{22–24} and others^{25–29} to promote photochemical transformations with high stereoselectivity. One of the salient features in the reported systems is that the same photoproduct is observed both in the presence and in the absence of Lewis acids.^{16–29} We were interested in utilizing the Lewis acid complexation to alter the outcome of the reaction by changing the product being formed in the photochemical transformations as we envisioned altering the type of intermediates participating in the reaction pathways.³⁰ In this report, we disclose our findings with maleimides^{31–34} in which the observed photoproduct is dictated by the mode of photocatalysis, viz., energy transfer or Lewis acid photocatalysis (Figure 1).

We began our investigation by evaluating the photoreaction of maleimides **1** with various alkenes **2** (Scheme 1).³⁵ Direct irradiation ($\sim 350 \pm 30$ nm) of maleimide **1a** with alkene **2a** did not lead to any noticeable conversion with complete recovery of the reactants. Photoirradiation at $\sim 420 \pm 30$ nm (16 h irradiation) of maleimide **1a** with alkene **2a** with thioxanthone (TX) as a photosensitizer led to an efficient reaction leading to photoproduct **3a** in 66% isolated yield

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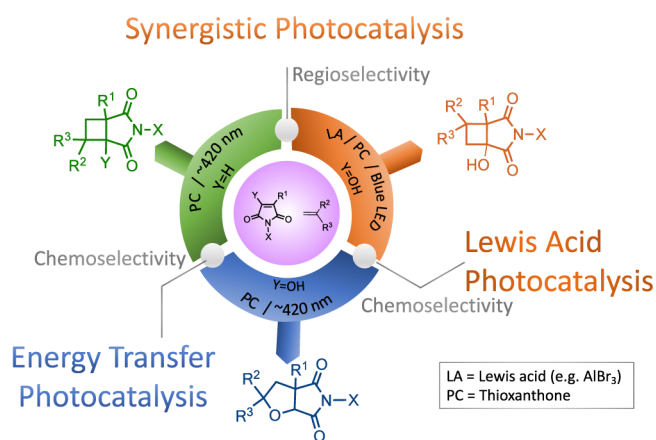


Figure 1. Controlling excited state reactivity via energy transfer vs Lewis acid mediated phototransformations.

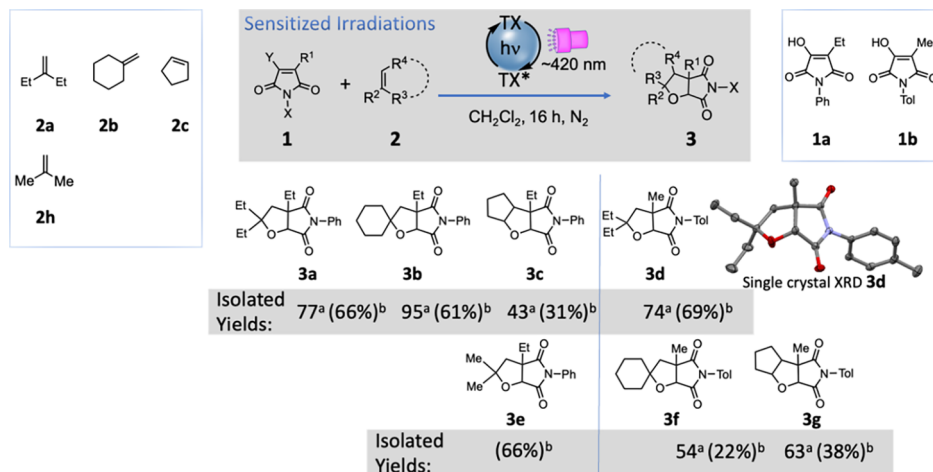
(Scheme 1). The photoproduct was characterized by NMR spectroscopy and HRMS.³⁵

The generality of the reaction using thioxanthone sensitizer was established by changing both the maleimide and the alkene.³⁵ Thioxanthone-sensitized photoreaction of **1a** with alkenes **2b** and **2c** led to the corresponding photoproducts **3b** and **3c** with yields (by ¹H NMR spectroscopy) of 95% and 43%, respectively. The compounds were isolated in 61% yield (for **3b**) and 31% yield (for **3c**). Varying the maleimide from **1a** to **1b** also led to similar reactivity. Thioxanthone-sensitized photoreaction of **1b** with alkenes **2a**, **2b**, and **2c** led to the corresponding photoproducts **3d**, **3e**, and **3f** in yields varying from 74% to 54% (by ¹H NMR spectroscopy; isolated yields varied from 69% to 22%). We were also successful in unambiguously establishing the structure of the photoproduct **3d** by single-crystal XRD.³⁵ In addition, a large-scale photocatalytic reaction under energy transfer sensitization led to efficient [3+2]-photocycloaddition of maleimide **1a** (0.5 g scale) and alkene **2a**, leading to photoproduct **3a** in 57% isolated yield (0.39 g of **3a**), showcasing the synthetic utility of the transformations. Due to the structural feature of maleimide **1**, we proceeded to investigate the effect of Lewis acids in promoting the phototransformation (Scheme 2). To our

surprise, blue LED irradiation ($\sim 455 \pm 20$ nm) of **1a** and **2a** with 50 mol % of AlCl_3 for 24 h led to the formation of photoproduct **4a** in 46% isolated yield (Scheme 2, top). The photoproduct was characterized by NMR spectroscopy and HRMS.³⁵ The structure was unequivocally established by single-crystal XRD (Scheme 2).³⁵ It is critical to note that the chemoselectivity in the photochemical transformations was observed under two different conditions employed, i.e., a [3+2]-type photochemical reaction^{36–39} leading to photoproduct **3** under energy transfer conditions and [2+2]-photocycloaddition leading to photoproduct **4** under Lewis acid mediated conditions (compare Schemes 1 and 2). To gauge the influence of triplet sensitizers under Lewis acid conditions, we also evaluated the photoreactivity of **1a** and **2a** in the presence of AlCl_3 and TX. Blue LED irradiation of **1a** and **2a** with 50 mol % of AlCl_3 and 10 mol % of TX for 5 h led to the formation of photoproduct **4a** in 74% isolated yield (Scheme 2, bottom). It is critical to note the synergistic effect of both the Lewis acid and the photosensitizer in promoting the transformation and impacting its efficiency and conversions. As shown in Scheme 2, blue LED irradiation in the presence of both the Lewis acid and thioxanthone sensitizer resulted in 74% isolated yield of photoproduct **4a** in just 5 h, while 24 h blue LED irradiation was required when Lewis acid alone was employed to promote the reaction, leading to 46% isolated yield. These observations (Schemes 1 and 2) necessitated an in-depth investigation into the role of Lewis acid and the sensitizer in controlling chemoselectivity and promoting the photochemical transformation.

We started our evaluation of the synergistic effect of Lewis acid and the triplet sensitizer on the phototransformation involving **1a** and **2a** under our standard conditions, viz., 50 mol % Lewis acid and 10 mol % of the thioxanthone sensitizer under blue LED irradiation for 5 h in dichloromethane at room temperature. Changing the Lewis acid from AlCl_3 to AlBr_3 resulted in a minor change in the isolated yield of the photoproduct **4a** (from 74% for AlCl_3 to 66% for AlBr_3 ; compare Table 1, entries 1 and 2). Changing the Lewis acid to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ resulted in 9% isolated yield of the photoproduct **4a** (Table 1, entry 3). Due to the significant drop in the isolated yield of the photoproduct **4a** upon changing the Lewis acid, we evaluated other aluminum-based Lewis acids. Both Et_3Al and

Scheme 1. Energy Transfer Sensitization Leading to Photocycloaddition of Maleimides **1a,b** with Alkenes **2a–c,h**



^aNMR yields. ^bIsolated yields. For clarity, hydrogens are not displayed in the single-crystal XRD structure of **3d**.

Scheme 2. Photoreactivity of Maleimide 1a with Alkene 2a in the Presence of Lewis Acid (Top) and in the Presence of Both the Lewis Acid and Thioxanthone Photosensitizer (Bottom)

Lewis Acid Photocatalysis

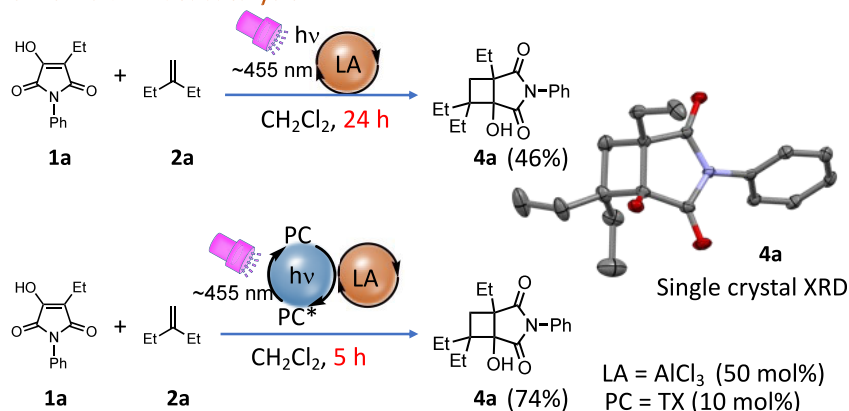
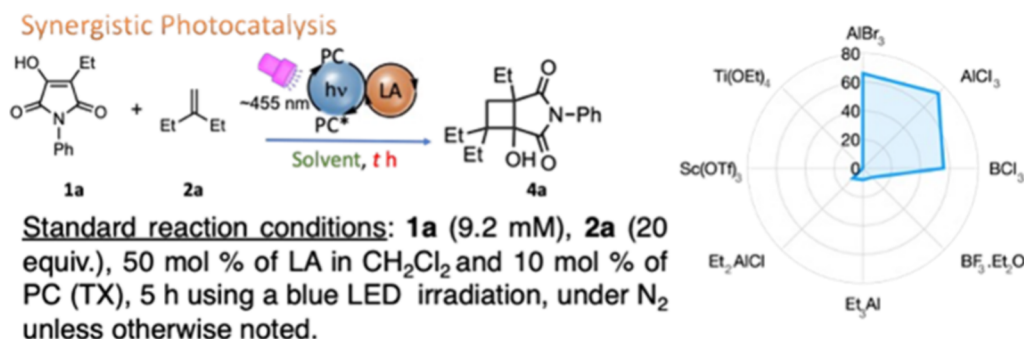


Table 1. Optimization of Photoreactivity of Maleimide 1a in the Presence of Lewis Acids and Thioxanthone



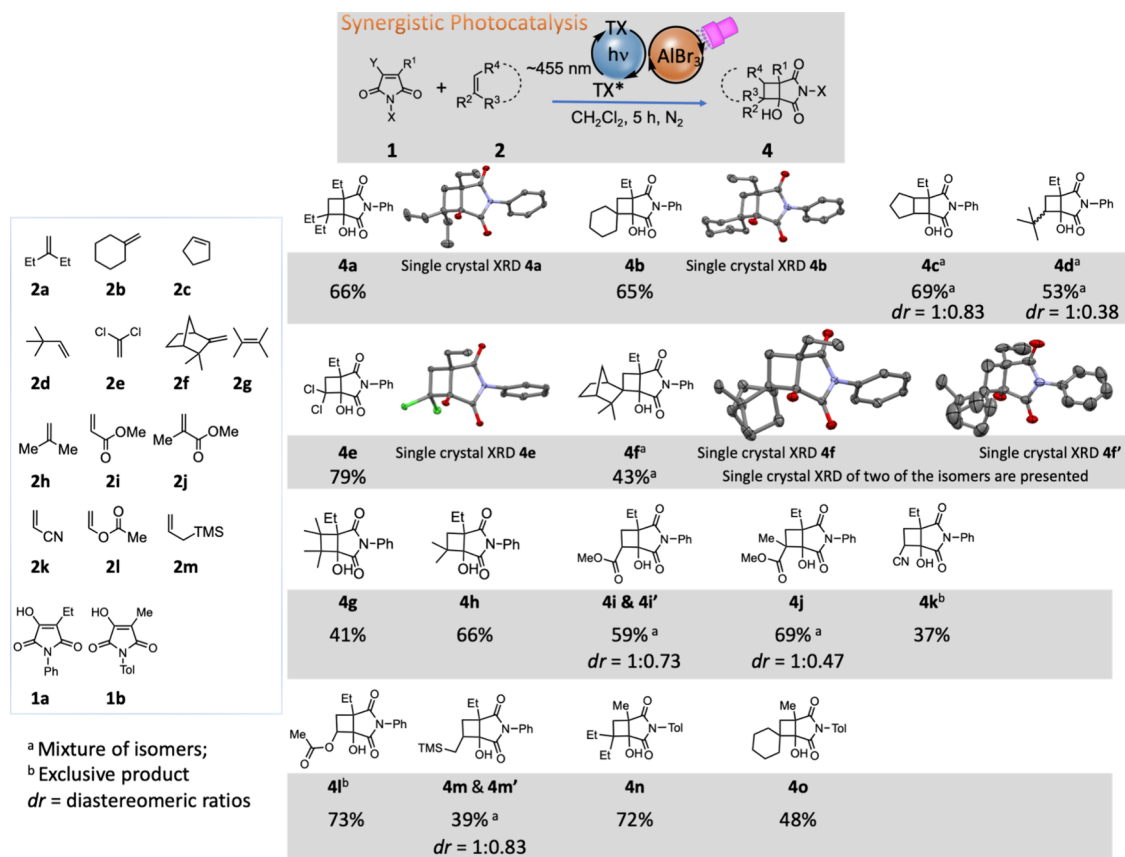
entry	variation from standard conditions	4a isolated yield (%)
1	standard conditions (LA = AlBr ₃)	66
2	standard conditions (LA = AlCl ₃)	74
3	standard conditions (LA = BF ₃ ·OEt ₂)	9
4	standard conditions (LA = Et ₃ Al)	8
5	standard conditions (LA = Et ₂ AlCl)	10
6	standard conditions (LA = BCl ₃)	56
7	standard conditions (LA = Sc(OTf) ₃)	-
8	standard conditions (LA = Ti(OEt) ₄)	-
9	standard conditions (no light)	-
10	standard conditions (solvent: CHCl ₃)	55
11	50 mol % TFA, 10 mol % TX, CH ₂ Cl ₂ , blue LED, 12 h	-
12	50 mol % TFA, 10 mol % TX, CH ₂ Cl ₂ , ~350 ± 30 nm, 12 h	-
13	CH ₂ Cl ₂ , no LA, no TX, ~350 ± 30 nm, 12 h	-

Et₂AlCl gave the identical photoproduct **4a** in 8% and 10% isolated yields respectively (Table 1, entries 4 and 5). Nonchelating Lewis acid BCl₃ resulted in lowering of the yield from 74% to 56% isolated yield (Table 1, entry 6). Lewis acids such as Sc(OTf)₃ and Ti(OEt)₄ did not result in photoproduct (Table 1, entries 7 and 8). Direct irradiation at ~350 ± 30 nm in the absence of both Lewis acid and thioxanthone did not result in photoproduct (Table 1, entry 13). In the absence of light from the standard conditions, no observable product was seen in the reaction, reinforcing the fact that the reaction originates from the excited state (Table 1, entry 9). Changing the solvent from dichloromethane to chloroform resulted in a slight drop in the isolated yield of the photoproduct **4a** to 55% from 66% (Table 1, compare entries 1 and 10). Photoirradiation in the presence of trifluoroacetic acid serving as the Brønsted acid (both at blue LED and ~350

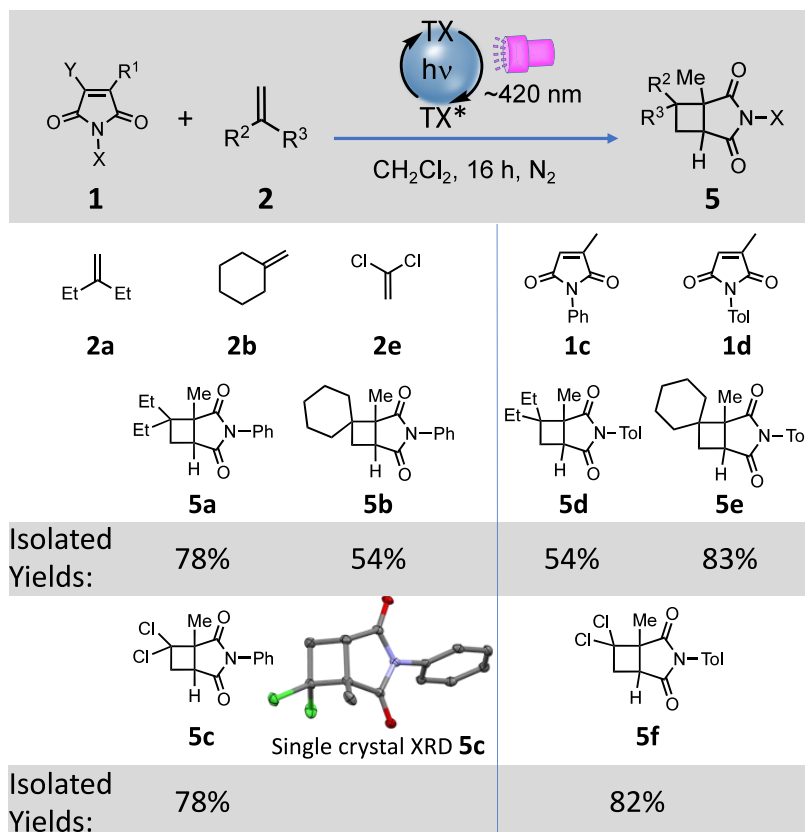
± 30 nm) did not yield the desired photoproduct (Table 1, entries 11 and 12), showcasing the need for the Lewis acid to promote the reaction.

With optimized conditions using 50 mol % Lewis acid and 10 mol % of the thioxanthone sensitizer under blue LED irradiation for 5 h in dichloromethane at room temperature, we then evaluated the generality of the Lewis acid promoted photochemical transformation by changing both the maleimide and the alkene (Scheme 3). In the first set of experiments, we employed hydroxy maleimide **1a** and systematically changed the type of alkene from **2a** to **2f** (Scheme 3, left) under synergistic photocatalytic conditions. Blue LED irradiation of **1a** with methylenecyclohexane **2b** with thioxanthone and AlBr₃ in CH₂Cl₂ for 5 h (standard conditions) led to 65% isolated yield of the photoproduct **4b**. Changing the alkene from 1,1-disubstituted to 1,2-disubstituted alkene did not significantly

Scheme 3. Synergistic Photocatalysis Involving Maleimides and Alkenes



Scheme 4. [2+2]-Photocycloaddition Involving Maleimides 1c/d with Alkenes



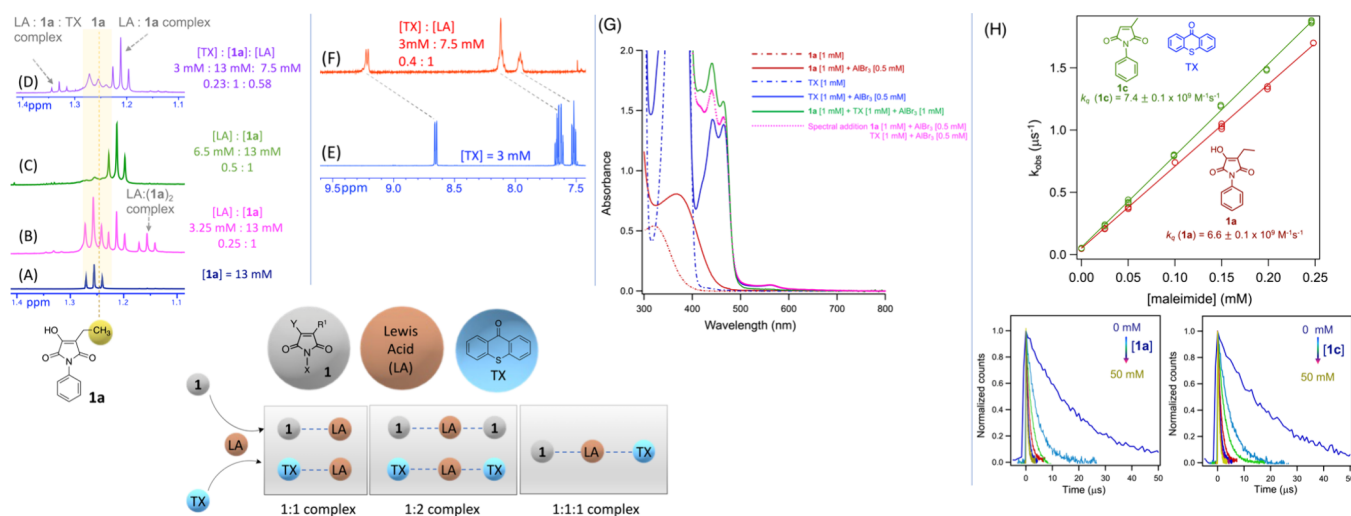


Figure 2. ¹H NMR spectroscopy in CDCl₃ (left) and UV–vis spectroscopy (middle) to understand synergistic photocatalysis. The dotted line in UV–visible absorbance profile corresponds to hydroxy maleimide (**1a**, red dotted trace) and thioxanthone (TX, blue dotted trace) in dry dichloromethane at room temperature. The solid line in the UV–visible absorbance profile correlates with complexed **1a** with AlBr₃ (red solid trace) and TX with AlBr₃ (blue solid trace), **1a**+TX with AlBr₃ (green solid trace), and spectral addition of **1a**+TX+AlBr₃ (pink dotted trace). Right: Determination of the bimolecular quenching rate constants *k_q* of quenching of thioxanthone triplet states by **1a** or **1c** using laser flash photolysis ($\lambda_{\text{ex}} = 355 \text{ nm}$, 7 ns pulse width). Triplet absorption decay rate constant monitored at 620 nm vs the concentration of **1a** or **1c** in argon-saturated acetonitrile solutions.

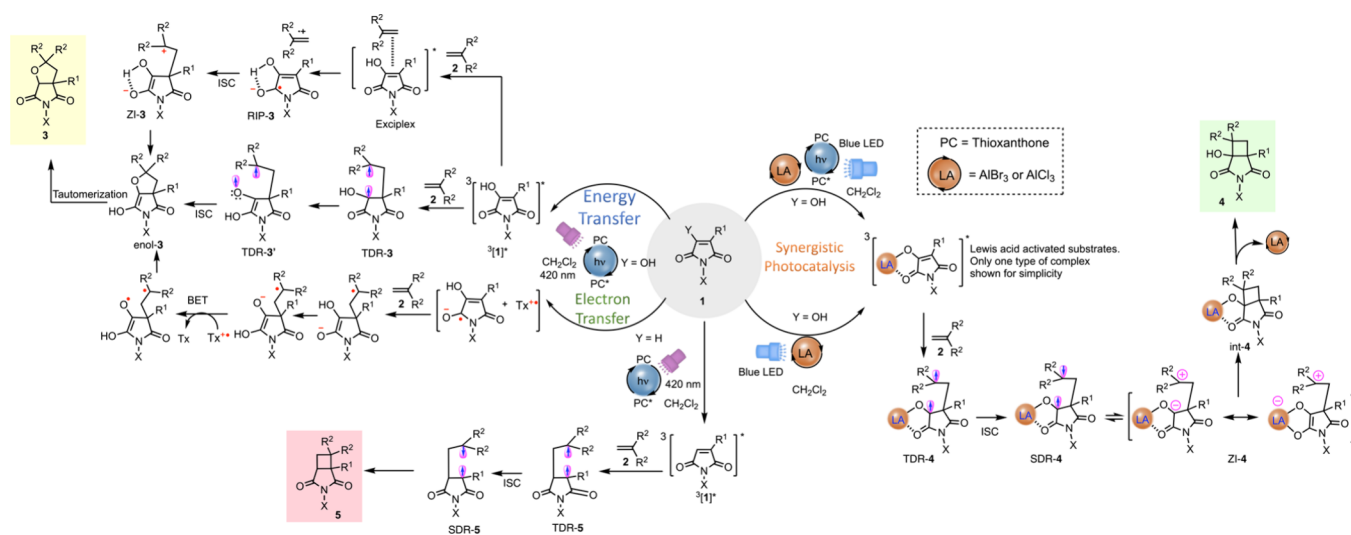
alter the photoproduct yield. For example, blue LED irradiation of **1a** with cyclopentene **2c** under standard irradiation conditions (Scheme 3) led to 69% isolated yield of the corresponding photoproduct **4c** (mixture of isomers). Employing monosubstituted alkene **2d** under the standard conditions led to 53% isolated yield of the photoproduct **4d** (mixture of isomers). The reaction was also tolerant to haloalkenes with 79% isolated yield of the photoproduct **4e** upon employing 1,1-dichloroethylene **2e**. Synergistic photocatalysis was also effective with bicyclic alkene **2f**, which gave 43% isolated yield of the photoproduct **4f** (mixture of isomers). To explore the reactivity of functional alkenes, which are useful synthetic building blocks, we employed readily available alkenes **2g–o** (Scheme 3). Photoreaction with maleimide **1a** under synergistic photocatalytic conditions with tetramethylethylene (**2g**) and isobutene (**2h**) resulted in the corresponding photoproducts **4g** and **4h** in 41% and 66% isolated yields, respectively. To showcase the versatility of the employed photocatalytic system, we used easily accessible methacrylate (**2i**), methyl methacrylate (**2j**), and acrylonitrile (**2k**) as an alkene partner. Photoreaction with maleimide **1a** under synergistic photocatalytic conditions with alkenes **2i–k** led to the corresponding photoproduct **4** with 59%, 69%, and 37% isolated yields. Photoreaction with maleimide **1a** under synergistic photocatalytic conditions with vinyl acetate **2l** resulted in photoproduct **4l** with 73% isolated yield. A point to note is that in the acrylate system the diastereomeric ratio (*dr*) was 1:0.73 in the photoproduct **4i** and 1:0.47 in photoproduct **4j**, while complete diastereocontrol was observed with vinyl acetate photoproduct **4l**. Employing allyl silane **2m** as the reactive partner for **1a** under synergistic photocatalytic conditions led to the corresponding cyclobutane photoproduct **4m/4m'** with an overall yield of 39%, showcasing substituent tolerance (trimethylsilane; TMS) under the reaction conditions (Scheme 3). Thus, the system was amenable to a broad scope of substrates. To assess the influence of the maleimide substituent, we evaluated maleimide **1b** with alkenes **2a** and **2b**

under standard conditions (Scheme 3, right), which gave the corresponding photoproducts **4n** and **4o** in 72% and 48% yields, respectively.

To elucidate the structural features of the maleimide that is responsible for the observed chemoselectivity, we evaluated maleimides **1c** and **1d**, which lack the hydroxy substituent on the maleimide skeleton. Photoirradiation at $\sim 420 \pm 30 \text{ nm}$ (16 h irradiation) of maleimide **1c/d** with alkene **2a/2b/2e** with TX as a photosensitizer led to an efficient reaction leading to corresponding photoproduct **5** in isolated yields varying from 54% to 83% (Scheme 4). The photoproduct structures were deciphered by NMR spectroscopy and HRMS.³⁵ Unambiguous characterization of the photoproduct **5c** was established by single-crystal XRD.³⁵ Closer inspection of the photoproduct **4** (derived from hydroxy maleimides **1a/b**) and photoproduct **5** (derived from maleimides **1c/d**, lacking the hydroxy substituent) shows that regiochemistry was profoundly impacted by the presence/absence of the hydroxy substituent on the maleimide skeleton. For example, photoirradiation at $\sim 420 \pm 30 \text{ nm}$ (16 h irradiation) of maleimide **1c** and alkene **2a** with TX as a photosensitizer resulted in photoproduct **5a** (78% isolated yield; Scheme 4), featuring a 1,2-relation between the *gem*-diethyl substituent and the bridge head methyl substituent. On the other hand, photoreactivity of hydroxy maleimide **1a** and **2a** in the presence of AlCl₃ and TX resulted in photoproduct **4a** (74% isolated yield; Table 1, entry 2), featuring a 1,3-relation between the *gem*-diethyl substituent and the bridge head ethyl substituent. It was clear that the regiochemistry of photocycloaddition in maleimides can be manipulated by employing Lewis acids.

To understand the intricacies of Lewis acid mediated control of excited state transformations involving maleimides, we utilized ¹H NMR and UV–vis spectroscopic investigations to appreciate the mechanistic details of the process (Figure 2).³⁵ Addition of Lewis acid to hydroxy maleimide **1a** led to complexation as revealed by the change in the proton resonance peaks (Figure 2A) of **1a**. We utilized the ethyl

Scheme 5. Mechanistic Rationale for the Observed Divergence in Energy Transfer and Electron Transfer vs Lewis Acid Mediated Photocatalysis



group resonances in **1a** as an NMR handle to gauge the interactions between **1a** and AlBr_3 (Figure 2A–D). The triplet centered around 1.25 ppm (Figure 2A) changed upon addition of various amounts of the Lewis acid. Upon employing 0.5 equiv or higher amount of AlBr_3 , a triplet resonance centered around 1.22 ppm (Figure 2C) was observed that was upfield shifted when compared to the triplet resonance of the uncomplexed maleimide **1a** (triplet resonance at 1.25 ppm). When less than 0.5 equiv of Lewis acid was employed, three distinct triplet resonances were observed (Figure 2B), which were tentatively assigned to the presence of uncomplexed **1a** at 1.25 ppm, $\text{1a}@\text{AlBr}_3$ complex at 1.22 ppm, and $(\text{1a})_2@\text{AlBr}_3$ complex at 1.15 ppm. In addition, the OH resonance of **1a** disappeared upon addition of the Lewis acid, indicating that the OH group was critical for Lewis acid complexation with maleimide (SI Figure S109).³⁵ Similarly, addition of Lewis acid to thioxanthone led to complexation, as revealed by the change in the thioxanthone proton resonances (Figure 2E,F). For example, the aromatic resonances centered around 7.6 and 8.6 ppm (Figure 2E) were shifted to ~ 8.0 and ~ 9.1 ppm (Figure 2F), respectively.

The interaction of a Lewis acid with hydroxy maleimide **1a** was further ascertained by a bathochromic shifted absorption (Figure 2G) in the presence of the Lewis acid (absorption spectra ending at ~ 480 nm in the presence of AlBr_3 when compared to ~ 390 nm in the absence of AlBr_3). Similarly, the interaction of a Lewis acid with thioxanthone ($\text{TX}@\text{AlBr}_3$) was ascertained from the bathochromic shift in the absorption (Figure 2G) in the presence of the Lewis acid (absorption spectra ending at ~ 592 nm in the presence of AlBr_3 when compared to ~ 420 nm in the absence of AlBr_3). Addition of a Lewis acid to a mixture of thioxanthone and **1a** showed that there is likely a synergistic interaction between them, leading to a ternary complex involving **1a**, AlBr_3 , and TX (Figure 2D). This conjecture is based on our observation of the ^1H NMR resonance of the methyl functionality in **1a**. When compared to the uncomplexed maleimide **1a** methyl triplet resonance centered around 1.25 ppm (Figure 2A) and the upfield shifted resonance for both $\text{1a}@\text{AlBr}_3$ and $(\text{1a})_2@\text{AlBr}_3$ complexes (Figure 2B,C), the methyl triplet resonance was downfield shifted to around 1.32 ppm (Figure 2D) for the ternary

complex involving **1a**, AlBr_3 , and TX. In addition, the methyl resonances were broadened (Figure 2D), indicating that there is a dynamic exchange occurring in the system within the NMR time scale. Based on these observations, we believe that there is a synergistic interaction between the Lewis acid (AlBr_3), thioxanthone, and **1a**. This conjecture is once again bolstered by our UV–vis studies, where the absorption spectra of **1a** and TX in the presence AlBr_3 (Figure 2G) were distinct when compared to **1a** with AlBr_3 and TX. A closer examination of the absorption spectra (Figure 2G) indicates that the UV–vis spectrum of the Lewis acid–substrate–thioxanthone (green trace in Figure 2G) has distinct absorption features and intensities when compared to the UV–vis of Lewis acid–substrate (solid red trace in Figure 2G), Lewis acid–thioxanthone (solid blue trace in Figure 2G), and the mathematical additive features of the individual complexes (Lewis acid–substrate and Lewis acid–thioxanthone; pink dotted trace in Figure 2G). It is our conjecture that a ternary complex featuring Lewis acid–substrate–thioxanthone likely coexists (dynamically) with Lewis acid–substrate and Lewis acid–thioxanthone complexes in solution. Examination of the transition centered at ~ 440 and ~ 465 nm observed with the $\text{TX}@\text{AlBr}_3$ complex showed a hyperchromic effect when the UV–vis spectrum was recorded for the mixture of **1a** with AlBr_3 and TX (Figure 2G). Thus, ^1H NMR and UV–vis spectroscopic investigations likely point to the involvement of a $\text{1a}-\text{AlBr}_3-\text{TX}$ complex in addition to the $\text{1a}-\text{AlBr}_3$ complex and $\text{TX}-\text{AlBr}_3$ complex under our reaction conditions. We also ascertained that photoinduced electron transfer in the system is endergonic, and hence the reaction likely proceeds via energy transfer.^{35,40–42}

As we employed thioxanthone as the photosensitizer for the reaction involving **1a** (Scheme 1) and **1c** (Scheme 4), we utilized transient absorption measurements to ascertain the rate constant for triplet energy transfer.⁴³ Laser excitation ($\lambda_{\text{ex}} = 355$ nm, pulse width = 7 ns) of an argon-saturated solution of TX in acetonitrile generated a triplet transient absorption spectrum, which was in agreement with previously published reports.⁴³ This triplet absorption of TX centered at ~ 620 nm was quenched by **1a**, leading to the formation of triplet **1a**, i.e., $^3\text{1a}^*$, with a bimolecular quenching rate constant $k_q^{\text{1a}} = (6.6 \pm$

$0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 2H). Similarly, the triplet of TX was quenched by **1c**, leading to the formation of triplet **1c**, i.e., $^3\text{1c}^*$, with a bimolecular quenching rate constant $k_q^{1c} = (7.4 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 2H). The near diffusion control rate constant for triplet energy transfer from TX to maleimides **1a** and **1c** shows that generation of the corresponding triplet excited maleimide is an efficient process.

Based on our photochemical investigations,³⁵ we propose the likely mechanistic pathway for the observed divergence in energy transfer vs Lewis acid mediated photocatalysis involving maleimides. In the presence of Lewis acid, hydroxy maleimides **1a/b** form dynamic complexes^{44,45} that can be excited either by directed irradiation (bathochromically shifted absorption) or by triplet energy transfer (Scheme 5). While we have proposed the Lewis acid–substrate complex coexisting (dynamically) with Lewis acid–substrate–thioxanthone ternary complex, at the present time we cannot pinpoint which of the species plays a dominant role in substrate activation during the photocatalytic cycle. Irrespective of the species, the activation of maleimides with Lewis acid occurs through deprotonation of the OH bond, leading to unique excited state reactivity. The triplet excited Lewis acid–maleimide complex reacts with alkene **2** to form the triplet diradical TDR-4, which intersystem crosses to ZI-4 (via SDR-4) en route to the formation of the observed photoproduct **4**. The triplet excited maleimide $^3[\text{1ab}]^*$, featuring a hydroxy substituent (triplet excited maleimides **1a** and **1b**), undergoes addition with alkene **2** to form a 1,4-triplet diradical TDR-3, which rearranges to form a 1,5-triplet diradical TDR-3' followed by intersystem crossing to enol-3, which tautomerizes to form the observed photoproduct **3**. At the present stage we cannot rule out the formation of a triplet exciplex leading to the formation of a radical-ion pair, RIP-3, that intersystem crossed to the zwitterion ZI-3⁴⁶ en route to the formation of photoproduct **3**. An alternative pathway via a photoinduced electron transfer from excited triplet TX to maleimide was also evaluated. Based on redox potential, this electron transfer will be endergonic, making this pathway less likely. In the case of triplet excited maleimide $^3[\text{1c}]^*$, which lacks a hydroxy substituent, undergoes addition with alkene **2** to form 1,4-triplet diradical TDR-5, which intersystem crosses to the singlet diradical SDR-5, leading to the formation of the observed photoproduct **5**.

Thus, our study has showcased that one can judiciously manipulate the excited state chemistry with a combination of substrate, Lewis acid, and the sensitizer. The synergistic interactions between the three (i.e., substrate, Lewis acid, and the sensitizer) control both the chemoselectivity and the regioselectivity in the reaction. We are in the process of understanding how excited state dynamics impact the reactivity and efficiency in such systems so that the process can be generalized for a variety of photochemical transformations. This will have a profound impact on the development of Lewis acid mediated photocatalytic reactions and uncover new excited state pathways.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c01185>.

Experimental procedures, characterization data (^1H and ^{13}C NMR spectroscopy, HRMS, XRD) of compounds,

electrochemical data, and photophysical measurements (PDF)

Single-crystal XRD data of **3d** (CCDC # 2270025) (CIF)

Single-crystal XRD data of **4a** (CCDC # 2270030) (CIF)

Single-crystal XRD data of **4b** (CCDC # 2270028) (CIF)

Single-crystal XRD data of **4e** (CCDC # 2270026) (CIF)

Single-crystal XRD data of **4f** (CCDC # 2270029) (CIF)

Single-crystal XRD data of **4f'** (CCDC # 2270322) (CIF)

Single-crystal XRD data of **5c** (CCDC # 2270027) (CIF)

■ AUTHOR INFORMATION

Corresponding Author

Jayaraman Sivaguru – Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States; orcid.org/0000-0002-0446-6903; Email: sivagj@bgsu.edu

Authors

Jayachandran Parthiban – Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States; orcid.org/0000-0002-5916-1701

Dipti Garg – Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States

Sapna Ahuja – Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States

Steffen Jockusch – Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403, United States; orcid.org/0000-0002-4592-5280

Angel Ugrinov – Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58103, United States

Complete contact information is available at:

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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