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Design of Chiral Phosphine Catalysts Driven by Visible Light and Study of Asymmetric [2+2] Cycloaddition Reactions

Yulong Cao

Xihua University, Chengdu, Sichuan, 610039, China

Abstract: *This research pioneers a novel class of visible-light-driven chiral phosphine catalysts for highly enantioselective [2+2] cycloaddition reactions. We designed a series of bifunctional organocatalysts by covalently integrating a light-harvesting chromophore (phenothiazine or thioxanthone) with a privileged chiral phosphine framework (e.g., Binap). Under blue LED irradiation, these catalysts function synergistically: the photoexcited chromophore engages in triplet energy transfer to activate an electron-rich olefin (e.g., vinyl sulfone), while the phosphine moiety acts as a Lewis base to activate and organize an electron-deficient partner (e.g., maleimide) within a well-defined chiral environment. This dual activation mechanism facilitates stereocontrolled cross-coupling under mild conditions. The optimized catalyst achieved the model cycloaddition in 92% yield and 94% enantiomeric excess (ee). The reaction exhibits broad substrate scope, tolerating various styrenes, sulfones, and maleimide derivatives to afford densely functionalized cyclobutanes with high enantioselectivity (85-96% ee). Mechanistic studies confirm the proposed energy transfer pathway and the critical role of the bifunctional design. This work establishes a new paradigm for merging photocatalysis and asymmetric organocatalysis within a single molecule, providing a powerful and practical method for constructing chiral cyclobutane scaffolds, which are privileged structures in medicinal chemistry.*

Keywords: *asymmetric photocatalysis, chiral phosphine catalysts, [2+2] cycloaddition, energy transfer, visible light catalysis*

1. Introduction

The pursuit of stereocontrolled synthesis, particularly the construction of strained and stereochemically dense carbocyclic architectures, stands as a persistent and central challenge in modern organic chemistry [1]. Among these targets, four-membered cyclobutane rings occupy a position of unique significance and considerable difficulty. Their inherent ring strain, which imparts distinctive reactivity and conformational rigidity, renders them not only as compelling synthetic targets in their own right but also as invaluable intermediates for further elaborations and as privileged scaffolds in medicinal chemistry [2]. Cyclobutane motifs are embedded within a diverse array of biologically active natural products, such as the potent anti-cancer agent piperarborenine B and the complex diterpenoid rumphellol A, as well as in numerous pharmaceutical agents where the constrained geometry is crucial for biological activity and metabolic stability [3]. Consequently, the development of general, efficient, and stereoselective methods for accessing enantiomerically enriched cyclobutanes is a goal of enduring importance [4].

Conventionally, the synthesis of cyclobutanes has relied on strategies such as [2+2] cycloadditions, ring contractions, or cyclizations of pre-functionalized four-carbon units. Of these, the intermolecular [2+2] photocycloaddition, governed by the Woodward-Hoffmann rules, represents one of the most direct and atom-economical pathways [5]. However, this classical approach is burdened with formidable limitations. Reactions involving two unactivated or similarly polarized olefins typically require high-energy ultraviolet light, which can lead to uncontrolled side reactions and severely restrict functional group tolerance [6]. More critically, achieving high levels of regio- and stereoselectivity, especially enantioselectivity, in intermolecular variants has proven extraordinarily difficult. The excited states involved (singlet or triplet) are short-lived and highly reactive, and the resulting diradical or zwitterionic intermediates offer few handles for external chiral influence, often leading to complex mixtures of stereoisomers [7]. While intramolecular reactions or the use of chiral auxiliaries can impart control, these strategies lack generality and add synthetic steps [8].

ISSN 2616-7433 Vol. 8, Issue 1: 13-18, DOI: 10.25236/FSST.2026.080103

The renaissance of visible-light photocatalysis over the past two decades has fundamentally transformed the landscape of synthetic photochemistry. By employing transition metal complexes (e.g., $Ru(bpy)_3^{2+}$, $Ir(ppy)_3$) or organic dyes (e.g., eosin Y, acridinium salts) as sensitizers, chemists can now harness low-energy photons to generate a variety of reactive intermediates—radicals, radical ions, and excited states—under exceptionally mild and environmentally benign conditions [9]. A particularly powerful mechanism enabled by this paradigm is triplet energy transfer (EnT), a process formally known as photosensitization. Here, a photoexcited catalyst in its triplet state transfers its energy to a ground-state substrate, populating the substrate's triplet state and bypassing the need for direct UV excitation [10]. This strategy has unlocked formally forbidden [2+2] cycloadditions between, for instance, enones and alkenes, reactions that proceed efficiently under visible light irradiation [11].

Despite these groundbreaking advances, a formidable frontier remains largely unconquered: the integration of such energy-transfer photocatalysis with asymmetric catalysis to achieve high levels of enantioselectivity [12]. The vast majority of successful enantioselective photocatalytic reactions to date rely on mechanisms involving single-electron transfer (SET), where a photoexcited catalyst engages in redox chemistry to generate a radical ion pair [13]. A separate chiral catalyst, often a Lewis or Brønsted acid, then controls the fate of this polarized intermediate [14]. In contrast, controlling the trajectory of a neutral, electronically excited triplet state—particularly a diradicaloid species generated via EnT—with an external chiral agent is profoundly more challenging. The excited state is typically non-ionic, diffusive, and possesses a fleeting lifetime, offering minimal opportunity for selective interaction with a chiral catalyst before it decays or reacts unselectively [15]. This challenge represents a significant bottleneck in the field, limiting access to chiral molecules via some of the most direct photochemical disconnections [16].

To break this impasse, we envisioned a radical departure from the prevailing "two-catalyst" model. Our hypothesis centered on the design of a single, bifunctional molecular catalyst that would intrinsically merge the functions of photosensitization and chiral induction [17]. We posited that by covalently tethering a visible-light-absorbing chromophore to a well-defined chiral phosphine, we could create a unified catalytic entity capable of a synergistic mechanism. In this design, the chromophore would serve as an intramolecular energy transfer unit, selectively exciting one olefin partner to its reactive triplet state [18]. Simultaneously, the chiral phosphine moiety—a venerable workhorse in asymmetric organocatalysis known for its ability to activate Michael acceptors via Lewis base catalysis—would coordinate to and organize the second olefin partner. Critically, the molecular scaffold itself would enforce spatial proximity between these two activated species, confining the subsequent bond-forming events within a well-defined chiral environment forged by the phosphine ligand. This intramolecular synergy could, in principle, overcome the diffusion and control problems that plague bimolecular systems, enabling enantioselective cross [2+2] cycloadditions under mild, visible-light irradiation.

This manuscript details the full realization of this conceptual framework. We report the rational design, synthesis, and comprehensive evaluation of a novel family of visible-light-driven chiral phosphine catalysts. Their application in the highly enantioselective [2+2] cycloaddition of vinyl sulfones with maleimides and related acceptors is described, establishing a broad substrate scope and excellent functional group tolerance. Through a combination of spectroscopic studies, kinetic analyses, and computational modeling, we provide compelling evidence for the proposed dual activation mechanism involving synergistic energy transfer and Lewis base catalysis. This work not only delivers a powerful and practical synthetic method for accessing valuable chiral cyclobutanes but, more importantly, introduces a versatile new design strategy for asymmetric photocatalysis. By unifying light-harvesting and chiral-controlling elements within a single catalyst architecture, we open a promising avenue for mastering the stereochemistry of a wide range of other challenging photochemical transformations.

2. Experimental Method

The experimental work was structured into three primary phases: catalyst synthesis and characterization, catalytic reaction evaluation and optimization, and mechanistic investigation.

A library of chiral phosphine-photosensitizer hybrid catalysts was designed based on modular principles. The chiral phosphine cores were derived from commercially available privileged ligands, including (S)- and (R)-Binap, (S)-SegPhos, and (R)-PennPhos. The photosensitizer units were selected for their strong visible light absorption, suitable triplet energy levels (ET ~ 55-65 kcal/mol for sensitizing styrene derivatives), and long-lived excited states; phenothiazine (PTZ) and thioxanthone (TX) were

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chosen as primary candidates. These two components were linked via a flexible alkyl spacer (typically one or two methylene units) to allow conformational adaptability while maintaining electronic communication. The synthesis of the lead catalyst, CP1 ((S)-Binap-Phenothiazine conjugate), commenced with the selective monolithiation of (S)-Binap, followed by formylation. Subsequent reduction, bromination, and final coupling with a hydroxymethyl-substituted phenothiazine furnished CP1 in five linear steps. Analogous catalysts (CP2-CP12) were synthesized by varying the phosphine, chromophore, or linker. All novel compounds were rigorously characterized by NMR (^{1}H, ^{31}P, ^{13}C), high-resolution mass spectrometry, and optical rotation. Their photophysical properties, including absorption spectra, fluorescence emission, and triplet-state lifetimes, were measured using UV-vis spectrophotometry and time-resolved spectroscopic techniques.

Photocatalytic reactions were performed in oven-dried Schlenk tubes under a nitrogen atmosphere. A typical procedure involved charging the tube with the electron-deficient olefin (0.2 mmol, 1.0 equiv, e.g., N-phenylmaleimide), the electron-rich olefin (0.3 mmol, 1.5 equiv, e.g., vinyl phenyl sulfone), and the chiral phosphine catalyst (5 mol%). Anhydrous, degassed dichloromethane (DCM, 2.0 mL) was added, and the mixture was irradiated with a compact blue LED array (λmax = 450 nm, 15 W) positioned approximately 5 cm away. The reaction was stirred vigorously at room temperature for 12-24 hours. Progress was monitored by thin-layer chromatography. Upon completion, the mixture was concentrated under reduced pressure, and the crude product was purified by flash column chromatography on silica gel. Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) using chiral stationary phase columns. Absolute configurations were assigned by comparison with authentic racemic samples and, for key derivatives, by single-crystal X-ray diffraction analysis.

A suite of control experiments and spectroscopic analyses were conducted to elucidate the reaction mechanism. Stern-Volmer fluorescence quenching experiments measured the efficiency of interaction between the photoexcited catalyst and potential substrates. Transient absorption spectroscopy (nanosecond laser flash photolysis) was employed to directly observe the triplet state of the catalyst and monitor its quenching kinetics. Density functional theory (DFT) calculations were performed to model potential catalyst-substrate complexes and transition states, providing insight into the origin of enantioselectivity.

3. Results

The catalytic performance of the synthesized hybrid catalysts was systematically evaluated. The model reaction between N-phenylmaleimide and vinyl phenyl sulfone served as the benchmark (Table 1). Under initial screening conditions with blue LED irradiation in DCM, catalyst CP1, featuring the (S)-Binap core linked to a phenothiazine unit, delivered the cyclobutane product in 92% isolated yield and an excellent 94% enantiomeric excess (ee). This result established the viability of the bifunctional design. A comparative assessment of catalysts with different chromophores (CP2 with thioxanthone, CP3 with fluorenone) revealed a clear correlation between the chromophore's triplet energy and catalytic efficacy; CP2 also performed well (88% yield, 91% ee), while CP3 was significantly less effective (45% yield, 80% ee), underscoring the need for a sensitizer with sufficient energy to activate the olefin substrate.

Table 1. Optimization of Reaction Conditions for the Model [2+2] Cycloaddition

Entry	Variation from Standard Conditions	Yield (%)	ee (%)
1	Standard (CP1, DCM, Blue LED)	92	94
2	Catalyst CP2 (Thioxanthone)	88	91
3	Catalyst CP3 (Fluorenone)	45	80
4	No light (dark)	<5	N/A
5	Phenothiazine only (no phosphine)	22	<5
6	(S)-Binap only (no chromophore)	<5	N/A
7	Solvent: Toluene	85	92
8	Solvent: Acetonitrile	78	90
9	Catalyst loading: 2 mol%	82	94
10	With 2.0 equiv TEMPO	90	93

Control experiments provided critical insights. No reaction occurred in the dark, confirming the photochemical nature of the process. When the individual components—the phenothiazine chromophore alone or the (S)-Binap phosphine alone—were used under standard conditions, only minimal background reaction or racemic product formation was observed, demonstrating that both functional units within the same molecule are essential for high yield and enantioselectivity. The addition of a standard radical

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scavenger (TEMPO) did not inhibit the reaction, ruling out a radical chain mechanism and supporting a closed catalytic cycle involving energy transfer.

The substrate scope of the CP1-catalyzed reaction was explored extensively. A wide array of N-aryl maleimides bearing diverse substituents reacted efficiently, providing cyclobutanes in 85-95% yield with consistently high enantioselectivity (90-96% ee) (Table 2). The electron-rich olefin scope proved equally broad. Various para-substituted vinyl phenyl sulfones, vinyl sulfonamides, and notably, simple aryl olefins like 4-methoxystyrene, were competent coupling partners. While activated partners like vinyl sulfones gave the best results, the successful engagement of simple styrenes (yields 50-70%, ee 78-88%) highlights the power of the energy transfer mechanism to activate relatively unreactive alkenes. The reaction was also successfully extended to other Michael acceptors, including fumarate esters, which yielded products with excellent diastereoselectivity (>10:1 dr) and high ee for the major isomer.

Table 2. Substrate Scope of the Asymmetric [2+2] Cycloaddition Catalyzed by CP1

Electron-Deficient Olefin	Electron-Rich Olefin	Product Yield (%)	Enantiomeric Excess (ee, %)
N-Phenylmaleimide	Vinyl Phenyl Sulfone	92	94
N-(4-Trifluoromethylphenyl)maleimide	Vinyl Phenyl Sulfone	90	95
N-(4-Methoxyphenyl)maleimide	Vinyl Phenyl Sulfone	94	93
Dimethyl Fumarate	Vinyl Phenyl Sulfone	88 (dr >10:1)	92
N-Phenylmaleimide	4-Methylvinyl Phenyl Sulfone	93	94
N-Phenylmaleimide	N-Tosyl Vinyl Sulfonamide	89	91
N-Phenylmaleimide	4-Methoxystyrene	65	88
N-Phenylmaleimide	Allylbenzene	58	82
Chalcone	Vinyl Phenyl Sulfone	75	85

Mechanistic investigations provided robust support for the proposed synergistic cycle. Stern-Volmer analysis showed that the fluorescence of CP1 was efficiently quenched by vinyl phenyl sulfone (KSV = 125 M^{-1}) but not by N-phenylmaleimide, indicating selective excited-state interaction with the energy-accepting olefin (Table 3). Transient absorption spectroscopy directly captured the triplet state of CP1 ($\tau T \approx 125$ μs) and demonstrated its rapid quenching by vinyl sulfone, confirming dynamic energy transfer. DFT calculations modeled a key intermediate where the phosphine of CP1 is coordinated to N-phenylmaleimide, creating a chiral pocket that pre-organizes the approaching vinyl sulfone. The calculated energy difference between the diastereomeric transition states leading to the (R)- and (S)-products was 2.1 kcal/mol, favoring the observed (R)-enantiomer and aligning with the high experimental ee.

Table 3. Summary of Key Mechanistic Evidence

Experiment	Key Observation	Interpretation
Stern-Volmer Quenching	KSV(Vinyl Sulfone) = 125 M^{-1}; KSV(Maleimide) ~ 0	Selective energy transfer from photoexcited catalyst to vinyl sulfone.
Transient Absorption	Triplet lifetime of CP1 (125 μs) reduced by vinyl sulfone ($k_q = 1.2 \times 10^9$ $M^{-1}s^{-1}$).	Direct observation of EnT from catalyst to substrate.
DFT Calculation	$\Delta\Delta G‡$ for competing pathways = 2.1 kcal/mol, favoring (R)-product.	Rationalizes the high enantioselectivity and its absolute sense.
Control Experiments	No reaction in dark; negligible yield/ee with separated components.	Confirms necessity of light and bifunctional catalyst structure.
Synthetic Application	Gram-scale synthesis (1.05 g, 90% yield, 93% ee).	Demonstrates practicality and scalability.

4. Discussion

The development and successful implementation of these visible-light-driven chiral phosphine catalysts constitute a significant conceptual advancement in the realm of asymmetric synthesis, particularly within the emerging field of synergistic photoorganocatalysis. The core achievement lies not merely in the provision of a practical synthetic method, but in the demonstration of a powerful new design paradigm: the covalent integration of a light-harvesting unit with a privileged chiral catalyst scaffold to create a single, bifunctional molecular entity capable of orchestrating complex, multi-step reaction sequences under mild photochemical conditions. This design elegantly addresses the fundamental challenge of stereocontrol in energy-transfer-mediated reactions by ensuring that the photogenerated, highly reactive triplet intermediate is formed in intimate proximity to a chiral, Lewis

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base-activated reaction partner. This enforced intramolecularity within a pre-organized chiral environment effectively circumvents the diffusion-controlled encounters and unselective background reactions that often plague systems employing separate photosensitizers and chiral co-catalysts.

The detailed structure-activity relationships elucidated through the evaluation of the catalyst library (CP1-CP12) offer profound insights for future catalyst design. The superior performance of catalysts bearing phenothiazine (CP1) or thioxanthone (CP2) chromophores, compared to the fluorenone-based CP3, underscores a critical design principle: the triplet energy (ET) of the sensitizer must be carefully matched to the substrate. The ET must be sufficiently high to exergonically sensitize the target olefin (e.g., vinyl sulfone, ET ≈ 60-62 kcal/mol), yet not so high as to necessitate impractically short-wavelength light for excitation or to promote undesired side reactions via energy transfer to other components. Furthermore, the nature of the tether linking the chromophore and the phosphine emerged as a subtle but crucial variable. A linker that is too rigid or too short may impede the necessary conformational adjustments for optimal substrate binding to both functional sites, while a linker that is too long or too flexible may diminish the effective molarity and erode the stereochemical control by allowing too much conformational freedom. The optimal one- or two-carbon methylene bridge found for CP1 appears to strike a delicate balance, providing enough flexibility for substrate accommodation while maintaining sufficient structural pre-organization to define a competent chiral pocket.

The remarkably broad substrate scope, encompassing not only activated vinyl sulfones but also simple styrenes and diverse Michael acceptors, speaks to the robustness and generality of the catalytic mechanism. The consistently high enantioselectivities observed across this range suggest that the stereodetermining step is largely insulated from variations in the energy-accepting olefin. This indicates that enantiocontrol is predominantly exerted during the interception of the prochiral triplet diradical (or its polarized equivalent) by the chiral, phosphine-bound Michael acceptor complex, rather than during the initial energy transfer event. This mechanistic feature is highly desirable, as it decouples the excitation step from the stereocontrol step, allowing the catalyst's chiral environment to function reliably across diverse substrate pairs.

However, a critical examination also reveals the current limitations and frontiers for further development. While maleimides and fumarates are excellent substrates, extending the methodology to more challenging but synthetically vital acceptors—such as acrylates, acrylonitriles, or nitroalkenes—will require iterative optimization of the phosphine's electronic and steric properties to modulate its Lewis basicity and the stability of the resulting zwitterionic adduct. The moderate yields obtained with simple styrenes point to potential inefficiencies in either the energy transfer efficiency for these substrates or competing unproductive decay pathways of their triplet states. Future catalyst generations might incorporate chromophores with even longer triplet lifetimes or tailored redox properties to better engage these less-activated partners. Perhaps the most ambitious future direction lies in achieving enantioselective [2+2] cycloadditions between two completely unfunctionalized olefins, a transformation that would require the catalyst to differentiate between two nearly identical hydrocarbon partners through subtle non-covalent interactions—a formidable task that will push the boundaries of supramolecular photocatalysis.

From a broader perspective, this work establishes a versatile blueprint for "dual-functional synergistic photocatalysis." The conceptual framework of appending a photosensitizer to a known chiral catalyst is inherently modular and generalizable. This strategy can be extrapolated well beyond phosphine catalysis. One can readily envision analogous designs where the chiral phosphine is replaced by a cinchona alkaloid-derived amine for iminium ion catalysis, a thiourea for dual hydrogen-bonding activation, or even a chiral transition metal complex for combined photoredox and transition metal catalysis. Similarly, the chromophore can be tailored—moving from phenothiazines to acridinium ions, porphyrins, or iridium complexes—to access different regions of the visible spectrum or to engage in single-electron transfer (SET) pathways instead of, or in concert with, energy transfer. This opens a vast and largely unexplored chemical space for the discovery of new catalytic manifolds.

Finally, the practical implications of this research extend to sustainable synthesis. By enabling powerful carbon-carbon bond-forming reactions at room temperature using low-energy visible light as the driving force, this methodology aligns with the principles of green chemistry. The ability to construct complex, chiral cyclobutane scaffolds—pharmacophores of high value—from simple starting materials in a single catalytic step represents a significant increase in synthetic efficiency. In conclusion, this study does more than introduce a new catalyst for a specific reaction; it provides a foundational design principle and a compelling proof-of-concept that will undoubtedly inspire and accelerate the development of the next generation of intelligent, multifunctional catalysts capable of harnessing light to perform previously impossible feats of asymmetric synthesis.

ISSN 2616-7433 Vol. 8, Issue 1: 13-18, DOI: 10.25236/FSST.2026.080103

5. Conclusion

In conclusion, we have developed a new class of chiral phosphine catalysts that operate under visible light to drive highly enantioselective [2+2] cycloaddition reactions. These bifunctional catalysts, which combine a triplet energy transfer photosensitizer with a chiral Lewis base in one molecule, facilitate a synergistic activation mechanism. This approach provides a general and practical method for synthesizing enantiomerically enriched cyclobutanes from readily available olefin precursors under mild conditions. The work establishes a powerful new strategy for asymmetric photocatalysis—the covalent integration of light-harvesting and chiral-controlling elements—which is likely to inspire the development of novel catalysts for a wide range of stereocontrolled photochemical transformations that are currently beyond reach.

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