

## ■ Asymmetric Catalysis | Hot Paper |

● Enantioselective [2+2] Photocycloaddition Reactions of Enones and Olefins with Visible Light Mediated by *N,N'*-Dioxide–Metal ComplexesHan Yu, Shunxi Dong, Qian Yao, Long Chen, Dong Zhang, Xiaohua Liu,\* and Xiaoming Feng\*<sup>[a]</sup>

**Abstract:** A 2-alkenylpyridine-bound *N,N'*-dioxide–Tb<sup>III</sup> complex has been found to absorb visible light to reach the excited state, leading to the direct visible-light-excited catalytic enantioselective [2+2] cycloaddition of 2-alkenylpyridines to various alkenes in the absence of an additional photosensitizer. Diverse enantioenriched cyclobutanes were successfully obtained (yields up to 70%, > 19:1 d.r., 92% ee). The new chiral terbium(III) complex features a bathochromic

shift, lower excitation energy, and facile intersystem crossing due to paramagnetic and heavy-atom effects, which enable the antenna 2-alkenylpyridines to be excited. For comparison, a chiral *N,N'*-dioxide–Sc<sup>III</sup> complex in combination with [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> was efficient in the enantioselective photocycloaddition reactions of 2'-hydroxychalcones with alkenes, thereby revealing that both substrates and metal salts have significant effects on the reaction.


## Introduction

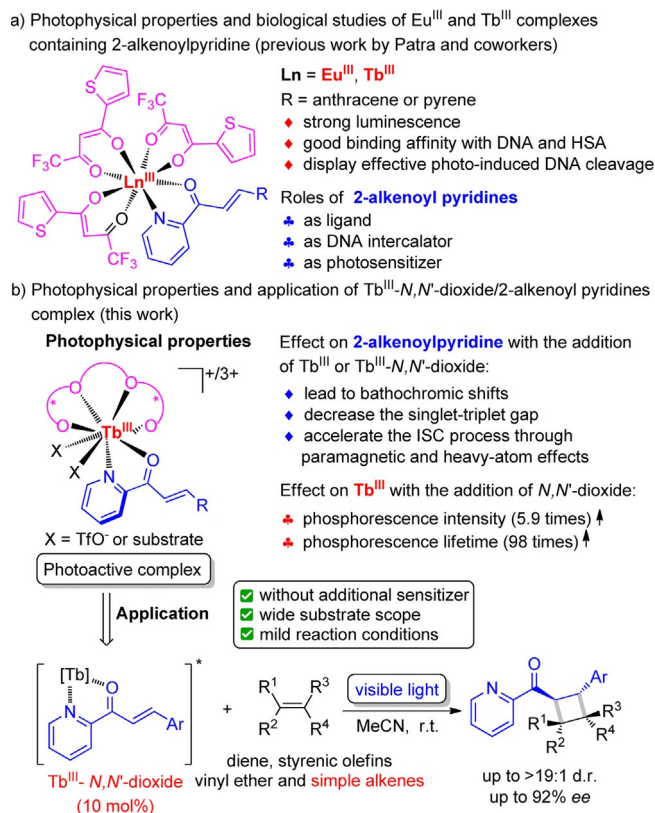
Enantioselective [2+2] cycloadditions of olefins, in particular [2+2] photocycloadditions, are one of the most efficient approaches to the construction of chiral cyclobutane compounds.<sup>[1]</sup> However, in the early stages of their development, catalytic enantioselective [2+2] photocycloadditions proved to be challenging, mainly due to competitive racemic background photoreactions and some side-reactions resulting from the highly reactive radical intermediates.<sup>[2]</sup> To date, several successful strategies for asymmetric catalytic [2+2] photocycloadditions have been developed separately by the groups of Bach,<sup>[3a,b,d,4]</sup> Yoon,<sup>[5]</sup> and Meggers.<sup>[6]</sup> Bach and co-workers first addressed this reaction through the use of either chiral hydrogen-bonding organic sensitizers<sup>[3]</sup> or chiral Lewis acids<sup>[4]</sup> as catalysts. The key point of chiral Lewis acid catalysis is the bathochromic shift of the UV absorption of the catalyst-activated substrate, which enables unselective background reactions to be suppressed through careful irradiation with a light source of appropriate wavelength.<sup>[4]</sup> Subsequently, Yoon and co-workers elegantly realized a handful of highly enantioselective catalytic [2+2] photocycloadditions under the synergistic catalysis<sup>[7]</sup>

of a chiral Lewis acid and a sensitizer.<sup>[5a,b]</sup> This stereocontrol protocol features the coordination of a chiral Lewis acid to an enone, which dramatically lowers the triplet energy of this bound substrate. Recently, Meggers and co-workers described a unique intermolecular [2+2] photocycloaddition reaction catalyzed by a chiral-at-metal<sup>[8]</sup> complex in which the chiral catalyst serves as a chiral Lewis acid and its complex with the substrate could act as the sensitizer.<sup>[6]</sup> In essence, the development of exogenous chiral ligand–Lewis acid catalysts that enable the feasible formation of excited-state organic intermediates with longer lifetimes is critical to broadening the scope of enantioselective photocycloaddition reactions.

Lanthanide (Ln) complexes have attracted great interest over the past two decades due to their stability, flexible coordination ability, and unique photophysical properties.<sup>[9–12]</sup> Lanthanide complexes have been widely used as luminescent probes, MRI contrast agents, luminescent metal–organic frameworks, and cellular imaging agents.<sup>[11]</sup> Very recently, Patra and co-workers reported the synthesis of Eu<sup>III</sup> and Tb<sup>III</sup> complexes containing 2-alkenylpyridine and three small 1,3-diketone ligands, which were subsequently found to present strong luminescence and display good binding affinity towards DNA and human serum albumin (HSA, Scheme 1a).<sup>[13]</sup> Our group has developed chiral tetradentate *N,N'*-dioxide ligands that can form powerful chiral Lewis acid catalysts with rare-earth metal salts and others.<sup>[10b,14]</sup> Intrigued by the well-understood platform of *N,N'*-dioxide–lanthanide metal complexes for asymmetric synthesis, we became interested in their luminescent properties and potential utility in asymmetric photocatalysis.<sup>[15,16]</sup> We envisioned that a high-level polydentate chiral *N,N'*-dioxide ligand and a suitable antenna<sup>[12]</sup> (such as 2-alkenylpyridine) could work in cooperation with a lanthanide ion

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Scheme 1. Studies on lanthanide complexes containing 2-alkenylpyridine.

to generate photoactive and luminescent lanthanide complexes (Scheme 1 b).

## Results and Discussion

To assess our hypothesis, we carried out UV/Vis studies on (*E*)-3-phenyl-1-(pyridin-2-yl)prop-2-enone (**1a**) in the presence of  $\text{Tb}(\text{OTf})_3$  or the  $\text{L}_4\text{-RaPr}_2\text{-Tb}(\text{OTf})_3$  complex (Figure 1 a; for the structures of the ligands  $\text{L}_n\text{-RaPr}_2$ , see Table 1). It was found that, with one equivalent of  $\text{Tb}(\text{OTf})_3$  or chiral  $\text{L}_4\text{-RaPr}_2\text{-Tb}(\text{OTf})_3$ , the absorption of **1a** at  $\lambda = 365$  nm increased gradually. The molar extinction coefficients are 280, 3580, and  $4760 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. The addition of Lewis acids changes the spectrum of **1a**, leading to bathochromic shift and strong absorption in the visible-light region at high concentration. This is in agreement with the results of previous work,<sup>[5a,b]</sup> and indicates that the complex  $\text{Tb}(\text{OTf})_3\text{-L}_4\text{-RaPr}_2\text{-1a}$  is photoactive. In addition, the luminescence of  $\text{Tb}(\text{OTf})_3\text{-1a}$  in the absence or presence of  $\text{L}_4\text{-RaPr}_2$  was also studied. Both the phosphorescence intensity (5.9 times, Figure 1 b) and lifetime (98 times) increased dramatically (see Figures S17–S19 in the Supporting Information) in the presence of  $\text{L}_4\text{-RaPr}_2$ . This suggests that the use of the multidentate  $N,N'$ -dioxide ligand minimizes the quenching of luminescence. Using 2-alkenylpyridine **1a** as a coordinating antenna, lanthanide luminescence begins with the excitation of **1a** from the ground state  $S_0$  ( $^1\text{a-Tb-L}$ ) to the singlet excited state  $S_1$  ( $^1\text{a-Tb-L}$ ). Intersystem crossing from  $S_1$  to the triplet excited state  $T_1$  is a spin-forbid-

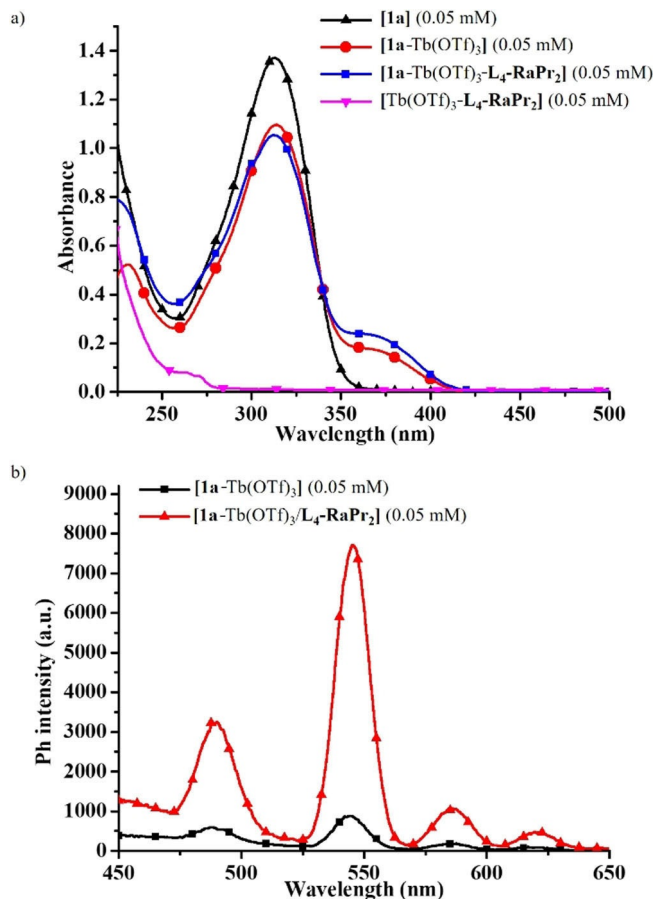


Figure 1. a) UV/Vis absorption spectra of 2-alkenylpyridine **1a** ( $c = 0.05$  mM in MeCN) in the presence of  $\text{Tb}(\text{OTf})_3$  or the  $\text{L}_4\text{-RaPr}_2\text{-Tb}(\text{OTf})_3$  complex. b) Phosphorescence spectra of  $[\text{1a-Tb}(\text{OTf})_3]$  and  $[\text{1a-Tb}(\text{OTf})_3\text{-L}_4\text{-RaPr}_2]$  ( $c = 0.05$  mM in MeCN). Delay time = 0.05 ms,  $\lambda_{\text{ex}} = 365$  nm, slit width = 12 nm.

den process. However,  $\text{Tb}^{\text{III}}$  as a heavy atom could largely promote the transition from  $S_1$  ( $^1\text{a-Tb-L}$ ) to  $T_1$  ( $^3\text{a-Tb-L}$ ).<sup>[17]</sup> Next, it is possible to transfer energy from the excited state of the antenna ( $^3\text{a-Tb-L}$ ) to the  $^5\text{D}_4$  excited state of  $\text{Tb}^{\text{III}}$  to yield  $\text{1a-Tb}^*\text{-L}$ . When the quenching conditions are minimized by the  $N,N'$ -dioxide ligand, lanthanide  $\text{Tb}^{\text{III}}$  emission clearly occurs involving the  $^5\text{D}_4 \rightarrow ^7\text{F}_j$  transition for  $j = 6, 5, 4$ , and  $3$ .<sup>[12]</sup>

The spectral data above provide proof-of-principle for the enantioselective [2+2] photocycloaddition of 2-alkenylpyridines with the chiral  $N,N'$ -dioxide- $\text{Tb}(\text{OTf})_3$  complex. The Lewis acid catalysis, along with the chiral environment created by the linear polydentate ligand, has a visible effect on the olefin [2+2] photocycloaddition reaction (Scheme 1 b). Here, we disclose our efforts in this area. The new four-carbon-linked chiral  $N,N'$ -dioxide  $\text{L}_4\text{-RaPr}_2\text{-Tb}^{\text{III}}$  complex was found to be efficient in the visible-light-excited [2+2] cycloaddition of 2-alkenylpyridines to diverse alkenes. The coordinated 2-alkenylpyridine itself acts as either a sensitizer or a reactant. Olefins, including a diene, styrene, vinyl ether, and simple alkenes, participated in the enantioselective photocycloaddition reaction with good results. For comparison, the synergistic catalysis of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  and a chiral  $N,N'$ -dioxide- $\text{Sc}^{\text{III}}$  complex enabled the photocycloaddition reactions of 2'-hydroxychalcones with alkenes.<sup>[18]</sup>

Initially, the [2+2] cycloaddition of 2-alkenoylpyridine **1a** to 2,3-dimethylbuta-1,3-diene (**2a**) was carried out without catalyst in MeCN by irradiation using a 23 W compact fluorescent light (CFL) bulb. The desired product **3a** was isolated in a yield of 68% with a diastereoselective ratio (d.r.) of 85:15 (Table 1, entry 1), which reveals a strong background reaction. Next, the

**Table 1.** Optimization of the reaction conditions for the [2+2] photocycloaddition of 2-alkenoylpyridine **1a**.<sup>[a]</sup>

Entry	Metal salt	Ligand	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>	d.r. <sup>[c]</sup>
1	–	–	68	0	85:15
2	Sc(OTf) <sub>3</sub>	L <sub>3</sub> -PrPr <sub>2</sub>	trace	0	–
3	Tb(OTf) <sub>3</sub>	L <sub>3</sub> -PrPr <sub>2</sub>	70	67	84:16
4	Tb(OTf) <sub>3</sub>	L <sub>3</sub> -PiPr <sub>2</sub>	65	64	83:17
5	Tb(OTf) <sub>3</sub>	L <sub>3</sub> -RaPr <sub>2</sub>	56	76	85:15
6	Tb(OTf) <sub>3</sub>	L <sub>2</sub> -RaPr <sub>2</sub>	62	71	85:15
7	Tb(OTf) <sub>3</sub>	L <sub>4</sub> -RaPr <sub>2</sub>	60	92	85:15
8 <sup>[d]</sup>	Tb(OTf) <sub>3</sub>	L <sub>4</sub> -RaPr <sub>2</sub>	0	–	–

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol), **2a** (1.0 mmol), and metal salt/L (1:1, 10 mol%) in MeCN (1.0 mL) at room temperature (r.t.) under irradiation with a 23 W CFL for 24 h. [b] Yield of the isolated product. [c] The ee and d.r. values were determined by ultraperformance convergence chromatography (UPC<sup>2</sup>) analysis. [d] Without light.

reaction was investigated with various metal salts in the presence of the ligand L<sub>3</sub>-PrPr<sub>2</sub> (see Table S1 in the Supporting Information), and it was found that only a trace amount of the desired product **3a** was isolated as a racemic mixture with the Sc<sup>III</sup>-L<sub>3</sub>-PrPr<sub>2</sub> complex as the catalyst (Table 1, entry 2). In contrast, the reaction occurred smoothly in the presence of N,N'-dioxide-lanthanide metal complexes. In particular, Tb<sup>III</sup> was a good choice in terms of enantioselectivity (entry 3; 70% yield, 67% ee, and 84:16 d.r.).<sup>[19]</sup> Encouraged by these promising results, N,N'-dioxides with different chiral backbones were evaluated. Compared with the (S)-pipecolic acid derived L<sub>3</sub>-PiPr<sub>2</sub> slightly better enantioselectivity was induced with the L-ramipril-derived L<sub>3</sub>-RaPr<sub>2</sub> as the ligand (Table 1, entries 4 and 5, 64% ee vs. 76% ee). Moreover, other parameters were also investigated, but no better results were observed (for details, see Tables S1 and S2). Gratifyingly, the linker of the ligands exhibits a significant influence on the enantioselectivity of the reaction. The new four-carbon-linked ligand L<sub>4</sub>-RaPr<sub>2</sub> was the most efficient as the desired product was provided in a yield of 60% with 85:15 d.r. and 92% ee (entry 7 vs. entries 5 and 6). It is noteworthy that the reaction did not occur without irradiation (entry 8).

With the optimized reaction conditions in hand, the substrate scope of the 2-alkenoylpyridines was tested in combination with diene **2a** (Table 2). Generally, moderate yields and

**Table 2.** Scope of the cycloaddition reaction with respect to 2-alkenoylpyridines.<sup>[a]</sup>

R = 4-Me ( <b>3b</b> )	62% yield, 91% ee, 6.5:1 d.r.
R = 4-OMe ( <b>3c</b> )	68% yield, 75% ee, 9.1:1 d.r.
R = 4-Br ( <b>3d</b> )	59% yield, 90/92% ee, 6.2:1 d.r.
R = 4-Cl ( <b>3e</b> )	53% yield, 90/92% ee, 5.7:1 d.r. <sup>[b]</sup>
R = 4-F ( <b>3f</b> )	67% yield, 90% ee, 5.7:1 d.r.
R = 3-F ( <b>3g</b> )	49% yield, 84% ee, 6.8:1 d.r.
R = 2-F ( <b>3h</b> )	51% yield, 87% ee, >19:1 d.r.
<b>3i</b>	59% yield, 90% ee, 4.8:1 d.r.
<b>3j</b>	51% yield, 92% ee, 5.6:1 d.r.
<b>3k</b>	66% yield, 87% ee, 5.6:1 d.r.

[a] All the reactions were carried out with **1** (0.1 mmol), **2a** (1.0 mmol), and Tb(OTf)<sub>3</sub>/L<sub>4</sub>-RaPr<sub>2</sub> (1:1, 10 mol%) in MeCN (1.0 mL) at room temperature under irradiation with a 23 W CFL for 24 h. Yield of the isolated product. The d.r. values were determined by <sup>1</sup>H NMR spectroscopy, and ee values were determined by UPC<sup>2</sup> analysis. The ee values of some minor isomers were not determined due to the lack of a separation method for the enantiomers. [b] The absolute configuration of the major isomer of **3e** was verified by X-ray crystallography as 1R,2R,3S.<sup>[20]</sup>

diastereoselectivities with good enantioselectivities were obtained regardless of the electronic nature and position of the substituents on the β-aryl groups (**3b** and **3d–3h**, 49–67% yields, 84–92% ee, and 5.7:1 to >19:1 d.r.), except for the *p*-methoxy-substituted substrate **3c** (68% yield, 75% ee, and 9.1:1 d.r.). Control experiments were carried out on the *p*-methoxy-substituted substrate **1c** that indicated that the lower ee value for the product **3c** was probably a result of the relatively rapid rate of an uncatalyzed cycloaddition (for details, see Table S8 in the Supporting Information). In addition, substrates bearing different substituents on the pyridine ring were also tolerated in this reaction system (59% yield, 90% ee, and 4.8:1 d.r. for **3i**; 51% yield, 92% ee, and 5.6:1 d.r. for **3j**). Moreover, the reaction between a heteroaryl 2-alkenoylpyridine and diene **2a** delivered the corresponding product **3k** with comparable results (66% yield, 87% ee, and 5.6:1 d.r.). The absolute configuration of the major isomer of the adduct **3e** was verified as 1R,2R,3S by single-crystal X-ray diffraction analysis.<sup>[20]</sup>

Next, a wide range of alkenes were also proven to be compatible with this reaction (Table 3, **3l–3q**, 25–70% yields, 72–83% ee, and 1.1:1 to >19:1 d.r.). The nature of the alkene had an appreciable effect on the outcome. Styrene underwent the cycloaddition to afford the corresponding product **3l** in a yield of 70% with a relatively low d.r. and a good ee for the two dia-



**Table 3.** Scope of the cycloaddition reaction with respect to alkenes.<sup>[a]</sup>

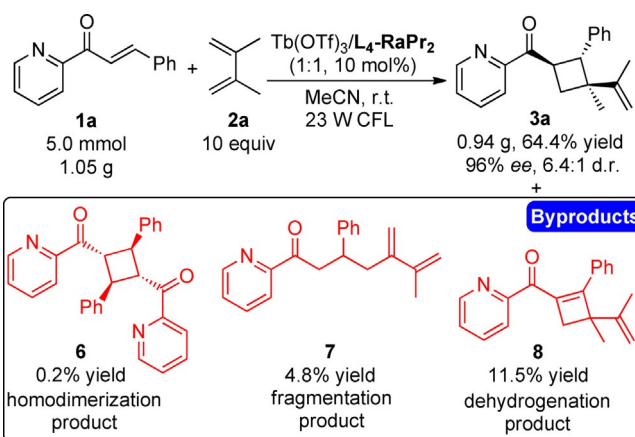
<p><b>1a</b> + <b>2</b> <math>\xrightarrow[\text{MeCN, r.t., 23 W CFL}]{\text{Tb(OTf)}_3/\text{L}_4\text{-RaPr}_2 \text{ (1:1, 10 mol\%)}}</math> <b>3</b></p>		
<p><b>3l</b> 70% yield 82/83% ee 1.8:1 d.r.</p>	<p><b>3m</b> 31% yield 82% ee &gt;19:1 d.r.</p>	<p><b>3n</b> 52% yield 78/77% ee 2.3:1 d.r.</p>
<p><b>3o</b> 55% yield 76/86% ee 1.5:1 d.r.</p>	<p><b>3p</b> 25% yield (72 h) 72/81% ee 1.1:1 d.r.</p>	<p><b>3q</b> 45% yield 84/75% ee 2.2:1 d.r.<sup>[b]</sup></p>

[a] Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol), **2** (1.0 mmol), and  $\text{Tb(OTf)}_3/\text{L}_4\text{-RaPr}_2$  (1:1, 10 mol%) in MeCN (1.0 mL) at room temperature under irradiation with a 23 W CFL for 24 h. Yield of the isolated product. The d.r. values were determined by  $^1\text{H}$  NMR spectroscopy, and the ee values were determined by UPC<sup>2</sup> analysis. [b] The absolute configuration of **3q**-major was determined to be 1*R*,2*R*,2*a**S*,7*a**R* by X-ray crystallography, and **3q**-minor was determined to be 1*R*,2*R*,2*a**R*,7*a**S*.<sup>[20]</sup>

stereomers (1.8:1 d.r., 82/83% ee). The reaction of **1a** with a vinyl ether occurred smoothly, and the desired product **3m** was isolated with 82% ee and >19:1 d.r., but in a yield of only 31%. Moderate results were obtained for 1,1-disubstituted alkenes (52% yield, 78/77% ee, and 2.3:1 d.r. for **3n**; 55% yield, 76/86% ee, and 1.5:1 d.r. for **3o**). Moreover, an aliphatic alkene with a long chain also reacted, although a low yield of the product **3p** was obtained (25% yield, 72/81% ee, and 1.1:1 d.r.). Indene, as a representative internal alkene, was tested in the present reaction protocol and the corresponding product **3q** was isolated in a yield of 45% with 2.2:1 d.r. and 84/75% ee. Moreover, the absolute configurations of both the major and minor diastereomers of **3q** were assigned by X-ray crystallography,<sup>[20]</sup> suggesting that our chiral catalyst is capable of excellent enantiofacial differentiation of 3-phenyl-1-(pyridin-2-yl)prop-2-enone. It is notable that in some cases the low yields were mainly caused by several unavoidable side reactions (see Scheme 2 for details).

To show the synthetic utility of the [2+2] cycloaddition of 2-alkenoylpyridine **1a** with the diene **2a**, a 5 mmol scale version of the reaction was conducted (Scheme 2). Better results were obtained (64% yield, 96% ee, and 6.4:1 d.r.) compared with the small-scale reaction. Meanwhile, the gram-scale reaction enabled us to isolate and assign the byproducts, including the homodimerization product **6** (0.2% yield),<sup>[20]</sup> the fragmentation product **7** (4.8% yield), and the dehydrogenation product **8** (11.5% yield).

For contrast, the [2+2] photocycloaddition reaction of the 2'-hydroxychalcone **4a** with the diene **2a** was also investigated



**Scheme 2.** Gram-scale reaction of **1a** and **2a**.

under similar conditions to the reaction with 2-alkenoylpyridine **1a** (Table 1, entry 7). However, the desired adduct **5a** was not detected. A UV/Vis study of 2'-hydroxychalcone **4a** showed that the addition of  $\text{Tb(OTf)}_3$  caused no variation in the absorption, but  $\text{Sc(OTf)}_3$  yielded a clear bathochromic shift (see Figure S15 in the Supporting Information). To our delight, by modifying the reaction conditions, the chiral cyclobutane **5a** was isolated in a yield of 96% with 4.2:1 d.r. and 90% ee (Table 4) when  $\text{Sc(OTf)}_3/\text{L}_3\text{-PiEt}_2\text{Me}$  was used as the Lewis acid catalyst with the addition of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  as the sensitizer upon irradiation with a 23 W CFL (for details, see Table S2).<sup>[21,22]</sup> Then, we went on to explore the generality of this synergistic catalytic photocycloaddition by examining the reactions of 2'-hydroxychalcones and alkene coupling partners (Table 4). Diverse substituents on the  $\beta$ -aryl group of 2'-hydroxychalcones were suitable for this transformation and gave comparable results (**5b–5h**; 80–99% yields, 84–92% ee, and 4.2:1–5.2:1 d.r.). Substrates bearing different substituents on the 2-acylphenol moiety were also applicable (93% yield, 90% ee, and 5.3:1 d.r. for **5i**; 95% yield, 90% ee, and 5.2:1 d.r. for **5j**), except for the 4'-fluoro- and 4'-bromo-substituted substrates. Yoon and co-workers<sup>[5a,b]</sup> used a blue LED lamp instead of a CFL bulb to conquer the uncatalyzed background cycloaddition with the photocatalyst. In our case, however, no better results were obtained under irradiation with a blue LED (10 W, 440–445 nm). Pleasingly, when the reaction was carried out without the photocatalyst  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  under irradiation with blue LEDs (10 or 20 W), the enantioselectivities of the products **5k** and **5l** were significantly improved (78% ee vs. 52% ee for **5k**; 76% ee vs. 37% ee for **5l**).<sup>[23]</sup> The same trend was observed with the  $\beta$ -heteroaryl substrate catalyzed by  $\text{Sc(OTf)}_3/\text{L}_3\text{-PiEt}_2\text{Me}$  with blue LED irradiation (**5m**; 56% yield, 91% ee, and 6.1:1 d.r.). Moreover, styrene also performed well in this transformation, affording the corresponding product **5n** in good yield and ee, albeit with a relatively low diastereoselectivity (86% yield, 88/87% ee, and 2.5:1 d.r.). Simple aliphatic alkenes and vinyl ethers did not yield the desired products, probably due to the relatively unstable 1,4-biradical intermediates.<sup>[24]</sup>

Control reactions between 2-alkenoylpyridine **1a** and diene **2a** for 5 h under irradiation with a 23 W CFL gave yields of 21,

**Table 4.** Scope of the cycloaddition reaction with respect to 2'-hydroxychalcones.<sup>[a]</sup>

	R = 4-H ( <b>5a</b> ) 96% yield, 90% ee, 4.2:1 d.r. R = 4-Me ( <b>5b</b> ) 88% yield, 84% ee, 4.4:1 d.r. R = 4-CF <sub>3</sub> ( <b>5c</b> ) 80% yield, 90% ee, 4.2:1 d.r. R = 4-Br ( <b>5d</b> ) 99% yield, 85% ee, 5.0:1 d.r. R = 4-Cl ( <b>5e</b> ) 86% yield, 87% ee, 4.9:1 d.r. R = 4-F ( <b>5f</b> ) 86% yield, 90% ee, 5.2:1 d.r. R = 3-F ( <b>5g</b> ) 93% yield, 88% ee, 4.8:1 d.r. R = 2-F ( <b>5h</b> ) 86% yield, 92% ee, 5.0:1 d.r.
	R = 5'-Cl ( <b>5i</b> ) 93% yield, 90% ee, 5.3:1 d.r. R = 4'-Me ( <b>5j</b> ) 95% yield, 90% ee, 5.2:1 d.r. R = 4'-Br ( <b>5k</b> ) 89% yield, 52% ee, 5.2:1 d.r. <sup>[a]</sup> 90% yield, 78% ee, 5.2:1 d.r. <sup>[b]</sup> R = 4'-F ( <b>5l</b> ) 85% yield, 37% ee, 5.0:1 d.r. <sup>[a]</sup> 87% yield, 76% ee, 5.0:1 d.r. <sup>[b]</sup>
	5m: 56% yield, 91% ee, 6.1:1 d.r. <sup>[b]</sup> 5n <sup>[c]</sup> : 86% yield, 2.5:1 d.r., 88/87% ee

[a] Unless otherwise noted, the reactions were carried out with **4** (0.1 mmol), **2a** (1.0 mmol), Sc(OTf)<sub>3</sub>/L<sub>3</sub>-PiEt<sub>2</sub>Me (1:1, 10 mol%), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (5 mol%), and 5 Å MS (20 mg) in iPrCN (1.0 mL) at room temperature under irradiation with a 23 W CFL for 24 h. Yield of the isolated product. The d.r. values were determined by <sup>1</sup>H NMR spectroscopy, and the ee values were determined by UPC<sup>2</sup> analysis. The ee values of some minor isomers were not determined due to the lack of a separation method for the enantiomers. [b] Without photocatalyst under irradiation with blue LEDs. [c] With styrene instead of **2a**.

30, and 53% of **3a** under conditions of no catalyst and in the presence of Tb(OTf)<sub>3</sub> (10 mol%) and the Tb(OTf)<sub>3</sub>/L<sub>4</sub>-RaPr<sub>2</sub> complex (10 mol%), respectively. Accordingly, the related conversions of **1a** also increased gradually, that is, 34, 67, and 94% in 5 hours, respectively. The enhanced reaction rate suggests that the terbium-*N,N'*-dioxide complex would probably lower the excited energy of **1a**, thereby enabling excitation of the chiral catalyst-substrate complex with visible light. The outcomes are consistent with the UV/Vis absorption spectra (Figure 1a). Therefore, the obtained ee values of the products are the results of competition between the chiral Lewis acid catalyzed process and the uncatalyzed racemic background cycloaddition reaction.

The structure of the chiral Tb<sup>III</sup>-L<sub>4</sub>-RaPr<sub>2</sub> complex was identified by X-ray crystallographic analysis. In contrast to the coordination of chiral *N,N'*-dioxide to other metal ions, including Sc<sup>III</sup>, Mg<sup>II</sup>, Ni<sup>II</sup>, and Co<sup>II</sup>, which form octahedral complexes,<sup>[14,25]</sup> the [Tb<sup>III</sup>(L<sub>4</sub>-RaPr<sub>2</sub>)(MeOH)<sub>3</sub>H<sub>2</sub>O] complex is eight-coordinate with a square antiprismatic geometry (Scheme 3a).<sup>[20]</sup> The L<sub>4</sub>-RaPr<sub>2</sub> ligand acts as a tetradentate acyclic ligand to form a cyclic lanthanide complex. The antenna 2-alkenoylpyridine **1a** involved in the coordination with Tb<sup>III</sup> was confirmed by HRMS

analysis of the mixture of **1a**, Tb(OTf)<sub>3</sub>, and L<sub>4</sub>-RaPr<sub>2</sub> (1:1:1) in MeCN, as the peak at *m/z* = 1380.4210 corresponding to the [L<sub>4</sub>-RaPr<sub>2</sub> + **1a** + Tb<sup>III</sup> + 2TfO<sup>-</sup>]<sup>+</sup> species (calcd for 1380.4213) was observed.

Based on the aforementioned efforts along with previous reports,<sup>[4-6,26]</sup> a possible mechanism can be proposed to elucidate the reaction process and chiral induction. As shown in Scheme 3b, the substrate **1a** coordinates to the chiral terbium-*N,N'*-dioxide complex to form the new photoactive chiral complex I. This complex is readily excited by visible light to reach its lowest singlet state (S<sub>1</sub>, intermediate II). After intersystem crossing (ISC),<sup>[17]</sup> the excited triplet state (T<sub>1</sub>, intermediate III) is generated. The production of terbium luminescence gives solid evidence for the generation of this intermediate T<sub>1</sub> (<sup>3</sup>**1a**-Tb-L). Intermediate III is subsequently attacked by alkene **2a** from its  $\alpha$ -*Re* face to produce the 1,4-biradical intermediate IV. After ISC and cyclization, the Tb-coordinated [2+2] cycloaddition product (intermediate V) is formed. With the release of the optically active cyclobutane **3a**, the catalyst is regenerated and participates in the next catalytic cycle. In addition, due to the high reactivity of intermediate III, other competitive pathways, including the regioselective [2+2] cycloaddition reaction with alkene **2a** and the homodimerization of **1a**,<sup>[27]</sup> may occur leading to several byproducts (shown in Scheme 2).

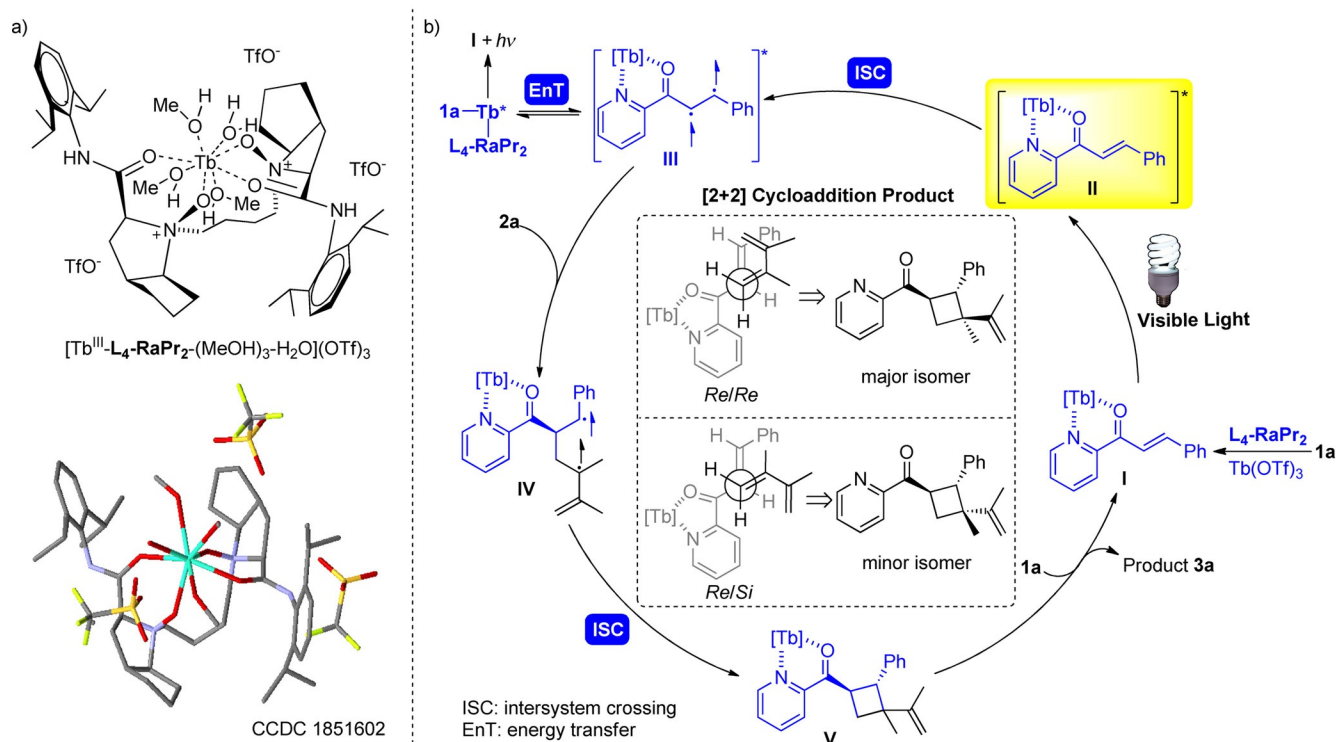
## Conclusions

We have developed an enantioselective photocycloaddition reaction between 2-alkenoylpyridines and olefins in the presence of a chiral Lewis acid catalyst. The 2-alkenoylpyridine itself acts as the antenna after coordinating to the chiral *N,N'*-dioxide-Tb<sup>III</sup> complex, absorbing visible light to reach its excited state. The paramagnetic and heavy-atom effects of the lanthanide complex make the intersystem crossing process from S<sub>1</sub> to T<sub>1</sub> more efficient, leading to a facile cycloaddition process. The square antiprismatic terbium complex of the novel four-carbon-linked L<sub>4</sub>-RaPr<sub>2</sub> ligand provides perfect facial selectivity of the bound enone, delivering optically active cyclobutene derivatives. For comparison, in the reactions of 2'-hydroxychalcones with alkenes, the chiral *N,N'*-dioxide-Sc<sup>III</sup> complex catalyst was efficient and enantioselective with the assistance of the photosensitizer [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>. The UV/Vis and phosphorescence spectra highlighted the new possibility of using a lanthanide metal-*N,N'*-dioxide complex as an asymmetric photocatalyst in cooperation with appropriate antenna, which is currently under investigation in our laboratory. In addition, the long-lived emissions of chiral *N,N'*-dioxide-Tb(OTf)<sub>3</sub> might lead to potential applications of lanthanide-based systems as luminescent probes and sensors.

## Experimental Section

### General experimental procedure for the asymmetric [2+2] photocycloaddition of 2-alkenoylpyridines

In a test tube, a mixture of L<sub>4</sub>-RaPr<sub>2</sub> (10 mol%), Tb(OTf)<sub>3</sub> (10 mol%), and 2-alkenoylpyridine (0.1 mmol) in MeCN (1.0 mL)



**Scheme 3.** Proposed mechanism for the photocycloaddition reaction between 2-alkenoylpyridines and alkenes.

was stirred at 35 °C for 30 min under N<sub>2</sub> atmosphere. The alkene (10 equiv) was added to this solution by syringe, and the resulting mixture was stirred under 23 W CFL irradiation at room temperature. The reaction progress was monitored by TLC. After 24 h, the solvent was removed in vacuo and the desired products were purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1:40 to 1:20).

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** cycloaddition • asymmetric catalysis • lanthanides • N,N'-dioxides • photochemistry

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