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Asymmetric Catalysis

Merger of Visible Light Induced Oxidation and Enantioselective Alkylation with a Chiral Iridium Catalyst

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Abstract: A single chiral octahedral iridium(III) complex is used for visible light activated asymmetric photoredox catalysis. In the presence of a conventional household lamp and under an atmosphere of air, the oxidative coupling of 2-acyl-1-phenylimidazoles with *N*,*N*-diaryl-*N*-(trimethylsilyl)methylamines provides aminoalkylated products in 61–93% yields with high enantiomeric excess (90–98% *ee*). Notably, the iridium center simultaneously serves three distinct functions: as the exclusive source of chirality, as the catalytically active Lewis acid, and as a central part of the photoredox sensitizer. This conceptionally simple reaction Scheme may provide new avenues for the green synthesis of non-racemic chiral molecules.

Asymmetric catalysis driven by visible light is a topic of high current interest.[1–5] Whereas asymmetric catalysis is considered an economic strategy to access enantiomerically pure chiral compounds, visible light can assist in generating reactive intermediates under surprisingly mild conditions, while at the same time providing an environmentally friendly and sustainable source of energy for activating chemical reactions. In most reported examples, this task is shared by two catalysts, a photoredox sensitizer for triggering light-induced redox chemistry, in combination with an asymmetric catalyst to provide the activation of one substrate and the required stereodifferentiation.[3,5] Examples for executing visible light activated asymmetric photoredox catalysis with single catalysts are rare.[4a,b,d] Notably, Melchiorre and co-workers reported photoactivated enamine catalysis in which a transient electron donor-acceptor (EDA) complex is capable of absorbing visible light and inducing a charge transfer.[4b,6] We disclose here that a simple chiral iridium complex is a very effective catalyst for the visible light activated α-aminoalkylation of 2-acyl-1-phenylimidazoles, thereby serving as a "2-in-1"-catalyst by combining photosensitized oxidation with asymmetric alkylation (Figure 1).

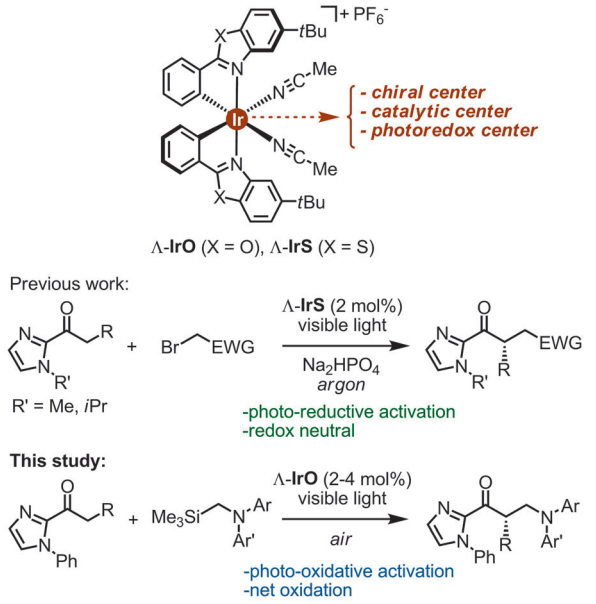

Figure 1. Previous work and this study regarding photoactivated asymmetric catalysis with chiral iridium(III) Lewis acids.

Previously, we reported that the chiral iridum complex Λ-**IrS** serves as an effective catalyst for the visible light induced enantioselective α-alkylation of 2-acyl imidazoles with electron-deficient benzyl bromides and phenacyl bromides under *reductive* activation (Figure 1).[7] We were wondering if this class of chiral iridium photocatalysts would also be capable of catalyzing asymmetric photoredox processes which instead proceed through *oxidative* chemistry and we chose the well-established oxidation of α-silylamines as our model system.[8–12] To start with, 2-phenylacetyl-1-methylimidazole (**1a**'') was treated with *N*,*N*-diphenyl-*N*-(trimethylsilyl)methylamine (**2a**) in the presence of the enantiomerically pure iridium complex Λ-**IrO**[13] (2 mol%), while exposed to air. Encouragingly, irradiation with visible light in the form of a standard 12 W energy saving household lamp for 20 h afforded the expected aminoalkylation product **3a**'' with 91% *ee*, albeit with a low yield of just 34% (Table 1, entry 1). Improved results were obtained when we modified the 2-acyl imidazole substrate. Accordingly, replacing the *N*-methylimidazole moiety (**1a**'') with *N*-isopropylimidazole (**1a**') provided the aminoalkylation product **3a**' with an increased yield of 48% and 90% *ee* after 20 h of irradiation

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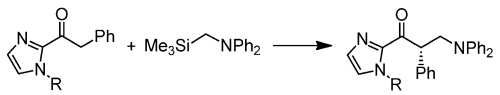
Table 1. Optimization of the enantioselective photoactivated α-aminoalkylation of 2-acyl imidazoles.[a]



1a'' (R = Me) **1a'** (R = *i*Pr) **1a** (R = Ph) — **2a** — **3a''** (R = Me) **3a'** (R = *i*Pr) **3a** (R = Ph)

Entry	*hν*[b]	Substrate	Catalyst (mol%)	*t* [h]	Yield [%]	*ee* [%][c]
1	visible light	**1a**''	Λ-**IrO** (2.0)	20	34	91
2	visible light	**1a**'	Λ-**IrO** (2.0)	20	48	90
3	visible light[d]	**1a**	Λ-**IrO** (2.0)	6.5	92	97
4	visible light	**1a**	none	20	0	nd
5	dark	**1a**	Λ-**IrO** (2.0)	48	18	94
6	visible light	**1a**	Λ-**IrS** (2.0)	20	51	97

[a] Reaction conditions: Reactions performed in CH_2Cl_2 (0.5 mL) with 2-acyl imidazole (0.4 M) and silyl amine (1.2 M) at room temperature under an atmosphere of air. [b] 12 W white light energy saving lamp (CFL). [c] Determined by chiral HPLC analysis; nd = not determined.[d] Almost identical results (6 h photolysis, 93% yield, 97% *ee*) were obtained using blue LEDs (6 W, $\lambda_{em} = (420 \pm 20)$ nm) instead.

(Table 1, entry 2). However, the best results were obtained with the *N*-phenylimidazole substrate **1a**, giving 92% yield and 97% *ee* after just 6.5 h of photolysis (Table 1, entry 3). Importantly, control experiments devoid of catalyst (no reaction) or performed in the dark (very sluggish and incomplete reaction after an elongated reaction time of 48 h) reveal that it is the combination out of chiral iridium complex Λ-**IrO** and visible light that is required for an efficient reaction (Table 1, entries 4 and 5). It is also worth noting that the catalyst Λ-**IrS**,[7] which was found superior for the previously reported asymmetric photo-reductive C–C bond formation, turned out to be inferior for the here investigated photo-oxidative activation (entry 6 compared to entry 3).

Next, we tested the scope of the asymmetric photoinduced α-aminoalkylation with catalyst Δ-**IrO**. Figure 2 shows that the reaction of a variety of 2-acyl imidazoles with *N*,*N*-diaryl-*N*-(trimethylsilyl)methylamines in the presence of Δ-**IrO** (2–4 mol%) and under air while illuminating with visible light provided the expected alkylation products in 61–93% yields and with high excellent enantioselectivities of 90–98% *ee*. With respect to silymethylamines, different substituents are tolerated in the phenyl groups (**3b**–**d**), and one phenyl was replaced by a naphthyl group (**3e**). With respect to 2-acyl imidazoles, steric, electron-donating, and electron-withdrawing groups can be placed into the phenyl moiety in the α-position to the carbonyl group (products **3f**–**i**), phenyl can be replaced by thiophenyl (product **3j**), and a 2-propionic imidazole (product **3k**) as well as a 2-butyric imidazole (product **3l**) were aminoalkylated in the α-postion of the carbonyl group with high enantioselectivities, although an increased catalyst loading of 4 mol% is required to achieve satisfactory results. Despite these excellent results, it has to be noted that the α-silyl and the two aryl groups, which reduce the oxidation potential of amines,[10] are required for obtaining satisfactory results (see Supporting Information).

We propose the following plausible mechanism as displayed in Figure 3. The catalytic cycle is initiated upon coordination of

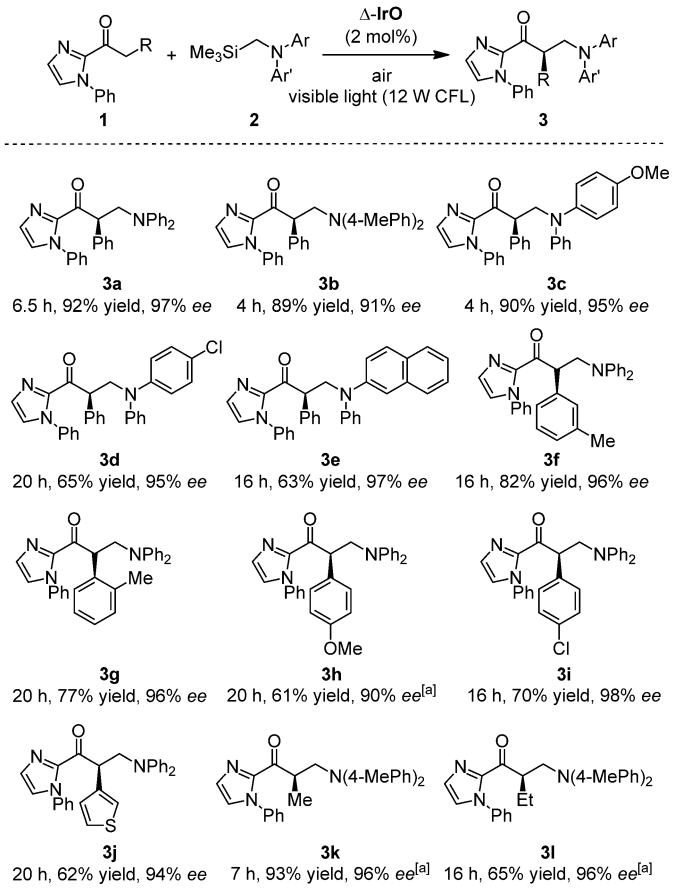


Figure 2. Substrate scope for the photoactivated asymmetric α-aminoalkylation of 2-acyl imidazoles.[a] Catalyst loading of 4 mol%.

the 2-acyl imidazole substrate **1** to the iridium complex Λ-**IrO** in a bidentate fashion under release of the two labile monodentate acetonitrile ligands to provide the substrate coordinated intermediate **A**. The subsequent reversible deprotonation in the α-position of the carbonyl group affords the nucleophilic iridium enolate intermediate **B**, which reacts with an electrophilic iminium ion that is generated by an iridium-photosensitized oxidation of the α-silylamine with oxygen serving as the terminal oxidant according to the shown and generally accepted photoredox catalysis cycle.[9–12] The addition of the iminium ion to the iridium enolate complex occurs in a stereocontrolled fashion dictated by the metal-centered chirality and provides the iridium-coordinated product **C**, which is subsequently released as the product **3** upon coordination to a new substrate molecule **1**, thereby initiating a new catalytic cycle.

A series of experiments support this mechanistic picture (Figure 4). We first investigated the catalytic cycle by verifying the involvement of the proposed nucleophilic iridium enolate intermediate **B**. Accordingly, upon reaction of an excess substrate **1a** with racemic Λ/Δ-**IrO** we could isolate the proposed complex **B** (R = Ph). A crystal structure is shown in Figure 4a and reveals that a Λ-configuration at the iridium center shields the *Si*-face of the α-enolate carbon atom and directs the addition of the electrophile to the *Re*-face, thereby being consistent with the observed *S*-configuration of the alkylation prod-

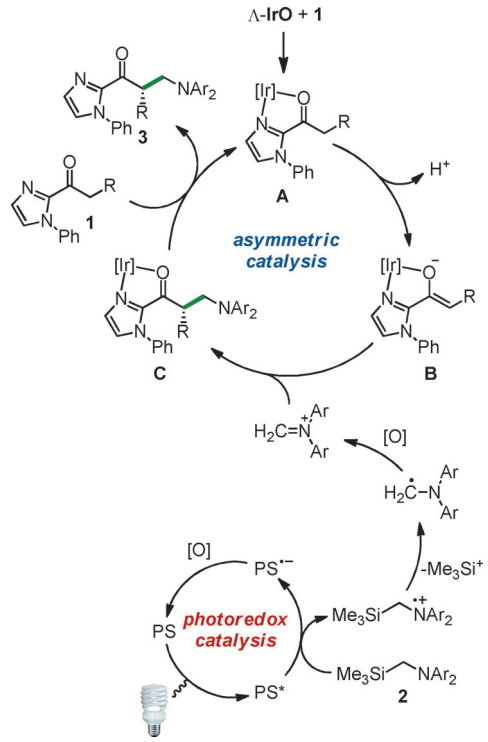
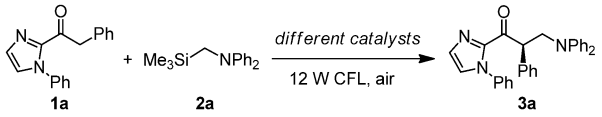


Figure 3. Plausible mechanism for the photoinduced asymmetric catalysis. PS = iridium photosensitizer, most likely intermediates **A** and **C**. [O] = oxidant in form of molecular oxygen and superoxide anion.

uct when using the catalyst with Λ-configuration at the metal. The involvement of an enolate complex in the catalytic cycle is further supported by a reaction of **1a** with the electrophile dibenzyl diazodicarboxylate catalyzed by Δ-**IrO** which afforded the α-amination product **4** in 87% yield and 89% *ee*, apparently through the intermediate formation of a nucleophilic iridium enolate complex (Figure 4b). Thus, Δ-**IrO** is capable of catalyzing enolate chemistry as has been recently also demonstrated for a related iridium[7] and rhodium[14] complex and the observed enantioselective C–C bond formation can be explained with the stereoselective reaction between the chiral iridium enolate **B** and an intermediate iminium ion. The formation of the electrophile through chemical oxidation—replacing the photosensitized oxidation—also provides the desired C–C bond formation product in an enantioselective fashion as shown for the oxidant *t*BuOOH (Figure 4b). The oxidative formation of the iminium ion intermediate starting from the oxidation of α-silyl amines along the pathway of photoinduced single-electron oxidation with a photosensitizer, followed by rapid desilylation, and further oxidation by air is well established[9–12] and consistent with the observation that the absence of air completely suppresses the formation of the desired product (Figure 4b).[15]

Next we verified the requirement for a photoredox process. We thereby exploited the circumstance that, in contrast to biscyclometalated iridium complexes which are well established photoredox sensitizers, this is not the case for the analogous rhodium complexes.[16] The replacement of iridium in the catalyst Δ-**IrO** with rhodium (Δ-**RhO**) therefore allows us to dissect the catalytic and photoredox activity of Δ-**IrO**, with the rhodium congener Δ-**RhO** only displaying a recently demonstrated activity for asymmetric enolate catalysis but presumably lacking photoactivity.[14] And indeed, the reaction of imidazole **1a** with amine **2a** in the presence of Δ-**RhO** (2 mol%) under irradiation with visible light provided the C–C bond formation product **3a** only in very low yield (6% after an elongated reaction time, compare entries 1 and 2 of Table 2). Revealingly,

Table 2. Single versus dual catalysis for the photoactivated α-aminoalkylation of 2-acyl imidazoles.[a]



Entry	Catalyst	*t* [h]	Conv. [%][b]	*ee* [%][c]
1[d]	Δ-**IrO** (2.0 mol%)	6.5	quant.	97
2	Δ-**RhO**[e] (2.0 mol%)	16	6	nd
3	$[Ir(ppy)_2(dtbbpy)]PF_6$ (1.0 mol%)	16	0	nd
4	$[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (0.5 mol%)	16	0	nd
5	Δ-**RhO** (2.0 mol%) + $[Ir(ppy)_2(dtbbpy)]PF_6$ (1.0 mol%)	24	84	94
6	Δ-**RhO** (2.0 mol%) + $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (0.5 mol%)	24	72	94
7	Δ-**RhO** (2.0 mol%) + TPP[f] (0.5 mol%)	24	30	90

[a] Reaction conditions: Reactions performed in CH_2Cl_2 (0.5 mL) with 2-acyl imidazole (0.4 M) and silyl amine (1.2 M) at room temperature under an atmosphere of air while illuminating with a 12 W white light energy saving lamp (CFL). [b] Determined by ^1H NMR. [c] Determined by chiral HPLC analysis; nd = not determined. [d] Shown for comparison. [e] Rhodium analogue of Δ-**IrO**. [f] *meso*-Tetraphenylporphyrin.

when we next complemented Δ-**RhO** with the established photosensitizers $[Ir(ppy)_2(dtbbpy)]PF_6$ (1.0 mol%)[1,17] or $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (0.5 mol%),[1,18] the reaction provided the product **3a** with good conversions and high enantioselectivities. Consistent with our proposed mechanism, neither the enolate catalyst Δ-**RhO** (Table 2, entry 2) nor photosensitizers (Table 2, entries 3 and 4) alone are capable of catalyzing the asymmetric photoreaction, apparently because asymmetric enolate catalysis and photosensitized amine oxidation have to proceed hand in hand, which can be achieved with a dual catalyst system (Table 2, entries 5 and 6) or even more efficiently with the single catalyst Δ-**IrO**. It is also worth noting that the weaker photooxidant but highly efficient single oxygen sensitizer *meso*-tetraphenylpropyhrin (TPP)[19,20] provides only a reduced yield of 30% after an elongated reaction time (Table 2, entry 7), thereby supporting the notion that singlet oxygen does not have a major contribution to the observed oxidation of the α-silylamines in this reaction scheme.

Finally, we evaluated the initial photoinduced electron transfer. It is safe to assume that at the beginning of the reaction, due to the bidentate nature of the 2-acyl imidazole substrate and a high substrate/catalyst ratio of 50, all the iridium catalyst will be captured by the imidazole substrate,[21] while an equilibrium may exist between the cationic intermediate **A** and the

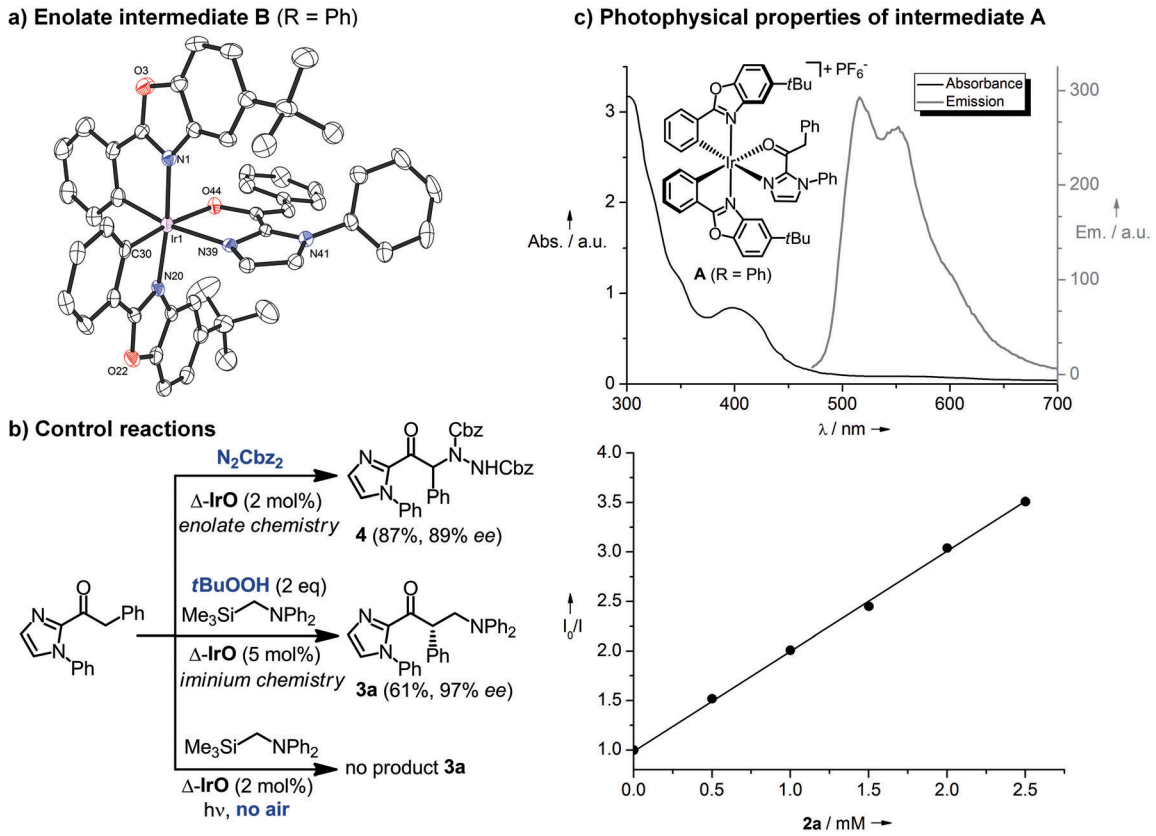


Figure 4. Mechanistic experiments. a) Crystal structure of an iridium enolate complex (proposed intermediate **B** with R = Ph). ORTEP drawing with 50% probability thermal ellipsoids. b) Control experiments. c) Photophysical properties of a substrate-coordinated iridium complex (proposed intermediate **A** with R = Ph). UV/Vis-absorbance and photoluminescence (λ_{ex} = 390 nm) spectra, and Stern–Volmer plot for quenching of the photoexcited iridium complex **A** (λ_{ex} = 390 nm, λ_{em} = 520 nm) with amine **2a**. I_0 and I = luminescence intensities in the absence and presence of the indicated concentrations of the amine **2a**, respectively. All experiments were performed in CH_2Cl_2.

deprotonated enolate form **B**. The involvement of the enolate complex **B** as a photosensitizer in this reaction was excluded based on a simple experiment in which we replaced Δ-**IrO** with the enolate complex and found that it was not capable of catalyzing the photoinduced reaction at all, whereas on the other hand the cationic intermediate **A** displayed the same catalytic activity compared to Δ-**IrO**. Thus, the substrate-coordinated intermediate **A** must be the active photosensitizer at the beginning of the reaction, probably complemented later by the related product-coordinated intermediate **C**. Indeed the substrate **1a** coordinated iridium complex **A** (R = Ph) absorbs visible light with a long wavelenth absorbance band in the visible region ($\lambda_{max,abs}$ = 398 nm) and its photoluminescence ($\lambda_{max,em}$ = 516 and 552 nm) is efficiently quenched by the α-silylamine **2a** in a dose-dependent fashion as shown with a Stern–Volmer plot in Figure 4c, which can be explained by a quenching of the excited state of **A** through electron transfer from the electron donor **2a**. Furthermore, cyclovoltammetry confirms that this electron transfer is thermodynamically feasible (see the Supporting Information).

In conclusion, we here reported that a single, simple chiral iridium complex catalyzes the visible light activated asymmetric aerobic α-aminoalkylation of 2-acyl imidazoles by simultaneously serving as a photosensitizer and a chiral Lewis acid, and thereby uniquely combining visible light induced oxidation with an enantioselective C–C bond formation. The photooxidative activation and net oxidation of the here featured asymmetric catalysis complements our previous work on a redox neutral reaction in which the photoactivation occured in a reductive fashion. It is fascinating that the metal-centered configuration (the exclusive source of chirality in the catalyst) retains throughout the catalysis, considering the oxidative conditions and the exposure to light. Future work will need to address the limited substrate scope of the here presented reaction scheme.[22] Considering the ability to perform reductive (previous work) and oxidative (this study) activation we believe that simple bis-cyclometalated chiral iridium complexes will be amenable as catalysts for a wide range of asymmetric conversions activated by visible light and work along these lines is ongoing in our laboratories.

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Keywords: asymmetric catalysis · iridium · metal-centered chirality · photoredox catalysis · visible light

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Asymmetric Catalysis

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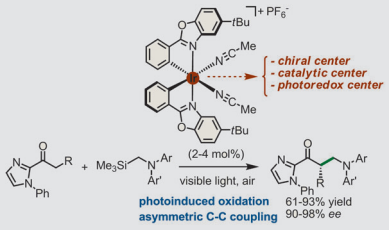
Merger of Visible Light Induced Oxidation and Enantioselective Alkylation with a Chiral Iridium Catalyst



Doing it all alone: A chiral iridium complex is used for visible light activated asymmetric photoredox catalysis by combining photoinduced oxidation with asymmetric C–C bond formation.