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Visible-Light-Promoted Generation of α-Ketoradicals from Vinyl-bromides and Molecular Oxygen: An Unprecedented Synthesis of Indenones and Dihydroindeno[1,2-c]chromenes**

*Santosh K. Pagire, Peter Kreitmeier, and Oliver Reiser**

Dedicated to Emeritus Prof. M. S. Wadia on the occasion of his 80th birthday

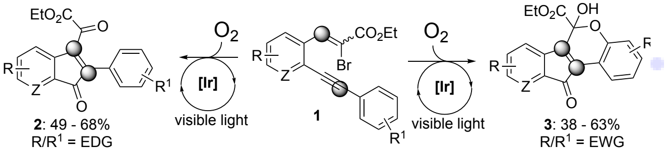
Abstract: *Ortho-alkynylated α-bromocinnamates can be converted by a visible light mediated photocascade reaction with molecular oxygen either to indenones or to dihydroindeno[1,2-c]chromenes. The one-step process features key photochemical steps, i.e. the initial activation of vinyl bromides by energy transfer giving rise to α-ketoradicals in the reaction with molecular oxygen followed by α-oxidation of an arene moiety by 6-π electrocyclization, and subsequent hydroxylation by electron transfer process from the same photocatalyst leads to the dihydroindeno[1,2-c]chromenes.*

Visible-light photoredox catalysis not only offers an alternate pathway to established transformations triggered by radical initiators such as peroxides and *n*-Bu_3SnH under thermal conditions but holds the promise to arrive at new bond forming reactions owing to the mild reaction conditions and functional group compatibility under which photocatalysts generally operate.[1] Recently, we found that *α*-bromochalcones can be coupled with a broad variety of electron rich heteroarenes[2] or alkenes[3] giving rise to polycyclic aromatic scaffolds. However, photochemical activation of vinyl halides is rare, requiring either an extended π-system or weak bonds as found in vinyl iodides.[4]

In general, vinyl bromides have much higher reduction potentials than typical photocatalysts in their excited states[2,5,6] (see also SI). Thus, ruthenium or iridium-based photocatalysts generally do not possess a sufficient excited-state reduction potential to transfer an electron and ultimately form a vinyl radical after bromide extrusion by an oxidative quenching cycle. In contrast, utilizing the reductive quenching cycle for the activation of vinyl bromides by having an amine present as a sacrificial electron donor results in simple dehalogenations.[2,6,7]

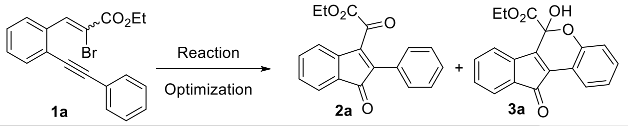
As an alternative to a direct photo-induced electron transfer, substrates can also be activated by energy transfer from the excited photocatalysts.[8] In line with such a mechanism, we report here the photochemical activation of vinyl bromides that is utilized in the coupling of *ortho*-alkynylated α–bromocinnamates **1** and molecular oxygen to give rise to indenones **2** or to dihydroindeno[1,2-c]chromenes **3**, depending on the electronic prerequisites of the substrates. As the key step in this process, the transformation of the vinyl bromides into *α*-ketoradicals is proposed, which is unambiguously supported by mechanistic studies and control experiments (*vide* infra).

Scheme 1: Photocatalyzed synthesis of indenones **2** an dihydroindeno[1,2-c]chromenes **3**



Exposing **1a** (E_{red} = –1.38 V vs. SCE, see SI) in an oxygen atmosphere to irradiation with 5 mol % [Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6[($E_{Ir(IV)/Ir(III)*}$ = –0.89 V vs. SCE; excited state life-time (*τ*) = 230 ns),[7a] [dF(CF_3)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtb-bpy = 4,4'-di-tert-butyl-2,2'-dipyridyl]) with blue ligh (LED_{455}, Table 1, entry 1), indeed resulted in a productive transformation, leading to **2a** and **3a**. In contrast, only E/Z-isomerizatio was observed in the absence of oxygen (Table 1, entry 2), which i in agreement with the proposed activation (*vide* infra) of vinyl bromides **1** by the photocatalyst *via* a diradical intermediate generate by a sensitization process.[10]

Table 1: Synthesis of **2a** and **3a**: Catalyst screening and reactio optimization[a]



Entry	Photocatalyst (mol %)	Temp. (°C)	Yield (%)[b]	
			2a	**3**
01	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (5)	rt	16	4
02[c,d]	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (5) no oxygen	rt	-	-
03	[Ir(ppy)$_2$(dtb-bpy)]PF_6 (5)	rt	10	2
04	*fac*[Ir(ppy)$_3$] (5)	rt	14	3
05	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (1)	rt	17	3
06	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (2)	60	20	6
07	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (1) no light	rt	-	-
08	no catalyst	rt	-	-
09	Ru(bpy)$_3$Cl$_2$ (5)	rt	5	26
10	Eosin Y (5), 530 nm	rt	3	8
11	[Cu(dap)$_2$Cl] (5), 530 nm	rt	-	-
12	Rose Bengal (5), 530 nm	rt	-	-
13	ZnCl$_2$/porphyrin (5), 530 nm	rt	-	-
14[e]	[Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 (5), DIPEA (3 equiv)	rt	-	-

Table 1: Reaction Conditions: [a] Substrate **1a** (0.5 mmol), photocatalyst (1-5 mol %), O_2, DMF, 72 h, rt, 60 °C, LED_{455}. [b] Isolated yields. [c] Under nitrogen. [d] E/Z-isomerization of **1a**, Z/E = 81:19 (before irradiation) to Z:E = 50:50 (after irradiation). [e] Dehalogenation product was identified by crude ^{1}H-NMR analysis.

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Supporting information for this article is available on the WWW under http://www.angewandte.org from the author

Other iridium photocatalysts such as [Ir(ppy)$_2$(dtb-bpy)]PF$_6$[11] ($E_{Ir(IV)/Ir(III)*}$ = –0.96 V vs. SCE, τ = 557 ns) [ppy = 2-phenylpyridine, dtb-bpy = 4,4’-di-tert-butyl-2,2’-dipyridyl] and neutral *fac*[Ir(ppy)$_3$][12] ($E_{Ir(IV)/Ir(III)*}$ = –1.73 V vs. SCE, τ = 1900 ns) [ppy = 2-phenylpyridine], (entries 3, 4) gave a similar product distribution, however, the product yields were lower.

In all cases we noted a deep red coloring of the solution in the course of the reaction, probably blocking the photo process, which could explain the incomplete conversion and long reaction time of the overall transformation. Lowering the catalyst concentration to 1 mol % (entry 5) gave almost identical results, indicating that catalyst deactivation was not the limiting factor of the reaction. A significant increase in yield was observed upon carrying out the reaction at 60 °C, which was found to be optimal in combination with 2 mol % catalyst loading (entry 6). In the absence of the iridium catalyst or light, no conversion of **1a** was observed (entries 7, 8).

Other photocatalysts such as [Ru(bpy)$_3$Cl$_2$][13] ($E_{Ru(III)/Ru(II)*}$ = –0.81 V vs. SCE, τ = 1100 ns) (bpy = 2,2’-bipyridine), Eosin Y,[14] and [Cu(dap)$_2$Cl][15] ($E_{Cu(II)/Cu(I)*}$ = –1.43 V vs. SCE, τ = 270 ns) [dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline], gave rise to low yields of **2a**/**3a** (Table 1, entries 9-11). Furthermore, no reaction was observed in the presence of rose bengal or ZnCl$_2$ / porphyrin, ruling out that the process is driven by singlet oxygen (Table 1, entries 12-13). A reductive quenching experiment by adding a tertiary amine (e.g. diisopropylethylamine, DIPEA) as a sacrificial electron donor (Table 1, entry 14), thus utilizing ground state reduction potentials of [Ir{dF(CF$_3$)ppy}$_2$(dtb-bpy)]PF$_6$ ($E_{Ir(III)/Ir(II)}$ = –1.37 V vs. SCE), only resulted in direct dehalogenation (99%).

Under the optimized reaction conditions (Table 1, entry 6), a variety of *ortho*-alkynylated α-bromocinnamates **1** (employed as E/Z mixtures) was subsequently tested (Table 2-4). A pronounced electronic effect was observed, which determined the overall course of the reaction: While *α*-bromocinnamates bearing +I (inductive donor) or +M (mesomeric / resonance donor) substituents yielded exclusively indenones **2b-k** (Table 2), derivatives with only electron withdrawing substituents gave rise to dihydroindeno[1,2-c]chromenes **3b-h** (Table 3). An *ortho* substituent R^1 overrides the electronic preference (*cf.* **2l**, Table 2 and **3i**, Table 3). However, a mixture of both products **2** and **3** was observed for electronically unbiased substrates **1** (Table 4). Notably, carrying out the reaction in a rotating film reactor enhanced the rate of the reaction (from 72 h/60 °C to 24 h/25 °C, see SI for more experimental details) due to the larger surface area of the resulting reaction mixture that was exposed to the oxygen atmosphere and visible-light irradiation (*cf* Table 2-4). Furthermore, performing the reaction in the advanced micro(flow)reactor systems[16] provides comparative yields but in very short reaction times of 15-40 minutes (Tables 2 and 3; also see the SI for detailed experimental set-up).

Table 2: Synthesis of indenones **2**[a]

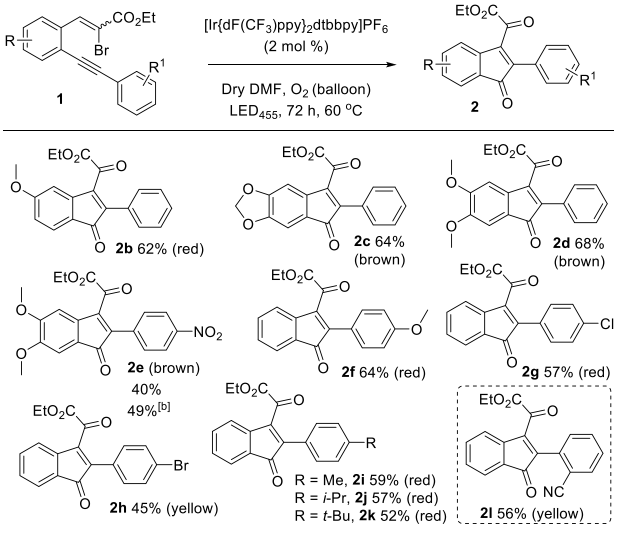


Table 3: Synthesis of dihydroindeno[1,2-c]chromenes **3**[a]

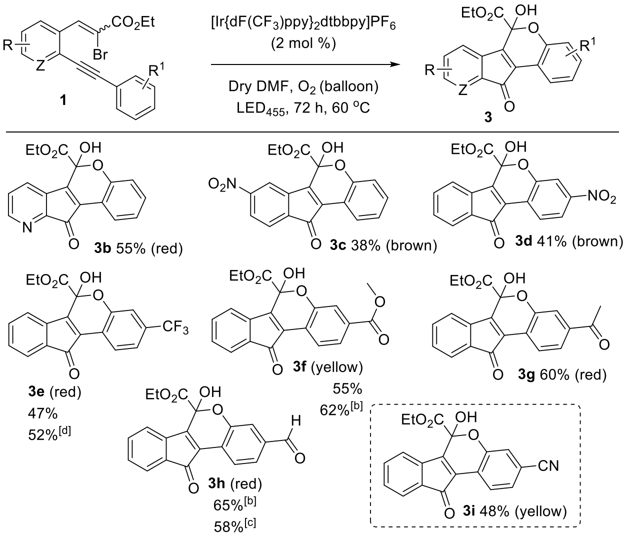
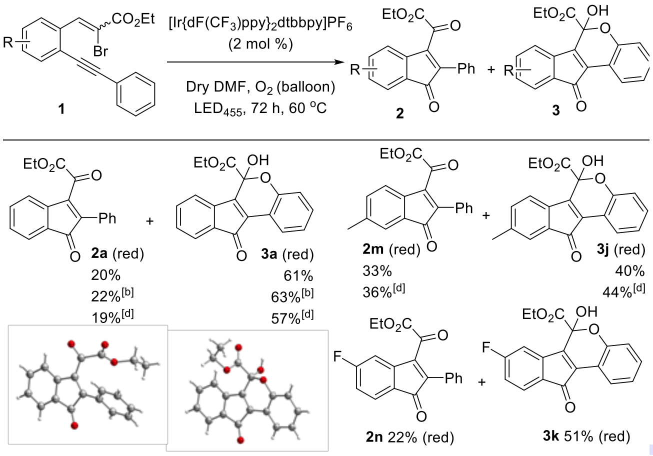


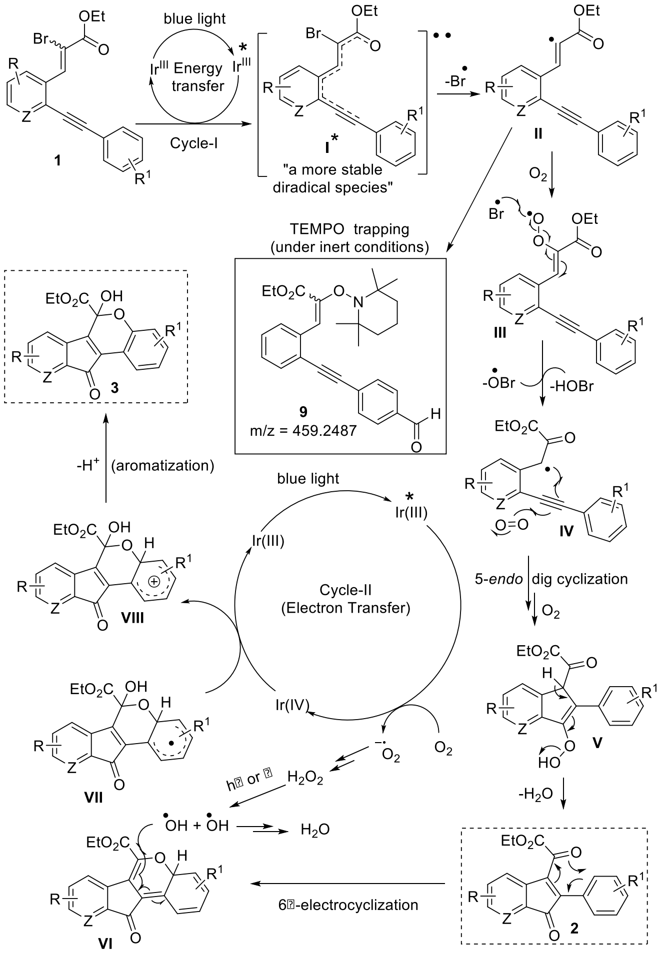
Table 4: Substrates **1**, leading to a mixture of **2** and **3**[a]



Tables 2-4: Reaction Conditions: [a] Substrate **1** (0.5 mmol, 1.0 equiv), photocataly (2 mol %), O$_2$ at 60 °C, in DMF, 72 h, LED$_{455}$, isolated yields of separated **2** and **3** ar stated. [b] Reaction performed on rotating film reactor with 1 mol % photocatalyst, r 24 h. [c] 2.0 mmol scale reaction. [d] Reaction performed on micro(flow)reactor with mol % photocatalyst, 40 min at rt (or 15 min at 60 °C). Compound color is mentioned i parentheses.

The mechanistic picture of this transformation is complex (Figure 1 The fluorescence quenching studies (see SI) revealed that th starting material **1a** strongly interacts with the photocatalysts. direct photoelectron transfer from the iridium(III)-catalyst to **1** i thermodynamically unfavorable due to the large difference i reduction potentials of substrates **1** and the employed photocatalys (*vide* supra). We, therefore, propose the generation of the activate vinyl bromide species **I*** (a more stable diradical species / a triple excited state)[10,17] by energy transfer from the excited *Ir(III) catalyst to **1**. Noteworthy, the [2+2]-cycloaddition of **1** was nc observed in contrast to the non-brominated analog **6** (Scheme 2, B) Also, no oxidation of the triple bond in **6** to the diketone occur under the reaction conditions,[18] thus, the reaction of **I*** via attack of oxygen on the triple bond appears to be unlikely. Instead, **I*** loses bromine Br• to form the critical vinyl radical **II**. Evidence for **II** is found by a trapping experiment with TEMPO giving rise to **9** as well as the 5-*exo*-trig cyclization reaction of **4** to **5** (Scheme 2, A). In addition, in the ESR spectra also a single radical species (*ge* = 1.984) was detected under inert atmospheric conditions at low temperature (See SI). In contrast, a direct *5-exo*-dig or *6-endo*-dig cyclization of **II** was not feasible, probably due to the unfavorable orientation of the reacting groups (See SI for the crystal structure of **1c**). Nevertheless, the vinyl radical intermediate **II** is capable of trapping molecular oxygen to give rise to intermediate **III**, which subsequently breaks down to the α-ketoradical **IV**. The independent generation of **IV** from **8** by photoinduced electron transfer in the presence of oxygen indeed gives rise to **2a** and **3a** (Scheme 2, C). It should be noted, however, that the conversion of **8** to **2a** and **3a** requires stoichiometric amounts of photocatalyst since the photoredox cycle cannot be closed in the absence of a sacrificial electron donor. The α-ketoradical **IV** then undergoes 5-*endo*-dig rather than 4-*exo*-dig cyclization[19] followed by trapping by a second molecule of oxygen to **V**. Elimination of water then leads to the observed indenones **2**. An isotope labeling experiment with pure $^{18}O_2$ and a mixture of $^{18/16}O_2$ proved that the oxygen atoms incorporated into the indenones **2** indeed stem from two different molecules of molecular oxygen (Scheme 3).

Figure 1: Proposed Reaction Mechanism



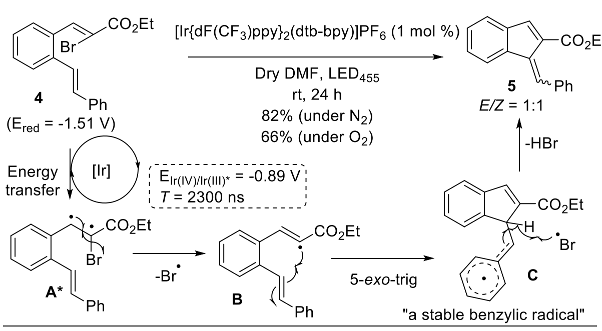
Indenones **2** having electron withdrawing substituents in either aromatic ring undergo facile 6π-electrocyclization, leading to dihydroindeno[1,2-c]chromenes **3**. The $^{18}O_2$ labeling experiment (Scheme 3) revealed that the termination of the electrocyclization by the introduction of a hydroxyl group also was ultimately derived from molecular oxygen.[14,20]

Independent experiments under visible light irradiation/photocatalyst or **IV** irradiation in the presence of oxygen (Scheme 2) with indenone **2** showed the feasibility of the 6π-electrocyclization reaction.[21] However, the yields obtained by this process were low compared to starting from the corresponding compounds **1**.

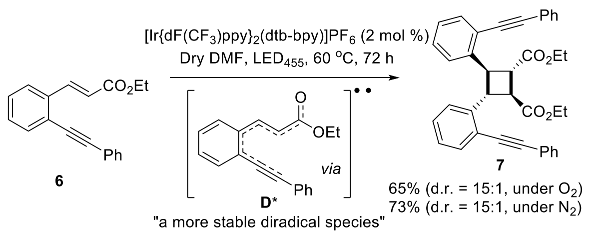
However, the electronic effect favouring electron poor starting materials **1** to preferentially undergo the cyclization to **3** rather than to **2** remains unclear at this point.

Scheme 2: Control experiments

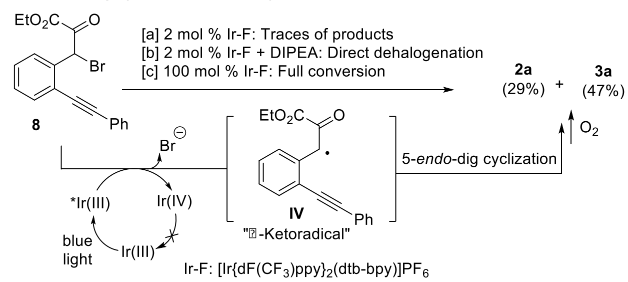
[A] With a double bond: Synthesis of Indenes[a]



[B] Without a bromine: Chemoselective [2+2]-cycloaddition[a]

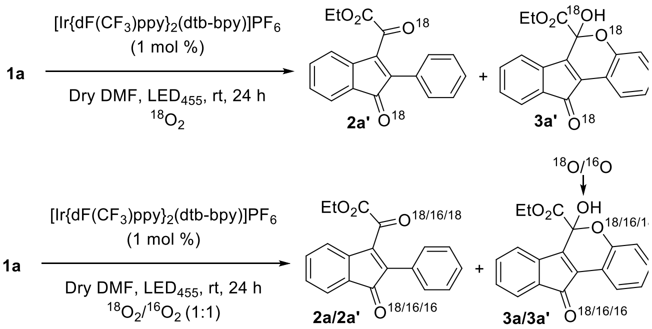


[C] 5-*endo*-dig cyclization: Direct synthesis of 2a and 3a[a,b,c]

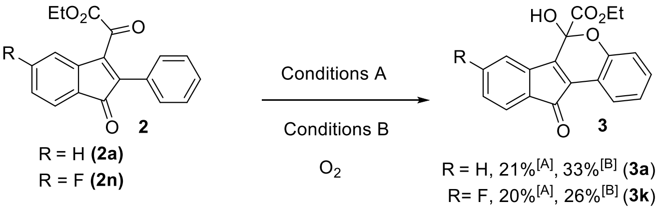


Reaction conditions: [a] Substrates **4**, **6** or **8** (0.5 mmol, 1.0 equiv [Ir{dF(CF$_3$)ppy}$_2$(dtb-bpy)]PF$_6$ (2 mol %), O$_2$ (or under N$_2$), at 60 °C (or at rt), i anhydrous DMF, 24-72 h, LED$_{455}$. [b] Substrate **8** (0.5 mmol, 1.0 equiv [Ir{dF(CF$_3$)ppy}$_2$(dtb-bpy)]PF$_6$ (2 mol %), DIPEA (2.2 equiv), O$_2$, at 60 °C, i anhydrous DMF, 72 h. [c] Substrate **8** (0.05 mmol, 1.0 equiv), [Ir{dF(CF$_3$)ppy}$_2$(dtl bpy)]PF$_6$ (100 mol %), O$_2$, at 60 °C, in anhydrous DMF, 12 h.

Scheme 3: Isotope labeling experiments



Scheme 4: 6π-electrocyclization



Conditions A: Substrate **2** (0.25 mmol, 1.0 equiv), [Ir{dF(CF$_3$)ppy}$_2$(dtb-bpy)]PF$_6$ (2 mol %), O$_2$, at 60 °C, in DMF, 72 h, LED$_{455}$. ***Conditions B:*** Substrate **2** (0.25 mmol, 1.0 equiv), UV-Light (125 W Hg-lamp, λ > 300 nm), O$_2$, at 60 °C, in anhydrous DMF, 72 h.

In summary, we have shown for the first time the generation of α-ketoradicals from vinyl bromides and molecular oxygen by energy transfer process operated by an Ir-F photocatalyst. The resulting vinyl radical **II**, being formed from a diradical intermediate upon bromine extrusion, could be engaged in a productive reaction cascade with up to three molecules of molecular oxygen, leading to complex molecule architectures in a single photochemical step under the mild reaction conditions. The newly obtained tetracyclic compounds **3** could serve as valuable building blocks in medicinal chemistry. Such compounds having a hetero-atom impregnated into the [6-5-6]-ABC skeleton were previously advertised as Taiwaniaquinoids related scaffolds by Panda *et al*,[22] which are closely related to the naturally occurring family of Taiwaniaquinoids possessing a common [6-5-6]-*abeo*-abietane carbon architecture with broad biological activities.[23]

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Photoredox Catalysis

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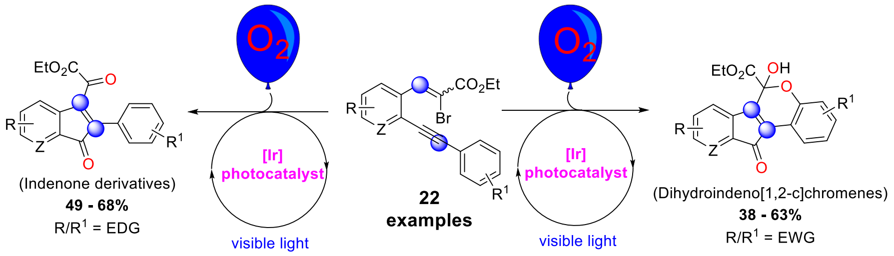
“Visible-Light-Promoted Generation of α-Ketoradicals from Vinyl-bromides and Molecular Oxygen: An Unprecedented Synthesis of Indenones and Dihydro-indeno[1,2-c]chromenes”



The activation of vinyl bromides by visible light photoredox catalysis and molecular oxygen is developed utilizing dual energy and electron transfer mechanisms using [Ir{dF(CF_3)ppy}$_2$(dtb-bpy)]PF_6 as a photocatalyst. Following this photocascade reaction mode, the synthesis of indenones or dihydroindeno[1,2-c]chromenes is possible from readily available ortho-alkynylated α-bromocinnamates.