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Evidence for Triplet Sensitization in the Visible-Light-Induced [2+2] Photocycloaddition of Eniminium Ions

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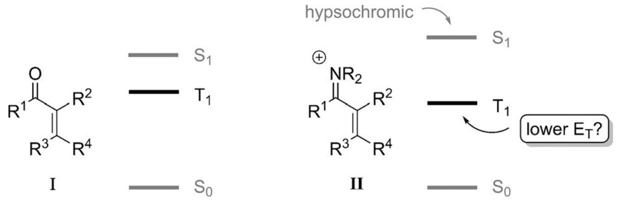
Abstract: *Eniminium ions were prepared from the corresponding α,β-unsaturated carbonyl compounds (enones and enals), and were found to be promoted to their respective triplet states by energy transfer. The photoexcited intermediates underwent intra- or intermolecular [2+2] photocycloaddition in good yields (50–78 %) upon irradiation at $\lambda = 433$ nm or $\lambda = 457$ nm. Iridium or ruthenium complexes with a sufficiently high triplet energy were identified as efficient catalysts (2.5 mol % catalyst loading) for the reaction. The intermolecular [2+2] photocycloaddition of an eniminium ion derived from a chiral secondary amine proceeded with high enantioselectivity (88 % ee).*

Whereas the [2+2] photocycloaddition chemistry of α,β-unsaturated carbonyl compounds (enones and enals) has been extensively explored,[1] the related α,β-unsaturated iminium ions (eniminium ions) have received little attention. Notable studies originate only from the group of Mariano, who investigated the intramolecular [2+2] photocycloaddition of eniminium ions[2] in the context of their pioneering work on the photochemistry of iminium ions.[3] They found that eniminium ions, upon direct excitation at $\lambda > 250$ nm, undergo a stereospecific [2+2] photocycloaddition that results from excitation of the respective ππ* transition. Attempts to generate enantioenriched cyclobutanes by using an eniminium ion derived from a chiral secondary amine led to a maximum enantiomeric excess (*ee*) of 82 % at 40 % conversion.[2b]



Scheme 1. Schematic energy diagram for the singlet (S) and triplet (T) states of α,β-unsaturated carbonyl compounds **I** and the respective eniminium ions **II**.

Scheme 1 illustrates the major difference in the photochemical behavior of enones **I** and eniminium ions **II**. The lowest-lying singlet state (S_1) of enones is of nπ* character and opens, despite its low absorption coefficient, a convenient entry to populate the reactive triplet state T_1 by direct excitation at long wavelengths ($\lambda = 300$–350 nm) followed by a symmetry-allowed[4] intersystem crossing (ISC). The S_1 state of eniminium ions is of ππ* character, and the absorption is shifted hypsochromically relative to the nπ* transition of the enone. As ISC to T_1 is notoriously slow[4] for the eniminium ion, subsequent reactions occur exclusively from the S_1 state. While it has been known for some time[5] that *E*/*Z* isomerization reactions occur from S_1 in photoexcited eniminium ions, it has only recently been disclosed by the Melchiorre group that this state can be quenched with appropriate electron donors to achieve enantioselective alkylation reactions.[6]

Considering recent interest in the catalysis of photochemical processes by visible-light-induced triplet sensitization,[7] we have explored the nature of the triplet state T_1 of eniminium ions in the present study. We speculated that this state would be accessible by carefully choosing a suitable triplet sensitizer, and we expected it to be an efficient intermediate in [2+2] photocycloaddition reactions. Our preliminary results are described in this Communication.

To investigate our hypothesis, we synthesized 3-(4-pentenyl)-cyclohex-2-enone (**1**),[8] which was readily converted into the eniminium salt **2** by treatment with pyrrolidine and azeotropic removal of water[9] (Scheme 2). The respective hexafluorophosphate salt precipitated and was recrystallized from ethanol. Enone **1** absorbs at $\lambda = 233$ nm ($\varepsilon = 15\,650\,\mathrm{M^{-1}\,cm^{-1}}$) and $\lambda = 320$ nm ($\varepsilon = 70\,\mathrm{M^{-1}\,cm^{-1}}$). The latter absorption was assigned to the forbidden nπ* transition, and the former absorption to the allowed ππ* transition. The eniminium salt **2** showed an absorption maximum at $\lambda = 270$ nm ($\varepsilon = 21\,320\,\mathrm{M^{-1}\,cm^{-1}}$). For the reasons mentioned above, the triplet energy of eniminium ion **2** could not be directly measured but its redox potential $E_{1/2}(\mathbf{2}^+/\mathbf{2}^\cdot)$ was determined as -1.39 V vs. SCE.[10,11] As expected from their absorption spectra, neither enone **1** nor the eniminium ion **2** showed any conversion when excited at an irradiation wavelength of $\lambda = 420$ nm.[12] We subsequently attempted to initiate the [2+2] photocycloaddition of eniminium ion **2** by addition of 2.5 mol % of an iridium or ruthenium catalyst (Table 1). The reactions were performed in MeCN solution,

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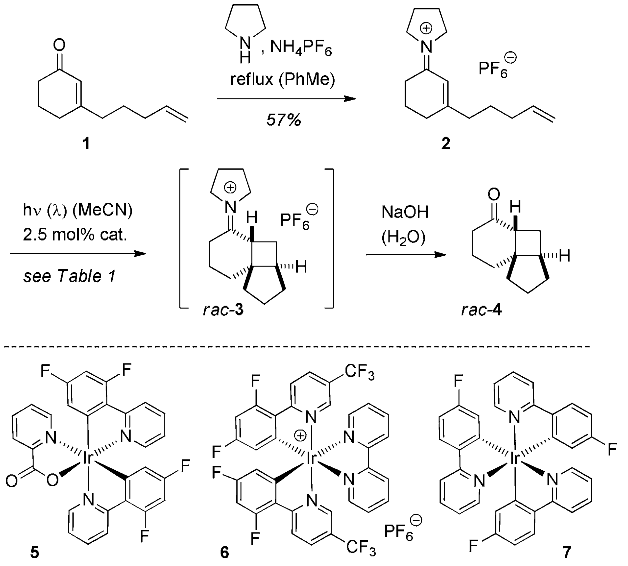


Scheme 2. Preparation of eniminium ion **2**, its sensitized [2+2] photocycloaddition reaction to products *rac*-**3** and *rac*-**4**, and structure of iridium complexes **5**–**7**.

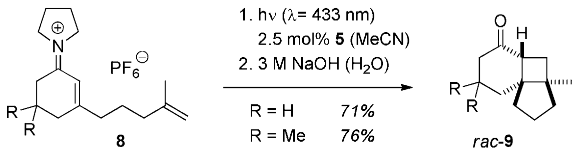
Table 1: [2+2] Photocycloaddition of eniminium salt **2** in the presence of various catalysts (see Scheme 2).

Entry[a]	λ[a] [nm]	Catalyst	E_T[b] [kJ mol^{-1}]	t[a] [h]	Product	Yield[c] [%]
1	420	**5**	256	20	*rac*-**4**	57
2	420	**6**	253	20	*rac*-**4**	44
3	420	**7**	245	20	–[d]	–
4	420	Ir(ppy)$_3$	231	20	–[d]	–
5	420	Ru(bpy)$_3$(PF$_6$)$_2$	193	20	–[d]	–
6[e]	420	**6**	253	2	*rac*-**3**	75
7[f]	433	**5**	256	2	*rac*-**4**	73
8[f]	433	**6**	253	2	*rac*-**4**	68

[a] The reactions were performed at room temperature with a substrate concentration of $c = 20$ mm in MeCN at the indicated wavelength (λ) and for the indicated period of time (t). An 1 m aqueous NaOH solution was used for hydrolysis unless otherwise indicated. [b] Tabulated or measured triplet energies for the respective iridium or ruthenium catalyst (see the main text). [c] Yield of isolated product. [d] No conversion was observed, and the starting material was re-isolated. [e] No aqueous work-up was performed. [f] A 3 m aqueous NaOH solution was employed for hydrolysis.

and the intermediate iminium ion *rac*-**3** was hydrolyzed by treatment with aqueous 1m NaOH solution.

The literature-reported cyclobutane *rac*-**4**[8b] was isolated as a single diastereoisomer from the reactions that were catalyzed by iridium complexes **5** and **6** (entries 1 and 2). The other catalysts, **7**, Ir(ppy)$_3$ (ppy = 2-phenylpyridine), and Ru(bpy)$_3$(PF$_6$)$_2$ (bpy = 2,2′-bipyridine), failed to induce the desired transformation (entries 3–5), and the starting material was recovered unchanged. The direct reaction of enone **1** to product *rac*-**4** was not catalyzed by complex **5** or **6**. In combination with the fact that iminium salt *rac*-**3** could be isolated from the reaction mixture in 75 % yield (entry 6), it is clear that the reaction proceeds via the eniminium ion and not via the enone. Further optimization experiments revealed that ketone *rac*-**4** was obtained in higher yields upon irradiation at $\lambda = 433$ nm[13] and upon work-up with 3m NaOH solution (entries 7 and 8). Under the conditions of entry 7, other eniminium ions **8** reacted equally well, and products *rac*-**9** were obtained in good yields (Scheme 3).



Scheme 3. Intramolecular iridium-catalyzed [2+2] photocycloaddition of eniminium ions **8**.

Most of the redox potentials and triplet energies of the photoexcited catalysts shown in Table 1 have been reported.[14] The triplet energy of compound **5** was determined from its luminescence emission[15] in MeCN solution (see the Supporting Information). We found no correlation between the excited-state redox potential of the catalysts and their viability in affording the cyclobutane product *rac*-**4**. The strongly reducing iridium complexes **7** and Ir(ppy)$_3$[16] failed to catalyze the [2+2] photocycloaddition while the much weaker reductant **6** [$E_{1/2}$(Ir^{IV}/Ir^{III*})[14c] = −0.55 V] was a very efficient catalyst. When comparing the tabulated triplet energies for the individual complexes (Table 1), there is, however, a very clear correlation. The [2+2] photocycloaddition ceases if the triplet energy E_T of the catalyst is below 250 kJ mol^{-1}. Vice versa, this figure provides an estimate for the triplet energy of the elusive T_1 state of eniminium ion **2**. The observation that enone **1** did not undergo an Ir-catalyzed [2+2] photocycloaddition (see above) is readily explained by its higher triplet energy compared to that of the eniminium ion.[17]

To gain more insight into the interaction between the photoexcited catalyst and eniminium salt **2**, quenching studies were performed in MeCN solution at a concentration of $c = 10$ μm. Luminescence quenching was observed for catalyst **5** (Figure 1 a), and the Stern–Volmer constant (K_{SV}) extracted

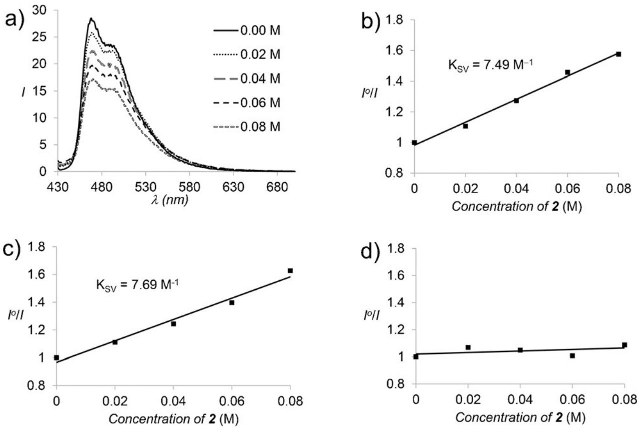
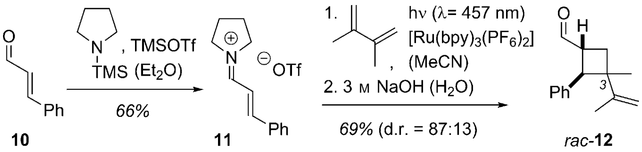


Figure 1. Quenching experiments of photoexcited iridium catalysts **5**, **6**, and Ir(ppy)$_3$ with eniminium ion **2** in MeCN solution. a) Decrease in the luminescence intensity of compound **5** upon addition of iminium salt **2**. Stern–Volmer plots (K_{SV} = Stern–Volmer constant) of the luminescence quenching for b) catalyst **5**, c) catalyst **6**, and d) Ir(ppy)$_3$.

from a plot of I^0/I versus the eniminium concentration was $7.49\,\mathrm{M}^{-1}$ (Figure 1b). The lifetime τ^0 of the excited state of catalyst **5**[15] was determined to be 970 ns, and it was shown that a dynamic quenching mechanism applies (see the Supporting Information). The quenching rate constant was calculated from K_{SV} and τ^0 as $k_q = 7.7\times10^6\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The luminescence intensity of catalyst **6** was similarly quenched by increasing concentrations of eniminium ion **2** (Figure 1c). The Stern–Volmer constant was calculated to be $7.69\,\mathrm{M}^{-1}$ in the case of catalyst **6**. The luminescence of the inactive iridium catalyst $Ir(ppy)_3$ (Table 1, entry 4) was not quenched by addition of eniminium ion **2** (Figure 1d). These results suggest that the photochemical reaction of eniminium ion **2** is initiated upon energy transfer from compounds **5** and **6** while energy transfer from $Ir(ppy)_3$ is not feasible based on the data from Table 1.

In a second set of experiments, we studied the intermolecular [2+2] photocycloaddition of eniminium ions derived from cinnamaldehyde (**10**). Eniminium ion **11** was readily prepared by treatment of aldehyde **10** with trimethylsilyl (TMS) triflate and *N*-trimethylsilyl pyrrolidine in diethyl ether (Scheme 4).[18] The absorption spectrum of compound



Scheme 4. Formation of eniminium ion **11** and its ruthenium-catalyzed [2+2] photocycloaddition to 2,3-dimethylbutadiene (d.r. = diastereomeric ratio).

11 shows a maximum at $\lambda = 330$ nm ($\varepsilon = 36840\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) but its triplet energy could not be determined. The redox potential $E_{1/2}(\mathbf{11}^+/\mathbf{11}^\bullet)$ was found to be −0.83 V.[10] Neither aldehyde **10** nor eniminium ion **11** showed any conversion when their solutions in MeCN were irradiated at $\lambda = 457$ nm[13] in the presence of 2,3-dimethylbutadiene. To our delight, we found that the desired [2+2] photocycloaddition of eniminium ion **11** could be triggered by the addition of 2.5 mol% of $Ru(bpy)_3(PF_6)_2$. The reaction was complete after four hours, and product *rac*-**12** was obtained upon hydrolysis in 69% as a mixture of two diastereomers. The relative configuration at C3 was different in the two diastereomers, and NOESY studies revealed that the major isomer *rac*-**12a** places the methyl group in *cis* orientation relative to the phenyl group. Under the same irradiation conditions, aldehyde **10** underwent hardly any conversion (≤ 10%) to product *rac*-**12**.

The following observations (see the Supporting Information) provide evidence for the fact that the ruthenium-catalyzed reaction proceeds via triplet energy transfer and not via electron transfer: a) The ruthenium complex $Ru(bpz)_3(PF_6)_2$ (bpz = 2,2′-bipyrazine), which is known to be a weak reductant in its excited state [$E_{1/2}(Ru^{III}/Ru^{II*})$[19] = −0.26 V], promoted the [2+2] photocycloaddition as efficiently as $Ru(bpy)_3(PF_6)_2$. b) Eosin Y (EY), with a triplet energy[20] of $E_T = 182$ kJ mol^{-1} and an excited-state reduction potential of $E_{1/2}(EY^{\bullet+}/EY^*)$[20] = −1.11 V, did not catalyze the reaction at $\lambda = 512$ nm. c) The reaction was catalyzed by typical triplet sensitizers such as benzil and thioxanthone,[21] albeit upon irradiation at short wavelengths. d) The regioselectivity of the [2+2] photocycloaddition can only be explained by a triplet pathway that proceeds via a 1,4-diradical. Addition of an intermediate radical **11**$^\bullet$ to 2,3-dimethylbutadiene would lead to the opposite regioisomer.

In a preliminary study of the substrate scope, other olefins were shown to react with eniminium ion **11** (Figure 2). Isoprene gave *rac*-**13** in a yield that was comparable to the yield recorded for *rac*-**12**. The lower diastereomeric ratio reflects the smaller size of the ethenyl group as compared to the 2-propenyl group. Likewise, 1,3-butadiene gave *rac*-**14** with a low diastereoselectivity at carbon atom C3. Alkynyl-substituted olefins, such as 2-methylhex-1-en-3-yne and (3-methylbut-3-en-1-ynyl)trimethylsilane, reacted smoothly to give products *rac*-**15** and *rac*-**16**.

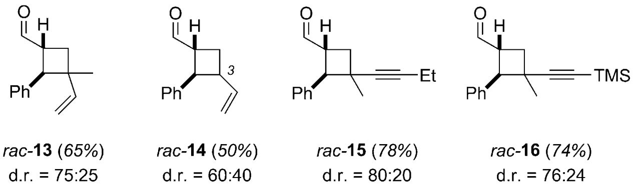
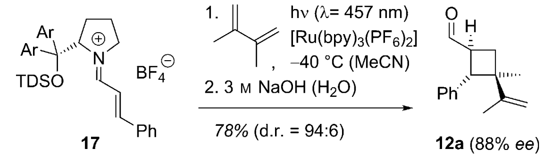


Figure 2. [2+2] Photocycloaddition products obtained by the reaction of eniminium ion **11** with different olefins ($\lambda = 457$ nm, catalyst: 2.5 mol% $Ru(bpy)_3(PF_6)_2$ in MeCN).

Additionally, we evaluated the potential of the triplet-sensitized [2+2] photocycloaddition of eniminium ions for enantioselective synthesis.[22] To meet this end, the known eniminium ion **17**[6] was prepared and subjected to a ruthenium-catalyzed reaction with 2,3-dimethylbutadiene (Scheme 5). The reaction was performed at −40 °C with 2.5 mol% of $Ru(bpy)_3(PF_6)_2$ as the catalyst. Complete conversion was observed after 3.5 h, and product **12a** was obtained essentially as a single diastereoisomer (d.r. = 94:6) and with 88% *ee*.



Scheme 5. Enantioselective ruthenium-catalyzed [2+2] photocycloaddition of eniminium ion **17** (Ar = 3,5-bis(trifluoromethyl)phenyl; TDS = *tert*-hexyldimethylsilyl) to cyclobutane **12a**.

In conclusion, we have collected evidence that eniminium ions can be promoted to their triplet states by sensitization with suitable iridium or ruthenium complexes upon irradiation with visible light ($\lambda = 433$ or 457 nm). This indirect activation mode allows for enantioselective [2+2] photocycloadditions of eniminium ions derived from chiral secondary amines. Transformations of this type could previously be conducted only via the respective singlet intermediate by short-wavelength irradiation ($\lambda = 250$–300 nm). More importantly, the hypothesis that the triplet state of an eniminium ion is lower in energy than the triplet state of the respective α,β-unsaturated carbonyl compound has been substantiated. Under conditions that allowed for sensitized [2+2] photocycloaddition reactions of the eniminium ions **2** and **11**, there was no or little conversion of the corresponding carbonyl compounds **1** and **10**. Along with thermal iminium ion catalysis[23] and photoinduced electron transfer (PET) to iminium ions,[6,24,25] triplet sensitization seems to offer another promising avenue for the in situ activation of carbonyl groups to explore new reactivity patterns.

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Conflict of interest

The authors declare no conflict of interest.

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[1] a) M. T. Crimmins, T. L. Reinhold, *Org. React.* **1993**, *44*, 297–588; b) P. Margaretha in *Molecular and Supramolecular Photochemistry, Vol. 12* (Eds.: A. G. Griesbeck, J. Mattay), Dekker, New York, **2005**, pp. 211–237; c) J. P. Hehn, C. Müller, T. Bach in *Handbook of Synthetic Photochemistry* (Eds.: A. Albini, M. Fagnoni), Wiley-VCH, Weinheim, **2009**, pp. 171–215; d) S. Poplata, A. Tröster, Y. Q. Zou, T. Bach, *Chem. Rev.* **2016**, *116*, 9748–9815.

[2] a) X. Cai, V. Chang, C. Chen, H.-J. Kim, P. S. Mariano, *Tetrahedron Lett.* **2000**, *41*, 9445–9449; b) C. Chen, V. Chang, X. Cai, E. Duesler, P. S. Mariano, *J. Am. Chem. Soc.* **2001**, *123*, 6433–6434.

[3] a) P. S. Mariano, *Acc. Chem. Res.* **1983**, *16*, 130–137; b) P. S. Mariano, *Tetrahedron* **1983**, *39*, 3845–3879.

[4] a) M. A. El-Sayed, *Acc. Chem. Res.* **1968**, *1*, 8–16; b) P. Klán, J. Wirz, *Photochemistry of Organic Compounds*, Wiley, Chichester, **2009**, pp. 38–39.

[5] a) G. Wald, *Science* **1968**, *162*, 230–239; b) R. F. Childs, B. D. Dickie, *Chem. Commun.* **1981**, 1268–1269; c) M. Pankratz, R. F. Childs, *J. Org. Chem.* **1988**, *53*, 3278–3283; d) K. Palczewski, *J. Biol. Chem.* **2012**, *287*, 1612–1619.

[6] M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre, *Nat. Chem.* **2017**, *9*, 868–873.

[7] For examples, see: a) Z. Lu, T. P. Yoon, *Angew. Chem. Int. Ed.* **2012**, *51*, 10329–10332; *Angew. Chem.* **2012**, *124*, 10475–10478; b) Y.-Q. Zou, S.-W. Duan, X.-G. Meng, X.-Q. Hu, S. Gao, J.-R. Chen, W.-J. Xiao, *Tetrahedron* **2012**, *68*, 6914–6919; c) R. Alonso, T. Bach, *Angew. Chem. Int. Ed.* **2014**, *53*, 4368–4371; *Angew. Chem.* **2014**, *126*, 4457–4460; d) Q. Liu, F.-P. Zhu, X.-L. Jin, X.-J. Wang, H. Chen, L.-Z. Wu, *Chem. Eur. J.* **2015**, *21*, 10326–10329; e) V. Mojr, E. Svobodová, K. Straková, T. Neveselý, J. Chudoba, H. Dvořáková, R. Cibulka, *Chem. Commun.* **2015**, *51*, 12036–12039; f) T. R. Blum, Z. D. Miller, D. M. Bates, I. A. Guzei, T. P. Yoon, *Science* **2016**, *354*, 1391–1395; g) A. Tröster, R. Alonso, A. Bauer, T. Bach, *J. Am. Chem. Soc.* **2016**, *138*, 7808–7811; h) J. Zhao, J. L. Brosmer, Q. Tang, Z. Yang, K. N. Houk, P. L. Diaconescu, O. Kwon, *J. Am. Chem. Soc.* **2017**, *139*, 9807–9810; i) V. Edtmüller, A. Pöthig, T. Bach, *Tetrahedron* **2017**, *73*, 5038–5047; j) N. Münster, N. Parker, L. van Dijk, R. S. Paton, M. D. Smith, *Angew. Chem. Int. Ed.* **2017**, *56*, 9468–9472; *Angew. Chem.* **2017**, *129*, 9596–9600; k) Z. D. Miller, B. J. Lee, T. P. Yoon, *Angew. Chem. Int. Ed.* **2017**, *56*, 11891–11895; *Angew. Chem.* **2017**, *129*, 12053–12057.

[8] a) I. de Miguel, B. Herrad, E. Mann, *Adv. Synth. Catal.* **2012**, *354*, 1731–1736; b) C. Brenninger, A. Pöthig, T. Bach, *Angew. Chem. Int. Ed.* **2017**, *56*, 4337–4341; *Angew. Chem.* **2017**, *129*, 4401–4405.

[9] S. Saba, D. Vrkic, C. Cascella, I. DaSilva, K. Carta, A. Kojtari, *J. Chem. Res.* **2008**, 301–304.

[10] All redox potentials are reported against a saturated calomel electrode (SCE) to allow for better comparison. Our own measurements were performed against a reference electrode of 0.01 M $Ag/AgNO_3$ in 0.1 M tetrabutylammonium hexafluorophosphate (MeCN, 25 °C). The potential against the SCE was thus obtained by adding 0.30 V to the measured potential; see: V. V. Pavlishchuk, A. W. Adison, *Inorg. Chim. Acta* **2000**, *298*, 97–102.

[11] Potentials originally reported against ferrocenium/ferrocene (Fc^+/Fc) were referenced to SCE by addition of 0.42 V to the reported potential; see: H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714–723.

[12] For the emission spectrum of the light source, see the Supporting Information.

[13] An LED lamp was used (for the emission spectrum, see the Supporting Information). For the reaction set-up, see: a) D. Rackl, V. Kais, P. Kreitmeier, O. Reiser, *Beilstein J. Org. Chem.* **2014**, *10*, 2157–2165; b) D. Lenhart, A. Pöthig, T. Bach, *Chem. Eur. J.* **2016**, *22*, 6519–6523.

[14] a) L. Flamigni, A. Barbieri, C. Sabatini, B. Ventura, F. Barigelletti, *Top. Curr. Chem.* **2007**, *281*, 143–203; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; c) A. Singh, K. Teegardin, M. Kelly, K. S. Prasad, S. Krishnan, J. D. Weaver, *J. Organomet. Chem.* **2015**, *776*, 51–59.

[15] a) E. Baranoff, B. F. E. Curchod, F. Monti, F. Steimer, G. Accorsi, I. Tavernelli, U. Rothlisberger, R. Scopelliti, M. Grätzel, M. K. Nazeeruddin, *Inorg. Chem.* **2012**, *51*, 799–811; b) S. Yi, J.-H. Kim, Y.-J. Cho, J. Lee, T.-S. Choi, D. W. Cho, C. Pac, W.-S. Han, H.-J. Son, S. O. Kang, *Inorg. Chem.* **2016**, *55*, 3324–3331.

[16] The reported values[14c] for $E_{1/2}(Ir^{IV}/Ir^{III*})$ against Fc^+/Fc are −1.86 V for **7** (−1.44 V vs. SCE)[11] and −1.97 V for $Ir(ppy)_3$ (−1.55 V vs. SCE).[11]

[17] The triplet energy of the closely related enone 3-methylcyclohex-2-enone was reported as $E_T = 283\ kJ\,mol^{-1}$; see: D. I. Schuster, D. A. Dunn, G. E. Heibel, P. B. Brown, J. M. Rao, J. Woning, R. Bonneau, *J. Am. Chem. Soc.* **1991**, *113*, 6245–6255.

[18] S. Lakhdar, T. Tokuyasu, H. Mayr, *Angew. Chem. Int. Ed.* **2008**, *47*, 8723–8726; *Angew. Chem.* **2008**, *120*, 8851–8854.

[19] M. Haga, E. S. Dodsworth, G. Eryavec, P. Seymour, A. B. P. Lever, *Inorg. Chem.* **1985**, *24*, 1901–1906.

[20] D. P. Hari, B. König, *Chem. Commun.* **2014**, *50*, 6688–6699.

[21] Triplet sensitization of an iminium ion by xanthone has been suggested to occur; see: C.-L. Tu, P. S. Mariano, *J. Am. Chem. Soc.* **1987**, *109*, 5287–5288.

[22] For a review, see: R. Brimioulle, D. Lenhart, M. M. Maturi, T. Bach, *Angew. Chem. Int. Ed.* **2015**, *54*, 3872–3890; *Angew. Chem.* **2015**, *127*, 3944–3963.

[23] a) K. A. Ahrendt, C. J. Borths, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2000**, *122*, 4243–4244; b) A. Erkkilä, I. Majander, P. M. Pihko, *Chem. Rev.* **2007**, *107*, 5416–5470.

[24] a) J. J. Murphy, D. Bastida, S. Paria, M. Fagnoni, P. Melchiorre, *Nature* **2016**, *532*, 218–222; b) A. Bahamonde, J. J. Murphy, M. Savarese, É. Brémond, A. Cavalli, P. Melchiorre, *J. Am. Chem. Soc.* **2017**, *139*, 4559–4567.

[25] For a review, see: Y.-Q. Zou, F. M. Hörmann, T. Bach, *Chem. Soc. Rev.* **2017**, DOI: https://doi.org/10.1039/C7CS00509A.

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