

Visible Light Uranyl Photocatalysis: Direct C–H to C–C Bond Conversion

Luca Capaldo,^{1b} Daniele Merli,^{1b} Maurizio Fagnoni,^{1b} and Davide Ravelli*^{1b}

Photogreen Lab, Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100 Pavia, Italy

Supporting Information

ABSTRACT: Uranyl nitrate hexahydrate performs as an efficient photocatalyst in the direct C–H to C–C bond conversion under blue light irradiation via hydrogen atom transfer (HAT). This uranyl salt enables the remarkable smooth functionalization of unactivated (cyclo)alkanes, ethers, acetals, and amides via radical addition onto electrophilic olefins. Dedicated electrochemical measurements on compounds and intermediates involved in the process were carried out to support the mechanistic proposal.

KEYWORDS: C–C bond formation, hydrogen atom transfer, photocatalysis, radical reactions, uranyl cation



Photoredox catalysis has deeply transformed the field of organic chemistry providing synthesis practitioners with a plethora of unconventional approaches, mainly based on radical intermediates.¹ These processes rely on the activation of an organic substrate through a single-electron transfer (SET) reaction promoted by the excited state of a purposely added catalyst. Indeed, despite the enhanced redox properties typical of excited states, the choice of the substrates is limited by the redox properties of the employed photocatalyst, albeit the incorporation of suitable redox-auxiliary groups² in one reactant facilitates the desired SET. To circumvent these limitations, notable efforts have been made to design an indirect photocatalyzed hydrogen atom transfer (*i*-HAT),³ where a photocatalytic cycle promotes the in situ generation of a thermal H atom abstractor (typically, an alkoxy radical RO• or an amine radical cation R₃N^{•+}, Scheme 1).^{3,4} Another useful approach to perform an *i*-HAT is through an intramolecular process, thus leading to a remote C–H bond functionalization.⁵

A more straightforward route for substrate activation makes use of a direct photocatalyzed HAT (*d*-HAT),³ where the excited photocatalyst cleaves directly a C–H bond in the

reagent (Scheme 1). Unfortunately, the development of such approach is severely limited by the scarcity of available photocatalysts able to promote this chemistry, with the added burden that most of them require highly energetic UV light to operate.^{6,7} Accordingly, there is an urgent need to develop synthetic protocols via *d*-HAT occurring under visible light irradiation, especially with the aim to forge C–C bonds from strong aliphatic C–H bonds, such as those embedded in alkanes, which is still considered as one of the “Holy Grails” in synthesis.⁸

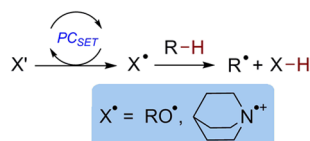
As an example, fluorenone,^{9a} acetophenone,^{9b} and uranyl nitrate hexahydrate¹⁰ were recently used to accomplish the C–H to C–F bond conversion in alkyl aromatics^{9a} or in alkanes^{9b,10} (Scheme 2).

On the other hand, the direct, visible-light photocatalyzed activation of a C–H bond in (cyclo)alkanes to forge C–C bonds still remains a challenge, and only two cases have been reported in the literature to date. First, 5,7,12,14-pentacenetetrone (PT, Scheme 2) was adopted as the photocatalyst in a radical allylation protocol, where cycloalkanes were converted into vinyl sulfones in a good yield by reaction with 1,2-bis(phenylsulfonyl)-2-propene.¹¹ Second, it was demonstrated that Eosin Y can function as an effective photoorganocatalyst for the visible-light derivatization of cyclohexane (Scheme 2), but despite the operational simplicity that allowed to run the reaction on a large scale by using continuous-flow technology, the yield of alkylated product was poor, and heating at 60 °C was necessary.¹²

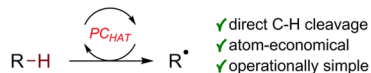
Pushed by our interest in photocatalysis via *d*-HAT by polyoxometalates, where an M=O (M: metal) functionality in the excited state is responsible for the relevant H-atom abstraction,¹³ we pursued the search for a robust photocatalyst that can operate in the visible light region. Accordingly, we

Scheme 1. Approaches for the Indirect (*i*-HAT) or Direct (*d*-HAT) Photocatalyzed Hydrogen Atom Transfer Reaction

Indirect HAT (*i*-HAT)



Direct HAT (*d*-HAT)



Received: January 21, 2019

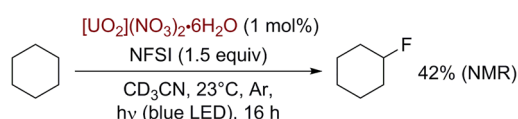
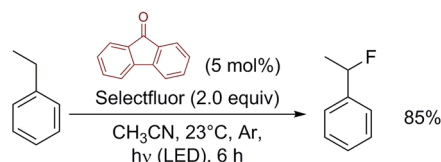
Revised: March 1, 2019

Published: March 5, 2019

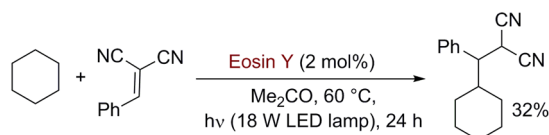
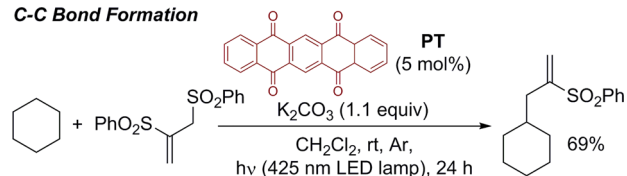
Scheme 2. Examples of Visible-Light-Photocatalyzed *d*-HAT in C–F (Upper Part) and C–C Bond Formation (Lower Part)

■ Visible Light *d*-HAT

C–F Bond Formation



C–C Bond Formation



chose uranyl nitrate hexahydrate $[\text{UO}_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a valid candidate.¹⁴ Since its discovery, the uranyl cation $[\text{UO}_2]^{2+}$ (oxidation state for U: +6) has received a great deal of attention for its photophysical and photochemical properties.¹⁵ The weak absorption band in the visible range has been proposed to involve the excitation of an electron from a π -orbital of the $\text{U}=\text{O}$ bond to a nonbonding orbital on the metal center.^{15c,16} This transition ultimately leads to the population of a triplet excited state endowed with free radical character, showing a lifetime in the domain of microseconds and a redox potential $E([\text{U}^{\text{VI}}\text{O}_2]^{2+*}/[\text{U}^{\text{V}}\text{O}_2]^{+})$ of +2.36 V vs SCE.^{15,16} Indeed, the reactive oxygen site of this state has the capability to generate C-centered radicals via homolytic cleavage of a C–H bond in organic compounds,¹⁰ especially in alcohols and arylaldehydes.¹⁷ Accordingly, we embarked on a study aimed to demonstrate that the uranyl cation is a valuable *d*-HAT photocatalyst to forge C–C bonds from unactivated C–H bonds (mainly from (cyclo)alkanes) under visible light irradiation.

We commenced our investigation by studying the addition of cyclohexane (**1a**) onto 2-benzylidenemalononitrile **2a**, chosen as a model Michael acceptor. After routine optimization of the reaction conditions (see Section 2 in Supporting Information), we found that uranyl nitrate hexahydrate (8 mol %) in an air-equilibrated acetone solution of **2a** in the presence of **1a** (5 equiv) under irradiation at 456 nm (40 W LED; light intensity: $400 \text{ W} \cdot \text{m}^{-2}$) gave the best results, with formation of the expected adduct **3** in 96% isolated yield (at complete conversion of **2a**). Notably, the residual uranium content in isolated **3** was determined by ICP-MS analysis to be $<20 \mu\text{g}/\text{kg}$ (see SI for details). We further demonstrated that the reaction required both light and photocatalyst to occur, while heating in refluxing acetone in the dark for 24 h did not afford any product. Moreover, the

process was inhibited in the presence of the radical scavenger TEMPO (see Table 1).

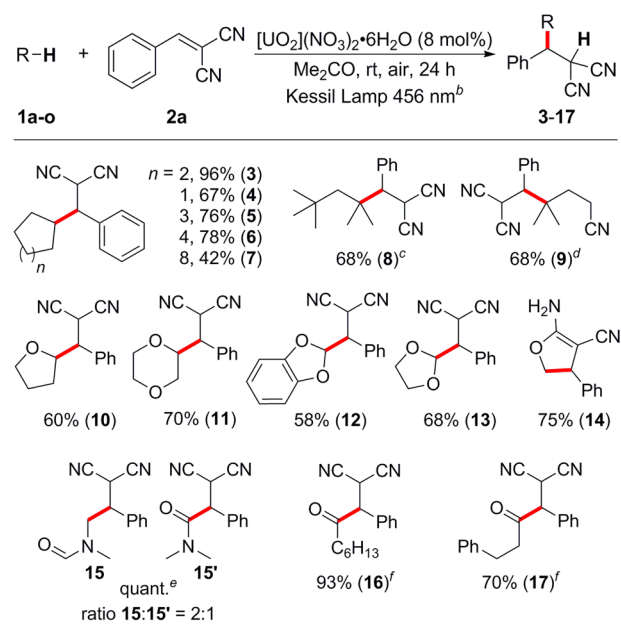
Table 1. Control Experiments for the Uranyl-Photocatalyzed C–H to C–C Bond Conversion

entry	variation from opt. conditions	2a consumption (%)	yield (%) ^a
1	none	100	95, 96 ^b
2	no light	<5	n.d.
3	dark, 60 °C ^c	<5	n.d.
4	no photocatalyst	<5	n.d.
5	N ₂ sparged solution	100	95
6	TEMPO (1 equiv)	<5	n.d.

^aAbsolute yields determined by means of calibration curves with authentic samples (see SI). ^bIsolated yield after flash column chromatography. ^cRefluxing acetone. n.d.: not detected. TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

Gratifyingly, the functionalization of unactivated methylene groups in several cycloalkanes occurred smoothly in good to excellent yields (see compounds **3–7**) under extremely mild conditions (Table 2). Interestingly, even acyclic isooctane (2,2,4-trimethylpentane, **1f**) was functionalized with a complete regioselectivity toward the methine site to afford **8** in 68% yield when the photocatalyst was used in 15 mol % amount. Isocapronitrile gave product **9**, confirming the same

Table 2. Scope of H-Donors **1 for the Alkylation of 2-Benzylidenemalononitrile **2a**^a**



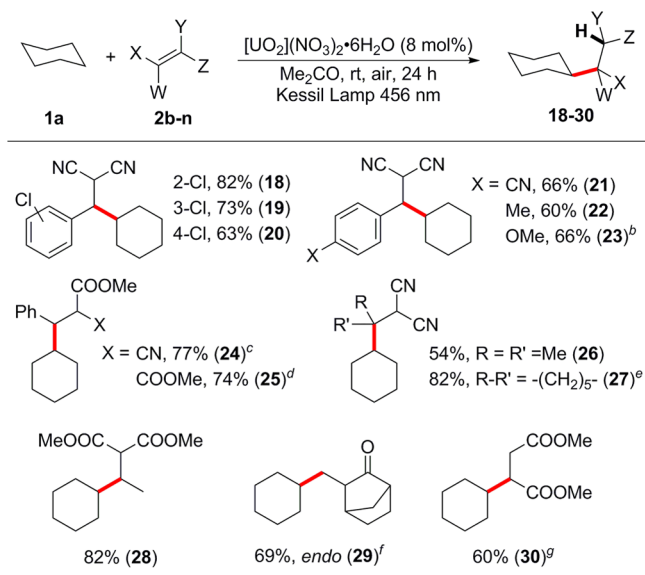
^aReaction conditions: **2a** (0.1 M), **1a–o** (5 equiv, unless otherwise noted); the structures of the starting materials are reported in Section 1 in the Supporting Information; isolated yields on a 1 mmol scale have been reported. ^bLight intensity: $400 \text{ W} \cdot \text{m}^{-2}$ at 5 cm. ^c20 equiv of **1f**, $[\text{UO}_2]^{2+}$ 15 mol %. ^d10 equiv of **1g**. ^e4 equiv of **1m**. ^f1 equiv of aldehyde.

selectivity toward the tertiary position. We then shifted our attention to the functionalization of oxygenated compounds, such as ethers and acetals, via the visible-light photocatalyzed generation of α -oxy and α,α -dioxy radicals, respectively.

Adducts **10–13** were then obtained in yields ranging 58–70%; notably, the photocatalyzed C–H cleavage in 1,3-dioxolane showed a complete selectivity toward the 2-position of the oxygenated ring. Methanol was then used as H-donor for the radical addition onto **2a**, which occurred in 75% yield, to afford compound **14** upon spontaneous cyclization. The functionalization was very efficient with dimethylformamide (DMF) since addition onto **2a** was quantitative. In the latter case, C–H activation was not regioselective, since both the adducts deriving from the α -amidoalkyl and the carbamoyl radicals were formed in a 2:1 ratio, respectively (compounds **15** and **15'**). Finally, the protocol could be easily adapted to perform an acylation starting from aliphatic aldehydes (compounds **16**, **17**, >70% yield), here used in an equimolar amount.

We then turned our attention to the scope of the olefin, by choosing **1a** as the model H-donor (Table 3). The substitution

Table 3. Scope of Electron Poor Olefins **2 for the Functionalization of Cyclohexane **1a**^a**



^aReaction conditions as in Table 2; the structures of the starting materials are reported in Section 1 in the Supporting Information. ^bComplete conversion after 96 h. ^cComplete conversion after 30 h. ^dComplete conversion after 65 h. ^e60% conversion of olefin **2k** was observed; yield based on the consumed olefin. ^fComplete conversion after 16 h, only *endo* diastereoisomer formed. ^gReaction performed in Me₂CO/H₂O 8:2.

pattern on the aromatic ring of the olefin **2a** was first tested. Neither the presence of a chlorine atom (products **18–20**, 63–82% yield) nor the electronic nature of the substituent (compounds **21–23**, ca. 60% yield) seemed to affect significantly the overall alkylation yield. However, the presence of an electron-donating group (e.g., OMe) required a longer irradiation time (96 h) to achieve complete conversion.

Similarly, the decrease of the electrophilicity of the olefin, resulting from the substitution of a CN with a COOMe group,¹⁸ did not affect the reaction yield, although the formation of adducts **24–25** required long reaction times, up

to 65 h. Finally, we tested olefins different from styrene derivatives. In particular, the β,β -disubstitution in isopropylidene malononitrile **2j** and cyclohexylidene malononitrile **2k** caused a slight drop in reactivity, and incomplete conversion of the olefin was observed in the latter case, with adduct **27** formed in 82% yield (based on 60% conversion of the olefin). When dimethyl ethylidene malonate **2l** was used, the reaction proceeded smoothly, affording **28** in 82% yield with complete conversion of the olefin. Reaction of **1a** with a conjugated ketone, such as 3-methylene-2-norbornanone **2m**, gave product **29** in 69% yield as the *endo* diastereomer, exclusively. In the alkylation of dimethyl maleate **2n**, product **30** was obtained in 60% yield in Me₂CO/H₂O 8:2 as the reaction medium.

To gain further insights into the HAT step, we performed a competition experiment in the presence of an equimolar C₆H₁₂/C₆D₁₂ (**1a/1a-d₁₂**) mixture (Figure 1a). A 74:26

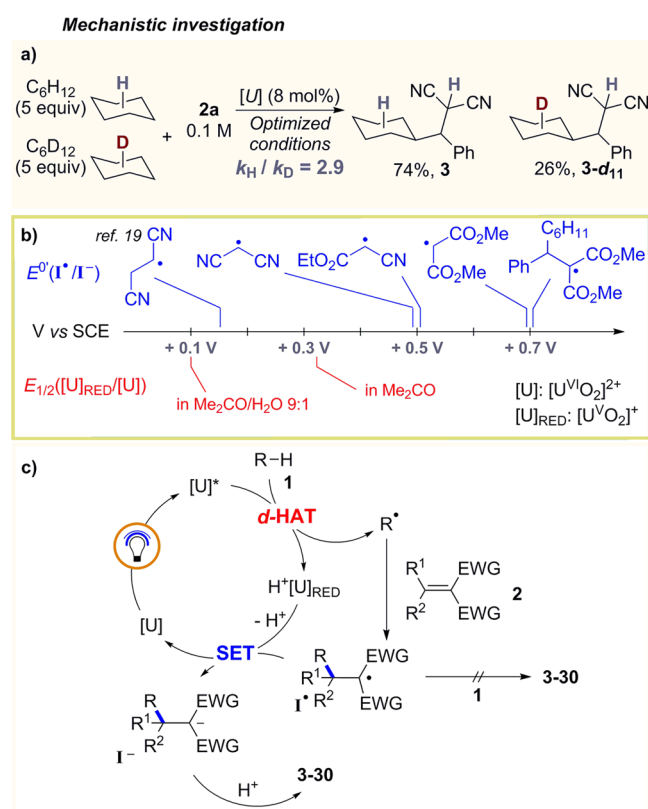


Figure 1. Mechanistic investigation: (a) deuteration experiment for KIE determination; (b) redox potentials of the involved species; (c) mechanistic proposal.

mixture of **3** and **3-d₁₁** was obtained, with a kinetic isotope effect (KIE) value of 2.9 (see also Scheme S2). This result is in accordance with that available in the literature^{15e} and was further confirmed by an independent Stern–Volmer experiment for the quenching of uranyl cation phosphorescence (see Table S5),¹⁵ where a KIE value of 3.5 has been determined.

We then focused our attention on the regeneration of the photocatalyst. We postulate that the catalytic cycle may be closed (in analogy with other metal-based *d*-HAT photocatalysts⁶ by an electron transfer process from the reduced photocatalyst ($\text{H}^+[\text{U}]_{\text{RED}} = \text{H}^+[\text{U}^{\text{V}}\text{O}_2]^+$) to the radical adduct (**I**[•]) resulting from the addition of the photogenerated radical (**R**[•]) onto **2**. As a matter of fact, the reaction worked better

when α,α -disubstituted styrenes **2a–i** were used. Accordingly, to test our hypothesis we decided to measure the redox potentials of the $\mathbf{I}^{\bullet}/\mathbf{I}^{-}$ couple for a set of $\mathbf{I}^{\bullet}(\text{CR})\text{X}_2$ radicals ($\text{X} = \text{CN}$ or COOR ; see Figure 1b). Thus, we generated in situ enolates $\mathbf{I}^{\bullet}(\text{CR})\text{X}_2$ from the corresponding active methylene derivatives (including compound **2S**, taken as a reference) upon addition of $(n\text{Bu})_4\text{N}^+\text{OH}^-$ and ran CV experiments (Figure S7). Interestingly, we found that all the redox couples were reversible, with moderately positive redox values $E_0'(\mathbf{I}^{\bullet}(\text{CR})\text{X}_2/\mathbf{I}^-(\text{CR})\text{X}_2) \geq +0.5$ V vs SCE, meaning that the generated intermediates \mathbf{I}^{\bullet} are remarkably prone to reduction. We believe that this interesting feature makes the closure of the photocatalytic cycle fast and efficient, compensating the weak reducing power of (protonated) $[\text{U}^{\text{V}}\text{O}_2]^+$ ($E_{1/2}([\text{U}^{\text{V}}\text{O}_2]^+/\text{[U}^{\text{VI}}\text{O}_2]^{2+}) = +0.32$ V vs SCE; nonreversible behavior; Figure S8). The process is likewise feasible when the adduct radical is stabilized by only one electron-withdrawing group (to give compounds **29–30**), since the redox potential of the succinonitrile radical $E(\text{NCCH}^{\bullet}\text{CH}_2\text{CN}/\text{NCCH}^-\text{CH}_2\text{CN})$ taken as a reference was reported to be $+0.165$ V vs SCE¹⁹ (Figure 1b). Thus, the reaction with dimethyl maleate **2n** proceeded satisfactorily in the presence of water, where the uranyl cation showed a more reversible behavior, with a slightly increased reducing power, $E_{1/2}([\text{U}^{\text{V}}\text{O}_2]^+/\text{[U}^{\text{VI}}\text{O}_2]^{2+}) = +0.10$ V vs SCE (Figure S8).

Moreover, we can safely exclude an electron transfer reaction between $\text{H}^+[\text{U}]_{\text{RED}}$ and the olefin since these have a redox potential $E(2/2^{\bullet-})$ more negative than -0.80 V vs SCE (Table S6).

A chain reaction mechanism may be excluded as well, since in most cases the BDE of the C–H bond to be cleaved is too strong (e.g., in cyclohexane the BDE is ca. 99.5 kcal·mol⁻¹).²⁰ In addition, an experiment performed in deuterated acetone allowed to prove that the solvent does not take part in the reaction (see Scheme S3 and Figure S11). In view of the above, our mechanistic proposal is reported in Figure 1c. In particular, the uranyl cation is excited under visible-light irradiation and, once in the excited state ($[\text{U}]^*$), is responsible for substrate activation via *d*-HAT. The thus-generated C-centered radical is readily intercepted by the electron-poor olefin **2** to give radical intermediate \mathbf{I}^{\bullet} . This species is then responsible for the reoxidation of the reduced form of the photocatalyst ($\text{H}^+[\text{U}]_{\text{RED}}$) to afford the desired Giese adduct.

In conclusion, we have demonstrated that uranyl cation can be used as a visible-light photocatalyst for *d*-HAT in C–C bond-forming reactions. The present approach is operationally simple and does not require any additive, thus confirming the robustness, efficiency, and selectivity of the *d*-HAT approach for the functionalization of strong C–H bonds. Notably, (cyclo)alkanes were readily alkylated via radical addition onto Michael acceptors in good to excellent yields. Furthermore, the electrochemical study allowed to propose a mechanistic scenario, where the nature of the olefin (and of the intermediates formed from it) plays a key role in the regeneration of the photocatalyst.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00287.

Experimental details about the used materials, sample preparation, experiments, electrochemical measurements, and analytical data (NMR) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: davide.ravelli@unipv.it

ORCID

Luca Capaldo: 0000-0001-7114-267X

Daniele Merli: 0000-0003-3975-0127

Maurizio Fagnoni: 0000-0003-0247-7585

Davide Ravelli: 0000-0003-2201-4828

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

L.C. and D.R. thank the MIUR for financial support (SIR Project “Organic Synthesis via Visible Light Photocatalytic Hydrogen Transfer”; Code: RBSI145Y9R).

■ REFERENCES

- (1) (a) *Photoorganocatalysis in Organic Synthesis*; Fagnoni, M., Protti, S., Ravelli, D., Eds.; World Scientific Publishing Co. Pte. Ltd.: Singapore, 2019, DOI: DOI: 10.1142/q0180. (b) *Visible Light Photocatalysis in Organic Chemistry*; Stephenson, C. R. J., Yoon, T. P., MacMillan, D. W. C., Eds.; Wiley-VCH: Weinheim, 2018. (c) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202. (d) Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*, No. 0052. (e) Parasram, M.; Gevorgyan, V. Visible Light-Induced Transition Metal-Catalyzed Transformations: Beyond Conventional Photosensitizers. *Chem. Soc. Rev.* **2017**, *46*, 6227–6240. (f) Xuan, J.; Lu, L.-Q.; Chen, J.-R.; Xiao, W.-J. Visible-Light-Driven Photoredox Catalysis in the Construction of Carbocyclic and Heterocyclic Ring Systems. *Eur. J. Org. Chem.* **2013**, *2013*, 6755–6770. (g) Reckenthaler, M.; Griesbeck, A. G. Photoredox Catalysis for Organic Syntheses. *Adv. Synth. Catal.* **2013**, *355*, 2727–2744.
- (2) (a) Yoshida, J.-i.; Kataoka, K.; Horcajada, R.; Nagaki, A. Modern Strategies in Electroorganic Synthesis. *Chem. Rev.* **2008**, *108*, 2265–2299. (b) Lin, S.; Lies, S. D.; Gravatt, C. S.; Yoon, T. P. Radical Cation Cycloadditions Using Cleavable Redox Auxiliaries. *Org. Lett.* **2017**, *19*, 368–371.
- (3) Capaldo, L.; Ravelli, D. Hydrogen Atom Transfer (HAT): A Versatile Strategy for Substrate Activation in Photocatalyzed Organic Synthesis. *Eur. J. Org. Chem.* **2017**, *2017*, 2056–2071.
- (4) Special issue on “Hydrogen Atom Transfer”, see: Costas, M.; Bietti, M. Uncovering the Complexity of the Simplest Atom Transfer Reaction. *Acc. Chem. Res.* **2018**, *51*, 2601–2602.
- (5) (a) Hu, X.-Q.; Chen, J.-R.; Xiao, W.-J. Controllable Remote C-H Bond Functionalization by Visible-Light Photocatalysis. *Angew. Chem., Int. Ed.* **2017**, *56*, 1960–1962. (b) Stateman, L. M.; Nakafuku, K. M.; Nagib, D. A. Remote C–H Functionalization via Selective Hydrogen Atom Transfer. *Synthesis* **2018**, *50*, 1569–1586.
- (6) (a) Ravelli, D.; Protti, S.; Fagnoni, M. Decatungstate Anion for Photocatalyzed “Window Ledge” Reactions. *Acc. Chem. Res.* **2016**, *49*, 2232–2242. (b) Ravelli, D.; Fagnoni, M.; Fukuyama, T.; Nishikawa, T.; Ryu, I. Site-Selective C–H Functionalization by Decatungstate Anion Photocatalysis: Synergistic Control by Polar and Steric Effects Expands the Reaction Scope. *ACS Catal.* **2018**, *8*, 701–713. (c) Suzuki, K.; Mizuno, N.; Yamaguchi, K. Polyoxometalate Photocatalysis for Liquid-Phase Selective Organic Functional Group Transformations. *ACS Catal.* **2018**, *8*, 10809–10825. (d) Tanielian, C. Decatungstate Photocatalysis. *Coord. Chem. Rev.* **1998**, *178–180*,

1165–1181. (e) Tzirakis, M. D.; Lykakis, I. N.; Orfanopoulos, M. Decatungstate as an Efficient Photocatalyst in Organic Chemistry. *Chem. Soc. Rev.* **2009**, *38*, 2609–2621.

(7) Li, H.; Zhang, M.-T. Visible-light-mediated C(sp³)-H activation by photo-induced hydrogen-atom transfer. *J. Photochem. Photobiol., A* **2018**, *355*, 109–113.

(8) Hartwig, J. F. Catalyst-Controlled Site-Selective Bond Activation. *Acc. Chem. Res.* **2017**, *50*, 549–555.

(9) (a) Xia, J.-B.; Zhu, C.; Chen, C. Visible Light-Promoted Metal-Free C–H Activation: Diarylketone-Catalyzed Selective Benzylic Mono- and Difluorination. *J. Am. Chem. Soc.* **2013**, *135*, 17494–17500. (b) Xia, J.-B.; Zhu, C.; Chen, C. Visible Light-Promoted Metal-free sp³-C–H Fluorination. *Chem. Commun.* **2014**, *50*, 11701–11704.

(10) (a) West, J. G.; Bedell, T. A.; Sorensen, E. J. The Uranyl Cation as a Visible-Light Photocatalyst for C(sp³)-H Fluorination. *Angew. Chem., Int. Ed.* **2016**, *55*, 8923–8927. (b) Wu, L.; Cao, X.; Chen, X.; Fang, W.; Dolg, M. Visible-Light Photocatalysis of C(sp³)-H Fluorination by the Uranyl Ion: Mechanistic Insights. *Angew. Chem., Int. Ed.* **2018**, *57*, 11812–11816.

(11) Kamijo, S.; Kamijo, K.; Maruoka, K.; Murafuji, T. Aryl Ketone Catalyzed Radical Allylation of C(sp³)-H Bonds under Photoirradiation. *Org. Lett.* **2016**, *18*, 6516–6519.

(12) Fan, X.-Z.; Rong, J.-W.; Wu, H.-L.; Zhou, Q.; Deng, H.-P.; Tan, J. D.; Xue, C.-W.; Wu, L.-Z.; Tao, H.-R.; Wu, J. Eosin Y as a Direct Hydrogen-Atom Transfer Photocatalyst for the Functionalization of C-H Bonds. *Angew. Chem., Int. Ed.* **2018**, *57*, 8514–8518.

(13) De Waele, V.; Poizat, O.; Fagnoni, M.; Bagno, A.; Ravelli, D. Unraveling the Key Features of the Reactive State of Decatungstate Anion in Hydrogen Atom Transfer (HAT) Photocatalysis. *ACS Catal.* **2016**, *6*, 7174–7182.

(14) Although the handling of uranium salts might trigger an instinctive concern, it is a common position that the main risks deriving from their use are associated with chemical toxicity, and not from radioactivity. Thus, a judicious use of PPE (Personal Protection Equipment) makes most common uranium compounds, such as uranyl nitrate or uranyl acetate, no more noxious than any other heavy metal complex. See: (a) Arfsten, D. P.; Still, K. R.; Ritchie, G. D. A Review of the Effects of Uranium and Depleted Uranium Exposure on Reproduction and Fetal Development. *Toxicol. Ind. Health* **2001**, *17*, 180–191. (b) Domingo, J. L. Reproductive and Developmental Toxicity of Natural and Depleted Uranium: A Review. *Reprod. Toxicol.* **2001**, *15*, 603–609.

(15) (a) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; The Macmillan Company, Pergamon Press: New York, 1964. (b) Jørgensen, C. K.; Reisfeld, R. Uranyl photophysics. *Struct. Bonding* **1982**, *50*, 121–171. (c) Burrows, H. D.; Kemp, T. J. The Photochemistry of the Uranyl ion. *Chem. Soc. Rev.* **1974**, *3*, 139–165. (d) Ghosh, R.; Mondal, J. A.; Ghosh, H. N.; Palit, D. K. Ultrafast Dynamics of the Excited States of the Uranyl Ion in Solutions. *J. Phys. Chem. A* **2010**, *114*, 5263–5270. (e) Wang, W.-D.; Bakac, A.; Espenson, J. H. Uranium(VI)-Catalyzed Photooxidation of Hydrocarbons with Molecular Oxygen. *Inorg. Chem.* **1995**, *34*, 6034–6039. (f) Mao, Y.; Bakac, A. Photocatalytic Oxidation of Toluene to Benzaldehyde by Molecular Oxygen. *J. Phys. Chem.* **1996**, *100*, 4219–4223.

(16) McGlynn, S. P.; Smith, J. K. The Electronic Structure, Spectra, and Magnetic Properties of Actinyl Ions: Part I. The Uranyl Ion. *J. Mol. Spectrosc.* **1961**, *6*, 164–187.

(17) (a) Matsushima, R. Mechanism of Quenching of the Uranyl Fluorescence by Organic Compounds. *J. Am. Chem. Soc.* **1972**, *94*, 6010–6016. (b) Sakuraba, S.; Matsushima, R. Photochemical Reactions of Uranyl Ions with Organic Compounds. II. The Mechanism of the Photo-Oxidation of Alcohols by Uranyl Ions. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2359–2363. (c) Sakuraba, S.; Matsushima, R. Photochemical Reactions of Uranyl Ions with Organic Compounds. IV. The Uranyl Fluorescence Quenching by Aliphatic Alcohols. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2915–2918. (d) Matsushima,

R.; Mori, K.; Suzuki, M. Photoreactions of the Uranyl Ion with Arylaldehydes in Solution. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 38–41.

(18) Allgäuer, D. S.; Jangra, H.; Asahara, H.; Li, Z.; Chen, Q.; Zipse, H.; Ofial, A. R.; Mayr, H. Quantification and Theoretical Analysis of the Electrophilicities of Michael Acceptors. *J. Am. Chem. Soc.* **2017**, *139*, 13318–13329.

(19) Magri, D. C.; Workentin, M. S. Redox Properties of Radicals. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgililoglu, C., Studer, A., Eds.; John Wiley & Sons, 2012, DOI: DOI: 10.1002/9780470971253.rad002.

(20) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, 2003.