



**HAL**  
open science

# Visible-light-induced 3d transition metal-catalysis: A focus on C–H bond functionalization

Olivier Baslé

► **To cite this version:**

Olivier Baslé. Visible-light-induced 3d transition metal-catalysis: A focus on C–H bond functionalization. *Current opinion in green and sustainable chemistry*, 2021, 32, pp.100539. 10.1016/j.cogsc.2021.100539 . hal-03421356

**HAL Id: hal-03421356**

**<https://hal.science/hal-03421356>**

Submitted on 9 Nov 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Visible light induced 3d transition metal-catalysis: A focus on C-H bond functionalization.

Author name: Olivier Baslé

Corresponding author: Olivier Baslé (olivier.basle@lcc-toulouse.fr)

Address: LCC-CNRS, Université de Toulouse, CNRS, Toulouse, France

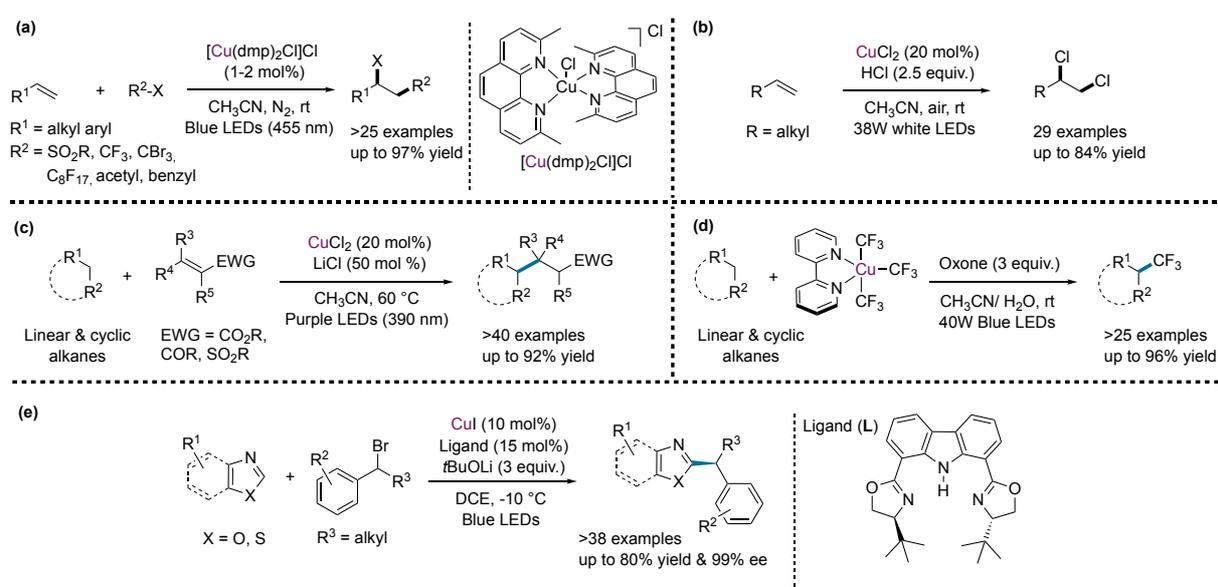
**Abstract:** *Transition metal catalysis under visible light irradiation has attracted considerable interest in the recent years. With the objective of breaking free from the use of noble metals, and as an alternative to traditional photoredox and dual catalysis, the implementation of this strategy with 3d transition metal complexes capable of both absorbing visible light and enabling catalysis has very recently led to the development of efficient photocatalytic systems for challenging organic synthesis, including C-H bond functionalization reactions.*

**Introduction:** Transition-metal photocatalysis has experienced tremendous developments in the last decades [1]. The most popular families of photocatalysts are Ru(II) polypyridyl and cyclometallated Ir(III) complexes owing to their strong absorbance in the visible light region where most organic molecules are transparent, and their sufficiently long-lived excited states to engage in outer-sphere electron or energy transfer to promote low energy reaction pathways [2,3]. Moreover, by merging photoredox catalysis and traditional transition metal-catalysis, the dual strategy has overcome intrinsic limitations of each approaches allowing for efficient and highly selective transformations that would be unfeasible under non-irradiative conditions [4,5]. Nevertheless, and despite remarkable achievement notably in combination with nickel catalysis [6,7], photoredox catalysis typically employs expensive organometallic complexes based on noble metals that are of economic and environmental concerns. Despite challenges associated with typically fast excited state deactivation and low photostability of 3d transition metal complexes [8], the long-standing interest in replacing noble metal in luminophores has led to recent discoveries of new photoactive complexes based on copper [9], nickel [10], cobalt [11], iron [12, 13], chromium [14, 15], and vanadium [16] exhibiting impressive photophysical properties whose applications as photoredox catalysts remain today relatively limited. On the other hand, a particular attention has been very recently given to visible light induced transition-metal catalysis, where the transition metal complex is capable of both absorbing visible light and enabling catalysis in the absence of an exogenous photosensitizer [17,18,19]. With the same objective of breaking free from the use of noble metals, the development of new photocatalytic systems solely based on abundant first-row transition metals has met with a number of resounding successes in very recent years [20]. The aim of this review is to highlight very recent advances in this emerging field of 3d transition metal catalyzed organic transformations under visible light with a special focus on C-H bond functionalization reactions.

**Visible light induced copper catalysis:** Among first-row transition metal, copper is by far the most studied alternative with already a variety of well-defined complexes capable of performing efficient transformation under visible light irradiation [21,22]. In a continuing effort to demonstrate the potential of copper-phenanthrolines complexes for visible light-mediated transformations, Reiser and co-workers recently reported on the use of  $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$  (dmp = 2,9-dimethyl-1,10-phenanthroline) as a low-priced and efficient photoredox catalyst for various atom transfer radical additions (Figure 1a) [23]. In this

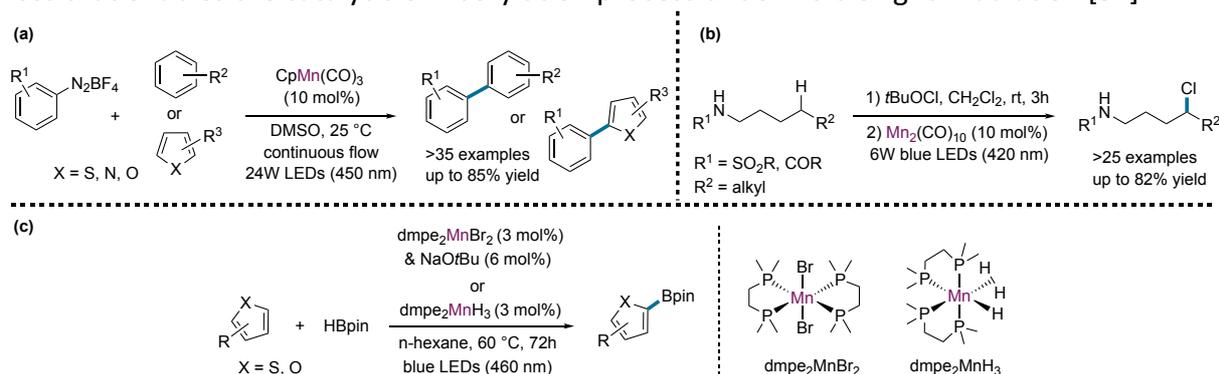
concern, and inspired by the seminal work of Kochi [24], Wan and co-workers have recently developed the blue light-induced vicinal dichlorination of alkenes by chlorine atom radicals generated through ligand-to-metal charge transfer excitation of  $\text{CuCl}_2$  (Figure 1b) [25]. More recently, Rovis and co-workers reported the photoinduced copper-catalyzed functionalization of unactivated  $\text{C}(\text{sp}^3)\text{-H}$  bonds via the coupling of alkanes with electron deficient olefins (Figure 1c) [26]. The photoactive cuprate catalyst formed *in situ* from  $\text{CuCl}_2/\text{LiCl}$  in acetonitrile undergoes ligand-to-metal charge transfer to generate chlorine radical capable of abstracting strong electron rich  $\text{C}(\text{sp}^3)\text{-H}$  bonds. While blue light irradiation (440 nm) can promote the desired transformation, improved catalytic activities were obtained using near ultraviolet light (390 nm) at 60 °C. Closely related to this work, Hong and co-workers very recently demonstrated that the photoexcitation of the bench stable  $\text{bpyCu}(\text{CF}_3)_3$  under blue light irradiation promotes trifluoromethylation of unactivated alkanes *via* the generation of trifluoromethyl radical as hydrogen atom transfer reagent (Figure 1d) [27].

Pioneered by the work of Fu and co-workers on photoinduced copper-catalyzed enantioselective cross-coupling reactions [28], the groups of Gong [29,30], Zhang [31] and Liu [32] recently contributed to the emergence of this research field by describing enantioselective alkylation of imine, dual carbofunctionalization of alkenes and decarboxylative alkylation with terminal alkynes, respectively. The most recent example was reported in 2021 by Zhang and coworkers, who developed an asymmetric alkylation of azoles catalyzed by a copper(I)/carbazole-based oxazoline ligand system under visible light irradiation (Figure 1e) [33]. A large variety of azoles and secondary 1-arylalkyl bromide substrates were efficiently engaged in this asymmetric photocatalytic C-H functionalization process to afford the desired chiral alkylated azole products in good yields and up to excellent enantioselectivity. Preliminary mechanistic studies evidenced that both the *in situ*-formed  $[\text{LCu}^{\text{I}}]$  and  $[\text{LCu}^{\text{I}}\text{-azole}]\text{Li}$  complexes absorb visible light in the range of 400-500 nm and that the latter is likely the photoactive species due to a larger Stern-Volmer constant measured using 1-bromoethyl benzene as quencher.



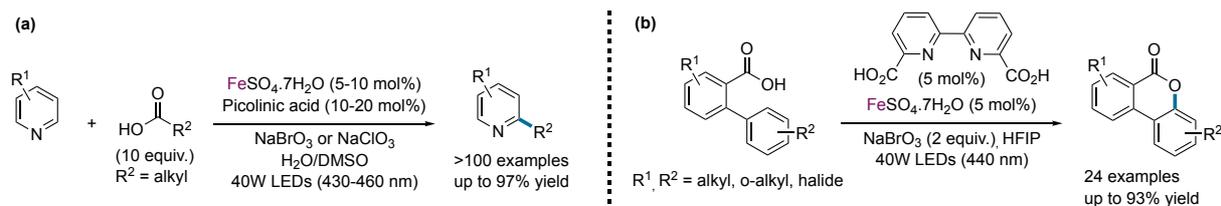
**Figure 1.** Visible light induced copper-catalysis

**Visible light induced manganese catalysis:** The use of manganese complexes in transition metal catalysis under visible light has recently emerged [34]. A relevant example was reported by Ackermann and co-workers who developed a visible light induced manganese-catalyzed C-H arylation in continuous flow (Figure 2a) [35]. Under blue light irradiation,  $\text{CpMn}(\text{CO})_3$  as catalyst allowed for the efficient arylation at room temperature of arenes and heteroarenes using aryl diazonium salts. Interestingly, based on mechanistic studies, the authors proposed that both substrates coordinate the manganese metal center to form a photochemically competent complex able to undergo single electron transfer from its excited state to reduce the aryl diazonium salt and generate the corresponding aryl radical. In 2020, Qu, Li, Zhang and coworkers reported the selective chlorination of unactivated  $\text{C}(\text{sp}^3)\text{-H}$  bonds of aliphatic amines catalyzed by  $\text{Mn}_2(\text{CO})_{10}$  under blue light irradiation (Figure 2b) [36]. Visible light induced Mn-Mn bond homolysis affords  $\text{Mn}(\text{CO})_5$  radical that abstracts the Cl atom of N-chlorosulfonamide to *in situ* generate amidyl radical undergoing 1,5-intramolecular hydrogen transfer followed by Cl atom transfer to produce the desired chlorinated product. The reaction performed under mild reaction conditions could notably provide efficient access to a large variety of alkyl chlorides in good yields. Very recently, Thomas and co-workers described a visible light induced manganese-catalyzed C-H borylation of furan and thiophene derivatives (Figure 2c). The photoactive Mn(I) hydride species,  $\text{dmpe}_2\text{MnH}_3$ , generated *in situ* from the dibromide precursor,  $\text{dmpe}_2\text{MnBr}_2$  (dmpe = 1,2-bis(dimethylphosphino)ethane), in the presence of pinacolborane (HBPin) and sodium tert-butoxyde (NaOtBu), is prone to hydrogen loss that enables the catalytic C-H borylation process under visible light irradiation [37].



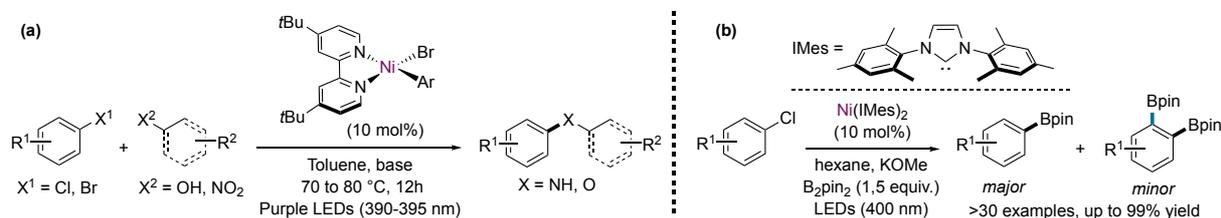
**Figure 2.** Visible light induced manganese-catalysis

**Visible light induced iron catalysis:** As an alternative to the challenging development of efficient Iron-based photosensitizers [12,13], new photocatalytic processes have been envisaged with the *in situ* formation of iron-substrate complexes that can generate radical species under visible light irradiation [38]. Inspired by the preliminary work of Sugimori [39], Jin and co-workers described in 2019 an efficient visible light-induced iron(II)-catalyzed decarboxylative alkylation of heteroarenes (Figure 3a) [40]. Also based on ligand-to-metal charge transfer of iron-carboxylates intermediates, Lei, Jin and coworkers have more recently developed an intramolecular aromatic C-H oxygenation of 2-biphenylcarboxylic acids catalyzed by  $\text{Fe}(\text{NO}_3)_3$ / 2,2'-bipyridine-6,6'-dicarboxylic acid and sodium bromate as terminal oxidant that exhibits a broad functionality tolerance (Figure 3b) [41].



**Figure 3.** Visible light induced iron-catalysis

**Visible light induced nickel catalysis:** In comparison to the broad application of nickel complexes as cocatalysts in dual photoredox catalysis [6,7], only very limited examples refer to the solely used of nickel photoredox catalysts in organic transformations [42, 43]. Nevertheless, recent studies by Doyle [44] Scholes [45], and Xue [46,47] have notably opened new perspectives in cross-coupling reactions thanks to the employment of Ni<sup>II</sup>-aryl halide complexes as pre-catalysts (Figure 4a). In 2020, Guo, Radius and Marder described a selective visible light-induced Ni-catalyzed borylation of chloroarenes [48]. Mechanistic investigations demonstrated that Ni<sup>I</sup>(IMes)<sub>2</sub>Cl generated *in situ* from Ni(IMes)<sub>2</sub> (IMes = 1,3-dimesitylimidazoline-2-ylidene) is the catalytic active species that undergoes under visible light irradiation chlorine abstraction from aryl chlorides to produce Ni<sup>II</sup>(IMes)<sub>2</sub>Cl<sub>2</sub> and aryl radical. The latter reacts with the anionic diborane B<sub>2</sub>pin<sub>2</sub>(OMe)<sup>-</sup> formed from B<sub>2</sub>pin<sub>2</sub> and KOMe (potassium methoxide) to afford the desired borylated product. Of particular interest, the authors also observed C-H bond borylation of chloroarenes to yield diborylated arenes as minor products (Figure 4b).



**Figure 4.** Visible light induced nickel-catalysis

**Conclusion:** First-row transition metal catalyzed organic transformations under visible light has recently emerged as a valuable alternative to traditional photoredox and dual catalysis that typically employ expensive organometallic complexes based on noble metals. Moreover, compare to ground stated transition metal catalysis, photoinduced 3d transition metal catalysis constitutes a greener approach allowing for milder reaction conditions, improved reactivity and selectivity, while enabling new challenging chemical transformations. Nevertheless, examples of photocatalytic processes solely based on 3d transition metal catalysts remains today relatively scarce and one might easily assume that it is only the beginning of the story.

#### Declaration of competing interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The author acknowledges the Centre National de la Recherche Scientifique (CNRS).

## References:

- <sup>1</sup> McAtee RC, McClain EJ, Stephenson CRJ: **Illuminating Photoredox Catalysis**. *Trends in Chemistry*, 2019, **1**: 111-125. <https://doi.org/10.1016/j.trechm.2019.01.008>.
- <sup>2</sup> Prier CK, Rankic DA, MacMillan DWC: **Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis**. *Chem. Rev.* 2013, **113**: 5322–5363. <https://doi.org/10.1021/cr300503r>.
- <sup>3</sup> Shaw MH, Twilton J, MacMillan DWC: **Photoredox Catalysis in Organic Chemistry**. *J. Org. Chem.* 2016, **81**: 6898–6926. <https://doi.org/10.1021/acs.joc.6b01449>
- <sup>4</sup> Twilton J, Le C, Zhang P, Shaw MH, Evans RW, Macmillan DWC: **The merger of transition metal and photocatalysis**. *Nat. Rev. Chem.* 2017, **1**: 0052. <https://doi.org/10.1038/s41570-017-0052>
- <sup>5</sup> Guillemard L, Wencel-Delord J: **When metal-catalyzed C–H functionalization meets visible-light photocatalysis**. *Beilstein J. Org. Chem.* 2020, **16**: 1754–1804. <https://doi.org/10.3762/bjoc.16.147>
- <sup>6</sup> Milligan JA, Phelan JP, Badir SO, Molander GA: **Alkyl Carbon–Carbon Bond Formation by Nickel/Photoredox Cross-Coupling**. *Angew. Chem. Int. Ed.* 2019, **58**: 6152–6163. <https://doi.org/10.1002/anie.201809431>
- <sup>7</sup> Zhu C, Yue H, Chu L, Rueping M: **Recent advances in photoredox and nickel dual- catalyzed cascade reactions: pushing the boundaries of complexity**. *Chem. Sci.*, 2020, **11**: 4051–4064. <https://doi.org/10.1039/D0SC00712A>
- <sup>8</sup> Förster C, Heinze K: **Photophysics and photochemistry with earth abundant metals – fundamentals and concepts**. *Chem. Soc. Rev.*, 2020, **49**: 1057-1070. <https://doi.org/10.1039/C9CS00573K>
- <sup>9</sup> Hamze R, Peltier JL, Sylvinson D, Jung M, Cardenas J, Haiges R, Soleilhavoup M, Jazzar R, Djurovich PI, Bertrand G, Thompson ME: **Eliminating nonradiative decay in Cu(I) emitters: >99% quantum efficiency and microsecond lifetime**. *Science*, 2019, **363**: 601-606. <https://doi.org/10.1126/science.aav2865>
- <sup>10</sup> Wong YS, Tang MC, Ng M, Yam VWW: **Toward the Design of Phosphorescent Emitters of Cyclometalated Earth-Abundant Nickel(II) and Their Supramolecular Study**. *J. Am. Chem. Soc.* 2020, **142**: 7638–7646. <https://doi.org/10.1021/jacs.0c02172>.
- <sup>11</sup> Pal AK, Li C, Hanan GS, Zysman-Colman E: **Blue-emissive cobalt(III) complexes and their use in the photocatalytic trifluoromethylation of polycyclic aromatic hydrocarbons**. *Angew. Chem. Int. Ed.* 2018, **57**: 8027–8031. <https://doi.org/10.1002/ange.201802532>.
- <sup>12</sup> Kjær KS, Kaul N, Prakash O, Chábera P, Rosemann NW, Honarfar A, Gordivska O, Fredin LA, Bergquist KE, Häggström L, Ericsson T, Lindh L, Yartsev A, Styring S, Huang P, Uhlig J, Bendix J, Strand D, Sundström V, Persson P, Lomoth R, Kenneth Wärnmark K: **Luminescence and reactivity of a charge-transfer excited iron complex with nanosecond lifetime**. *Science* 2019, **363**: 249–253. <https://doi.org/10.1126/science.aau7160>.
- <sup>13</sup> Wenger OS: **Is iron the new ruthenium**. *Chem. Eur. J.* 2019, **25**: 6043–6052. <https://doi.org/10.1002/chem.201806148>.
- <sup>14</sup> Treiling S, Wang C, Förster C, Reichenauer F, Kalmbach J, Boden P, Harris JP, Carrella LM, Rentschler E, Resch-Genger U, Reber C, Seitz M, Gerhards M, Heinze K: **Luminescence and light-driven energy and electron transfer from an exceptionally long-lived excited state of a non-innocent chromium(III) complex**. *Angew. Chem. Int. Ed.* 2019, **58**: 18075–18085. <https://doi.org/10.1002/anie.201909325>.
- <sup>15</sup> Jiménez JR, Poncet M, Miguez-Lago S, Grass S, Lacour J, Besnard C, Cuerva JM, Campana AG, Pigué C: **Bright Long-Lived Circularly Polarized Luminescence in Chiral Chromium(III) Complexes**. *Angew. Chem. Int. Ed.* 2021, **60**: 10095-10102. <https://doi.org/10.1002/anie.202101158>.
- <sup>16</sup> Dorn M, Kalmbach J, Boden P, Pöpcke A, Gómez A, Förster C, Kuczelinis F, Carrella LM, Büldt LA, Bings NH, Rentschler E, Lochbrunner S, González L, Gerhards M, Seitz M, Heinze K: **A vanadium(III) complex with blue and NIR-II spin-flip luminescence in solution**. *J. Am. Chem. Soc.* 2020, **142**: 7947–7955. <https://doi.org/10.1021/jacs.0c02122>.
- <sup>17</sup> Parasram M, Gevorgyan V: **Visible light-induced transition metal-catalyzed transformations: beyond conventional photosensitizers**. *Chem. Soc. Rev.*, 2017, **46**: 6227-6240. <https://doi.org/10.1039/C7CS00226B>.
- <sup>18</sup> Cheng WM, Shang R: **Transition metal-catalyzed organic reactions under visible light: recent developments and future perspectives**. *ACS Catal.* 2020, **10**: 9170–9196. <https://doi.org/10.1021/acscatal.0c01979>.
- <sup>19</sup> Larsen CB, Wenger OS: **Photoredox catalysis with metal complexes made from earth-abundant elements**. *Chem. Eur. J.* 2018, **24**: 2039–2058. <https://doi.org/10.1002/chem.201703602>

- <sup>20</sup> Abderrazak Y, Bhattacharyya A, Reiser, O: **Visible-light-induced homolysis of earth-abundant metal-substrate complexes: a complementary activation strategy in photoredox catalysis.** *Angew. Chem. Int. Ed.* 2021, <https://doi.org/10.1002/anie.202100270>.
- <sup>21</sup> Hossain A, Bhattacharyya A., Reiser, A: **Copper's rapid ascent in visible-light photoredox catalysis.** *Science*, 2019, **364**: eaav9713. <http://dx.doi.org/10.1126/science.aav9713>.
- <sup>22</sup> Zhong M, Pannecoucke X, Jubault P, Poisson T : **Recent advances in photocatalyzed reactions using well-defined copper(I) complexes.** *Beilstein J. Org. Chem.* 2020, **16**: 451-481. <https://doi.org/10.3762/bjoc.16.42>.
- <sup>23</sup> Engl S, Reiser O: **Making Copper Photocatalysis even more robust and economic: Photoredox Catalysis with [Cu<sup>II</sup>(dmp)<sub>2</sub>Cl]Cl.** *Eur. J. Org. Chem.* 2020, **10**: 1523-1533. <https://doi.org/10.1002/ejoc.201900839>.
- <sup>24</sup> Kochi JK: **Photolyses of Metal Compounds: Cupric Chloride in Organic Media.** *J. Am. Chem. Soc.* 1962, **84**: 2121–2127. <https://doi.org/10.1021/ja00870a025>.
- <sup>25</sup> Lian P, Long W, Li J, Zheng Y., Wan X: **Visible-light-induced vicinal dichlorination of alkenes through LMCT excitation of CuCl<sub>2</sub>.** *Angew. Chem. Int. Ed.* 2020, **59**: 23603–23608. <https://doi.org/10.1002/anie.202010801>.
- <sup>26\*</sup> Treacy SM, Rovis T: **Copper catalyzed C(sp<sup>3</sup>)-H bond alkylation via photoinduced ligand-to-metal charge transfer.** *J. Am. Chem. Soc.* 2021, **143**: 2729–2735. <https://doi.org/10.1021/jacs.1c00687>. Of special interest. Using a simple system based on CuCl<sub>2</sub>/LiCl in CH<sub>3</sub>CN, functionalization of unactivated C-H bonds of alkanes is reported.
- <sup>27</sup> Choi G, Lee GS, Park B, Kim D, Hong SH: **Direct C(sp<sup>3</sup>)-H trifluoromethylation of unactivated alkanes enabled by multifunctional trifluoromethyl copper complexes.** *Angew. Chem. Int. Ed.* 2021, **60**: 5467-5474. <https://doi.org/10.1002/anie.202012263>.
- <sup>28</sup> Kainz QM, Matier CD, Bartoszewicz A, Zultanski SL, Peters JC, Fu GC : **Asymmetric copper-catalyzed C-N cross-couplings induced by visible light.** *Science*, 2016, **351**: 681–684. DOI: 10.1126/science.aad8313.
- <sup>29</sup> Han B, Li, Yu Y, Gong L: **Photocatalytic enantioselective  $\alpha$ -aminoalkylation of acyclic imine derivatives by a chiral copper catalyst.** *Nature Commun.* 2019, **10**: 3804. <https://doi.org/10.1038/s41467-019-11688-7>.
- <sup>30</sup> Li Y, Zhou K, Wen Z, Cao S, Shen X, Lei M, Gong L: **Copper(II)-Catalyzed Asymmetric Photoredox Reactions: Enantioselective Alkylation of Imines Driven by Visible Light.** *J. Am. Chem. Soc.* 2018, **140**: 15850–15858. <https://pubs.acs.org/doi/10.1021/jacs.8b09251>.
- <sup>31</sup> Zhang Y, Sun Y, Chen B, Xu M, Li C, Zhang D, Zhang G: **Copper-Catalyzed Photoinduced Enantioselective Dual Carbonylfunctionalization of Alkenes.** *Org. Lett.* 2020, **22**: 1490–1494. <https://pubs.acs.org/doi/10.1021/acs.orglett.0c00071>.
- <sup>32</sup> Xia HD, Li ZL, Gu QS, Dong XY, Fang JH, Du XY, Wang LL, Liu XY: **Photoinduced Copper-Catalyzed Asymmetric Decarboxylative Alkynylation with Terminal Alkynes.** *Angew. Chem. Int. Ed.* 2020, **59**: 16926–16932. <https://doi.org/10.1002/anie.202006317>.
- <sup>33\*</sup> Li C, Chen B, Ma X, Mo X, Zhang G : **Light-Promoted Copper-Catalyzed Enantioselective Alkylation of Azoles.** *Angew. Chem. Int. Ed.* 2021, **60**: 2130 –2134. <https://doi.org/10.1002/anie.202009323>. of special interest. Under visible light irradiation, high enantioselectivity is obtained for the cross-coupling of azoles and secondary alkyl bromides catalyzed by copper.
- <sup>34</sup> Nuhant P, Oderinde MS, Genovino J, Juneau A, Gagn Y, Allais C, Chinigo GM, Choi C, Sach NW, Bernier L, Fobian YM, Bundesmann MW, Khunte B, Frenette M, Fadeyi OO: **Visible-Light-Initiated Manganese Catalysis for C-H Alkylation of Heteroarenes: Applications and Mechanistic Studies.** *Angew. Chem. Int. Ed.* 2017, **56**: 15309 – 15313. <https://doi.org/10.1002/anie.201707958>.
- <sup>35</sup> Liang YF, Steinbock R, Yang L, Ackermann L: **Continuous Visible-Light Photoflow Approach for a Manganese-Catalyzed (Het)Arene C-H Arylation.** *Angew. Chem. Int. Ed.* 2018, **57**: 10625–10629. <https://doi.org/10.1002/anie.201805644>.
- <sup>36\*</sup> Liu RZ, Li J, Sun J, Liu XG, Qu S, Li P, Zhang B: **Generation and Reactivity of Amidyl Radicals: Manganese-Mediated Atom-Transfer Reaction.** *Angew. Chem. Int. Ed.* 2020, **59**: 4428–4433. <https://doi.org/10.1002/anie.201913042>. of special interest. Regioselective chlorination of unactivated C(sp<sup>3</sup>)-H bonds is achieved under visible light irradiation using Mn<sub>2</sub>(CO)<sub>10</sub> as catalyst.
- <sup>37</sup> Britton L, Skrodzki M, Nichol GS, Dominey AP, Pawluć P, Docherty JH, Thomas SP: **Manganese-Catalyzed C(sp<sup>2</sup>)-H Borylation of Furan and Thiophene Derivatives.** *ACS Catal.* 2021, **11**: 6857–6864. <https://doi.org/10.1021/acscatal.1c01563>
- <sup>38</sup> Zhou WJ, Wu XD, Miao M, Wang ZH, Chen L, Shan SY, Cao GM, Yu DG: **Light Runs Across Iron Catalysts in Organic Transformations.** *Chem. Eur. J.* 2020, **26**: 15052-15064. <https://doi.org/10.1002/chem.202000508>.
- <sup>39</sup> Sugimori A, Yamada T: **Visible light- and gamma ray-induced alkylation in pyridine ring. Effective alkylation with visible light in the presence of iron(III) sulfate.** *Chem. Lett.* 1986, **15**: 409–412. <https://doi.org/10.1246/cl.1986.409>.

- 
- <sup>40</sup> Li Z, Wang X, Xia S, Jin J: **Ligand-Accelerated Iron Photocatalysis Enabling Decarboxylative alkylation of heteroarenes.** *Org. Lett.* 2019, **21**: 4259–4265. <https://doi.org/10.1021/acs.orglett.9b01439>.
- <sup>41</sup> Xia S, Hu K, Lei C, Jin J: **Intramolecular aromatic C–H acyloxylation enabled by iron photocatalysis.** *Org. Lett.* 2020, **22**: 1385–1389. <https://doi.org/10.1021/acs.orglett.0c00002>.
- <sup>42</sup> Grübel M, Bosque I, Altmann PJ, Bach T, Hess CR: **Redox and photocatalytic properties of a Ni<sup>II</sup> complex with a macrocyclic biquinazoline (Mabiq) ligand.** *Chem. Sci.* 2018, **9**: 3313–3317. <https://doi.org/10.1039/C7SC05320G>.
- <sup>43</sup> Mandal T, Das S, De Sarkara S: **Nickel(II) tetraphenylporphyrin as an efficient photocatalyst featuring visible light promoted dual redox activities.** *Adv. Synth. Catal.* 2019, **361**: 3200–3209. <https://doi.org/10.1002/adsc.201801737>.
- <sup>44\*</sup> Ting SI, Garakyaraghi, S, Taliaferro CM, Shields BJ, Scholes GD, Castellano FN, Doyle AG: **3d-d excited states of Ni(II) complexes relevant to photoredox catalysis: spectroscopic identification and mechanistic implications.** *J. Am. Chem. Soc.* 2020, **142**: 5800 – 5810. <https://doi.org/10.1021/jacs.0c00781>. of special interest. An in-depth study on excited state nickel(II) species and their implications in catalysis.
- <sup>45</sup> Tian L, Till NA, Kudisch B, MacMillan DWC, Scholes GD: **Transient absorption spectroscopy offers mechanistic insights for an iridium/nickel-catalyzed C–O coupling.** *J. Am. Chem. Soc.* 2020, **142**: 4555–4559. <https://doi.org/10.1021/jacs.9b12835>.
- <sup>46</sup> Yang L, Lu HH, Lai CH, Li G, Zhang W, Cao R, Liu F, Wang C, Xiao J, Xue D: **Light-promoted nickel catalysis: etherification of aryl electrophiles with alcohols catalyzed by a Ni<sup>II</sup>-aryl complex.** *Angew. Chem. Int. Ed.* 2020, **59**: 12714–12719. <https://doi.org/10.1002/anie.202003359>.
- <sup>47</sup> Li G, Yang L, Liu JJ, Zhang W, Cao R, Wang C, Zhang Z, Xiao J, Xue D: **Light-promoted C–N coupling of aryl halides with nitroarenes.** *Angew. Chem. Int. Ed.* 2021, **60**: 5230–5234. <https://doi.org/10.1002/anie.202012877>.
- <sup>48\*</sup> Tian YM, Guo XN, Krummenacher I, Wu Z, Nitsch J, Braunschweig H, Radius U, Marder TB: **Visible-Light induced Ni-catalyzed radical borylation of chloroarenes.** *J. Am. Chem. Soc.* 2020, **142**: 18231–18242. <https://doi.org/10.1021/jacs.0c08834>. of special interest. Unique borylation of C(sp<sup>2</sup>)-H bond is reported in the presence of nickel catalyst under visible light irradiation.