Chlorination

Zitierweise: *Angew. Chem. Int. Ed.* **2020**, *59*, 23603–23608
Internationale Ausgabe: doi.org/10.1002/anie.202010801
Deutsche Ausgabe: doi.org/10.1002/ange.202010801

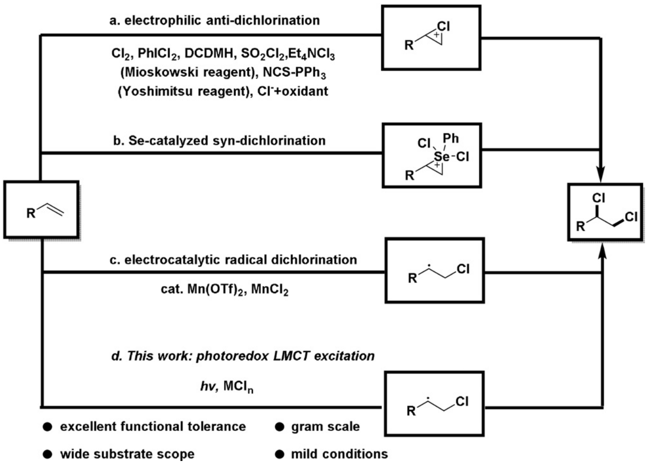
Visible-Light-Induced Vicinal Dichlorination of Alkenes through LMCT Excitation of $CuCl_2$

*Pengcheng Lian, Wenhao Long, Jingjing Li, Yonggao Zheng, and Xiaobing Wan**

Abstract: *This work demonstrates photoredox vicinal dichlorination of alkenes, based on the homolysis of $CuCl_2$ in response to irradiation with visible light. This catalysis proceeds via a ligand to metal charge transfer process and provides an exciting opportunity for the synthesis of 1,2-dichloride compounds using an inexpensive, low-molecular-weight chlorine source. This new process exhibits a wide substrate scope, excellent functional group tolerance, extraordinarily mild conditions and does not require external ligands. Mechanistic studies show that the ready formation of chlorine atom radicals is responsible for the facile formation of C–Cl bonds in this synthetic process.*

Chlorination reactions are among the oldest and most fundamental organic transformations, and they have been extensively studied.[1] As an example, the free radical substitution reaction of methane with molecular chlorine is commonly taught in undergraduate courses and is a standard process for the industrial synthesis of chlorinated solvents.[2] First discovered in 1877,[3] the vicinal dichlorination of carbon–carbon double bonds has attracted much attention owing to the importance of the dichlorinated products. However, the use of molecular chlorine as the chlorination reagent suffers from inherent drawbacks, including the high toxicity and corrosiveness of the chlorine and the harsh conditions and poor selectivity associated with the reactions. Consequently, a series of alternatives have been developed based on the ionic dichlorination reactions of alkenes.[4] These include the Willgerodt reagent ($PhICl_2$),[4c] SO_2Cl_2,[4d] the Mioskowski reagent (Et_4NCl_3),[4w] NCS-PPh_3 (the Yoshimitsu reagent),[4n] and combinations of chloride salts and oxidants,[4l,m,o,x,z] among others (Scheme 1 a). These electrophilic addition reactions typically exhibit *anti* selectivity as a result of the formation of a chloriranium ion as the reaction intermediate. Enantioselective versions of such reactions have been well-established, and have been reported by the Borhan,[5a] Snyder,[5e] Hennecke,[5f] Nicolaou,[5d] and Burns[5b,c,g] groups. In 2015, a pioneering study demonstrating the catalytic *syn*-dichlorination of alkenes was performed by Denmark and co-workers based on a key selenium intermediate (Scheme 1 b).[6b] Recently, Lin's group developed the Mn-catalysed radical dichlorination of alkenes using electricity as the primary energy source and supplying chlorine via $MgCl_2$ (Scheme 1 c).[7] Despite such successes, the majority of existing dichlorination methods have certain disadvantages, including the use of hazardous oxidants in stoichiometric quantities, the need for harsh conditions, and narrow substrates scopes. The diversity of naturally ccurring polychlorinated compounds,[8] particularly chlorosulfolipids, poses significant challenges and requires the development of more practical techniques for the vicinal dichlorination of alkenes. Specifically, a wider range of substrates and milder reaction conditions would be beneficial. Our group proposes that catalysis driven by visible light has promise as an approach to devising creative and powerful strategies to address these issues.

Compared to traditional thermal reactions, visible-light-induced reactions are typically carried out under more sustainable and milder conditions (typically room temperature).[9] Over the past decade, great progress has been made in this field, which has become an important complement to its thermal counterpart. More importantly, it has become possible to achieve chemical conversions that are either difficult or impossible to induce by non-photochemical processes. Reactions promoted by visible light are often associated with the use of d^6 transition-metal complexes, including those based on Ru^{II} and Ir^{III}, which undergo metal-to-ligand charge transfer (MLCT) such that small molecules can be activated to construct more complex compounds. In sharp contrast, the use of ligand-to-metal charge transfer (LMCT) is underdeveloped and only a few examples of the



Scheme 1. Vicinal dichlorination of alkenes.

---

[*] P. Lian, W. Long, J. Li, Y. Zheng, Prof. Dr. X. Wan
Key Laboratory of Organic Synthesis of Jiangsu Province
College of Chemistry, Chemical Engineering and Materials Science
Soochow University
199 Ren-Ai Road, Suzhou, Jiangsu 215123 (P. R. China)
E-mail: wanxb@suda.edu.cn

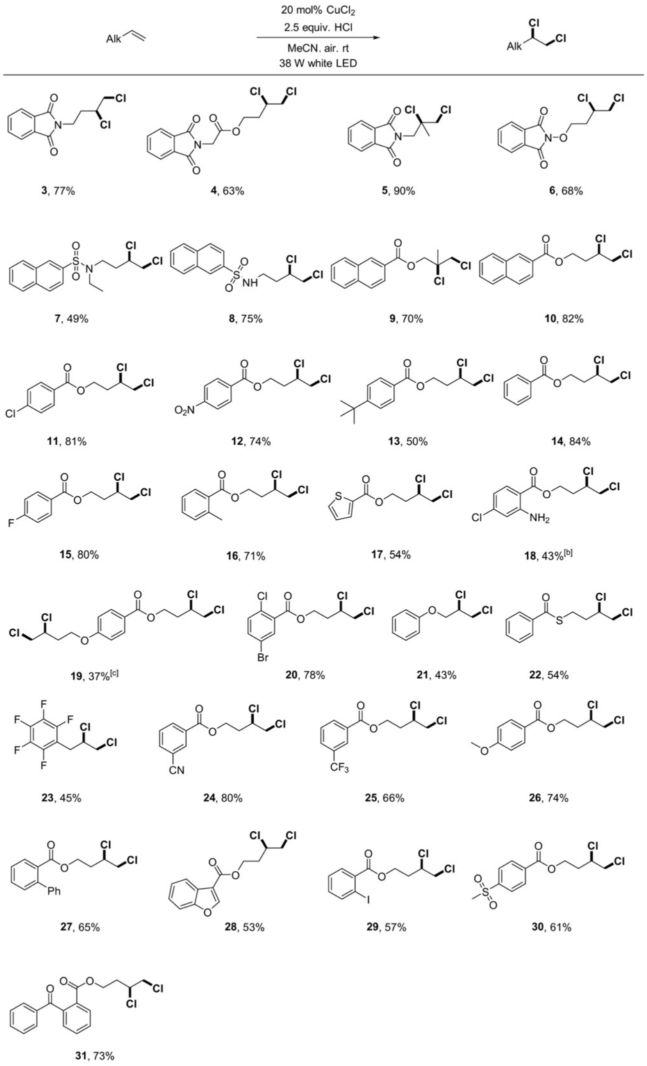
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202010801.

application of this process in synthetic chemistry have been reported in recent years.[10] In nature, chlorine typically exists in the form of inorganic chloride salts, and so it would be ideal to use Earth-abundant chloride salts as chlorine sources under photocatalytic conditions. However, this remains a formidable challenge given the fact that the oxidation potential of the chloride anion is much higher than the oxidation potentials of common photocatalysts. We envisioned that chlorine radicals could be generated under visible light as a result of the LMCT excitation of chloride salts and could attack alkenes to provide a novel yet elegant dichlorination technique (Scheme 1 d).

Based on the previously demonstrated facile LMCT excitation of cerium salts,[10b,e–i,l] we initially examined the application of $CeCl_3{\cdot}7H_2O$ to the dichlorination of the aliphatic alkene **1**. However, none of the desired product **2** was obtained upon irradiation with a 38 W white LED (Supporting Information, Table S1, entry 1). A variety of chloride salts, including those based on main group and transition metals, were subsequently assessed but none delivered a significant amount of **2** (for details, see Table S1 in the Supporting Information).

In 1962, Kochi demonstrated that an unfiltered mercury radiation could promote $CuCl_2$ homolysis, then worked with a variety of substrates to deliver corresponding products.[11a] More recently, the ability of Cu-based complexes to function as visible light photocatalysts has been recognized and extensively investigated, leading to exciting new possibilities for unprecedented chemical transformations.[12] Encouraged by these pioneering works, we examined the use $CuCl_2$ to induce the vicinal dichlorination of alkenes via a photoredox process. Using this approach, the desired product **2** was obtained in 82 % yield (Supporting Information, Table S1, entry 11), which appeared to show the feasibility of our hypothesis. We subsequently reduced the amount of the Cu salt that was employed and incorporated a low molecular weight nucleophilic chlorine source to promote the desired dichlorination reaction. After extensive screening, the optimized conditions were determined to comprise the use of $CuCl_2$ (20 mol %) as the catalyst and hydrochloric acid (2.5 equiv) as the chlorine source in 0.5 mL MeCN under air with irradiation by a 38 W white LED for 72 h. Under these optimized conditions, **1** was transformed into **2** with a high 85 % yield. Standard LMCT catalysis normally requires ligands to accelerate the homolysis of complexes.[10] In contrast, the present $CuCl_2$-catalyzed process successfully transferred the chlorine atom to the alkene substrate without requiring exogenous ligands. Blank experiments showed that dichlorination did not proceed in the absence of light, even with heating (Supporting Information, Table S1, entries 17 and 18). Switching the solvent to acetone resulted in a slight decrease in the yield of product **2** (Supporting Information, Table S1, entry 19). Furthermore, a good yield of **2** was obtained under oxygen (Supporting Information, Table S1, entry 20). Notably, this photocatalytic process generated water as the only side product and proceeded under mild conditions, both of which are quite different from traditional electrophilic chlorination methods.

Having established the optimised conditions, we set out to explore the scope of this reaction. As depicted in Scheme 2, a variety of substituents, both electron-withdrawing (NO_2, SO_2, carbonyl, CN, ester, CF_3, F, Cl, Br, I) and electron-donating (phthalimide, *N*-hydroxyphthalimide, acetal, Me, *t*-Bu, ether) were well-tolerated in this vicinal dichlorination reaction, and the desired products **3**–**31** could be isolated in moderate to good yields. Even sulphonamides having free N−H groups reacted well to afford the dichlorinated products in satisfactory yields (**7** and **8**). Interestingly, the presence of heteroatoms such as oxygen and sulfur did not significantly decrease the efficiency of this reaction, such that the desired dichlorides **17** and **28** were obtained in moderate yields. In particular, alkenes containing oxidatively labile amine groups were transformed into the dichloride product **18**, providing an opportunity for further elaboration. The reaction also proceeded using thioate and pentafluorobenzene substrates to



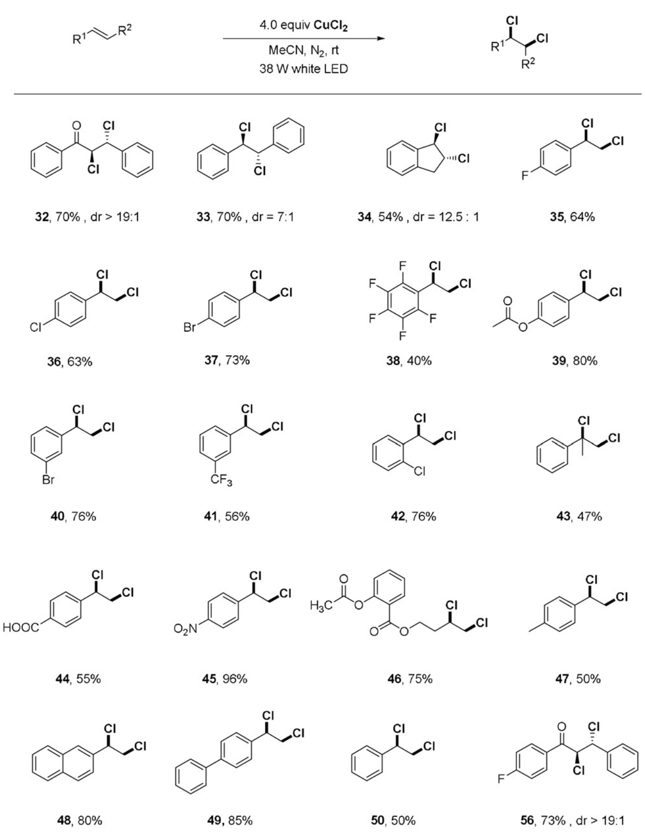
Scheme 2. [a] Reaction conditions: alkenes (0.2 mmol), $CuCl_2$ (0.04 mmol, 0.2 equiv), HCl (0.5 mmol, 2.5 equiv, 37 % in water) in MeCN (0.5 mL) irradiation with 38 W white light LEDs at ambient temperature for 72 h. [b] 1.0 mL MeCN was used. [c] 1.0 mmol HCl (37 % in water) was used.

give moderate yields (**22** and **23**). A diene was also found to be a viable substrate, affording the desired product **19** in a diminished but synthetically useful yield.

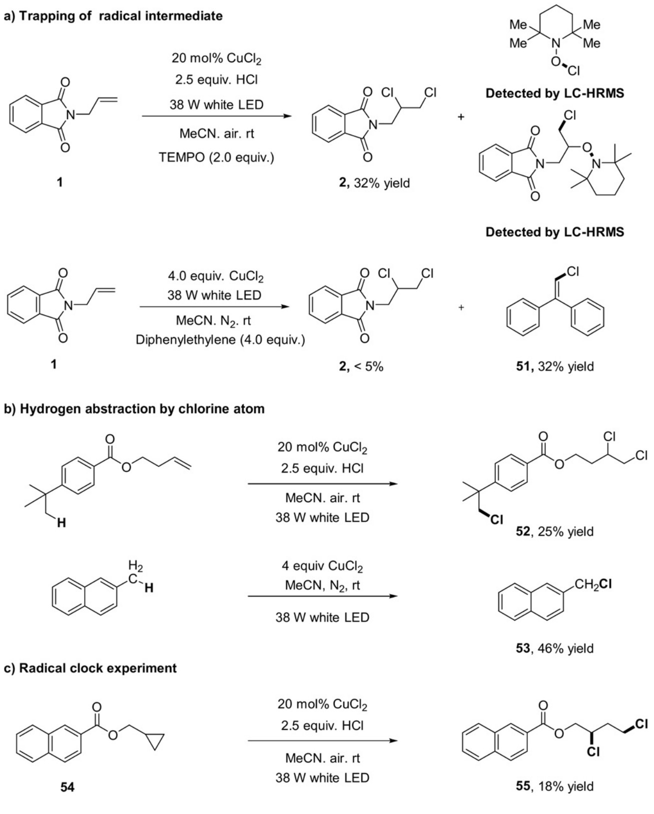
To further highlight the utility of our method, the reaction was conducted on a larger scale (5 mmol, 1.1 g), and readily afforded the 1,2-dichloride product **12** in a 63% yield [Eq. (1)].

Subsequently, chalcone was employed to investigate the stereochemistry of this vicinal dichlorination reaction. Only a small amount of the dichloride product was obtained owing to the generation of undesired by-products. However, the 1,2-*trans*-dichloride product **32** was achieved as the single stereoisomer in 70% yield when $CuCl_2$ was used as the chlorination reagent under a nitrogen atmosphere (Scheme 3). Both (*E*)-stilbene and indene delivered the desired dichloride with high stereoselectivity (**33**, **34**), as anticipated. We attribute this stereoselectivity to the steric and electrostatic repulsion provided by the previously installed Cl substituent, such that the $CuCl_2$ preferentially attacks from the opposite side.[13] Various substituted styrenes were also assessed with regard to this transformation, with the results shown in Scheme 3. The reaction proved generally applicable to mono-substituted, 1,2-disubstituted and 1,1-disubstituted alkenes. Styrenes with electron-rich, electron-poor or sterically hindered substituents on the aromatic ring were tolerated, giving dichlorides in moderate to excellent yields. The chemoselectivity of this protocol is especially significant, as free carboxyl, ether, fluoro, chloro, bromo, iodo, ester, nitro, and trifluoromethyl groups were all readily tolerated. Aliphatic alkenes were also suitable substrates for this reaction (**46**).

A variety of preliminary studies were carried out to gain information regarding the associated reaction mechanism. The addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was found to inhibit the formation of **2** (Scheme 4a) and electrospray ionization–high-resolution mass spectrometry showed that both chlorine and aliphatic radicals were trapped by this compound. Similar result was obtained when diphenylethylene was used as the trapping reagent. Notably, benzylic and aliphatic C−H bonds could be activated by the chlorine radical via hydrogen atom abstraction, leading to the corresponding products in moderate yields (Scheme 4b). Additional insights were obtained from a radical clock experiment with a compound having a cyclopropane moiety (**54**) that was found to open to generate a linear 1,3-dichloride (**55**) in 18% yield (Scheme 4c). Further mechanistic research also proved the difference and superiority of



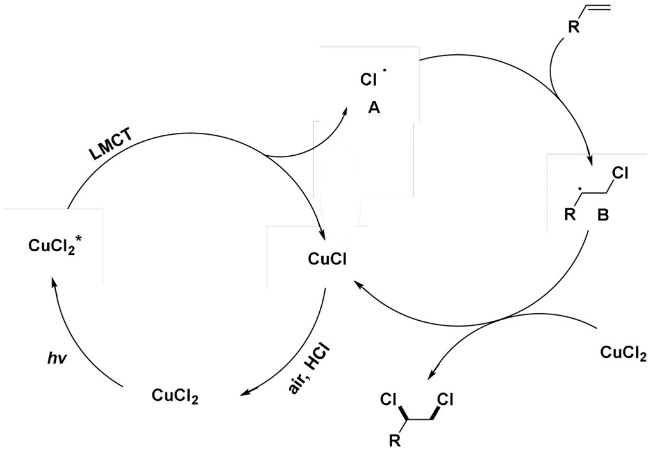
Scheme 3. Reaction conditions: alkenes (0.2 mmol), $CuCl_2$ (0.8 mmol, 4.0 equiv) in MeCN (5 mL) irradiation with 38 W white light LEDs at ambient temperature for 72 h.



Scheme 4. Probe for the possible mechanism.

our method with the previous methods (for details, see Section 4 in the Supporting Information). Based on these results, we propose that the visible-light-induced homolysis of $CuCl_2$ and subsequent chlorine atom transfer are responsible for the C−Cl bond formation. Harsh conditions are typically required to generate chlorine radicals, such as the excitation of molecular chlorine by UV light. Although the homolysis of high-valence transition metals[10n,o,q,14] and the electrolysis of manganese salts[7] have been shown to effectively generate these radicals, the present method is mild, employs visible light and uses commercially available $CuCl_2$.[15]

On the basis of the above, a plausible mechanism was presented in Scheme 5. Initially, the irradiation of $CuCl_2$ with visible light produces an excited state ($CuCl_2$*). LMCT then takes place to generate chlorine atom radical **A**, which rapidly adds to the alkene to produce the C-centered radical **B**. Finally, the reaction of radical **B** and $CuCl_2$ forms the dichloride product and CuCl.



Scheme 5. Proposed catalytic cycle.

In summary, this work achieved the first-ever vicinal dichlorination of alkenes promoted by visible light. This process is mechanistically distinct from, and thus complementary to, existing synthetic methods. A variety of control experiments demonstrated that the LMCT excitation of $CuCl_2$ plays a pivotal role in triggering the smooth generation of chlorine radicals as a key intermediate. In contrast to traditional electrophilic chlorination methods, this photocatalytic methodology is compatible with a broader spectrum of alkene substrates, including styrenes and aliphatic alkenes, terminal and internal alkenes, and simple and functionalized alkenes. Overall, 49 examples are described with substrates bearing a wide range of functional groups, such as cyano, sulfide, sulfonyl, ester, amide, and protic groups (NH_2, COOH) as well as nitro and halides moieties, offering a direct and practical approach to the construction of 1,2-dichloride products in generally good yields. Further investigations of asymmetric variants and other chemical transformations based on the LMCT excitation of Cu^{II} complexes are currently underway in our laboratory.

Acknowledgements

This work was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), NSFC (grant numbers 21971175 and 21572148). We thank Michael Judge, MSc, from Liwen Bianji, Edanz Editing China (www.liwenbianji.cn/ac), for editing the English text of a draft of this manuscript.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · cupric chloride · dichlorination · LMCT · photoredox

---

[1] a) S. Patai, Z. Rappaport, *The Chemistry of Halides, Pseudo-Halides and Azides, Supplement D2*, Wiley, Hoboken, **1995**; b) R. C. Larock, *Comprehensive Organic Transformation: A Guide to Functional Group Preparation*, 2nd ed., Wiley-VCH, New York, **1999**, pp. 629–640.

[2] a) L. G. Wade, J. W. Simek, *Organic Chemistry*, 9th ed., Pearson, Upper Saddle River, **2017**; b) J. G. Smith, *Organic Chemistry*, 6th ed., McGraw-Hill, New York, **2020**.

[3] A. Atterberg, O. Widman, *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 1841–1844.

[4] For reviews on dichlorination of alkenes, see: a) A. J. Cresswell, S. T.-C. Eey, S. E. Denmark, *Angew. Chem. Int. Ed.* **2015**, *54*, 15642–15682; *Angew. Chem.* **2015**, *127*, 15866–15909; b) "Halogenation and Halocyclization of Alkenes": A. Andries-Ulmer, T. Gulder in *Science of Synthesis: Catalytic Oxidation in Organic Synthesis*, *Vol. 1* (Ed.: K. Muniz), Thieme Medical Publishers, Stuttgart, **2017**, pp. 389–428; For selected examples on this topic, see: c) J. C. Sarie, J. Neufeld, C. G. Daniliuc, R. Gilmour, *ACS Catal.* **2019**, *9*, 7232–7237; d) X. Zeng, C. Gong, J. Zhang, J. Xie, *RSC Adv.* **2016**, *6*, 85182–85185; e) W.-S. Huang, L. Chen, Z.-J. Zheng, K.-F. Yang, Z. Xu, Y.-M. Cui, L.-W. Xu, *Org. Biomol. Chem.* **2016**, *14*, 7927–7932; f) F. J. Seidl, N. Z. Burns, *Beilstein J. Org. Chem.* **2016**, *12*, 1361–1365; g) H. Egami, T. Yoneda, M. Uku, T. Ide, Y. Kawato, Y. Hamashima, *J. Org. Chem.* **2016**, *81*, 4020–4030; h) A. Shemet, D. Sarlah, E. M. Carreira, *Org. Lett.* **2015**, *17*, 1878–1881; i) S. E. Denmark, N. Carson, *Org. Lett.* **2015**, *17*, 5728–5731; j) T. Moriuchi, Y. Fukui, S. Kato, T. Kajikawa, T. Hirao, *J. Inorg. Biochem.* **2015**, *147*, 177–180; k) U. Hennecke, M. Wilking, *Synlett* **2014**, *25*, 1633–1637; l) M. Stodulski, A. Goetzinger, S. V. Kohlhepp, T. Gulder, *Chem. Commun.* **2014**, *50*, 3435–3438; m) P. Swamy, M. M. Reddy, M. A. Kumar, M. Naresh, N. Narender, *Synthesis* **2014**, *46*, 251–257; n) Y. Kamada, Y. Kitamura, T. Tanaka, T. Yoshimitsu, *Org. Biomol. Chem.* **2013**, *11*, 1598–1601; o) J. Ren, R. Tong, *Org. Biomol. Chem.* **2013**, *11*, 4312–4315; p) A. P. Brucks, D. S. Treitler, S.-A. Liu, S. A. Snyder, *Synthesis* **2013**, *45*, 1886–1898; q) P. B. Thorat, B. Y. Bhong, N. N. Karade, *Synlett* **2013**, *24*, 2061–2066; r) D. X. Hu, G. M. Shibuya, N. Z. Burns, *J. Am. Chem. Soc.* **2013**, *135*, 12960–12963; s) T. Kitamura, Y. Tazawa, M. H. Morshed, S. Kobayashi, *Synthesis* **2012**, *44*, 1159–1162; t) X. Liu, L. Wang, J. Zou, *Chin. J. Chem.* **2011**, *29*, 2097–2100; u) A. Podgoršek, M. Jurisch, S. Stavber, M. Zupan, J. Iskra, J. A. Gladysz, *J. Org. Chem.* **2009**, *74*, 3133–3140; v) A. L. Boyes, M. Wild, *Tetrahedron Lett.* **1998**, *39*, 6725–6728; w) T. Schlama, K. Gabriel, V. Gouverneur, C. Mioskowski, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2342–2344; *Angew. Chem.* **1997**, *109*, 2440–2442; x) I. E. Markó, P. R. Richardson, M. Bailey, A. R.

Maquire, N. Coughlan, *Tetrahedron Lett.* **1997**, *38*, 2339 – 2342; y) K. Sakai, K. Sugimoto, S. Shigeizumi, K. Kondo, *Tetrahedron Lett.* **1994**, *35*, 737 – 740; z) P. F. Richardson, I. E. Markó, *Synlett* **1991**, 733 – 736.

[5] For representative examples on enantioselective dichlorination of alkenes, see: a) B. Soltanzadeh, A. Jaganathan, Y. Yi, H. Yi, R. J. Staples, B. Borhan, *J. Am. Chem. Soc.* **2017**, *139*, 2132 – 2135; b) M. L. Landry, D. X. Hu, G. M. McKenna, N. Z. Burns, *J. Am. Chem. Soc.* **2016**, *138*, 5150 – 5158; c) D. X. Hu, F. J. Seidl, C. Bucher, N. Z. Burns, *J. Am. Chem. Soc.* **2015**, *137*, 3795 – 3798; d) K. C. Nicolaou, N. L. Simmons, Y. Ying, P. M. Heretsch, J. S. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 8134 – 8137; e) S. A. Snyder, Z.-Y. Tang, R. Gupta, *J. Am. Chem. Soc.* **2009**, *131*, 5744 – 5745; f) V. Wedek, R. Van Lommel, C. G. Daniliuc, F. De Proft, U. Hennecke, *Angew. Chem. Int. Ed.* **2019**, *58*, 9239 – 9243; *Angew. Chem.* **2019**, *131*, 9339 – 9343; g) M. L. Landry, N. Z. Burns, *Acc. Chem. Res.* **2018**, *51*, 1260 – 1271.

[6] For dichlorination of alkenes using Se, see: a) B. B. Gilbert, S. T.-C. Eey, P. Ryabchuk, O. Garry, S. E. Denmark, *Tetrahedron* **2019**, *75*, 4086 – 4098; b) A. J. Cresswell, S. T.-C. Eey, S. E. Denmark, *Nat. Chem.* **2015**, *7*, 146 – 152; c) C. Paulmier, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, *172*, 25 – 54; d) A. M. Morella, D. A. Ward, *Tetrahedron Lett.* **1985**, *26*, 2899 – 2900; e) A. M. Morella, D. A. Ward, *Tetrahedron Lett.* **1984**, *25*, 1197 – 1200.

[7] N. Fu, G. S. Sauer, S. Lin, *J. Am. Chem. Soc.* **2017**, *139*, 15548 – 15553.

[8] For references on natural polychlorinated products, see: a) P. Sondermann, E. M. Carreira, *J. Am. Chem. Soc.* **2019**, *141*, 10510 – 10519; b) P. Moosmann, R. Ueoka, M. Gugger, J. Piel, *Org. Lett.* **2018**, *20*, 5238 – 5241; c) J. Boshkow, S. Fischer, A. M. Bailey, S. Wolfrum, E. M. Carreira, *Chem. Sci.* **2017**, *8*, 6904 – 6910; d) A. M. Bailey, S. Wolfrum, E. M. Carreira, *Angew. Chem. Int. Ed.* **2016**, *55*, 639 – 643; *Angew. Chem.* **2016**, *128*, 649 – 653; e) S. Krautwald, C. Nilewski, M. Mori, K. Shiomi, S. Omura, E. M. Carreira, *Angew. Chem. Int. Ed.* **2016**, *55*, 4049 – 4053; *Angew. Chem.* **2016**, *128*, 4117 – 4121; f) W.-J. Chung, C. D. Vanderwal, *Angew. Chem. Int. Ed.* **2016**, *55*, 4396 – 4434; *Angew. Chem.* **2016**, *128*, 4470 – 4510; g) A. R. White, B. M. Duggan, S.-C. Tsai, C. D. Vanderwal, *Org. Lett.* **2016**, *18*, 1124 – 1127; h) C. Nilewski, C. Le Chapelain, S. Wolfrum, E. M. Carreira, *Org. Lett.* **2015**, *17*, 5602 – 5605; i) S. S. Tartakoff, C. D. Vanderwal, *Org. Lett.* **2014**, *16*, 1458 – 1461; j) W.-J. Chung, C. D. Vanderwal, *Acc. Chem. Res.* **2014**, *47*, 718 – 728; k) W.-J. Chung, J. S. Carlson, C. D. Vanderwal, *J. Org. Chem.* **2014**, *79*, 2226 – 2241; l) W.-J. Chung, J. S. Carlson, D. K. Bedke, C. D. Vanderwal, *Angew. Chem. Int. Ed.* **2013**, *52*, 10052 – 10055; *Angew. Chem.* **2013**, *125*, 10236 – 10239; m) C. Nilewski, E. M. Carreira, *Eur. J. Org. Chem.* **2012**, 1685 – 1698; n) D. K. Bedke, C. D. Vanderwal, *Nat. Prod. Rep.* **2011**, *28*, 15 – 25; o) T. Umezawa, M. Shibata, K. Kaneko, T. Okino, F. Matsuda, *Org. Lett.* **2011**, *13*, 904 – 907; p) D. K. Bedke, G. M. Shibuya, A. R. Pereira, W. H. Gerwick, C. D. Vanderwal, *J. Am. Chem. Soc.* **2010**, *132*, 2542 – 2543; q) T. Yoshimitsu, N. Fukumoto, R. Nakatani, N. Kojima, T. Tanaka, *J. Org. Chem.* **2010**, *75*, 5425 – 5437; r) J. S. Kanady, J. D. Nguyen, J. W. Ziller, C. D. Vanderwal, *J. Org. Chem.* **2009**, *74*, 2175 – 2178; s) D. K. Bedke, G. M. Shibuya, A. Pereira, W. H. Gerwick, T. H. Haines, C. D. Vanderwal, *J. Am. Chem. Soc.* **2009**, *131*, 7570 – 7572; t) C. Nilewski, R. W. Geisser, E. M. Carreira, *Nature* **2009**, *457*, 573 – 576; u) C. Nilewski, R. W. Geisser, M.-O. Ebert, E. M. Carreira, *J. Am. Chem. Soc.* **2009**, *131*, 15866 – 15876; v) M. Ohtawa, S. Ogihara, K. Sugiyama, K. Shiomi, Y. Harigaya, T. Nagamitsu, S. Omura, *J. Antibiot.* **2009**, *62*, 289 – 294; w) G. M. Shibuya, J. S. Kanady, C. D. Vanderwal, *J. Am. Chem. Soc.* **2008**, *130*, 12514 – 12518.

[9] For selected reviews on photoredox, see: a) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034 – 10072; *Angew. Chem.* **2018**, *130*, 10188 – 10228; b) M. Parasram, V. Gevorgyan, *Chem. Soc. Rev.* **2017**, *46*, 6227 – 6240; c) J. K. Matsui, S. B. Lang, D. R. Heitz, G. A. Molander, *ACS Catal.* **2017**, *7*, 2563 – 2575; d) J.-R. Chen, X.-Q. Hu, L.-Q. Lu, W.-J. Xiao, *Acc. Chem. Res.* **2016**, *49*, 1911 – 1923; e) M. D. Kärkäs, J. A. Porco, Jr., C. R. J. Stephenson, *Chem. Rev.* **2016**, *116*, 9683 – 9747; f) E. C. Gentry, R. R. Knowles, *Acc. Chem. Res.* **2016**, *49*, 1546 – 1556; g) T. Koike, M. Akita, *Acc. Chem. Res.* **2016**, *49*, 1937 – 1945; h) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075 – 10166; i) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035 – 10074; j) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322 – 5363.

[10] For representative examples on LMCT catalysis, see: a) S. Xia, K. Hu, C. Lei, J. Jin, *Org. Lett.* **2020**, *22*, 1385 – 1389; b) K. Wadekar, S. Aswale, V. R. Yatham, *Org. Biomol. Chem.* **2020**, *18*, 983 – 987; c) K. Zhang, L. Chang, Q. An, X. Wang, Z. Zuo, *J. Am. Chem. Soc.* **2019**, *141*, 10556 – 10564; d) A. Sagadevan, M. F. Greaney, *Angew. Chem. Int. Ed.* **2019**, *58*, 9826 – 9830; *Angew. Chem.* **2019**, *131*, 9931 – 9935; e) V. R. Yatham, P. Bellotti, B. König, *Chem. Commun.* **2019**, *55*, 3489 – 3492; f) J. Schwarz, B. König, *Chem. Commun.* **2019**, *55*, 486 – 488; g) A. Hu, J.-J. Guo, H. Pan, H. Tang, Z. Gao, Z. Zuo, *J. Am. Chem. Soc.* **2018**, *140*, 1612 – 1616; h) A. Hu, J.-J. Guo, H. Pan, Z. Zuo, *Science* **2018**, *361*, 668 – 672; i) A. Hu, Y. Chen, J.-J. Guo, N. Yu, Q. An, Z. Zuo, *J. Am. Chem. Soc.* **2018**, *140*, 13580 – 13585; j) A. Hossain, A. Vidyasagar, C. Eichinger, C. Lankes, J. Phan, J. Rehbein, O. Reiser, *Angew. Chem. Int. Ed.* **2018**, *57*, 8288 – 8292; *Angew. Chem.* **2018**, *130*, 8420 – 8424; k) Y. Qiao, E. J. Schelter, *Acc. Chem. Res.* **2018**, *51*, 2926 – 2936; l) Y. Qiao, Q. Yang, E. J. Schelter, *Angew. Chem. Int. Ed.* **2018**, *57*, 10999 – 11003; *Angew. Chem.* **2018**, *130*, 11165 – 11169; m) C. F. Harris, C. S. Kuehner, J. Bacsa, J. D. Soper, *Angew. Chem. Int. Ed.* **2018**, *57*, 1311 – 1315; *Angew. Chem.* **2018**, *130*, 1325 – 1329; n) Y. Li, K. Zhou, Z. Wen, S. Cao, X. Shen, M. Lei, L. Gong, *J. Am. Chem. Soc.* **2018**, *140*, 15850 – 15858; o) M. K. Nielsen, B. J. Shields, J. Liu, M. J. Williams, M. J. Zacuto, A. G. Doyle, *Angew. Chem. Int. Ed.* **2017**, *56*, 7191 – 7194; *Angew. Chem.* **2017**, *129*, 7297 – 7300; p) B. J. Shields, A. G. Doyle, *J. Am. Chem. Soc.* **2016**, *138*, 12719 – 12722; q) H. Yin, P. J. Carroll, J. M. Anna, E. J. Schelter, *J. Am. Chem. Soc.* **2015**, *137*, 9234 – 9237; r) S. J. Hwang, D. C. Powers, A. G. Maher, B. L. Anderson, R. G. Hadt, S.-L. Zheng, Y.-S. Chen, D. G. Nocera, *J. Am. Chem. Soc.* **2015**, *137*, 6472 – 6475.

[11] For $CuCl_2$-mediated transformations under thermal or irradiation conditions, see: a) J. K. Kochi, *J. Am. Chem. Soc.* **1962**, *84*, 2121 – 2127; b) R. P. Arganbright, W. F. Yates, *J. Org. Chem.* **1962**, *27*, 1205 – 1208; c) P. P. Nicholas, R. T. Carroll, *J. Org. Chem.* **1968**, *33*, 2345 – 2349; d) W. C. Baird, J. H. Surridge, M. Buza, *J. Org. Chem.* **1971**, *36*, 3324 – 3330; e) S. Uemura, O. Sasaki, M. Okano, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1482 – 1484; f) E. Cervone, F. Diomedi-Camassei, *J. photochem.* **1979**, *11*, 321 – 332; g) E. Cervone, F. Diomedi-Camassei, *J. Photochem.* **1981**, *15*, 203 – 212; h) A. S. Mereshchenko, P. K. Olshin, A. M. Karimov, M. Y. Skripkin, K. A. Burkov, Y. S. Tveryanovich, A. N. Tarnovsky, *Chem. Phys. Lett.* **2014**, *615*, 105 – 110; i) V. P. Charpe, A. Sagadevan, K. C. Hwang, *Green Chem.* **2020**, *22*, 4426 – 4432.

[12] For selected examples on photoredox Cu-catalyzed reactions, see: a) A. Hossain, A. Bhattacharyya, O. Reiser, *Science* **2019**, *364*, eaav9713; b) A. Sagadevan, V. K. K. Pampana, K. C. Hwang, *Angew. Chem. Int. Ed.* **2019**, *58*, 3838 – 3842; *Angew. Chem.* **2019**, *131*, 3878 – 3882; c) Ref. [10o]; d) P. Xiao, C.-X. Li, W.-H. Fang, G. Cui, W. Thiel, *J. Am. Chem. Soc.* **2018**, *140*, 15099 – 15113; e) X.-Y. Yu, Q.-Q. Zhao, J. Chen, J.-R. Chen, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2018**, *57*, 15505 – 15509; *Angew. Chem.* **2018**, *130*, 15731 – 15735; f) A. Hazra, M. T. Lee, J. F. Chiu, G. Lalic, *Angew. Chem. Int. Ed.* **2018**, *57*, 5492 – 5496;

Angew. Chem. **2018**, *130*, 5590 – 5594; g) Ref. [10k]; h) C. Minozzi, A. Caron, J.-C. Grenier-Petel, J. Santandrea, S. K. Collins, *Angew. Chem. Int. Ed.* **2018**, *57*, 5477 – 5481; *Angew. Chem.* **2018**, *130*, 5575 – 5579; i) W. Zhao, R. P. Wurz, J. C. Peters, G. C. Fu, *J. Am. Chem. Soc.* **2017**, *139*, 12153 – 12156; j) Q.-Y. Meng, X.-W. Gao, T. Lei, Z. Liu, F. Zhan, Z.-J. Li, J.-J. Zhong, H. Xiao, K. Feng, B. Chen, Y. Tao, C.-H. Tung, L.-Z. Wu, *Sci. Adv.* **2017**, *3*, e1700666; k) A. Sagadevan, V. P. Charpe, A. Ragupathi, K. C. Hwang, *J. Am. Chem. Soc.* **2017**, *139*, 2896 – 2899; l) A. C. Hernandez-Perez, S. K. Collins, *Acc. Chem. Res.* **2016**, *49*, 1557 – 1565; m) Q. M. Kainz, C. D. Matier, A. Bartoszewicz, S. L. Zultanski, J. C. Peters, G. C. Fu, *Science* **2016**, *351*, 681 – 684; n) G. Fumagalli, P. T. G. Rabet, S. Boyd, M. F. Greaney, *Angew. Chem. Int. Ed.* **2015**, *54*, 11481 – 11484; *Angew. Chem.* **2015**, *127*, 11643 – 11646; o) C. Meng, K. Yang, X. Fu, R. Yuan, *ACS Catal.* **2015**, *5*, 3760 – 3766.

[13] Similar stereoselectivity was observed in Mn-catalyzed electrochemical dichlorination of alkenes; see Ref. [7].

[14] W. Liu, J. T. Groves, *J. Am. Chem. Soc.* **2010**, *132*, 12847 – 12849.

[15] During the preparation of our manuscript, the group of Hwang reported visible light-induced aerobic oxidation of diarylalkynes catalysed by $CuCl_2$; for details, see Ref. [11i].

Manuscript received: August 6, 2020
Accepted manuscript online: September 11, 2020
Version of record online: October 25, 2020